Parameters Affecting Dephosphorization of Stainless Steel

Literally study on dephosphorization with highest possible chromium retention

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Abstract
A literary study has been made to find parameters affecting dephosphorization of stainless steel. Ways to lower phosphorus content without major loss of chromium in order to decrease the production costs of Sandvik AB’s stainless steel. The study was conducted with respect to oxidizing dephosphorization and parameters affecting dephosphorization are carbon and chromium content, temperature and slag properties. It was revealed that higher carbon content and basicity is beneficial to the dephosphorization process. However, the choice of temperature, chromium content and flux were dependant on which way dephosphorization was approached. A method of refining chromium in slag using an electric arc furnace (EAF) was also discovered. This made it possible to extract 97% of all chromium in slag. The conclusions are that in order for Sandvik to successfully remove phosphorus, scrap metal with higher carbon content should be used, together with a basic CaO slag with constituents of e.g. Li$_2$O$_3$ and CaF$_2$. A deslagging step can be added to the argon oxygen decarburizer (AOD) process in order to remove the phosphorus bound to the slag, before decarburization.
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1 Introduction

1.1 Background

Stainless steel consists mostly of iron, chrome and nickel with lower amounts of other substances and impurities such as phosphorus. Chrome and nickel is required for the steel to receive a protective oxide layer and become stainless steel.

This report will primarily focus on the parameters affecting the phosphorus content in steelmaking, with chromium losses in mind, for the electric arc furnace (EAF) and the argon oxygen decarburizer (AOD) processes.

Phosphorus is mostly an unwanted substance in both regular and stainless steel. Phosphorus reduces the plasticity and toughness of the steel if the content is too high. During solidification the phosphorus segregates at the grain boundaries which lead to cold embrittlement. At lower temperatures this phenomenon is even more serious. [1, 2] For regular steelmaking, the phosphorus is removed by oxidizing it to the slag and then by removing the slag. For stainless steelmaking, the process cannot be repeated as easily without oxidizing chromium as well.

Common oxidation of phosphorus in a metal bath follows eq. (1), where phosphorus in the bath reacts with dissolved oxygen and oxygen ions of the slag phase. [1]

\[
P + \frac{5}{2}[O] + \frac{3}{2}(O^{2-}) = (PO_4^{3-}) \quad \text{eq. (1)}
\]

Also, phosphorus may react according another reaction, eq. (2): [18]

\[
2[P] + 5[FeO] = (P_2O_5) + 5(FeO) \quad \text{eq. (2)}
\]

In order to lower the amount of phosphorus from 150 ppm to 100 ppm, the degree of dephosphorization, \( \eta_P \) has to be at least 33%. This value is calculated by the formula below, eq. (3). Change of phosphorus content divided by initial content.

\[
\eta_P = \frac{[\Delta P]}{[P_i]} \times 100 \quad \text{eq. (3)}
\]

In addition to oxidizing dephosphorization there is reducing phosphorization. This has not been surveyed in this report, due to not being deemed relevant for Sandvik.

Today the low phosphorus content in Sandvik’s steel is achieved by purchasing scrap metal with already low phosphorus content. If it is possible to lower the amount of phosphorus in the process of making stainless steel, cheaper scrap metal with higher phosphorus content would lower the costs. Although there is no deliberate focus on dephosphorization in Sandvik’s steel production, the dephosphorization process is taking place in the interface between the slag and the melt. [3].
At Sandvik the scrap metal to be melted in the EAF is selected depending on which steel is to be manufactured. For low phosphorus steels, scrap metal which already have a low content of phosphorus is chosen. During the melting process lime (CaO) and dolomite (CaMg(CO$_3$)$_2$) is added. CaF$_2$ is also added in order to increase the solubility of the slag. When the process is finished, and it is time for tapping, the temperature of the molten crude steel is about 1700°C. [3, 4]

The melt is then transferred to the AOD converter where several steps of refining takes place such as decarburization, reduction and desulphurization. The decarburizing step removes dissolved carbon from the melt and is controlled by ratios of oxygen and inert gas. The reduction step recovers valuable oxidized alloys from the slag, such as chromium, by adding components/elements with a higher affinity for oxygen. The desulphurization step removes sulphur from the melt by having a high concentration of lime in the slag and by reducing the amount of oxygen in the melt by adding, for example, aluminium. When these steps are finished and the right temperature is reached the steel is ready for tapping. [3].

1.2 Aim
The goal with the project is to summarize factors which affect removal of phosphorus in stainless steel in order to lower content from 150 ppm to 100 ppm with minimum chromium loss. This will allow cheaper scrap metal to be purchased as raw material. This will be made by a literature study to investigate what has been published on the subject and in consideration for Sandvik AB’s production.

2 Method
A literally survey was done from the open literature. Articles where dephosphorization of stainless steel or steel containing chromium had been researched were sought after. These articles were evaluated and the methods used for removing phosphorus were investigated. The methods and results in the articles were compared and the factors influencing dephosphorization were discovered. These articles were found using the KTH library search tools alongside google. Key search words were: dephosphorization, phosphorus, steel, stainless, chromium, AOD, EAF, basicity, and slag. Also a field trip to Sandvik AB in Sandviken was made to acquire more information regarding their conditions and how their steel production processes worked. The found factors and methods were then evaluated with Sandvik’s conditions and equipment in mind. What Sandvik could do to dephosphorize their steel was decided.
3 Results

Experiments found in the open literature were analyzed to acquire the parameters affecting dephosphorization and possible chromium retention. Parameters most treated in experiments, affecting the dephosphorization and chromium retention were:

- Flux composition
- Slag basicity
- Carbon and chromium content
- Temperature

After-treatment of the AOD slag for chromium extraction:

- Chromium recycling

3.1 Flux composition:

In steelmaking, fluxes are added to the slag in order to increase removal of impurities and to protect the lining of the vessel. The dephosphorization reaction, as well as other reactions, takes place in the interface between metal and slag. Therefore it is important that the slag has a high mobility, i.e. high liquidity. In order to remove phosphorus, the flux needs to increase the phosphorus capacity of the slag and lower the viscosity. K. Kitamura et al [5] write that oxidation of phosphorus is best achieved using a slag containing Li₂CO₃, Na₂CO₃ or BaO which are more basic than CaO. Slags containing barium, with fluxes based on BaO, have high phosphate capacity. Since Barium both is toxic and expensive, the more available CaO is commonly used. [1] As more flux is added and more Cr₂O₃ enters the slag, its viscosity increases. [6] A Li₂CO₃-CaO-CaF₂-FeO flux was added in the experiments conducted by Murahashi et al [7] and it is stated that this flux has a good phosphorus capacity.

A common way to decrease viscosity and melting point of slag is to add fluorite, CaF₂. This allows a lower temperature and less chromium losses. In slags with a high amount of CaO, fluorite stabilizes the slag by increasing the phosphate capacity when forming fluorophosphates. This decreases the surface tension between melt and slag thanks to its ability to dissolve oxides. Fluxes containing CaF₂ are cheap and have great metallurgical properties but have shown environmental problems however. [1].

3.2 Slag basicity:

A slag’s basicity is defined as the ratio in weight percent between the basic oxides and the acid oxides present in the slag. Karbownikczek et al [1] defines the basicity in their experiments as eq. (4):

\[
\text{Basicity} = \frac{\text{CaO} + \text{FeO}}{\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{P}_2\text{O}_5 + \text{Cr}_2\text{O}_3} \quad \text{eq. (4)}
\]
The basicity of the slag which leaves Sandvik’s EAF is about 1.5-2. Since CaO, has good dephosphorization ability and $4\text{CaO} \cdot \text{P}_2\text{O}_5$ is stable at temperatures that occur during steelmaking, the basicity is increased with a higher concentration of CaO. If the basicity is too high by adding more than enough CaO, the melting temperature of the slag will be increased. If the CaO cannot be fully melted it will lead to an increase of slag viscosity and decrease of mobility, which leads up to slowing down the dephosphorization. The activity of FeO will decrease when the basicity gets higher than its optimum, which will slow down the dephosphorization reaction. FeO can increase the dissolution of CaO in the slag. However, if the FeO content is too high it will dilute the CaO, reducing its concentration. [2]

When Si is removed from the metal, the efficiency of lime is increased. This reduces the amount of CaO that react with silica and form calcium silicate, $2\text{CaO} \cdot \text{SiO}_2$. This results in more calcium phosphate being able to form and reducing the consumption of CaO. [8] After their experiments in the AOD, Qiu et al [2] mean that the dephosphorization of the hot metal reaches its peak at a slag basicity of approximately 3.5 to 4.5 as shown in figure (1). They also mention that increasing the basicity to a certain value also means a cost increase.

![Fig. (1). Effect of basicity on degree of dephosphorization.][2]

The influence of slag basicity was also investigated by Karbowniczek et al [1], who conclude that a high basicity is conducive to dephosphorization. This can be viewed in figure (2) that shows how the degree of dephosphorization depends on the basicity. Also, a higher basicity increases dephosphorization independently of temperature, chromium content and the decomposition of the dephosphorization mixture.
3.3 Carbon and chromium content:

Industrial experiments on making low phosphorus stainless steel from high chromium pig iron with approximately 3.6% carbon content and utilizing a Li$_2$CO$_3$-flux, proven effective at dephosphorization, were examined by Murahashi et al [7]. High chromium pig iron was melted in the EAF and sent to the AOD converter where the pig iron is carburized to a carbon content of approximately 5%. The high carbon content makes it possible to oxidize phosphorus to the slag without oxidizing any serious amount of chromium as well. The phosphorus rich slag is then removed and replaced by a new slag and flux. By removing the slag, only small amounts of phosphorus will be reduced back to the melt. This can be repeated to very low phosphorus contents in the melt. When the desired phosphorus content has been met, the melt can be decarburized. The experiments show a reduction of the phosphorus content from 260ppm to 60ppm with only 1 percentage chromium loss. [7]

S. Kitamura et al [9] states that a higher carbon content is needed if dephosphorization is to be accomplished using a CaO based slag. At lower carbon contents a BaO based slag is needed. In their experiments, the carbon content varied from 2% to 6% showing both an increase of dephosphorization rate and decrease of chromium loss at higher carbon contents. Karbowniczek et al [1] had a carbon content varying from 2.07% to 3.66% and could not find what impact it had on the degree of dephosphorization. Scrap metal with higher carbon content is also a cheaper raw material than scrap metal with less carbon content. [10]

According to the positive interaction coefficient seen in table 1 between phosphorus and carbon, high carbon content in the melt will favor dephosphorization by increasing the phosphorus activity in the melt. This will displace the equilibrium to the right, making the phosphorus migrate to the slag. (eq.1, 2) [1, 7] According to the negative interaction coefficient seen in table 1 between phosphorus and chromium, high chromium content in the melt will disfavor the dephosphorization by decreasing the phosphorus activity in the melt. This will displace the equilibrium to the left, making the phosphorus stay in the melt, in eq. (1, 2). [1, 7].
In the same way the interaction coefficient between chromium and carbon is negative. In oxidation of chromium, higher carbon content will decrease the activity of chromium which will displace the equilibrium towards \([\text{Cr}]\), making the chromium stay in the melt. [1, 7]. This is also shown in experiments by S. Kitamura et al. [9]

Table (1). Interaction coefficients with respect to phosphorus, carbon, chromium, nickel, oxygen, sulphur and silicon. [1, 11].

<table>
<thead>
<tr>
<th>i</th>
<th>P</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.062</td>
<td>-0.053</td>
</tr>
<tr>
<td>O</td>
<td>0.13</td>
<td>-0.14</td>
</tr>
<tr>
<td>C</td>
<td>0.126</td>
<td>-0.12</td>
</tr>
<tr>
<td>Si</td>
<td>0.118</td>
<td>-0.0043</td>
</tr>
<tr>
<td>S</td>
<td>0.028</td>
<td>-0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>0, -0.004, -0.006</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.016 ≥ -0.030</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4 Temperature:
Qiu et al [2] state that higher temperatures can improve the dephosphorization rate since high temperature improves the liquidity and basicity of the slag and increases the interaction between melt and slag. However, the oxidation of phosphorus is not improved by a higher temperature since the process will produce a lot of heat. As seen in figure (3), the dephosphorization rises from low temperature and reaches a maximum at 1773 K and decreases for higher temperatures. The flux in the experiments was CaO based with basicity between 3.5-4.5 and the degree of dephosphorization changed with temperature. [2].

Fig. (3). Effect of temperature on dephosphorization. [2]
To keep the chromium loss to a minimum, Karbowniczek et al. [1] argues that the process temperature should be low. Also, they received greater degree of dephosphorization at lower temperature as seen in the experiments conducted and in figure (4) and (5).

3.5 Chromium recycling:
Experiments to retrieve chromium from the AOD slag by reducing the chromium oxide to a metal phase in the EAF was made by Adamczyk et al [12]. Chromium rich slag from the AOD can be processed in the EAF where \( \text{Cr}_2\text{O}_3 \) is reduced by carbon electrodes or reduction agents and separated to a metallic phase which in turn can be retrieved and recycled. The metallic phase mostly contains chromium, but also iron, manganese, vanadium, silicon and carbon. More than 97% of both metallic and mineral bound chromium in the slag can be recovered. If temperatures in the EAF are higher than 1700 °C a reduction agent in the EAF is needed to reduce the \( \text{Cr}_2\text{O}_3 \), otherwise the carbon electrodes will suffice. Slag with high chromium content has shown to be of less practical use as a building material. Adamczyk et al [12] argues that this makes it not only economically favorable to retrieve the chromium from the slag based on the sole value of chromium, but also for the management and the enhanced practical use of the slag. This is however a very energy costly process.

4 Discussion

4.1 Flux and slag basicity:
According to the results, the slag basicity of Sandvik’s steel is too low in order to achieve a good dephosphorization. To Increase the basicity, a higher amount of the basic oxides must be added, and decrease the amount of the acid oxides. Maruhashi et al desiliconized the metal during the carburization, meaning that \( \text{SiO}_2 \) was produced. Since \( \text{SiO}_2 \) is an acid oxide, removing this by deslagging and adding new slag by adding \( \text{CaO} \), should increase the basicity significantly. This does
also mean that less CaO will react with SiO$_2$, resulting in higher efficiency of the CaO as it can react with more phosphorus. Adding more CaO would increase basicity, but also adding CaF$_2$ or other fluidizers would be important in order to get a good slag viscosity. Adding a flux of Li$_2$O$_3$ or Na$_2$O$_3$ should also increase dephosphorization, as it is done by Murahashi et al where a CaO based flux containing Li$_2$O$_3$ is added. Phosphorus content below 100 ppm was achieved using this slag. If Sandvik would use this type of flux with such basic compounds, dephosphorization without the loss of chromium might be possible.

4.2 Carbon and Chromium content:
As the results show, during the AOD process, high carbon content in the melt will displace the equilibrium to the right, oxidizing the phosphorus to the slag. In the same way, high carbon content will keep chromium in the melt. However, the critical carbon content for best chromium retention and phosphorus oxidation is not found. Karbowniczek et al argues that carbon content between 2.07% and 3.66% will benefit the dephosphorization. This is a relatively low carbon content compared to Maruhashi et al’s experiment, having up to 5.5% carbon content after carburization, although a deslagging process was needed. The degree of dephosphorization is greater for Maruhashi et al’s experiment, further verifying that high carbon content favors dephosphorization. In addition the chromium retention was also greater. As stated earlier Sandvik’s steel leaves the EAF with a carbon content of approximately 1%. The low carbon content will decrease the dephosphorization.

At present there is no deslagging in the AOD at Sandvik, since the slag contains oxidized elements such as chromium, which are being reduced back to the steel later. However if the phosphorus can be removed before the decarburization, as in the experiment of Maruhashi et al, the slag should not contain any high amounts of these valuable elements. Then the metal can be decarburized as usual after deslagging, although the higher carbon content means this will take longer time. This would result in the AOD becoming a bottleneck for the entire steel making process. If Sandvik would use this method to dephosphorize, a scrap metal with higher carbon content would be preferable which would lower the raw material costs. Also, higher carbon content would lower the melting point of the metal, so the scrap melting process should be less energy consuming.

4.3 Temperature:
Temperature affects dephosphorization in two ways. Higher temperature is conducive if a faster rate of dephosphorization is desired since it improves the interaction between melt and slag, and lower temperatures would be conducive for a dephosphorization when keeping chromium losses to a minimum is desired. High temperature would be appropriate to implement when following the theory of Adamczyk et al, since chromium lost to the slag will be recycled. If increased carbon content would be used, a high temperature would also speed up the necessary decarburization.
4.4 Chromium recycling:
Experiments conducted by Adamczyk et al argue that the best method to retain chromium in stainless steelmaking production is to recycle the AOD slag. By treating the slag in the EAF and separating the chromium rich metal phase, more than 97% of the chromium present in the slag can be salvaged. Meaning a more extensive dephosphorization can be conducted since the chromium lost to the slag will be recycled. With this method, the steelmaking process can continue as normal except a deslagging process in needed. Also, the separated metallic phase only have elements present in normal steels meaning that no processing is needed. However, to retain the chromium, the slag must be treated in the EAF. To further enhance dephosphorization this method can be combined with a higher basicity, higher carbon content and higher temperature. Whether or not this would be economically profitable has not been investigated. A cheaper scrap metal can be used, since phosphorus can be removed, but increasing the amount of CaO to raise the basicity, carburize, etc would mean a certain cost. And if the chromium is to be extracted from the slag, usage of an EAF is required, which is costly.
5 Conclusions and recommendations
With this report several factors affecting removal of phosphorus in stainless steel have been treated and the following conclusions what Sandvik AB could do to dephosphorize were made:

- Choice of flux is dependant on which way the dephosphorization is approached.
In order to raise the phosphorus capacity of the slag, Sandvik can add a special flux. A CaO based slag containing basic compounds, e.g. Li$_2$O, could be used.
- Increase Basicity
As a high basicity shows to be beneficial for dephosphorization, Sandvik should increase the slag basicity. In comparison to the results, the basicity of the Sandvik’s slag is presently too low to achieve good dephosphorization.
- Increase the Carbon content
Higher carbon content showed to be conducive for dephosphorization and chromium retention. Scrap with higher carbon content would raise the levels without any further processing, which would also be cheaper.
- Choice of temperature is dependant on which way the dephosphorization is approached.
Lowering Sandvik AB’s high process temperature in the AOD from 2000 K to 1773 K would favor dephosphorization.
- Recycling chromium
Recycling AOD slags in the EAF would eliminate chromium loss.

6 Acknowledgements
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7 References


