CHAPTER 3

MASS BALANCE AND THEORETICAL CALCULATIONS

This chapter deals with the mass balance calculations for the melt and other theoretical calculations related to the reduction of composite pellets in smelting reduction process. An attempt is made to develop a mathematical model/formulation for mass balance in smelting reduction process and empirical relations for calculation of degree of reduction for composite pellets.

The basis for mass balance calculation can either be *weight* (1 kg or 1 tonne) or *mole* (1 mole). From industrial application point of view, *weight-basis* is more useful and has far greater relevance than *molar-basis*. In fact, it is more convenient to make efficient use of materials by weighing than that by counting moles. Therefore, *weight* is taken as the basis for development of mathematical model/formulation for mass balance calculations.

3.1 Importance of Mass Balance

The product output of any process depends on the amount of raw materials consumed and the chemical reactions taking place. Aim of mass balance calculations is to estimate the in-flow and out-flow of materials. These are essential part of plant records and routine calculations for plant operation. Such exercise is widely employed to obtain the accurate composition of a product with available raw materials and also for design of furnaces. A relatively complete accounting can be made from the knowledge of what species goes into the system and what species comes out from the system, with little or no need to consider the complexities and mechanisms of the processes within the system [156].

Before attempting to calculate the raw material requirements of a process, it is desirable to first obtain a clear picture of the process. The best way to do this is to draw a *block diagram*. These are very important for saving time and eliminating mistakes.

3.2 Material Balance Procedure

Material balance is essentially an application of the *law of conservation of mass*, i.e., *the mass of an isolated system remains constant irrespective of the changes occurring within the system.* It forms a sound basis for material balance calculations. The following equation describes in words the principle of general material balance applicable to processes both with and without chemical reactions.

$$\begin{pmatrix} Acculu lation\ of\ mass \\ within\ the\ system \end{pmatrix} = \begin{pmatrix} Input\ through \\ system\ boundaries \end{pmatrix} - \begin{pmatrix} Output\ through \\ system\ boundaries \end{pmatrix} \quad \ldots\ldots..(3.1)$$

The above equation can be written simply as:

$$(Acculu lation) = (Input) - (Output) \quad \ldots\ldots..(3.2)$$

The equation reduces further when there is no accumulation within the system, i.e., steady state. In that case one can write:

$$(Input) = (Output) \quad \ldots\ldots..(3.3)$$

This is applicable to a *batch process* which involves treatment of a given mass of materials in a process after which the products are taken out. If a process is operated such that, over long periods, continuous streams of materials enter into the processing unit and continuous streams leave the same then it is called a *continuous process.* In such a process, one is concerned with the rate of input and rate of output of materials. If the continuous process runs at steady state, then the chemical compositions of the input materials and output materials remain unchanged and there can be no accumulation within the system either. In such a situation, the material balance equation is written as:

(Rate of input of materials into the system)
= (Rate of output of materials from the system) ....(3.4)

In other words, for both batch process and continuous process, whatever goes in that must come out. It should be noted that material balance holds on the total mass of materials but not on moles. For material balance, a convenient basis of calculation is to be chosen. In continuous processes, it is either unit time (per hour or per day) or unit mass of product (e.g. one tonne of hot metal production for the blast furnace). For batch process, it is either the entire batch or unit mass of product [156].

3.3 Development of Mathematical Model for Mass Balance

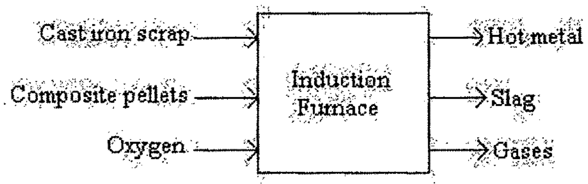

Fig. 3.1: Block diagram for melting in an induction furnace.

The process of smelting of composite pellets in an induction furnace is represented by the block diagram as shown in Figure 3.1. The input and output of the process are shown there itself. Table 3.1 also shows the input and output of the smelting of composite pellets in an induction furnace.

Table 3.1: Input and output (mass balance) of smelting process

Input (kg)	Output (kg)
Cast iron scrap (W_1)	Hot metal (W_3)
Composite pellets (W_2)	Gases and volatiles (W_{12}, W_{13}, W_{19}, W_{20}, W_{21})
Oxygen required from atmosphere (O_8)	Slag (W_{22})
Total input $= (W_1 + W_2 + O_8)$	Total output $= (W_3 + W_{12} + W_{13} + W_{19} + W_{20} + W_{21} + W_{22})$

Assumptions:

i) Basis of mass balance calculation is one tonne of hot metal produced,
ii) Loss of iron (Fe) to slag occurs in the form of FeO,
iii) Removal of sulphur occurs in the form of CaS only,
iii) No other elements (including iron) are oxidized during melting of cast iron scrap,
iv) 90 pct of carbon forms CO gas and remaining 10 pct forms CO_2 gas, and
vi) Fe_2O_3 present in composite pellets is reduced by the carbon present in composites.

Iron (Fe) balance

Fe input = Fe output

$\Rightarrow$ (Fe coming from cast iron scrap + Fe coming from composite pellets)

= (Fe present in hot metal produced + Fe loss to slag) .... (3.5)

$$\Rightarrow \left(\frac{W_1 \times I_1}{100} + \frac{W_2 \times F_1 \times F_2 \times F_3}{100 \times 100 \times 100}\right)\left(1 - \frac{F_4}{100}\right) = \frac{W_3 \times I_2}{100}$$

$$\Rightarrow \frac{1}{100} \times \left(W_1 \times I_1 + \frac{W_2 \times F_1 \times F_2 \times F_3}{10^4}\right) \times \left(\frac{100 - F_4}{100}\right) = \frac{W_3 \times I_2}{100}$$

$$\Rightarrow \frac{(W_2 \times F_1 \times F_2 \times F_3)}{10^4} = \left[\frac{100\,(W_3 \times I_2)}{(100 - F_4)} - (W_1 \times I_1)\right]$$

Therefore, weight of composite pellets require (W_2),

$$W_2 = \frac{10^4}{F_1 \times F_2 \times F_3}\left[\frac{100\,(W_3 \times I_2)}{(100 - F_4)} - (W_1 \times I_1)\right] \qquad \text{...........(3.6)}$$

Iron (Fe) loss to slag with respect to total Fe input, (W_4)

= (Total Fe input) x (Pct of Fe loss to slag)

= (Fe coming from cast iron scrap + Fe coming from composite pellets) x (Percent of Fe loss to slag)

$$\Rightarrow W_4 = \left(\frac{W_1 \times I_1}{100} + \frac{W_2 \times F_1 \times F_2 \times F_3}{100 \times 100 \times 100}\right) \times \frac{F_4}{100} \qquad \text{........(3.7)}$$

$$\left[Fe + \frac{1}{2}O_2 = FeO\right] \qquad \text{.........}(3a)$$

(56) (16) (72)

$$\textit{Since, weight of FeO form, } W_5 = \frac{72}{56} \times W_4 \qquad \text{........(3.8)}$$

Now, by substituting the Eq (3.7) *in Eq* (3.8), *we get*:

$$W_5 = \frac{72}{56} \times \frac{F_4}{10^4}\left[(W_1 \times I_1) + \left(\frac{W_2 \times F_1 \times F_2 \times F_3}{10^4}\right)\right] \qquad \text{........(3.9)}$$

Weight of oxygen require for oxidation of Fe loss to slag (O_1);

$$\textit{Since, } O_1 = \frac{16}{56} \times W_4$$

$$\Rightarrow O_1 = \frac{16}{56} \times \frac{F_4}{10^4} \times \left[(W_1 \times I_1) + \left(\frac{W_2 \times F_1 \times F_2 \times F_3}{10^4}\right)\right] = \frac{16}{72} \times W_5 \qquad \text{.....(3.10)}$$

SiO_2 balance

SiO_2 input = SiO_2 output

⇒ (SiO_2 in terms of Si present in cast iron scrap + SiO_2 present in iron ore of composite pellets + SiO_2 present in lime of composite pellets + SiO_2 present in coal ash of composite pellets) = (SiO_2 in terms of Si in hot metal produced + SiO_2 goes to slag) ....(3.11)

$$\Rightarrow \frac{W_1 \times I_3}{100}\left(\frac{60}{28}\right)+\frac{W_2 \times F_1 \times F_5}{100\times 100}+\frac{W_2 \times L_1 \times L_2}{100\times 100}+\frac{W_2 \times C_1 \times A_1 \times A_2}{100\times 100\times 100}=\frac{W_3 \times I_4}{100}\left(\frac{60}{28}\right)+W_6$$

$$[Si + O_2 = SiO_2] \qquad \text{.............}(3b)$$

(28) (32) (60)

Since, 28 kg of Si forms 60 kg of SiO_2

$$\therefore \left(\frac{W_1 \times I_3}{100}\right) \text{ Kg of Si forms } \left(\frac{60}{28}\times\frac{(W_1 \times I_3)}{100}\right) \text{ Kg of } SiO_2$$

Therefore, weight of SiO_2 *goes to slag* (W_6):

$$W_6 = \frac{60}{28\times 10^2}(W_1 \times I_3 - W_3 \times I_4)+\frac{W_2}{10^4}\left((F_1 \times F_5)+(L_1 \times L_2)+\frac{(C_1 \times A_1 \times A_2)}{100}\right) \text{.......}(3.12)$$

Now, weight of SiO_2 *form due to oxidation of* Si (Y_1):

$$Y_1 = \frac{60}{28\times 10^2}(W_1 \times I_3 - W_3 \times I_4) \qquad \text{........}(3.13)$$

Weight of oxygen require for oxidation of silicon (O_2):

$$O_2 = \frac{32}{28\times 10^2}(W_1 \times I_3 - W_3 \times I_4) \qquad \text{............}(3.14)$$

MnO balance

MnO input = MnO output

⇒ (MnO in terms of Mn present in cast iron scrap + MnO present in iron ore of composite pellets + MnO present in coal-ash of composite pellets) = (MnO in terms of Mn present in hot metalproduced + MnO goes to slag) .... (3.15)

$$\Rightarrow \frac{W_1 \times I_5}{100}\left(\frac{71}{55}\right)+\frac{W_2 \times F_1 \times F_6}{100\times 100}+\frac{W_2 \times C_1 \times A_1 \times A_3}{100\times 100\times 100}=\frac{W_3 \times I_6}{100}\left(\frac{71}{55}\right)+W_7$$

$$\left[Mn+\frac{1}{2}O_2 = MnO\right] \qquad \text{............}(3c)$$

(55) (16) (71)

Therefore, weight of MnO goes to slag (W_7):

$$W_7 = \frac{71}{55\times10^2}(W_1\times I_5 - W_3\times I_6) + \frac{W_2}{10^4}\left(F_1\times F_6 + \frac{C_1\times A_1\times A_3}{100}\right) \quad ....(3.16)$$

Weight of MnO form due to oxidation of Mn (Y_2):

$$Y_2 = \frac{71}{55\times10^2}(W_1\times I_5 - W_3\times I_6) \quad ....(3.17)$$

Weight of oxygen require for oxidation of manganese (O_3):

$$O_3 = \frac{16}{55\times10^2}(W_1\times I_5 - W_3\times I_6) \quad ....(3.18)$$

P_2O_5 balance

P_2O_5 input = P_2O_5 output

⇒ (P_2O_5 in terms of phosphorous present in cast iron scrap + P_2O_5 present in iron ore of composite pellets + P_2O_5 present in coal-ash of composite pellets) = (P_2O_5 in terms of phosphorous present in hot metal produced + P_2O_5 goes to slag) ....(3.19)

$$\Rightarrow \frac{W_1\times I_7}{100}\left(\frac{142}{62}\right) + \frac{W_2\times F_1\times F_7}{100\times100} + \frac{W_2\times C_1\times A_1\times A_4}{100\times100\times100} = \frac{W_3\times I_8}{100}\left(\frac{142}{62}\right) + W_8$$

$$\left[2P + \frac{5}{2}O_2 = P_2O_5\right] \quad ....(3d)$$

(62) (80) (142)

Therefore, weight of P_2O_5 goes to slag (W_8):

$$W_8 = \frac{142}{62\times10^2}(W_1\times I_7 - W_3\times I_8) + \frac{W_2}{10^4}\left(F_1\times F_7 + \frac{C_1\times A_1\times A_4}{100}\right) \quad ....(3.20)$$

Weight of P_2O_5 form due to oxidation of phosphorous (Y_3):

$$Y_3 = \frac{142}{62\times10^2}(W_1\times I_7 - W_3\times I_8) \quad ....(3.21)$$

Weight of oxygen require for oxidation of phosphorous (O_4):

$$O_4 = \frac{80}{62\times10^2}(W_1\times I_7 - W_3\times I_8) \quad ....(3.22)$$

CaO balance

CaO input = CaO output

$\Rightarrow$(CaO present in lime of composite pellets + CaO present in coal-ash of composite pellets) = (CaO goes to slag + Loss of CaO in the form of CaS to slag) ....(3.23)

$$\Rightarrow \frac{W_2 \times L_1 \times L_3}{100 \times 100} + \frac{W_2 \times C_1 \times A_1 \times A_5}{100 \times 100 \times 100} = (W_9 + W_{16})$$

Therefore, weight of CaO goes to slag (W_9):

$$W_9 = \frac{W_2}{10^4}\left(L_1 \times L_3 + \frac{C_1 \times A_1 \times A_5}{100}\right) - W_{16} \qquad ....(3.24)$$

Al_2O_3 balance

Al_2O_3 input = Al_2O_3 output

$\Rightarrow$ (Al_2O_3 present in iron ore of composite pellets + Al_2O_3 present in coal-ash of composite pellets + Al_2O_3 present in lime of composite pellets) = (Al_2O_3 goes to slag) ....(3.25)

$$\Rightarrow \frac{W_2 \times F_1 \times F_8}{100 \times 100} + \frac{W_2 \times C_1 \times A_1 \times A_6}{100 \times 100 \times 100} + \frac{W_2 \times L_1 \times L_4}{100 \times 100} = W_{10}$$

Therefore, weight of Al_2O_3 *goes to slag to* (W_{10}):

$$W_{10} = \frac{W_2}{10^4}\left(F_1 \times F_8 + \frac{C_1 \times A_1 \times A_6}{100} + L_1 \times L_4\right) \qquad ....(3.26)$$

MgO balance

MgO input = MgO output

$\Rightarrow$ (MgO present in coal-ash of composite pellets + MgO present in lime of composite pellets) = (MgO goes to slag) ....(3.27)

$$\Rightarrow \frac{W_2 \times C_1 \times A_1 \times A_7}{100 \times 100 \times 100} + \frac{W_2 \times L_1 \times L_5}{100 \times 100} = W_{11}$$

Therefore, weight of MgO goes to slag (W_{11}):

$$W_{11} = \frac{W_2}{10^4}\left(\frac{C_1 \times A_1 \times A_7}{100} + L_1 \times L_5\right) \qquad ....(3.28)$$

Carbon balance

Carbon input = Carbon output

$\Rightarrow$(Carbon coming from coal in composite pellets + Carbon coming from cast iron scrap) = (Carbon present in hot metal produced + Carbon converted into CO and CO_2 gases) ....(3.29)

$$\Rightarrow \frac{W_2 \times C_1 \times F_9}{100 \times 100} + \frac{W_1 \times I_9}{100} = \frac{W_3 \times I_{10}}{100} + W_C$$

Therefore, weight of carbon converted into CO *and* CO_2 *gases* (W_C):

$$W_C = \frac{1}{100}\left(\frac{W_2 \times C_1 \times F_9}{100} + W_1 \times I_9 - W_3 \times I_{10}\right) \qquad \text{..............(3.30)}$$

$$As \left[C + \frac{1}{2}O_2 = CO \right] \qquad \text{................(3e)}$$

(12) (16) (28)

Assuming that 90 pct carbon converts into CO gas and remaining 10 pct into CO_2 gas, the weight of CO gas form after reduction of iron oxide present in composite pellets (W_{12}):

$$W_{12} = \frac{28}{12} \times W_C \times 0.90 \qquad \text{.............(3.31)}$$

Weight of oxygen require for CO gas formation (O_5):

$$O_5 = \frac{16}{12} \times W_C \times 0.90 \qquad \text{.............(3.32)}$$

$$As \left[C + O_2 = CO_2 \right] \qquad \text{...............(3f)}$$

(12) (32) (44)

Weight of CO_2 gas form (W_{13}):

$$W_{13} = \frac{44}{12} \times W_C \times 0.10 \qquad \text{.............(3.33)}$$

Weight of oxygen require for CO_2 gas formation (O_6):

$$O_6 = \frac{32}{12} \times W_C \times 0.10 \qquad \text{............(3.34)}$$

Oxygen balance

Oxygen input = Oxygen output

⇒(Oxygen coming from iron ore present in composite pellets + Oxygen requires from atmosphere for oxidation of elements) = (Oxygen consumes for formation of FeO, SiO_2, MnO and P_2O_5 + Oxygen consumes for formation of CO and CO_2 gases)

.... (3.35)

$$As\left[Fe_2O_3 \rightarrow 2Fe + \frac{3}{2}O_2\right] \qquad ....(3g)$$

(160) (112) (48)

Oxygen coming from iron ore present in composite pellets (O_7):

$$O_7 = \left(\frac{W_2 \times F_1 \times F_2}{100 \times 100}\right) \times \frac{48}{160} \qquad ....(3.36)$$

Now, Oxygen require from atmosphere for oxidation of elements (O_8):

⇒ O_8 = (Oxygen consumes for formation of FeO, SiO_2, MnO and P_2O_5 + Oxygen consumes for formation of CO and CO_2 gases) – (Oxygen coming from iron ore present in composite pellets)

⇒ $O_8 = [(O_1 + O_2 + O_3 + O_4 + O_5 + O_6) - O_7]$ ....(3.37)

Sulphur balance

Sulphur input = Sulphur output

⇒ (Sulphur coming from cast iron scrap + Sulphur coming from coal-ash present in the form of SO_3 in composite pellets) = (Sulphur present in hot metal produced + Sulphur goes to slag) ....(3.38)

$$S + \tfrac{3}{2}O_2 = SO_3 \qquad ....(3h)$$

(32) (48) (80)

$$\Rightarrow \left(\frac{W_1 \times I_{11}}{100}\right) + \left(\frac{32}{80}\right) \times \left(\frac{W_2 \times C_1 \times A_1 \times A_8}{100 \times 100 \times 100}\right) = \left(\frac{W_3 \times I_{12}}{100}\right) + W_{14}$$

Therefore, weight of sulphur goes to slag (W_{14}):

$$W_{14} = \frac{1}{10^2}(W_1 \times I_{11} - W_3 \times I_{12}) + \frac{W_2}{10^6} \times \left(\frac{32}{80}\right) \times (C_1 \times A_1 \times A_8) \qquad ....(3.39)$$

As [CaO + S → CaS + ½ O_2] ....(3i)

(56) (32) (72)

Amount of CaS form due to reaction of sulphur with CaO (W_{15}):

$$W_{15} = \frac{72}{32} \times W_{14} \qquad ....(3.40)$$

Amount of CaO that converts into CaS (W_{16}):

$$W_{16} = \frac{56}{72} \times W_{15} \qquad ....(3.41)$$

Other balances

Amount of other oxides except SiO_2, MnO, FeO, Al_2O_3 and P_2O_5 coming from iron ore present in composite pellets (W_{17}):

$$W_{17} = \left(\frac{W_2 \times F_1 \times F_{11}}{100 \times 100}\right) \qquad \text{.............}(3.42)$$

Amount of FeO (W_{18}) that goes to slag due to presence of Fe_2O_3 in coal-ash:

$$As\ [Fe + Fe_2O_3 \rightarrow 3FeO] \qquad \text{............}(3j)$$

(56) (160) (216)

$$W_{18} = \frac{216}{160} \times \left(\frac{W_2 \times C_1 \times A_1 \times A_9}{100 \times 100 \times 100}\right) \qquad \text{..............}(3.43)$$

Amount of dextrose present in composite pellets (W_{19}):

$$W_{19} = \left(\frac{W_2 \times F_{12}}{100}\right) \qquad \text{............}(3.44)$$

Amount of volatile matters present in coal of composite pellets (W_{20}):

$$W_{20} = \left(\frac{W_2 \times C_1 \times F_{13}}{100 \times 100}\right) \qquad \text{..............}(3.45)$$

Amount of moisture present in coal of composite pellets (W_{21}):

$$W_{21} = \left(\frac{W_2 \times C_1 \times F_{14}}{100 \times 100}\right) \qquad \text{.............}(3.46)$$

Weight of slag produced (W_{22}):

$$W_{22} = (W_5 + W_6 + W_7 + W_8 + W_9 + W_{10} + W_{11} + W_{15} + W_{17} + W_{18}) \qquad \text{........}(3.47)$$

3.4 Stoichiometric Coal Requirement for Reduction of Iron Oxides

$$Fe_2O_3 + 3\,C = 2\,Fe + 3\,CO \qquad \text{.........(3.48)}$$

$$(160) \quad (36) \quad (112) \quad (84)$$

Since, reduction of 160 kg of Fe_2O_3 requires 36 kg of carbon

$$\therefore \textit{Reduction of W kg of } Fe_2O_3 \text{ requires } \left(\frac{36}{160}\times W\right) \textit{kg of carbon} \qquad \text{...........(3.49)}$$

$$\textit{Since, } W = W_0 \times \frac{F_2}{100} \qquad \text{..............(3.50)}$$

$$\text{and, } F_2 = \frac{160}{112}\times F_{10} \qquad \text{..............(3.51)}$$

From Eq (3.49) to (3.51), we get:

$$W_{car} = \frac{36}{160}\times W_0 \times \frac{160}{112}\times\frac{F_{10}}{100}$$

$$= \frac{36}{112\times 100}\times W_0 \times F_{10} \qquad \text{............(3.52)}$$

Since, F_9 kg of carbon is present in 100 kg of coal

$$\therefore \left(\frac{36}{112\times 100}\times W_0 \times F_{10}\right) \text{kg of carbon will be present in} \left(\frac{100\times 36\times W_0 \times F_{10}}{F_9 \times 112\times 100}\right) \text{kg of coal}$$

$$= \left(\frac{0.3214\times W_0 \times W_{10}}{F_9}\right) kg \text{ of coal.} \qquad \text{...........(3.53)}$$

Alternatively, it means that

$\left(\frac{0.3214\times W_0 \times F_{10}}{F_9}\right)$ kg of coal is required for the reduction of W_0 *kg* of iron ore

$$\text{Here, } \left(\frac{C_{fix}}{Fe_{tot}}\right)_{\text{stoichiometric ratio}} = 0.3214$$

$$\text{If } \frac{Fe_{tot}}{C_{fix}} = r$$

The amount of coal required for reduction of W_0 kg of iron ore in composite pellet (W_{coal}):

$$W_{coal} = \frac{W_0 \times F_{10}}{r \times F_9} \qquad \text{................(3.54)}$$

3.5 Measurement of Degree of Reduction

The degree of reduction can be obtained through single measurement of weight loss when a gaseous reductant is used. For reduction of iron oxides by carbon, the degree of reduction can not be found out directly from the weight loss of the sample, since this is made up of both oxygen and carbon losses. It is not possible to delineate the two unless the released gases are analyzed and their volumes are measured. Accordingly, such reactions have been studied with the help of gas chromatograph attach with the reduction chamber. Even this method runs into trouble when coal is used in place of carbon. Alternatively, the reaction product can be chemically analyzed after each test run, but this procedure is time consuming, more expensive and would give only intermittent information.

For ore-coal composite pellets, the weight loss of the sample arises not only from oxygen and carbon loss, but also the loss of volatile matters and residual moisture present in pellets [8]. Since only weight loss of the sample is not sufficient, some additional measurements are required for estimating the degree of reduction (α), which is defined as follows.

$$\alpha = \frac{weight\ of\ oxygen\ removed\ from\ iron\ oxide}{total\ weight\ of\ remvable\ oxygen\ present\ in\ iron\ oxides} \times 100$$

$$= \frac{\Delta W_0}{W_0^i} \times 100 \qquad \text{............(3.55)}$$

3.5.1 Review of methods for measurement of degree of reduction in composite pellets

For determining the degree of reduction for carbothermic reduction, research workers have employed various techniques. Most of the investigations have employed carbon, such as graphite, coconut char and coal char as reductant. In these cases, the product gas consists of CO and CO_2 only and its analysis is straight forward. However, that would not be the case if coal is used, because the other gases such as H_2, CH_4 etc would also be present.

Reeve et al [157] determined the rates of reduction of the composite pellet with iron oxide and char or coke. The progress of reaction was monitored by the increase in pressure within the constant volume system as measured by 0 to 760 mm absolute pressure transducer connected to a side arm in the cold part of the system. No information is available about the method of calculation of degree of reduction.

Srinivasan and Lahiri [158] mixed powders of natural hematite and graphite and prepared pellets by hand for reduction studies. They measured the progress of reduction with time by noting the weight changes in the pellet and product gas analysis. The amount of CO_2 absorbed in a given time interval was determined from the increase in weights of the absorption tubes. The amount of CO present in the out coming gas stream was determined from the weight change and CO_2 absorption data. At any instant, the degree of reduction was evaluated from the above data.

Shrivastava and Sharma [159] prepared a core pellet from the mixture of iron ore and coal and further coated it with the iron ore only. They determined the degree of reduction by using Eq. (3.55). Loss in weight due to carbon loss was calculated by estimating remaining carbon content in reduced pellet after each reduction. It was not clear how it was done. Oxygen loss was calculated by subtraction of other losses.

Dey et al [160] studied the reduction characteristics of hematite-noncoking coal composite pellets (size of fines from 40 to 80 μm, 10 mm pellets), and they found that reduction follows mixed kinetic laws which are dependent on temperature as well as on the degree of reduction. The data for 1173 K and 1223 K are fitted well by Jander's model. At 1273 K and above, and for α values less than 0.5, the data are fitted by a parabolic model $(\alpha \sim t^2)$, and for α values greater than 0.5, the data are fitted by Jander's model.

Prakash [150] carried out non-isothermal kinetic studies on reduction of iron ore-coal mixture under increasing temperature conditions up to 1273 K at 15 K min^{-1}. No external gas was used and the samples were allowed to establish their own atmosphere. Simultaneous thermal analysis plots showed step wise reduction of iron ore (coupled with oxidation of coal) and a change of reaction mechanism at about 973 K. In the case of

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thermal analysis data the degree of reduction (α) was expressed in terms of a pseudo-kinetic parameter, the fraction of reaction *(f_R)*, defined as:

f_R = (weight loss at time t) / (maximum possible weight loss) ....(3.56)

Dutta and Ghosh [27] employed non-isothermal method to determine the degree of reduction for iron ore-coal composite pellet. They passed argon at known flow rate through the reaction chamber containing composite pellet and then to analyze the composition of exit gas by gas chromatograph at several interval of time. In another method, further reduction of the partially reduced composite pellet was carried out by hydrogen in a thermogravimetric set-up. This allowed measurement of residual oxygen of iron oxide present in the partially reduced composite pellet and thus determination of degree of reduction.

The *degree of reduction*, $\alpha = \left(\Delta W_O / W_O^i\right) \times 100$ ....(3.57)

Where, ΔW_O = weight of oxygen removed from iron oxide

W_O^i = total initial weight of oxygen present in iron oxide

i) Rate of oxygen loss (W_o^* in g.s^{-1}) associated with evolution of CO and CO_2 was given as

$$W_O^* = \left(\frac{16Q}{22400}\right) \times \left(X_{CO} + 2X_{CO_2}\right) \qquad ....(3.58)$$

Where, Q = total gas flow rate at the exit, cm^3.s^{-1}

X_i = volume fraction of species *i* (CO, CO_2, CH_4 and H_2).

By graphical integration of W_O^* as function of time, total oxygen loss from iron oxide (ΔW_O in g) due to evolution of CO and CO_2 can be estimated as:

$$\Delta W_O = \int_0^t W_O^* \, dt$$ Where, t is the time in second.

ii) From Eq. (3.57); the degree of reduction can also be calculated after hydrogen treatment,

$$\alpha = \left(\frac{\Delta W_O}{W_O^i}\right) \times 100 = \left(\frac{W_O^i - \Delta W_O^H}{W_O^i}\right) \times 100 \qquad ....(3.59)$$

Where, ΔW_O^H = total oxygen loss during hydrogen reduction.

Hence, from oxygen loss data of hydrogen reduction of reduced pellets and total initial oxygen of composite pellet before non-isothermal / isothermal reduction, the degree of reduction can be calculated using Eq. (3.59).

Agrawal et al [161] prepared composite pellets of iron ore and coal using dextrine as binder. They used fraction of reaction *(f_R)* to study the extent of reaction of ore-coal composites. Isothermal reduction tests were performed at 1223 to 1373 K for 5 to 60 minutes. Reduced pellets were analyzed for fraction of reduction 'F' values, whereas 'f_R' values were obtained from weight loss measurements. Fraction of reaction *(f_R)* is defined as the ratio of weight loss of reacting mixture to the maximum possible weight loss (MPWL). This MPWL could be either the theoretically determined weight loss or an experimentally determined value. Based on the definitions of 'F' and 'f_R', a theoretical relationship between these two parameters was established [162]. The relationship can be expressed as:

$$F = f_R \times \left(1 + \frac{K_2 \times C_1}{K_1 \times F_1}\right) - \left(\frac{Weight\,loss\,from\,coal}{K_1 F_1}\right) \qquad \text{...............(3.60)}$$

Where, F = fraction of reduction, f_R = fraction of reaction, K_1 = Pct oxygen in ore, K_2 = Pct (moisture + volatile matter + fixed carbon) in coal, F_1 = Pct ore in the pellet, and C_1 = Pct coal in the pellet.

El-Geassy et al [46] prepared iron ore-fuel oil composite pellets containing 5 to 15 pct fuel oil as a binder and reducing material. These composite pellets were isothermally and non-isothermally reduced at 1023 to1273 K in a flow of H_2 and N_2 gases. The total weight loss resulting from oxygen removal from the reduction of Fe_2O_3 and from the thermal decomposition of fuel oil was continuously recorded as a function of time at different reduction conditions. The actual reduction extent at a given time was calculated from the chemical analysis of partially reduced samples at a given time and temperature.

Santos and Mourao [48] studied the reaction between iron oxides and carbon at temperature higher than 1473 K employing solid carbon or carbon dissolved in liquid iron as reductant. Iron oxides-carbon composite pellets were submitted for thermogravimetric analysis under inert gas in the range of 1473 to 1623 K. The fraction of reaction (f_R) was calculated by employing the expression,

$$f_R = \frac{W_i - W_t}{\Delta W_{\max}} \qquad \text{............(3.61)}$$

Where, W_i = initial weight of pellet

W_t = weight of pellet at time t

$\Delta W_{\max}$ = maximum weight loss attained by the pellet

Mourao et al [163] studied the kinetics of the carbothermic reduction of iron oxides using different materials (iron ore-charcoal composite pellets and iron ore-coke composite pellets) in the temperature range 1173 to 1373 K under argon and C/Fe_2O_3 ratio of 3. The main experimental technique employed was thermogravimetry in which the weight of the sample was registered as a function of time. Both isothermal as well as non-isothermal reduction studies were carried out and the parameter employed in the kinetic analysis was the reacted fraction (F), defined as:

$$F = \frac{\Delta W_t}{\Delta W_{\max}} = \frac{W_0 - W_t}{W_0 - W_f} \qquad \text{............(3.62)}$$

Where, W_0 = initial weight of the sample

W_t = weight of sample at time t

W_f = final weight of the sample attained in the experiment

Yang et al [164] prepared hematite-graphite composite pellets using a cold isostatic press and studied the carbothermic reduction of hematite in hematite-graphite composite pellets in an induction heating furnace at temperatures of 1373 to 1673 K. By use of the isothermal reduction method, effects of temperature, carrier gas flow rate and graphite particle size on the carbothermic reduction rate of hematite were investigated experimentally. A high frequency induction furnace (15 kW, 100 kHz) was used to heat a graphite crucible in which a high temperature isothermal zone was maintained. The reduction was greatly promoted because the contact area between the graphite and the iron oxide particles was remarkably increased and the heat conduction was greatly enhanced. Since increasing temperature can greatly activate the indirect reduction and the carbon solution loss reaction, the carbothermic reduction of hematite was greatly promoted.

With the assumption that the total amount of reduction of iron oxides by CO is equal to the amount of the carbon solution loss reaction, the overall reduction can be expressed as:

$$Fe_2O_3 + 3C = Fe + 3\,CO \qquad \text{..........(3.63)}$$

Since the molar ratio of Fe_2O_3 to C in the hematite-graphite composite pellets is 1: 3, the reduction degree (α) can be defined as the ratio of the pellet mass loss to the theoretical pellet mass loss on the assumption that the reaction (3.63) is completed. Thus the reduction degree (α) can be given as follows:

$$\alpha = \frac{(W_0 - W_f)\times 100}{W_0 \times \left(\dfrac{3M_{CO}}{M_{Fe_2O_3} + 3M_C}\right)} \qquad \text{...........(3.64)}$$

Where, W_0 = weight of pellet before reduction (g)

W_f = weight of pellet after reduction (g)

M_i = molecular weight of species *i* (g/mol)

Chowdhury et al [165] developed a semi-empirical model to determine the course of reduction of iron ore-graphite composite pellets over time in a laboratory scale side heated packed bed reactor attached with a tailor made bottom hanging thermogravimetric set-up. The particle size of less than 150 µm for both the ore and graphite powders were selected for the preparation of the composite pellets. The degree of reduction was estimated through weight loss and corresponding gas analysis. Assuming no CO in the exit gas, and neglecting any volatile loss, the degree of reduction (α) may be calculated by using the following relationship:

$$\alpha = \frac{\frac{32}{44}\times W_r}{f_o \times W_h}\times 100 \qquad \text{...........(3.65)}$$

Where, W_r is the weight loss during reduction, W_h is the weight of hematite in the pellet and f_o is the fraction of oxygen in hematite.

However, by knowing the exit gas composition, the degree of reduction may be calculated more accurately. If the volumetric ratio of CO/CO_2 in the exit gas is Z, the atomic ratio of oxygen/carbon (O/C) in the exit gas may be expressed in terms of Z as follows:

$$\frac{O}{C}=\frac{Z+2}{Z+1} \qquad \text{............(3.66)}$$

The weight ratio of oxygen/carbon (W_O/W_C) can also be expressed in terms of outgoing gas composition Z as follows:

$$\frac{W_O}{W_C}=\frac{Z+2}{Z+1}\times\frac{16}{12}=\frac{4Z+8}{3Z+3} \qquad \text{...........(3.67)}$$

and

$$\frac{W_O}{W_O+W_C}=\frac{4Z+8}{7Z+11} \qquad \text{...........(3.68)}$$

Then the degree of reduction (α) can be represented more precisely as

$$\alpha=\frac{\left(\frac{W_O}{W_O+W_C}\right)\times W_r}{f_o\times W_h}\times 100=\frac{\left(\frac{4Z+8}{7Z+11}\right)\times W_r}{f_o\times W_h}\times 100 \qquad \text{........(3.69)}$$

Wang et al [43] calculated the degree of reduction (α) for iron ore-coal pellet as follows:

$$\alpha=\frac{\textit{Total oxygen loss from iron oxides}}{\textit{Total removable oxygen present in iron oxides}}\times 100$$
$$=\frac{\Delta m_o}{m_o}\times 100 \qquad \text{..........(3.70)}$$

Total weight loss of a pellet (Δm_t, g), after reduction, is represented by

$$\Delta m_t=\Delta m_f+\Delta m_o+\Delta m_c \qquad \text{...........(3.71)}$$

Where, Δm_f = weight loss of volatiles in composite pellets, g

Δm_o = weight loss of oxygen in iron oxides, g

Δm_c = weight loss of carbon in composite pellets, g

Again, $\Delta m_f=m\times f_v$ ....(3.72)

Where, f_v = factor of devolatilization for iron ore-coal pellet

m = initial weight of composite pellets, g

Suppose that the final reactive result of reduction of iron oxides by carbon can be treated as a non-elementary homogeneous reaction:

$$Fe_xO_y + C = Fe_xO_{y-1} + CO \qquad \text{.........(3.73)}$$

Therefore, $\Delta m_c = \frac{12}{16} \times \Delta m_o = \frac{3}{4} \times \Delta m_o$ ....(3.74)

Now, Eq. (3.72) and (3.74) are substituted in Eq. (3.71) giving

$$\Delta m_t = (m \times f_v) + (\Delta m_o) + (\frac{3}{4} \times \Delta m_o)$$

$$= (m \times f_v) + (\frac{7}{4} \times \Delta m_o)$$

$$\therefore \Delta m_o = \frac{4}{7}[\Delta m_t - (m \times f_v)] \qquad \text{..........(3.75)}$$

Now, Eq. (3.75) is substituted in Eq. (3.70) giving

$$\alpha = \frac{4}{7m_o}[\Delta m_t - (m \times f_v)] \times 100 \qquad \text{.........(3.76)}$$

Eq. (3.76) is the original equation developed by Wang et al to calculate the degree of reduction (α) for iron ore-coal pellet.

Now, this equation is further modified by the author by incorporating the following.

Total removable oxygen present in iron oxide can be calculated as:

$$m_o = m \times f_{ore} \times \rho_{ore} \times f_o \qquad \text{...........(3.77)}$$

Where, f_{ore} = fraction of ore in composite pellets

f_o = fraction of oxygen in iron oxides

ρ_{ore} = purity of iron oxide

m = initial weight of the composite pellets, g

Now, f_v can be calculated as:

$$f_v = f_{coal} \times f_{vm} \qquad \text{...........(3.78)}$$

Where, f_{coal} = fraction of coal present in composite pellets

f_{vm} = fraction of volatile matters in coal

The fractional weight loss (f_{wl}) of a pellet is represented by

$$f_{wl} = \frac{\textit{Total weight loss of composite pellets}}{\textit{Initial weight of composite pellets}} = \frac{\Delta m_t}{m} \qquad \text{.........(3.79)}$$

Where, f_{wl} = fractional weight loss of pellet

Δm_t = total weight loss of composite pellets, g

m = initial weight of composite pellets, g

Now, Eq. (3.77), (3.78) and (3.79) are substituted in Eq. (3.76) giving

$$\alpha = \frac{4}{7} \times \left[\frac{(m \times f_{wl}) - (m \times f_{coal} \times f_{vm})}{(m \times f_{ore} \times \rho_{ore} \times f_o)} \right] \times 100$$

$$= \frac{400}{7} \times \left[\frac{f_{wl} - (f_{coal} \times f_{vm})}{(f_{ore} \times \rho_{ore} \times f_o)} \right] \qquad ....(3.80)$$

Eq. (3.76) takes into account of total release of volatiles in composite pellets while calculating the degree of reduction. However, the release of volatiles from composite pellet is gradual and occurs over a wide range of temperatures (523 to 1200 K). Therefore, the values of the degree of reduction (α) calculated by Wang et al's Eq. (3.76) at temperatures below 1200 K turn out lower than the actual degree of reduction. Further, non-isothermal reduction of composite pellets by thermal analyzer does not provide continuous recording of separate release of volatiles. Considering the above, a term f_{vr} is incorporated in Eq. (3.80) and hence, the modified equation of Wang et al is as follows:

$$\alpha = \frac{400}{7} \times \left[\frac{f_{wl} - (f_{coal} \times f_{vm} \times f_{vr})}{(f_{ore} \times \rho_{ore} \times f_o)} \right] \qquad ....(3.81)$$

Where, f_{vr} represents fraction of volatiles released at time t or at a particular temperature during reduction. In present investigation, Eq. (3.81) is used to calculate the degree of reduction of composite pellets.