

DESIGN OF IMPROVED $\text{Al}_2\text{O}_3 - \text{SiC} - \text{C}$ BASED TROUGH CASTABLE SUITABLE FOR HIGH MnO IN SLAG

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ABSTRACT

Good quality iron ore is depleting day by day and steel makers have started to use low grade iron ores having high quantity of impurities particularly manganese oxides. Manganese oxides present in iron ore reduced to MnO by CO and partially into Mn in reducing atmosphere inside the blast furnace. Both Mn and MnO dissolved into molten metal and slag followed by aggravate the refractory corrosion and erosion.

The consistent performance of trough castable is very important to maintain the whole chain of steel production while giving constant supply of hot metal. The erosion and corrosion of $\text{Al}_2\text{O}_3 - \text{SiC} - \text{C}$ trough castable happen in three stages namely decrease in viscosity of slag, increase in the wettability of refractory surface and formation of different low eutectic compounds which penetrate easily into the refractory lining. The optimum use of silicon carbide is also important to control the penetration of slag inside the castable lining.

In this present work, one new trough castable in $\text{Al}_2\text{O}_3 - \text{SiC} - \text{C}$ system is designed while taking special care in matrix part. An improved matrix is designed in combination of various reactive alumina, carbonaceous compounds and antioxidants, thereby enhancing, one, its non wettability to molten metal/slag and, two, its packing density upon casting. The improved castable is installed in several integrated steel plants and there is significant improvement in performance where MnO in slag is remarkably high.

INTRODUCTION

In absence of good quality iron ores and to reduce the overall manufacturing cost, low grades iron ores are being used in most of the steel making units. The low grade iron ores are having different oxides like MnO , B_2O_3 , TiO_2 etc. and presence of these oxides adversely affects the performance of refractory particularly for blast furnace hearth and trough working lining. The

major concern is manganese oxide which reduced to MnO and finally to Mn . Elemental Mn and MnO are dissolved¹ in hot metal and slag respectively and aggravate the refractory erosion. The presence of Mn in hot metal and MnO in slag results significant changes in refractory performance in blast furnace trough working lining. In general, $\text{Al}_2\text{O}_3 - \text{SiC} - \text{C}$ based low cement or ultra low cement castables are used as working lining refractory for blast furnace trough. While using good quality iron ores the MnO content varies from 0.2 to 0.5% in slag. But it may go upto 3% while using low grades iron ore. The MnO present in slag affects the refractory through different mechanisms. It forms several low eutectic compounds² with other oxides like $\text{Mn}_2\text{Al}_4\text{Si}_3\text{O}_{18}$ (1180°C), $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (1200°C), MnSiO_3 (1293°C), Mn_2SiO_4 (1347°C) and lowering the viscosity of the slag. Later on, it increases the wettability of refractory surface while changing the wetting angle below 90° between solid and liquid. The wettability is the measurement of spreading of liquid over the solid surface and control the rate of penetration³ and corrosion. More spreading means more penetration and reactions with refractory material and damage the refractory lining very fast. TiO_2 , another oxide present in low grade iron ores, also forms different low eutectic compounds^{4,5} resulting lowering the viscosity of slag and therefore indirectly help to aggravate the penetration and corrosion of refractory.

Presence of Al_2O_3 in slag increases the slag viscosity and maintains a dynamic balance while forming AlO_4^{5-} . But in presence of MnO the dyanamic balance is disturbed and the reverse reaction may take place while decreasing AlO_4^{5-} as well as the viscosity of the slag. On the other hand, MnO destroys the AlO_4^{5-} and SiO_4^{4-} tetrahedron⁶ and simplifies the slag structure resulting the decreasing slag viscosity.

The slag viscosity is determined about the oxide structure present in slag particularly silica tetrahedra. It has been investigated by IR study

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and found that the Si-O bond⁷ moves backwards towards high frequency near 1368 cm⁻¹. This phenomenon may attribute to bond stress and spatial structure effect resulting peak position migration in ionic compound. Along with Mn²⁺ presence of Mg²⁺ and Ca²⁺ also change the Si-O bond orientation and simplifies the structure and finally resulting the decrease in slag viscosity.

In the present works different castable formulations have been studied while changing the aggregate as well as additives. Few more additives were added for strengthening the matrix to control the penetration of slag followed by corrosion so that the rate of corrosion can be controlled.

EXPERIMENTAL

At first, two synthetic slags were prepared having the similar chemical composition of an integrated steel plant with MnO as low as 0.3% and as high as 1.5%. In this plant standard MnO in slag was ~ 0.3% and with low grades iron ores the MnO content in slag has increased to ~ 1.5%. The rate of liquid formation of two different slags and in present of slags along with working lining refractory material (Al₂O₃ – SiC – C castable) were studied with an advanced software technology at temperature in between 1200^oC and 1600^oC. While measuring the rate of liquid formation with temperature the working lining refractory and slag were mixed in 1:1 ratio.

Later on, five different Al₂O₃ – SiC – C castables were designed to study the various properties. Free flow and tap flow were measured for all the samples as per internal method followed by measurement of BD, CCS and PLC after firing at different temperatures. Since the castables are having SiC and carbonaceous materials, firing was carried out in reducing atmosphere. Slag corrosion test was conducted in an induction furnace at 1550^oC in presence of high MnO slag collected from one integrated steel plant. Microstructure of samples after slag corrosion test was analyzed through optical microscope to understand the mechanism of slag penetration and corrosion.

Out of five recipes the best recipe was selected for plant trial. During plant trial, the performance of working lining refractory material was monitored in terms of hot metal throughput (HMT). The performance of newly designed material is compared with existing material to correlate the results obtained specifically improvement in slag corrosion resistance during

development of this material and actual performance while used it in integrated steel plant.

RESULTS AND DISCUSSIONS

Chemical composition of hot metal and slag along with temperature are the controlling factors about the performance of trough working lining refractory. In hot metal C, Si, S and Mn are the major constituents which are responsible to control the rate of corrosion/erosion. Similarly, in slag SiO₂, Al₂O₃, MgO, FeO and MnO are the major constituents. The variation of any constituent either in hot metal or in slag may increase or decrease the overall performance of trough working lining material. The variation in hot metal temperature is also directly proportional with the rate of corrosion/erosion (wear rate). In Table I, the effect of different constituents present in hot metal on refractory in terms of corrosion behaviour is mentioned. The same is mentioned for slag in Table II. The effect of hot metal temperature (tapping temperature) on corrosion rate of refractory is shown in Fig.1.

Table I : Effect of different constituents present in hot metal on wear rate of trough working lining refractory

Increasing of	Rate of wear	Reason	Results
[C]	Decrease	Antioxidant	Improves in oxidation resistance of SiC and C
[Si]	Increase	Metal viscosity become lower	Formation of low eutectic and more penetration into refractory castable
[S]	Increase	-do-	-do-
[Mn]	Increase	Reacted with SiC	-do-

The rate of penetration of metal inside the refractory lining depends upon the viscosity of the hot metal. While increasing the Si and S content in hot metal there is more penetration due to formation of low eutectic compounds whereas with increasing amount of Mn it reacts with SiC followed by penetration.

In case of slag, increasing quantity of SiO₂ and Al₂O₃ is in favour of low penetration due to increasing of slag viscosity. But MgO, FeO and MnO accelerate the penetration while increasing the quantity in slag. The presence of MgO results the formation of low eutectic compounds whereas FeO and MnO react with SiC followed by penetration inside the refractory lining. This is also supported by Al₂O₃ – SiO₂ – MnO ternary phase diagram (Fig. 2)

Table II : Effect of different constituents present in slag on wear rate of trough working lining refractory

Increasing of	Rate of wear	Reason	Results
[SiO ₂]	Decrease	Slag viscosity become higher	Less penetration
[Al ₂ O ₃]	Decrease	-do-	-do-
[MgO]	Increase	Slag viscosity become lower	Formation of low eutectic and more penetration into castable
[MnO]	Increase	-do-	-do-
[FeO]	Increase	Reacted with SiC	-do-

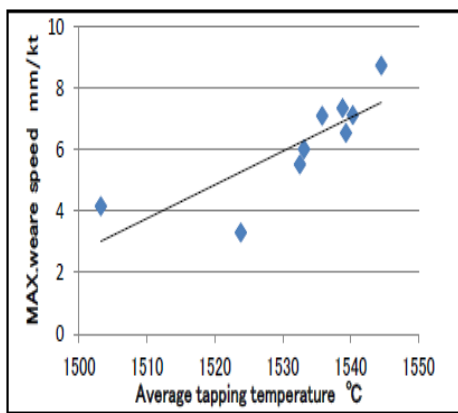


Fig. 1. Effect of tapping temperature on wear rate of working lining refractory of trough

Tapping temperature is directly proportional to the wear rate of working lining castable. Higher tapping temperature is responsible for higher wear rate. Due to high tapping temperature, the viscosity of both hot metal and slag decreases resulting more penetration and corrosion.

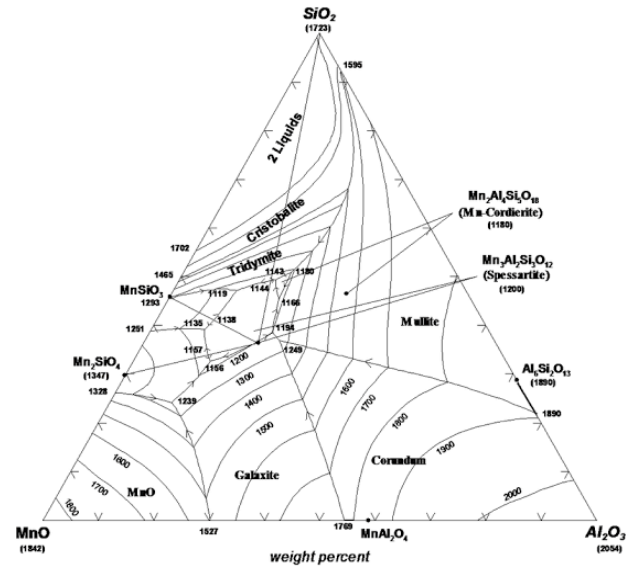


Fig. 2. Al₂O₃ – SiO₂ – MnO ternary phase diagram

The hot metal and slag chemistry of an integrated steel plant is given in Table – III and Table – IV. During this period the plant was using low grades iron ores having high MnO.

Table III : Hot metal chemistry while using low grades iron ore

Sample No	C%	% Si	% Mn	% S	% P
1	4.63	0.67	0.446	0.018	0.111
2	4.54	0.55	0.419	0.019	0.107
3	4.49	0.45	0.413	0.025	0.111
4	4.45	0.38	0.367	0.033	0.114
5	4.52	0.49	0.546	0.015	0.122
6	4.6	0.61	0.489	0.015	0.129
7	4.54	0.52	0.449	0.022	0.121
8	4.51	0.49	0.442	0.022	0.12
9	4.44	0.32	0.443	0.02	0.118
10	4.48	0.38	0.473	0.018	0.116

In general, MnO content in slag is in between 0.2 to 0.5% when good quality iron ores are used. But the same is increased to as high as 1.6% when low

grades iron ore were used. The significant increase in MnO in slag affects the refractory lining severely while increasing the specific rate of corrosion and reduced the overall throughput of hot metal. Due to unexpected throughput there is shortage of hot metal and entire steel making process is disturbed.

Table IV : Slag chemistry while using low grades iron ores.

Sample No	Temp (°C)	% CaO	% MgO	% SiO ₂	% Al ₂ O ₃	% MnO
1	1494	35.09	7.79	35.96	18.16	1.12
2	1496	36.32	8.75	34.44	17.77	0.87
3	1509	36.19	8.88	34.29	18.06	0.81
4	1499	37.15	7.96	34.44	17.71	0.88
5	1503	35.39	7.53	35.93	18.31	0.86
6	1495	35.36	8.01	35.59	18.24	0.92
7	1493	36.22	8.51	34.51	18.07	1.01
8	1482	36.22	7.73	34.62	17.83	1.61
9	1498	35.57	6.45	36.12	18.46	1.33
10	1498	35.16	7.03	36.54	17.92	1.32

To understand the rate of liquid phase formation of slag having low MnO (0.3%) and high MnO (1.5%), one special simulation technique was adopted in laboratory. With the same technique the slag samples were mixed with castables in 1:1 ratio and measured the rate of liquid phase formation. The chemical composition of castable considered in this study is mentioned in Table – V and the slag chemistry (MnO = 0.3% and MnO = 1.5%) along with the chemistry of samples while mixing with castable in 1: 1 ratio is shown in Table – VI.

Table V: Chemical composition of Al₂O₃-SiC-C castable

% SiO ₂	% CaO	% Al ₂ O ₃	% TiO ₂	% Fe ₂ O ₃	% SiC	% C
3.59	1.02	73.49	1.76	0.47	y	z

The rate of liquid formation for four samples (two slags and two castable+slag composite) is shown in Fig.3. In the temperature range of 1200°C to 1250°C, the rate of liquid phase formation is higher when the slag is having 1.5% MnO. In case of mixture of slag and castable the rate is higher above 1260°C specifically maximum rate is observed at 1310°C.

Table VI: Chemical composition of slag and castable + slag (1:1) samples

Sample description	% SiO ₂	% CaO	% Al ₂ O ₃	% MgO	% TiO ₂	% MnO	% Fe ₂ O ₃	% SiC	% C
① Slag/Past	36.3	34.2	18.53	9.34	0.58	0.3	0	0	0
Slag/Current	35.8	33.8	18.31	9.23	0.57	1.5	0	0	0
Slag/Past +Trough castable	19.9	17.6	46.03	4.75	1.17	0.15	0.14	0.5y	0.5z
Slag/Current +Trough castable	19.7	17.4	45.91	4.69	1.17	0.75	0.14	0.5y	0.5z

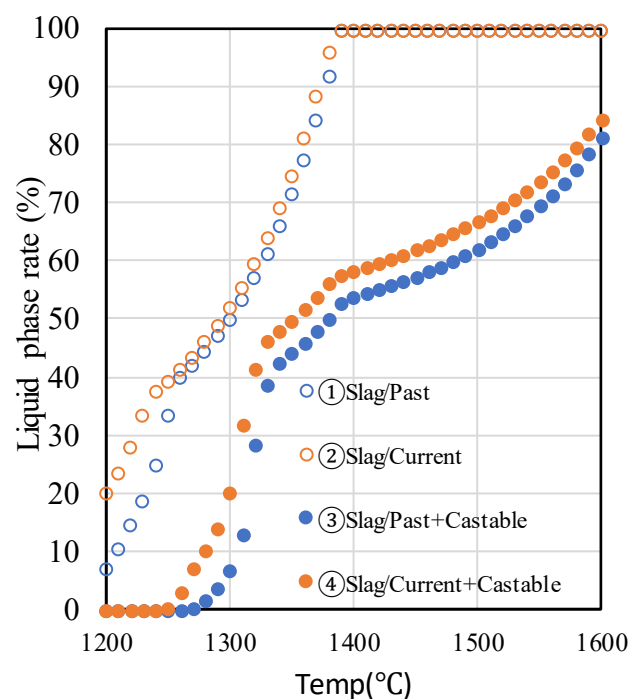


Fig. 3. Rate of liquid phase formation with temperature

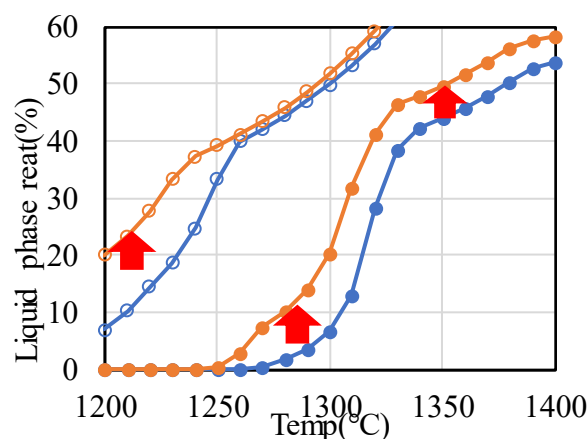


Fig. 4. Rate of liquid phase formation with temperature (Enlarged view)

In Fig. 4 enlarged view is shown for better understanding. While calculating it has been

observed that the rate of liquid phase formation is 19% higher when the slag is having MnO of 1.5% against the slag having MnO of 0.3%.

To design suitable Al₂O₃ – SiC – C castable having better slag corrosion resistance against high MnO slag, specifically for slag runner, five different recipes are formulated. The recipes are shown in Table VII. Out of five recipes, two recipes (E1 and E2) were standard and performance was good when MnO in slag was in between 0.2% to 0.5%. Three new recipes (T-1, T-2 and T-3) were formulated while changing the ratio of different base raw materials, introduction of new additives and increasing the quantity of additives.

Table VII: Design of recipes

	E-1	E-2	T-1	T-2	T-3
Fused Al ₂ O ₃	a	a	a	a	a
Sintered Al ₂ O ₃	b	b	b	b+c	b
Silicon carbide	d	d	d	d-c	d
Reactive Al ₂ O ₃	e	e	e	e-f	e
Binder	g	g	g	g	g
Micro silica	h	h	h	h-α	h
Carbon	j	j	j	j+f	j
Additive 1	k	k-α	k-α	k+1	k-2α
Additive 2	x	x+α	x+α	x+α	x+2α
Additive 3	y	y+β	y-β	y	y-2β
Additive 4	z	z-β	z+β	z	z+2β

Since flow of this castable is very important, free flow and tap flow were measured for three trial recipes and compared with existing materials. As an example, free flow and tap flow are shown in Fig.5 and Fig.6 for two samples (E1 and T-2).



Fig. 5 Free flow of castable E-1, (Left) and T-2, (Right)

Slag corrosion test was conducted in an induction furnace at 1550⁰C with the slag collected from integrated steel plant. The chemical composition of slag is shown in Table – VIII.



Fig. 6 Tap flow of castable E-1, (Left) and T-2, (Right)

Table VIII: Chemical analysis of slag

Constituent	% by Wt.
CaO	36.22
MgO	7.73
SiO ₂	34.62
Al ₂ O ₃	17.83
FeO	0.45
MnO	1.51
Na ₂ O	0.11
K ₂ O	0.34
TiO ₂	0.58

The appearance of samples after slag corrosion test is shown in Fig.7 and penetration depth is shown in Fig.8.

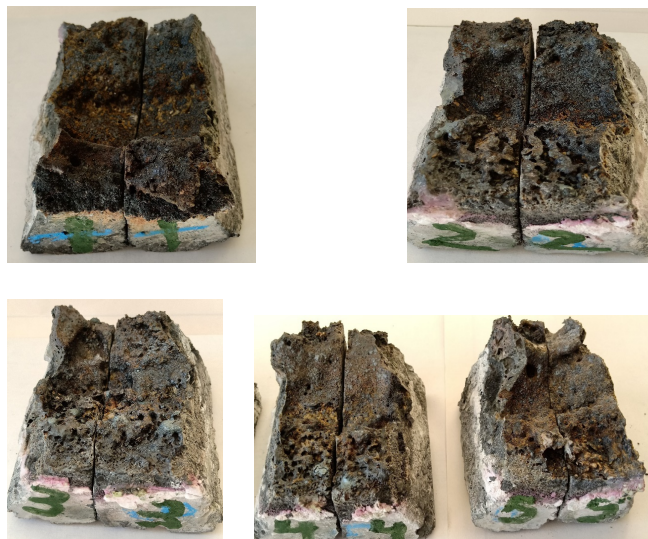


Fig. 7 Appearance of samples after slag corrosion (Clockwise – E1, E2, T-3, T-2, T-1)

Corrosion depth of all five samples is measured and shown in Fig.9. The minimum corrosion depth is observed in T-2 recipe and maximum is in E-1

followed by E-2, T-1 and T-3. The corrosion depth for T-1 and T-3 is almost same. Minimum corrosion depth indicates, T-2 recipe is having better slag corrosion resistance against high MnO slag. Considering E-1 as base material, there is about 40% improvement in slag corrosion resistance in T-2.

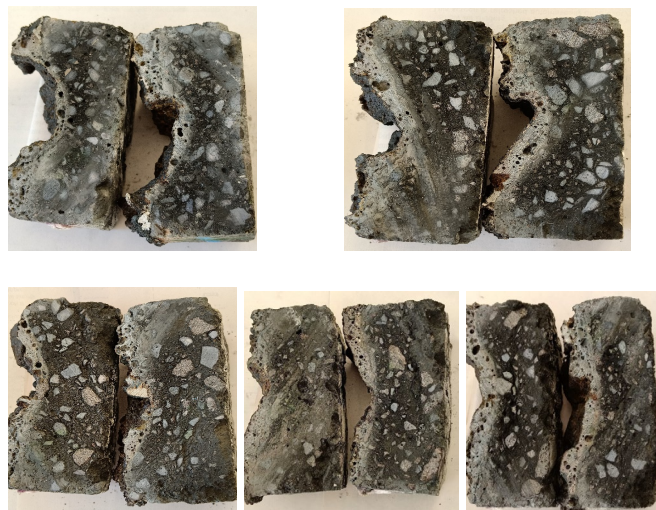


Fig. 8 Appearance of cut surface after slag corrosion (Clockwise – E1, E2, T-3, T-2, T-1)

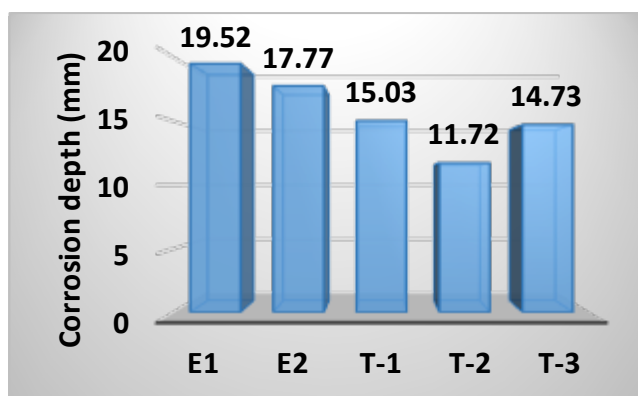


Fig. 9 Corrosion depth for different samples

Microstructure analysis is done through optical microscope for sample E-1 (maximum corrosion depth) and T-2 (minimum corrosion depth). The major phases are identified as corundum and silicon carbide for both the samples. For E-1, the penetration of slag occurs through matrix and matrix gets affected followed by grains dissolution (Fig.10). But in case of T-2, the penetration occurs through grain boundaries and minimum grain dissolution is observed and matrix is less affected. The recipe of T-2 is designed in such a way that it diverts the penetration from matrix to grain

boundaries and thus showing less penetration followed by less corrosion. Apart from various additives, T-2 recipe is having different amount of microsilica and carbonaceous compounds than others. The ratio of fused alumina and sintered alumina is also different in T-2.

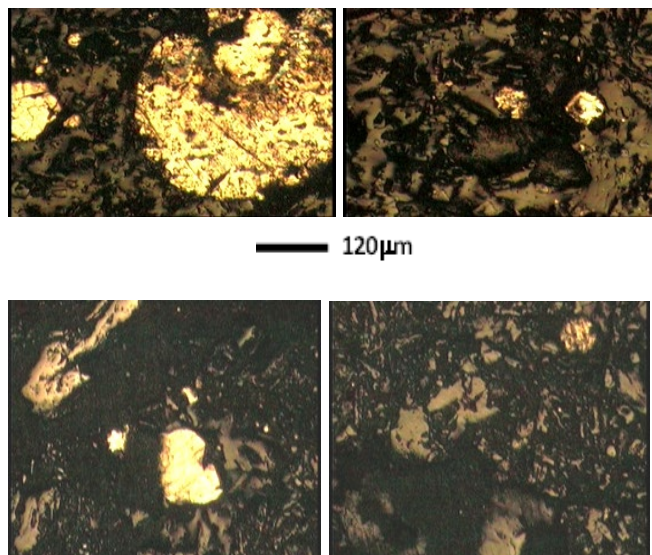


Fig. 10 Optical micrograph of E-1 (Top) and T-2 sample after slag corrosion (Interphase between slag and refractory)

Table IX: Hot metal throughput

Sl No	Material	HM throughput (MT)	Average HM throughput (MT)
1	E-1	101230	108801
2	E-1	110897	
3	E-1	110789	
4	E-1	111328	
5	E-1	109765	
6	T-2	154458	154118
7	T-2	136119	
8	T-2	142855	
9	T-2	162608	
10	T-2	174552	

Since T-2 recipe gave best results for slag corrosion resistance, this recipe was selected to be taken for plant trials. This material was applied in three different plants in slag runner. In all plants there is significant improvement in hot metal throughput. In Table IX, the hot metal throughput

for an integrated steel plant is given for E-1 castable and T-2 castable.

The actual performance with T-2 castable is ~ 41% higher than the existing castable which is supporting the outcome of slag corrosion test conducted in laboratory scale in induction furnace while designing this castable. Now, both supplier and steel makers are happy with this new castable suitable for high MnO slag.

CONCLUSIONS

Due to non-availability of good quality iron ores, most of the steel makers have started using low grades iron ores. Use of low grades of iron ores is a challenge for refractory manufacturers to maintain the similar performance of trough as different oxides, particularly MnO, has a strong effect on the performance of trough castable, specifically for slag runner. MnO, present in slag, affects the refractory in three ways while forming different low eutectic compounds resulting lowering the slag viscosity followed by penetration and corrosion of refractory. On the other hand, presence of MnO in slag increase the wettability of slag while lowering the solid angle between slag and refractory. To overcome the high corrosion of slag, one castable has been designed while changing the matrix with different additives. This newly designed castable shows ~ 40% improvement in slag corrosion resistance against the existing material. The newly designed castable is performing well in different plants and the actual throughput is increased in between 35% to 45% which is in line with slag corrosion behaviour observed in laboratory scale.

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