Introduction

The oxygen converter process (LD and its derivatives) is the main method of carbon and low-alloy steelmaking, annual production approaching 60% of total crude steel production (900 Mt). The oxygen converter process is essentially oxidizing refining of high carbon hot metal to medium or low carbon crude steel. Besides the primary refining action, decarburization of iron melt with controlled end-content of carbon, the process aims to eliminate of impurities, P, Ti, V and melt scrap using the extra heat released in exothermic oxidation reactions. Together with impurity elements, Si is totally and Mn partially oxidized and slagged. A schematic diagram of the process is presented in Figure 1 and the progress of oxidation-slag forming reactions in a 55 ton LD-converter at Koverhar steelworks, Finland, in Figure 2a and b.

Several reaction environments are suggested for the total oxygen converter process: I. The primary oxidation zone, the ‘hot spot’ or the oxygen jet-iron bath impingement surface, at which very high temperatures have been reported1–4 II. The metal bath near the hot spot into which oxygen-rich iron melt and even primary oxides penetrate and react with fresh high carbon melt1,3,5,6; III. Substantial
amounts of metal droplets, splashed by the vigorous oxygen jet or suspended by bubble bursting, are circulating in the slag and furnace atmosphere (10–80% of total mass of slag have been reported to be iron droplets during the main de-carburization period (Huitu13, 1974). Directed interaction between the molten iron and slag bulks also takes place, but due to the insignificant area of mutual interface its role is obviously of less importance except possibly for the final period of blowing characterized by a low carbon monoxide generation rate. (For reaction environments see Figure 1.)

Slag has in the LD-process various functions and roles. Primarily, it is spontaneously formed by the non-volatile oxides resulting in the oxidation of hot metal minor constituents and iron (SiO₂, MnO, P₂O₅, TiO₂, VOₓ, and FeO). In order to flux the impurity oxides to form a low melting, fluid slag, lime and sometimes doloma (a mixture of CaO and MgO) and, if necessary, fluorspar (CaF₂) are charged into the converter. Secondly, molten slag is a reaction environment for impurity elimination like desulfurization and dephosphorization, although ladle treatments have diminished the importance of the LD-process in this respect. Slag, when forming an emulsion with carbon monoxide and metal droplets — slag foaming—obviously plays some role in post-combustion of primary reaction products. In the first case the interaction of the oxygen jet with the bath is characterized by more intensive iron bath mixing and lower iron bath mixing intensity, and hard blowing with 'low lance' and bottom stirring (in combined blown converters), these reactions are followed by secondary oxidation-reduction reactions, especially by decarburization taking place on the surface of metal droplets circulating in the slag.

Formation of slag

Slag formation starts with the dissolution of oxygen in iron melt and simultaneous oxidation of iron and minor bath constituents in the oxygen jet impact zone. As the bath temperature in the impact zone is very high, over 2000°C, iron can dissolve a great amount of oxygen (up to 1 wt%)

• promotes dephosphorization at least at a high carbon level
• increases the oxidation rate of Mn, V, Ti etc.
• increases refractory wear
• raises the risk of slag slopping out of the furnace.

Figure 3. The 'slag path' in CaO-SiO₂-(FeO+MnO)-pseudo ternary diagram for a customary LD-converter blow at Koverhar steelworks during a tests campaign (Huitu13, 1974) and end composition of slags in a series heats of low manganese hot metal to low and high carbon steels (2000). End temperatures of the blows, reported varied within a range of 1673 to 1730°C.
saturation range (see Figure 3). The evaluation of the slag path passing the high temperature liquidus surfaces such as the dicalcium silicate nose or liquidus surfaces of the tricalcium silicate or lime and corresponding precipitation of solid phases from the melt, is somewhat obscured by the fact that slags are multicomponent phases and the slag temperatures have been reported to exceed, even by several hundred degrees, the average temperature of the iron bath.

**Converter slag as reaction environment**

**Thermodynamic consideration**

The overall slagging reactions can be expressed by a general formula

\[ O(g) + 2\alpha M_{\text{Fe}}(l) = 2\beta M_{\text{O}2}(l), \]

or

\[ 2O(g) + 2\alpha M_{\text{Fe}}(l) = 2\beta (M_{\text{O}2} + \beta_{\text{Fe}}), \]

if oxygen dissolution is separated as an independent step. The direct decarburization reaction is correspondingly:

\[ [O + [C]]_{\text{Fe}} = CO(g). \]

The driving forces or affinities of the oxidation-slagging reactions (relative to the stoichiometry of gaseous oxygen) are

\[ A_s = \left[ \frac{\partial G}{\partial x_s} \right]_g = A_s^0(\Delta R_{G}G_s) - RT \left[ \frac{a_{\text{M}_{\text{O}2}}}{a_{\text{O}_2}^{\text{g}}} \right] \left[ \frac{a_{\text{M}_2\text{O}2}}{a_{\text{M}}^{2\beta \text{O}2}} \right] \]

and

\[ A_i = A_s^0 + RT \left[ \frac{\partial G}{\partial x} \right]_{\text{Fe}^2} = \left[ \frac{\partial G}{\partial x} \right]_{\text{Fe}^2}^{\text{g}} \]

\[ \left[ a_{\text{M}}^{\beta \text{O}2} \right]_i = \left[ \gamma_{\text{M}_{\text{O}2}} \right]^{\text{g}} \times \left[ x_{\text{M}_{\text{O}2}} \right]^{\text{g}}, \]

respectively, the partial molar reaction energy of the \( j \)-th reaction (the first derivative of system Gibbs energy relative to reaction extent), the affinity of the reaction, the standard affinity of the \( j \)-th reaction, the standard Gibbs energy change in the \( j \)-th reaction, the activity of the oxide component in the slag and alloy component in molten iron. \( \gamma_{\text{M}_{\text{O}2}} \), \( \gamma_{\text{M}_2\text{O}2} \), and \( x_{\text{M}_{\text{O}2}} \) are the activity coefficients and mole fractions of components in slag and molten iron phases.

Local affinities at phase boundaries (slag/bath, slag/droplet, bath/gas slag/gas, etc.) control the progress of similar reactions of the components in the same solution phase (iron melt or slag). The magnitude of the reaction affinity depends on the standard affinity \( A^0 = (\Delta G^0) \) and activities (chemical potentials) of reaction components in solution phases. The local reaction affinities controlling the distribution of oxygen between the oxidation reaction of minor elements in the iron bath and iron i.e. the mutual progress of oxidation reactions, change with the time and temperature evolution of the process. In the same way, the local affinities of secondary oxidation reactions by iron (and other oxides in slag, like manganese oxide) control the progress of decarburization vs. oxidation of other minor constituents of iron droplets in the slag environment. This thermodynamic control of the oxidation reaction explains why iron is oxidized and slugged in soft blow. Weak mixing in iron bath results in slow transport of minor bath constituents (Si, Mn, Ti, V, C, etc.) from the bath interior to the superficial layers where oxidation takes place and from which iron droplets are splashed or burst into the slag. These layers are the pattering out of minor elements, their activities in metal phase and, accordingly, reaction affinities are decreased relative to iron. Iron oxidation becomes thus thermodynamically favourable.

The standard affinities of oxidation-slagging reactions presented in Table I demonstrate the general tendency of hot metal constituents to be oxidized and slugged. Titanium, silicon and manganese are under any blowing practice oxidized and slugged in the very early stage of the blow. According to the experience of steel plants having high vanadium hot metal, problems can occur in slugging of vanadium, especially when the aim is to produce high carbon steel with appropriate low vanadium content. The well-known behaviour of manganese (see Figure 2)—oxidation in the beginning of the blow and back reduction from the slag—is obviously a complex phenomenon in which the relatively strong effect of temperature on the carbon reduction equilibrium (see Table II, a 99-fold increase in equilibrium constant from 1300 to 1800°C), but also the changes in the chemical potential (activity coefficient) of reaction components (manganese in iron melt and oxide in the slag) play a significant role. Low standard affinity of phosphorus oxidation explains the problems in slugging—low standard affinity is to be compensated by decreasing the chemical potential (activity coefficient) of phosphorus oxide in slag. The low affinity of sulphur oxidation reaction explains why sulphur cannot be removed from the iron melt in the converter by direct oxidation to sulphur dioxide (or sulphate ion into the slag) but rather in reduced form as sulphide into highly basic slags.

**Consideration of oxidation-slagging reactions on the base of test runs at Koverhar steel plant**

A series of test runs was carried out in the LD converters of 55 ton nominal capacity at the Koverhar steel plant of Ovako Oy Ab (presently Fundia Wire Oy Ab of Rautaruukki Group) from 1974–1975, with the aim to find the optimal slag path and conditions for deP and deS. Direct

| Table I | Standard affinities \( (A^0 = -\Delta G^0) \) of oxidation-slagging reactions |
|---|---|---|---|
| T/C | \( \Delta G^0 / \text{kJ} \) | T/C | \( \Delta G^0 / \text{kJ} \) |
| 1300 | -647.775 | 1300 | -329.892 |
| 1500 | -616.422 | 1500 | -309.954 |
| 1700 | -585.695 | 1700 | -290.278 |
| 1300 | -633.424 | 1300 | -309.495 |
| 1500 | -594.152 | 1500 | -273.915 |
| 1700 | -555.325 | 1700 | -238.437 |
| 1300 | -513.966 | 1300 | -499.621 |
| 1500 | -487.636 | 1500 | -533.557 |
| 1700 | -461.109 | 1700 | -567.172 |
| 1300 | -380.235 | 1300 | -278.588 |
| 1500 | -353.034 | 1500 | -265.056 |
| 1700 | -325.961 | 1700 | -244.962 |
sampling of metal and slag was performed every 2–3 min during the blowing period. The study consisted of three MSc. theses supervised by one of the authors (Holappa). These results have not been published previously.

**Evolution of iron bath and slag composition in the LD-blow**

The typical evolution of iron bath and slag composition in a test heat presented in Figures 2a and 2b can be qualitatively explained by the mutual control of oxidation reactions by reaction affinities. During the first minutes of the blow, silicon and manganese having the highest reaction affinities are oxidized. With the progress of the blow, the affinity relations change due to changes in the bath and slag composition and temperature effect on the standard thermodynamic properties, as well as partial molar properties (activity coefficients) in solution phases. Manganese oxide in slag starts to be reduced due to these effects. Iron oxide added in the form of converter dust has negative oxidation affinity (positive affinity for reduction by carbon) and it tends to be reduced from the very beginning of the blow. The slag bath of the test blow in the CaO-SiO2-FeO ternary diagram is presented in Figure 3 with the end composition of some slags from contemporary blowing practice of the same plant (2000). Even when the diagram does not quantitatively correspond to multicomponent slag, as it is strictly valid only for the CaO-SiO2-FeO ternary, it rather reliably predicts calcium silicate precipitation conditions.

The slag path control was much more important in the past (in the middle ’70s at the Koverhar steel plant) than in contemporary oxygen steelmaking, as dephosphorization and desulphurization were at that time basically carried out in the converter. The early hit of the dicalcium silicate nose had a negative effect on these refining reactions. In modern steel plants deS treatment, and in some plants, deP treatment are carried out in separate ladle refining stations and time and temperature passing the dicalcium silicate ‘nose’ is no longer so critical. The end compositions of six contemporary end slags presented in Figure 3 seem to be at the tricalcium silicate or lime saturation field rather than saturated by dicalcium silicate.

The role of slag as a secondary oxidation environment is demonstrated in Figures 4 and 5 in which the evolutions of carbon and manganese content in the bath and metal droplets circulating in the slag are compared. Carbon content in droplets collected from the foaming slag is, as a rule, lower than in the samples taken from the bath due to oxidation by slag constituents (FeO, MnO, etc.) Manganese content in droplets roughly follows the oxidation-reduction behaviour demonstrated by the bath and slag analyses (Figure 2). The mass fraction of droplets in slag varied

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**Table II**

<table>
<thead>
<tr>
<th>Mn(0)</th>
<th>Fe3O4(0)</th>
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<tr>
<td><strong>T/°C</strong></td>
<td><strong>ΔG°/kJ</strong></td>
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<td>1300</td>
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<tr>
<td>1800</td>
<td>-113.22</td>
</tr>
<tr>
<td><strong>K2073/K1573</strong></td>
<td>99</td>
</tr>
</tbody>
</table>

| **T/°C** | **ΔG°/kJ** | **K** | **ΔG°/kJ** | **K** |
| 1300 | -108.00 | 3.86E+03 | 66.90 | 6.00E-03 |
| 1400 | -126.34 | 8.80E+03 | 48.55 | 3.05E-02 |
| 1500 | -144.62 | 1.82E+04 | 30.30 | 1.28E-01 |
| 1600 | -162.85 | 3.48E+04 | 12.15 | 4.58E-01 |
| 1700 | -181.03 | 6.20E+04 | -5.90 | 1.43E+00 |
| 1800 | -199.15 | 104300 | -23.85 | 3.99E+00 |
| **K2073/K1573** | 27 | 665 |

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![Figure 4](image-url)  
**Figure 4.** Carbon content in the iron bath (solid lines) and in iron droplets sampled from the slag (dotted lines) in five test runs at Koverhar steelworks (Väinölä, 1975)

![Figure 5](image-url)  
**Figure 5.** Manganese content in the metal bath and droplets circulating in the foaming slag in a test run at Koverhar steelworks (Väinölä 1975)

![Figure 6](image-url)  
**Figure 6.** Mass fraction of iron droplets in slag and the foam height in five test runs at Koverhar plant (Väinölä, 1975). The distance from bath surface to converter mouth was estimated to be close to 5 m
between a few and 25 per cent (Figure 6) which is of the same magnitude as values presented by Price\textsuperscript{14} but much lower than high values up to 80% presented by some other investigators.\textsuperscript{16,14,15} The majority of particles was observed to belong to a range 0.3 to 1 mm in the sample taken in the middle of the blow (11 min).

**Slag foaming**

Figure 7 shows the slag to steel mass ratio for a set of Koverhar converter blows. The range from 40 to 90 kg slag per 1 ton of steel is obviously within the range of common practice. Binary Fe-C melts give a good approximation for hot metal density. Density varies with temperature and composition, ranging from 7.1 ±0.1 g·cm\(^{-3}\) (high carbon hot metal at 1300°C) to 6.9 g·cm\(^{-3}\).\textsuperscript{17} A rough estimate for converter slag consisting of CaO, SiO\(_2\), FeO, MnO within typical composition and temperature ranges of the oxygen converter process is 2.8 ±0.1 to 3 ±0.1 g·cm\(^{-3}\).\textsuperscript{18} If the slag to steel mass ratio at the end of a converter blow varies within 0.04 to 0.1, the slag to steel volume ratio rises from almost zero in the beginning of the blow to 0.10/0.25 towards the end of the blow.

Foam height as a function of blowing time is presented as an average for all test runs in Figure 6 and for one specified blow in Figure 2b, from which can be seen that the maximum height of the foam was reached when slag mass approached 70% of the end slag amount. This behavior was approximately confirmed in other test runs as well. The Koverhar plant developed in the middle '70s a practice using reactive converter dust as the source of iron oxides in order to guarantee rapid formation of foaming slag, even when the blow was started with low lance i.e. hard blow practice was utilized\textsuperscript{19}. There is very little available experimental knowledge on the effect of slag in general or of slag foaming on post-combustion. Farrand and co-writers\textsuperscript{20} report that foaming slag decreases the post-combustion ratio and increases the heat transfer efficiency to the bath. It is, however questionable if the results of trials in the KOBM furnace can be directly transferred to top blown converters, with or without inert gas bottom stirring.

In general, slag is considered to dampen metal ejections and dust formation from the converter during the blow. If a converter is operated with a very low amount of slag, heavy metal ejections and skull formation can be attained. The properties of slag are, however, of utmost importance.

Fluid, strongly oxidizing slag is favourable for oxidation reactions but can result in slag slopping out from the converter. Slopping often occurs if slag formation is delayed, for some reason, and a high amount of oxygen is ‘loaded’ into the slag by soft blow, ore/dust addition, etc. Intensive CO formation anyway results in formation of slag-metal emulsion, slag formation starts, secondary and tertiary oxidation reactions take place vigorously, and enhanced gas formation leads to heavy slopping. Proper control of slag formation and foaming is a central measure in slopping prevention.

Chemical wear of refractory lining depends, among others, on its interaction with slag/emulsion, liquid metal and gas phase including O\(_2\) blow. The most important mechanism is the dissolution of lining into the slag. Rapid slag formation in order to bind and neutralize acid SiO\(_2\) forming in the blow beginning, is a key point. Highly oxidizing hot slag dissolves magnesia or dolomite lining readily. Use of doloma lime can greatly improve the lining life. Recently, slag splashing has become an established practice to prolong converter life\textsuperscript{21}. The residual slag in the converter after tapping is splashed by a violent nitrogen flow around the converter wall. Lining lives over one year are reported. The procedure itself, as well the consequences to the converter process, are fairly complex and the slag should be strictly adjusted for the treatment\textsuperscript{22}.

**Concluding remarks**

The importance of oxygen steelmaking explains the huge amount of research dedicated to the process. In spite of that, we still do not have unambiguous understanding on the all-important features of the process such as the role of slag as the environment for oxidation reactions of carbon and other hot metal constituents or post-combustion.

Basic thermodynamics of reactions and phases seem to be nowadays fairly well established, but there is still need for better data for minor components in slags (e.g. Mn, Ti and V oxides).

The oxygen top-blowing process results in steep gradients in and between the different zones in the converter concerning temperatures, concentrations/activities, surface tension of phases, phase fractions, etc. To better understand the complicated interfacial reactions and phenomena, more work is needed to describe the movement (flow) of liquids, solids and gases inside the converter, including circulation of metal droplets and slag, as well as the role of oxygen blow and escaping gases.

**References**