

An important phenomenon in oxygen steelmaking is splashing, i.e. ejection of liquid metal droplets from the bath surface because of the impact of the jet on the bath. Investigations on this were carried out primarily in water models with gas blown from a single-hole top lance. It seems that there is a critical minimum depth of the impact cavity for the onset of splashing and splashing is an integral part of BOFs under the blowing conditions employed. The ejected droplets exhibit a size distribution ranging from about 0.2 mm to 10 mm.

17.2.2 Chemical Interactions between Jet and Bath

When a molecule of oxygen strikes the surface of the liquid impure iron, it may interact in any of the following ways.

- Reaction with dissolved carbon, etc. directly
- Reaction with Fe first to form FeO, which subsequently reacts with dissolved solutes
- Dissolution of gaseous oxygen into liquid iron as atomic oxygen.

From a kinetic point of view, the probability of the occurrence of the first is very low, and that of the second is high. Taking note of the fact that a total quantity of oxygen corresponding to about 3% of the mass of iron has to be absorbed in about 15 minutes blowing time, and that the solubility of oxygen in liquid iron is about 0.25 wt. %, the probability of the third mechanism is also low. Hence, the second mechanism, viz. gaseous oxygen first forming FeO, which subsequently reacts with the dissolved solutes is accepted as the major method of the transfer of oxygen.

Oxidation of iron is exothermic. The heat released in the impact zone takes time to dissipate. This causes a large increase of temperature around the impact zone. It has been known as the *hot spot*, whose temperature is above 2000°C, as inferred from experimental measurements in the laboratory.

Since the oxidation of molten iron to FeO is a simple reaction, it can be assumed to be very fast at such high temperatures. This was originally considered to be the reason why refining was possible within a very short time. Later, it was found that the ejection of a very large number of metal droplets from the impact zone (s), and the large specific surface area (i.e. surface area/volume ratio) of the droplets, makes the gas–metal interfacial area for the refining reactions (decarburisation in particular) extremely large. Hence, from a kinetic viewpoint, this reaction is more or less instantaneous. Therefore, it is the rate of supply of oxygen, rather than the rate of oxidation of iron, that is now accepted as the rate limiting step in the process. As a result, blowing velocities and the total supply of oxygen within the shortest possible time have received increasing attention in BOF steelmaking.

17.2.3 Chemical–Thermal Interactions of the Jet with the Surroundings

The oxygen jet also interacts with the surrounding gaseous atmosphere, both chemically and thermally. Also, there is no doubt that it interacts with the slag–metal–gas emulsion formed above the bath surface, but this is being ignored owing to the complexity. Of special importance, is the reaction of the oxygen jet(s) with the CO gas evolved because of the reaction of carbon

dissolved in metal with oxygen. This leads to the formation of some CO_2 , particularly in regions well above the bath. The exit gas from the BOF contains about 20 volume percent CO_2 initially, and about 5% towards the end of the blow.

This is known as *post-combustion* inside the converter. It is beneficial since oxidation of CO to CO_2 is also exothermic and supplies heat for the endothermic steps (see Chapter 15, Section 15.2 for details). The jet also physically entrains the gases from the surrounding atmosphere. As a result, by the time the oxygen jet reaches the impact zone, it contains some amount of CO and CO_2 and its temperature becomes higher.

17.3 COMPOSITION AND TEMPERATURE CHANGES DURING THE BLOW

In Chapter 15, the thermochemical and thermodynamic aspects of reactions in primary steelmaking with specific reference to basic oxygen processes were discussed and hence, these will not be repeated.

The composition and temperature of the bath changes during the progress of the blow for the reasons enumerated already. The exact magnitude of the changes is illustrated in Figure 17.3 (Deo and Boom, 1993) based on data from the 300 tonne combined blown BOF converter at Hoogovens IJmuiden, Netherlands (now Corus). This converter is equipped with facilities for

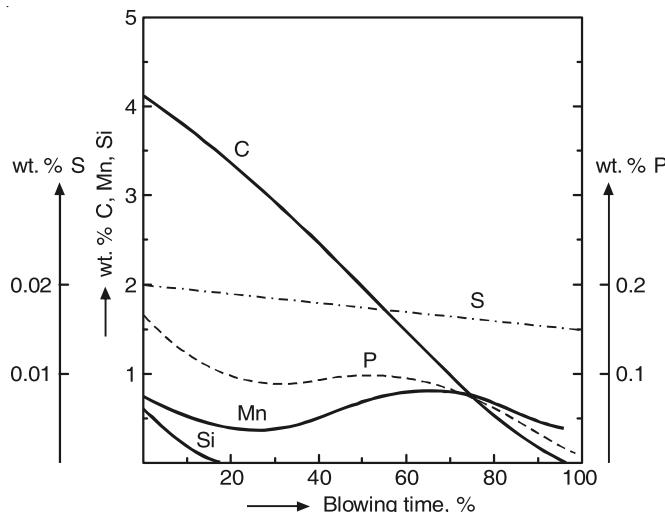


Figure 17.3 Change of bath composition with blowing time for 300 tonne BOF.

bottom stirring by inert gas using four symmetric bottom tuyeres. It was found that the temperature of the bath gradually rises from 1250–1450°C initially to about 1600–1680°C at the end of the blow essentially because of exothermic oxidation of Si, C and Fe. Silicon dissolved in iron gets eliminated in the form of silica right from the start of the blow. Silicon is the first element to get oxidised owing to the much higher stability of SiO_2 as compared to the other oxides. To make sure that this silica is assimilated in the slag as soon as it is formed (otherwise,

it would attack the basic vessel lining), lime addition is also begun right from the start of the blow. Once silicon is removed, oxidation of carbon dissolved in the bath to CO starts and continues almost throughout the blow. Significant removal of phosphorus occurs primarily towards the end of the blow.

Figure 17.4 (Deo and Boom, 1993) shows the change in slag composition during the blow for the same converter. The temperature of the slag is always slightly higher than that of the metal—in the initial stages, the difference can be as high as 100°C, but as the blow progresses,

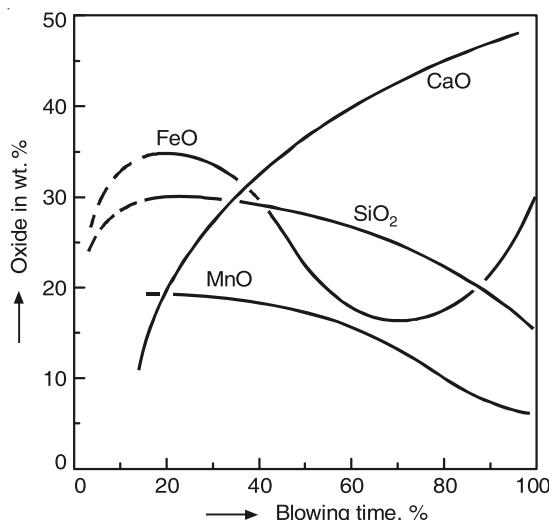


Figure 17.4 Change of slag composition with blowing time (for the same converter as in Figure 17.3).

the difference decreases, till at the end of the blow, the slag temperature is around 30–50°C higher. Often at the end of the oxygen blowing period in combined blown converters (like in Hoogovens), about two minutes of argon stirring is carried out to bring down the temperature difference. Post-blow stirring not only helps in temperature/composition homogenisation, but can contribute significantly towards dephosphorisation since the slag at this stage is rich in FeO and has high basicity. Figure 17.4 also depicts how the concentration of CaO in the slag increases continuously during the blow because of progressive dissolution of lime. The FeO concentration in the slag is initially high when the slag volume is limited, but as the blow progresses and more and more slag is formed, the FeO concentration goes down. Towards the end of the blow, the C–O reaction subsides and oxygen begins to react with iron in the bath (rather than carbon) leading once again to higher concentration of FeO in the slag.

It is to be understood that the quantity of slag, which is nil at the beginning, keeps increasing during the blow as lime dissolution continues. The total amount of lime used depends primarily on the silicon content in hot metal so that a CaO/SiO₂ ratio of at least 3.0 is maintained in the final slag to ensure adequate refining of the metalloids. The extent of lime added can be 60–70 kg/tls for 0.5–0.7% silicon hot metal and as high as 100 kg/tls for hot metal with around 1.2% silicon.

17.3.1 Slag Path and Lime Dissolution in Slag

As noted in Chapter 15, Section 15.3.1, Fe is present in slag as Fe^{2+} and Fe^{3+} ions (i.e. as FeO and Fe_2O_3). The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio varies, to a very large extent, during the blowing period, but it is not determined on a routine basis. Therefore, the standard practice is to assume that the total iron present in slag is in the form of FeO . The ternary phase equilibrium diagram at 1600°C for the $\text{CaO}-\text{SiO}_2-\text{FeO}$ (or Fe_2O_3) system has been presented in Figure 15.1, while Figure 15.2 depicted the change in composition for a commercial slag containing other minor constituents as well.

Such changes in the composition of slag during oxygen blowing in various practices have been reported in such pseudo-ternary diagrams. These changes are commonly referred to as *Slag Path*. Figures 17.5(a) and (b) (Turkdogan 1996) show some examples. In Figure 17.5(a), curve I is that reported in Hoogovens' IJmuiden plant, whereas curve II is for Mannesman's practice in Germany. Two other practices are also included in Figure 17.5(b). The practice adopted in each plant is based on certain advantages and disadvantages; for example, it has been claimed that following curve A gives better decarburisation while the path given by curve B results in better dephosphorisation.

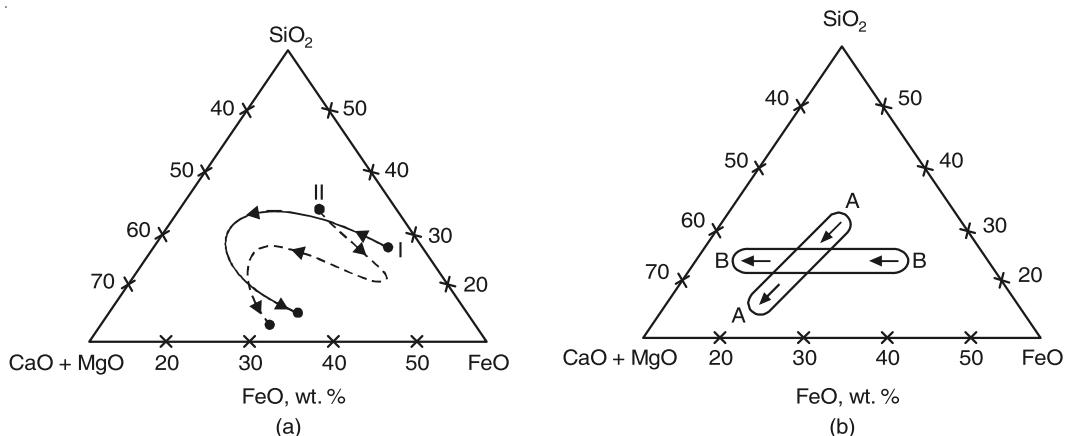


Figure 17.5 Changes in composition of slag during oxygen blowing for various BOF steelmaking practices.

17.3.2 Kinetics of Lime Dissolution

Evolution of slag composition during the BOF blow depends primarily on the rate of dissolution of the solid lime particles into the slag. Besides some plant investigations in BOF converters, several studies on the rate and mechanism of lime dissolution have been carried out in the laboratory. The salient findings are summarised below.

- The rate of dissolution is controlled by mass transfer in the slag.
- Smaller lime particles dissolve faster because of the larger specific surface area. In industrial practice, the particles would have a range of sizes.

- Lime particles having a larger volume fraction of pores are more reactive, and dissolve faster than less porous lime, since the slag is able to penetrate into the pores with consequent increase in the surface area for reaction, and the particles tend to disintegrate into smaller sizes owing to such penetration as well as the lower strength of porous lime. If CaCO_3 is calcined at a lower temperature for a longer time it is more porous. However, too low a temperature and/or too short a time of calcining results in a lime containing unacceptable percentage of undissociated CaCO_3 .
- The commonly accepted test for lime reactivity is the standard slaking test in which water is added at room temperature and the rise in temperature is measured.
- During dissolution of lime, a solid impervious high melting outer coating of dicalcium silicate tends to form (see Figure 15.1). It is important to break this layer by fluxing agents. FeO is a powerful agent. It reacts with dicalcium silicate and forms a low melting $\text{CaO}-\text{FeO}-\text{SiO}_2$ liquid. MnO has a similar effect.
- Higher temperatures are expected to increase rate of dissolution as a general rule of kinetics. However, it has been reported that lime sinters rapidly at 1600°C and above, making it dense and thus slowing down the rate.
- The final BOF slags have been found to contain some undissolved CaO particles, both free as well as with a coating of dicalcium silicate. The content of free CaO can range between 5% and 10% of the slag weight, in some cases.

17.4 KINETICS OF CARBON–OXYGEN REACTION IN BOF; SLAG–METAL–GAS INTERACTION

Elimination of carbon from liquid iron is quantitywise the most major reaction in the BOF and occurs throughout the blow. Important kinetic features of the carbon–oxygen reaction will now be discussed based on experimental investigations in the original BOFs with only a top lance (i.e. LD converter) and in modern BOFs with concurrent inert gas injection through bottom tuyeres, as well as in laboratories.

1. The specific decarburisation rate is expressed as $(-d[W_C]/dt)$, where $[W_C]$ is the weight per cent carbon in the bath at any instant of time t after the oxygen blowing starts. $-dW_C/dt$ is a function of blowing time and exhibits three stages, as shown in Figure 17.6. Initially, oxidation of silicon dominates. The decarburisation rate increases as the silicon content goes down. The middle stage corresponds to the maximum decarburisation rate and is ideally characterised by a steady value. The last stage is characterised by decreasing $-dW_C/dt$, since the carbon concentration is low and the emulsion subsides.
2. The steady value of $-dW_C/dt$ is proportional to the oxygen blowing rate as shown in Figure 17.7 (Meyer, 1969). This indicates that the decarburisation reaction is very fast and is essentially limited by the rate of supply of oxygen.
3. At the peak decarburisation period, vigorous evolution of CO causes the formation of a *slag–metal–gas emulsion*, which fills-up a considerable portion of the inner volume of the converter. The emulsion subsides in the last stage of decarburisation (Figure 17.6).

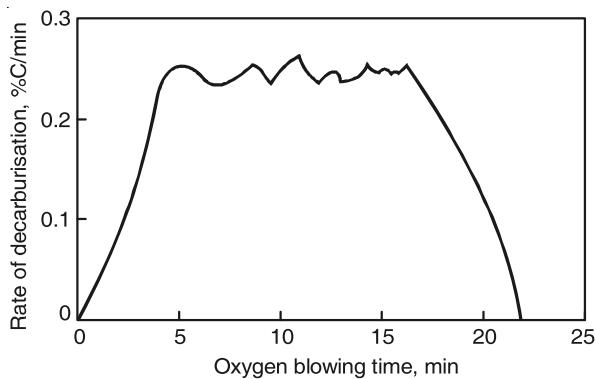


Figure 17.6 Change of decarburisation rate during oxygen blowing in BOF steelmaking (schematic).

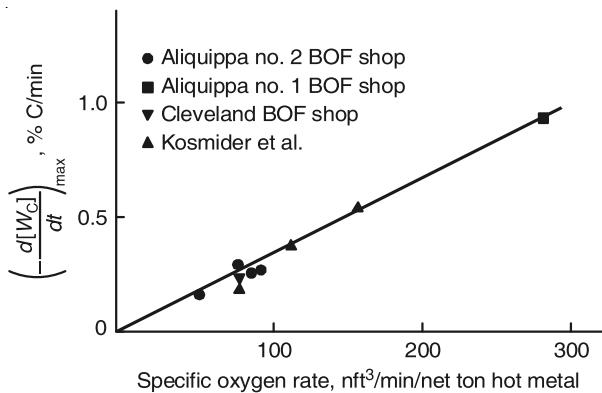


Figure 17.7 Peak (steady state) decarburisation rate as a function of specific oxygen blowing rate.

17.4.1 Foams and Emulsions in Basic Oxygen Steelmaking

An emulsion is a heterogeneous system consisting of at least one immiscible liquid or gas intimately dispersed in a second liquid in the form of droplets or bubbles. A foam is an overgrown gas–liquid emulsion in which the gas bubbles occupy a proportionately larger volume of the system. A typical foam contains 80%, or more, of gas by volume. By this definition, the emulsion in BOFs may be called foam as well, since here the gas volume is 80 to 90%.

The entire slag is assumed to be present in the emulsion and constitutes the continuous liquid phase. Foaming of steelmaking slags was observed in earlier primary steelmaking processes as well. *The slag foam is transient* in nature and is sustained by vigorous CO evolution. The more the viscosity of the slag, the greater is the foam height. In this context, it may be mentioned that the undissolved lime particles suspended in the slag increase the *effective viscosity* of the slag, and thus contribute to more foaming.

The emulsion in basic oxygen converters also contains a significant proportion of liquid metal droplets. The impingement of the jet on to the bath surface causes splashing of metal droplets as already mentioned in Section 17.2.1. It is further enhanced by the ejection of droplets following vigorous evolution of CO. Though estimates vary over a wide range, it is generally agreed that the slag–metal–gas emulsion may contain as much as 80 weight per cent metal. Therefore, in reality, the oxygen jet in BOFs is surrounded by the emulsion during a major part of the blow. This is schematically shown in Figure 17.8.

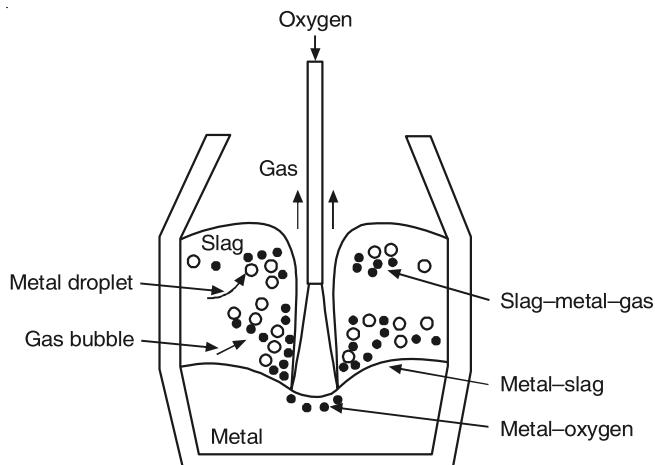


Figure 17.8 Representation of regions in top-blown oxygen steelmaking (schematic).

17.4.2 Mechanism of Carbon–Oxygen Reaction

Samples of the emulsion collected from converter ejections revealed that the metal droplets are hollow (Meyer 1969). This was attributed to the generation of CO gas inside the droplets. Laboratory experiments confirmed this phenomenon. Reaction of carbon in metal droplets with FeO in the surrounding molten slag is responsible. The excessive pressure of the generated CO even leads to the disintegration of the droplets.

Experimental observations by several investigators indicate a wide range of droplet sizes in the emulsion, varying from 0.1 mm to 25 mm. Estimates of droplet–slag interfacial area range from 8 to 250 m² per tonne of metal. For a 150 t converter, therefore, it may range from 1200 m² to 37500 m². It has also been found that the metal droplets are purer than the bulk metal in the bath.

In view of the above, Meyer et al. concluded that the very high rate of peak decarburisation is a result of such a high slag–metal interfacial area in the emulsion. The reacted droplets settle down into the bath and fresh droplets get ejected, leading to continuous refining in the emulsion. Though some investigators differed with this conclusion in the beginning, at present it has been generally accepted that the carbon–oxygen reaction occurs in different parts of the converter—in the impact zone primarily, in the emulsion, and lesser in other locations in the bath.