Lecture 5: Physico-chemical properties of slag

Contents

Introduction

Viscosity

Basicity

Oxidation and reduction potential of slag

Slag foaming

Operational advantages

Quantification of slag foaming

Keywords: Foaming, electric steelmaking, basicity of slag, steelmaking reactions

Introduction:

This lecture discusses the physico-chemical properties of slag which are relevant in steelmaking. Slag is a multi-component system and in steelmaking it consists of acidic oxides such as SiO_2 and P_2O_5, and basic oxides such as FeO, CaO, MgO etc. In some slags Al_2O_3 is also present. In the last lecture we noted that acidic oxides are network formers, whereas basic oxides are network breakers.

Viscosity:

Viscosity controls the fluidity of slag. The slag should be fluid so that it can be removed easily during tapping of steel. In fact fluidity is inversely proportional to viscosity of slag. In general viscosity of a slag is a function of temperature, composition and percent solid present in slag.

Viscosity of any slag composition decreases with the increase in temperature as given by the following expression:

$$\eta_0 = A \exp\left(\frac{E}{RT}\right) \qquad\qquad (1)$$

η_0 is viscosity, A is an empirical constant, E is activation energy, T is temperature and R is gas constant. For a given temperature, addition of basic oxides decreases rapidly the viscosity of a slag which contains SiO_2 and P_2O_5. The decrease in viscosity is greater with alkaline oxides like Na_2O and fluorides like CaF_2 as compared with CaO and MgO for the reasons discussed in lecture 3.

Alumina acts as a network breaker in an acidic slag and network former in a basic slag.

Presence of solid particles in slag increases the viscosity of slag as shown in the following expression:

$$\eta = \eta_0 (1 - \epsilon)^{-2.5} \qquad\qquad (2)$$

Where ϵ is volume fraction of solids in slag

If volume fraction of the solid is in between 5% to 10%, viscosity of slag increases by 114% to 130%.
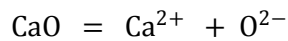
Basicity:

Basicity can be understood either from ionic or from molecular nature of slag. The ionic nature of slag assumes slag to consist of ions. In slags, acidic oxides can accept one or several O^{2-} ions, whereas a basic slag is a donor of O^{2-} ions. For example, 1 mole of SiO_2 can accept 2 moles of O^{2-} ions so that each tetrahedron in hexagonal structure becomes independent of each other. Similarly each mole of P_2O_5 can accept 3 moles of O^{2-} ions. Thus

$$\left.\begin{array}{l} SiO_2 + 2O^{2-} = SiO_4^{4-} \\ P_2O_5 + 3O^{2-} = 2(PO_4)^{3-} \end{array}\right\} \qquad\qquad (3)$$
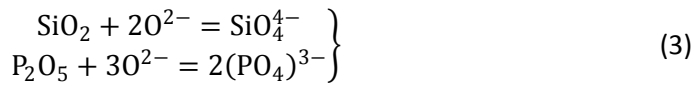
Amphoteric oxides behave as bases in presence of acid or as acids in presence of a base:

$$\left.\begin{array}{l} Al_2O_3 + O^{2-} = Al_2O_4^{2-} \\ Al_2O_3 = 2\,Al^{3+} + 3O^{2-} \end{array}\right\} \qquad\qquad (4)$$

Bases can supply O^{2-} ions

$$CaO = Ca^{2+} + O^{2-}$$

In a neutral slag enough oxygen ions will be present to ensure that each tetrahedron remains independent of each other. In binary $CaO - SiO_2$, slag will become neutral when CaO is 66.7%, which corresponds to the formation of $2CaO.SiO_2$. Slag will be basic only when CaO content is more than 66.7%. Basicity can be expressed in terms O^{2-} ions which are in excess than that required, thus satisfying the requirements of acidic oxides. In 100 g of slag

$$n_{O^{2-}} = \left(n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO}\right) + \cdots - \left(2n_{SiO_2} + 3n_{P_2O_5} + n_{Al_2O_3}\right) \qquad\qquad (5)$$

In industrial practice ionic definition of basicity is not useful; the molecular approach is more useful. The molecular approach assumes slag to consist of chemical compounds. The basicity of slag is

$$B = \frac{\text{weight \% CaO}}{\text{weight \% SiO}_2} \qquad (6)$$

In presence of different basic oxides, the different strength of the basic oxides should be considered. In a slag which contains CaO, MgO, SiO_2 and P_2O_5, the basicity is

$$B = \frac{(\text{weight \% CaO} + 0.66 \text{ weight \% MgO})}{(\text{weight \% SiO}_2 + \text{weight \% P}_2O_5)} \qquad (7)$$

In slag/metal reactions which involve desulphurization and dephosphorization, the concept of free lime in slag is useful. Free lime in CaO, SiO_2 and P_2O_5 slag is that amount which is available after the formation of neutral compound like $2CaO. SiO_2$, $3CaO. P_2O_5$

$$\text{Free lime (Kg)} = \text{Kg CaO} + 112/60 \text{Kg}(SiO_2) + 168/142 \text{Kg} (P_2O_5) \qquad (8)$$

For 100 ton hot metal with 1% silicon and 0.2% P the calculation shows that free CaO in slag would be available when CaO content exceeds 4540Kg.

Oxidation and reduction potential of slag

It refers to the capability of slag to transfer oxygen to and from the molten steel bath. FeO content of slag determines the oxidation potential of slag. Thus activity of FeO in slag is an important parameter. The equilibrium between FeO of slag and oxygen of steel is
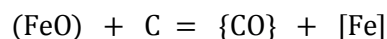
$$(FeO) = [Fe] + [O]$$
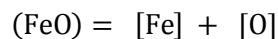
$$K = \frac{a_{(FeO)}}{a_{[O]}} \qquad (9)$$

 The activity of oxygen in metal is proportional to the activity of FeO in slag.

Slag foaming:

Foam is a dispersion of gas bubbles in a liquid. A liquid is said to be foaming when gas bubbles could not escape through the liquid and as a result height of the liquid increases. In steelmaking, slag foaming can occur due to the following reactions:

$$(FeO) + C = \{CO\} + [Fe]$$

This reaction occurs within the slag. The other reaction

$$[C] + [O] = \{CO\}$$
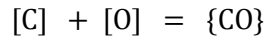
This reaction occurs at the gas/metal interface. In both the cases when the CO gas bubbles are unable to escape through the slag, the slag is said to be foaming. If the reaction between carbon and oxygen occurs deep into the bath i.e. reaction 2 then gas bubbles have enough time to grow in size and can easily escape through the slag layer as compared to when the gas bubbles are produced by reaction 2. The reaction 2 occurs within the slag

Is slag foaming desirable? Yes to the extent that slag should not flow out of the reactor. Slag foaming enhances the reaction area. In electric steelmaking foamy slag practice prevents the transfer of heat of the arch to the refractory lining.

Operational advantages: A foaming slag

- Shields molten steel against atmospheric oxidation
- Acts as a thermal barrier to prevent heat losses
- Shields the refractory lining particularly in electric arc furnace
- Control heat transfer from the post combustion flame

Quantification of slag foaming:

Foaming index = Foam layer thickness/ average gas velocity

Low foaming index means easy escape of gas bubbles which can be obtained either by smaller gas bubbles or higher gas velocities. Foam life is directly proportional to foaming index

Increase in slag viscosity increases foaming index. Presence of solid particles and surface active agents increases the foaming index. Addition of calcium fluoride decreases the foaming index by decreasing the viscosity of slag. Foaming index (FI) can be calculated from the physical properties of slag and size of the gas bubble:

$$FI = \frac{115 \, \eta_o (1-\epsilon)^{-2.5}}{(\rho\gamma)^{0.5} (d_b)^{0.9}} \qquad\qquad (10)$$

$\epsilon = $ Volume fraction of solids in slag

$\rho = $ Slag density kg/m^3

γ = Surface tension of slag N/m

d_b = Gas bubble diameter in m

Calculate the foaming index slag of composition 60% CaO, 35% Al_2O_3 and 5% S_iO_2 at 1773 K slag from the following data:

$\eta_o = 3.5 \frac{Kg}{ms}, \rho = 2500 \frac{Kg}{m^3}, \gamma = 1.1$ N/m and $d_b = 0.005$ m and 0.01m.

Substituting the value of the variables in eq. 10 we get

$FI = 904s$ for $d_b = 0.005$ m and 485 s for $d_b = 0.01$ m.

If the volume fraction of solid particles in slag is 0.1

$FI = 1175$ s for $d_b = 0.005$ m and 631 s for $d_b = 0.01$ m.

Note that foaming index increases to 1.3 times due to presence of solid particles in slag.

Consider a slag of composition 55% CaO, 35% Al_2O_3 and 1% C_aF_2 at 1873 K whose $\eta_o = 0.7$ Kg/ms, $\rho = 2700$ Kg/m^3 and $\gamma = 1.4$ N/m and $d_b = 0.01$m. This slag would have foaming index 9s. Foaming tendency decreases drastically due to production of CaF_2 in slag.

Reference to lectures 3 and 4

A.Ghosh and A.Chatterjee:: Ironmaking and steelmaking

Zhang and Fruehan: Metallurgical and Materials Trans. B, 26(8), 1995