Modern hot metal desulfurization

Modern Hot Metal Desulfurization And Dephosphorization Technologies

Introduction

The purpose of phosphorus and sulfur removal is to decrease the concentration of these particles along with the undesired inclusions (oxides, borides, nitrides, carbides, and chlorides) to accomplish the final product quality requirements [5]. Dephosphorization involves low temperature, high slag basicity (CaO/ SiO2 ratio) and high oxygen activity whereas desulphurization entails high temperature, high slag basicity (CaO/ SiO2 ratio) and low oxygen activity. Initially, dephosphorization was performed by the addition of iron ores in the blast furnace runner. Soda ash (Na2CO3) was used in the blast furnace house during desulphurization. Subsequently, dephosphorization was improved by the subsurface injection of reagents in vessels, such as torpedo or submarine cars. Desulfurization was enhanced by co-injection of lime and magnesium into the hot metal transfer ladles [6].
The following dephosphorization and desulphurization technologies are reviewed:

1. Dephosphorization by the multirefining converter (MURC) process

2. Dephosphorization using CaO aggregates

3. Desulfurization by Magnesium

4. Desulfurization by flux injection using a new kinetic model

5. Desulfurization by the CFD modeling

1. Dephosphorization By The Murc Process

The multirefining converter (MURC) process claims to improve the efficiency of the dephosphorization procedure by reducing the cost and minimizing the slag volume. It is a new hot metal pretreatment in which dephosphorization and decarburization processes are developed in the same converter for further reduction of the decarburization slag.

The MURC process reduces the amount of slag by 50 % in comparison to the conventional pretreatment processes (30 %). The decarburization slag is continuously recycled (Figure 1). A low basicity dephosphorization slag is discharged from the MURC due to the high amount of total iron in the slag (T Fe) and no desiliconization treatment of the hot metal. This results into a valuable utilization of the dephosphorization slag in the steelmaking process.

2. Dephosphorization Using Cao Aggregates

The multiphase dephosphorization slag is analyzed through the addition of calcium ferrite flux powder into hot metal. It is observed that high [Si] content (0. 15 %) shows a similar CaO efficiency for dephosphorization than low [Si] content (0. 00 %). The low [Si] content exhibits calcium phosphate (3CaO. P2O5) whereas high [Si] content shows a combination of calcium silicate (2CaO. SiO2), and calcium phosphate. The formation of these solid phases explains a similar CaO efficiency under different [Si] content.

3. Desulfurization By Magnesium

Desulfurization is enhanced by the stirring effect of Mg bubbles in the hot metal. The reaction speeds up by the addition of lime and CaC2. These desulfurization reagents were tested in ArcelorMital Indiana Harbor. The typical inclusions before reagent injection were TiC and MnS. TiO2 is added to protect the graphite lining in the blast furnace. MgS + TiC and MgS were the most frequent inclusions after the reagent injection. MnS inclusions were not observed after this stage. This means, most of these inclusions floated up at the end of desulphurization. Further improvement of desulfurization can be achieved by Al addition. The latter reacts with lime to form lower melting point calcium aluminates.

4. Desulfurization By Flux Injection Using A New Kinetic Model

Desulfurization is performed by introducing powder reagents (CaO, calcium carbonate, calcium diamide carbonate) into the hot metal using either core wired or a carrier gas (nitrogen). This creates a complex variety of interfaces in torpedo ladles (Figure 2) [7]. There are two reaction modes that are present in the heterogeneous/ immiscible phases. The first mode is related to the transitory reaction between the liquid steel and powder particles. The second mode is the permanent reaction between the slag on the surface and the molten steel.

Desulfurization in torpedo ladles. The interfaces are: (1) Jet zone; (2) bubbles and particles rise in the plume zone; (3) bubbles emerge in the breakthrough zone; (4) slag zone; (5) gas-slag-metal emulsion forms in the dispersion zone; (6) metal reacts with lining in the lining zone; (7) lowest stirring intensity in the intermediate zone

Several parameters influence the desulfurization of hot metal and are predicted by a new model of submerged powder injection. The total amount of the flux is considered to be liquid at steelmaking temperature and the injection rate along with the time lapse can be determined. The total sulfur removal rate for both the permanent contact (top slag) and transitory (injection powder) mode is obtained by the following equation,

The right hand side of the reaction is related to the transitory reaction. This equation is only useful during the powder injection. After that, the right hand side becomes worthless.

Sulfide solubility in slag is restricted. Once the sulfide solubility limit is reached, a pure sulfide phase grows within the slag to absorb the excess of sulfur. Sulfide saturation may occur before the slag and metal reach equilibrium. The speed of the reaction is reduced until the sulfur content is dropped. Excess of sulfur in permanent reactions produces a reversion reaction and further desulphurization cannot occur. The transitory reaction removes the excess of sulfur by the continuously addition of fresh powder into the torpedo ladle. It is also recommended to deslag after powder injection.

Figure 3 is divided into [% S] wt % and reaction rate. The experimental results are obtained from the 20 CaO-60CaF2-20Al2O3 (by weight) powder injection under an argon atmosphere into 3. 4-3. 8 kg cast iron at 1310 °C. Once the slag (permanent-contact reaction) experiences an excess of sulfur at 420 s, the sulfur concentration decreases continuously until 950 s. The contributions of the permanent and transitory reactions are also displayed. The permanent reaction increases with time until it is saturated. The transitory reaction never approaches to saturation conditions. The difference between these two reactions is not significant large. Therefore, the contribution of these both reactions is generally equal.

5. Desulfurization By CFD Modeling

Synthetic slag is used on the desulfurization process due to its reuse in several treatments. The sulfur is transferred to the synthetic slag followed by slag regeneration. Slag regeneration is performed by the oxygen injection to produce gaseous sulfur dioxide (Equation 3). The sulfur distribution also differs from the slag and the metal once desulfurization begins (Figure 4). A porous plug at the bottom of the vessel is used to inject nitrogen in the hot metal. The fluid velocity is increased to optimize the desulfurization rate to improve sulfur transport. Therefore, CFD analyzes the desulfurization and slag regeneration processes to optimize the plug position and calculate the drift velocity of gas bubbles, desulfurization rate, among other parameters, for future design of desulphurization processes.

Conclusions

Multirefining converter (MURC)

(1) Dephosphorization and decarburization are carried out in the same converter, reducing the slag volume for better industrial, economical and environmental purposes

(2) The dephosphorization efficiency is increased by greater amounts of CaO to produce solid phases, such as 3CaOP2O5 and 2CaSiO2

Desulfurization by Mg

(1) TiC particles are nucleation sites for MnS and MgS

(2) MgS inclusions are the most frequent particles after the reagent injection

Desulfurization by flux injection using a new kinetic model

(1) A new model is developed to evaluate and identify separately the transitory and permanent reactions

(2) This model helps to predict the excess of sulfur to avoid reversion of it in the hot metal

(3) The contributions of the transitory and permanent contact reactions are observed to be in a similar proportion, concluding equal influence in the powder injection technique

CFD Modelling

(1) The desulfurization and slag regeneration are successfully modeled using thermal and transport mechanisms

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