Decarburization control during stainless steel making in an EAF

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Abstract
During the production of stainless steel in the electric arc furnace (EAF) there is a phase when oxygen is injected to oxidize unwanted elements, mainly carbon and silicon. Within this decarburization phase unfortunately also elements valuable to the process like iron and chromium get oxidized. This causes an economical loss and a bad environmental impact.
Since it is not possible to continuously measure the carbon content of the melt during decarburization, an alternative indirect control strategy has been developed. This control strategy is based on thermochemical calculations, a model describing the elements oxidation during oxygen injection and the measurement of carbon emissions from the EAF. To monitor the carbon emissions (CO\textsubscript{2}, CO) of the process during decarburization, an off-gas analysis system has been installed at an industrial EAF.
This new control strategy was tested in a number of exemplary heats and showed good results throughout. The control of the decarburization phase by monitoring the carbon emissions leads on average to a decrease of the oxygen consumption and therefore a decrease in tap-to-tap time. Compared to the previous decarburization strategy the oxygen consumption could be decreased by up to 24\% for single heats (~ 8 minutes of injection time). The chromium losses to the slag could also be decreased significantly, which is equal to a saving of ferrochrome input of about 8 kg/t steel. Concluding also the influence of this new decarburization control strategy on the EAF’s energy demand and energy efficiency has been investigated and there is no negative influence on both of them.

Keywords
chromium scorification, stainless steel, off-gas analysis, electric arc furnace

Introduction
Rising costs for energy and raw materials in the last few years have encouraged the European steel industries to research new melting strategies in order to decrease the production cost of steelmaking. The environmental awareness for minimizing CO\textsubscript{2} emissions among the European steel industries has meanwhile increased as well. By minimizing waste and excess material, e.g. through a well-defined process control, the European steel industries intend to decrease the cost of steelmaking as well as contribute towards decreasing the direct and indirect CO\textsubscript{2} emissions caused during the production of steel.
During stainless steelmaking in the electric arc furnace at Deutsche Edelstahlwerke (DEW) oxygen is injected into the furnace in order to oxidize unwanted tramp elements, mainly silicon and carbon, in the steel melt. The aim is to reduce the concentration of tramp elements in the melt to the target level for tapping.
Due to the less noble property of iron and chromium, i.e. the higher affinity to oxygen and oxidation at lower oxygen partial pressure, the oxidation of silicon and carbon is accompanied by an extensive slagging of chromium and iron. This is the reason why at the moment approx. 97\% of all chromium losses during EAF-based stainless steelmaking take place in the EAF [1].
Since chromium is an expensive alloy, stainless steel producers have to minimize chromium losses during the steelmaking process. Apart from economical reasons, the chromium slagging should also be minimized for environmental reasons, since the landfilling of EAF slags and dusts containing chromium can lead to the formation of Cr species in the eluate of the respective landfill.
Known metallurgical strategies to decrease the chromium slagging during oxygen injection into liquid steel, for example the decrease of the CO activity by dilution with injected argon gas or the use of vacuum technology as well as the operation at very high temperatures of the liquid steel, are not applicable in the EAF.
Therefore a new strategy had to be developed to increase the efficiency of the oxygen injection into the EAF. This increased efficiency should lead directly to a decrease of chromium and iron losses to the slag.
The basic principle of this new strategy is to control the oxidation process during the refining period. The approach used in this research is to monitor the oxidation products in the off-gas, i.e. CO and CO₂. An off-gas analysing system provides precise information to control the efficiency of the oxygen injection and to identify critical points of silicon and carbon oxidation. These critical points can be used to determine the end of efficient oxygen injection and thereby excess chromium and iron oxidation can be prevented.

This decarburization control (DC) strategy has been tested at Deutsche Edelstahlwerke and the influence of decarburization control on the chromium yield during stainless steel production has been investigated in a number of trials. Additionally the influence of this new strategy on EAF energy demand and energy efficiency has been assessed, with the objective being to understand the influence of the efficient oxygen injection on other EAF characteristics.

Thermodynamic calculations
Since many oxidation and reduction reactions in the EAF take place simultaneously, the element reactions during oxygen injection in the EAF are complicated. In addition there are interdependencies between the presence of a specific element and another elements oxidation. So temperature, oxygen partial pressure as well as steel and slag composition determine the elements oxidation [2,3].

In order to understand this decarburization process, thermodynamic calculations were carried out based on exemplary industrial heat data and the FactSage thermodynamic database [4]. The amount and composition of scraps, alloys and slag additives added into the EAF before the start of the refining period were taken from an exemplary industrial heat at DEW. They were evaluated according to their chemical composition and then based on the FactSage database a free energy data file for the used set of elements and their corresponding phases were generated. The continuous oxygen injection during the decarburization phase was then reproduced by stepwise thermodynamic calculations, increasing the amount of added O₂ by 100 kg in each step. For each step the equilibrium composition of steel and slag as well as the corresponding masses were determined by thermodynamic calculations.

When examining the results of the thermodynamic equilibrium calculation it has to be considered, that these calculations do not take other influencing processes such as heat and mass transfers or reaction kinetics into account. The calculations are also based on the assumption of a homogenous elements and temperature distribution. Figure 1 presents the mass of oxidized elements as a function of the cumulative oxygen injection. In these calculation results, two critical points with regard to the decarburization process can be identified. The first critical point correlates with the end of the intense silicon oxidation and the beginning of the intensive decarburization.

**Figure 1: Results of thermodynamic calculation of the oxidation of Fe, Cr, Si, C for an exemplary heat**

The second critical point correlates with a decreasing gradient of carbon oxidation. Therefore the results of the thermodynamic calculations show the existence of three stages in the decarburization process. In the early stage the injected oxygen is most likely to intensely oxidize silicon before the first critical point appears at 4.8 kg O₂/t_steel cumulative oxygen injection for this particular heat. This is in agreement with results obtained by other researchers, e.g. [5,6]. During the middle stage the injected oxygen intensively oxidizes carbon and also leads to chromium slagging. The mass of oxidized carbon increases in this stage linearly with an increasing cumulative oxygen injection, whereas the chromium oxidation follows an exponential path. By the time the carbon concentration in the melt reaches a critical value, the second critical point appears at 18.3 kg O₂/t_steel. In the end stage decarburization decreases and on the other hand the oxidation of chromium becomes more intensive. Meanwhile the slagging of iron takes place in small amounts from the beginning of the early stage and becomes more noticeable in the end stage.

Therefore, in accordance with this model of the decarburization process, a measurement of the carbon content in the off-gas as an indicator for the progression of the decarburization process should provide the possibility to identify the second critical point as a terminating condition for the oxygen injection during the course of a heat in the EAF.

Industrial measurements and plant trials
The industrial measurements and plant trials were conducted at an AC-EAF of DEW. A duplex process-route for stainless steelmaking at DEW involves an EAF and a VOD. The EAF melts down scrap, ferro-alloys and other raw materials to produce liquid steel. The usual amounts of oxygen injection at the EAF are in the range of 6 to 30 kg O₂/t_steel depending on stainless steel grades. After tapping from the EAF,
the liquid steel is charged into the VOD in order to achieve a very low carbon concentration. Based on the results of the thermodynamic calculations, an off-gas analysing system has been installed at the EAF’s primary dedusting system to investigate the oxidation process in the refining period. As explained above the carbon content (CO, CO₂) of the off-gas should be a good indication of the progression of the decarburization process and is therefore of particular interest. A steep decrease of the carbon content should indicate that the second critical point of decarburization has been reached. The off-gas analysing system consists of water-cooled probes for gas sampling, temperature and gas velocity measurement (differential pressure probe), gas filters, analyzers and data acquisitioning (Figure 2).

Figure 2: Off-gas analysing equipment with off-gas sampling and analysing, temperature measurement, volume flow measurement and data acquisition. To measure CO and CO₂ concentrations, analyzers based on infrared absorption spectrometry have been employed and the oxygen concentration has been measured with a paramagnetic O₂ analyzer. The off-gas temperature was measured using coated thermocouples. From the differential pressure measurement of the off-gas flow, the off-gas volume flow rate as well as the off-gas mass flow rate have been calculated. The off-gas mass flow rates were checked with carbon mass flow rates and a complete carbon mass balance.

Initially two measurement points were tested (Figure 3). Measurement point A is located at the hot gas duct directly after the EAF elbow. At this point the influence of leak air at the gap between elbow and hot gas duct is minimal and it is possible to measure the direct EAF off-gas. Point B is located about 30 m downstream of point A and allows the measurement of the off-gas composition after complete post-combustion.

As a result of test measurements, point B was chosen for further measurements, since long-time off-gas measurements at point A are difficult because of the extreme conditions (e.g. high temperature, highly inhomogeneous species distribution in radial direction). At point B on the other hand these measurements can easily be conducted because of the less demanding measurement conditions and furthermore the post-combustion with leak air does not influence the monitoring of the decarburization process since hardly any carbon is added to the off-gas by the leak air.

Results of measurements and trials
At the chosen measurement point B after post-combustion the CO concentrations in the off-gas were found to be lower than 2000 ppm. Therefore the contribution of carbon monoxide to the total carbon mass balance is only up to 0.19 kg/t steel, which is about 2 % of the total carbon mass oxidized. For this reason, the installation of a CO analyzer is less important at this measurement point and the decarburization process can be monitored with a CO₂ analyzer alone.

The industrial measurements also showed that it is possible to monitor the decarburization process using...
the off-gas analysing system for both austenitic (Figure 4) and ferritic (Figure 5) stainless steel heats.

![Figure 4: CO₂ concentration in the off-gas during the refining period for an exemplary austenitic stainless steel heat](image)

**Figure 4:** CO₂ concentration in the off-gas during the refining period for an exemplary austenitic stainless steel heat.

![Figure 5: CO₂ concentration in the off-gas during the refining period for an exemplary ferritic stainless steel heat](image)

**Figure 5:** CO₂ concentration in the off-gas during the refining period for an exemplary ferritic stainless steel heat.

The results of the off-gas measurements show a higher second critical point for the ferritic heat when compared to the austenitic heat. This can be explained by the higher input of carbon-rich chromium alloy for ferritic steel heats which leads to a higher carbon concentration in the liquid steel. In accordance with the results of the model of the decarburization process, the off-gas measurements also show the existence of three consecutive stages in the decarburization process. Furthermore a few differences between the calculation results and the results of the off-gas analysis are clearly evident. These differences can be explained by considering the fact that the elements oxidation does not merely depend on thermodynamics, but also on other phenomena such as mass and heat transfer, fluid dynamics and kinetics. The differences are also due to inhomogeneous temperature and elements distributions inside the liquid steel during the refining period. A good example of this is the injection zone directly in the range of the oxygen lance which has the highest oxygen concentration and temperatures [2]. The restricted oxygen capacity of the silicon in this zone leads to carbon oxidation from the early stage on. One of the differences between the results of the thermodynamic calculations and off-gas measurements is, that the off-gas measurements show the occurrence of decarburization from the early stage on and therefore it can be expected that chromium slagging also begins in the early stage and continues until the end of the oxygen injection. In contrast the thermodynamic calculations showed negligible chromium slagging during the early stage. During the early stage of oxygen injection the rate of silicon oxidation is controlled by the silicon mass transfer in the liquid steel [5]. In the course of the early stage the chemical reaction between carbon and oxygen at the steel-gas interface becomes the rate determining mechanism of decarburization, as carbon and oxygen mass transfer are sufficiently high during this stage [5,7,8]. The peak value of the decarburization rate in the middle stage and the duration of the middle stage depend on the oxygen mass flow rate during injection. The intensive decarburization in the middle stage takes place until the carbon concentration in the liquid steel reaches a critical value, which depends on the oxygen mass flow rate [2], temperature, CO partial pressure [5] as well as steel and slag composition [9]. In the end stage of the decarburization process the decarburization rate is controlled by the mass transfer of carbon in liquid steel [2]. The carbon oxidation decreases after the decarburization process reaches the second critical point. This is due to the decreasing carbon concentration in the liquid steel which leads to a decrease in the driving force of the decarburization reaction kinetics, the concentration difference [C] – [C]eq, as well as a decrease in carbon activity. Since the EAF used for this investigation is not equipped with argon bottom stirring or other means to increase the decarburization rate in the end stage, the carbon concentration of the liquid at tapping is higher than the equilibrium value. At DEW the required low carbon values are achieved by subsequent treatment in a vacuum oxygen decarburization (VOD) process.

**Slag analyses.** Results of slag analyses conducted for these first measurements show that the Cr₂O₃ concentration in the slag varies between 5.47 and 11.40 wt% (mean value 8.07 wt%, Table 1).

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>SiO₂</th>
<th>Cr₂O₃</th>
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<td><strong>Mean</strong></td>
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<td>3.26</td>
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<td>8.07</td>
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<tr>
<td><strong>Standard deviation</strong></td>
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<td>1.74</td>
<td>2.32</td>
<td>0.79</td>
<td>2.86</td>
<td>1.80</td>
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**Table 1: Result of slag analyses (without DC)**

The relatively low FeO concentration in the slag demonstrates that iron is not intensively oxidized in the EAF. A coordinated evaluation of the results of slag analyses, off-gas measurements, analyses of tapped steel and thermodynamic calculations lead to the conclusion, that higher FeO and Cr₂O₃ concentrations in the slag strongly correlate with high amounts of excess oxygen in the end stage [9].
The results of slag analyses also show a positive correlation between the FeO and Cr$_2$O$_3$ concentration in the slag (Figure 6).

Figure 6: Correlations between the Cr$_2$O$_3$, FeO and CaO concentrations in the slag
This correlation could possibly be due to the simultaneous chromium and iron oxidation by oxygen as well as the simultaneous reduction of chromium and iron oxides by silicon. Nevertheless higher FeO and Cr$_2$O$_3$ concentrations in the slag result in lower CaO concentrations. With the exception of FeO and CaO, no significant correlations between Cr$_2$O$_3$ and other slag components could be found.

Plant trials. Phase 1 and phase 2 of the plant trials delivered good results. Using the off-gas analysis system to control the decarburization process, can prevent high carbon concentrations in the tapped steel. Threshold for the carbon concentration at tapping is about 1 wt% at DEW. Finishing oxygen injection at the second critical point always led to carbon concentrations in the liquid steel in the range of 0.4 to 0.8 wt%.

For most of the heats in the trials by using the decarburization control the oxygen consumption could be decreased in relation to the precalculated amounts. For a particular heat the oxygen consumption could even be decreased by up to 24 % compared to the precalculated injection amount. For this specific EAF this is equivalent to a decrease of oxygen injection time by up to 8 minutes (Figure 7).

Figure 7: Decrease of oxygen injection and its distribution during plant trials
Four out of fifteen heats on the other hand did not reach the second critical point during injection of the predetermined amount of oxygen. This circumstance may indicate that these heats had a higher carbon input than estimated from the available scrap database, so the oxygen injection should not have ended at the predetermined amount. Instead it should have continued till the off-gas analysis showed the typical decrease of carbon concentrations in the off-gas.

However, during these trials the oxygen injection could not be continued beyond the precalculated amount, since this would have resulted in an excessively high liquid steel temperature, which would have disturbed the further process. Since the decrease of injected oxygen in phase 1 of the plant trials did not result in higher silicon concentrations than usual in the tapped steel, the silicon was charged in its nominal amount during phase 2.

Increase of chromium and iron yield. Using decarburization control leads to FeO concentrations in the slag varying between 0.47 and 1.71 wt% (mean value 0.88 wt%), while the Cr$_2$O$_3$ concentrations are in the range of 1.37 to 8.35 wt% (mean value 4.29 wt%) as can be seen in Table 2.

Table 2: Result of slag analyses for the plant trials (with DC)
These mean values are equal to a decrease of FeO mass in the slag of about 76 % from 5.4 kg/t down to 1.3 kg/t. Meanwhile the mass of Cr$_2$O$_3$ in the slag decreased by 51 % from 12.3 kg/t to 6.0 kg/t (Table 3), which is equivalent to a saving of chromium alloy input of approximately 950 kg per heat. Therefore the new strategy of oxygen injection has proven to significantly decrease chromium and iron oxidation.

Table 3: Comparison of the mean values for FeO and Cr$_2$O$_3$ mass in the slag with and without DC
Furthermore, lower Fe$_2$O$_3$ concentrations in the slag can decrease the wear rate of the EAF refractory [2,5]. Additionally due to lower Cr$_2$O$_3$ and Fe$_2$O$_3$ concentrations in the slag less, CaO input and therefore less slag mass can be achieved. This leads to an additional economic benefit since less slag needs to be treated and deposited.

EAF energy demand. Electrical energy and the chemical energy released from exothermic elements oxidation together deliver the energy for scrap melting and overheating of the liquid steel in the investigated EAF. The electrical energy input is well known from operational data of the EAF. The chemical energy input on the other hand is
determined by the mass of oxidized elements, which is calculated from mass balances, i.e. the difference between output and input.

\[ E_{\text{chem}} + E_{\text{el}} = E_{\text{steel}} + E_{\text{slag}} + E_{\text{off-gas}} + E_{\text{cooling-water}} + E_{\text{others}} \] (1)

The amount of energy released by elements oxidation can be calculated by multiplying the mass of the oxidized element with the specific exothermic enthalpy change of the elements oxidation reaction, \( \Delta H_{i,\text{ox}} \).

\[ E_{\text{chem}} = \sum \Delta H_{i,\text{ox}} (m_{i,\text{in}} - m_{i,\text{out}}) \] (2)

For the determination of the chemical energy input, in this investigation carbon is assumed to be completely oxidized to CO₂.

The electrical and chemical energy inputs contribute approximately 59 % and 41 %, respectively, to the total energy input. While the electrical energy input varies in the range of 419 to 600 kWh/t_steel (average 483 kWh/t_steel), the total energy input is in the range of 609 to 1093 kWh/t_steel with an average of 827 kWh/t_steel (Figure 8).

**Energy efficiency.** The EAF’s energy efficiency \( \eta_{\text{EAF}} \) is determined as the ratio between steel enthalpy, \( H_{\text{steel}} \), and the total energy input (eq. 3). The steel enthalpy thereby is calculated following the model of moderately non-ideal diluted iron alloy melt, in which the mixing enthalpy is disregarded (eq. 4) [10].

\[ \eta_{\text{EAF}} = \frac{H_{\text{steel}}}{E_{\text{chem}} + E_{\text{el}}} \] (3)

\[ H_{\text{steel}} = m_{\text{Fe}} \cdot \Delta h_{\text{Fe}} + \sum m_i \cdot \Delta h_i \] (4)

In this work an increase of steel enthalpy or tapping temperature with a higher amount of injected oxygen could not be observed (Figure 9). The energy efficiency of the investigated EAF meanwhile varies in a wide range between 37 % and 68 % with an average efficiency of 48 % (Figure 10). The energy efficiency decreases with a higher total energy input.

**Productivity.** A higher EAF productivity with a higher amount of injected oxygen has been reported by Jones [11]. In contrast to his work, this investigation shows a decrease of productivity when the chemical and electrical energy inputs increase (Figure 11). Compared to the case with no DC, the EAF productivity with DC correlates even more strongly with the chemical and total energy input. In general higher productivity can be achieved with lower
chemical and total energy input when the
decarburization can be well controlled.
By decreasing the total amount of injected oxygen at
a given restricted volume flow rate of the oxygen
lances, a shorter tap-to-tap time can be obtained.
This shorter tap-to-tap time increases the
productivity. And therefore the productivity and the
chemical energy input, which is depending on the
amount of injected oxygen, are negatively correlated.

Figure 11: Electrical and chemical energy input vs.
EAF productivity for heats with and without DC
Since the efficient oxygen injection leads to lower
chromium and iron oxidation, less metal slagging
occurs. A higher metal yield due to this reduced
metal slagging also contributes to an increase of the
EAF’s productivity.

Based on these results the efficient oxygen injection
using the presented decarburization control method
is suggested to achieve higher productivity as well as
lower energy losses without detrimentally influencing
its main purpose, which is to oxidize tramp elements,
mainly silicon and carbon.

Conclusion
Optimal decarburization and minimal chromium and
iron oxidation are beneficial for stainless steelfaking
in the EAF. In this work the optimization of elements
oxidation at Deutsche Edelstahlwerke was performed
by the application of an off-gas analysing system.
Using the results from thermodynamic-based
calculations combined with slag and off-gas
measurements proved to be a promising method to
not only monitor the elements oxidation but also
increase the efficiency of oxygen injection.
As a result, a new EAF process control strategy for
the decarburization process during the refining period
of stainless steelmaking based on an off-gas
analysing system has been developed. By ending the
oxygen injection at the 2nd critical point of
decarburization, high chromium and iron slagging can
be prevented. The application of the off-gas
analysing system to control the decarburization
process increases the efficiency of oxygen injection,
which leads to a decrease of the oxygen
consumption for the investigated heats by on average
approximately 10%. For a particular heat the oxygen
injection could even be decreased by up to 24%.

This is equivalent to a decrease of the injection time
of up to 8 minutes and this in turn increases the
EAF’s productivity.
During the plant trials the implemented
decarburization control decreased the mean values
of chromium and iron oxides in the slag by 76% and
50%, respectively, and therefore minimized
chromium and iron losses to the slag. The decrease
of chromium loss to the slag is equal to a saving of
ferrochrome input by about 8.6 kg/t_steel. The
decarburization control can also maintain the carbon
concentration in the tapped steel below the threshold
of 1 wt%. Due to the efficient oxygen injection 
FeO_x concentrations in the slag are low. Thus a
competitive FeO_x and CrO_y reduction by silicon can
be avoided, so that the consumption of silicon, as the
sole reductant at the investigated EAF, can be well
controlled. Furthermore, due to the lower CrO_y and
FeO_x content of the slag, less CaO input and less
slag mass can be achieved. As less slag needs to be
treated and deposited, this leads to an additional
economic benefit.

Regarding the influence of this new control strategy
on energy demand, energy efficiency and productivity
of the EAF, this paper suggests that the
decarburization control results in no increase of the
electrical energy demand. In fact contrary to
increasing the total energy input, shorter tap-to-tap
times through optimized oxygen injection could be a
significant source for a decrease of energy losses,
since Kirschen [12] reported that the energy losses
through water-cooling and the off-gas during the
refining period are approximately 2 kWh/(t_steel min)
and 3-5 kWh/(t_steel min), respectively.
An interesting approach for further research on this
topic would be the development of a control algorithm
to automatically identify the 2nd critical point of
decarburization from real-time off-gas measurement
data. This would allow for integrating this new control
strategy as an automatic real-time control into the
EAF’s process control system.

Abbreviations
[C] actual carbon concentration in liquid steel
[C]_eq equilibrium carbon concentration
DC decarburization control
DEW Deutsche Edelstahlwerke GmbH
E energy
EAF electric arc furnace
H enthalpy
VOD vacuum oxygen decarburization

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