Hot Corrosion of Slag Line in Plaster of Tundish in Continuous Casting of Steel

S. M. Siadati[1*], A. Monshi[2], E. Karamian[3], S. Alikhani[4] and A. Salehian[5]

1, 2, 3- Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran
4, 5- Isfahan Iron and Steel Mill

Abstract

Plasters are produced from a light refractory material, mainly MgO (M.P. 2800°C), a binder, and a void forming substance for insulating purposes. Different oxides from the slag penetrate into these voids and provide low melting-point phases such as rhodonite ($MnSiO_3$) (1290°C), tephorite (Mn_2SiO_4) (1345°C), merwinite ($Ca_3MgSi_2O_8$) (1575°C), monticellite ($CaMgSiO_4$) (1490°C), and enstatite ($MgSiO_3$) (1560°C). XRF, XRD, and microanalysis by EDX were used to investigate and evaluate the penetration of different oxides to distances below the slag-plaster interface. Results show that SiO_2 and MnO are the most deteriorating while alumina and calcite are the least harmful. It is suggested that rice husk cover on melt, which is rich in SiO_2, be replaced with insulating powders rich in Al_2O_3 and CaO, and that slag basicity be increased in order to decrease the slag line hot corrosion of plaster.

Keywords: Corrosion, Slag, Plaster of tundish, Slag line.

1- Introduction

Iron and steel making industries use about 70% of the global refractory production[1]. The tundishes of continuous ingot or billet casting machines are intended to absorb the kinetic energy of the steel stream flowing from the steel teeming ladle, to partially separate the nonmetallic inclusions, to serve as a mold providing a reservoir of liquid metal, and to help the uniform distribution of molten steel in the mold[2]. The quality of the liquid product delivered from the tundish to the mold, thus, highly depends on the degree of interaction of slag and possible gases with the refractory phases[3, 4]. Typically, tundish linings are composed of three layers. The working lining or plaster is a high MgO-content material, which is directly exposed to steel[5]. Currently, there are different types of tundish linings available in the market. These, in roughly chronological order of introduction into the market, include 'bricked', 'gunnable', 'board', 'sprayable', and the more recently in-situ formed 'dry' systems[6]. In order to use the tundish as more than just a steel reservoir for feeding the caster, different tundish flux formulations have been proposed. The fluxing composition is both insulating and basic, which performs the following

* *Corresponding author:*
Tel: +98- 511- 6630834 Fax: +98- 311- 3912752
E- mail: s_m_siadati@ma.iut.ac.ir
Address: Dept. of Materials Engineering,
Isfahan University of Technology, Isfahan, 84156-8311, Iran
1. M.Sc. Student
2. Associate Professor
3. Ph.D.Student
4. M.Sc.
5. B.Sc.

three vital functions as it covers the liquid metal in the tundish:
1. Thermal insulation of the liquid steel;
2. Provision of a barrier to reoxidation; and
3. Assimilation of slag and inclusions, thereby, cleansing the steel[7, 8].

Tundish flux must have a number of essential characteristics in order to achieve its objectives. These are: a) It must have a high capacity for adsorbing different types of nonmetallic inclusions over long periods of time; b) It must be neutral with respect to the steel being cast and the refractories used in the tundish; c) It must be viscous while not impeding the operation of the stoppers; and d) The overall volume of the harmful precipitates that are formed must be small. The raw material of tundish flux is usually the ash of burned rice paring. This by-product of rice production contains both SiO_2 and a small amount of carbon.

The backup lining is generally composed of Al_2O_3 and SiO_2 (andalusite castable) and is the thickest part of the tundish lining which is made to be used several hundreds of times. This backup lining has a low reactivity with magnesia materials to form a surface working layer and to have affinity for the safety lining. The third component of the tundish refractory system is a safety lining. This highly insulating lining is sandwiched between the backup lining and the tundish steel shell to provide thermal insulation and keep the shell temperature below its critical range throughout the operating campaigns of a tundish[1, 7, 8]. In order to provide insulation to preserve heat in the molten steel, an inert barrier must be provided between the steel and the backup lining to act as a parting plane for easy deskulling. Steelmakers use

coating materials to line the tundish plaster rather than running directly on the backup lining[8].

The plaster is usually composed of the following:

• Basic refractory composition such as magnesia and olivine;

• Density reducing filler materials like inorganic or organic fibers (ceramic or glass fibers, paper fibers), expended inorganic or organic materials (polystyrene beads), foaming agent (sodium louryl sulphate), etc.;

• A plasticizer to enhance the ability of the composition to adhere to itself and the surfaces to which it is applied, such as silica fume; and

• Some compositions can contain other additives like a binder to promote initial gelling properties when mixed with water (alkaline earth phosphate or aluminum phosphate) and also imparting high temperature strength to the composition.

Penetration of melt and slag into porous plaster causes sintering of this inert barrier and its possible reaction with permanent liner. Dissolution of the refractory material at the interface with slag is caused by some chemical reaction and or diffusion of reacting species into the plaster[9]. The diffusion of MgO is first associated by the formation of a solid solution or magnesiuwustite, $(Mg, Fe)O$ [10].

The aim of this research is to investigate the reactions and the phases developing when the slag penetrates into the plaster of the tundish used in Isfahan Iron and Steel Mill in central part of Iran.

2- Experimental

A plaster used for 6 sequences and about 500 minutes to produce 31Mn5 steel was selected for hot corrosion studies of the slag line. Table (1) shows the chemical analysis of the steel.

Table 1. Chemical analysis of 31Mn5 steel.

%C	%Si	%Mn	S,P	$C_{equivalent}$
0.28-0.38	0.35-0.55	1-1.3	<0.045	0.46-0.55

The slag from the last sequence was collected from different areas on top of the melt. Slags were collected from different regions and milled in a ball mill for 3 hours to become fine and homogenous. The chemical analysis of the slag was studied by XRF (Table 2). Small samples from different depths of slag penetration in the tundish plaster were carefully taken for phase analysis by XRD and microstructure observations by SEM. The intensity of

peaks in XRD patterns were used for semiquantitative analysis of phase changes.

3- Results and Discussion

Table (2) shows the XRF analysis of the homogenized slag and one point of 3-4 cm depth from the slag-plaster interface, together with the analysis of the unused plaster.

XRF shows that more than 98% of the slag is composed of SiO_2, CaO, MnO, MgO, Al_2O_3, and FeO. Accounting for nearly 55% of the slag, SiO_2 and MnO have a stronger destructive effect. CaO accounting for nearly 20% of the slag is basic and less harmful to the basic MgO grains, as the main body of the plaster. Most of the SiO_2 comes from the rice husk used as the insulator cover on top of the steel melt.

The steel should have 1-1.3% Mn (Table 1), about 0.1-0.2% of which comes from iron ore and the rest must be provided by ferromanganese. CaO comes from the lime used as a flux in the converter, where the iron is changed to steel. About 8% of Al_2O_3 comes from Al ingot thrown into the steel melt to absorb oxygen to form Al_2O_3 and to provide mild steel.

MnO is a low melting oxide. Phase diagrams show that this oxide makes eutectics with other oxides of the slag to produce compounds with melting temperatures of 1200-1400°C. This means that this oxide is very destructive at high quantities. When MnO is associated with SiO_2, the slag is more fluid and penetrative. Table (3) shows the possible phase formations with their melting points.

These possible phases at the steel making temperature of 1600°C are all liquid and produce a low viscosity slag which can easily penetrate into the porous plaster. XRF results of a depth of 3-4cm from the slag-plaster interface shows that more than 30% of the MgO in the plaster is missing (thus 58.8% remaining from a total of 90%). This MgO must have reacted with other oxides to form low melting compounds in the slag. In place of this missing MgO, other oxides, mainly SiO_2, have penetrated into the plaster. Al_2O_3, MnO, CaO, and FeO are also present in a decreasing order. Alumina and calcite are less corrosive, since these oxides can produce spinel $(MgO.Al_2O_3)$ and MgO-CaO solid solution with MgO both of which are high temperature resistant. Al^{3+} is smaller than Ca^{2+} (their radii being 0.51Å and 0.99Å, respectively).

Table 2. XRF analysis of homogenized slag and a point of 3-4 cm depth from slag-plaster interface, together with the analysis of unused plaster.

	SiO_2	CaO	MnO	MgO	Al_2O_3	FeO	Na_2O	TiO_2	K_2O	SO_3
slag	37.4	19.33	17.17	10.86	7.44	6.3	0.53	0.5	0.19	0.07
3-4 cm depth	17.3	6.72	7.45	58.83	7.68	0.92	0.17	0.52	0.13	0.12
Unused plaster	4.5	3.2	–	90	0.4	0.8	0.05	–	–	–

Table 3. Possible phase formation with their melting points.

Melting point(°C)	Chemical composition	phase
1290	$MnO.SiO_2$	rhodonite
1345	$2MnO.SiO_2$	tephorite
575	$CaO.MnO.2SiO_2$	johannsenite
1355	$CaO.MnO.SiO_2$	Glaucochroite
1575	$Ca_3MgSi_2O_8$	merwinite
1490	$CaMgSiO_4$	monticellite
1560	$MgSiO_3$	enstatite
1560	$MnO.Al_2O_3$	galaxite
1205	$2FeO.SiO_2$	fayalite
1750	$MgO.Fe_2O_3$	Magnesioferrite
1454	$2CaO.MgO.2SiO_2$	akermanite

Table 4. EDX oxide analysis of different regions under the interface.

	Region1(near the interface)	Region 2(Middle parts)	Region3(deep inside plaster)
%MgO	72.2	75.5	82.6
%SiO₂	16.6	13.2	10.3
%Al₂O₃	5.8	4.4	3.6
%CaO	5.5	6.8	2.8
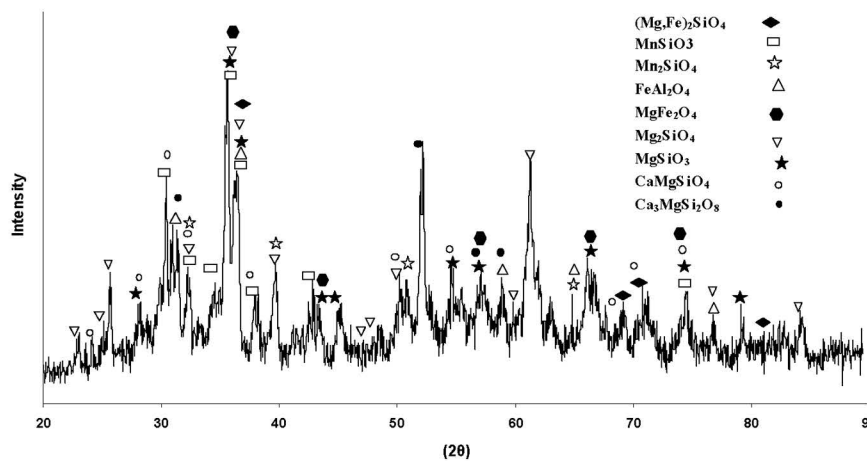
Fig. 1. XRD peaks of homogenized slag.
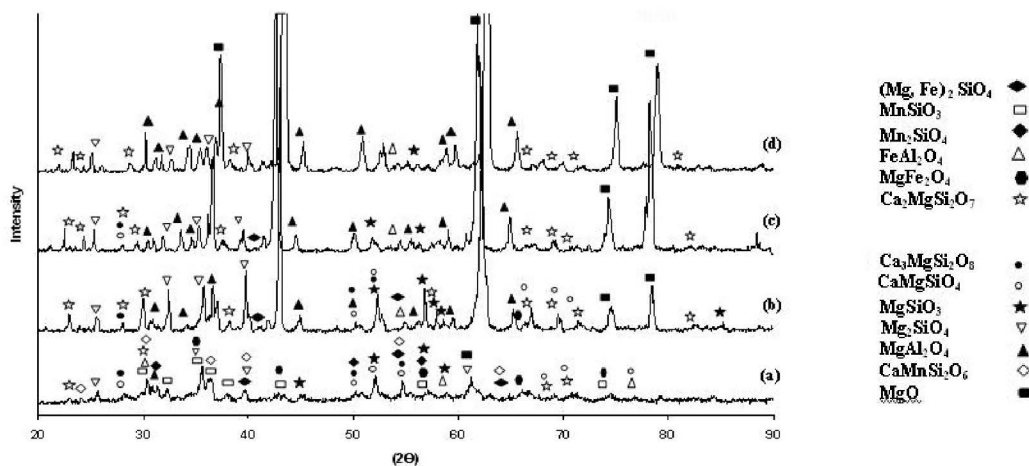
Fig. 2. XRD peaks and related phases for respectively 0, 1.5, 3, 4 cm from the slag-plaster interface in a, b, c, d.
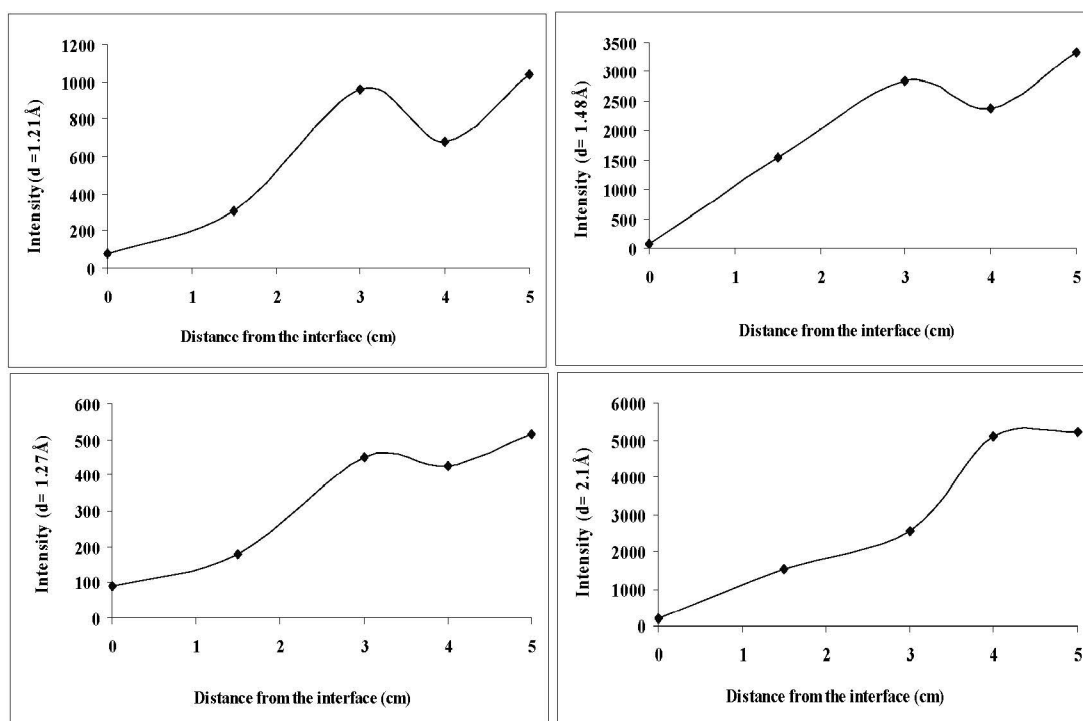
Fig. 3. The variation of intensity in 4 stronger peaks of MgO vs. distance from the interface.
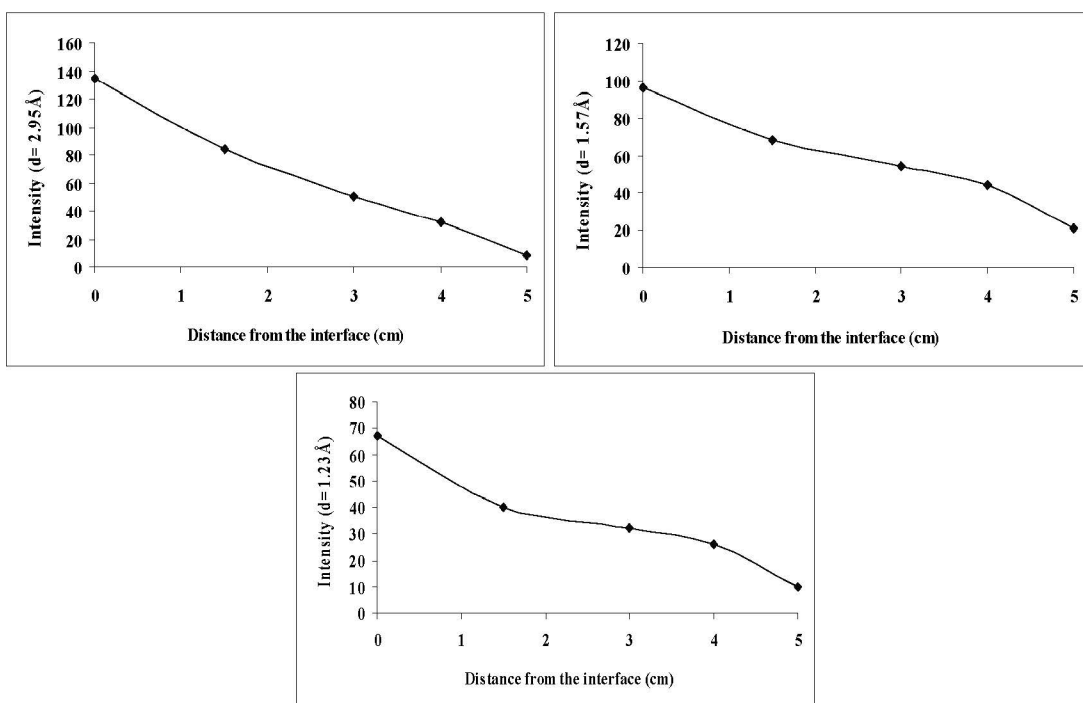

Fig. 4. The variation of intensity in peaks of $FeAl_2O_4$ vs. distance from the interface.

Figure (1) shows XRD peaks of the homogenized slag and the phases identified. Figure (2) compares XRD patterns and their related phases of : a) The slag, b) 1.5cm below the interface, c) 3cm below the interface, and d) 4cm below the interface. The variations of intensity in the 4 strongest peaks of MgO are illustrated in Figure (3). These peaks are from the set of planes with *d* values of $d_1=1.21Å$, $d2=1.48Å$, $d3=1.27Å$, and $d4=2.1Å$ angstroms, respectively.

The trend is towards higher concentrations of magnesite at farther distances from the interface, as expected. Some fluctuations might contribute to the formation of phases containing MgO such as $MgAl_2O_4$ ($MgO.Al_2O_3$) and the like.

Figure (4) shows the variation of peaks of $FeAl_2O_4$ ($FeO.Al_2O_3$) *vs.* distance from the interface. Maximum concentration for this phase is observed at the interface, which decreases as it gets deeper into the plaster. Figure (5) shows the phase concentration for $MnSiO_3$. It is seen that at deeper sections, penetration of MnO and SiO_2 decreases and so does the formation of this phase. However, the formation of small amounts of this low temperature phase can be destructive. Forsterite (Mg_2SiO_4) is shown in Figure (6). Its maximum concentration is observed at about 1.5 cm below the interface. This is because the quantity of SiO_2 is high but that of MgO is low at the interface. Moreover, both oxides are optimal at this depth. At deeper sections, MgO is frequent while SiO_2 is limited, and $2MgO.SiO_2$ can not be formed extensively. Forsterite is a high temperature phase (its melting point being about 1800°C) and its presence is beneficial. Similar phase changes are shown for $MgSiO_3$ or $MgO.SiO_2$ (Figure 7), Ca_3MgSiO_4 or $CaO.MgO.2SiO_2$ (Figure 8), and $CaMgSiO_4$ or $CaO.MgO.SiO_2$ (Figure 9). Figure (11) shows the XRD pattern for the unused plaster.

The quantity of MnO in the slag is higher than that of MgO and phase formation of $MnSiO_3$ decreases with increasing penetration depth (Figure 5). However, $MgSiO_3$ gains its maximum value at about 1.5 cm below the interface where both MgO and SiO_2 are considered to be at their optimal levels (Figure 7). The ratio of $\frac{MgO}{SiO_2}$ for forsterite is 2 and for enstatite it is 1. Formation of Mg_2SiO_4 at the interior parts of the plaster is more favorable than that of $MgSiO_3$ due

to the lack of SiO_2 and the availability of MgO. Since forsterite is more refractory than enstatite, it is beneficial from a corrosion point of view. Similarly, $Ca_3MgSi_2O_8$ and $CaMgSiO_4$ have their maximum quantities at about 1.5 cm below the interface, where the ternary oxides (CaO, MgO, and SiO_2) are at their optimal levels. Unfortunately, these are low melting point phases which cause the interior layers of the plaster to melt and scale through time, thus limiting the effective life of the plaster.

EDX analysis by electron microscopy was performed at different depths at intervals of about 2cm (Table 4). Figure (10) shows the SEM images of these points together with the EDX peaks.

It should be noted that the values of XRF and the EDX in Table 2 are semiquantitative due to the absorption and enhancement of elements with respect to each other. This means that the energy ($E = h\nu = \frac{hc}{\lambda}$) emitted as a result of excitement of some elements by the *Niobium* XRF lamp can be consumed by some other elements to generate more excitement than originally received from the *Nb* XRF lamp. This leads to the absorption of the first group and the enhancement of the second. Therefore, the analysis for the first group is less and for the second group is more than the realistic due to elemental variations in this study, these phenomena become much more complex. XRD peaks are also influenced by the presence of elements that absorb X rays more than others, but fluctuations are less sensitive.
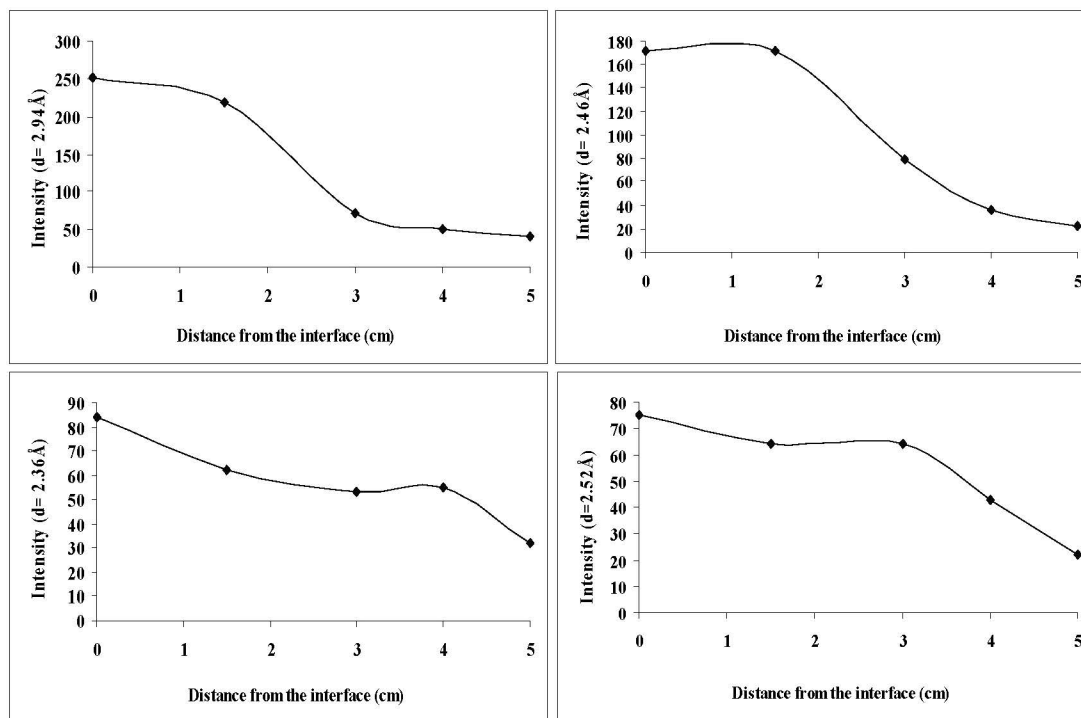

Fig. 5. The variation of intensity in peaks of $MnSiO_3$ vs. distance from the interface.
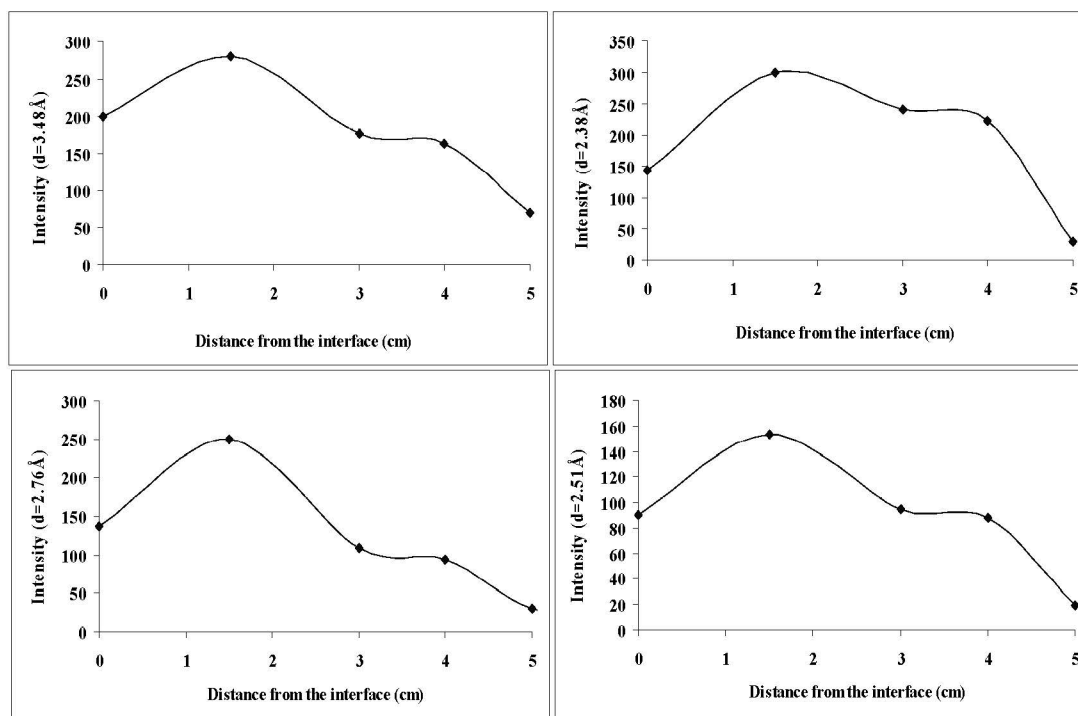
Fig. 6. The variation of intensity in peaks of Mg_2SiO_4 vs. distance from the interface.
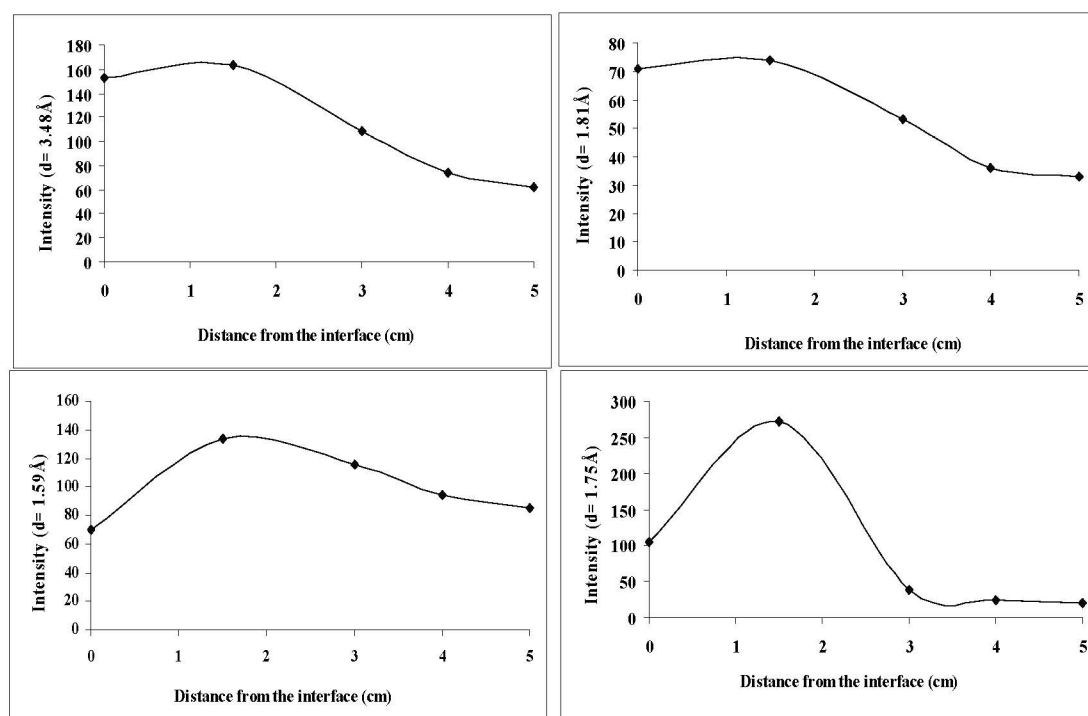

Fig. 7. The variation of intensity in peaks of $MgSiO_3$ vs. distance from the interface.

Figure (11) confirms that phosphate phases exist in the unused plaster. This comes from using sodium phosphate binders, such as sodium hexametaphosphate and sodium tripolyphosphate in the production of plaster. These phosphates develop low melting point compounds which are harmful at the high temperatures of steelmaking in continuous casting due to the hot corrosion of the plaster.
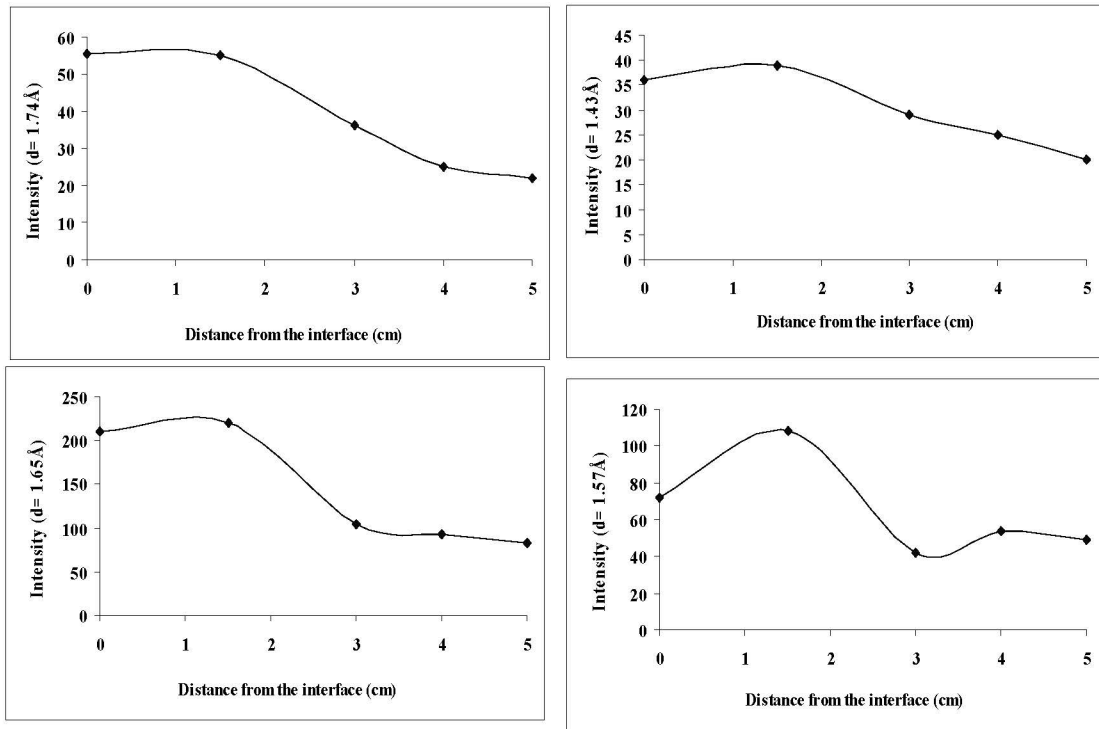
Fig. 8. The variation of intensity in peaks of $Ca_3MgSi_2O_8$ vs. distance from the interface.
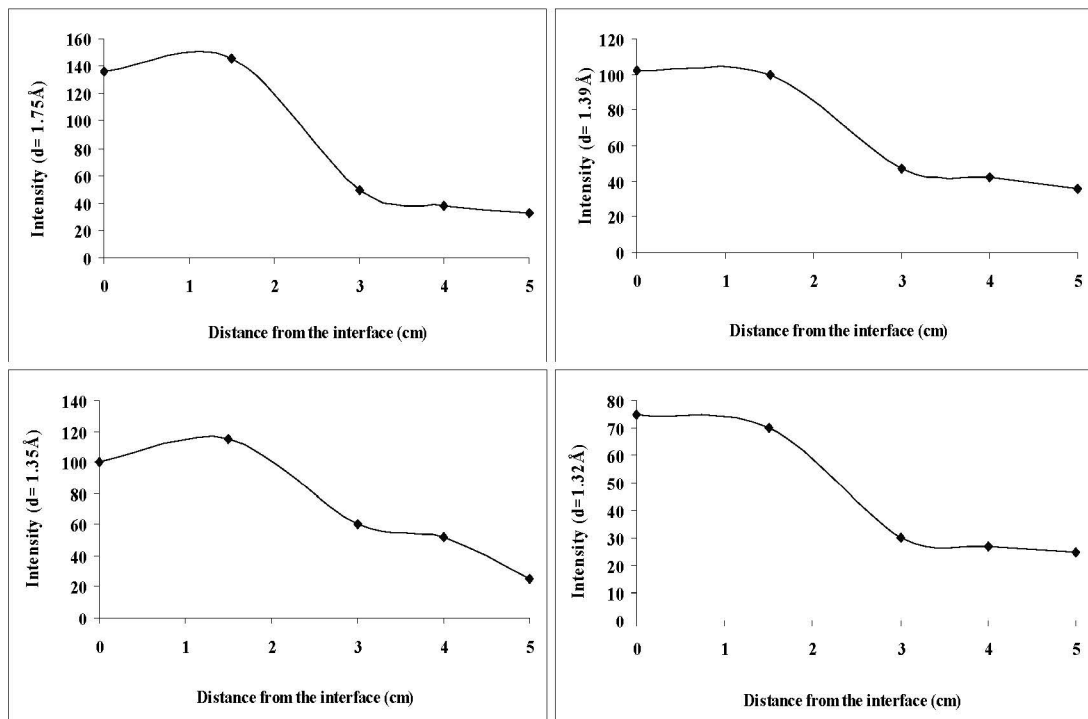

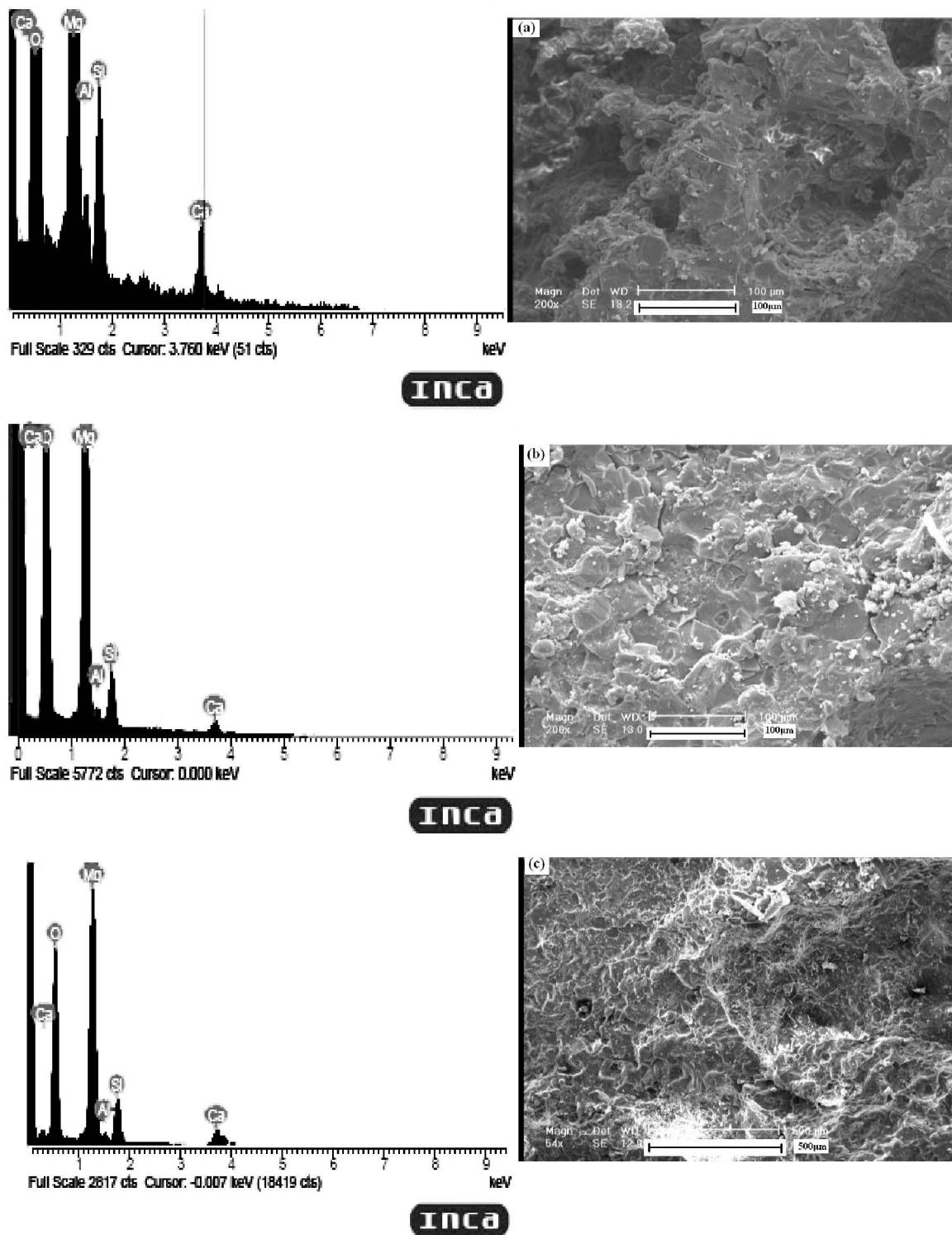*Fig. 9. The variation of intensity in peaks of $CaMgSiO_4$ vs. distance from the interface.*

Fig. 10. SEM and EDX of 3 different region of plaster (a) near the interface, (b) middle parts and (c) deep inside plaster.
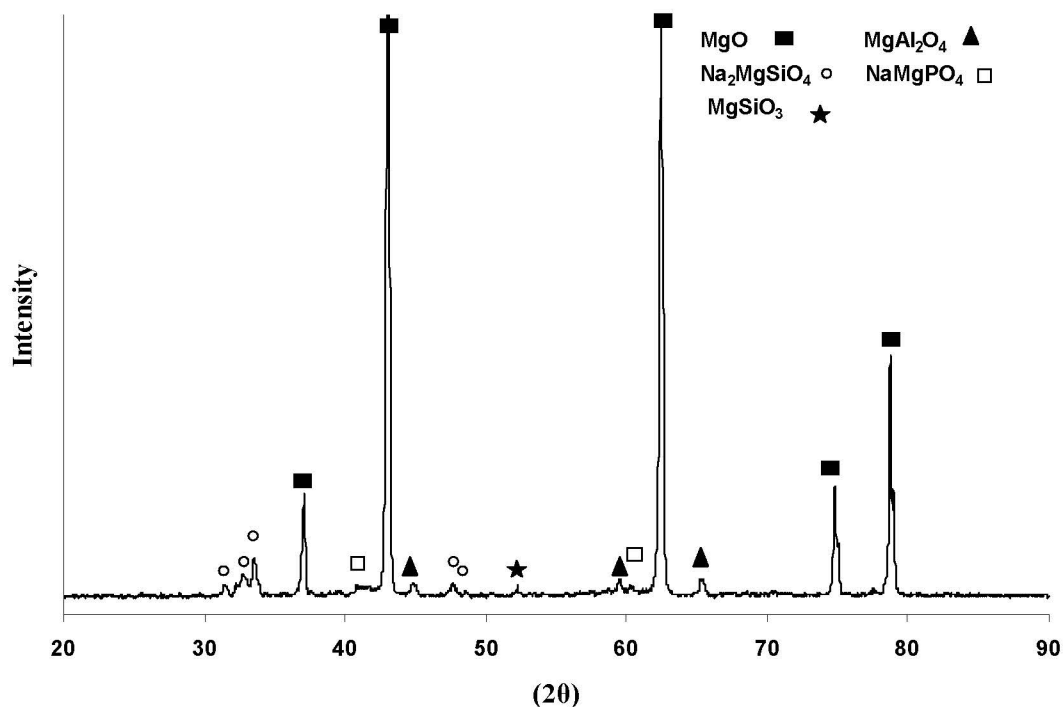
Fig. 11. XRD pattern of unused plaster.

4- Conclusions

• Plasters are produced with high porosity to act as an insulator, but the side effect is the penetration of different oxides from the slag and the accelerated hot corrosion of the slag line.

• Oxides such as SiO_2 and CaO react with MgO grains (Melting Point 2800°C) in plaster and produce low melting phases such as merwinite, $Ca_3MgSi_2O_8$(1575°C); monticellite, $CaMgSiO_4$(1490°C); enstatite, $MgSiO_3$(1560°C); and akermanite, $Ca_2MgSi_2O_7$(1454°C).

• The most deteriorating oxides in the slag are SiO_2 and MnO. These two oxides produce rhodonite, $MnSiO_3$ (1290°C) and tephorite, Mn_2SiO_4 (1345°C). Alumina and calcite are less harmful.

• It is suggested that rice husk cover on melt which is rich in SiO_2 be replaced with an insulating powder rich in Al_2O_3 and CaO. The basicity of the slag is also suggested to be increased in order to decrease the slag line hot corrosion of the plaster.

References

[1] S. I. Kataoka: Conf. Proc. of Refractories for Steelmaking in Japan, UNITCER 93., Brazil, (1993), 27.

[2] Y. V. Materikin and V. A. Molochkov: Refractories for consumer, 24 (1983), 108.

[3] J. P. Birat, C. Chow, T. Emi: The Making, Shaping and Treating of Steel, The AISI Steel Foundation, Pennsylvania, (1998), 1513.

[4] A. McLean: Proc. of Steelmaking, ISS-AIME, (1998), 23.

[5] Committee on Technology: International Iron and Steel Institute, Brussels, 1985.

[6] B. M. Moshtaghioun, A. Monshi: J. Mat. Proc. Tech., 196 (2008), 52.

[7] L. J. Heaslip, J. D. Dorricott: US patent 5 366 535, 1994.

[8] B. M. Moshtaghioun, A. Monshi: J. Mater. Sci., 42 (2007), 6720.

[9] L. A. Leasky, A. E. Machale: Ceram. Trans., 4 (1989), 453.

[10] J. Liu, M. Guo, P. T. Jones, F. Verhaeghe, B. Blanpain, P. Wollants: J. Euro. Ceram. Soci., 27 (2007), 1961.