Bath Smelting Slag Reactions
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Introduction
During the past decade there has been a tremendous worldwide effort to develop direct ironmaking processes that use coal in place of coke and have lower capital costs than the traditional blast furnace and coke oven route. A family of processes based on "bath smelting" of iron oxides using coal directly in a high energy intensity reactor and relying on post-combustion of CO and H\textsubscript{2} to be energy efficient have been under development. These processes include the AISI Direct Ironmaking process, the DIOS process, the ROMELT process, the CCF process, and the Hlsmelt process. The COREX process, which uses coal directly, has been commercially implemented and is not based on the concept of bath smelting.

Bath smelting processes can be categorized into "deep slag" and "liquid metal bath" reactors. In the "deep slag" reactors, most of the critical process phenomena occur in a thick slag layer which separates the metal from the oxygen/air jets and post-combusted gases. Post-combustion of CO and H\textsubscript{2} generated from coal devolatilization, and the reduction and primary combustion reactions take place in and above a foamed slag. Most of the energy generated from post-combustion is consumed in the slag phase. "Deep slag" reactors are employed by the AISI Direct Ironmaking, DIOS, ROMELT and CCF processes.

The Hlsmelt process utilizes a "liquid metal bath" reactor and the reduction and coal devolatilization reactions take place as the injected ore and coal pass through the metal phase. Post-combustion is conducted in the top space above the metal bath and heat is transferred to the bath via metal and slag droplets ejected into the top space. Detailed process descriptions are presented in other publications.\textsuperscript{1-6}

The results presented in this paper were obtained during a six year, $68.6 million collaborative program conducted by the American Iron and Steel Institute (AISI) and the United States Department of Energy (DOE).\textsuperscript{7-9} The research and development program, including pilot plant operations and laboratory research, resulted in the successful development of post-combustion smelting technology for the production of hot metal from iron ore pellets or steel plant waste oxides using coal. The AISI is currently pursuing efforts to commercialize the direct ironmaking and waste oxide recycling processes.

In this paper, the critical reactions and basic phenomena occurring in the slag in the bath smelting of iron are discussed. A schematic diagram of the "deep slag" reactor, indicating where some of the critical reactions occur, is shown in Figure (1). The role of the slag is of great importance in the bath smelting process. A typical smelting slag has a CaO/SiO\textsubscript{2} ratio of 1-1.3 and contains 7-13% Al\textsubscript{2}O\textsubscript{3}, 8-15% MgO and 2-6% FeO.
The key phenomena involving the slag discussed are listed below. The discussion will primarily be limited to reactions taking place in the slag although some of the basic principles apply to reactions occurring in the liquid metal bath as well.

• Coal Devolatilization
• Ore Dissolution
• Reduction Reactions
• Slag Foaming
• Post-combustion and Heat Transfer
• Sulfur Reactions

**Coal Devolatilization**

The coals used in the smelting processes have volatile matter ranging from 10-20% to 30-40% for low and high volatile coals respectively. Since devolatilization takes place at lower temperatures (500-1000 °C) than smelting temperatures (1450-1550 °C), the volatiles, which have considerable energy content, evolve shortly after the coal enters the vessel. Coal devolatilization has been extensively studied by Sampaio et al.\(^\text{10}\) It was found that the percentage of devolatilization is (i) independent of the coal type (ii) the same in a gas phase as in a slag phase and (iii) primarily controlled by heat transfer. Typical results shown in Figure (2) indicate that the volatiles are released within a few seconds.

**Ore Dissolution**

In all the bath smelting processes except the ROMELT process, the iron ore is pre-reduced using the reduction potential in the off-gas exiting the smelter. In the AISI process, the pre-reduction is done in a shaft furnace while in the DIOS and Hlsmelt processes, circulating fluidized beds are used. In the CCF process, a melting cyclone is used for pre-reduction. Thus, the iron oxides charged to the smelter can be in the form of lumps or pellets, fines, or molten oxides. These are gravity charged into the slag and iron oxide fines can also be injected.

Ozturk and Fruehan\(^\text{11}\) examined the rate of dissolution of wustite and hematite pellets and typical results are shown in Figure (3). The rate was found to be fast and was controlled by heat transfer. Calculations indicate that less than 1% of the slag would be comprised of undissolved pellets. Iron ore fines and molten iron oxides would dissolve even faster. During operation of the pilot plant, slag from the smelter was sampled periodically and undissolved pellets were never found in the slag samples. Therefore, it can be concluded that the dissolution of ore is a rapid phenomena and will not be process limiting in any way.

**Reduction of Iron Oxide**

The main reactions in smelting are the reduction of FeO dissolved in the slag. Reduction takes place through two main reactions: by carbon in the coal char (1) and by carbon dissolved in the metal droplets present in the slag (2).

\[
\begin{align*}
\text{(FeO) } + \text{ C (char) } &= \text{ Fe } + \text{ CO} \\
\text{(FeO) } + \text{ C (in Fe droplets) } &= \text{ Fe } + \text{ CO}
\end{align*}
\]

These reactions were extensively studied in laboratory experiments.\(^\text{12,13}\) It was found that the overall reactions take place via a combination of gas-metal (or char)
Figure 1: Schematic diagram of a "deep slag" smelting reactor indicating chemical reactions.

Figure 2: Fraction of volatile matter evolved as a function of time for three coal sizes (3, 6 and 9 mm) and two coal types (LD - low volatile and HDE - high volatile). Constant volume pressure experiments performed at 1793 K under high heating rate conditions.\textsuperscript{10}
Figure 3: Rate of dissolution of a wustite, a hematite, and a hematite pellet heated to 1073 K in 40% CaO-40% SiO\textsubscript{2}-20Al\textsubscript{2}O\textsubscript{3} slag at 1723 K.\textsuperscript{11}

Figure 4: Volume of CO evolved for the reaction of Fe-C drops with FeO in slag for low sulfur metal.\textsuperscript{12}
and gas-slag reactions represented by reactions (3) and (4) respectively.

\[
\begin{align*}
\text{CO}_2 + \text{C} & \text{ (char or in Fe droplets)} = 2 \text{ CO} \quad (3) \\
\text{CO} + (\text{FeO}) & = \text{Fe} + \text{CO}_2 \quad (4)
\end{align*}
\]

Typical results are shown in Figures (4) and (5) for the slag-metal and slag-carbon reactions respectively. The rate of reaction (1) is primarily controlled by the mass transfer of FeO to the gas-slag interface. The rate of reaction (2) is controlled by a combination of mass transfer of FeO and the chemical kinetics for reaction (3). The rate of reaction (2) depends on the CO\textsubscript{2} pressure at the interface which, in turn, depends on the FeO content of the slag because it is determined by the equilibrium conditions for reaction (4).

\[
P_{\text{CO}_2} = \frac{K_4 \ (%\text{FeO}) \ \gamma_{\text{FeO}} \ C \ \text{PCO}}{a_{\text{Fe}}} \quad (5)
\]

where,
- \(K_4\) is the equilibrium constant for reaction (4)
- \(\gamma_{\text{FeO}}\) is the activity coefficient of FeO
- \(C\) is a constant converting mole fraction into weight percent
- \(a_{\text{Fe}}\) is the activity of Fe

At high sulfur levels in the metal, the rate of reduction by metal droplets is controlled by reaction (3) and the rate can be computed by the partial pressure of CO\textsubscript{2} given by equation (5) and the independently measured rate for dissociation of CO\textsubscript{2}. As shown in Figure (6), the computed rate agrees with the measured rate.

Therefore, both reactions depend on the FeO content of the slag and the reduction rate in the smelting processes can be expressed as shown in equation (6).

\[
R = (k_d A_d + k_c A_c) (%\text{FeO}) \quad (6)
\]

where \(k_d\) and \(k_c\) are the rate constants for reactions (1) and (2) respectively determined from laboratory experiments, and \(A_d\) and \(A_c\) are the surface area of the droplets and char in the slag respectively. Generally, the amount of char and iron droplets increase as the slag weight \((W_s)\) increases. Therefore, the reduction rate can be simply expressed as:

\[
R = k W_s (%\text{FeO}) \quad (7)
\]

The rate constant \(k\) can be computed based on a knowledge of the amount and size of char and metal droplets in the slag and the rate constants obtained in the laboratory experiments for reactions (1) and (2).

Equation (7) has been found to reasonably represent the rate of reduction in the AISI and DIOS processes. Figure (7) shows the rate of reduction obtained at the AISI pilot plant with that calculated using equation (7). During pilot plant operation, the amount of char in the slag varied between 15\% and 35\% of the slag weight. As can be seen, the agreement between the measured and estimated reduction rates is good.

Based on the current understanding of the reduction of iron oxides from slag, it is possible to predict and control the rate of reduction during smelting in "deep slag" processes. This understanding is also directly applicable in process control during operation and in the scale-up of smelting reactors.
Less information is available for "liquid metal bath" reactors such as Hlsmelt. However, indications are that the rates of reduction of the injected particles in the iron bath is rapid and does not limit the overall production rate.

**Slag Foaming**

In the bath smelting processes, the specific gas flow rate, defined as the volumetric flow rate of the off-gas per unit vessel volume is large due to the prevailing smelting temperature and the direct use of coal. This results in considerable foaming of the slag and plays a significant role in the smelting process. Slag foaming increases the depth of the slag layer thereby further separating the gas phase from the liquid metal bath. The extent of slag foaming can impact post-combustion and heat generation, heat transfer, the amount of dust exiting the smelter, and stable operation of the smelting reactor. Slag foaming also has important implications with respect to the scale-up of smelting reactors.

Slag foaming is a complex phenomenon and it has been shown that the slag volume is proportional to the off-gas volumetric flow rate \( Q \) through the foam index \( \Sigma \).\textsuperscript{14-15} \[ V_f = \Sigma Q \quad (8) \]
\[ H_f = \Sigma V_g \quad (9) \]

where, \( H_f \) is the foam height and \( V_g \) is the superficial gas velocity.

Figure (8) shows typical results for the variation in the foam height with the superficial gas velocity. The foam index or the ability of a slag to foam depends on the properties of the slag, in particular, its viscosity. It was also found that the foam index was approximately inversely proportional to the bubble size. A general correlation to predict the foam index in terms of the properties of the slag and the bubble size was developed using dimensional analysis and is shown in Figure (9).

Small bubbles (< 3mm) are generated by the reduction reactions while large bubbles arise from char oxidation and bottom stirring. Therefore, the gas bubbles in the slag fall into two size distributions. Furthermore, other operating parameters also affect foaming. In particular, coal char greatly reduces foaming. It was found that the antifoam effect is primarily a result of the non-wetting nature of carbonaceous materials with slag which causes smaller foam bubbles to coalesce and reduces their residence time in the slag. In addition to the weight of char in the slag, the char size was also found to be a critical factor in controlling the slag foam. In general, the size of the char particles should be larger than the size of the gas bubbles for suppression of slag foaming.

Figure (10) shows the variation in the foam volume with the volumetric flow rate of the off-gas. The solid line represents a foam index of 0.5 seconds. As can be seen from Figure (10), the foam index measured during pilot plant operation was less than 0.5 seconds. This is consistent with the predicted foam index based on laboratory studies. Slag foaming is also affected by the lance position and the slag height was found to be inversely related to the lance position.
Figure 5: CO evolution rate for the reaction of FeO in slag with coke spheres.
1. Diameter = 1.5 cm and Initial FeO content = 10%. 2. Diameter = 1.42 cm and Initial FeO content = 8%.

Figure 6: The observed and computed rates of reduction of FeO from slag by iron-carbon droplets as a function of the reciprocal of the sulfur content.\textsuperscript{12}
Figure 7: Measured rates of reduction in the AISI smelter compared to the predicted rates (solid lines) as a function of the FeO content of the slag. Data for operation at slag weight of 4-5 tonnes. Solid lines represent calculated rates for 15% and 35% char in slag.

Figure 8: Foam height of CaO-SiO$_2$-FeO slags as a function of the superficial gas velocity at 1773 K.$^{14}$
Figure 9: The results of dimensional analysis considering the effect of the bubble size.\(^{16}\)

\[ N_\Sigma = \sum \mu g/\sigma, \quad M_0 = \mu^4 g/\sigma^3 p, \quad \text{and} \quad A_r = \rho^2 D_0^3 g/\mu^2 \]

Figure 10: Variation in the measured foam volume in the AISI smelter with the off-gas volumetric flow rate.
The laboratory studies and pilot plant work resulted in the development of an adequate understanding of the slag foaming phenomena such that it was possible to reasonably predict the extent of foaming based on the foam index, off-gas flow rate, char weight and lance height. This understanding was successfully utilized in process control during operation of the pilot plant and in scale-up.

**Post-combustion and Heat Transfer**

In the smelting reactor, the energy generation and energy utilization rates per unit reactor volume are high. The endothermic requirement for the rapid reduction reactions is satisfied by a combination of primary combustion of carbon and post-combustion of CO and H₂. At a post-combustion degree (PCD) of 40%, more than half the energy is supplied by post-combustion. The operating parameters affecting the PCD, which is defined below, include raw material and oxygen distribution, thickness of the slag layer, lance height, char weight and the operating pressure.

\[
PCD = 100 \times \frac{\%CO_2 + \%H_2O}{\%CO + \%CO_2 + \%H_2 + \%H_2O} \tag{10}
\]

The oxygen lance delivers oxygen through two sets of nozzles. Primary oxygen is delivered using "hard" jets which penetrate through a substantial portion of the slag layer. Primary oxygen is used mainly for the combustion of carbon. Post-combustion oxygen is delivered using "soft" jets and penetrates only the upper region of the slag. The consumption of oxygen involves the following phenomena: (i) Entrainment of furnace gases into the oxygen jet, (ii) Combustion of CO and H₂ in furnace gases with oxygen, and (iii) reaction of CO₂ and H₂O in the jet with char and Fe droplets which reduces the PCD.

In view of the above, it is imperative that the slag layer be adequately deep so that contact between the CO₂ and H₂O in the jet with the metal bath is minimized. Further, an adequately deep slag layer will result in a lower density of char and metal droplets per unit slag volume. This will lower the extent of reaction between CO₂ and H₂O in the jets with char and metal droplets and result in a higher post-combustion degree. The lance position relative to the slag height, defined as the lance gap, also affects post-combustion. Figure (11) shows the effect of the lance gap on the post-combustion degree for operation with an adequately deep slag layer. It is evident that a higher lance gap results in a higher post-combustion degree. This is because at a higher lance position relative to the slag height, the contact between the CO₂ and H₂O, in the post-combustion jets, with char and iron droplets present in the slag is reduced.

Heat transfer in the smelting process takes place via radiation and convection. The efficiency of heat transfer from combustion in the primary oxygen jets is high due to the fact that the jets penetrate through a substantial portion of the slag layer. The efficiency and mechanism of heat transfer from post-combustion is critical to the overall energy efficiency of the smelting process. If radiation were the main mode of heat transfer then the heat transferred will be related to the cross-sectional area of the
furnace. In this situation, the production rate will scale-up with the cross-sectional area. On the other hand, if convection is the main mode of heat transfer then the heat transferred can be related to a volumetric component. In such a case, the production rate can be scaled-up with the corresponding volumetric component.

Figure (12) shows the total heat transferred per unit vessel cross-sectional area as a function of the post-combustion degree for smelting reactors operating at different production rates. As can be seen, the total heat transferred per unit cross-sectional area at a given post-combustion degree is different for reactors operating at different production rates. This implies that radiation is not the main mode of heat transfer. Consequently, heat transfer and the production rate do not scale-up with the cross-sectional area of the smelting reactor.

Figure (13) shows the total heat transferred per unit total slag volume as a function of the post-combustion degree. The total slag volume represents the volume of the entire slag including the gas bubbles. It is evident that the total heat transferred per unit slag volume at a given post-combustion degree is the same irrespective of the production rate the reactor is operated at. This indicates that convection plays a significant role in heat transfer. The plot for the post-combustion heat transferred per unit slag volume as a function of the post-combustion degree shows is very similar to Figure (13) except that the values of post-combustion heat transferred per unit slag volume are correspondingly lower.

From Figures (12) and (13), it can be concluded that heat transfer is the bath smelting process scales-up according to the slag volume and not according to the cross-sectional area of the reactor. This is because convection makes a significant contribution to the total heat transferred in the process. It is worthwhile to note that heat transfer by convection occurs to slag, metal and char droplets in the free space, char and metal droplets in the slag, and circulation of the slag itself. Calculations indicate that the rates of heat transfer obtained during smelter operation can be explained by the heat transferred to metal droplets and char in the free space and slag.

**Sulfur Reactions**

Extensive investigations to study the thermodynamic and kinetic behavior of sulfur in the smelting process were conducted. Sulfur is introduced into the smelting reactor primarily with coal. The amount of sulfur retained in the slag and metal is dependent on the sulfur input, the rate at which sulfur is removed in the gas phase from the slag, and the amount of sulfur reporting to the gas phase during coal devolatilization and combustion. The sulfur partition ratio, \( L_s \), which is defined as the ratio of the weight percent of sulfur in the slag to that in the metal is largely determined by the chemical composition of the slag and temperature.

As in other iron and steelmaking processes, the sulfur partition ratio was found to be affected by the \( \text{CaO}/\text{SiO}_2 \) ratio in the slag and the \( \text{FeO} \) content of the slag. Figure (14) shows the variation in the sulfur partition ratio with the \( \text{CaO}/\text{SiO}_2 \)
Figure 11: Measured Post-combustion Degree in the AISI smelter as a function of the lance gap for operation with medium volatile coal.

Figure 12: Total heat transferred per unit vessel cross-sectional area for smelting reactors as a function of the post-combustion degree.
Figure 13: Total heat transferred per unit slag volume for smelting reactors as a function of the post-combustion degree.

Figure 14: Variation in the measured sulfur partition ratio in the AISI smelter with the weight ratio of CaO/SiO$_2$ in the slag.
ratio in the slag. The scatter in the data is a result of the variation in the slag FeO content and temperature. Figure (15) shows the effect of the slag FeO content on the sulfur partition ratio. Based on the pilot plant data, it was concluded that a higher sulfur partition ratio was favored by higher CaO/SiO₂ ratio in the slag, lower slag FeO content, and higher smelting temperature.

Sulfur transfer between the metal and the slag can be represented by the reaction shown below.

\[(\text{CaO}) + S = (\text{CaS}) + Q\]  \hspace{1cm} (11)

The sulfur partition ratio, \(L_s\), is related to the activity of oxygen in the metal by the expression shown below.

\[
L_s = \frac{K_{11} \gamma_{\text{CaO}} X_{\text{CaO}} f_s}{\gamma_{\text{CaS}} \gamma_{\text{S}} a_0 C_1} \hspace{1cm} (12)
\]

where,

\(K_{11}\) is the equilibrium constant for reaction (11)
\(\gamma_{\text{CaO}}\) is the Raoultian activity coefficient for \(\text{CaO}\)
\(X_{\text{CaO}}\) is the mole fraction of \(\text{CaO}\)
\(f_s\) is the Henrian activity coefficient for sulfur in the metal
\(\gamma_{\text{CaS}}\) is the Raoultian activity coefficient for \(\text{CaS}\)
\(a_0\) is the Raoultian activity for oxygen in the metal
\(C_1\) is a constant converting mole percent of sulfur in the slag to weight percent

The measured sulfur partition ratio obtained during pilot plant operation was compared with those predicted assuming the activity of oxygen was controlled by the \(\text{C-CO, Al-Al}_2\text{O}_3, \text{Mn-MnO, Si-SiO}_2,\) and \(\text{Fe-FeO}\) reactions. It was found that the predicted and measured values for \(L_s\) were in good agreement when the activity of oxygen was assumed to be controlled by the \(\text{Fe-FeO}\) reaction. Figure (16) shows the measured and predicted sulfur partition ratios. It can be concluded that the oxygen potential at the slag-metal interface is controlled by the \(\text{Fe-FeO}\) reaction and that the sulfur partition ratio can be predicted for a given slag composition and temperature.

A kinetic model to estimate the sulfur content in the slag and metal was developed. The variation in the sulfur content of the slag with time can be expressed as shown below.

\[
(%S)_t = \frac{C_2 - (C_2 - C_3 (%S)_0) e^{-C_3 t}}{C_3} \hspace{1cm} (13)
\]

\[
C_2 = 100 \left( \frac{\alpha F^C_S + \beta F^R_S}{W_s + W_m} \right) L_s \hspace{1cm} (14)
\]

\[
C_3 = \frac{dW_s}{dt} + \frac{1}{L_s} \frac{dW_m}{dt} + k_s \hspace{1cm} (15)
\]

\[
L_s = \frac{(%S)}{[%S]} \hspace{1cm} (16)
\]

where,

\([%S]\) is the sulfur content in the metal
\((%S)_t\) is the slag sulfur content at time=\(t\)
\((%S)_0\) is the slag sulfur content at time=0
\(\alpha\) is the fraction of sulfur, from coal, that enters the slag and metal
\(F^C_S\) is the sulfur input from coal (kg/min)
\(\beta\) is the fraction of sulfur, from recycled dust, that enters the slag and metal
\(F^R_S\) is the sulfur input from recycled dust (kg/min)
\(W_s\) is the slag weight (kg)
\(W_m\) is the metal weight (kg)
Figure 15: Comparison between measured sulfur partition ratios in the AISI smelter and those predicted, assuming Fe-FeO equilibrium, at 1500 °C as a function of the FeO content of the slag.

Figure 16: Comparison between the measured sulfur partition ratio in the AISI smelter with those predicted assuming the oxygen potential is controlled by the Fe-FeO reaction.
Figure 17: Comparison between predicted and measured sulfur levels in the metal and slag after batch addition of FeS$_2$ to the smelter slag.
$k_s$ is the rate constant for sulfur removal from the slag to the gas (kg/min %S)
$rac{dW_s}{dt}$ and $rac{dW_m}{dt}$ are the slag and metal production rates (kg/min) respectively.

At steady state, the sulfur content in the slag can be expressed as shown below.

$$\text{(S)}_{ss} = \frac{100}{\frac{dW_s}{dt}} \left( \alpha F_S^C + \beta F_S^R \right) + \frac{1}{L_s} \frac{dW_m}{dt} + k_s$$

The validity of this model was tested at the pilot plant in experiments where large additions of FeS$_2$ were made to the slag. Samples of the slag and metal were periodically taken and the sulfur content in the metal and slag were analyzed. The measured and predicted values of the sulfur content in the metal and slag were in good agreement as shown in Figure (17).

Thus, it can be concluded that detailed investigations helped develop a reasonably comprehensive understanding of the thermodynamic and kinetic behavior of the sulfur reactions. This allowed the sulfur path and the sulfur content in the metal, slag, and gas in the smelting process to be predicted.

Conclusions

The role of the slag in the smelting process is significant. The slag participates in all the critical process phenomena. As part of the AISI-DOE collaborative program to develop a coal based ironmaking process, extensive investigations were conducted to understand some of the key process phenomena such as coal devolatilization, ore dissolution, reduction of iron oxides, slag foaming, post-combustion and heat transfer, and the sulfur reactions. The studies combined laboratory and pilot plant research and resulted in a reasonable understanding of the smelting process and the role of the slag. Models based on fundamental principles of thermodynamics, kinetics, and heat and mass transfer were developed to explain the various phenomena. These models were validated using operating data from smelting reactors.

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