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Unique functions of slags in steelmaking

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Slags have many useful functions in iron and steel making. In particular, slags are used to remove impurities such as sulphur, phosphorus and inclusions from the metal, and a large amount of research has been done in this area. Slags also insulate the metal thermally and form reactions with the atmosphere such as reoxidation and nitrogen pick-up. However, slags serve other more unique functions, several of which are reviewed in this paper. The role of slags in new iron smelting processes with regards to reduction of ore and gaseous desulphurization are discussed. In iron smelting processes, much of the reduction occurs by the reaction of carbon in the char and the metal suspended in the slag with iron oxide dissolved in slags. The slags also react with the gas resulting in sulphur removal from the process. The mechanisms of these reactions and pilot plant data for these processes are given in this paper.

Slag formation within ferrous burden materials affects the cohesive zone and the performance of the blast furnace. Recent theoretical and experimental findings on this topic are presented. In the electric arc furnace, foamed slags are used to allow for higher power operation and productivity. Of particular interest, foaming in stainless steel production is more difficult than for normal steels. The foam index, or the ability of the slag to foam, for stainless steelmaking is similar to that for carbon steelmaking slags. The poor foaming is due to the lack of gas generation for the foam. Methods to increase foaming in stainless steelmaking are discussed.

Introduction

Slags are present in virtually all iron and steelmaking processes and have many functions. In particular, slags are used for the removal of impurities such as sulpghur, phosphorus and non-metallic inclusions. These areas have been the subject of an enormous amount of research. Slags also thermally insulate the metal and prevent reactions with the atmosphere in ladle processes. However, slags also have unique functions in a number of processes. In this paper several unique functions of slag in iron smelting, the blast furnace and the electric arc furnace (EAF) are presented along with recent research on these subjects.

Iron smelting

Over the past twenty years a number of direct iron smelting processes have been developed. In these processes, ore and coal are fed directly into a slag-metal bath at about 1500°C and the ore is reduced producing an iron carbon saturated metal. The processes eliminate cokemaking and, in several cases, ore agglomeration. The most highly developed of these processes are HIsmelt, DIOS and AISI which have recently been reviewed in detail.[1] The slag in these processes serves many functions including the refining of sulphur and phosphorus and heat transfer from post combustion. Two unique functions of slags in these processes are reduction and gaseous desulphurization. An evaluation of these processes, including reaction mechanisms and plant data, has been given in a recent publication.[1]

Reduction

In the DIOS and AISI processes, the ore, which may be partially reduced, typically by about 30% to FeO, is gravity fed into a large volume foaming slag.[1] The iron oxide dissolves into the slag which typically has 30–40% CaO, 25–40% SiO_2, 5–10% Al_2O_3, 5–8% MgO, and 3–7% FeO along with sulphur, phosphorus and other minor components. The actual slag chemistry depends on the ore used and other factors. The added coal becomes char and is suspended in the slag; typically 10–15% of the slag by weight is char. There are also Fe-C metal droplets in the slag which are ejected into the slag from the metal. The FeO is reduced out of the slag by the carbon in the char and metal.

$$(FeO) + C = Fe + CO \qquad [1]$$

As discussed elsewhere[1] in detail the rate of reduction (R) $\frac{\text{ton Fe}}{\text{hr}}$ can be given by:

$$R = kW_s(\%FeO) \qquad [2]$$

k = overall constant
W_S = weight of slag
$(\%FeO)$ = FeO content of the slag

The rate is shown to be a function of slag weight in Figures 1 and 2 and of FeO content in Figure 3. Remarkably the rate constants for three different vessels; two AISI and one DIOS vessel are in good agreement.

In HIsmelt the ore is injected into the metal where it is partially reduced, the partially reduced ore then enters the slag and is dissolved. In this case the reduction R is given by:

$$R = R_m + kW_s(\%FeO) \qquad [3]$$

where RM is the additional reduction done in the metal.

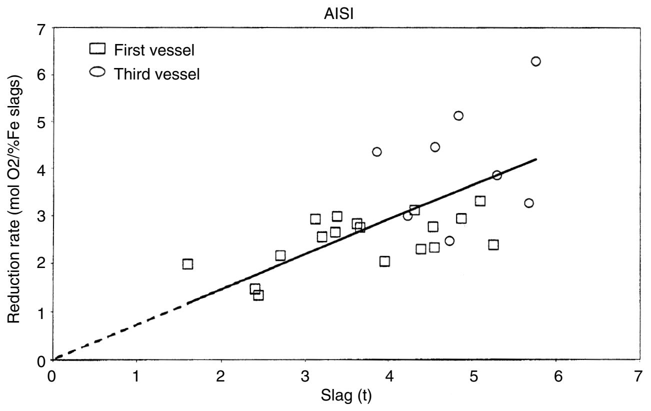

Figure 1. Rate of reduction versus slag weight for AISI (1550°C)

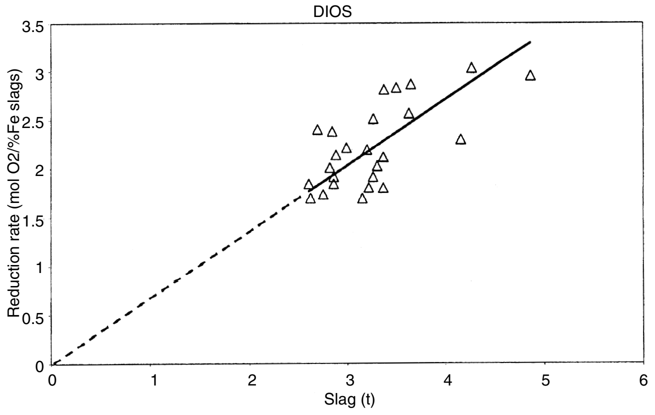

Figure 2. Rate of reduction versus slag weight for DIOS at Sukai Works (1550°C)

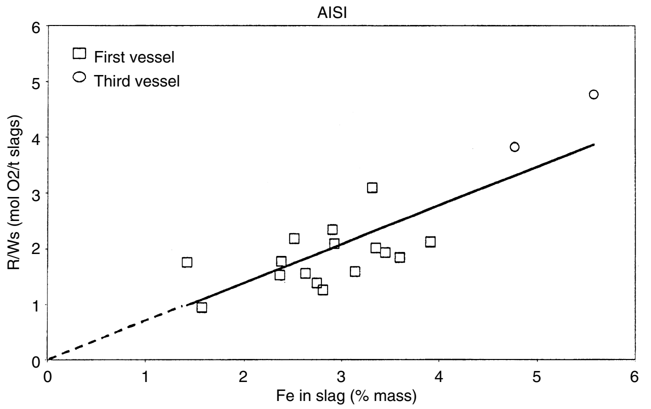

Figure 3. Rate of reduction versus Fe_T in slag for AISI (1550°C)

HIsmelt conducted several trials in which the ore injection was stopped and only reduction in the slag was possible. The results of these lists were used to compute the rate constant for reduction from the slag and was determined to be in agreement with that from AISI and DIOS. The analysis indicates that about 60% of the reduction occurred in the slag and 40% as the injected ore travelled through the metal in HIsmelt. The relationship between reduction rate versus FeO in the slag is shown in Figure 4. The intercept indicates the reduction in the metal, the additional reduction is done in the slag.

Gaseous desulphurization

In the new processes, coal is used directly, increasing the sulphur input into the reactor. Also, the process is run under more oxidizing conditions, higher FeO in the slag. Therefore, the sulphur distribution ratio between slag and metal (L_S) is much lower for smelting than for a blast furnace, possibly resulting in higher sulphur contents in the metal. However, in all three processes, gaseous desulphurization occurs. Sulphur primarily is introduced into the process with the coal and with recycled materials.

There are possibly two mechanisms for gaseous desulphurization. First, when the coal is added much of the organic sulphur is released into the gas and, as the coal burns, sulphur gaseous species are released. Also, due to the high temperature, and volume of gas, sulphur gaseous species are released from the slag. Much of this sulphur is recaptured from the off gas and may be re-introduced into the system with the recycled dust. When there is no recycle materials as much as 90% of the sulphur injected into the reactor leaves in the gas phase. The sulphur in the recycled materials is primarily FeS and CaS. When these are injected most of this sulphur enters the slag where it can be removed in the gas phase or be transferred to the metal.

The steady state sulphur content of the slag and metal is given by:

$$(\%S)=\frac{100\left(\alpha F_C^{\,S}+\beta F_S^{\,R}\right)}{\frac{dW_S}{dt}+\frac{1}{L_s}\frac{dW_M}{dt}+k} \qquad [4]$$

$$(\%S)=\frac{(\%S)}{L_S} \qquad [5]$$

(%S) = sulphur content of slag
[%S] = sulphur content of metal
1 = fraction of sulphur from coal entering slag
1 = fraction of sulphur from recycle entering slag
F_S^R = rate of sulphur input from recycle
F_S^C = rate of sulphur input from coal
WS = slag weight
WM = metal weight
LS = sulphur partition ratio
k = first order rate of removal of S from the gaseous species $\left(\frac{mass}{t(\%S)}\right)$

The first order rate constant depends on the actual rate controlling mechanism. For example, if the rate is controlled by mass transfer, the rate constant involves the

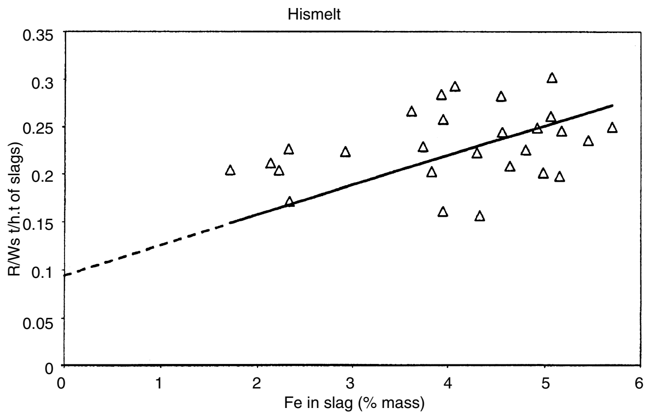

Figure 4. Rate of production versus Fe in slag for HIsmelt (1550°C)

mass transfer coefficient and the reaction surface area. If the gas is in equilibrium with the slag it is related to the equilibrium pressures of SO_2, H_2S and S_2 and the volume of gas. Results of pilot plant studies by AISI indicate maybe that perhaps α is relatively small (<0.25) and β is relatively large (>0.75). Also, results by HIsmelt indicate the k is relatively large.

If the slag is in equilibrium with the gas phase the rate of removal (R_S) is given by (6).

$$R_S = \frac{V_g(32)}{RT}\left('p_S'(\%S) + 2p_{s_2}(\%S)^2 \right) \qquad [6]$$

where $'p_S'$ = sum of SO_2 and H_2S pressures for 1%S in the slag
p_{S_2} = pressure of S_2 for 1%S in the slag
V_g = Volume rate of gas generation

If liquid phase mass transfer is controlling the rate, R_S is given by::

$$R_S = \frac{Am\rho}{100}\left[(\%S) - (\%S)_S\right] \qquad [7]$$

where A = slag-gas surface area
m = the mass transfer coefficient
ρ = density of the slag
$(\%S)_S$ = surface sulphur concentration

If both processes are affecting the rate, mixed control, the rate is given by:

$$R_S = \frac{(\%S)}{\dfrac{RT}{32V_g\,'p_s'} + \dfrac{100}{Am\rho}} \qquad [8]$$

In this case the pressure of S_2 is neglected or $'p_S'$ has an additional term which is approximately p_{S_2} divided by $(\%S)$ at steady state.

It is useful to estimate the rates for the two limiting cases given by Equations [6] and [7]. The pressures of the sulphur bearing gaseous species at 1773 K in equilibrium with a slag with a basicity of 1.15, and 130, 5% FeO and 0.5% S are listed in Table I. In Table II the assumptions used in the calculation and in Table III the computed rates are summarized. For 50% post combustion and the coals listed previously the volume of gas 1050 and 3075 m^3 (STP)/t for O_2 and air respectively.[3] To use Equation [6] it is necessary to know the production rate which is assumed to be 10 t/h in this example. The estimate rate of sulphur removal is approximately 0.66 and 1.92 kg for O_2 and air as the combustion, respectively.

The problem in using Equation [7] is estimating the slag-gas surface area. The planar surface area of a 10 t/h reactor is about 15 m^2. However, the total surface area will be much larger. For HIsmelt it would be the area of the slag droplets while for AISI-DOE type processes it would be that of the slag foam. In either case, a conservative estimate would be 100 to 200 m^2. To put this in perspective, one tonne of slag particles with an average Sauter diameter of 1 cm would have an area of about 100 m^2. The value of m is estimated to be 1.5×10^{-5} m/s. Using these values, the rate for liquid phase mass transfer control for a slag containing 0.5%S would be 0.22 to 0.44 kg/s.

Whereas mass transfer is expected to be the more important process, gas saturation or equilibrium should not be neglected and mixed control should be considered. For HIsmelt (enriched air) and AISI-DOE (O_2), the mixed control rates will range from 0.20 to 0.35 and from 0.17 to 0.26 kg/s respectively for the assumed case. If the oxygen potential of the gas increases, the temperature increases, or slag basicity decreases, the rate of vaporization increases. However, the overall rate only increases slightly since it is primarily controlled by mass transfer.

It is now possible to estimate the sulphur content at steady state using Equation [4]. For a coal containing 1%S and consumption of 600 kg/t and consumption of 600 kg/(t of hot metal), the sulphur input is 6 kg/t.[3] If the fraction entering the slag-metal system (α) is equal to one, the slag is 200 kg/t of hot metal and L_S is two the steady state sulphur content can be estimated. Using a value of k equal to 0.5 kg S/(%S), for k the steady state sulphur content, when adding coal only and no recycle would be 0.65%S, which is generally higher than observed. Even if the rate of sulphur vaporization was twice as high as estimated the steady state level would be 0.54%S. This indicates that the fraction of sulphur actually entering the slag-metal system from the burning of coal is less than one. Presumably, the first atom of S from FeS_2 in the coal goes off directly as well as an organic sulphur. This represents roughly about half the sulphur so (α) may only be 0.5 which reduces predicted steady state sulphur to 0.25 to 0.3%, which is similar to that observed.

In any case, over 75% of the sulphur leaves in the gas phase either by vaporization during the combustion of the coal or by vaporization from the slag. Much of this sulphur

Table 1
Equilibrium pressure of SO_2, H_2S and S_2 with smelting gas 50% post combustion using O_2 or air and slag containing 0.5%S

Gas	CO	CO_2	H_2	H_2O	N_2
O_2	0.39	0.31	0.05	0.16	
Air & O_2	0.20	0.15	0.03	0.09	0.49
B	Gas	SO_2	H_2S	S_2	
1.15	Air + O_2	0.023	0.015	0.063	
1.30	Air + O_2	0.014	0.008	0.018	
1.15	O_2	0.024	0.015	0.063	
1.30	O_2	0.014	0.009	0.016	

Table II
Assumed conditions for computing the rate of vaporization for assumed cases and steady state sulphur content

PC 50%
Production 10 t/h Hot Metal
Slag-Gas Area 100 m^2
Temperature 1500°C
600 kg of coal (1%S) per tonne hot metal
200 kg of slag per tonne of hot metal
0.5% Sulphur in slag for rate calculations

Table III
Computed rates for assumed conditions given in Table II

	Rates of Sulphur vaporization kg/s	
	O_2 (AISI-DOE)	HIsmelt (air)
Saturation	0.66	1.92
Mass Transfer	0.22–0.44	0.22–0.44
Mixed Control	0.17–0.26	0.20–0.35

is converted to CaS and FeS by reaction with CaO and FeO in the dust as it cools. If the dust is recycled then the sulphur input will increase as well as the steady state sulphur content. The sulphur content of the metal can be reduced by limiting recycling or attempting to control the off gas system to reduce the amount of sulphur gaseous species reacting to form CaS and FeS.

Cohesive zone in the blast furnace

In general, slags perform useful functions in iron making and steel making. However, in some cases, they may cause problems. All ferrous burden materials added to a blast furnace contain gangue, the major component often being SiO_2. As the ore is reduced the FeO reacts with the gangue materials forming a slag which causes the burden materials to soften. The zone in which softening begins and the burden materials completely melt is called the cohesive zone. In this zone, the gas flow through the furnace is affected. In general, a cohesive zone low in the furnace and a short zone is desired.

To understand the basic phenomena involved in softening and melting a multi-faceted research program is being performed. The research includes characterization of the burden materials with respect to gangue chemistry and distribution, observation of melting using a laser confocal microscope, softening/melting experiments of pellets with x-ray observations, and thermochemical modelling to predict phases present.[4–5]

In this paper, only the softening/melting experiments and modelling aspects for commercial acid and basic pellets will be briefly discussed. More details can be found in other publications.[4–5] The simplified chemical composition of the pellets are given in Table IV. Other types of pellets and burden materials have been also studied. The experimental set-up is shown in Figure 5. Six pellets were in the reactor for each experiment. The samples were subjected to a 100 kpa load and the displacement was measured with a Linear Variation Displacement Transducer (LVDT). The pellets were prereduced to 60 or 80% to simulate conditions in the blast furnace prior to being put into the apparatus.

Typical results with regards to the displacement or compression of the pellets as a function of temperature are shown in Figures 6 and 7. From the behaviour of the curves, the softening and melting temperatures can be determined. These are given in Table V for the pellets in question. It is clear that the softening of the acid pellets occur earlier and the melting zone is larger. This was confirmed by x-ray observations as shown in Figures 8 and 9. Since reduction is occurring during the heating, the temperature rate of the cohesive zone would be more accurately defined as the softening at 60% reduction and melting at 80% reduction.

As is well known, the lower softening temperature of the acid pellets is due to the reactions of SiO_2 and FeO forming a low melting point slag. Thermo-chemical modelling of the evolution of the slag phase is being conducted using

Table IV
Simplified pellet composition

	wt per cent					
	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	Basicity
Acid	92	4.9	0.3	1.2	0.6	0.23
Basic	90	4.0	0.4	4.2	1.0	1.05

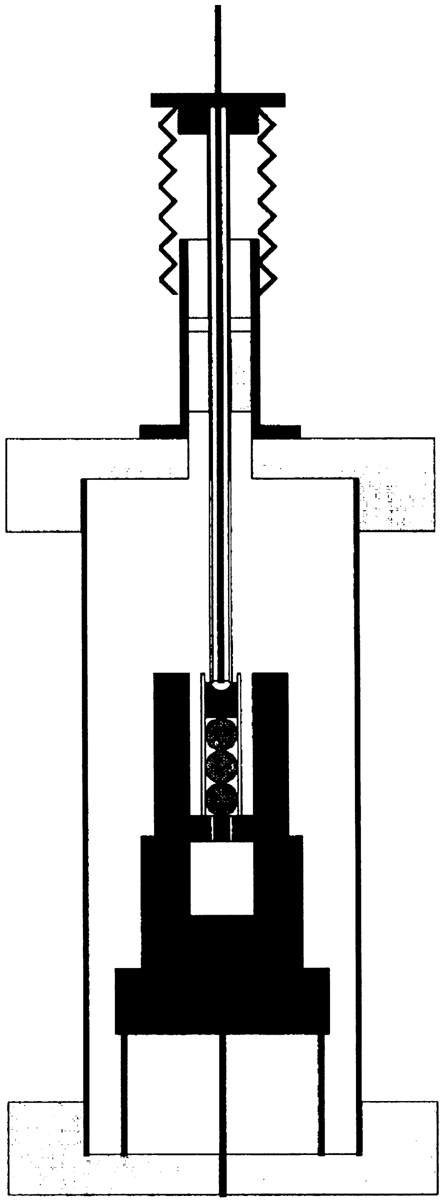

Figure 5. Experimental apparatus for measuring and observing softening and melting of ferrous materials

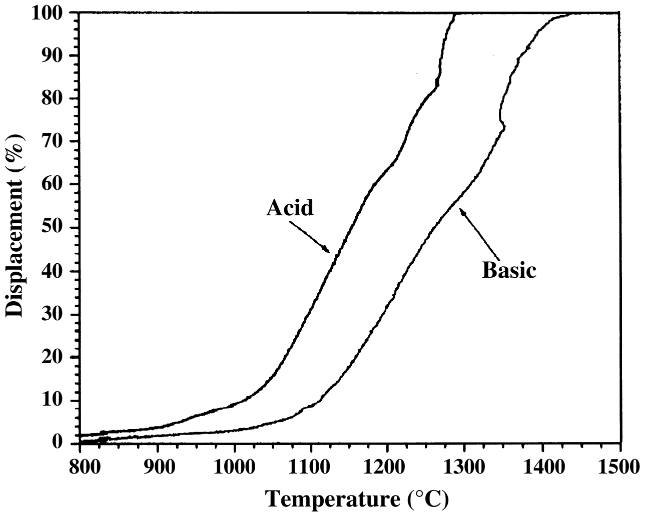

Figure 6. Displacement versus temperature curves for pellets at 60% reduction

FACTSAGE. For example, the fraction of each phase is plotted versus temperature as a function of temperature in Figures 10 and 11. It is evident that the temperature at which the slag begins to form is lower for the acid pellets. For example, the first liquid slag is formed at 1130°C and 1180°C for the acid and basic pellets respectively. These calculations indicate higher softening temperatures than observed, possibly because the calculations are for the bulk composition. The local composition may have lower melting gangue compositions and are being investigated. Therefore, thermo-chemical modelling is being done on the local gangue composition, as well as the bulk composition, since the pellets are not homogeneous. From the results of the multi-faceted research the design of the chemistry of pellets and sinters as well as the charging pattern for mixed burden should be optimized to improve the operation of the blast furnace.

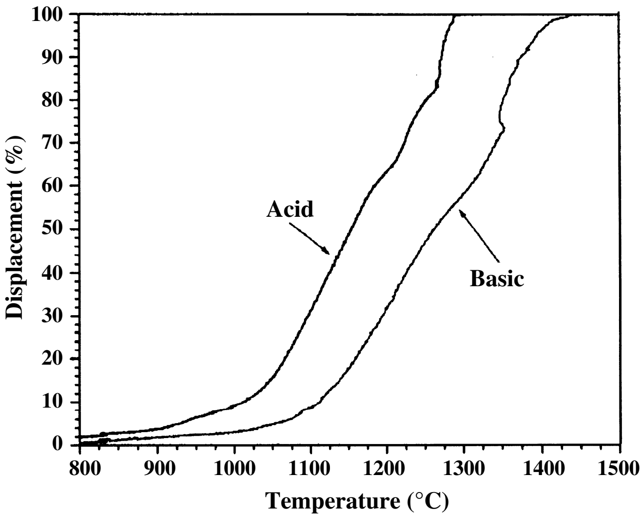

Figure 7. Displacement versus temperature curves for pellets at 80% reduction

Table V
Softening and melting temperatures for acid and basic pellets at 60% and 80% reduction obtained for displacement temperature curves

	Acid	Basic
60% Reduction	**(°C)**	**(°C)**
Softening	1042	1100
Melting	1271	1354
80% Reduction		
Softening	1070	1015
Melting	1356	1384
T	314	284

ΔT Melting 80% - Softening (60%)

Slag foaming in the EAF

Slag forming in the EAF in which the foamed slag protects the refractories from the electrical arc allows for longer arcs or higher voltages. This results in higher energy input and, therefore, higher productivity. In most cases the foam is generated by injecting carbon into the slag where it reacts with FeO, reaction (1), producing CO which causes the slag to foam. The ability of a slag to foam is characterized by its foaming index (Σ) which can be defined by Equations [9] and [10].

$$\sum = \frac{H_f}{V_g} \qquad [9]$$

$$V_g = \frac{Q}{A} \qquad [10]$$

H_f = foam height
V_g = gas velocity
Q = gas flow rate
A = container cross section area

The foam index for typical stainless steelmaking slags was determined by measuring the foam height as a function of superficial gas velocity in laboratory experiments.[6] Typical results for stainless steelmaking slags are shown in Figure 12. The foam index for these slags was similar to that for normal steelmaking slags without chrome oxide. When second phase precipitates begin to form these particles stabilize the foam by increasing the slag viscosity. However, when the amount and size of the second phase particles become large it is not possible to foam the slag. This behaviour is shown in Figure 13.

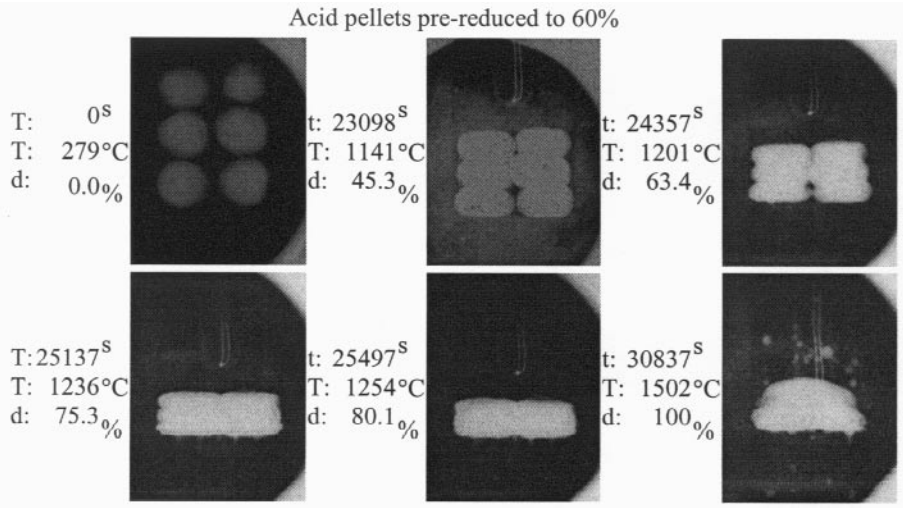

Figure 8. X-ray observations for acid pellets with 60% reduction under load

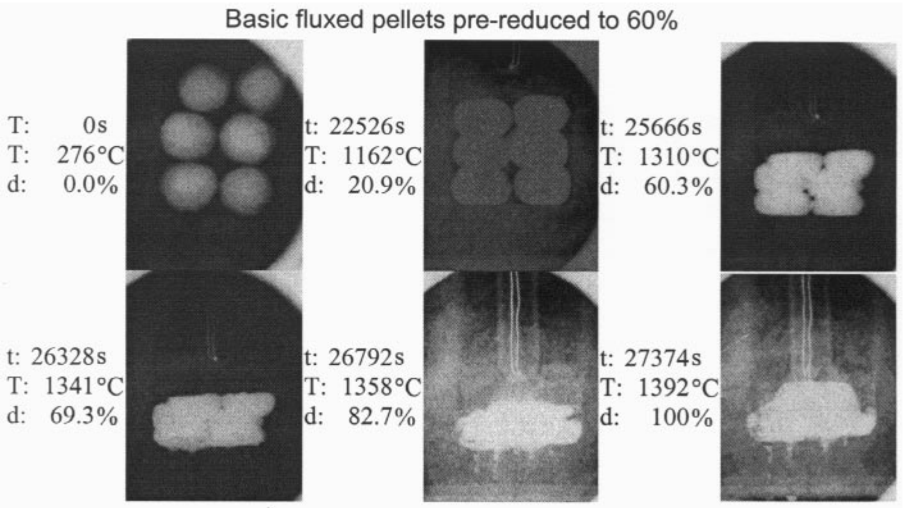

Figure 9. X-ray observation for basic pellets with 60% reduction under load

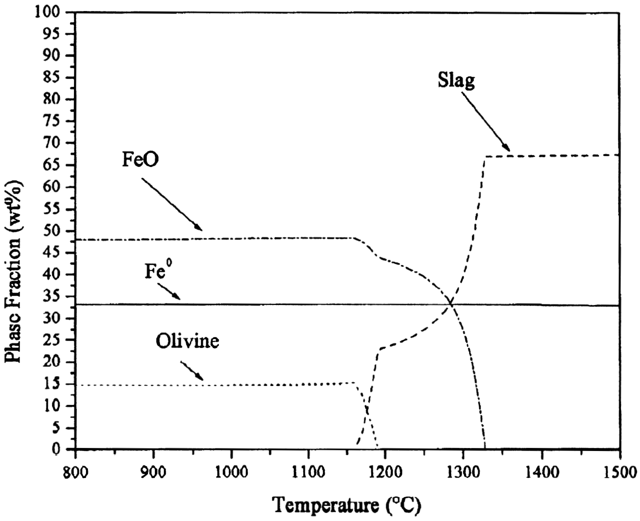

Figure 10. Thermo-chemical calculation by FACTSAGE of phase fractions for acid pellets (60% reduction)

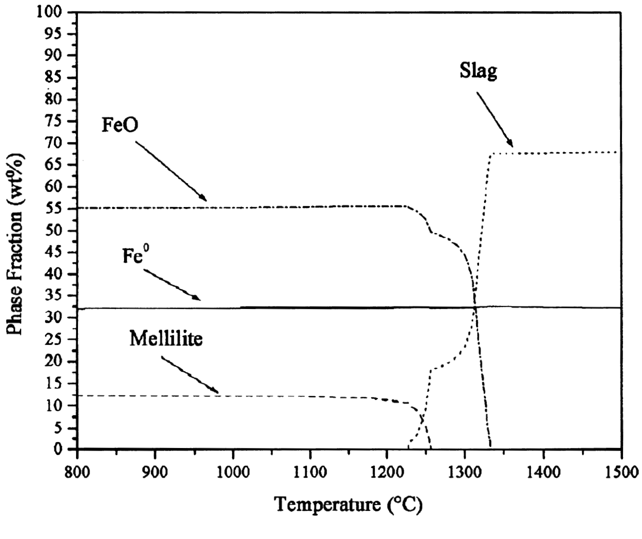

Figure 11. Thermo-chemical calculation by FACTSAGE of phase fractions for basic pellets (60% reduction)

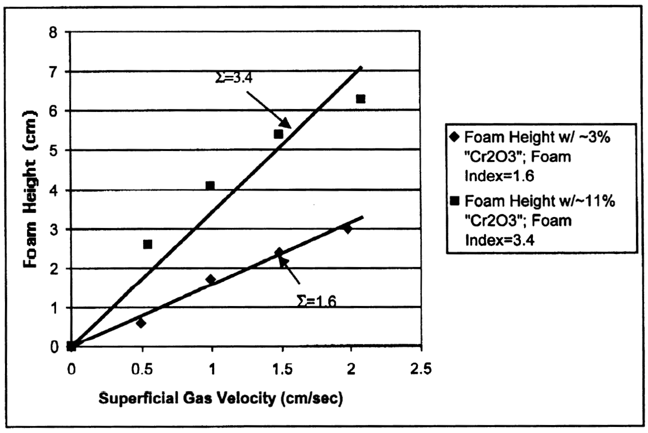

Figure 12. Typical experimental results of foam index measurements for stainless steelmaking slags

The inability to foam a stainless steelmaking slag is not due to a low foam index but, rather, the inability to generate gas at a sufficient rate. The gas is generated by the reaction of injected carbon with either FeO or 'CrO' in the slag. Stainless steelmaking slags have little FeO and the main reducible oxide is CrO.

$$(FeO) + C = CO + Fe \qquad [11]$$

$$(CrO) + C = C + Cr \qquad [12]$$

The rate of reaction (12) is much slower than reaction (11) which would explain the poor foaming in stainless steelmaking. The rates of reactions (11) and (12) were measured in the laboratory using a constant volume pressure increase technique (CVPI). In the experiments, a carbon cylinder is submerged into the slag and the rate of CO generation is determined by the pressure increase in a closed vessel. Typical results for FeO reduction are shown in Figure 14, the rate for CrO was too slow to be measured using this technique. The researchers were able to explain the results based on the rate of oxidation of carbon by CO_2 which is a gaseous intermediate in the reaction sequence. The pressure of CO_2 in the case of CrO is very low due to the stability of CrO. Therefore, the poor foamability of

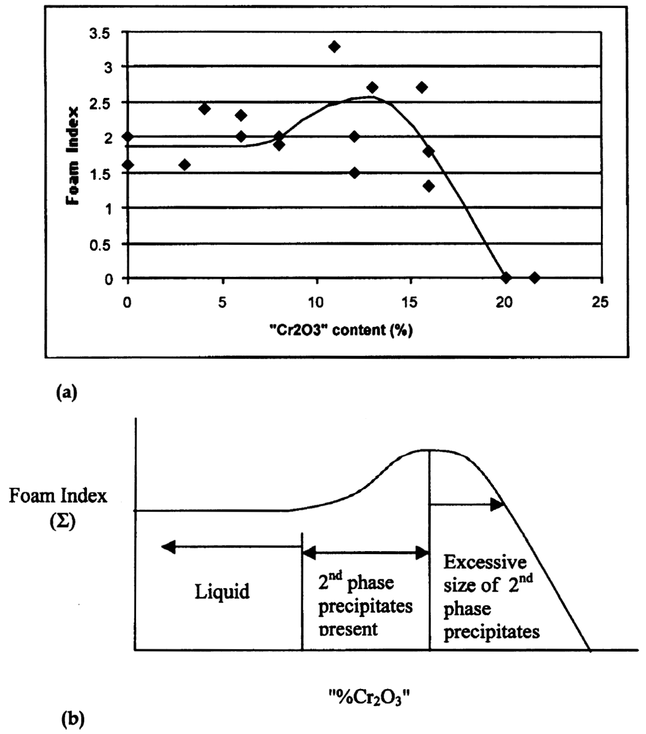

Figure 13. The effect of 'CrO' content on the foam index (a) theoretical (b) experimental

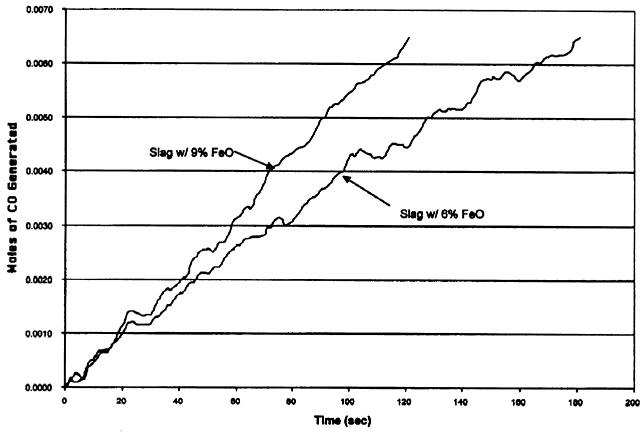

Figure 14. Rate of reaction of carbon with typical carbon steel EAF slags at 1823K

slags in stainless production is due to the slow rate of reaction of carbon with CrO dissolved in the slag.

Since poor foaming is due to the lack of gas generation additives, which will generate gas, could provide adequate foaming. A number of additives such as limestone ($CaCO_3$), NiO plus carbon, waste oxide briquettes containing FeO and carbon and calcium nitrate were investigated[6]. For example, when $CaCO_3$ is added, CO_2 gas is generated.

$$CaCO_3 = CaO + CO_2 \qquad [13]$$

Typical results on the rate of gas evolution from $CaCO_3$ are shown in Figure 15. It was concluded that the rate was controlled by heat transfer. In all cases, the rate of gas generation was sufficient to provide foaming of the slag. The rate of dissociation of $CaCO_3$ was shown to be controlled by heat transfer to the particle by radiation.

Simple models to predict foaming were developed. In the case of $CaCO_3$, after a sufficient amount of $CaCO_3$ is added a steady state rate of gas generation and foam height will be achieved. As injection of $CaCO_3$ begins the rate of injection is faster than for CO_2 generation because the area of $CaCO_3$ is limited. As the $CaCO_3$ in the slag increases, the rate of dissociation increases until it equals the rate of injection. The steady state foam height (H_f) is given by:

$$H_f = \frac{IRT\Sigma}{A} \qquad [14]$$

I = $CaCO_3$ injection rate (moles/second)
R = gas constant
T = absolute temperature
Σ = foam index
A = area of furnace

Simplified calculations based on the rate of $CaCO_3$ dissociation can be used to predict the steady state amount of $CaCO_3$ in the slag and the foam height achieved. For example, for the following conditions:

- $CaCO_3$ injection rate 2.2 kg/s
- $CaCO_3$ average size 1 cm diameter
- Temperature 1873 K
- Furnace diameter 5.0 m.

It will take 80 kg of $CaCO_3$ in the slag to achieve steady state and the foam height will be 50 cm.

In the case of slag foaming the slag is providing an important function. In understanding the basic phenomena it is possible to develop methods to improve foaming.

Conclusions

In addition to their normal functions, slags also have unique functions in several iron and steelmaking processes. In iron smelting it is the reaction medium for the reduction of the ore. The slag can also be used as a medium for gaseous desulphurization and, possibly, as a method to reduce the sulphur content of the metal. In the blast furnace, the slag formed in ferrous burden materials determine the position and size of the cohesive zone which, in turn, affects the operation of the furnace. Finally, foamed slags are used in the EAF to allow for long arcs, more power input and, consequently, higher productivity. Understanding the process has led to methods of obtaining better foaming, particularly in the production of stainless steel. In general, learning the basic phenomena involved in these and other unique functions of slags will lead to improved processes.

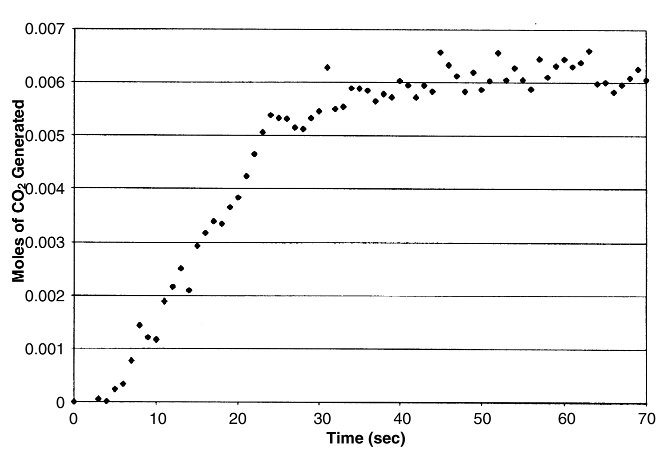

Figure 15. The rate of gas evolution from $CaCO_3$ 6 mm diameter in a stainless steelmaking slag at 1823K

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