Title: Iron and Steelmaking

Code: 618-3013

Author: Jiří Bažan, Ján Kret

Edition: first, 2015

Number of pages: 135 p.

Academic materials for the Economics and Management of Industrial Systems study programme at the Faculty of Metallurgy and Materials Engineering.

Proofreading has not been performed.

Execution: VŠB - Technical University of Ostrava
18. FUNDAMENTALS OF STEELMAKING TECHNOLOGY IN ELECTRIC ARC FURNACES ................................................................. 102
19. DEOXIDATION OF THE STEEL AND ALLOYING ............................................. 107
20. SECONDARY METALLURGY OF STEEL ............................................................ 112
21. STEEL CASTING .............................................................................................. 119
LITERATURE ........................................................................................................ 135
PART A

IRONMAKING

- How to study – steel production
- Production of pig iron in a blast furnace
- Oxidation zones of a blast furnace
- Counter flow of a charge and gas in a blast furnace
- Heat exchange in a blast furnace
- Reduction of iron oxides in a blast furnace
- Reduction of iron oxides by carbon
- Reduction of iron oxides by hydrogen
- Effect of a share of direct reduction on the specific consumption of coke
- Reduction of other elements in a blast furnace
- Blast furnace slag
- Desulphurization in a blast furnace
- Types of pig irons
HOW TO STUDY

Course name:

IRONMAKING

You have received a study package designed to guide you through the 1st semester of Master's degree program in Economics and Management of Industrial Systems. Study package contains an integrated study textbook Part I – Ironmaking for the combined studies, including a study guide.

Prerequisites:

This course assumes previous completion of the course Theory of Technological Processes.

SUBJECT GOAL AND STUDY OUTCOMES

Objective:

To provide students with wider theoretical knowledge of the theory and the technology of production of pig iron with a focus on chargé materials and their treatment, technological principles of production and basic chemical, thermal and physical phenomena and processes in the production of pig iron.

Study outcomes:

Acquired knowledge:

- The student will be able to formulate physical – chemical processes occurring in production of pig iron.

Acquired skills:

- The student will be able to use basic theoretical knowledge and technological principles in pig iron production.
- The student will be able to apply pig iron production knowledge under the operational conditions.
Who is this subject intended for

The subject is integrated into the master's degree program in Economics and Management of Industrial Systems, but the subject can also take an interested part from any other field of study, if the required prerequisites are met.

Used and recommended literature is listed at the end of each section.

The way of communication with tutors

During the study are expected:

- A semester project on a given topic from the field: charge materials, technology of iron making, physical-chemical processes taking place in sintering of ores and iron production,
- The project will be monitored by the teacher within 14 days after submission and the results will be emailed to students through the IS,
- Completion of the credit test and test results will be communicated to students after its completion.

Questions about an assigned topic is possible to consult with tutor (Doc. Ing. Ján KRET, CSc.):

- On the telephone number 597 324 464
- Via e-mail: jan.kret@vsb.cz
1. PRODUCTION OF PIG IRON IN A BLAST FURNACE

CHAPTER DIVISION

- Basic terms
- Description of a blast furnace plant
- Main parts of a blast furnace, description and function
- Composition of a charge in the production of pig iron in a blast furnace
- Agglomeration and pelletization of iron ores
- Requirements to individual components of a blast furnace charge

Time for the study: 120 mins

Objective: After reading this chapter

- You will understand the purpose and function of individual operations of a blast furnace plant
- You will understand the function and importance of individual parts of a blast furnace
- You will become familiar with the basic characteristics of individual parts of a blast furnace charge
- You will understand the sense and methods of agglomeration and pelletization of ores
- You will understand the principle of calculating the amount of individual components of a blast furnace charge
- You will know that a blast furnace is a reducing aggregate

Interpretation:

Iron

Not only the chemically pure element but also various kinds of technical iron are known as iron. Technical iron contains a number of elements that change its properties. These properties are mostly affected by carbon, whose presence to approximately 2.14 % of volume enables iron (steel) to be moulded when heated. Iron with the highest carbon content loses
these properties and is brittle both when cold and after heating. Such alloys of iron with a carbon content of about 4.2 to 5.0 % produced in a blast furnace are called cast iron, also pig iron ranks among them.

**Pig Iron**

Pig iron is an alloy of iron with carbon (about 4.5 %), silicon, manganese, sulphur, phosphorus and other elements. It is produced by reduction of iron oxides, in the liquid state, in blast furnaces. This term usually also refers to a liquid product produced by smelting reduction (SRI; *Translator’s Note: Smelting Reduction Iron*), manufactured without a blast furnace and without coke.

Pig iron is divided into steel-making pig iron, which is intended for further processing to steel by various refining processes, and foundry pig iron, from which cast iron is produced by re-melting.

**Directly Reduced Iron**

Directly reduced iron is a product of iron (steel) direct reduction from ores in the solid state (at a temperature lower than the melting point) and without coke – DRI (*TN: direct-reduced iron*), HBI (*TN: Hot-Briquetted Iron*), sponge iron.

**Brief History of Iron Production**

According to most historians, the first iron used by man was of meteoritic origin. It does not contain carbon; therefore, it is soft, malleable. It usually contains an admixture of nickel. It was directly applicable to production of tools.

![A bloomery furnace](image)

*Note: 1- stone lining, 2 - earth or sand, 3 - refractory clay, 4 - furnace chamber, 5 – open slag drain, 6 - space for char, 7 – mass of iron and slag (“bloom”)*
Even though there is evidence of iron production in crucibles already in ancient times, reduction of lump ores by charcoal was used for its practical use at the beginning of iron industry. Charcoal provided necessary heat and reducing gas. Reached temperature did not exceed 1000 °C. The product was a conglomerate of reduced iron and slag. Slag used to be removed by forging, initially manually and later by means of a water wheel. Ascending need for iron led to intensification of its production.

Air was blown into a furnace and the height of the furnace was increased. Temperature at the bottom of the furnace was being increased until iron was melted. The melt was carburized and the manufactured iron ceased to be malleable. Thereby iron production is divided into two stages:

- **Production of carburized pig iron (ironworks)**
- **Refining (making malleable) pig iron by oxidation (steelworks)**

**Description of a Blast Furnace Plant**

A blast furnace plant does not operate only its own blast furnaces but also a number of preparatory and auxiliary operations with relative autonomy.
Profile of a blast furnace and its dimensions are adapted to technology of process, see Figure. The bottom cylindrical part of the profile is called a hearth, wherein pig iron and slag are accumulated and periodically discharged through tap holes. Tuyeres through which hot wind and additional fuels are blown extend into the upper part of a hearth. A hearth continues in a bosh which has a frustoconical shape with a wider upper base. The bosh shape ensures necessary deflection of hot gas flows from oxidation areas of furnace lining which would otherwise be prematurely destroyed. Smooth passage of bosh to a shaft is ensured by a belly. A shaft having a frustoconical shape, resp. shape of two truncated cones is the most voluminous part of a blast furnace. Preheating of raw materials, decomposition of carbonates and indirect reduction take place in a shaft which is characterized by a cohesive zone. The upper part of a furnace is called a throat and it serves for filling the furnace with a charge and for removing charging gas out of the furnace.
Production of pig iron in a blast furnace

Scheme of a blast furnace

Diagram of a blast furnace profile with marked technological zones
A Blast Furnace Charge and Its Treatment

A blast furnace charge consists of ore, fluxes and fuel.

The ore part of a charge consists of iron ores and concentrates, manganese ores and various types of scrap containing iron. These ore parts are usually contained in a charge as products of a high-temperature treatment i.e. as agglomerate or pellets. Agglomerate currently comprises about 70% of a metal-bearing charge, pellets about 30%. Compared with pellets, agglomerate has higher strength in reduction and higher alkalinity. It has a less favourable shape of a grain and lower iron content. Pellets have the ideal shape and higher iron content but they are usually acidic, during reduction they tend to swell and they disintegrate. Iron ores are the basic source of iron.

Iron Ores

A rock of appropriate chemical and mineralogical composition, of which iron of required composition can be obtained at reasonable cost, is considered iron ore. From the chemical point of view, iron ores can be divided into four groups.
Anhydrous Oxides

- Iron oxide, Fe₂O₃, hematite (blood ore). In the pure state, it contains 70% of iron, in the nature about 60%. It crystallizes in the trigonal system, it is non-magnetic, coloured dark red and its gangue usually contains a lot of SiO₂.
- Ferrous-ferric oxide, Fe₃O₄, magnetite. The iron content in the pure state is 72.4% of iron, in the nature to 68%. It has ferromagnetic properties and crystallizes in the cubic system. It is usually hardly reducible.

Hydrated Oxides, Fe₂O₃ . nH₂O – limonite or brown hematite. We divide hydrated oxides into four types according to the content of chemically bound water (n).

- Hydro-hematite
- Goethite
- Limonite
- Turite

All hydrated oxides contain substantially less iron than it corresponds to pure minerals. Before being used in a blast furnace, they are always freed from chemically bound water (by dissociation).

Carbonates

- Siderite, (chalybite), FeCO₃, contains 48.3% of Fe, 13.8% of O₂ and 37.9% of CO₂ in the pure state. It has a grey colour, crystallizes in the trigonal system, and prior to use is always freed from CO₂ by dissociation.

Silicates

- Chamosite [Fe,Mg]₁₅Al₁₀Si₁₁O₅₂.₁₆H₂O. It is mined very rarely and has no practical importance.

Reusable Material

Many wastes from industrial processes can serve as a substitute for iron ores or fluxes due to their chemical composition and properties.

We rank steel scrap, iron scales, metallurgical dusts and sludges, steel-making slag, etc. among the most frequently used reusable materials. Proportion of reusable material in a blast furnace charge depends on the content of detrimental substances in this material.

Most of fine-grained materials, especially waste in the form of dusts and sludges, are not only ineligible for direct processing in a metallurgical production unit but they are also a big
trouble in transport. For this reason, it is almost always necessary to form these materials into lumps.

Properties of such modified material (pellets or agglomerate) must be suitable for its further processing or handling.

**Agglomeration of Iron Ores and Concentrates**

Agglomeration, or sintering iron ores, is to heat a dust agglomeration mixture (ore part, fuel, additives) to such a temperature that surface of each grain of a charge starts to melt and the formed melt creates liquid bridges between grains, which, after solidification, ensure formation of a solid porous material - agglomerate.

A charge for the production of agglomerate consists of agglomeration ore of a grain size below 10 mm, coke of a grain size below 3 mm and alkaline additives of a grain size below 3 mm. The top surface layer is ignited after mixing and pre-pelletizing of the mixture, a zone of combustion and sintering is created (combustion front), which moves towards a grate because of a sucked air flow and in the layer, there are formed different zones, see Figure. When the combustion front reaches the grate, the agglomerate production process is finished.

![Scheme of agglomeration charge sintering in three different stages of the process](image)

*Note: 1 - combustion and sintering zone, 2 - intense heat zone, 3 - drying zone, 4 – pre-wetting zone, 5 - condensation zone, 6 - original charge, 7 - cooling zone of an agglomerate*

In the following Figure, there is a diagram showing operational continuous method of the agglomerate production on a sinter strand.
A blend of agglomeration ore, fine-grained concentrate, additives and fuel is wetted before sintering. It is pre-pelletized in a pelleting drum in order to reduce the proportion of fine-grained particles and to increase air-permeability of a mixture. The pre-pelletized blend, placed on a sintering device, is ignited by a strong external source of heat on the top surface layer and combustion continues then gradually due to sucked air also in other parts of the layer in direction of sucked air and so it ensures creation and cooling of the melt. Combustion temperatures range between 1300 to 1500 °C.

The sintering process is finished when fuel is burnt above a grate. Agglomerate leaves the sintering device, is further broken off, sorted, cooled and transported to storage tanks of blast furnaces. Certain portion of small and dust fraction remains after sorting, it is called
reversible agglomerate. This reversible agglomerate is added to agglomeration mixture and makes up around 25% and it is re-sintered. Larger quantity of reversible agglomerate decreases the yield and performance of the sintering device. Reversible agglomerate has a favourable effect on air-permeability of the sintered mixture during sintering because it has a larger grain size than micropellets of the sintered mixture and also that it heats up the charge. Beside that, it contains components which already underwent sintering and therefore heat consumption for sintering reversible agglomerate is then lower than for sintering raw ore.

**Pelletizing Iron Ores**

Pelletization is a lumpiness adjustment of fine-grained materials by combustion to the form of pellets. In doing so, also properties of pelletized materials substantially change. A charge for pelletization does not contain fuel even at high-temperature solidification. Gas is commonly used as fuel. The pellet production consists of 2 stages:

- **Formation of raw pellets**
- **Hardening of pellets, which can be high-temperature (burning) or low-temperature (chemical-catalytic) by means of bonding agents.**

Raw pellets are formed in pelletizing drums or in pelletizing disks. Pelletizing drums have higher productivity but they require sorting of products. Capillary forces and binding forces of a bonding agent are the crucial binding force in pelletizing. Pelletizing plants usually recycle their own dust wastes without any problems. Nevertheless, they rank among significant air polluters since they are technologies working with very fine grained materials and they use combustion of natural gas as an energy source. Pelletization as a complex technology is currently not industrially used in the Czech Republic (pellets are imported from abroad).

**Quality Requirements for Ore Raw Materials**

The most important characteristics of ore raw materials are:

- **Chemical properties, especially content of iron, basicity and content of pollutants (S, P, Cd, Zn, Pb, As, Na$_2$O, K$_2$O, etc.)**
- **Physical properties – humidity, lumpiness, granulometric homogeneity, density, flow properties, porosity and magnetic properties**
- **Technological properties:**
  - Strength characteristics, especially abrasion. *Strength of ore materials is ascertained by the drum peel test and strength is given by a percentage share of*
pieces of ore material, that have dimension larger than 6.3 mm (PISO 6.3) after the test. Also the parameter abrasion is determined; it is given by a percentage share of pieces of ore material, which have dimension smaller than 0.5 mm (OISO 0.5) after the test. Pellets are tested for compressive strength on a pellet

- **Reducibility** – a summary of raw material properties which determine the rate of conversion of iron oxides to metal by treatment with reductant is called reducibility. A measure of reducibility is represented by a weight loss of an ore sample per time unit, caused by transition of oxygen into gas

- **Thermoplastic properties (softening of ores)** - are given by a temperature of beginning of softening and a temperature of softening end. The difference between these temperatures is referred to as the softening interval. Values of these temperatures are measured from ore sample deformation under loading at rising temperature. The temperature of beginning of softening shall be as high as possible, the value of the softening interval shall be as small as possible

**Slag-Forming Components (Fluxes)**

Elements and compounds that are not reduced pass into slag. Alkaline components (limestone and dolomite) which form slag while passing to liquid phase in order to bond permanently acidic tailings components of ores and other undesirable impurities we consider fluxes.

Fluxes ensure formation of blast furnace slag with optimum chemical composition and with optimum technological properties. Limestone, dolomitic limestone and dolomite are the most commonly used fluxes.

**Fuels**

Blast furnace coke is the prevailing fuel in production of pig iron. In a blast furnace, coke does not act only as fuel but also as reductant, carburizer and supporting framework. A part of blast furnace coke may be replaced by fuels in liquid or gaseous state, blown by tuyeres into a blast furnace hearth (oil, natural gas, tar, etc.). Replacement rate of coke by injected fuels depends on economical favourableness and on technological factors. Blast furnace coke should have high calorific value, sufficient strength (MICUM, CSR), adequate flammability, reactivity (CRI), ignition temperature and optimal lumpiness.
Carbon content and low content of ash and detrimental additives (S, P, As) are important from the chemical point of view.

From the physical point of view, it is especially density, porosity, specific heat capacity and flow properties.

Composition of a blast furnace charge is based on the material balance of charged raw materials and expected products. A value of free bases of the component $RO_m$ is determined for each component of a charge. In a simplified way:

$$RO_m = (CaO_m + MgO_m) - B_2 (SiO_{2m} + Al_2O_{3m})$$  \hspace{1cm} (1)

where: $B_2$ is required basicity of slag

Amount of basic admixtures per a given component is then calculated:

$$V_m = \frac{RO_m}{RO_v}$$  \hspace{1cm} (2)

where: $RO_m$ is a value of free bases of m-th component

$RO_v$ - a value of free bases of a basic admixture

Amounts of basic admixtures for individual components of a charge are summed and we get a total amount of basic admixtures. In the exact calculation, transition of silicon into pig iron, evaporation of elements and other parameters are taken into account.

Amount of fuel (reductant, coke) was in the past determined according to the richness of charge by "Šárek's diagram". Nowadays, the required amount of fuel is determined by means of statistical mathematical models or from the heat balance of the blast furnace process. Proportion of coke (fuel) in a charge depends besides amounts and composition of charged materials also on their quality, on structural and technological parameters of a blast furnace, on required quality and composition of pig iron and on other parameters. Portion of individual charge raw materials is usually quoted in units of measurement i.e. calculated per unit of produced pig iron. Specific fuel consumption in a modern blast furnace is currently around 470 - 500 kg t\(^{-1}\) of pig iron.
Summary of Terms:

- A blast furnace plant, pig iron, slag
- A blast furnace, its main parts
- Components of a blast furnace charge and their role in the process of pig iron production
- The principle of a blast furnace charge calculation;
- An overview of chemical and physical processes in each part of a blast furnace

Questions

- What operations does a blast furnace plant include?
- What are the main parts of a blast furnace?
- Which three components are always present in a blast furnace charge?
- Explain the concept of agglomeration and pelletization.
- What do we mean by pig iron, sponge iron (DRI), smelting reduction (SRI)?
- Which are the most important characteristics of ore raw materials and coke?
- Based on what is the amount of alkaline additives in a charge determined?
- What does the term “free bases” mean?
- What are advantages of agglomerate compared to pellets?
2. **OXIDATION ZONES OF A BLAST FURNACE**

**CHAPTER DIVISION**

- Location, purpose and description of oxidation zones in a blast furnace
- Composition and properties of blast furnace wind
- Physico-chemical processes taking place in front of tuyeres
- Utilization of oxidation zones to control temperature and composition of reducing gases

**Time for the study:** 60 mins

**Objective:** After reading this chapter

- You will understand basic functions of oxidation zones in a blast furnace;
- You will ascertain effect of composition and properties of blast furnace wind on chemical and thermal processes in a blast furnace
- You will have an overview of physical, chemical and thermal processes taking place in front of tuyeres
- You will know compositions, amounts and properties of gases escaping from oxidation zones.

**Interpretation:**

In the upper part of a hearth about half a meter below the edge of bosh, there are openings spaced around a perimeter of the hearth, through which heated air – blast furnace wind - is injected into a blast furnace by means of special devices (tuyeres).

Coke, which together with other raw materials descends from a throat into a hearth, gets to an oxidation zone in front of individual tuyeres where intensive combustion of the coke carbon takes place in a flow of blown wind.

\[
C_{(k)} + O_2 = CO_2 \quad (3)
\]

As there is surplus of carbon in a hearth, carbon dioxide is reduced to carbon monoxide and this product of Boudouard reaction in a blast furnace is essential for reducing zones of
a blast furnace. CO thus always escapes from oxidation zones as a product of coke combustion.

\[ C_{(k)} + CO_2 = 2 CO \]  \hspace{1cm} (4)

In areas with a lack of oxygen, the carbon of coke is burnt imperfectly to CO.

\[ C_{(k)} +0,5 O_2 = CO \]  \hspace{1cm} (5)

Blown wind contains natural moisture and is also often intentionally wetted. In the reaction of the coke carbon with water vapour, also hydrogen which becomes another component of the reducing gas arises besides carbon monoxide.

\[ C_{(k)} + H_2O = H_2 + CO \]  \hspace{1cm} (6)

Nevertheless, the reducing gas is significantly enriched with hydrogen while hydrocarbon fuels are injected into a hearth through jets located in tuyeres. This replaces a portion of coke and increases reducing ability of gas but it cannot replace the gas in its function of “supporting framework”, therefore further significant increase in amount of injected fuel is not realistic.

Boudouard reaction as well as reaction of hydrogen with the coke carbon is highly endothermic reaction and decreases temperature in a given area. Cost of coke is approximately one-third of the total cost of pig iron production. From the physical point of view, combustion of coke in oxidation zones may be considered gasification of solid coke which frees up space in the lower part of a blast furnace for the descent of next batch. Besides CO, H₂, N₂, hearth gas leaving oxidation zones contains also SO₂ from oxidation of the sulphur of coke burning in front of tuyeres. But this component of the gas dissolves in dribbling pig iron and returns to a hearth where desulphurization is carried out.
Summary of Terms:
- Blast furnace wind, combined wind, substitute fuels
- Combustion of the fuel carbon in front of BF tuyeres
- Boudouard reaction
- Water vapour reaction
- Amounts and compositions of gases escaping from oxidation zones

Questions
- What is the composition of blast furnace wind?
- What is the temperature of the blast furnace wind nowadays?
- What speed is the blast furnace wind injected at into a furnace?
- What does oxygen in oxidation zones react with?
- Where is Boudouard reaction carried out in an oxidation zone?
- What is the role of nitrogen in the blast furnace wind?
- What happens with water vapour in an oxidation zone?
- Why cannot H₂O and CO₂ exist beyond the boundary of oxidation zones?
- What is the composition of the reaction gases beyond the oxidation zone?
3. COUNTER FLOW OF A CHARGE AND GAS IN A BLAST FURNACE

CHAPTER DIVISION

✓ Fundamental condition of blast furnace operation
✓ Vertical forces applied to lumps of a charge in a blast furnace
✓ Loss of gas pressure in the granular layer
✓ Possibilities of gas flows controlling in a BF
✓ External, internal and normal operation of a BF

Time for the study: 60 mins

Objective: After reading this chapter

- You will understand necessity of a smooth descent of a charge and flow of furnace gases
- You will learn about forces acting on individual lumps of a charge
- You will learn about basic characteristics of gas flow through a granular layer
- You will know how the external and internal operation of a blast furnace manifest themselves

Interpretation:

Operation of a blast furnace is conditioned by continuous descent of a blast furnace charge and continuous flow of reducing gases in the opposite direction. It means that forces acting downwards on particles of a charge must be greater than forces acting against the descent of a charge – kinetic energy of gas, frictional forces and buoyancy force of coke immersed in pig iron or slag.
G = \rho_m \cdot g \cdot h \tag{7}

where: \( \rho_m \) is density of charge grains

\( \rho_g \) – gas density
\( g \) – gravitational acceleration
\( h \) – distance from a backfill surface

V = 0.5 \cdot \rho_g \cdot w_g^2 + T + A \tag{8}

where: \( w_g \) is gas velocity
\( T \) – frictional forces
\( w_g \) – gas velocity
\( A \) – buoyancy force of coke immersed in slag and pig iron

Kinetic energy of gas, i.e. velocity of flowing reducing gases, has a determinative role. Ability of a granular charge to let the gaseous phase through is commonly assessed by its air-permeability. As air-permeability of a charge in a blast furnace cannot be monitored continuously and with sufficient accuracy, this parameter is usually replaced by the loss of gas pressure in a certain height.

The loss of gas pressure at a certain height is usually calculated by means of the so-called Ergun equation:

\[
\Delta P = \frac{\xi \cdot \frac{1-\varepsilon}{\varepsilon^3}}{d \cdot \Phi} \cdot \rho_0 \cdot \omega_0^2 \cdot \frac{T}{T_0} \cdot \frac{P_0}{P}
\tag{9}
\]

where: \( \Delta P \) is loss of gas pressure in a granular layer, [Pa]
\( \xi \) – coefficient of aerodynamic resistance, [1]
\( \varepsilon \) – voidage of a layer, [m$^3$.m$^3$]
\( \Delta h \) – height of the assessed column, [m]
Counter flow of a charge and gas in a blast furnace

\[ d \quad \text{mean linear dimension of grains, [m]} \]
\[ \Phi \quad \text{coefficient of grain shape, [1]} \]
\[ \rho_0 \quad \text{gas density, [kg.m}^{-3}\text{]} \]
\[ w_0^2 \quad \text{velocity of gas flow, [m.s}^{-1}\text{]} \]
\[ T \quad \text{real temperature of gas, [K]} \]
\[ T_0 \quad \text{standard temperature of gas, [K]} \]
\[ P \quad \text{real pressure, [Pa]} \]
\[ P_0 \quad \text{standard pressure, [Pa]} \]

We need to know values of the aforementioned quantities, respectively to calculate them from available values, in order to come to the calculation of a pressure loss in a granular layer.

Since granulometric composition of a charge (ratio of coke and ore) is different in different distances from the axis of a blast furnace, there is different voidage and so different velocity of reducing gases flow. Also different velocity of descending of a solid charge in different distance in the radial direction is a consequence of that. A charge descends unevenly in a blast furnace in the radial direction. Technologically, this unevenness shall be intentional, it shall be controlled.

We distinguish three types of blast furnace operation based on this unevenness.

- **Inner (central) operation of a blast furnace is such an operation in which gas flows and a charge descends mainly in the axis of a furnace. Descent of a charge at furnace walls is slow**

- **Outer (peripheral) operation of a blast furnace is such an operation in which gas flows and a charge descends mainly at furnace walls and only little in the central part of a furnace**

- **Regular operation of a blast furnace is a compromise between the mentioned furnace operations; distribution of gas flows is arranged on purpose in a radial cross-section of a furnace**

Distribution of gas flows in a blast furnace presupposes knowledge of their arrangement. In a throat of a blast furnace (above a charge), temperature and gas composition are measured in the axis of a furnace and in each octant around circumference (at a furnace wall).

Hearth gas leaving oxidation zones has a high temperature (up to 2000 °C) and contains carbon in the form of CO (no CO\(_2\)). In the areas where gas flows quickly, it has not enough
time to be cooled and there is then not enough time for CO to be reduced to CO$_2$. During the peripheral operation, there will be high temperature of gas and low CO$_2$ content at the wall of a throat. During the central operation on the contrary, there will be high temperature and low CO$_2$ content in the axial part of a furnace, see Figure.

Central and peripheral (circumferential) operation of a blast furnace

Gas flows are mostly controlled from above (by pouring). We pour an air-permeable charge (coke) into places where we want to support gas flowing. We pour smaller impermeable charge (the ore part) where we want to suppress the flowing. We rank also size of a charge, order of charged components, etc. among the control parameters. A bell-less top charging system provides much better conditions for gas flows controlling in a blast furnace than a bell type charging system.

Gas flows may be controlled also from below by means of parameters of the blast furnace wind.
Productivity Management of Blast Furnace

The condition of the blast furnace operation is a continuous drop of the charge and flowing of the reduction gases. The faster drop of the charge, the higher the blast furnace productivity.

The basic method of increasing the furnace productivity is the increase of the amount of the blown wind. Increased amount of the wind makes it possible to burn more coke, produce more heat and more reduction gas. By burning larger quantity of coke more space for the descent of the charge is cleared. Further increase in the amount of blown wind causes the decrease in the rate of the productivity growth up to the stop point of the charge. With increase of the amount of wind increases its flowing rate, which increases the force that counteracts the decrease of the charge, see Figure. For the further growth of productivity it is necessary to reduce the gas flow rate through the batch. All measures to reduce the rate of the gas flow lead to an increase of productivity.

In practice are used two basic methods to increase the productivity.
The method of high pressure inside furnace top: the method is based on reduction of the gas drain at the exit of blast furnace by means of so called throttling system so called expander. The gas pressure increases in the shaft of the blast furnace and its volume decreases and thus also the gas flow rate in m.s\(^{-1}\) or m\(^3\).s\(^{-1}\). Rate in g.s\(^{-1}\) or mol.s\(^{-1}\) remains the original. The gas density increases. Reduction of the gas rate reduces the force counteracting the drop of the batch and accelerates its descent.

The enrichment of the blast furnace wind with the oxygen: increasing the oxygen content in the blown wind at the same amount of burned coke reduces the portion of nitrogen in the wind and in the reduction gas, in consequence of which the gas volume reduces and hence its flow rate. Consequences are the same as in the first method.

A certain possibility of the increase of productivity is also the increase of the weight of the charge, for example by replacing sinter with pellets. The pellets contain more iron (are heavier) and a greater bulk density (an ideal shape of the grain).

Summary of Terms:

- Air-permeability of a charge column in a BF
- The loss of gas pressure in a granular layer
- The inner operation of a blast furnace
- The outer operation of a blast furnace
- The regular operation of a blast furnace
- Controlling a counter flow of a charge and gas in a blast furnace

Questions

- What is the condition for a charge descent in a blast furnace?
- What forces act downwards on grains of a charge?
- What forces act upwards on grains of a charge?
- What is the air-permeability of a granular layer?
- What is the pressure loss in a granular layer?
- How does granularity of a charge influence the pressure loss and voidage of the charge?
- Does the grain shape influence the air-permeability of a charge?
- Why do hydrocarbon substitute fuels reduce the TFT?
- What methods are used to increase productivity of the blast furnace?
4. HEAT EXCHANGE IN A BLAST FURNACE

CHAPTER DIVISION

✓ Basic laws of heat exchange in a blast furnace
✓ Definition of basic zones of a blast furnace in terms of heat exchange
✓ Description of the principle of heat transfer in a blast furnace

Time for the study: 60 mins

Objective: After reading this chapter

- You will know how the external and internal operation of a blast furnace manifest themselves
- You will understand the principle of heat exchange in a blast furnace
- You will become familiar with division of a blast furnace into 3 basic zones in terms of heat transfer
- You will learn which part of a blast furnace is the most important in terms of heat transfer

Interpretation:

Reducing gas escaping from oxidation zones having temperature of about 2200 °C flows at high speed towards a throat and meanwhile transfers its heat to a charge. The gas is cooled this way to a temperature that is always higher than the temperature of the outer atmosphere. A charge is heated from an inlet temperature, which is usually equal to the temperature of the outer atmosphere, to the mean temperature of liquid products at an outlet about 1450 – 1500 °C. The course of temperatures was ascertained by calculation and measurement, see Figure below. In view of these temperature circumstances, a blast furnace can be uprightly divided into 3 parts (zones):

- $H_1$ – upper zone of heat exchange (thermally preparatory zone)
- $H_2$ – middle zone of heat exchange (thermally inefficient zone, idle zone)
- $H_3$ – lower zone of heat exchange (production zone)
A blast furnace can therefore be compared to two heat exchangers connected to each other by thermally inefficient zone.

The existence of a thermally inefficient zone proves that in the production zone, practically perfect heat exchange takes place. Temperature of the gaseous and solid phases in the middle zone practically become equal (the temperature difference is 10 to 50 K). It is impossible to lower the height of a blast furnace by the height of the middle zone, because a number of chemical and physical processes are carried out here. Comparison of temperatures at the end of the production zone enables to draw up the heat balance of the zone.

In the upper zone of heat exchange, there is always an excess of heat. For example, an increase in an inlet temperature of a charge would be reflected only by a decrease in the height of the middle zone and an increase in the temperature of outgoing gas. Heat does not get into the production zone where it is exploitable and increased temperature of gas complicates its escape from a blast furnace.

Solving equations of heat transfer in different zones is based on the assumption that the amount of heat passed by gas on a charge equals to the amount of heat received by the charge.

\[ G_g \cdot c_g \cdot dt_g = G_m \cdot c_m \cdot dt_m \]  

(10)

Knowledge of input and output temperatures and of equality of temperatures in the middle zone enables to determine boundary conditions for each zone so that differential equations for different zones can be compiled.
Heat Exchange in a blast furnace

Summary of Terms:
- Thermally preparatory zone, idle zone, production zone
- Water equivalent of a charge, water equivalent of gas
- Heat content of a charge, heat content of gas

Questions
- Why is there excess of heat always in the upper zone of heat exchange?
- Which is the most important zone of heat exchange?
- What are the inlet temperature of a charge and the initial temperature of gas?
- In which part of a blast furnace is the heat transfer most intensive and why?
5. REDUCTION OF IRON OXIDES IN A BLAST FURNACE

CHAPTER DIVISION

✓ Characteristics of individual iron oxides
✓ Affinity of elements for oxygen
✓ Richards-Ellington diagram
✓ Basic theory of reduction
✓ Reductants in a blast furnace

Time for the study: 100 mins

Objective: After reading this chapter

- You will understand basic characteristics of individual iron oxides
- You will understand what we mean by wüstite
- You will understand the importance of affinity for oxygen for reduction and oxidation reactions
- You will know how to use the Richardson diagram
- You will know the dissociation theory of iron oxides reduction
- You will know the adsorption theory of iron oxides
- You will know which elements or compounds are used to reduce iron oxides in a blast furnace

Interpretation:

Iron Oxides

Hematite (α-Fe₂O₃) is the most widespread iron oxide on Earth. It crystallizes in the trigonal system and has the lattice type of corundum (a = b = c = 5.4271 Å, α = β = γ = 55° 15.8’). Maghemite (γ - Fe₂O₃) has the cubic lattice as magnetite, is magnetic (which is used in the magnetic ore beneficiation).
Magnetite $\text{Fe}_3\text{O}_4$ ($\text{Fe}_2\text{O}_3$.FeO) crystallizes in the cubic system and forms a lattice type of spinels. A basic cell has the dimensions of $a = b = c = 8.41$ Å.

Wüstite is actually vacant FeO and can be denoted by the general formula $\text{Fe}_{1-y}\text{O}$ where $y$ is the concentration of vacancies. ($0.0463 < y < 0.1674$). Each vacancy of iron is compensated by two trivalent iron ions. It has a cubic crystal lattice and at the temperature of 570 °C, it is $y = 0.05$.

Rough idea of the structure is shown in following Figure.

![Structure of the lattice of wüstite](image)

Basic parameters of individual oxides are depicted in the sector of the binary diagram Fe-O in the following Figure.

![The binary iron – oxygen diagram](image)
The reduction order of individual iron oxides and also of other oxides with carbon may be determined from the Richards-Ellington diagram, see Figure.

Carbon monoxide, carbon and hydrogen are the basic reductants in a blast furnace; they are oxidized to carbon dioxide, carbon monoxide and water vapour during the reduction process. CO contributes the most to the reduction (40 to 60 %) and hydrogen the least (3 to 20 %) but importance of the reduction with hydrogen grows when hydrocarbon fuels are injected.

Since the products formed in a blast furnace are continuously being exhausted, there is no risk that the reduction would be reversible and metal would be re-oxidized in a blast furnace.
Reduction of iron oxides in a blast furnace

Reducing mechanism is explained in two ways. Earlier theory (dissociation) explains the mechanism in two stages:

\[ \text{MeO} = \text{Me} + 0.5 \text{O}_2 \quad (1^{\text{st}} \text{ stage}) \]  
\[ \text{R} + 0.5 \text{O}_2 = \text{RO} \quad (2^{\text{nd}} \text{ stage}) \]  
\[ \text{MeO} + \text{R} = \text{Me} + \text{RO} \quad (13) \]

In the first stage, dissociation of oxide takes place and in the second stage, reductant is oxidized by released oxygen.

The second, more modern concept of the mechanism (adsorption) assumes three successive steps.

\[ \text{MeO} + \text{R} \to \text{MeO} \cdot (\text{R})_{\text{ads}} \quad (1^{\text{st}} \text{ stage}) \]  
\[ \text{MeO} \cdot (\text{R})_{\text{ads}} \to \text{Me} \cdot (\text{RO})_{\text{ads}} \quad (2^{\text{nd}} \text{ stage}) \]  
\[ \text{Me} \cdot (\text{RO})_{\text{ads}} \to \text{Me} + \text{RO} \quad (3^{\text{rd}} \text{ stage}) \]  
\[ \text{MeO} + \text{R} \to \text{Me} + \text{RO} \quad (17) \]

The first stage represents adsorption of a gaseous reductant on a reaction surface of metal oxide, the second stage represents a course of the reduction and the third stage represents desorption of gaseous products of the reduction of the reaction surface. Difficulty of the reduction is also directly related to dissociation tension caused by the dissociation of oxide.

We can say that the lower the dissociation tension of carbon at a given temperature, the more difficult the reduction of oxide. The explanation is that the dissociation tension of carbon is closely related to free enthalpy change, whose negative value is a measure of the affinity of an element for oxygen; therefore, the difficulty of reduction is given by the stability of oxide in the metal.

Temperature dependence of chemical affinity of oxygen for iron is shown in the following Figure.

Fe\(_2\)O\(_3\) has the highest dissociation tension, thus it is reduced most easily, on the contrary, FeO has the lowest dissociation tension from the temperature of approximately 570 °C and therefore, it is reduced worst. So at temperatures higher than 570 °C, the reduction order will be as follows:

\[ \text{Fe}_2\text{O}_3 \to \text{Fe}_3\text{O}_4 \to \text{FeO} \to \text{Fe} \quad (18) \]

At temperatures below 570 °C, FeO is thermodynamically unstable and spontaneously changes to Fe\(_3\)O\(_4\) and iron.
Summary of Terms:
- Hematite, magnetite
- Wüstit
- Reduction order of iron oxides
- Oxygen affinity
- Reduction mechanism
- Dissociation tension
- Reduction agents

Questions
- What does “y” in the formula for wüstite mean?
- Explain the term “affinity for oxygen”.
- Which reduction mechanism is more accurate?
- What is the dissociation tension?
- What reductants do you know?
6. REDUCTION OF IRON OXIDES BY CARBON

CHAPTER DIVISION

✓ Fundamentals of thermodynamics of iron oxide reduction by carbon
✓ Gradual reduction of iron oxides by carbon
✓ Baur-Glässner-Boudouard diagram
✓ Direct and indirect reduction
✓ Degree of utilization of reducing gas

Time for the study: 120 mins

Objective: After reading this chapter

- You will understand the basic thermodynamic laws of the reduction of iron oxides by carbon
- You will learn the principle of Baur-Glässner-Boudouard diagram construction
- You will know zones of stability of individual iron oxides
- You will understand dependence of the position of the reduction beginning of individual oxides on temperature and composition of reducing gas
- You will learn the possibilities of Baur-Glässner-Boudouard diagram application in practice

Interpretation:

An iron ore charge brings the necessary amount of iron in the form of its oxides or other compounds which contain these oxides into a blast furnace. Agglomerate, pellets and lump ore are the main components of an iron ore charge. These iron ore raw materials are subjected to reduction. The order of iron oxides reduction at temperatures higher than 570 °C:

\[ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \]  \hspace{1cm} (19)

From iron oxides, only \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) are contained in ores. Free \( \text{FeO} \) only occurs as a part of siderite and in agglomerate in pellets in various bonds. It is apparent from
following Figure that FeO is thermodynamically unstable at temperatures below 570 °C and spontaneously decomposes according to the equation:

$$4 \text{FeO} = \text{Fe}_3\text{O}_4 + \text{Fe} \quad (\Delta H^{\circ}_{298} = -40\,612 \text{ kJ})$$  \hspace{1cm} (20)

It means that the order of reduction below 570 °C is:

$$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$$ \hspace{1cm} (21)

Accordingly, the reactions take place:

\(\bowtie\) Above 570 °C:

$$3 \text{Fe}_2\text{O}_3 + \text{CO} = 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 \quad (\Delta H^{\circ}_{298} = 2667 \text{ kJ})$$ \hspace{1cm} (22)

$$\text{Fe}_3\text{O}_4 + m\text{CO} = 3\text{FeO} + \text{CO}_2 + (m-1)\text{CO} \quad (\Delta H^{\circ}_{298} = 2667 \text{ kJ})$$ \hspace{1cm} (23)

$$\text{FeO} + n\text{CO} = \text{Fe} + \text{CO}_2 + (n-1)\text{CO} \quad (\Delta H^{\circ}_{298} = -13942 \text{ kJ})$$ \hspace{1cm} (24)

\(\bowtie\) Below 570 °C:

$$\text{Fe}_3\text{O}_4 + p\text{CO} = 3\text{Fe} + 4\text{CO}_2 + (p-4) \quad (\Delta H^{\circ}_{298} = -15156 \text{ kJ})$$ \hspace{1cm} (25)

The coefficients m, n and p represent the volumes of CO necessary for the formation of the corresponding volume of CO\(_2\) in the respective equilibrium gaseous mixture (CO +CO\(_2\)).

From the known dependences of Gibbs energy change
Reduction of iron oxides by carbon

\[ \Delta G^\circ = -RT \ln K_p \]  

(26)

\[ \Delta G^\circ = a + bT \]  

(27)

It is possible to derive the dependence of the equilibrium composition of gas on a temperature. For example for the reduction of magnetite, the relation can be derived:

\[ \log K_p = \log \left( \frac{p_{CO_2}}{p_{CO}} \right) = -\frac{1834}{T} + 2.17 \]  

(28)

A value of the coefficient “m” for this reaction can be calculated from the equation:

\[ \frac{1}{m-1} = \frac{\%CO_2}{\%CO} = K_p \]  

(29)

\[ m = \frac{K_p + 1}{K_p} \]  

(30)

Graphical representation of the dependences calculated for individual reactions is shown in following Figure.

![Graphical representation of the dependences calculated for individual reactions](image)

*Balances between iron, wüstite, magnetite, (CO + CO₂) mixture and carbon*

The diagram includes also the equilibrium curve of Boudouard reaction which is particularly important for the FeO - C system. The graph is known as the Baur-Glässner-Boudouard diagram.

From the thermodynamic point of view, the intersections of Boudouard equilibrium curves with the equilibrium curves of reduction reactions represent beginnings of direct
Reduction of iron oxides by carbon

reduction of magnetite and wüstite, see Figure below. Indirect reduction is carried out at temperatures to about 800 °C, in the range of 800 to 1100 °C, both types of reduction take place and above the temperature of 1100 °C, only direct reduction occurs.

Direct reduction of solid iron oxides can take place through the gas phase and in conjunction with Budouard reaction whose equilibrium depends on both the temperature and the total gas pressure; it has a significant influence on the proportions of individual types of reduction in the overall process.

\[
\begin{align*}
\text{FeO} (s) + \text{CO} (g) & \rightarrow \text{Fe} (s) + \text{CO}_2 (g) \quad (\Delta H_{298}^\circ = -13.9 \text{ kJ}) \\
\text{CO}_2 (g) + \text{C} (s) & \rightarrow 2\text{CO} (g) \quad (\Delta H_{298}^\circ = 166.2 \text{ kJ}) \\
\text{FeO} (s) + \text{C} (s) & \rightarrow \text{Fe} (s) + \text{CO} (g) \quad (\Delta H_{298}^\circ = 152.2 \text{ kJ})
\end{align*}
\]

Degree of utilization of reducing ability of gas (CO) depends on values of the coefficients m, n, p and is expressed by the relation:

\[
\eta = \frac{\text{CO}_2}{\text{CO} + \text{CO}_2}
\]

**Summary of Terms:**

- Individual reduction equations by means of CO and C
- Coefficients of CO excess – m, n, p
- Initial temperature of the direct reduction
- Importance of Boudouard reaction for the course of the direct reduction
- Baur-Glässner-Boudouard diagram
- Utilization coefficient of CO in a blast furnace

**Questions**

- Which reduction reactions by means of carbon are exothermic and which are endothermic?
- Explain the principle of Baur-Glässner-Boudouard diagram construction.
- Which iron oxides are easily reducible and which are reducible with difficulties?
- Why does Baur-Glässner-Boudouard diagram contain the equilibrium curve of Boudouard reaction?
- What is the physical importance of intersections of the Boudouard reaction curve with curves of reduction reactions?
7. REDUCTION OF IRON OXIDES BY HYDROGEN

CHAPTER DIVISION

✓ Fundamentals of thermodynamics of iron oxide reduction by hydrogen
✓ Chemical equations of reduction of individual iron oxides by hydrogen
✓ Comparison of equilibria of reduction equations by carbon and hydrogen
✓ Degree of utilization of hydrogen in a blast furnace

Time for the study: 60 mins

Objective: After reading this chapter

- You will understand the basic thermodynamic laws of the reduction of iron oxides by hydrogen
- You will familiarize yourself with the gradual reduction of iron oxides by hydrogen
- You will be able to compile Baur-Gläsner diagram for reduction by hydrogen
- You will understand the difference between the reduction by carbon and by hydrogen from the thermodynamic and kinetic perspective

Interpretation:

Reactions of iron oxides with hydrogen are analogous to the reactions of these oxides with carbon monoxide; they differ in reaction enthalpy and values of the coefficients m, n, p.

The course of reactions of iron reduction by hydrogen at a temperature:

⇒ Above 570 °C:

3 Fe₂O₃ + H₂ = 2 Fe₃O₄ + H₂O       (ΔH°₂₉₈ = 11 304 kJ)     (35)

Fe₃O₄ + m'H₂ = 3FeO + H₂O(g) + (m’-1)H₂       (ΔH°₂₉₈ = 67 826 kJ)     (36)

FeO + n’ = Fe + H₂O + (n’-1)H₂       (ΔH°₂₉₈ = -13 942 kJ)     (37)
Below 570 °C:

\[
\text{Fe}_3\text{O}_4 + p\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O} + (p' - 4)\text{H}_2 \quad (\Delta H^\circ_{298} = -15156 \text{ kJ})
\] (38)

Graphical depiction of dependences of the equilibrium gas composition on temperature for individual reduction reactions by hydrogen is shown in Figure below.

---

Balances between iron, wüstite, magnetite and the gas mixture of (H\(_2\) + H\(_2\)O)

Reducing ability of hydrogen is used mainly at high temperatures but its participation in the reduction is reflected only a little by change in the chemical composition of gas. The reason is that formed water vapour reacts with the carbon of coke, so the reduction by hydrogen proceeding at high temperatures manifests itself in its consequence as the direct reduction.

\[
\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}
\] (39)

\[
\text{H}_2\text{O} + \text{C}_k = \text{H}_2 + \text{CO}
\] (40)

\[
\text{FeO} + \text{C}_k = \text{Fe} + \text{CO}
\] (41)

The equilibrium degree of utilization of hydrogen:

\[
\hat{n}_{\text{H}_2} = \frac{H_2\text{O}}{H_2 + H_2\text{O}}
\] (42)

A comparison of the thermodynamic equilibria of the Fe-O-H system with the Fe-O-C system implies that the degree of utilization of both reducing gases (H\(_2\), CO) is approximately the same at the temperature of 820 °C, see following Figure. At this temperature, it is \(m = m'\), \(n = n'\).
Below the temperature of 820 °C, CO is a better reductant; hydrogen is then a better reductant above this temperature. This, however, applies only in terms of thermodynamics. In terms of kinetics, hydrogen is a better reductant also below this temperature due to better diffusion ability.

![Diagram of thermodynamic equilibrium of the Fe-O-C and Fe-O H system](image)

**Summary of Terms:**
- Chemical equations for the reduction of various iron oxides
- Coefficients of hydrogen excess for various reduction equations – m’, n’, p’
- Baur - Gläsner diagram for reduction with hydrogen
- Reduction ability of carbon and hydrogen
- Degree of utilization of hydrogen in the blast furnace

**Questions**
- What are the sources of hydrogen in a blast furnace?
- What has a larger atomic diameter, carbon (CO) or hydrogen?
- What is the better reductant at temperatures above 820 °C, carbon or hydrogen?
- Can be hydrogen the better reductant also at temperatures below 820 °C?
- Do the coefficients of a reductant excess differ for hydrogen and carbon?
- Under which conditions are coefficients of excess equal (m = m’, n = n’, p = p’)?
- May Boudouard reaction take place during the reduction by hydrogen?
8. EFFECT OF A SHARE OF DIRECT REDUCTION ON THE SPECIFIC CONSUMPTION OF COKE

CHAPTER DIVISION

- Advantages and disadvantages of direct reduction
- Advantages and disadvantages of indirect reduction
- CDR diagram
- Utilization of CDR diagram for optimization of the specific consumption of coke (carbon)
- The amount of carbon for the direct reduction, indirect reduction and heat requirements
- Utilization of CDR diagram for controlling a blast furnace

**Time for the study: 120 mins**

**Objective:** After reading this chapter

- You will understand that the total consumption of carbon in a blast furnace is not determined by the sum of needs for direct, indirect reduction and for heat requirements but by the maximum value thereof
- You will become familiar with the meaning of the term “degree of direct reduction of wüstite”
- You will become familiar with CDR diagram construction and determination of the optimum degree of the direct reduction of wüstite
- You will understand the possibilities of using the CDR diagram in controlling consumption of coke (carbon) in production of pig iron

**Interpretation:**

For the production of pig iron in a blast furnace, carbon is needed for direct reduction, indirect reduction and for heat requirements (endothermic reaction, heating and melting).

The fact that the overall consumption of carbon is not the sum of the three mentioned needs but it is the maximum value thereof, is an advantage of blast furnace iron production.
This is due to the fact that the carbon of coke burnt in front of tuyeres releases heat - \( C_t \) during combustion (to CO) and a combustion product (CO) is used for indirect reduction. Similarly, the product of direct reduction (CO) is further utilized for indirect reduction.

A blast furnace can therefore operate in a "thermal region" right of \( r_{dopt} \) (see following Figure) where the consumption of carbon (of coke) is determined by its consumption on heat (\( C_t \)) or in the chemical region left of \( r_{dopt} \) where the carbon consumption is determined by the consumption on the reduction (\( C_i \)). When we plot the real consumption of coke and the real \( r_d \) into the diagram, it is possible to identify measures to reduce consumption of carbon (of coke). The measures may be taken in the field of furnace operation (external, internal operation, etc.), or in the field of charge quality (reducibility of an ore charge, reactivity of coke).

Currently, the principle “the lower degree of direct reduction, the smaller specific consumption of coke” (Grüner principle) is no more valid. This principle was applicable in the past for small, poorly-cooled blast furnaces and an untreated charge, where a very large amount of carbon was needed to cover heating needs (upper line of \( C_t \) in the right part of the Figure). The \( C_t \) line is shifted downwards by improvements of furnace structures and adjustment of a charge and the minimum consumption of carbon is at the optimum degree of direct reduction of wüstite - \( r_{dopt} \).

### Summary of Terms:

- Carbon needed for the indirect reduction
- Carbon needed for the direct reduction
- Carbon needed for heat
- Degree of the direct reduction of FeO
- Optimum degree of the direct reduction of FeO

**Questions**

- What is the degree of the direct reduction of wüstite?
- What is the degree of the indirect reduction of wüstite?
- What is the optimum degree of the direct reduction of wüstite?
- What is the “Grüner principle”?
- Why is the “Grüner principle” not applicable in modern blast furnaces?
- Does the reduction of heat requirements shift $r_{\text{dopt}}$ to higher or to lower values?
- Why is the carbon consumption on heat in the direct reduction higher than in the indirect reduction?
- How can the CDR diagram be used for minimizing the specific consumption of coke?
9. REDUCTION OF OTHER ELEMENTS IN A BLAST FURNACE

CHAPTER DIVISION

✓ Reduction of manganese in a blast furnace
✓ Reduction of silicon in a blast furnace
✓ Reduction of phosphorus in a blast furnace
✓ Reduction of other elements in a blast furnace
✓ Yields of individual elements in a blast furnace
✓ Modification of the pig iron composition out of a blast furnace

Time for the study: 100 mins

Objective: After reading this chapter

- You will understand regularities of manganese reduction in a blast furnace from a charge and from slag
- You will familiarize yourselves with the effect of manganese on the properties of pig iron and slag
- You will understand regularities of silicon reduction in a blast furnace from a charge and from slag
- You will learn the possibilities of controlling the silicon content in pig iron
- You will understand the cause of the complete reduction of phosphorus in a blast furnace
- You will know why titanium is added to a blast furnace charge (or wind)

Interpretation:

Reduction of Manganese

Manganese is contained in ores as MnO, MnO₂, Mn₂O₃, Mn₃O₄ oxide and also as MnCO₃ carbonate. These oxides are further comprised of silicates and manganese ferrites. Manganese oxides are further divided into:
Reduction of other elements in a blast furnace

- **Easily reducible:** MnO₂ and Mn₂O₃ to form Mn₃O₄ and oxygen.
- **Reducible with difficulties:** Mn₃O₄ and particularly then MnO are very stable and hardly reducible oxides.

The least manganese (0.1 to 0.3 %) is usually in hematite and magnetite ores, while siderites contain 2 – 12 % of manganese. Iron ores with 12 to 30 % of manganese are called iron-manganese, while ores rich in manganese are known as manganese.

MnO is manganese oxide of the greatest importance in the reduction in a blast furnace. It is reducible only by carbon at high temperatures.

\[2 \text{Mn}(s) + O_2 = 2 \text{MnO}(s) \quad (\Delta H^{\circ}_{298} = -770 \, 371 \, \text{kJ}) \quad (43)\]

Similarly for the reaction:

\[2 \text{Mn}(l) + O_2 = 2 \text{MnO}(l) \quad (\Delta H^{\circ}_{298} = -688 \, 310 \, \text{kJ}) \quad (44)\]

Manganese dioxide MnO₂ (pyrolusite) is an essential mineral of Chiatura and Nikopol manganese ores.

**Reaction of formation of MnO₂:**

\[\text{⇑ Above 525 °C:} \]

\[2 \text{Mn}_2\text{O}_3 + O_2 = 4 \text{MnO}_2 \quad (\Delta H^{\circ}_{298} = -160 \, 773 \, \text{kJ}) \quad (45)\]

For reaction of formation of Mn₂O₃

\[\text{⇑ Above 900 °C:} \]

\[4 \text{Mn}_3\text{O}_4 + O_2 = 6 \text{Mn}_2\text{O}_3 \quad (\Delta H^{\circ}_{298} = -212 \, 689 \, \text{kJ}) \quad (46)\]

Mn₃O₄ (hausmannite) is similar in its structure to magnetite. For reaction of formation of Mn₃O₄:

\[\text{⇑ Above 1180 °C:} \]

\[6 \text{MnO} + O_2 = 2 \text{Mn}_3\text{O}_4 \quad (\Delta H^{\circ}_{298} = -463 \, 897 \, \text{kJ}) \quad (47)\]

From the thermodynamic point of view, the least stable oxide is then MnO₂ (pyrolusite), belonging to the sphere of higher oxides, which is reduced by carbon monoxide and hydrogen to Mn₂O₃ already at room temperature. In the conditions of a blast furnace, the reaction is irreversible and strongly exothermic:

\[2 \text{MnO}_2 + \text{CO} \rightarrow \text{Mn}_2\text{O}_3 + \text{CO}_2 \quad (\Delta H^{\circ}_{298} = -202 \, 767 \, \text{kJ}) \quad (48)\]
Identically then from the thermodynamic point of view, the oxide Mn$_2$O$_3$ (manganite) is less stable. The reduction takes place in the presence of carbon monoxide or hydrogen. In the conditions of a blast furnace, this reaction is irreversible and strongly exothermic and it is completed already at temperatures of 400 – 500 °C:

$$3 \text{Mn}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Mn}_3\text{O}_4 + \text{CO}_2 \quad (\Delta H^o_{298} = -176 809 \text{ kJ}) \quad (49)$$

The oxide Mn$_3$O$_4$ (hausmannite) is the next from a number of more difficult to reduce. But the reduction in the conditions of a blast furnace is reversible and takes place in the temperature range of 600 – 1000 °C:

$$\text{Mn}_3\text{O}_4 + \text{CO} = 3 \text{MnO} + \text{CO}_2 \quad (\Delta H^o_{298} = -51 205 \text{ kJ}) \quad (50)$$

Higher manganese oxides, if present in a blast furnace charge, can thus be reduced by carbon monoxide and hydrogen. However, it is also possible that larger pieces of Mn$_3$O$_4$ are not completely reduced to MnO in the temperature zone of the indirect reduction and they will be partly reduced by carbon:

$$\text{Mn}_3\text{O}_4 + \text{CO} = 3 \text{MnO} + \text{CO}_2 \quad (\Delta H^o_{298} = -51 205 \text{ kJ}) \quad (51)$$

Indirect reduction of higher manganese oxides is accompanied by the release of considerable heat, which is one of the causes of high temperature of charging gas and substantial losses of manganese by volatilization.

Reduction of manganese from the MnO oxide by carbon monoxide or hydrogen is not possible. Reduction of manganese is only possible by carbon and is strongly endothermic.

$$\text{MnO} + \text{C (k)} = \text{Mn} + \text{CO} \quad (\Delta H^o_{298} = 268 290 \text{ kJ}) \quad (54)$$

The direct reduction of manganese from MnO is carried out similarly to the reduction of wüstite in the presence of a gaseous phase. These are endothermic reactions. High temperature, which ensures the necessary concentration of CO in the gas from Boudouard reaction, is an important prerequisite for the course of reduction:

$$\text{MnO} + \text{CO} = \text{Mn} + \text{CO}_2 \quad (\Delta H^o_{298} = 102 032 \text{ kJ}) \quad (55)$$

$$\text{CO}_2 + \text{C(k)} = 2 \text{CO} \quad (\Delta H^o_{298} = 166 258 \text{ kJ}) \quad (56)$$

$$\text{MnO} + \text{C(k)} = \text{Mn} + \text{CO} \quad (\Delta H^o_{298} = 268 290 \text{ kJ}) \quad (57)$$
Nevertheless, much more favourable conditions for direct contact of MnO with carbon contained in coke are in the liquid phase. The direct reduction is reversible and is carried out in the reverse direction intensively at the temperatures of 600 to 700 °C. In the conditions of a blast furnace, the course of the reaction is insignificant because at the indicated temperatures, manganese is not reduced yet. The oxidation of manganese by carbon monoxide then occurs according to the following reactions:

\[
\begin{align*}
2 \text{CO} &= \text{CO}_2 + \text{C} \\
\text{Mn} + \text{CO}_2 &= \text{MnO} + \text{CO} \\
\text{Mn} + \text{CO} &= \text{MnO} + \text{C}
\end{align*}
\]

Released carbon is similar to carbon released during carbon monoxide decay while iron and manganese act catalytically. At the temperatures of intensive reduction of MnO oxide, i.e. above 1300 °C, carbides of manganese, of which carbide Mn\(_3\)C predominates, are formed; this formation of manganese carbides in a blast furnace cannot be avoided. If we consider e.g. the reaction:

\[
3 \text{MnO} + 4 \text{C} \text{(k)} = [\text{Mn}_3\text{C}] + 3 \text{CO} \quad (\Delta H^{\circ}_{298} = 263 \text{ kJ})
\]

At the temperature around 1200 °C, a substantial portion of MnO passes into primary slag and combines with SiO\(_2\) before being reduced.

**Reduction of Manganese from Slag**

Final blast furnace slag will always contain a certain part of Mn if we add it to a charge, because the reduction at a certain concentration of MnO ceases. The concentration of MnO in slag is then dependent on richness of slag in manganese, height of hearth temperature, alkalinity and specific amount of slag. If we want to reach low concentration of MnO in slag, it is necessary to ensure:

- *A charge poor in Mn*
- *High temperature in a hearth*
- *High alkalinity of slag*
- *Large specific amount of fuel*

To increase a content of manganese in pig iron, presence of CaO and MgO oxides, which have higher chemical affinity for SiO\(_2\) than MnO has, is necessary. The positive effect of increased alkalinity of slag on the manganese reduction proceeds as follows:
Reduction of other elements in a blast furnace

\[
\begin{align*}
\text{MnSiO}_3 + 2 \text{CaO} &= \text{Ca}_2\text{SiO}_4 + \text{MnO} \quad (\Delta H^{o}_{298} = -23600 \text{ kJ}) \quad (62) \\
\text{MnO} + \text{C (k)} &= \text{Mn} + \text{CO} \quad (\Delta H^{o}_{298} = 64080 \text{ kJ}) \quad (63) \\
\text{MnSiO}_3 + 2 \text{CaO} + \text{C (k)} &= \text{Mn} + \text{Ca}_2\text{SiO}_4 + \text{CO} \quad (\Delta H^{o}_{298} = 169482 \text{ kJ}) \quad (64)
\end{align*}
\]

Presence of CaO in slag is more efficient than presence of MgO because binding energy of Ca\textsuperscript{2+} with silicate anions is approximately twice as high as binding energy of Mg\textsuperscript{2+}. Nevertheless, a certain concentration of MgO in slag is beneficial as it reduces viscosity of slag. For this reason in the production of ferromanganese, a part of limestone is then usually replaced with dolomite. Reduced viscosity of slag allows then to increase its alkalinity without risking that difficulties arise during tapping.

**Reduction of Silicon**

Part of the silicon that is reduced in a blast furnace always passes into pig iron. The rest of the unreduced silicon passes into slag, where it is one of the essential components. Tailings of iron and manganese ores, with only minor exceptions, contain SiO\textsubscript{2} and SiO\textsubscript{2} also occurs in the ash of coke. Silicon dissolves in iron in all proportions and forms the silicides FeSi, Fe\textsubscript{3}Si\textsubscript{2} and Fe\textsubscript{2}Si\textsubscript{5}. At high temperatures, only FeSi is stable. Besides SiO\textsubscript{2}, which is thermodynamically stable, three metastable oxides exist:

- \( \text{SiO} \)
- \( \text{Si}_2\text{O}_3 \)
- \( \text{Si}_3\text{O}_4 \)

SiO is also called (silicon monoxide or silicon suboxide), it has a considerable importance for the blast furnace process, especially due to its minuscule density. This property causes difficulties during the blast furnace process at excessive temperature in a hearth.

It is obtained by reaction of silicon with SiO\textsubscript{2} in a vacuum furnace at temperatures of 1420 to 1500 °C:

\[
\text{Si (s) + SiO}_2 (s) = 2 \text{SiO (g)} \quad (\Delta H^{o}_{1423} = 322385 \text{ kJ}) \quad (65)
\]

Reduction of silicon with hydrogen takes place even at very high temperatures only in negligible extent:

\[
\text{SiO}_2 (s) + 2 \text{H}_2 = \text{Si (s) + 2 H}_2\text{O (g)} \quad (\Delta H^{o}_{298} = 386860 \text{ kJ}) \quad (66)
\]
Reduction of other elements in a blast furnace

Calculations revealed that the reduction of SiO$_2$ by hydrogen and carbon monoxide only leads to the formation of SiO and the reaction area must be completely freed from the gaseous reaction products. Silicon reduction from SiO$_2$ in a blast furnace is only possible by carbon while the reaction takes place in two stages:

\[
\text{SiO}_2(s) + C(k) = \text{SiO}(g) + \text{CO} \quad (\Delta H^{\circ}_{298} = 157,880 \text{ kJ}) \quad (67)
\]

\[
\text{SiO}(g) + C(k) = \text{Si}(s) + \text{CO} \quad (\Delta H^{\circ}_{298} = -5,720 \text{ kJ}) \quad (68)
\]

\[
\text{SiO}_2(s) + 2 \text{C}(k) = \text{Si}(s) + 2 \text{CO} \quad (\Delta H^{\circ}_{298} = 637,064 \text{ kJ}) \quad (69)
\]

Reduced silicon combines with iron to form silicate iron FeSi which is stable only at high temperatures $T_1 = 1420 \, ^\circ\text{C}$. This lowers the temperature attributable to the reduction of silicon from SiO$_2$ by carbon.

\[
\text{Fe}(s) + \text{Si}(s) = \text{FeSi}(s) \quad (\Delta H^{\circ}_{298} = -80,387 \text{ kJ}) \quad (70)
\]

Effect of silicon dissolution in iron on a temperature of the reduction is greater than effect of manganese dissolution in iron on the reduction of MnO, which relates to the formation of silicide. The reduction of silicon in the presence of iron:

\[
\text{SiO}_2(s) + 2 \text{C} = [\text{Si}] + 2 \text{CO} \quad (71)
\]

At the temperatures of the silicon reduction, iron, which gradually becomes saturated with carbon, is already reduced. It must, therefore, be assumed that this carbon also contributes to the reduction of silicon:

\[
2 [\text{C}] + \text{SiO}_2(s) = [\text{Si}] + 2 \text{CO} \quad (72)
\]

In a blast furnace, a portion of SiO$_2$ combines still in the solid state with CaO to form silicates and thus the reduction of silicon becomes significantly more difficult. E.g. silicon reduction of CaSiO$_3$ according to the reaction:

\[
(\text{CaSiO}_3) + 2 \text{C}(k) = \text{Si} + (\text{CaO}) + 2 \text{CO} \quad (\Delta H^{\circ}_{298} = 828,903 \text{ kJ}) \quad (73)
\]

The reaction starts to proceed at temperatures exceeding 1400 $^\circ\text{C}$ and to achieve 1.8 % of Si in iron, temperatures above 1600 $^\circ\text{C}$ are needed. In a blast furnace, Si is reduced from molten slag into iron. When passing SiO$_2$ or solid silicates into slag, the ratio changes again and the silicon reduction temperature decreases.

Transition of SiO$_2$ into molten slag changes also kinetic conditions of the silicon reduction. The reduction is carried out faster, probably due to improved contact of SiO$_2$ with the coke carbon and also due to possibility of SiO$_2$ reaction with carbon which is dissolved in iron.
Controlling the Silicon Content in Pig Iron

Basic factors influencing the silicon reduction in a blast furnace and its dissolution in pig iron include:

- temperature in a hearth
- chemical composition and physical properties of slag
- amount of slag
- reducibility of an ore charge

Temperature in a hearth determines temperature of slag in this part of a furnace and a content of silicon in pig iron is directly proportional to the temperature of slag. Insufficient heating of slag causes that it contains a lot of FeO which may oxidize silicon and reduce its content in pig iron. Also MnO acts similarly. Concentration of MnO is to some extent dependent on the concentration of silicon in iron.

Oxidation of Silicon

\[
2 \text{(FeO)} + [\text{Si}] = 2 \text{[Fe]} + (\text{SiO}_2) \quad (\Delta H^{\circ}_{298^\circ} = -405\,073 \text{ kJ})
\]

(74)

Larger specific amount of slag is advantageous for the reduction of silicon but it increases the specific consumption of coke and decreases productivity. Concentrations of FeO and MnO in the primary slag depend on reducibility of an ore charge. Increased pressure of gas limits the reduction of silicon in a blast furnace.

Temperature dependence of silicon reduction degree

Note: 1 - from vacant SiO\textsubscript{2} in the presence of iron, 2 - from vacant SiO\textsubscript{2} without the presence of iron, 3 - from slag in the presence of iron, 4 - from slag without the presence of iron
Reduction of Phosphorus

Phosphorus contained in a charge, is mostly in the form of phosphorite \( \text{Ca}_3\text{P}_2\text{O}_8 \) or also as vivianite \( \text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \).

Reduction of phosphorus in a blast furnace is almost perfect. Alkalinity of slag in the range that is common in the production of any kind of pig iron almost does not affect the degree of phosphorus reduction. Its concentration in pig iron cannot be then affected otherwise than by selecting appropriate raw materials.

The main cause of the inability to transfer phosphorus into slag consists in reducing atmosphere of a blast furnace and in relatively high temperatures in a hearth.

Reduction of Titanium

In a blast furnace, reduction of titanium takes place only directly.

\[
\text{TiO}_2 + 2\text{C}_k = \text{Ti} + 2\text{CO} \tag{75}
\]

TiC is a final product which dissolves in iron.

Reduction of Chromium

Chromium is reduced with big difficulties by carbon at high temperatures.

\[
7\text{FeCr}_2\text{O}_4 + 34\text{C} = 2\text{Cr}_7\text{C}_3 + 7\text{Fe} + 28\text{CO} \tag{76}
\]
Reduction of Zinc

Zinc melts at 420 °C and boils at 907 °C. Temperature of ZnO reduction is slightly higher. Sphalerite ZnS can react both with carbon in the presence of CaO.

\[ \text{ZnS} + \text{CaO} + C_k = \text{Zn} + \text{CaS} + \text{CO} \]  \hspace{1cm} (77)

and with iron

\[ \text{ZnS} + \text{Fe} = \text{Zn} + \text{FeS} \]  \hspace{1cm} (78)

Smitshonite ZnCO\textsubscript{3} decays relatively easily

\[ \text{ZnCO}_3 = \text{ZnO} + \text{CO}_2 \]  \hspace{1cm} (79)

and released ZnO is reduced by carbon

\[ \text{ZnO} + C = \text{Zn} + \text{CO} \]  \hspace{1cm} (80)

Reduction of Arsenic

Arsenic is one of the elements that degrade pig iron. Its reduction is carried out very easily and almost completely.

\[ \text{As}_2\text{O}_5 + 2\text{CO} = \text{As}_2\text{O}_3 + 2\text{CO}_2 \]  \hspace{1cm} (81)

\[ \text{As}_2\text{O}_3 + 3\text{CO} = 2\text{As} + 3\text{CO}_2 \]  \hspace{1cm} (82)

Summary of Terms:

- Direct reduction of manganese
- Yield of manganese
- Monoxide (suboxide) of silicon
- Controlling silicon content in pig iron
- Adjusting pig iron composition out of a furnace
- Nodal positions, internodal – interstitial positions
- Protection of hearth lining
- Accumulation of zinc in a blast furnace

Questions

- What is the yield of manganese in steel-making and foundry pig iron?
- Why has the manganese content in pig iron been recently reduced?
- Does higher temperature increase or decrease the manganese content in pig iron?
- Is silicon from SiO₂ reduced directly or indirectly?
- Does the presence of iron support or hinder the reduction of silicon?
- Which factors enable to control the iron content in pig iron?
- Why is the production of pig iron with a high content of silicon more expensive?
- How can the phosphorus content in pig iron be controlled?
- Why is titanium added to a blast furnace?
- Why is zinc considered a detrimental element?
10. BLAST FURNACE SLAG

CHAPTER DIVISION

✔ Definition and types of blast furnace slag
✔ Basic characteristics of blast furnace slag
✔ Self-regulation ability of slag
✔ Role of blast furnace slag
✔ Utilization of blast furnace slag

Time for the study: 60 mins

Objective: After reading this chapter

- You will repeat the molecular and the ionic theory of slags
- You will understand the basic principles of the crystal structure of silicates
- You will know self-regulation mechanism of slag in a blast furnace
- You will familiarize yourselves with the influence of chemical composition and temperature on characteristics of slag
- You will know the basic methods of blast furnace slag utilization

Interpretation:

Emergence of Blast Furnace Slag

Oxides, which were not reduced to metal, comprise slag together with some other elements of a charge. They are in particular CaO, MgO, SiO₂, Al₂O₃, MnO, BaO, small amounts of titanium oxide and iron oxide, oxides of alkali metals, vanadium and other elements. Also sulfates CaS, MgS, BaS, MnS, Na₂S, K₂S pass into slag and in case there is chromium in a charge, slag contains also its carbides.

Temperature of the beginning of charge softening may be considered the initial temperature of slag emergence in a blast furnace. Temperature interval between the
beginning of softening of a charge and complete melting is not fixed and may vary depending on the ratio of substances present. At the same time, new chemical compounds and solid solutions which reduce the melting point of present or emerging substances are formed.

Slag that emerges is called primary slag and its formation is preceded by sintering of partially reduced agglomerate. This sintering is not only of physical nature, since new chemical compounds or solid solutions are formed already in its course. Primary slag is characterized by a high content of FeO, resp. MnO. The MnO content depends primarily on its amount in a charge. Temperature distribution and hence primary slag emergence areas can be very different according to the type of manufactured pig iron, mineralogical composition of raw materials, furnace volume, temperature of the blown wind and other technological conditions.

Primary slag gradually descends through a charge to zones with higher temperatures and its viscosity decreases. It passes into closer contact with hot coke, reduction of iron is completed and remaining amount of SiO₂, CaO, MgO and Al₂O₃ dissolves. This changes chemical composition of slag and its volume increases. At the highest temperatures, also manganese, phosphorus and silicon are reduced from slag but ash from burnt coke passes in it in the area of tuyeres. In these zones, slag is also temporarily enriched with FeO and other oxides of metals (from oxidizing areas), which are later re-reduced. This way, composition and properties of slag permanently change, the slag is therefore called transition slag.

Final slag must then have such chemical composition and physical properties to be able to desulphurize pig iron as perfectly as possible, ensure perfect reduction of iron and high reduction degree of manganese and finally, to flow easily from a furnace. This slag usually contains from 0.5 % to 0.8 % of FeO. It is also necessary to take into consideration further utilization of blast furnace slag (content of MgO, Al₂O₃ etc.)

The so called self-regulation ability of slag is important for blast furnace operation. Its principle consists in the matter of fact that if slag has a high content of FeO and MnO, it has low viscosity (high flowability), flows quickly into a hearth, it has not enough time to be heated up by blowing gas and its viscosity is relatively lower. Consequently, velocity of slag flow slows down. On the contrary, when the content of FeO and MnO is low, slag flows slowly, it has time enough to heat up and due to lower viscosity, it flows faster.
Properties of Blast Furnace Slag

Alkalinity is the most important chemical characteristics of blast furnace slag which is usually expressed by means of a simple or an extended relationship:

\[
P_1 = \frac{w_{(CaO)}}{w_{(SiO_2)}} \quad (83)
\]

\[
P_2 = \frac{w_{(CaO)} + w_{(MgO)}}{w_{(SiO_2)} + w_{(Al_2O_3)}} \quad (84)
\]

where: \( P_1, P_2 \) is the value of basicity of slag, [1]

\( w \) - mass fraction of a component in slag, [1]

Basicity can also be defined as the ratio of alkaline and acidic components (oxides) of slag. Value of alkalinity usually ranges between 0.9 to 1.2 while total content of these four basic oxides in blast furnace slag is usually around 95 wt. %.

As already mentioned, slag is not only “desulphurizer” but is also perceived as by-product intended for further processing for the following reasons:

- **reduction of the total cost of pig iron production**
- **its further utilization in construction and elsewhere**

In practice, the terms short and long slag are often used. These terms relate to the rate of slag solidification. When the time interval of the operating temperature after slag solidification is short - we talk about short slag (alkaline), when this interval is long, we talk about long slag (acidic).

*Viscosity dependence of slag on its temperature*

*Note: 1 - long slag, 2 – short slag*
According to slag characteristics (its alkalinity, temperature) and of course according to requirements of sales department, gravel, cobblestones, granules for the cement industry, slag wool to be used as insulating material, etc. are further produced of blast furnace slag. Recently, possibilities of using blast furnace slag in the field of cleaning polluted water as a replacement of cement, etc., are examined.

∑ Summary of Terms:

- Basicity of slag, viscosity of slag, melting point of slag
- Basic silicate tetrahedron $\text{SiO}_4^{4-}$
- Self-regulating ability of slag
- Short slag, long slag
- Primary, transition, final slag
- Specific amount of slag
- Slag granules

❓ Questions

- What does blast furnace slag emerge of?
- Which 4 oxides compose approximately 95% of blast furnace slag?
- Explain the principle of the molecular theory of slags.
- Explain the principle of the ionic theory of slags.
- Which are the most important characteristics of blast furnace slag?
- What is the importance of the $O / Si$ ratio in blast furnace slag?
- What is primary, transition and final slag in a blast furnace?
- What is short and long slag?
- What is the self-regulating ability of slag?
- What is currently the specific amount of slag for Czech blast furnaces?
- What purposes is blast furnace slag used for?
11. DESULPHURIZATION IN A BLAST FURNACE

CHAPTER DIVISION

✓ Sources and forms of sulphur in a BF
✓ Mechanism of desulphurization in a blast furnace
✓ Thermodynamics of desulphurization reactions in a blast furnace
✓ Desulphurization by means of CaO and other compounds
✓ Desulphurization out of a blast furnace

Time for the study: 120 mins

Objective: After reading this chapter

- You will understand the structure of sulphur sources in a BF
- You will know mechanism of desulphurization in a blast furnace
- You will know which desulphurizers are used in a blast furnace
- You will familiarize yourselves with thermodynamics of desulphurization reactions in a blast furnace
- You will know factors influencing the effectiveness of desulphurization in a blast furnace
- You will understand the effect of the presence of some elements on improvement or deterioration of desulphurization in a blast furnace
- You will understand why a blast furnace desulphurizes more effectively than steel-making aggregates

Interpretation:

Yet in the fifties of the last century, the presence of sulphur in pig iron was a totally undesirable phenomenon. Today, the presence of sulphur in steel can be assessed as mainly undesirable, with the exception of steels with controlled sulphur content, such as cutting steels i.e. better machinable steels with increased content of sulphur (e.g. in the range of 0.035 % - 0.055 %). Presence of sulphur in steel causes so called red-short (red-hot, sulphur)
embrittlement. Sulphur also reduces resistance of steel to corrosion, impact toughness and its electro-technical properties. It acts detrimentally also in grey cast iron where it causes gas unsoundness of castings.

Sulphur enters into the process of pig iron production by means of charged raw materials, mainly through coke (up to 90%), an ore charge (ore raw materials contain approx. 0.013% of sulphur) and only minimally through alkaline admixtures. Sulphur is present in coke in three modifications; as organic, sulphide and sulphate sulphur in the total amount to 1%. Considerable amount of sulphur is also brought by substitute fuels (heavy oils, coal dust, etc.). In an ore charge after heat treatment by agglomeration or pelletization and dissociation, sulphur is present in the form of FeS. Coke descending through a blast furnace shaft warms up in the reducing environment but otherwise it changes only minimally. Likewise sulphur contained therein. When entering oxidation zones, temperature of coke reaches approximately 1500 °C. The coke carbon is oxidized in front of tuyeres to CO and sulphur to SO$_2$. SO$_2$ contained in gas ascends along with reducing gases, it gets into contact with drops of descending pig iron in counter-flow, is adsorbed on their surface and reacts to FeS. In a blast furnace, we therefore desulphurize from FeS.

The highest degree of desulphurization occurs mostly in a blast furnace hearth under tuyeres where droplets of pig iron containing FeS pass through a layer of alkaline slag whose height prior to tapping reaches 1 meter. Each drop of pig iron has its own surface. The sum of surfaces of individual drops gives a very large interfacial boundary due to which desulphurization is very intensive. The effect is enhanced yet by the matter of fact that while descending, a drop of pig iron still encounters further fresh slag. This desulphurization is called “upper” and the major part of sulphur is removed here. Next phase of desulphurization (lower) takes place at a contact area of pig iron layer with slag. Share of this desulphurization is the same as in a steel-making plant and is of little importance because it is limited by diffusion of sulphur and oxygen to interfacial boundary and diffusion of products of reactions into the mass of metal and slag.

In a blast furnace, iron is desulphurized by substances having higher affinity for sulphur than iron has. They are CaO and MgO in particular. As a blast furnace hearth is, beside melts, filled with coke (carbon) and blast furnace slag contains very little FeO, it is possible to write the reaction of desulphurization in the form:

$$\text{[FeS]} + (\text{CaO}) + C(\text{coke}) = \text{[Fe]} (l) + (\text{CaS}) + \text{CO(g)} \quad (\Delta H^{\circ}_{298}=152300 \text{ J}) \quad (85)$$
Its equilibrium constant has the form:

\[
K_a = \frac{a_{Fe(l)} a_{(CaS)} p_{CO(g)}}{a_{FeS} a_{(CaO)} a_{(coks)}}
\]  

(86)

where:  
\(a\) is activity of a given component  
\(p_{CO(g)}\) - partial pressure of CO, [Pa]

If it can be assumed that \(a_{Fe(l)} = 1\) and \(a_{(cokes)} = 1\) and if we express \(a_{(CaS)}\) as a product \(\gamma_{(S)} \cdot \chi_{(S)}\), we can express the equilibrium in the form:

\[
K_a = \frac{\gamma_{(S)} \cdot \chi_{(S)} \cdot p_{r,CO(g)}}{\gamma_{[s]} \cdot \chi_{[s]} \cdot \gamma_{(CaO)} \cdot \chi_{(CaO)}}
\]  

(87)

where:  
\(\gamma_{(S)}\) is activity coefficient of sulphur in slag  
\(\gamma_{[s]}\) - activity coefficient of sulphur in pig iron  
\(p_{r,CO(g)}\) - relative partial pressure of CO, [Pa]  
\(\chi_{(S)}\) - the mole fraction of sulphur in slag  
\(\chi_{[s]}\) - the mole fraction of sulphur in pig iron, [1]  
\(\chi_{(CaO)}\) - the mole fraction of CaO in slag, [1]

Partition coefficient of sulphur \(L_s\) is then a measure of desulphurization ability of slag:

\[
L_s = \frac{\chi_{(S)}}{\chi_{[s]}} = K_s \frac{\gamma_{[s]} \gamma_{(CaO)} \chi_{(CaO)}}{\gamma_{(S)} p_{r,CO(g)}}
\]  

(88)

Presence of some elements significantly affects desulphurization by increasing or decreasing activity coefficient of sulphur. Carbon, silicon and phosphorus increase the activity coefficient most significantly, see the following Figure. Content of these elements in a blast furnace is substantially higher than in steel-making processes. This is why there are markedly better conditions for desulphurization in a blast furnace than in a steel-making plant.

The mentioned equations imply that desulphurization of pig iron in a blast furnace is positively affected by:

- increased temperature at which the value of equilibrium constant \(K_s\) increases
o increased basicity of slag ($a_{(CaO)}$)

Activity of CaS in slag and partial pressure of CO cannot be reduced in a blast furnace.

Reduction in the sulphur content in pig iron by increasing temperature in a hearth and basicity of slag is accompanied by increase in specific consumption of coke and heat. Experience has shown that such reduction in the sulphur content in pig iron is effective only to a certain limit. When the need for the sulphur content in pig iron is less than 0.01 %, it is more advantageous to install out-of-furnace desulphurization outside the steelmaking plant, which is capable to reduce the sulphur content approximately ten times. This is a separate device wherein dust complex desulphurizers are injected into a mass of pig iron. Installation of such device is only effective, if investment and operating costs of out-of-furnace desulphurization are less than saving in blast furnace operation. Saving in the pig iron production arise because we do not need to desulphurize – specific consumption of coke and heat decreases and it is possible to work with acidic slag.

Dependence of sulphur activity coefficient on the content of accompanying elements

<table>
<thead>
<tr>
<th>Summary of Terms:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Upper and lower desulphurization</td>
</tr>
<tr>
<td>- Partition coefficient of sulphur</td>
</tr>
<tr>
<td>- Specific amount of slag</td>
</tr>
<tr>
<td>- Out-of-furnace desulphurization of pig iron</td>
</tr>
</tbody>
</table>
Desulphurization in a blast furnace

Questions

- Which compound do we desulphurize in a blast furnace from?
- Which is the raw material bringing most sulphur into a blast furnace?
- What happens with sulphur in oxidation zones of a blast furnace?
- Which properties of slag influence desulphurization?
- Which elements enhance the activity coefficient of sulphur most (improve desulphurization)?
- Why are conditions during desulphurization in a blast furnace better than in a steel-making plant?
- Which measures can reduce the sulphur content in iron in a blast furnace?
- What is the partition coefficient of sulphur?
- Why is it more advantageous to desulphurize outside a blast furnace than in it, if very low sulphur content is required (below 0.01%)?
12. TYPES OF PIG IRONS

CHAPTER DIVISION

- Quality of produced pig iron
- Traditional division of pig irons
- Pig iron according to European Standards
- Special pig irons
- Basic technical-economic indicators of pig iron production

Time for the study: 60 mins

Objective: After reading this chapter

- You will understand the term quality of pig iron
- You will familiarize yourselves with basic types of produced pig irons
- You will understand the concept and structure of the new European Standard on division of pig irons
- You will familiarize yourselves with the basic technical-economic indicators of pig iron production

Interpretation:

Pig irons

The term pig iron means an alloy of iron and carbon with the content of carbon exceeding 2% that contains elements of the amount equal or lower than specified in the standard. Currently in the Czech Republic, the Standard ČSN EN 10001 (420041) is valid, which is identical to EN 10001/1990 and has been published with the approval of CEN (TN: the European Committee for Standardization, French: Comité Européen de Normalisation). Pig iron is intended for further processing in a liquid state to steel or cast iron. Pig iron is supplied either in liquid or solid state in the form of pigs or other similar products, or in granular form. Based on chemical composition, pig iron is divided into:
Types of pig irons

- unalloyed pig iron
- alloyed pig iron

**Unalloyed pig iron** is, according to further processing, divided into:

- steel-making pig iron
- foundry pig iron
- other unalloyed pig irons

**Steel-making pig irons** are further divided into pig irons with low phosphorus content and with high phosphorus content.

**Foundry pig irons** are divided into common irons, for which it is not recommended to use various traditional names as irons with low, medium or high phosphorus content, hematite, Cleveland, etc. but abbreviations given by the standard such as Pig-P1 Si, Pig-P3 Si, Pig-P6 Si, Pig-P12 Si and Pig-P17 Si, then into spheroidal graphite irons, spheroidal graphite irons with higher manganese content and irons with low carbon content.

**Alloy pig irons** are divided into spiegeleisen and other alloy irons.

In the practice of Czech blast furnace plants, traditional division of pig irons into steel-making, foundry and special pig irons is still used. Indicative composition of steel-making grade pig iron:

- C - 4.5 %
- Mn - below 1 %
- Si - below 1 %
- S - below 0.03 %
- P - below 0.2 %

In individual manufacturing plants, produced pig irons are further divided into quality grades according to the content of sulphur.

- Grade I → S < 0.01
- Grade II → S < 0.02
- Grade III → S < 0.03

A company standard also usually specifies the maximum content of other elements according to the product range of a company (e.g. – Cr, P, Cu, Mn, Ti, etc.)

Indicative composition of foundry grade pig iron (foundry grade pig iron common):
Types of pig irons

- C - 4.3 %
- Mn - below 1 %
- Si - 1.6 to 4.2 %
- S - below 0.03 %
- P - below 0.3 %

Furthermore, “foundry specials” cold or hot depending on required content of Si or Mn are produced. Low phosphorous foundry pig iron – hematite, which has a very low content of phosphorus (to 0.15 %), is often produced. Sporadically, ferromanganese is produced in blast furnaces.

Blast furnace plants enable to supply pig irons in accordance with customers’ requirements. Special requirements for quality of pig iron, however, require special composition of a blast furnace charge, which will be reflected in the price of produced pig iron.

**Basic technical-economical indicators**

The production, consumption and cost indicators count among the basic technical-economical indicators of pig iron production. However, since the price of pig iron produced is governed by its quality, evenness of the chemical composition and temperature of the iron counts among the technical-economical indicators.

- Specific consumption of coke is coke consumption recalculated per unit of produced pig iron.
- Specific fuel consumption is coke and substitute fuels consumption recalculated per unit of produced pig iron.
- Measuring occurrence of slag is slag resulting amount recalculated per unit of produced pig iron.
- Daily productivity of the blast furnace can be expressed as the ratio of daily consumption of coke ($K_d$) and its measuring consumption ($k_m$)

$$P_d = \frac{K_d}{k_m} \quad [t.d^{-1}] \quad (89)$$

- To assess the intensity of the work of variously sized blast furnaces is used volumetric coefficient of burning coke intensity

$$I = \frac{K_d}{V_0} \quad [t.m^3.d^{-1}] \quad (90)$$

where: $V_0$ is a useful volume of blast furnace or square index of hearth load
\[ i = \frac{K_d}{A_n} \quad [\text{t.m}^{-2}.\text{d}^{-1}] \]  

where: \( A_n \) is a cross-sectional area of the hearth on the tuyeres level

Coefficient of utilization of the useful volume of blast (\( k_0 \), or KIPO) is the ratio of useful volume of the furnace and the daily productivity

\[ k_0 = \frac{V_0}{P_d} \quad [\text{m}^3.\text{t}^{-1}.\text{d}] \]  

Of equal importance is the inverse value of this indicator known as an indicator of measuring productivity

\[ P_m = \frac{P_d}{V_0} \quad [\text{m}^3.\text{t.d}^{-1}] \]  

### Summary of Terms:
- Quality of pig iron
- Steel-making grade pig iron
- Foundry grade pig iron
- Technical-economical indicators of pig iron production

### Questions
- What is the composition of steel-making pig iron?
- What is the composition of foundry pig iron?
- What kinds of special pig irons do you know?
- How is a blast furnace “re-charged” from the production of steel-making grade pig iron to the production of foundry grade pig iron?
- How are pig irons divided according to the new European Standard?
- Which are the most important technical-economical indicators of the blast furnace work?
PART B

STEELMAKING

- How to study – steel production
- Description of steel
- Theoretical fundamentals of steelmaking
- Refractories
- Fundamentals of steelmaking technology in oxygen converters
- Fundamentals of steelmaking technology in tandem furnaces
- Fundamentals of steelmaking technology in electric arc furnaces
- Deoxidation of the steel and alloying
- Secondary metallurgy of steel
- Steel casting
- Literature
HOW TO STUDY

Course name

STEELMAKING

You have received a study package designed to guide you through the 1st semester of Master’s degree program in Economics and Management of Industrial Systems. Study package contains an integrated study textbook Part II – Steelmaking for the combined studies, including a study guide.

Prerequisites:

This course assumes previous completion of the course Theory of Technological Processes.

SUBJECT GOAL AND STUDY OUTCOMES

Objective:

To provide students with the knowledge and theoretical understanding of the processes taking place in steel production, with a focus on physical - chemical processes, technological principles of the production of primary steel aggregates, processes and deoxidation and alloying of steel, secondary metallurgy and steel casting.

Study outcomes:

Acquired knowledge:

- The student will be able to formulate physical – chemical processes occurring in production of steel in primary aggregates like converters, tandem furnaces and electric arc furnaces, including the deoxidation and alloying, secondary metallurgy and steel casting.

Acquired skills:

- The student will be able to use basic theoretical knowledge and technological principles in steel making.
- The student will be able to apply steel making knowledge under the operational conditions.
Who is this subject intended for

The subject is integrated into the master's degree program in Economics and Management of Industrial Systems, but the subject can also take an interested part from any other field of study, if the required prerequisites are met.

Used and recommended literature is listed at the end of this section.

The way of communication with tutors

During the study are expected:

- A semester project on a given topic from the field: the theoretical foundations of steel making, steel making technology in primary aggregates, deoxidation and alloying, secondary metallurgy and steel casting,
- The project will be monitored by the teacher within 14 days after submission and the results will be emailed to students through the IS,
- Completion of the credit test and test results will be communicated to students after its completion.

At the beginning of the semester, students will be assigned individual topics of Semestral project. Students will be given more detailed instructions at the beginning of tuition. Questions about an assigned topic is possible to consult with tutor (Prof. Ing. Jiří BAŽAN, CSc. or Ing. Ladislav SOCHA, Ph.D.):

- Within the listed consulting hours
- On the telephone number 597 325 231 and 597 323 534,
- Via e-mail: jiri.bazan@vsb.cz or ladislav.socha@vsb.cz
13. DESCRIPTION OF STEEL

CHAPTER DIVISION

✓ Basic terms
✓ Description of steel

Time for the study: 30 mins

Objective: After reading this chapter

- You will understand the term steel, its basic elements and other components

Interpretation:

Alloys in which the predominant element is Fe are collectively called the „technical iron“. If this alloy can be formed in the plastic state temperature (below the melting temperature), then such kind of technical iron is referred to as „steel“.

In addition to the basic element – Fe – steel contains:

- The common accompanying elements – C, Si, Mn, P, S
- Special accompanying elements that are added to the steel in order to obtain special properties or mechanical values. These include e.g. Cr, Ni, W, Mo, V, Ti, Nb, Zr, etc.
- Accompanying elements from the group of non-ferrous metals - Cu, As, Sb, Sn, Bi, Zn, etc. These elements are harmful to the steel and can’t be removed from the steel by conventional procedures
- Gases - nitrogen, hydrogen, oxygen
- In the steel there are also always present products of reactions taking place in the metal or reactions of metal with refractory materials (corrosion, erosion). Due to its non-metallic nature it is referred to as „non-metallic inclusions“

At the present time there’s produced around 5 million tons of steel per year in ČR and around 1600 million tons of steel per year in the world.
Summary of Terms:
- Usual and special accompanying elements, gases, non-metallic inclusions

Questions
- Steel – explain the term
- Elements in the steel and their influence on the properties of steel
14. THEORETICAL FUNDAMENTALS OF STEELMAKING

CHAPTER DIVISION

✓ Metallurgical rules determining the behaviour of elements in steel production
✓ The molten steelmaking slags
✓ The basic steelmaking reactions

Time for the study: 240 mins

Objective: After reading this chapter

- You will be able to define the theoretical rules of the behaviour of elements in steel production
- You will understand the importance and the role of molten slag
- You will understand the basic reactions occurring in steelmaking - oxidation of C, Si, Mn, P and reaction of desulfurization

Interpretation:

Metallurgical rules determining the behaviour of elements in steel production

Whether and to what amount the element passes from the charge or from the furnace atmosphere to steel is primarily determined by its affinity to oxygen, respectively stability of its oxides at temperatures of steelmaking processes, then the degree of oxidation effect of individual periods in steel production, chemical behaviour of the element in the liquid metal (its solubility, respectively the ability to react with other elements dissolved in the iron), the chemical behaviour of its oxides in the slag and temperature.

The rate of the chemical affinity of the reacting components is the maximum useful work that the reaction releases during the return course, respectively decrease in free enthalpy (Gibbs energy) corresponding reaction.

\[(\text{affinity})_{p,T} = - (\Delta G)_{p,T}\] (94)
The condition of spontaneous course of any metallurgical reaction in the considered direction is a positive value of chemical affinity reacting components, respectively negative value change in the free enthalpy ($\Delta G < 0$).

If we express the free enthalpy of the chemical reaction by change in enthalpy $\Delta H$ and change of entropy $\Delta S$, then for the affinity of the components applies

$$(\text{affinity})_{p, T} = - \Delta H + T \cdot \Delta S \quad (95)$$

where:

$\Delta H = H_2 - H_1$ \text{ is thermal effect of the reaction at constant pressure, [J]}

$\Delta S = S_2 - S_1$ \text{ - entropy change in chemical reaction, [J.K$^{-1}$]}

$H_1 ; S_1$ \text{ - enthalpy and entropy of components entering the reaction, [J] ; [J.K$^{-1}$]}

$H_2 ; S_2$ \text{ - enthalpy and entropy of the reaction products, [J] ; [J.K$^{-1}$]}

$T$ \text{ - temperature, [K]}

Equation (95) shows that at low temperatures the reaction heat $\Delta H$ has a greater influence on affinity, while influence of entropy component $T \cdot \Delta S$ grows at higher temperatures. The absolute values of entropy $S_1$ and $S_2$ are dependent on the state of the substances. The substances in the gaseous state have high entropy values, the substances in the condensed state have low values. Sign before the $\Delta S$ depends on change of the mole number of the gaseous components of the reaction and starting substances $\Delta n$. In reactions accompanied by increase in the number of moles of gaseous components, where $\Delta n > 0$ (for example $2 \text{C(S)} + \text{O}_2(\text{g}) = 2 \text{CO(\text{g})}$, or $[\text{C}] + [\text{O}] = \text{CO(\text{g})}$) is $S_1 < S_2$ and $\Delta S > 0$. The affinity of the elements during such a chemical reaction grows with increasing temperature. In reactions associated with the reduction in the number of moles of gaseous components, where $\Delta n < 0$, (for example $2 \text{CO(\text{g})} + \text{O}_2(\text{g}) = 2 \text{CO}_2(\text{g})$, or $2 \text{Me(\text{s})} + \text{O}_2(\text{g}) = 2 \text{MeO(\text{s})}$) is $S_1 > S_2$ and $\Delta S < 0$.

The following figure shows the elements affinity to oxygen dependence on a temperature during formation of the respective oxides.

The affinities of the elements were calculated assuming unit activities of the starting substances and reaction products. In case that oxidation reaction occurs between the components dissolved in the molten iron, activities of reactants will be identified by their content in the iron and also by other factors (especially composition of liquid alloy and temperature) whose effect is quantified in the value of the activity coefficient

$$a_{[X]} = f_{[X]} \cdot [X] \quad (96)$$
where: \( a_{[X]} \) is activity of element X in the molten iron, [1]

\( f_{[X]} \) - activity coefficient of element X, [1]

\([X]\) - element content in the molten iron, [%]

Influence of the composition of the polycomponent molten iron on the activity coefficient of element X can be expressed through the interaction coefficients as follows

\[
\log f_{[X]} = e^x_{[X]} + e^R_{X[R_1]} + e^R_{X[R_2]} + e^R_{X[R_3]} + \ldots \quad (97)
\]

where: \( e^x_{[X]}, e^R_{X[R_1]}, e^R_{X[R_2]}, e^R_{X[R_3]} \) is interaction coefficients expressing the influence of the components X, R\(_1\), R\(_2\), R\(_3\) on the activity of X in the molten iron, [1]

\([X], [R_1], [R_2], [R_3]\) - element content in the molten iron, [%]

**Molten steelmaking slags**

The importance and role of slags in the production and steel refining lies in ensuring:

- A main course of metallurgical reactions
- An intensity reduction of transmission of gasses \((H_2, N_2)\) of the furnace atmosphere to steel
Theoretical fundamentals of steelmaking

- A regulation of the heat transfer between the gaseous atmosphere and the molten metal
- An absorption of non-metallic inclusions

In the creation of steel slag are involved:

- The oxides formed by oxidation of iron and other elements in the molten metal
- The sulphides formed during desulfurization of the metal
- The slag-forming additives (added on purpose) providing desired physical and chemical properties of slag
- The materials coming into the slag during corrosion of linings

Chemical composition of steel slags is given by number of factors, e.g. whether it is refining by blowing oxygen, deoxidation or secondary refining of steel; whether it is an basic or acidic process or what aggregate or technological stage is melting process in.

In terms of tasks, which steel slag serves, especially in terms of reactions between metal and slag, respectively metal and lining, we define two terms – the basicity and the oxidizing ability of the slag.

The basicity according to molecular theory of slags can be put both as a ratio of weight contents of basic and acidic oxides, e.g.

\[
B_1 = \frac{\% \text{CaO}}{\% \text{SiO}_2}
\]  

\[
B_2 = \frac{\% \text{CaO}}{\% \text{SiO}_2 + \% \text{P}_2\text{O}_5}
\]  

\[
B_3 = \frac{\% \text{CaO} + \% \text{MgO}}{\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3}
\]

The ion theory of slags uses Lewis electron theory of acids and basics to express the basicity. According to this theory, activity of free oxygen ions \(\text{aO}_2^{-}\) is used as a measure of basicity in oxide melts. Sources of these ions are basic oxides with ionic bond in the lattice (CaO, MgO, MnO, FeO etc.), which is easily dissociated. Acidic oxides (SiO\(_2\), P\(_2\)O\(_5\) etc.) characterized by a stable covalent bond in the molecules are, however, in molten slag able to bond free oxygen ions to create complex anions (e.g. \(\text{SiO}_4^{4-}\), \(\text{SiO}_3^{2-}\), \(\text{PO}_4^{3-}\) etc.) and thus reduce the activity of \(\text{O}_2^{-}\) ions.
Oxidation ability of slags shows their ability to dissolve oxygen in the metal. Since iron oxide is the main source of oxygen in the steel, the oxidation ability of the slag is described by the activity of FeO (Molecular theory), or by the product of activities of ferrous and oxygen ions ( Ionic theory).

Reactions occurring during production and refining of steel

Refining oxidation reactions in the steelmaking furnaces take place predominantly due to the oxygen gas injection. In the area of direct contact of gaseous oxygen with the liquid metal occur following reactions

\[
2 \text{Fe(l)} + O_{2(g)} = 2 (\text{FeO}) \quad (101)
\]
\[
[\text{Si}] + O_{2(g)} = (\text{SiO}_2) \quad (102)
\]
\[
2 [\text{Mn}] + O_{2(g)} = 2 (\text{MnO}) \quad (103)
\]
\[
2 [\text{C}] + O_{2(g)} = 2 \text{CO}(g) \quad (104)
\]

The bulk of gaseous oxygen is consumed by reaction (101). Emerging FeO partially passes into the slag and partially is the source of oxygen in metal by reaction

\[
(\text{FeO}) = \text{Fe(l)} + [\text{O}] \quad (105)
\]

Reaction (105) creates conditions for the oxidation of other elements directly in the metal bath

\[
[\text{Si}] + 2 [\text{O}] = (\text{SiO}_2) \quad (106)
\]
\[
[\text{Mn}] + [\text{O}] = (\text{MnO}) \quad (107)
\]
\[
[\text{C}] + [\text{O}] = \text{CO}(g) \quad (108)
\]

With the emergence of the slag containing FeO are also created conditions for the oxidation of other elements at slag/metal interface.

\[
2 (\text{FeO}) + [\text{Si}] = (\text{SiO}_2) + 2 \text{Fe(l)} \quad (109)
\]
\[
(\text{FeO}) + [\text{Mn}] = (\text{MnO}) + \text{Fe(l)} \quad (110)
\]
\[
(\text{FeO}) + [\text{C}] = \text{CO}(g) + \text{Fe(l)} \quad (111)
\]
\[
5 (\text{FeO}) + 2 [\text{P}] = (\text{P}_2\text{O}_5) + \text{Fe(l)} \quad (112)
\]
Emerging oxides create the liquid slag. In acidic processes resulting slag is composed of oxides FeO, MnO, SiO₂ and their compounds (FeSiO₃, Fe₂SiO₄, MnSiO₃, Mn₂SiO₄). Dephosphorization in acidic processes does not occur, because equilibrium of the strongly exothermic reaction (112) is at high temperatures moved entirely to the left. That is because in acidic slag is all MnO bound to SiO₂, reaction (107), (110) are completely shifted to the right and produced „acidic“ steel contains hardly any manganese (0.02 ~ 0.03 % Mn). On the contrary, high SiO₂ content in the slag (in the end of melting process as high as 65%) causes, that even produced steel contains silicon before deoxidation (~ 0.1 až 0.2 % Si).

In basic processes the added lime is dissolving and strongly basic CaO displaces manganese oxide and iron oxide from silicates.

\[(\text{Fe}_2\text{SiO}_4) + 2 \text{(CaO)} = (\text{Ca}_2\text{SiO}_4) + 2 \text{(FeO)} \] (113)

\[(\text{Mn}_2\text{SiO}_4) + 2 \text{(CaO)} = (\text{Ca}_2\text{SiO}_4) + 2 \text{(MnO)} \] (114)

In alkaline slags is therefore all SiO₂ bound to Mono-, Di-, and Tricalcium silicate and therefore even the silicon content in the refined steel is zero. On the contrary in consideration of the reaction (114) elevated content of free MnO in the slag shifts the equilibrium of the reaction (110) to the left and therefore the refined „basic“ steel contains 0.15 to 0.2 % manganese.

**Dephosphorization of steel** by reaction (112) ensures the oxidizing and basic slag, and the activity of emerging P₂O₅ is reduced by the reaction with calcium oxide

\[4 \text{(CaO)} + (\text{P}_2\text{O}_5) = (\text{Ca}_4\text{P}_2\text{O}_9) \] (115)

Regarding dephosphorization, the optimal content of CaO in the slag is 40 to 45 % and 15 to 20 % of FeO. Too high content of CaO in the slag, as well as the metal temperature below 1500°C negatively affect the rate of dephosphorization because the slag is too viscous.

The significance of high content of CaO in the slag increases especially at the end of melting, where the high temperature shifts the equilibrium of strongly exothermic reaction (112) to the left, and only reduced activity of P₂O₅ can compensate this negative effect. In certain steel technologies, „slag off“ methods and creation of new slag are used for reduction of the content and therefore the activity of P₂O₅.

**The most important refining reaction is the oxidation of carbon – decarburization reaction.** This reaction due to emerging bubbles of CO stirs the bath, ensures the course of reactions between the slag and metal, creates conditions for reduction of
hydrogen and nitrogen content in the steel, for flotation and separation of inclusions and also the thermal effect involved in the heating of steel is important. Oxidation of carbon is accompanied by the formation of gas phase – CO bubbles, to whose nucleation is necessary to provide energy, which is at least equal to the surface energy of these bubbles. Therefore, so-called “Homogenous” carbon reaction \((10^4)\) requires significant oxygen supersaturation of the bath. These kinetic difficulties associated with the nucleation of bubbles are also the reasons of course delay of the carbon reaction in the process of refining pig iron (after complete oxidation of silicon), even if the corresponding balanced activities of oxygen with regard to silicon and carbon in the molten pig iron are almost identical.

Other curiosity of carbon oxidation while forming carbon monoxide, affinity of carbon to oxygen with increasing temperature is growing, see the Figure above. This decarburization process curiosity is used in vacuum processes in the manufacture of stainless steel.

**Transmission and distribution of sulphur between the molten metal and the slag**

show reactions

\[
\text{Fe}_\text{(l)} + [S] = (\text{FeS}) \\
(\text{FeS}) + (\text{CaO}) = (\text{CaS}) + (\text{FeO}) \\
\text{Fe}_\text{(l)} + [S] + (\text{CaO}) = (\text{CaS}) + (\text{FeO}) \\
[S] + (\text{CaO}) = (\text{CaS}) + [O]
\]

The largest share of sulphur is removed from the metal by its absorption in the slag. Only in the oxygen converter (LD and OBM) is 10 to 15% of the removed sulphur oxidized to \(\text{SO}_2\). Equations \((118)\) and \((119)\) are equal when it comes to expression of desulphurisation of steel. The relation between them is given by equation \((105)\) describing the distribution of oxygen between the slag and the metal. From the equations for the balanced constants of the equations \((118)\) and \((119)\) can be derived conditions ensuring low sulphur content in the metal.

\[
[S] = \frac{a_{(\text{CaS})} \cdot a_{(\text{FeO})}}{K_{118} \cdot a_{(\text{CaO})} \cdot f_s} \\
[S] = \frac{a_{(\text{CaS})} \cdot a_{[O]}}{K_{119} \cdot a_{(\text{CaS})} \cdot f_s}
\]

**These are:**

- *The high activity of (CaO) in the slag (basic slag)*
- *The low activity of (FeO) in the slag (reducing slag)*
Such a chemical composition of the metal, which increases the activity of sulphur in the metal (value of $f[S]$)

- The low oxygen activity in the metal (deoxidized steel)
- The low activity (CaS) in the slag (it can be reduced by slagging off the slag)
- The enthalpy of the reaction of desulphurization of steel is endothermic. Increased temperature therefore positively influences the thermodynamics of desulphurization, and also improves kinetic conditions of desulphurization and reduces the viscosity of the slag

∑ **Summary of Terms:**

- Affinity to oxygen, molten slag, characteristics, theory of slag, reactions occurring during the production and refining of steel

❓ **Questions**

- What is the affinity of chemical reaction
- Steelmaking slags, molecular and ionic theory
- The role of steelmaking slags
- Reaction of decarburization, oxidation of Mn and Si
- Reaction of dephosphorization
- Reaction of desulphurization
15. REFRACTORIES

CHAPTER DIVISION

✓ Classification of refractories
✓ Properties of refractories
✓ Characteristics of basic refractories and their use

Time for the study: 120 mins

Objective: After reading this chapter

- You will get an idea about a distribution and properties of refractories and you will be able to characterize individual materials in terms of their chemical nature and use

Interpretation:

Classification of refractories

Technological processes are carried out at very high temperatures, their effects together with the furnace setting lay extraordinary demands on fire-resistant materials.

In metallurgy, refractories are used to line-up the working parts of equipment (furnaces, ladles, etc.) for the operational security. They have, together with the structural solution of lining, major impact on performance, the possibility of intensification, use of time and economy of operation.

Classification of fire-resistant materials can be made from various aspects, such as:

○ By form
  - shaped materials (bricks, blocks)
  - non-shaped materials (grained materials)

○ By porosity
  - highly dense (porosity up to 3%)
- very dense (porosity 3-10%)
- dense (porosity 10-16%)
- medium dense (porosity 16-20%)
- common (porosity 20-30%)
- porous (porosity 30-45%)
- expanded (porosity 45-75%)
- highly expanded (porosity of 75%)

- By the chemical nature
  - acidic - basic component is SiO$_2$
  - neutral - basic component is Al$_2$O$_3$ and SiO$_2$
  - basic - at least 40% MgO

**Monitored properties of refractories**

- fire resistance (°C)
- resistance to deformation under load in the heat (°C at a pressure of 0.2 MPa)
- strength (MPa)
- changes in length at 1400 °C (%)
- volume density (kg.m$^{-3}$)
- porosity (%)
- rate of absorption (%)
- resistance to changes of temperature
- chemical stability (in relation to the influence of steel, slag)

**Characteristics of basic refractories:**

**Dinas**

It contains min. 93 wt. % SiO$_2$ – it is an acidic material. It is made from pure quartzites and quartzes containing up to 98 wt. % SiO$_2$. Products are moulded from a working material that is prepared by mixing the quartzitic pulp with additives. Subsequent firing is controlled so as to achieve the desired degree of modification conversion of SiO$_2$ quartz to cristobalite and tridymite.

**Characteristics:**

- to temperatures of 300 °C undergoes a significant volume changes
- above 300 °C insensitive to temperature changes
Refactories

- high resistance to deformation in the heat
- high fire-resistance
- due to its acidic nature it is not usable in alkaline slag environment

Fire clays

Fire clay building materials belong to the most common types of refractory materials. They are universal materials successfully used for a variety of linings. The basic components of fire clay building materials are SiO$_2$ and Al$_2$O$_3$, whose total share amounts to min. 93%. Other oxides present in fire clay are impurities from raw materials acting as addition – they reduce heat resistance and other thermal properties. Heat resistance of fire clay materials increases with increasing content of Al$_2$O$_3$, which is up to 40% for common types.

Fire clay building materials are made of the mixture of opening material and binding constituent by pressing followed by firing at a temperature guaranteeing obtaining a product with a constant volume. As opening materials used in the production of the common types of fire clay are used kilned shale, in the production of high-aluminium building materials fused alumina or sintered mullite (3Al$_2$O$_3$.2SiO$_2$) are used. As a binding constituent, heavy clays with high heat resistance are used that are added to the working material in various amounts. The opening material forms the skeleton of the product and the considerable extent determines the properties of the fired material.

Properties:

- Resistance to sudden changes of the temperature
- Low resistance to deformation in the heat
- Limited use of temperature range

According to the preparing method we distinguish following fire-clay:

- Plain
- Hard
- Semi-hard
- Expanded
- Acidic

Special groups consist of fire-clays with high contents of Al$_2$O$_3$ (up to 80 %) – called high-aluminium materials.
Magnesite Materials

Building materials based on MgO are typically alkaline. They have found the widest use in the metallurgical industry for its high heat resistance and good resistance to basic slags.

The feedstock for the production of magnesite building materials is a sintered fired magnesite with a low content of CaO, SiO₂ and Al₂O₃. The pressing material for the production of blocks is usually prepared by mixing of several kinds of clinkers with complementary properties.

Properties:

- high strength
- resistance to mechanical stress
- poor resistance to temperature changes
- resistance to effect of basic slags

A substantial increase in resistance of alkaline building materials to sudden temperature changes is achieved by adding chrome ore. This produces two groups of products containing Cr₂O₃, these are:

- magnesite-chrome building materials – in the mass prevails the magnesite clinker over the chrome ore (MgO content above 55%)
- chrome-magnesite building materials – chrome ore constituent exceeds the share of magnesite clinker (MgO content of 25 up to 54%)

Chromium oxide Cr₂O₃ is during firing and during actual use of building material dissolved in MgO and improves its properties. By firing at very high temperatures, so called direct link between the magnesite component and chrome ore can be achieved, thus it makes it possible to obtain products with increased strength at the operational temperatures and higher resistance to liquid alloys.

∑ Summary of Terms:

- Refractory materials, properties, production. Classification by chemical nature

❓ Questions

- Characteristics, basic classification of refractory materials
- Acidic, neutral and basic refractories
16. FUNDAMENTALS OF STEELMAKING TECHNOLOGY IN OXYGEN CONVERTERS

CHAPTER DIVISION

- Steel production in top-blown converters
- Steel production in bottom-blown converters
- Combined methods of oxygen blowing

Time for the study: 120 mins

Objective: After reading this chapter

- You will be able to describe the construction of top-blown and bottom-blown oxygen converter
- You will understand the technological process of production in individual aggregates

Interpretation:

Steel production in top-blown converters (LD)

LD converters replaced the production in Siemens-Martin furnaces in the world and their application meant a rapid increase of steel production.

The first oxygen converter was developed and industrially applied in 1952 in Linz and Donawitz, Austria. The process is therefore referred to as LD. Currently this is the most used type of oxygen converter, although already many variations have been developed, in particular bottom-blown converters and converters with combined blowing.
The basis of LD process is refining pig iron with oxygen which is top-blown into the bath of liquid metal by water-cooled copper nozzle, placed in the axis of the basic-lined converter. Purity of oxygen must be min. 99.5%.

Scheme of top-blown oxygen converter and the overall layout are shown in the following Figures.
Oxygen converter is lined with basic refractories. It consists essentially of its own body, tilting mechanism, nozzle and dedusting equipment.

The heat weight for the first LD converters was 30 to 35 tons; currently the largest number of oxygen converters operate with heat weight from 150 to 250 tons and the biggest converters operate with heat weight up to 400 tons.

The following Figure shows dimensions and shapes of converters for different heat weight.

Basic metal charge is formed by molten pig iron (about 72%) and steel scrap (about 28%), further fluxes are added (slag-forming additives, e.g. lime, diluent, magnesite, etc.), furthermore it is also possible to add iron ore, sinter, return slag, etc., especially for the bath cooling and treatment of slag.

This process is mainly used for the production of medium and low carbon steels. The duration of the heat, including repair times, charging, pouring pig iron, finishing and tapping takes about 50 minutes, the time of oxygen blowing takes 18 minutes from this time. The intensity of the blowing is about 2.5 to 3.5 m³·t⁻¹·min⁻¹.

The entire process has the following stages:

- **Repair of linings**
- **Charging of fluxes, additives and charging of steel scrap**
- **Charging (pouring) of pig iron**
- **Oxygen blowing (finishing)**
- **Tapping coupled with the deoxidation and alloying**
Repair of the linings is currently performed so that during tapping of steel the slag, to which granulated MgO is added, is left in the converter. It is followed either by tilting of the converter on sides or splash of the slag using oxygen blowing. This will spray a slag (coat) on the walls and it will harden them.

Charging of steel scrap together with lime and diluents is performed by charging boxes using crane so that the entire operation is carried out during one time interval.

Pouring pig iron is performed immediately after attaching charge from the ladle using a crane.

It’s followed by oxygen blowing using an oxygen, water-cooled copper nozzle, examples of which are shown in the following Figure.

During oxygen blowing, which takes about 18 minutes, individual accompanying elements are oxidized according to the following scheme.
At the same time due to the exothermic effect of individual oxidation reactions the temperature of the bath increases.

☞ Tapping of the final steel is performed by tilting the converter and discharging all of the steel into a ladle. Due to other procedures (secondary metallurgy) the outflow of converter oxidation slag into the ladle is prevented.

☞ During tapping, deoxidation of steel and alloying, scattering of ferro-alloys and additives into the flow of tapped steel are performed, again using the crane.

**Steel production in bottom-blown converters (OBM, Q-BOP, OXYVIT)**

During bottom-blowing of oxygen into the converter’s bath, temperature increases up to 2500 °C in the tuyeres area positioned at the bottom. To avoid undesirable lining melting of the converter bottom in the area of tuyeres, oxygen is brought into the liquid metal using double-wall concentric tuyeres by whose external parts are brought gaseous hydrocarbons and by inner part gaseous oxygen and dust lime. Tuyeres are placed in the bottom of the converter in a circle, ellipse or a cross in a total number of about 14 tuyeres.

When using methane, it breaks down in the tuyere orifice and partially oxidizes according to following reactions

\[
\text{CH}_4(g) \rightarrow [\text{C}] + 2\text{H}_2(g) \tag{122}
\]

\[
[\text{C}] + [\text{O}] \rightarrow \text{CO}_2(g) \tag{123}
\]
The heat effect of this process is endothermic.

Processes that are going on around the nozzle are schematically shown in the following Figure.

Processes that are going on around the tuyeres

The individual stages of the process are the same as in case of LD converter.

The shape of the bottom-blown converter is compared to LD converter characterized by lower specific volume (0.6 to 0.8 m³.t⁻¹ of steel) and also by smaller ratio of height to outer diameter (H : D = 1.2 to 1.0) – see the comparison.
The cross section of the hall of converter steel plant during the Q-BOP and LD process

The metal charge is also formed by poured pig iron and steel scrap, where in this way it is possible to process its higher share than in the LD process.

When the oxygen passes through the bath, the individual accompanying elements are oxidized. The advantage of these converters are small temperature differences of the bath and its chemical homogeneity, because the blowing intensity is lower than in the LD converter. Therefore it doesn’t come to over-oxidation of the bath, oxidation reactions occur near the equilibrium state, which increases the yield of metal, reduces manganese burn and it makes it possible to work with smaller amount of slag. Due to decomposition of CH₄, during which hydrogen is produced as the product, though produced steels contain about 2 ppm more hydrogen.

The course of the heat in oxygen converter during the Q-BOP and LD process
Fundamentals of steelmaking technology in converters

The dependence between the content of C in the metal and FeO in the slag during steelmaking LD and Q-BOP process

The dependence of [S] content in the steel to [S] content in the pig iron in case of slag basicity $B = 3.5$ at the Q-BOP and LD process

Combined ways of blowing

Converters with combined blowing join the advantages of LD and OBM – higher productivity and simplicity of LD with technological advantages of bottom-blowing. They make it possible to run the oxidation process in the vicinity of the equilibrium state and thus improve the conditions for dephosphorization and desulphurization of the steel. Top-blown converters are therefore complemented by alternative bottom-blowing of Ar, N$_2$, O$_2$, CO$_2$, C$_m$H$_n$, together with solid slag forming additives using nozzles or porous blocks. Development focuses on specially modified bottom-blown converters into which, together
with oxygen, fuel – oil, gas or dust coal is additionally brought. Thus blown converters enable processing of higher amounts of steel scrap. KMS process is known for example, where oxygen and coal is blown into the bath along with dust lime.

All new oxygen converter processes assume the maximum utilization rate of reaction vessel followed by the completion of the cast by secondary metallurgy methods in the vessel outside the convertor.

Possible options are shown in the following Figures.
The arrangement of the converter – combined oxygen blowing

Summary of Terms:
- Construction of top-blown and bottom-blown oxygen converter
- Production technology of individual converters

Questions
- Construction of LD converter
- Construction of bottom-blown converter
- Converters with combined blowing
- Technology of production in LD converters
- Technology of production in bottom-blown converters
17. FUNDAMENTALS OF STEELMAKING TECHNOLOGY IN TANDEM FURNACES

CHAPTER DIVISION

- The construction of tandem furnace
- The steelmaking technology

Time for the study: 120 min

Objective: After reading this chapter

- You will understand the structure of tandem furnace and you will be able to describe the technological process of production in this aggregate

Interpretation:

The construction of tandem furnace

The tandem furnace consists of two hearths, where one is used for preheating and melting of the batch, while the second one is used for the process of refining by the gaseous oxygen. The tandem furnace operates without regenerators and the waste gases heat, mainly CO and heat generated by post-combustion of CO to CO₂, is used for the heating or melting of the charge – see the picture. After each tapping the function of each hearth is reversed.
The actual furnace consists of two folding rectangular hearths closed with the vault from top. In the front wall of each hearth, there is a charging door, there are also hearth flues on both sides of the furnace. Under the hearth flues, the slag chamber is placed. Telescopic nozzle (primary) for supplying the refining oxygen, which extends obliquely into the hearth through the hearth flue, is placed on stands on both sides of the furnace. The quantity of the refining oxygen is about 14 000 m$^3$.hour$^{-1}$ and post-combustion mixture approximately 4 000 m$^3$.hour$^{-1}$. Due to furnace vault it vertically extends above each post-combustion (secondary) nozzle that brings a mixture of oxygen and air in a ratio of about 1:1 for additional oxidation of CO 99.5% purity oxygen is used. A transfer channel, which transfers waste gases, is placed between both hearths. The scheme of the furnace is clear from the following Figures.
The lining consists of two layers – safety and working, which is named powdery basic refractory material with a thickness of 300 to 400 mm.

The technology of steelmaking

The basic nature of steelmaking in tandem furnaces (T-furnaces) is to utilize physical heat of waste gas and the chemical heat of carbon monoxide to preheat the solid part of the batch first and the liquid part of the batch later. The actual refining of pig iron happens during the oxygen blowing on the surface of liquid metal. These furnaces are currently operating only in ArcelorMittal Ostrava, a.s., with a melt weight of 220 t in each hearth.

The production process in T-furnace takes place in the refining hearth, where additional components oxidize in the metal bath. The resulting oxides SiO₂, MnO, P₂O₅, FeO pass into the slag. Resulting waste gases (carbon monoxide) are discharged through the transfer channel into the preheating hearth, where they preheat the fixed metal-slag batch and afterwards also
the poured pig iron. Through the secondary nozzle of this hearth oxygen is blown, which helps to complete the combustion of CO to CO$_2$ according to the equation

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$$  \hspace{1cm} (124)

Which is an exothermic reaction subsequently allowing the increase of steel scrap amount to about 33% of the total metallic charge weight.

The manufacturing process starts with the charging of the batch with a prior tapping and inspection of the lining of the hearth. In order to shorten the time of the charging, the special containers are used for burdening, so that it is possible to take all of the steel scrap to the T-furnace in only one or two intervals. Placing of the steel scrap is followed by soaking (approximately 10% of the refining time) and then the lime burdening. Another warming-through continues until the pig iron is poured, which should be completed before tapping the melt from the refining hearth.

The tandem furnace batch is formed by liquid pig iron, steel scrap (approximately 33% metallic charge) and slag-forming additives – lime and diluents.

The actual refining process of the oxygen blowing begins after the end of tapping in the side hearth. Approximately in one third of the refining time, the primary foamed slag is raked off, after which the addition of lime and diluents creates the new slag. In the middle of refining (time of refining of the bath with oxygen) the first test of the metal and slag is taken and the temperature of the bath is measured. In the second half of refining, the treatment of the slag as necessary is performed, either by addition of lime and diluents or by the change of oxygen blowing regime.

The following Figure shows the change of the chemical composition of the metal bath during the oxygen blowing
The change of the chemical composition of the metal bath in T-furnace

It is followed by tapping in the refining hearth and the whole technological process is reversed. The total processing time in each hearth is approximately 70-80 minutes. The following pictures show the change in the position of refining and post-combustion nozzles based on the change of the individual hearths, and furthermore the schedule of the refining process in individual hearths for both variants of the process.

It also contains photographs of ArcelorMittal Ostrava a.s. furnaces.
Fundamentals of steelmaking technology in tandem furnaces

**Scheme of the first variant**

Refining schedule in T – furnace Variant I

**Scheme of the second variant**

Refining schedule in T – furnace Variant II
Fundamentals of steelmaking technology in tandem furnaces

Tandem furnace – ArcelorMittal Ostrava a.s.

Tandem furnace – front view ArcelorMittal Ostrava a.s.

Tandem furnace - ArcelorMittal Ostrava a.s.
Summary of Terms:

- Construction of T-furnace
- Technology of steel production in T-furnace

Questions

- Construction of T-furnace
- Technology of steel production in T-furnace
- Differences in production technology compared to LD converter
18. FUNDAMENTALS OF STEELMAKING TECHNOLOGY IN ELECTRIC ARC FURNACES

CHAPTER DIVISION

✓ The construction of electric arc furnace
✓ The steelmaking technology

Time for the study: 120 min

Objective: After reading this chapter

- You will be able to describe the construction of the electric arc furnace including electric parts
- You will understand the actual course of the technological process in this aggregate

Interpretation:

The construction of the electric arc furnace

Electric arc furnaces were used as the main steel aggregates for the production of alloyed and high-grade steel for a long time. In the last twenty years, however, the look at their usage has started to change completely and today they are also used as a device to quick melt of the steel scrap and production of crude steel. Further processing of crude steel – part of refining, deoxidation as well as alloying shifts are made in secondary metallurgy. The goal is to maximize the significant electric power, which has increased in modern UHP (Ultra High Productivity) compared to conventional EOP furnaces from the usual 100 to 200 kW.t\(^{-1}\) of steel maximum power to 300 to 600 kW.t\(^{-1}\) and in the future possibly even more.

EOP are mostly built as a three-phase folding AC (alternating current) furnaces adapted for top charging with automatic movement of electrodes. The heat source is an electric arc which burns between graphite electrodes and conductive batch. In recent years several furnaces working with DC (direct current) were built worldwide. The aim was to reduce the consumption of graphite electrodes and to improve the working environment.
The electric arc furnace

The electric arc furnace consists of the actual furnace, motion mechanisms and electrical equipment. The outer part of the furnace (the door and the shell) are made of the steel sheet of welded or riveted construction. In the front part of the furnace there is a handling area, in the back part of the furnace there is a tapping hole. The construction of the arc is formed by a circular frame equipped with the water cooling. In the arc there are apertures for the passage of electrodes.

The furnace is lined in several layers with refractory bricks based on magnesite. The last working layer of the hearth lining is made by tamping down the ground dolomite or magnesite. The lining of the roof is made of shaped bricks, silica or chromium-magnesite. Charging of the batch for these furnaces is performed either by charge box or charge bucket.
Technology of steelmaking

The entire process of steelmaking has the following stages:

- **furnace turnaround**
- **furnace charging**
- **melting process**
- **the oxidation and the reduction period**
- **alloying**
- **tapping**

➢ The furnace turnaround is performed immediately after the end of tapping. Damaged areas, especially in the area of the „slag line“ are repaired using gunned refractories (rotafrite or magnesite) with a grain size up to 10 mm. Repairs can be done manually or by using special slings.

➢ Charging of the batch is carried out by burn in an off state so that its duration is as short as possible, using the charge boxes or buckets. The steel scrap, solid pig iron, coke or fragments of electrodes form the metal batch. Batch further consists of lime, diluents. Further the feed ore is added to the batch to achieve the oxidation of accompanying elements.

➢ In a phase of melting process, due to burning of arcs between the electrode and the metal batch, its melting occurs and gradually the complete meltdown of the batch. In this phase
is already occurring the partial oxidation of accompanying elements (especially steel dephosphorization) joined with the production of slag. The melting process phase ends with the complete meltdown of the batch in the furnace.

- In a phase of oxidation, dephosphorization of the metal bath (low temperature, high oxidizing ability and high basicity of the slag), the connection with the skimming of the slag (deslagging) with a high content of $4\text{CaO}.\text{P}_2\text{O}_5$ occur. This is followed by oxidation of carbon and other elements with addition of iron ore or oxygen blowing into the bath. The last part of the oxidation phase is the carbon oxidation without the addition of iron ore (pure boil). Since at the end of the oxidation phase the required carbon content in the metal should be achieved, oxidation of carbon must be terminated by the external interference, for example by preliminary deoxidation of the bath and by the skimming of the oxidation slag.

- The point of the reduction phase of the melting process is to achieve the required desulphurization and alloying of the bath. After skimming of the oxidation slag and realization of the preliminary deoxidation of the bath, a new slag from the lime and diluents is created. Reductants are added as well (coke, FeSi, …), which are used for reduction of the residual FeO in the slag by equations

\begin{align}
\text{In case of FeSi} & \quad \text{(Si)} + \text{(FeO)} \rightarrow \text{(SiO)} + \text{Fe}_\text{(l)} \\
& \quad \text{(SiO)} + \text{(FeO)} \rightarrow \text{(SiO}_2\text{)} + \text{Fe}_\text{(l)} \\
& \quad \text{(SiO}_2\text{)} + 2\text{(CaO)} \rightarrow \text{2CaO}.\text{SiO}_2 \\
\text{In case of carbon} & \quad \text{(CaO)} + \text{(C)} \rightarrow \text{(CaC}_2\text{)} + \text{CO}_\text{(g)} \\
& \quad \text{(CaC}_2\text{)} + 2\text{(FeO)} \rightarrow \text{(CaO)} + 2\text{CO}_\text{(g)} + 3\text{Fe}_\text{(l)}
\end{align}

The process of deoxidizing reactions reduces the content of FeO in the slag below 1%, and thus supports the process of the desulphurization reaction

$$\text{Fe}_\text{(l)} + /\text{S}/ + \text{(CaO)} \rightarrow \text{(CaS)} + \text{(FeO)}$$

- At the end of the reduction phase, the alloying of the bath to the prescribed chemical composition is performed. The temperature of the bath is also adjusted to the desired value.

In remelting process of the steel scrap and steel-making in UHP furnaces, the portion of the meltage, which is attributable to the reduction period, moves outside of the furnace
(secondary metallurgy), thus the high power transformer EOP and the specific options of these devices are better used.

➢ It’s followed by the steel tap into the casting ladle.

More modern high performance furnaces are intensified with oxygen. Fuel burners as well as direct computer control are used there and the walls and roofs are water-cooled. In addition, the consumption of energy and graphite electrodes decreases. The duration of the melting process is at UHP reduced to less than 2 hours.

Currently, at the time when steel mills are equipped with secondary metallurgy devices, the procedures presented within the reduction phase are performed on these devices, beyond the basic manufacturing aggregate.

∑ Summary of Terms:
- The construction of electric arc furnace
- Technology of steel-making process in the electric arc furnace

❓ Questions
- The construction of EOP
- The electric scheme of EOP
- The technology of steel-making process in EOP
The steel is made by oxidation processes and therefore at the end of the melting process in the metal bath, a certain amount of dissolved oxygen remains. The oxygen content in the metal bath after the oxidation of accompanying elements depends on the composition of the metal (especially carbon content) and the slag (activity of FeO), on the bath temperature and the type of the manufacturing process.

The deoxidation task is to reduce the oxygen content in the liquid steel to the required level, since during the cooling, solidification and crystallization of the steel the solubility of oxygen significantly decreases, which leads to the formation of oxides SiO₂, MnO, FeO, CO etc.
conditioning the formation of voids, pores and pollution of the solified steel with non-metallic oxide inclusions. This is reflected in the poor formability and deterioration of mechanical properties of steel.

According to the degree of deoxidation steel is divided into:

- **Killed steel** – oxygen content is reduced to the level where during the casting and solidification process the carbon reaction doesn’t take place anymore
- **Rimmed (unkilled) steel** – during the casting and solidification process the oxidation of carbon whilst forming CO bubbles occurs
- **Semi-killed steel** – the link between the killed and unkillled steel

According to the method of performance deoxidation is divided into:

- precipitation
- diffusion
- using synthetic slags
- vacuum carbon deoxidation

**Precipitation deoxidation**

The substance of precipitation deoxidation lies in the additive of deoxidation elements – substances with higher affinity towards oxygen than that of iron – into the steel, whilst forming insoluble oxides in the steel.

\[
m \, [X] + n \, [O] = X_m O_n \text{ (s, l, g)}
\]  

(131)

Deoxidation ability of the elements used in the precipitation deoxidation can be most fully assessed according to the value of the equilibrium content of oxygen calculated from the equilibrium constant of the reaction (131) for the element

\[
K_{131} = \frac{a_{X,O}}{f_{[X]}^m \cdot [\%X]^m \cdot f_{[O]}^n \cdot [\%O]^n}
\]  

(132)

\[
[\%O] = a \sqrt{\frac{a_{X,O}}{f_{[X]}^m \cdot [\%X]^m \cdot f_{[O]}^n \cdot K_{131}}}
\]  

(133)

In the value of the equilibrium constant, affinity of deoxidation element towards oxygen and temperature influence is contained. Significant is also the influence of the chemical composition of the steel on deoxidation ability of the elements hidden in the activity coefficients \( f_{[X]} \) a \( f_{[O]} \). (Their values can be calculated using the interaction coefficients).
Deoxidation of the steel and alloying

If the product of deoxidation is pure oxide, then \( a_{x_o} = 1 \).

If the product of deoxidation is unsaturated solution, then \( a_{x_o} < 1 \), which positively reflects in the value of the equilibrium oxygen content. This fact is used in deoxidation with complex additives (e.g. FeSiMn, FeSiAl etc.).

Alloying

Deoxidation of the steel is closely associated with the alloying. The residual content of deoxidation element (above the theoretical equilibrium content) increases the value of the corresponding element in the steel – element alloys the bath.

That part of the deoxidation element, which participates in the deoxidation is called iron loss of the element and that part of the deoxidation, which increases the content of the element in the steel is called utilization.

Ferroalloys

Appropriate elements in the form of ferroalloys (iron alloys) are used to deoxidation and alloying.

For precipitation deoxidation of the steel, FeMn, FeSi and solid aluminium are mostly used. Ferroalloys of the other elements with high affinity to oxygen (FeTi, FeV, FeNb, FeCr, FeW, FeMo, FeCaSi etc.) used to alloy steel or modification of inclusions are added later into the deoxidized steel to reduce the iron loss of precious nonferrous metals.

The main advantage of the precipitation deoxidation is the ease of performance, the speed and the effect of the process of the chemical reaction. The main disadvantage is the pollution of the steel with non-metallic inclusions.

Diffusion deoxidation

The substance of diffusion deoxidation lies in creating the imbalance between the activity of oxygen in the metal and the activity of FeO in the slag by reaction

\[
(\text{FeO}) = \text{Fe}_\text{(l)} + [\text{O}] \tag{134}
\]

The thermodynamic condition of the process of the reaction (134), right to left, is the dissimilarity derived from the equation for the equilibrium constant of this reaction

\[
a_{[\text{O}]} > K_{134} \cdot a_{\text{FeO}} \tag{135}
\]
In practice, e.g. in the reduction melting phase in EAF it is necessary to deoxidize the slag deeply (deactivate) by FeSi, Al or carbon. The advantage of this method of deoxidation lies in the fact that it is not accompanied by formation of deoxidation products in the steel, which means its higher cleanliness. The significant disadvantage limiting its usefulness is the slow progress limited by diffusion processes.

**Deoxidation of steel with synthetic slag**

The principle of the diffusion deoxidation – see equation (135) is also applied in deoxidation of steel with synthetic slag. The difference lies in the technology of implementation. When the steel is being deoxidized with a synthetic slag, the steel is poured from above into a pre-molten synthetic slag located in the ladle. Due to the formation of the emulsion of slag and steel it comes to increasement of the interfacial surface and the intense turbulence in the droplets of metal and slag. This speeds up processes at the slag-metal interface and removes the main disadvantage of the diffusion deoxidation. The synthetic slag may be acidic and basic, but with a minimum content of FeO (up to 0.5%).

Using basic slag (calcium-aluminate) the steel can be simultaneously also desulphurized.

**The vacuum carbon deoxidation of the steel**

It is a reduction of oxygen content in the metal using the carbon reaction under reduced pressure. The equilibrium constant of decarburization reaction and its dependence on the temperature shows equation

\[
[C] + [O] = CO_{(g)}
\]

\[
log K_{136} = log \frac{P_{CO}}{a_{[C]} \cdot a_{[O]}} = \frac{1168}{T} + 2.07
\]

According to the principle of action and reaction the reduced pressure shifts the reaction equilibrium (136) to the right. This is evident also from equation (137), when at a constant temperature by reducing the pressure e.g. from \(P_{CO} = 0.1\) MPa to \(P_{CO} = 0.01\) MPa must also simultaneously ten times decrease the product of activities \(a_{[C]} \cdot a_{[O]}\) to keep the value of the equilibrium constant \(K_6\) unchanged. The significant effect of the reduced partial pressure of CO at equilibrium oxygen activity is shown in the following Figure.
Deoxidation of the steel and alloying

Summary of Terms:
- The role of deoxidation
- The precipitation deoxidation
- The diffusion deoxidation
- The deoxidation under the synthetic slag
- The vacuum carbon deoxidation
- The alloying of the steel

Questions
- The role of deoxidation
- The principle of precipitation deoxidation
- The principle of diffusion deoxidation
- The principle of deoxidation with the synthetic slag
- The principle of vacuum carbon deoxidation
- Ferroalloys, alloying of the steel

The equilibrium between the activity of oxygen and activity of carbon for the selected partial pressures of CO
20. SECONDARY METALLURGY OF STEEL

CHAPTER DIVISION
✓ Clarification of the term, the role of secondary metallurgy of the steel
✓ Degassing of the steel
✓ Blowing of inert gases in steel
✓ Reheating of the steel
✓ Injection of powder additives

Time for the study: 120 min

Objective: After reading this chapter
- You will be able to define the role of secondary metallurgy of the steel
- You will be able to describe some basic processes of secondary metallurgy

Interpretation:

Clarification of the term, the role of secondary metallurgy of the steel

The second half of the 20th century was in the steelmaking characterized by increasing user demand for the quality of steel (energy, chemical industry, unconventional production engineering etc.), or in relation to the increasement of the utility properties of traditional products.

The limiting factor of further increasement of the furnace units productivity – has became the length of the finishing phase of the melt after the melting of the charge. Naturally therefore technical solutions enabling to convert some technological operations during the finishing of the melt outside of the furnace aggregate appeared. These solutions have led to the emergence of new steel technologies, collectively referred to as secondary metallurgy – treatment of molten steel in the ladle (ladle metallurgy, ladle refining).
The current secondary metallurgy makes it possible to successfully fulfil the basic requirements – on the one hand the need to reduce production costs and on the other hand to enhance the quality of manufactured materials.

**Degassing of the steel**

Dissolution of gases (hydrogen, nitrogen) in molten steel can be expressed as follows

\[
\frac{1}{2} X_2(g) = \%X / 1
\]

The equilibrium constant is then given by equation

\[
K_x = \frac{f_x \cdot \%X /}{\sqrt{P_x}}
\]

The content dependence of atomically dissolved gas in the molten steel on its pressure at a constant temperature can be expressed as follows

\[
\%X / = \frac{K_x \cdot \sqrt{P_x}}{f_x}
\]

From the above it is evident that the content of dissolved gas in the steel will be lower, the lower the partial pressure of gas above the bath is. Therefore to reduce the gas content in the molten steel, vacuum degasing methods are used.

The next section describes the most commonly used methods.

**The method of degasing in a ladle (VD - Vacuum Degassing)**

This process is characterized by a simple procedure and the high grade possibility of steel processing. Processed slag-free steel is tapped from the production aggregate. Subsequently it is transported to the caisson together with the new synthetic slag with a desired chemical composition that is needed for the following chemical reactions (especially desulphurization). Possible heat loss of the steel must be compensated either by increasement of the tapping temperature in the production aggregate or by heating at ladle furnace. Therefore it is very important to consider the desired length of the steel processing on VD and the quantity of alloy additions.

Sufficient mixing of the melt is ensured by blowing of inert gas through the blowing block, placed in the bottom of the ladle, which provides a high transfer of the mass in the ladle bath.
VD process is particularly advantageous for refining and modification of the steel requiring low contents of hydrogen, nitrogen and sulphur at the same time.

Vacuum processing of the molten steel by the recirculating way (RH-Ruhrstahl-Heraeus process)

Due to vacuum in the vacuum chamber, the melt is transported by the supply snorkel to the chamber. By supplying inert gas to this snorkel, the mixture of metal and gas of lower density is created, so that it moves up to the vacuum chamber. Gases contained in the steel are released, degassed steel flows through the output snorkel back to the ladle where it mixes with other metal. In this way the steel circulates between the ladle and RH chamber.

Vacuum processing of the molten steel by lifting method (DH – Dortmund Hüttenunion process)

Due to difference of the pressure between the vacuum chamber and the surrounding atmosphere in the inlet neck, the column of liquid steel forms and portion of the steel gets into the vacuum chamber where the process of degassing takes place. After degassing the chamber lifts up (or the ladle drops) and degassed steel flows back to the ladle. This process continues until the desired degree of degassing is achieved. The ladle content must go through the vacuum chamber at least 3x.
Blowing of the inert gas into the steel

Inert gas (usually Ar) is blown into the bath typically through porous ceramic blocks built in the bottom of the ladle. Porous structure of ceramic blocks allows creation of the soft and evenly dispersed bubbles.

Blowing of inert gases can also be performed via the top lance inserted through the roof of the ladle. This method ensures especially intensive mixing of the bath.
Effects of refining with inert gases

- The chemical homogenization of the bath
- The thermal homogenization of the bath
- The improvement of the non-metallic inclusions coagulation
- The carrying out of non-metallic inclusions partly due to the flow of the steel and partly also due to sticking of inclusions on bubbles (flotation)
- The reduction of the gas content in the steel (hydrogen, nitrogen). The substance is the difference of partial pressures of gases that should be removed from the bath and inert gas. This difference allows the diffusion of gases into the argon bubbles, by which they are carried out above the bath

Reheating of the steel

Reheating of the steel is used to achieve the required and accurate casting temperature and also to secure the process of refining reactions.

The most commonly used device is the ladle furnace (LF), that for reheating electric arcs burning between the graphite electrodes and the bath are used. At the same time, this device is also used for steel refining (desulphurisation and improving of metallurgical cleanliness).
Powder additives injection

There is a number of devices allowing the powder additives injection (alloying, refining, modification) into the volume of the steel (below the surface).

The principle is clear from the following Figure, when the individual additives are injected through the nozzle. The carrying medium is usually argon.
Summary of Terms:
- The secondary metallurgy of steel

Questions
- Explain the concept and the role of secondary metallurgy of steel
- Methods and the principle of degassing of the steel
- Methods and effects of blowing of inert gases into the steel
- Methods of reheating of the steel
- Powder additives injection into the steel
21. STEEL CASTING

CHAPTER DIVISION

- Casting steel into moulds
- Segregation, solidification of steel
- Continuous casting of steel
- Tundish in continuous casting of steel
- Prospects of continuous casting of steel

Time for the study: 150 min

Objective: After reading this chapter

- You will be able to describe ways of steel casting into moulds
- You will be able to characterize the concept of steel segregation
- You will be able to describe the basic construction elements of continuous casting of steel and their role
- You will be able to describe the development trends in continuous casting of steel

Interpretation:

The liquid steel produced in steel aggregates is after tapping, deoxidation and other secondary metallurgy treatment casted (castings, ingots or continuous casts) and further processed at the mills or forges.

After pouring the steel into the mould, respectively crystallizer, there is the immediate contact of the metal with the cold wall, resulting in the temperature drop of the steel and in the beginning of its crystallization.

At the present time in ČR is about 10 % of the total steel production casted traditionally (into the moulds) and 90 % is casted in continuous casting devices.
Steel casting into moulds

It is performed in the steel casting hall. Cast-iron moulds – moulds are located either on mobile ingot casting car or on the casting field. The steel is casted into moulds either directly from the tapping ladle or through the tundish, which is provided with sealable drains – casting from the top.

Scheme of casting from the top through the tundish shows following Figure.

![Example of steel casting from the top from the casting ladle over the tundish into moulds placed in the ingot casting car](image)

When **casting from the bottom** steel is not casted into moulds directly, but through the casting sprue and inlet channels. It then rises evenly in all moulds simultaneously. Moulds in this way of casting can be also placed on ingot casting car or in casting pits. The shape of moulds follows the requirement of rolling mills. Casting steel from the bottom shows the following scheme.

![Casting from the bottom scheme](image)
Comparison of casting steel into mould from the top and from the bottom

Some advantages of casting from the top compared to casting from the bottom are:

- Less labor-intensity and consumption of refractory materials in the preparation of casting kit (no knocking down of an old and a new lining of casting systems in casting slabs, etc.);
- Smaller losses of steel (in particular the losses arising from the casting from the bottom by solidification of steel in the casting system – so called „bones”);
- Better storing of the thermal center of the ingot which is in the process of solidification in its upper part;
- Smaller possible degree of additional contamination of steel by contact with the casting ceramics;
- Smaller drop in temperature of steel between the ladle and mould etc.

Some disadvantages of casting from the top compared to casting from the bottom are:

- Greater chance of developing certain defects, such as scales (steel spray);
- In many cases a greater time interval for the ladle casting in casting from the top is required than in casting from the bottom (when casting from the bottom, it is possible to cast simultaneously from example 64 small ingots);
- Larger number of closures of the ladle and thus greater ceramic closing mechanism wear off;
- Worse monitoring and regulation of casting speed, a greater moulds wear off, etc.

Segregation, solidification

The steel ingot has internal discontinuities, contains non-metallic particles of different chemical composition and size and points of different chemical composition of the steel. Differences of the chemical composition of the metal are formed by limited solubility of accompanying and alloying elements in the steel during solidification. Inevitably different concentration of additive is accordingly in new crystals than in the former melt from which they originated. The described phenomenon is generally called the segregation.

The segregation has a big impact on the quality of casted and moulded steel. It is a basic process of formation of steel heterogeneity, which can be influenced to certain extent by the suitable metallurgical composition of basic batch materials (e. g. by limiting the concentration
of accompanying elements), production technology and casting, but perfect homogeneity of the steel product can not be achieved.

The equilibrium and effective distribution coefficient

The tendency of elements to segregation expresses the equilibrium distributive coefficient

$$k_o = \frac{C_S}{C_L}$$  \[(141)\]

where: $C_S$ is concentration of the element in the solid phase

$C_L$ - concentration of the element in the liquid phase

Which indicates the differential solubility of elements in liquid and solid phase.

Casting from the bottom scheme

Note: $C_L, C_S$ – initial concentration of additives in the liquid and solid phase;

$A, B$ – the concentration of additives in the melt and solid phase

Values of equilibrium distributive coefficients for individual elements shows following Figure.

From the Figure it is evident that the greatest tendency toward segregation (the difference between the content of the element in the liquid and solid phase) have elements with low $k_o$ value (oxygen, sulphur, phosphorus, carbon).
The equilibrium distribution coefficient does include neither the influence of solidification speed nor the influence of flowing speed and therefore the effective distributive coefficient was introduced

\[
k = \frac{k_o}{k_o + (1-k_o) \cdot e^{-\delta/D}}
\]

(142)

where: \( v \) is the rate of solidification, \([\text{cm.s}^{-1}]\)

\( \delta \) - the thickness of the diffusion layer before the interfacial interface, \([\text{cm}]\)

\( D \) - the diffusion coefficient of additives in the melt, \([\text{cm}^2\text{s}^{-1}]\)

According to this relationship the value increases (the effect of segregation decreases) with increasing solidification speed and decreasing flowing speed (increasing value \( \delta = 1/v \)).

The structure of ingot from the killed steel

The following Figure shows the internal structure of killed ingot. At the beginning of the crystallization, due to rapid cooling of the metal by contact with the mould, the chill zone is formed. It is formed by small crystals which emerge at high cooling rate, when there is a high number of spontaneously arising centers which do not have time to develop. With increasing thickness of this layer and simultaneous heating of the mould walls conditions of drawing off the heat are changing – columnar crystals are formed.
Steel casting

The cooling rate decreases, but it is still intense enough to form columnar crystals. The growth of these crystals takes place until the temperature gradient of the liquid part of the ingot on the border of solidification of the steel does not reach the minimum value. Then the growth of columnar crystals stops.

It is followed by a zone, where crystals due to the decreasing temperature gradient and released latent heat of crystallization, grow in all directions - equiaxed zone is formed.

Structure of crystallization process of the ingot

Structure of ingot from killed steel
Steel casting

The continuous casting of steel

The continuous casting of steel is a technology that replaces the existing procedure of steel casting in the ingot way. Extension of this technology is not only caused by ever increasing demands for quality of produced steel, but also by economic and production indicators.

The principle of the continuous casting can be defined as a technological process, wherein the liquid steel is being continuously processed to blank, which can have various shapes as required for subsequent forming. Different shapes of blanks and their terminology are shown in the following Figure. When casting steel on CCM is initially treated steel brought in the casting ladle from the secondary metallurgy device and placed into a ladle turret, which allows manipulation with casting ladles for the purpose of continuous refilling of the tundish. The tundish is another part of CCM which is there for dividing the steel into individual casting streams, which supply the liquid steel into the crystallizers (moulds), which represents the primary cooling zones. The crystallizer consists of copper shell, which is water cooled. This leads to the formation of casting crust which forms the shell of the liquid core blank.

After exit from the crystallizer the blank consists of the casting crust on the cross-section, while the liquid core remains in the middle. After exiting the crystallizer it gets into the secondary cooling zone, where it is cooled with such intensity that it is solidified on the entire cross-section at the end of this zone.

Last but one technological step represents the division of the blank at the end of the secondary cooling zone at the desired lengths for subsequent rolling mill processing. Finally the blank gets to the cooling bed, ie. tertiary cooling zone, where it is cooled with the surrounding atmosphere.

Examples of different types of blanks and their terminology
The construction development and division of CCM

The continuous casting devices can be divided according to their construction development into several groups. The first group constitutes the vertical CCM. The development of this basic construction of vertical CCM led to its modification and formed the radial (arc) CCM. This type of CCM represents a new group which has been structurally further developed and at the present time accounts for the predominant type of CCM used around the world including the Czech Republic.

Specific requirements of small steel mills and the production of high-grade steels led to the emergence of another construction group called the horizontal CCM.

The radial (arc) CCM

The radial CCM is the modified vertical casting. It is characterized by placement of the main parts of the casting machine along so called casting arc through which the blank goes. In this type of CCM solidification of the blank starts in the crystallizer, further continues on the downward, curved path, when the secondary cooling system affects the blank, whereby the complete solidification throughout the cross-section of the blank is according to conditions used for the process of the casting terminated either still on the curved path or not until in the horizontal path of the blank. Therefore the straightening of the blank takes place at either completely solidified cross-section or with the blank containing the liquid core.

This type of the radial CCM can be divided into two basic types, which have been further developed according to the requirements and capabilities of individual steel mills. The first type is the radial (arc) CCM with the straight crystallizer. This type of CCM is characterized in that the blank begins to solidify in the straight crystallizer, then continues into the subsequent vertical part, where its walls get a sufficient thickness and afterwards proceeds to the bending zone, where it is deformed into an arc shape. Another shape deformation of the blank takes place at the crossing to the horizontal part of the path.

The second type is the radial (arc) CCM with the curved crystallizer. In this case the blank begins to solidify in a curved crystallizer, wherein in the subsequent part of the downward path of the identical radius the blank is not a subject of the shape deformation which takes place at the crossing to the horizontal part of the path.
The horizontal CCM

The horizontal CCM is intended primarily for smaller steel mills with a wide quality range of products. The basic scheme of this device is characterized by the arrangement of individual parts in the horizontal direction. This type of CCM has not broaden much in the steel industry and it is rather on the decline. It is also used during the casting of non-ferrous metals.
The comparison of ingot casting and continuous casting

Among the advantages of continuous casting is a greater yield of steel (about 10 to 15% in comparison with the steel casting into the moulds), eliminating the need for soaking furnaces and blooming mill or slabling mill, lower energy intensity, shortening of the product cycle, higher productivity of work, often smaller necessary of hall space, the possibility to cast blanks with a shaped traverse cross-section, the higher degree of chemical homogeneity of the blank, even more mechanical properties of rolled products.

Overall a better quality of continuously casted steel is related both to the different character of cooling so the fact that to control this process (e.g. in terms of elimination of the creation supposition of external and internal cracks, etc.) is necessary to protect also the improvement of the produced liquid steel quality.

The tundish in continuous steel casting

The tundish represents one of the most important technological nodes of the continuous casting device and it is placed between the casting ladle and the crystallizer.

The tundish itself is composed of welded steel shell with an internal multilayered refractory lining and usually also elements affecting the steel flow in the tundish (such as impact pads, dams etc.). Furthermore to reduce the heat loss of the liquid steel and to improve the heat balance, tundishes are equipped with roofs. The control of the flowing steel is solved by the system of stopper rods or slide-valve gates.
The tundish is comprised of not only its own vessel, but it has a whole range of other devices, that have an impact on the flow and purity of steel, see the Figure below.

Prospects of continuous casting of steel

The development is focused mainly on casting forms of close shapes of products - NNSC (Near Net Shape Continuous Casting)

- The beam blank (also dog bone) for the production of beams
- The circular shapes of different diameters for the manufacture of tubes and circular products – rings, wheels
From mentioned schemes arise the basic advantages of this device:

- The minimalization of the correction of the blank shapes in rolling mills
- The increasement of the equipment power
- The reduction of cos

Casting of the thin slabs, hot strips and direct rolling plates

Production processes are usually classified according to the thickness of the billet cast:

- Thin slabs with a thickness of 20 to 80 mm and a width of 1500 to 2000 mm,
- Strips with a thickness of 1 to 6 mm and a width of 1200 to 1500 mm,
- Thin strips or foils with a thickness of about 0.02 to 0.5 mm and a width of 300 mm.
Furthermore they are classified according to the continuous casting of thin slabs into two subgroups according to the casting speed:

- Normal casting speed $3$ to $7\, \text{m.min}^{-1}$ with a thickness of slab $40$ to $80\, \text{mm}$
- High performance casting speed $15\, \text{m.min}^{-1}$ with a thickness of slab $40$ to $60\, \text{mm}$

The strips are characterized by a thickness of $2$ to $8\, \text{mm}$ and a casting speed of $30$ to $60\, \text{m.min}^{-1}$.

*ISP process with a reduction of the thickness under the crystallizer (the thickness of the slab after reduction: $15 – 25\, \text{mm}$)*

The direct strip casting

It includes e.g. systems of continuous casting on one roll, between two rotating rollers, between the belt and the roll and casting between two rotating strips.

The scheme of the casting between **two rotating copper rollers that are cooled** shows the following Figure. This device is called „CASTRIP“ and works in Crawfordsville (fa Nucor).
Comparison

At the end of the chapter is a scheme which shows a comparison of continuous casting of classical slabs (200 to 300 mm), thin slabs (50 to 60 mm) and hot strips (0.7 to 1.8 mm).

The comparison is made with respect to:
- The construction and arrangement of the entire device,
- The casting speed,
- The intensity and complexity of the device,
- The range of rolling sequences,
- The length of the device to the strips reeler
Comparison of CCM
### Summary of Terms:

- The steel casting into moulds, the segregation, the solidification of the steel
- The continuous steel casting, the tundish during the continuous casting of steel
- Perspectives of the continuous steel casting

### Questions

- Steel casting into moulds from the top and the bottom, comparison
- Segregation phenomena during the solidification of the steel
- The construction of the continuous steel casting device
- The tundish of continuous steel casting
- Prospects of continuous steel casting
LITERATURE

[18] www.steeluniversity.org