EXPERIENCES IN PHYSICOCHEMICAL MODELLING OF OXYGEN CONVERTER PROCESS (BOF)

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Abstract

Oxygen converting of hot metal (LD/BOF) is contemplated as an object of simulation. Oxygen converting is a highly complex thermo-chemical process comprising a series of matter and energy transformation and transportation steps that makes the simulation very challenging. The basic principles of CONSIM 5 oxygen converter simulator are presented. Simulator is a comprehensive combination of a physical model with several empirical submodels describing all properties and processes that affect the final result of a converter blow, final mass and composition of steel, slag, dust and converter gas as well as the end temperature of steel. CONSIM simulator is used for simulation of series of high and low carbon steel blows. Simulated steel temperatures, oxygen consumption, blow time and iron oxide content of slag are compared with measured values. Problems of simulation and requirements for quantitative simulation of oxygen converter process are discussed.

Introduction

The oxygen converter process (LD/BOF and its derivatives) is the main method of carbon and low alloy steelmaking, annual production approaching to 60% of total crude steel production (over 1 Gton /2005). BOP is essentially an oxidising refining process in which high carbon hot metal (3.7 to 4.5%C) is converted to low or medium carbon raw steel with low impurity content by oxidizing carbon and a series of minor constituents that are slagged. It is a highly complex thermochemical process in which the target is beyond a complex route ranging from converter charge with all its properties to the thermo-chemical state of steel and slag in the end of the blow. Complexity of the process makes simulation model aiming to quantitative prediction of end point very challenging.

Chemical and metallurgical high temperature processes can be categorised to stationary, continuous processes and non-stationary batch processes into which category various converter processes belong. From a simulation point of view the main difference between the continuous and batch processes lays there, that in the reactors of former type of processes there are stationary temperature, mass and velocity profiles without any accumulation of mass or energy, whereas in the latter type of processes the chemical and thermal evolution proceed in time and there is both mass and energy accumulation (+ or -) in the reactor. Simulation models might range from pure mathematical formulation of process on the basis of practical experience, empirical data on the process and its state to a pure physical model describing the progress of matter and energy transformation and transportation processes proceeding in the reactor on a
theoretical basis. For non-stationary processes dynamic simulation is preferable instead of static mass and energy balance calculations.

Even if physical models alone are not sufficient basis for process control and automation of highly complex thermochemical processes like oxygen converting they cannot be substituted by empirical static or dynamic models based on statistical analysis of process data even if such modern powerful tools as fuzzy logics or neural networks are applied. Simulation based on physical models is

- necessary for understanding of highly complex processes and can be used in education as well as for developing, designing and ruling of processes and individual runs of batch processes
- better tool for process control than static models?
- not a rival for empirical static and dynamic models but all types of models should be combined in order to get the maximum precision in description of the process evolution!

A physical model for oxygen converter process is a combination of dimensional, thermochemical and rate phenomena characteristics of the process, simulation based on the model aims to quantitative description the chemical and thermal evolution of individual heats in the particular technological environment.

Characteristics of BOP as an object of simulation

Oxygen converter process is characterised in Figure 1 as a subject of simulation. In the process oxygen is blown with high velocity (up to double velocity of sound) to the surface of the metal bath and so called hot spot is formed at surface area where the oxygen jet impinges the surface (zone I). In this zone all iron melt constituents including iron are obviously “burned”. Oxidation products are dissolved in slag except for carbon monoxide, which is passing the slag layer and forming the major component of converter gas. Intensive oxygen jet is inducing fluid flows (circulation) in iron bath and forces highly oxidised metal and even molten oxidation products from the iron bath surface to penetrate into the bath (zone III), where these react with “fresh metal” of high impurity element content [1].

On the other hand the rigorous oxygen jet and gas bubbles rising in the bath bring small droplets of iron melt into the slag (zone II)- 10-80% of total mass of slag have been reported to be iron droplets [2,3,4,5]. Heat evolved in highly exothermal oxidation reactions is consumed in heating and melting the charge materials, heating of iron bath, slag and carbon oxides formed in carbon oxidation and partly lost into the environment during and between the blows (1 to 7 in Figure 1). Circulations in iron bath (A in Figure 1.) caused by oxygen jet, rising gas bubbles and inert gas purging through bottom tuyeres in combined blown converters transport the minor iron melt constituents (C, Si, Ti, Mn, P, V etc.) into the upper bath layers. Remarkable amounts of dust up to 3 % of the iron bath mass is formed by mechanical transport of small particles by off-gas and evaporation of volatile components at the very high temperature of “hot spot”. Part of the primary carbon monoxide is oxidised in interaction with oxides (especially iron oxides) in slag or directly with oxygen jet.

Oxidation reactions proceed obviously in three zones: at iron melt surface (I), in the superficial layers of the bath when high oxygen melt and fresh metal with high impurity content are mixed (III) and at the surface of iron droplets circulating in slag (III). The most significant mass transfer step is obviously convection transport of metal from the bulk to the superficial layers where oxidation takes place (zones I, II and III). Except for carbon oxides the other oxidation products (SiO₂, MnO, P₂O₅, and Fe₂O) dissolve into the slag, into which lime also dissolves gradually along with the evolution of oxidation of silicon, iron and other metal bath constituents.
In the “start up” period of a converter blow, when bath temperature is low, slag might be saturated by di-calcium silicate but approaches and probably even reaches lime saturation in the later stages of the blow.

**Figure 1.** Chemical and thermal phenomena in LD processes and its derivatives

Temperature in converter baths is not uniform. In “hot spot” i.e. at the oxygen - molten iron impinging surface temperature is reported to exceed 2000°C [5,6,7] at the same time as non-melted scrap in the converter pot keeps the adjacent bath temperature hundreds of degrees lower. Slag temperature is reported to exceed markedly the medium temperature of molten iron at least in early stages of blow [6,8].

The evolution of the main chemical reactions, oxidation of minor hot metal components that are competing of the same oxygen, is obviously controlled by two main factors: 1) thermodynamic affinity of competing oxidation reactions and 2) mass transfer of oxidising components from the bulk of molten iron bath to the reaction environments at the superficial layers of the bath where the oxidation reactions take place. Chemical resistance of oxidising reactions i.e. chemical kinetics plays obviously secondary role due to high temperature. The mutual role of thermodynamics, i.e. affinities of chemical reactions and mass transfer is demonstrated clearly by practical experience from LD process. The general order of oxidation of minor hot metal constituents and iron, demonstrated in Figure 2 (supported by a great number of information in metallurgical literature from 60ies and 70ies, a.o. references [5 and 9]) follows standard affinities of individual oxidation reactions (Table I.). If the iron bath is effectively mixed the main component, iron with more than 80 atomic percent of total bath composition starts to be oxidised first with low contents of thermodynamically more favourable alternatives, titanium, silicon, carbon, manganese etc. Sulphur is practically not oxidised in converter process due to its low oxidation affinity but is removed, if at all, by slagging as sulphide (CaS, MgS). On the other hand the well known method to reverse the thermodynamically more favourable oxidation of
minor hot metal constituents to iron oxidation in top blown LD-converter is high lance blowing. This decreases the intensity of iron bath mixing and, accordingly, the rate of convective transport of minor constituents from iron bath bulk to the superficial oxidation layers, concentrations of minor constituents in these layers where oxidation takes place and, finally, decreases oxidation affinity of carbon and minor metal bath components relative to iron (see Equations 4 to 6 for reaction affinity). This leads further growth in iron oxidation rate.

Figure 2. Chemical evolution of iron bath in a blow of 50 ton LD converter at Koverhar steelworks (Huitu 1974[10])

Table I. Standard affinities of iron bath constituent oxidation relative to one mole of oxygen ($A^\circ = -\Delta_RG^\circ$)[11]

<table>
<thead>
<tr>
<th>T/°C</th>
<th>$\Delta_RG^\circ$</th>
<th>T/°C</th>
<th>$\Delta_RG^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(l) + O$_2$(g) = TiO$_2$(l)</td>
<td>1.894Fe(l) + O$<em>2$(g) = 2Fe$</em>{0.947}$O(l)</td>
<td>4/5V(l) + O$_2$(g) = V$_2$O$_5$(l)</td>
<td>2Mn(l) + O$_2$(g) = MnO(l)</td>
</tr>
<tr>
<td>1300</td>
<td>-647.8</td>
<td>1300</td>
<td>-633.4</td>
</tr>
<tr>
<td>1500</td>
<td>-616.4</td>
<td>1500</td>
<td>-594.1</td>
</tr>
<tr>
<td>1700</td>
<td>-585.7</td>
<td>1700</td>
<td>-555.3</td>
</tr>
<tr>
<td>Si(l) + O$_2$(g) = SiO$_2$(l)</td>
<td>2C(s) + O$_2$(g) = 2CO(g)</td>
<td>S(l) + O$_2$(g) = 2SO$_2$(g)</td>
<td>4/5P(l) + O$_2$(g) = 2/5P$_2$O$_5$</td>
</tr>
<tr>
<td>1300</td>
<td>-633.4</td>
<td>1300</td>
<td>-499.6</td>
</tr>
<tr>
<td>1500</td>
<td>-594.1</td>
<td>1500</td>
<td>-533.6</td>
</tr>
<tr>
<td>1700</td>
<td>-555.3</td>
<td>1700</td>
<td>-567.2</td>
</tr>
</tbody>
</table>

* stoichiometric iron oxide, FeO
It is obvious that a physical model aiming to quantitative prediction of the end temperature and composition (carbon content) of steel should include the above mentioned major features, thermodynamic control of oxygen distribution between the oxidation reactions and mass transfer in iron bath. All secondary chemical reactions and thermal processes including heat losses should be also be taken into account and connected to these major features, if the aim of simulation is reliable prediction of steel properties in the end of the blow.

**Principles of CONSIM simulation program**

Oxygen converter process is a combination of chemical, thermal and mass transfer processes (as all chemical and metallurgical processes!). The total oxidation reactions proceed in a complex way in several steps in several reaction environments mentioned above. Besides the primary reactions a series secondary reactions are combined with them. Charge components, lime or doloma and fluorspar react with oxidised hot metal components or oxides charged in converter (iron ore, converter dust) and form a molten slag. Extra fuel like ferro-silicon, coke etc. are dissolving in iron melt and reacting with oxygen. Carbon monoxide formed in primary oxidation of hot metal carbon reacts with oxides (especially with iron oxides) in slag and directly with primary oxygen and forms carbon dioxide. Distribution of primary oxygen between the competing oxidation reactions is controlled by affinities of oxidation reactions in various reaction environments.

The primary reactions of oxygen converting, oxidation of hot metal constituents are of three general types

\[
\begin{align*}
O_2 (g) & \leftrightarrow 2[O] \text{ for oxygen dissolution in iron melt} \\
O_2(g) + 2[C] & \leftrightarrow 2\text{CO(g) for gaseous products (mainly carbon)} \\
O_2(g) + 2\alpha/\beta[M] & \leftrightarrow 2\beta(M_\alpha O_\beta) \text{ for other constituents} \\
& \quad \text{(Si, Ti, V, Mn, P, Fe etc.) that are slagged}
\end{align*}
\]

Isothermal-isobaric affinity of oxidation reactions in the chemical reaction zones controls the distribution of oxygen amongst the reactions and, accordingly, the mutual rates of oxidation of minor elements and iron in metal phase. Affinities (reaction potentials) of primary oxidation reactions are

\[
\left( \frac{\partial G}{\partial \xi_{(1)}} \right) = \Delta_R G_{(O)} = \Delta_R G^{o}_{(O)} + RT \ln \left( \frac{a_2^{[O]}}{(p_{O_2} / p^o)} \right)
\]

\[
= \Delta_R G^{o}_{(O)} + RT \ln \left( \frac{\gamma_2^{[O]} x_2^{[O]}}{(p_{O_2} / p^o)} \right)
\]

(4)

\[
\left( \frac{\partial G}{\partial \xi_{(C)}} \right) = \Delta_R G_{(C)} = \Delta_R G^{o}_{(C)} + RT \ln \left( \frac{(P_{CO} / p^o)^2}{a_2^{[C]}} \left( \frac{p_{O_2}}{p^o} \right) \right)
\]

\[
= \Delta_R G^{o}_{(C)} + RT \ln \left( \frac{\gamma_2^{[C]} x_2^{[C]} (P_{CO} / p^o)^2}{(n_{CO}/n^o)^2} \right)
\]

(5)

\[
\left( \frac{\partial G}{\partial \xi_{(M)}} \right) = \Delta_R G_{(M)} = \Delta_R G^{o}_{(M)} + RT \ln \left( \frac{a_2^{2\alpha/\beta}}{a_2^{0}(M_{\alpha}O_{\beta})} \left( \frac{p_{O_2}}{p^o} \right) \right)
\]


\[
\Delta_R G^0 (M) = RT \ln \left( \frac{\gamma^{2/\beta} (M_{o}O_{\beta})^{x_i} \gamma^{2/\beta} (M_{o}O_{\beta})^{x_i}}{\gamma^{2/\beta} (M_{e}O_{\beta})^{x_i} \gamma^{2/\beta} (M_{e}O_{\beta})^{x_i}} \right)
\]

The concentrations \((x_i)\) and activities \((a_i)\) of oxidising elements in various reaction environments are controlled by the rate of their oxidation and mass transfer rate of their transport from molten iron bulk.

Principles of simulation applied in CONSIM series of programs and persons participated in developing the program principles and encoding it are presented in references \([12,13,14,15,16,17,18,19]\). The principles of the central reaction model of CONSIM 5 program is shown in Figure 3. The above described three oxidation zones of actual converter are substituted by one generalised reaction zone in order to avoid a complex program structure based on too meagre information. Oxidation and oxygen consumption proceeds in small (differential) individual (for each iron bath component) steps, reaction affinities of each oxidation reaction controlling the order of steps. Concentration of each oxidising component and, accordingly, reaction affinity (Equations 4 to 6) of each oxidising component is controlled by individual oxidation rate, intensity of convection transport, that is related to energy dissipation in iron bath from top and bottom blow and individual diffusivities of oxidising components in iron melt. Energy dissipation model used in CONSIM is presented in reference \([20]\). Mass transfer and oxidation rates are assumed to be equal. Mass transfer rate algorithm is written on the base of surface renewal model \([21]\). The concentrations (mole fractions) of oxidising components in metal phase of generalised reaction zone are finally expressed by equation

\[
\frac{s_{x_i} b_{x_i}}{b_{x_i}} = \frac{M_{Fe} * Pa}{e^{y} \* D^{1/2} \* \rho} * m_{n_i}
\]

\(s_{x_i}, b_{x_i}, D, m_{n_i}, e, M_{Fe}, \rho\) in equation are surface and bulk concentration of iron bath constituents, diffusivity and molar oxidation rate of oxidising components, energy dissipated by top and bottom blows to the iron bath, molar mass of iron. \(y\) and \(Pa\) are parameters to be assessed. Thermochemical data for computing the reaction potentials and enthalpies are from source \([12]\), for computing activity coefficients (in Equations 4 to 6) of components in iron and slag melts from sources \([22]\) and \([23]\), respectively. Diffusivities of components in molten iron are from various sources \([5,24,25]\).

There are models and subprograms for all other matter and energy transformation and transportation processes including 1) reduction of slag oxides, mainly iron oxides (= secondary oxidation of iron melt constituents), 2) post combustion of carbon monoxide, 3) melting and dissolution of charge materials in slag or in iron melt, 4) heating of solid charge materials, molten phases and gas by heat released in exothermic reactions, 5) heat losses during and between the blows. The progress of each process is connected with the oxygen consumption and accordingly with time as oxygen blow rate is known. The mean temperature of iron and slag bath is assumed to be equal. Several parameters should be assessed against properties measured at actual converter.
Simulation of blows in 50-ton LD-converter

Two test series of blows in 50-ton LD-converter at Fundia Wire Oyj (now Ovako Steel), Koverhar Steel Plant from the year 2000 are simulated. At that time the bottom stirring facilities were not yet installed at Koverhar converters and simulation is thus performed using only top blow mode. Target for CONSIM 5 program used for simulation can be carbon content, temperature or blow time. Analysed end carbon contents were used as targets. Several parameters in subprogram should be assessed against the process data from actual converter i.e. test series data. The total number of parameters adjusted to give acceptable fit for end temperature for the set of high carbon heats was six: one in mass transfer, heat loss, slag reduction and dust formation models and two in post combustion model.

Simulation results are presented in Figures 4 to 8 for an individual blow. In Figures 9 to 12 the reported end temperatures, iron oxide contents in slag, oxygen consumption and blow times of 15 low carbon and 21 high carbon steel blows are compared with simulated values.
Figure 4. Simulated evolution of iron bath composition for a low carbon steel blow (heat Nr. 48824)

Figure 5. Evolution of slag composition in simulated blow.
Figure 6. Simulated oxidation rates

Figure 7. Simulated temperature evolution
Figure 8. Simulation report for the blow Nr. 48824

Figure 9. Simulated and observed end temperatures and iron oxide contents in slag in high carbon steel blows
Figure 10. Simulated and observed oxygen consumption and blow times in low carbon steel blows

Figure 11. Simulated and observed end temperatures and iron oxide contents in slag in low carbon steel blows
Simulation gives qualitatively the typical chemical and thermal evolution of LD-process (Figures 4 to 6) observed in industrial scale tests carried out in 60
P
ies and 70
P
ies, shown in Figure 3 for iron melt evolution at Koverhar steelworks test runs from middle.

The fit rate of reported and simulated values presented in Figs. 9-12 is generally satisfactory. The fit rate was lowest for amount of blown oxygen – the simulated values are as a rule larger than the reported ones for both series of heats. The weak correlation in oxygen consumption is strange as the compatibility in blow time was rather good. Any rational explanation for this disagreement was not found. A notable observation is that the fit between simulated and measured values of low carbon heats using parameters adjusted using data from the high carbon blow series is acceptable. This although the average values of blow parameters and charge for high and low carbon steel blows are different (see Table II.)

Table II. Average data for simulated series of low and high carbon blows

<table>
<thead>
<tr>
<th></th>
<th>Blow rate Nm³/min</th>
<th>Lance height m</th>
<th>wt% C</th>
<th>Scrap ton</th>
<th>Converter dust + ore ton</th>
<th>FeSi ton</th>
<th>Lime ton</th>
<th>CaF₂ ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low C</td>
<td>134</td>
<td>1.00</td>
<td>0.033</td>
<td>5.89</td>
<td>0.96</td>
<td>0.030</td>
<td>2.61</td>
<td>0.007</td>
</tr>
<tr>
<td>High C</td>
<td>120</td>
<td>1.15</td>
<td>0.686</td>
<td>2.15</td>
<td>1.05</td>
<td>0.099</td>
<td>3.15</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Concluding remarks

Experience on CONSIM 5 simulator shows that simulation based on thermodynamic, thermochemical and mass transfer models combined with simple sub-models on measured data from industrial converter is able to describe qualitatively all the essential features of the process. Simulator is a useful tool for process analysis and for development of process control measures.
The next logical step is to use simulator as a substitute for static model of oxygen converter process. This necessitates a reliable feedback interface reading charge and end data from converter data base for optimisation of some essential program parameters, especially those included in mass transfer, heat loss and dust formation models.

Experience has also shown usefulness, even necessity, to base the sub-models on correct mathematical formulation of the interconnection between the sub-phenomena and the main physical and technological characteristics of the process, its main progress variables. Such sub-phenomena are scrap melting, post combustion, reduction of slag oxides (especially iron oxides) and heat loss. Proper mathematical formulation of sub-models gives good basis to obtain quantitative result by optimising model parameters against measured data. Fluid flow modelling aiming to connect the dimensional and dynamic parameters of oxygen top blow and inert gas bottom stirring with flow characteristics in iron bath would be highly useful. Even a simple but mathematically proper model for mass transfer of minor iron melt constituents to the oxidation environments with one-two parameters to be optimised using process data would greatly improve the accuracy of simulation.

Availability all necessary data from the process and its reliability is highly important. Standardising of blowing practise would also greatly increase the reliability of simulation. Experience has further proven that errors and mistakes are easily generated and difficult to locate in codes of simulation programs of such highly complex, non-stationary batch process as oxygen converting where the end properties are a result of a number of relative independent phenomena.

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