Quantifying sources of variation in process analytical measurements

Jellema, R.H.

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Production of steel; from iron ore to soda cans

Production of steel is a complex process in which iron ore is reduced to metallic iron. Further refinery of the formed iron to steel is performed by carefully removing and adding certain elements such that finally the product meets certain quality standards. The description of the production of steel given in this chapter concerns the steel production process currently in use at the Hoogovens steel company. In the future, probably other methods such as thin slab casting of steel will become more common because of the decreased time between order and delivery. This introduction to the production of steel should help the reader to put the research presented in this thesis into perspective. Therefore, a general description of the production process is given with some more detail of those parts of the production process that were included in the research.

2.1 Raw materials

For the production of steel mainly two raw materials are of importance: iron ore and coke. Besides these two, other materials such as scrap, pure (or near to pure) metals and gas like oxygen and argon are used during the production process. Iron ore and coke, however, are the two starting materials which are fed into the blast-furnaces.

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*The information presented in this chapter has been gathered from a technical report and personal communications.*

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2.1.1 Iron ore

The solid crust of the earth consists for approximately 5% of Iron (Fe). Concentrated regions of iron oxide are found as magmatic or sedimentary deposit. Magmatic iron ores originate from molten magma that penetrated the solid crust of the earth. The ferrous compounds crystallized at an early stage and precipitated to layers of iron oxide which can become huge such as Swedish magmatic iron ore reserves in Kiruna and Malmberget (5 and 6 in Figure 2.1). These reserves consist mainly of $\text{Fe}_3\text{O}_4$ and therefore are called magnetite ores. Magnetite ores consist for 72.4% of Fe.

Another source of iron ore is sedimentary iron ore. Iron minerals became concentrated when, due to erosion (wind, water, frost), parts of the earth crust were transported to, for instance, the bottom of the sea. Due to selection (based on particle size and other physical properties) natural concentration took place. The so-called sedimentary iron ore is found as haematite ($\text{Fe}_2\text{O}_3$) which consists for 70% of Fe. Haematite is found at for instance Carol Lake, Mount Wright and Itabira (1 and 4 in Figure 2.1).

A third kind of iron ore is of lateritic origin. This kind of ore is a residual of
2.1 Raw materials

Figure 2.2: Drawings of two forms in which coke is used for steel making: sinter (5-25 mm) and pellets (10-15 mm).

material which resided after all other components of the rock was washed away by water. Again, natural concentration occurred leaving the water containing oxide limonite \((\text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O})\) behind which contains approximately 50-60% of Fe. Places where oxide limonites are found are Orinoco, Goa and Robe River (2, 10 and 12 in Figure 2.1).

Iron ore dug from the mines has to be prepared in such a way that an optimal process control is possible in the blast-furnace. Many factors have a certain influence on the efficiency of the blast-furnace process. One of those factors is the quality of the iron ore which has to comply with two important properties:

- The reducing gasses which flow through the blast-furnace must not be obstructed (open structure of the ore).
- The reducing gasses must be able to reach the iron ore in order to let reduction of oxidic iron take place quickly (high surface to volume ratio of the ore).

A good permeability of the blast-furnace can be obtained by choosing the right particle size of the charge (between 5 and 50 mm). Besides that, the particles need to be strong enough during reduction in order to prevent crumbling of the particles which would reduce the permeability. Two forms of prepared iron ore are used in the blast-furnace namely sinter and pellets (Figure 2.2).

Production of sinter

Sinter production is started by mixing iron ore, coke (fuel) and additives together to produce a homogeneous mixture. Water and quicklime are added in order to produce micropellets. In the sinter furnaces, the small particles are baked together to form larger particles of sinter. The temperature in the
furnace (1300 °C) is high enough to ignite the fuel (coke) which is mixed with the iron ore. The temperature increases to 1400 °C which is just high enough to let the iron ore particles melt together. The large slabs of sinter are broken and cooled down. The cooled down sinter is sieved and particles in between 5 and 25 mm are used for the blast-furnaces.

Production of pellets

Pellets or balls of iron ore are formed from very fine particles of iron ore and additions. As a first step in producing pellets, iron ore and additions are ground thoroughly to form particles smaller than 0.045 mm. After grinding, the powdered material is mixed with water to form so-called green pellets. These green pellets are still wet and soft and have to be baked into hard pellets. After baking at a temperature of 1320 °C, the pellets are sieved and the fraction smaller than 3 mm is used for the production of sinter. The fraction in between 3 and 25 mm is used in the blast-furnaces.

2.1.2 Coke

For the production of coke, coals are used. These coals originate from the remains of plants that lost their gaseous constituents such as hydrogen, carbon dioxide and methane under influence of temperature and pressure. The more gaseous constituents are lost, the higher the carbon concentration becomes. An increase in carbon content results in a change of appearance ranging from brown vegetable mould through black graphite and transparent diamond. The coals used for steel production contain in between 18 and 35% gaseous components. The coke which is produced from the coals have three main functions in the blast-furnace process:

- Fuel in order to keep and bring the furnace up to the right temperature.
- Reduction of iron oxide to atomic iron.
- Means to maintain the permeability of the blast-furnace charge for gases.

As a first step in forming coke for the blast-furnace, the coals are broken into pieces. After breaking, 70% of all particles must be smaller than 2 mm. The particles of coal are prepared by heating in coke ovens until approximately 1000 °C. During this process, the coals are isolated from air. The gaseous compounds are separated from the solid carbon and the small particles of coal melt together thereby forming the coke which is needed. The coke is “well
done" at this stage of the process. At that moment the coke has been heated during a period of in between 16 and 20 hours. After this time, the coke is removed from the coke machine and to prevent the coke from burning it is quenched with water. The cooling is performed with a predestined amount of water to ensure that the water content is in between 4 and 5%. The coke is sieved and three fractions are distinguished:

- 0-20 mm: Used for iron ore preparation.
- 20-35 mm: Fine coke for usage in blast-furnace.
- > 35 mm: Rough coke for usage in blast-furnace.

Besides the coke produced in the coke ovens, also powdered coals are used in the blast-furnaces. These so-called injection coals are produced by grinding the coals in ball mills.

### 2.2 Blast-furnaces

In Figure 2.3 a schematic drawing of a blast-furnace is presented. The mouth of the furnace is situated at the top and is shut off from the air by means of a gas lock which consists of 2 valves. The base material of steel (sinter, pellets and coke) and additional material is elevated to the mouth and cast into the top of the blast-furnace above the small valve (Figure 2.3a). When the small valve is opened, the material enters the space in between the small and the large valve (Figure 2.3b). The small valve is closed again and the space in between the upper and the lower valve is filled further by repeating the above sequence. After a few sequences, the small valve is closed and the large valve is opened. The usage of the two valves prevents contact between air and contents of the blast-furnace. As soon as the large valve is opened, the raw material falls into the furnace via armour plating (Figure 2.3c) that can direct the material to predestined places in the furnace. Other types of blast-furnaces exist but the description of other set-ups is beyond the scope of this chapter.

Iron ore is a mixture of mainly iron oxides and gangue[^1^]. In the blast-furnace, iron oxide is reduced to metallic iron and it is thereby separated from the gangue. The gangue appears as slag floating on the surface of the liquid metal. The processes of reduction and separation can only take place when heat and a reducing agent are provided and here is where the coke comes back into the

[^1^]: Gangue is the commercially worthless matter in metal or mineral deposit.
Figure 2.3: Schematic presentation of a blast-furnace and the use of valves for filling the blast-furnace: a) both valves closed; b) small valve opened, large valve closed; c) small valve closed, large valve opened, the material falls into the blast-furnace shaft.
picture. Coke works both as a reducing agent and as a source of heat. Also, coke has a high melting point and therefore serves as a kind of matrix which gives porosity to the contents of the blast-furnace. Porosity is needed for both flow of liquid metal and flow of gas. Without this porosity, the furnace would clog.

Filling of the blast-furnace is performed almost continuously. While new solid material is added to the top, preheated air with a temperature between 950 and 1300 °C (even higher when powdered coals are injected) is blown in at the bottom. Coke, close to the points of entrance of the preheated air burns intensively and at those points, temperatures between 2000 and 2400 °C can be reached.

The coke in the blast-furnaces will burn and the formed carbon dioxide will reduce immediately to carbon monoxide due to the intense heat (equation 2.1).

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \\
CO_2 + C & \rightarrow 2 CO
\end{align*}
\] (2.1)

The carbon monoxide will react with the iron oxide. An example of such a reaction is presented in equation 2.2 in case of the iron oxide Fe\(_2\)O\(_3\).

\[
\begin{align*}
3 \text{Fe}_2\text{O}_3 + \text{CO} & \rightarrow 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 \\
\text{Fe}_3\text{O}_4 + \text{CO} & \rightarrow 3 \text{FeO} + \text{CO}_2 \\
\text{FeO} + \text{CO} & \rightarrow \text{Fe} + \text{CO}_2
\end{align*}
\] (2.2)

This type of reduction is also known as indirect reduction and takes place in the upper part of the blast-furnace where the temperatures are in between 570 and 1000 °C. Lower in the blast-furnace where temperatures above 1000 °C prevail, the CO\(_2\) formed according to equation 2.2 immediately reduces back to carbon monoxide according to equation 2.3 due to the high temperature and the abundance of carbon (coke).

\[
\begin{align*}
\text{FeO} + \text{CO} & \rightarrow \text{Fe} + \text{CO}_2 \\
\text{CO}_2 + C & \rightarrow 2 \text{CO}
\end{align*}
\] (2.3)

Combining both reactions in equation 2.3 and deleting equal components on both sites of the equation, equation 2.4 is obtained which is known as direct reduction. Indirect reduction is preferred because that type of reduction is less energy consuming.

\[
\text{FeO} + C \rightarrow \text{Fe} + \text{CO}
\] (2.4)
2.2.1 Tapping

The liquid metal formed in the blast-furnace is called hot metal (sometimes referred to as pig iron) and still needs to be converted to steel. Hot metal and slag flow out of the blast-furnace and are separated from each other by means of a skimmer (Figure 2.4). The hot metal (which still contains some slag) is cast into torpedos (Figure 2.5) which transport it to the steel factory by railway.
Table 2.1: Examples of the composition of a number of steels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Properties</th>
<th>Added elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloyed, refined steel</td>
<td>High strength and toughness</td>
<td>Ni, Cr, V, Mo, Wo</td>
</tr>
<tr>
<td>Durable steel</td>
<td>Higher durability</td>
<td>Mn, sometimes Cr or Mo</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Resistant to rust and acid</td>
<td>Extra Cr, Ni, Mo, Ti</td>
</tr>
<tr>
<td>Heat resistant steel</td>
<td>Resistant to high temperatures.</td>
<td>Cr or Cr and Ni, possibly Ti</td>
</tr>
<tr>
<td>Alloved tool steel</td>
<td>Suitable for exhaust pipes of motors</td>
<td>Wo, Cr, V, Co</td>
</tr>
</tbody>
</table>

2.3 Steel Production

Many different procedures have been invented for the conversion of hot metal into steel (Frischen, Puddle process, Bessemer process, Siemens-Martin process, Thomas process, Oxygen steel processes and electrical processes such as arc-furnace, induction-furnace and resistance-furnace). All techniques have in common that the carbon is reduced to an acceptable level by means of combustion. The production of pure oxygen can be performed in an economically sound way and therefore, at Hoogovens, oxygen is blown on the liquid metal bath to reduce the carbon content in the metal bath.

2.3.1 What is steel?

Steel is malleable iron. The reason why the hot metal produced in the blast furnace is not referred to as steel is that the carbon content is too high and therefore, the hot metal is not malleable. During the reduction process in the blast-furnace, carbon has been dissolved in the liquid iron and appears as iron carbide (Fe₃C) or as graphite in the iron. The amount of carbon in hot metal ranges from 4 to 4.5% and causes the solid material to be hard and brittle. Milling or welding of this material is not possible. Reduction of the carbon content below a concentration of 1.9% results in obtaining a material that is referred to as steel. Summarizing, in the blast-furnace carbon is added to remove oxygen bonded to iron and in the next phase, oxygen is added to the liquid metal bath to remove dissolved carbon.

Many different types of steel exist of which a number are summarized in Table 2.1. Even small differences in concentration can make a large difference in properties of the steel product.
Table 2.2: Typical desired concentrations in hot metal for the oxygen steel process.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in hot metal</th>
<th>Concentration in steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.06%</td>
<td>0.06%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35%</td>
<td>0.35%</td>
</tr>
<tr>
<td>Si</td>
<td>0.01%</td>
<td>0.01%</td>
</tr>
<tr>
<td>P</td>
<td>0.02%</td>
<td>0.02%</td>
</tr>
<tr>
<td>S</td>
<td>0.1%</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

2.3.2 Oxygen steel process

Hot metal is the main base material for the oxygen steel process. To guarantee continuity of the process, certain elements have to be present in a certain concentration as shown in Table 2.2 for most types of steel.

Phosphorus and sulphur need to be removed from the hot metal. Adding simultaneously oxygen and lime causes most of the phosphorus to end up in the slag layer that floats on top of the hot metal. For the desulphurization, lime is needed as well. Before further processing the material, the slag layer is removed to prevent the sulphur from re-entering the hot metal at a later stage of the process.

Besides hot metal, also scrap is an important base material. The concentrations in scrap material are already at or near the target concentrations if the material originates from the own factories. Scrap material obtained from other sources are added as well but may contain significantly different concentrations than those apparent in own scrap. Due to this diversity, input of scrap has to be controlled such that target concentrations of certain elements, which are difficult to remove, are not exceeded. Refinement of hot metal is based on the oxidation or combustion of undesirable elements. Some elements more readily bind to oxygen and are therefore more easy to remove than others. In the process of oxidation the sequence of combustion is as follows: silicon, manganese, carbon, iron. Carbon oxide escapes as a gaseous compound while silicon oxide, manganese oxide and iron oxide are absorbed by the slag layer. Oxidation of the various elements frees a huge amount of energy in the form of heat which is used for melting scrap material. Addition of solid scrap is needed to prevent the convertor from being damaged by extensive heat development.

A pear shaped convertor is used for the oxygen steel process. Oxygen (99.6 %) is blown on the surface of the steel bath in order to oxidize the undesirable elements. The convertor is loaded with liquid hot metal (75%), solid scrap (25%) and additional material (for example lime to form a slag
layer). After loading the convertor, oxygen is blown on the surface of the liquid metal. The blowing of oxygen on the surface takes place with such a force that the slag layer floating on top of the liquid metal is blown aside. Temperatures in the range of 2500 - 3000 °C are reached at the spot where direct contact between metal surface and oxygen occurs. In order to obtain a good mixing effect, gas (argon) that enters the convertor through holes in the bottom, is blown through the liquid metal. This helps to homogenize the contents of the convertor in both temperature and composition.

When the batch of steel has reached the target composition and temperature, the batch is cast into a ladle while additional materials such as ferrous manganese and aluminium are added. The amount and type of additions are dependent upon the demand of the customer. When the steel is cast into the ladle, part of the slag is cast into the ladle as well. The steel in the ladle is transported to the stirring station or to the vacuum ladle degasser.

At the stirring station, the inert gas argon is blown through the liquid steel to obtain homogeneity in both content and temperature. Ladle additions are made as well depending upon the type of steel to be prepared. The time needed to obtain the target temperature and the amount of additions needed to obtain the target concentrations are estimated from measurements and models. Before sending the batch of steel to the casting machines, a final sample is taken and measured through spark optical emission spectrometry (see Chapter 4).

After the conversion of hot metal into steel in the convertor, the obtained material contains a lot of dissolved oxygen. One method of removing the oxygen from the steel bath is by addition of aluminium and/or silicon to the steel. A disadvantage of this method is that inclusions such as Al₂O₃ and SiO₂ will evolve. As inclusions are not allowed in some types of steel, the vacuum ladle degasser has been developed with which dissolved gas in the steel bath can be removed without adding aluminium or silicon to the steel bath. Still, aluminium is added to the steel bath to remove oxygen but the aluminium oxides are allowed to migrate to the slag layer by extending the waiting time between degassing and further processing of the liquid steel. The vacuum ladle degasser is used when:

- Only an extremely low level of inclusions is allowed.
- A very low carbon concentration has to be obtained.
- A very low hydrogen concentration has to be obtained.

In the vacuum ladle degasser (Figure 2.6) the pressure is reduced from 1000 mbar to 0.7 mbar. Due to this low pressure, dissolved gas in the steel bath will
diffuse more readily from the dissolved to the gaseous state. To obtain a low pressure, a so-called vacuum vessel is immersed into the steel bath. Next, the pressure is reduced by pumping gas out of the vacuum vessel which consists of two snorkels. Through one of these snorkels, argon or nitrogen gas is entered. The combination of blowing and suction, causes the steel bath to be pumped around. When the target concentrations are reached, atmospheric pressure is retained and the batch of steel is transported to the casting machine.

2.3.3 Continuous Casting process

A schematic representation of the continuous casting machine is shown in Figure 2.7. A ready made batch of steel coming from the stirring station or the vacuum ladle degasser is cast into the so-called tundish (a) through the submerged entry nozzle or SEN (b). The steel flows through the two outlets
(e) into the mould (c) where the steel is shaped into slabs (d) or blooms. In order to obtain slabs of a certain length, cutting torches are used to cut the slabs into pieces of a certain length. Figure 2.8 shows a more detailed presentation of the continuous casting machine.

The tundish serves both as a buffer and a distribution tank. A buffer is needed to be able to cast a number of ladles of steel after each other without interrupting the casting process. From the tundish, the steel flows into the moulds in which the steel is cooled down and shaped as rectangular slabs while moving continuously (Figure 2.9).

During the casting process, the steel surface in the tundish is covered with a powder which has three purposes:

- To prevent the steel bath from cooling.
- To prevent oxidation of aluminium.
- To absorb non-metallic compounds such as aluminium oxide.

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The steel can be cast into blooms or slabs. The research was focussed on the production of slabs and therefore, only the casting of slabs of steel will be discussed.
Figure 2.8: Schematic presentation (side view) of the casting machine.

Figure 2.9: A slab of steel ejected from the casting machine is cut while moving out of the mould.
To grease the mould, casting powder is added to the mould. The molten powder is a good heat conductor and provides for a good heat conduction between the solidified surface and the mould. In the mould, a solid layer of steel of about 15 mm is formed. Further solidification takes place in the remainder of the casting machine under influence of cooling by water or a mixture of water and air. The formed slabs are cut into pieces of desired length by means of oxygen-methane burners which move along with the slab while cutting the slabs.

2.4 Rolling Mills

2.4.1 Hot milling

Slabs of steel with a maximum thickness of 228 mm can be reduced to a minimum thickness of 1.5 mm by means of hot milling. Before this process, the steel is heated to a temperature in the range of 1150-1270 °C. Heating of the material has two purposes: improvement of the structure on a microscopic scale and facilitation of the milling process. Milling is performed by means of pressure practised on the steel slabs by means of a series of cylinders as shown schematically in Figure 2.10.

The slab becomes thinner and thereby also longer. At the end of the milling process, the steel is rolled onto reels. The rolls of steel can be transported to customers outside the steel company or processed further to improve durability or to transform the steel into products like thin plates for soda cans.

2.4.2 Cold milling

Further reduction of the hot milled product with a thickness of 2-5 mm to a product with a thickness of 0.15-3 mm is possible by means of cold milling. Cold milling of steel is performed because:
• it results in a product with a higher surface quality than the half product, hot milled steel:

• the thickness of the final result can be controlled better than is the case with hot milling:

• a thinner product is needed and this is possible with the cold milling process.

During hot milling, an oxidized surface is formed on the steel surface due to oxidation by oxygen from the surrounding air. This oxide hide is capable of doing much damage to the milling cylinders of the cold milling machine and therefore the oxide hide has to be removed before cold milling. Removal takes place by means of pickling of the oxide surface through acid. During the pickling the iron oxide on the surface of the steel is reduced according to the chemical reactions presented in equation 2.5.

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 6 \text{HCl} & \rightarrow 2 \text{FeCl}_3 + 3 \text{H}_2\text{O} \\
\text{Fe}_3\text{O}_4 + 8 \text{HCl} & \rightarrow \text{FeCl}_2 + 2 \text{FeCl}_3 + 4 \text{H}_2\text{O} \\
\text{FeO} + 2 \text{HCl} & \rightarrow \text{FeCl}_2 + \text{H}_2\text{O}
\end{align*}
\]

(2.5)

Three different chemical reactions are shown because the oxide layer consists of haematite (\(\text{Fe}_2\text{O}_3\)), magnetite (\(\text{Fe}_3\text{O}_4\)) and wüstite (\(\text{FeO}\)). After removal of the oxide layer, the steel plate is rinsed with water and dried by air. Next the surface is covered with an emulsion of 25% oil in water to reduce the friction between mills and steel plate.

The thickness is reduced by the cold milling machine which is presented schematically in Figure 2.11. The extra support rolling mills are needed to prevent the working mill from bending due to the high pressure. Due to the strong transformation during milling, the structure of the cold milled material has changed dramatically which results in a very tough but breakable material.

In order to obtain a strong material that is less vulnerable to breaking, an annealing treatment is performed after cold milling the thin plate. An improved structure on microscopic scale is obtained by means of controlled heating of the cold milled plate material.

A final milling process (post milling) after the annealing treatment is performed to improve the crystalline structure of the steel plate.
2.5 Further handling

To give added value to the product, the cold milled plate material can be further processed by means of galvanization, tinning or painting. Applications for these kind of thin covered plate material can be found in automobile industries, ceilings, walls, prefab buildings, central heating boilers, venetian blinds, etc.

Tinplate is used for the production of, for example, soda cans. The process of tinning is performed by means of electrolysis. Finally, from the iron ore described in the beginning of this chapter, the material is produced that forms the basis for soda cans. It should have become clear that process control and scheduling play important roles in the total process of steel making. The process steps are strongly tied together and therefore improvement of one process phase involves many of the other process phases. A high standard in process control and therefore also a high standard in analytical measurements is needed in order to meet the targets given by the customers.