Abstract

The AOD is by its very nature and purpose a large generator of CO₂. The total CO₂ emission from the process can be divided into two parts - the direct part which is proportional to the carbon removal from the metal and the indirect part which is related to the consumption of additives such as reduction agents, slag formers and alloys. The production of the additives typically required for a heat causes large emissions of CO₂, in fact, often larger than what is generated from the direct part. By applying a real-time adaptive optimization of the oxygen to inert gas ratio over small time increments, the overall carbon removal efficiency is increased while the consumption of reduction agents and slag formers are decreased. This removes unnecessary production costs and minimizes the total emission of CO₂.

In this paper a process concept with optimized gas administration over a large number of time increments is compared with a more traditional process practice. The work is based on industrially proven process models integrated in the UTCAS software package for converter management and control. Finally, this paper concludes on how the suggested process can be applied in actual plant operation.

Introduction

In the mid 1950s, studies performed by Union Carbide showed that low carbon concentrations could be reached without excessive chromium oxidation by adding argon together with the oxygen during decarburization. This work led to the first commercial AOD installation in Joslyn, USA 1968 1). A decarburization process based on a stepwise decrease of the oxygen to inert ratio according to table 1 was gradually established. This practice made it possible to reach low carbon concentrations while keeping the carbon removal efficiency – or CRE – relatively high.

Table 1. Typical stepwise decarburization for an 18%Cr, 8%Ni grade.

<table>
<thead>
<tr>
<th>Oxygen/Inert</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/1</td>
<td>C ≥ 0.6</td>
</tr>
<tr>
<td>1/1</td>
<td>0.6 &lt; C ≥ 0.25</td>
</tr>
<tr>
<td>1/3</td>
<td>0.25 &lt; C ≥ 0.07</td>
</tr>
<tr>
<td>1/5</td>
<td>C &lt; 0.07</td>
</tr>
</tbody>
</table>

In modern steelmaking, much of this original strategy is still accepted and applied. Even if ratios and conditions varies and are calculated by process control systems, it is common that the number of steps is limited to between four and six.

By dividing the decarburization period in a large number of short time increments and by determining the oxygen/inert ratio for each such increment based on predicted thermodynamic conditions, it is possible to further increase the CRE.
An increase in CRE will lead to less oxidation of other dissolved elements, mainly chromium, and the required amounts of reduction agents will decrease. The amount of required lime is often determined by the amount of reduction agents since it is common to aim for a specified basicity of the slag.

The production of one tone of FeSi(75%) causes four tons of CO$_2$ emission$^2)$ and same figure for the production of lime is 0.985 tons$^3$.

**Theory**

When oxygen is injected into a stainless steel bath, chromium and iron will oxidize. Decarburization occurs when dissolved carbon reduces the chromium and iron. If only chromium is considered, the overall reaction can be expressed as in equation 1$^4$)

$$Cr_2O_3(\text{slag}) + 3C \rightarrow 2Cr + 3CO(g)$$

The equilibrium equation for this reaction is given by equation 2$^4$)

$$K = \left( \frac{a_{Cr}^2 \cdot p_{CO}^3}{a_C^3 \cdot a_{Cr_2O_3}} \right)$$

where $a_C$, $a_{Cr}$ and $a_{Cr_2O_3}$ are the activities of carbon, chromium and chromium oxide respectively, $p_{CO}$ is the partial pressure of carbon monoxide (CO) in the gas phase and $K$ is the equilibrium constant.

Based on equation 2 and the assumption that $a_{Cr_2O_3}$ equals unity, the equilibrium carbon concentration [$\%C_e$] can be calculated according to equation 3$^4$)

$$[\%C_e] = \frac{f_C^{[\%Cr]} \cdot f_{Cr}^{1/3} \cdot p_{CO}}{f_{Cr}^{[\%Cr]} / f_C^{1/3}}$$

where $f_C$ and $f_{Cr}$ are the activity coefficients of carbon and chromium respectively and [$\%Cr$] is the concentration of chromium. From this equation, it is evident that the equilibrium carbon content is lowered if $p_{CO}$ is decreased. By rearranging equation 3, an expression for the equilibrium partial pressure of CO is obtained as shown in equation 4

$$p_{COeq} = \frac{[\%C] \cdot f_C^{K^{1/3}}}{(f_{Cr}^{[\%Cr]})^{2/3}}$$

where $p_{COeq}$ is the partial pressure of CO which is in equilibrium with given concentrations of carbon and chromium at a given temperature.

Under conditions where all injected oxygen has reacted with carbon (CRE = 100), the partial pressure of CO can according to the gas law be determined by equation 5$^4$)

$$p_{CO} = \frac{Q_{CO}}{Q_{CO} + Q_{inert}} \cdot p_{Tot}$$

where $Q_{CO}$ is the volumetric amount of generated CO, $Q_{inert}$ is the volumetric amount of injected nitrogen or argon and $p_{Tot}$ is the total pressure.

By combining equations 4 and 5, the oxygen to inert gas ratio can be optimized for any combination of carbon/chromium concentration and temperature. This statement is valid under...
the condition that no free oxygen is available in the system, i.e. that the oxygen flow rate is adequately low and stirring sufficiently high to allow all injected oxygen to react.

**Method**

This work compares the stepwise decarburization practice according to table 1 with two alternative practices based on the theory as described above.

The calculations, figures and illustrations are based on simulations made in the UTCAS system for an 80 ton AOD. The calculation models used has been validated in several industrial installations in daily production for more than ten years.

In all cases, the start conditions and the beginning of the process are the same (Fig. 2) and in all cases the final target carbon concentration is 0.020%.

![Fig. 1: Start conditions and beginning of process](image)

In all cases, the total flow was kept constant a 133 nm\(^3\)/minute. No additions were simulated from the starting point until the final carbon target.

The results of the comparisons have focused on the amounts of FeSi and lime required to fully reduce the slag, to reach a final Si concentration of 0.300% and a slag basicity of 1.70.

**Results**

Fig. 2 illustrates the simulated process based on the blowing practice according to table 1. This is referred to as Case 1.

Fig. 3 illustrates an alternative process with short time increments. The duration of each increment is 24 seconds and the oxygen/inert ratio has been individually optimized with respect to maximized CRE. This is referred to as Case 2.

Fig. 4 illustrates a second alternative process – Case 3. Here, the oxygen part of the optimized ratio was multiplied with a factor > 1 while the inert part was equally reduced. The ambition was to reach the same decarburization time as for Case 1.

In Fig. 5, the CRE values over time for the three cases are compared.
Fig. 2: Case 1 process. X-axis = time in minutes, Y-axis = %C, Bars = gas mix/flow rates, Green(light) line = %C over time, Black(dark) line = temperature over time.

Fig. 3: Case 2 process – CRE optimization.

Fig. 4: Case 3 process – adjusted CRE optimization.
The main results for all cases are summarized in table 2. The reduced consumptions and CO$_2$ emissions as follows from comparing Case 2 with Case 1 are presented in table 3.

Table 2: Result summary

<table>
<thead>
<tr>
<th>Case</th>
<th>Dec Time</th>
<th>Peak Temp</th>
<th>End Temp</th>
<th>FeSi (kg)</th>
<th>FeSi (kg/ton)</th>
<th>Lime (kg)</th>
<th>Lime (kg/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26:30</td>
<td>1754</td>
<td>1754</td>
<td>1196</td>
<td>14.74</td>
<td>1985</td>
<td>24.47</td>
</tr>
<tr>
<td>2</td>
<td>31:40</td>
<td>1734</td>
<td>1647</td>
<td>927</td>
<td>11.43</td>
<td>1238</td>
<td>15.27</td>
</tr>
<tr>
<td>3</td>
<td>26:32</td>
<td>1746</td>
<td>1694</td>
<td>970</td>
<td>11.96</td>
<td>1357</td>
<td>16.73</td>
</tr>
</tbody>
</table>

Table 3: Reduction in consumption and related CO$_2$ emissions when comparing Case 1 with Case 2. All values as kg/ton produced steel.

<table>
<thead>
<tr>
<th>FeSi CO$_2$ rel.</th>
<th>Lime CO$_2$ rel.</th>
<th>CO$_2$ total</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.31</td>
<td>-9.20</td>
<td>-22.30</td>
</tr>
</tbody>
</table>

Case 2 shows the lowest consumption of FeSi and lime but also the longest decarburization time. The peak temperature as well as the temperature at the end of decarburization is also significantly lower. Case 3 ends up at about the same decarburization time as Case 1 but the consumption figures are still quite low compared to Case 1.

It is also interesting to note that the total carbon amount removed from the steel, recalculated to CO$_2$ emission, equals 29.2 kg/ton produced steel.

**Discussion**

In comparing the different cases, it is clear that the process times as well as the temperature profiles are different and this study does not directly consider the impact of these variables. In real production, the total scope must be evaluated and boundary conditions defined. Limitations for process time, highest peak temperature and temperature after decarburization must be determined.
In many cases time is critical but there are also situations when it is not. During periods when the converter is the bottleneck, the shortest refining time is the obvious choice. During other periods, CRE optimization will be more cost efficient and above all reduce the CO₂ emissions. The relatively lower temperature would also be beneficial for lining lifetime.

The lower slag output will also result in less metal oxide and less entrapped metal droplets in the slag resulting in higher yield.

As shown in Case 3, it is possible to find compromise solutions where the pure CRE optimization practice can be adjusted to meet different boundary conditions, for instance maximum decarburization time.

The computer systems used for process design and control should have the ability to recognize and adapt to such boundary conditions in a dynamic way so that the best practice under the given circumstances can be generated. It is also important that the valve station is able to handle frequent changes in ratios and to control flow rates with precision.

This study has only focused on the CO₂ emissions from the production of FeSi and lime. Future work should include other greenhouse gases and also consequential emissions from mining, enrichment, transportation and handling. Emissions related to other materials such as aluminum, dolomite and fluorspar should be investigated.

**Conclusions**

By applying a decarburization practice based on short time increments with individually optimized oxygen/inert ratios, it is possible to increase the overall CRE compared to a more typical stepwise practice. The increased CRE will lead to a reduced consumption of FeSi and lime, potentially up to 22.5% and 37.6% respectively. This will not only reduce production costs but also significantly lower the total CO₂ emissions with up to 22.3 kg/ton produced steel.

A practice entirely focused on CRE optimization will prolong the decarburization time and end at lower temperature compared to a reference practice with higher final oxygen/inert ratios. This practice will lead to the lowest CO₂ emissions related to the consumption of FeSi and lime and should with respect to the environment be applied when possible.

By allowing the CRE optimization model to work under the restriction of boundary conditions, it is possible to dynamically generate practices that will satisfy different target criteria such as decarburization time and still keeping the CRE relatively high.

Even if the fundamental theory behind maximizing CRE as briefly described in this paper has been known and accepted for many years, its application in day-to-day production is far from common. As the awareness of how the greenhouse gases effects the climate has increased over the recent years, all steel producers should have good reasons to evaluate current practices.

The world production of crude stainless steel during 2009 was more than 24 million tons. This figure indicates the potential for a significant reduction of CO₂ emissions.

A wide implementation of the dynamic CRE optimization concept in process design and real-time control would in a global perspective lead to huge positive environmental effects and help us to a greener future world.
References
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