TECHNOLOGY OF PRODUCTION
OF STEEL IN CONVERTERS

Didactic Text

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PREFACE

Study support to the subject *TECHNOLOGY OF PRODUCTION OF STEEL IN CONVERTERS* is primarily intended for students of combined studies. In the combined form of study, there is a much smaller proportion of direct contact teaching, which makes this study much more difficult for students. Our study support to the subject *TECHNOLOGY OF PRODUCTION OF STEEL IN CONVERTERS* can help you to eliminate this handicap to a certain extent. These is not a new textbook, there are enough of those. The study support is a replacement, if possible, for the lack of direct instruction and interlink to a subsequent study of professional literature itself, whether it be textbooks or other publications.

When writing this support I have tried to maximize the clarity of the text. This cannot be achieved, at least in my opinion, without some simplification, reduction and sometimes even inaccuracy. If someone feels that simplification is too much, I apologize in advance. But my experiences in teaching this subject led me to a result which is just this text.

Despite careful checking of the text, it is almost certain that I did not avoid errors, typing errors, etc., maybe even factual mistakes. I will be most grateful, if you notify me about them so I can gradually correct them. You can notify me either directly during classwork or by email to zdenek.adolf@vsb.cz.

I wish all of you who will use this study support, a lot of strength in your study!

The Author
1 STEEL – CHARACTERISTICS, IMPORTANCE, CLASSIFICATION

Chapter Structuring
✓ Characteristics of steel
✓ Basic raw materials for production of steel
✓ Importance of steel

Time for Study: individual

Target After studying this chapter, you will be able to
- characterize steel and its properties that allow its applicability in practice.
- 

Interpretation

Steel is an alloy of iron with carbon and other metal and non-metallic elements.

Steel contains:
- desirable elements—intentionally added to steel in order to improve its properties: Mn, Si, Cr, Ni, W, Mo, V, Ti, Al, Nb and others
- undesirable elements which get into steel during the metallurgical process and largely deteriorate its properties: S, P, H, N, O and others.

Hydrogen, nitrogen and oxygen are gases atomically dissolved in steel. Hydrogen increases brittleness and decreases resistance to corrosion—it is always undesirable, nitrogen causes so called “ageing of steel”—increase in brittleness and loss of plastic properties of steel due to nitrides formation during exploitation of steel (in chrome-nickel steels, nitrogen can be an alloyant). In produced steel, oxygen is to be found in form of inclusions or atomically dissolved. Again, it deteriorates properties of steel products.

In steel production, oxygen is an essential oxidizing agent that ensures refining of pig iron.
**Steels** contain up to 1.7 wt. % of carbon, **cast iron** contains more than 1.7 wt. % of carbon. Steels and cast iron rank among **technical alloys of iron**. In a heated state, steels are malleable; cast iron is brittle both in a cold state and after heating.

### 1.1 Basic Raw Materials for Production of Steel

**Pig iron** is a product of iron ores processing in a blast furnace. Steel-making pig iron contains: C (4.3 – 4.6 wt. %), Mn (0.5 – 0.7 wt. %), Si (0.5 – 0.7 wt. %), P (0.10 – 0.17 wt. %), S (0.010 – 0.025 wt. %). This chemical composition corresponds to blast furnaces in the Czech Republic. Foundry pig iron contains more Si (1.25 – 3.25 wt. %), P (0.23 – 0.70 wt. %), Mn (0.40 – 1.30 wt. %).

In a charge of a steel-making furnace, pig iron is used in liquid form (if loaded into EAF, then in form of ingots).

**Steel scrap** carries elements used for deoxidation and alloying of steel and so called “trace elements”, which deteriorate properties of steel even in low concentrations (As, Sb, Pb etc.), into steels. Steel scrap must be classified according to present alloyants.

Deoxidizing agents and alloyants are added into steel as:
- ferroalloys (FeMn, FeSi, FeMnSi, CaSi, FeTi, FeCr, FeMo, FeVb, FeB, FeV, etc.),
- technically pure metals (Al, Ni etc.).

### 1.2 Importance of Steel

Steel is one of the most important industrial and construction commodities. Nowadays (2011, 2012), its worldwide production is more than 1.5 billion tons per year. In the Czech Republic it is 5.5 to 6.5 million tons per year.

Growing demands for its production result from its extraordinary properties:

- **large flexibility of properties**

  Steels, depending on chemical composition, presence of non-metallic inclusions and mainly on heat and mechanical processing (rolling, forging), are characterized by an extraordinary range of properties, such as hardness of tool steels, good formability of automotive sheet metals, corrosion resistance of steels alloyed with chromium, strength and elasticity of structural steels, durability (rails) also at high temperatures (blades for steam turbines)

- **recyclability**

  Worn-out steel products are usable as steel scrap in the production of new steel and that at lower cost than when produced from pig iron. Recyclability, especially after sorting, approaches 95 to 100%. This is more than other major commodities such as construction materials, glass, plastics, paper and electro-technical products.
Steel has also disadvantages such as high specific weight (approx. 7000 kg.m³), very high manufacturing costs and environmental pollution during its production (significant air pollution, dust, waste water, slag landfill).

Steel is produced in following types of products:
- flat products - metal sheets,
- long products - bars, sections, rails, wires,
- special products - boilers for the energy industry, autoclaves for the chemical industry,
- pipes for the oil industry, pipes for product pipelines.

### Summary of Terms of the Chapter

- It is mentioned in the “Chapter Structuring”

### Questions to the Taught Curriculum

- Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”
2 HISTORICAL DEVELOPMENT OF INDUSTRIAL PRODUCTION OF STEEL

Chapter Structuring

- Beginnings of industrial production of steel in converters and open-hearth furnaces
- Production of steel in electric furnace
- Current oxygen steel-making technologies

Time for Study: individual

Target: After studying this chapter you will gain information about beginnings of industrial production of steel and current technologies of its production.

Interpretation

Historically the oldest industrial method of steel production is represented by production of steel in converters.

1855 – Henry Bessemer patented technology of production of steel by blowing air into molten pig iron through tuyeres in the bottom of a converter with acid lining. Content of Si in pig iron and silicon dioxide in slag were determining parts of the process. During refining, pig iron could not be desulfurized or dephosphorized. Due to short time of refining (about 20 minutes), productivity of a converter (with capacity up to 30 t) was extremely high.

1878 – Sidney Gilchrist Thomas patented the alkaline converter lining. This lining enabled dephosphorization and desulfurization of steel through alkaline slag, in which calcium oxide is a dominant component. Composition of pig iron was a limiting condition of Thomas alkaline process, as it required high content of phosphorus from 1.7 to 2.5 wt. %, providing a source of heat for heating up a charge, since the silicon content in this case was limited. Oxidation of phosphorus improved heat balance of the process, which is compared to the Bessemer process characterized by higher proportion of slag.

Both types of converters used air as a refining agent. Nitrogen in the air cooled orifices of tuyeres, but increased the nitrogen content in metal, especially in case of work under
alkaline slag. Simultaneously, nitrogen deteriorated heat balance of a melt thus converters could handle only limited quantity of steel scrap (Thomas: 3 to 5%; Bessemer 4 to 7% of a metal charge).

In the Czech lands of the Austro-Hungarian Empire, the Bessemer process was for the first time introduced in 1865 in Vitkovice and the first Thomas converter was built in 1879 in the Vojtesska metallurgical plant of the Kladno Ironworks.

Steel production in Bessemer converters was in the 20's of the last century completely crowded out by Thomas converters. Last melting in Thomas converters took place in 1978 in the Poldi Kladno steelworks.

Development of open-hearth furnaces, known as Siemens-Martin (Translator Note: hereinafter SM), coincided with first converters.

1864 - Pierre Emile Martin joined his metallurgical knowledge with the Friedrich Siemens' patent and used its regenerative preheating to achieve required temperatures also in furnaces producing steel from pig iron and steel scrap in a fiery furnace. These furnaces ensured heating of a charge by combustion of fuel gases (blast furnace gas, coke gas, generator gas) by preheated air in regenerators.

Latticework of regenerators was heated up to 1100 - 1300°C with heat of the exhaust gases from the furnace. When reversed the direction of flow, air and fuel gases in regenerators were preheated and then in burners of a furnace they were burnt and released heat was used to heat up a charge.

Initially, acid-lined furnaces were used and after 1878 also SM furnaces began to use alkaline lining. Significantly longer duration of melting was a disadvantage of SM process compared to converters; initially it was 20 hours, over the years after intensification of the process 15 hours or less, but never less than 8 hours.
Advantages of SM process:

- ability to process any amount of steel scrap
- much lower dependence on composition of pig iron
- ability to produce even highly demanding quality of steel at the time, when methods of secondary metallurgy were not known yet.

Therefore SM process became a successful competitor to converter processes at the end of the 19th century and the first half of the 20th century. In our country, SM process was introduced in 1871 in Vitkovice and later also in other steelworks.

1900 - In the early 20th century, also electrical energy began to find its use in production of steel in electric arc furnaces (EAF) and also in induction furnaces (EIF). In 1901 the Frenchman Paul Louis Heroult and also the Italian Stassane melted high carbon steel using an electric arc. In the same year, the Swede Kjellin constructed the first induction furnace. Emergence of new technologies in steel production was associated both with new discoveries in the field of industrial production of electricity and with a need to process ever-increasing amounts of steel scrap. Also the increasing need for alloy steels was another incentive to produce electrosteel.
In the Czech lands, they began to produce electrosteel in the Poldi Kladno Ironworks and in Vitkovice in the years 1908 to 1914.

1952 - Steelmakers returned to the converter steel production at a qualitatively higher level in 1952, when first melting was carried out in the above blown converter in Linz at the firm Voest-Alpine Stahl AG (Fig. 4). Compared to historical converters, this so-called LD process uses pure oxygen for refining of steel; oxygen is blown under the surface of bath from above through a lance positioned perpendicularly to the axis of a converter. As a result of this new principle, area of highest temperatures is enclosed in mass of metal and thus it is sufficiently distant from lining. Blowing of pure oxygen also enabled to increase proportion of steel scrap in a charge to approx. 25% and significantly reduce volume of emerging exhaust gases and nitrogen content in produced steel.

![Figure 4. Scheme of LD converter](image)

Technologically mastered industrial production of cheap pure oxygen is an essential condition for development of oxygen processes in steel production, which was met in Europe during World War II and that is why Europe became the cradle of oxygen processes.

1967 - Even this highly effective method of steelmaking was not the last developed and industrially used manufacturing technology. First of all, the German steelworks, that still in the sixties of the 20th century produced steel in Thomas converters, considered replacement of air with oxygen. Specifically, the Maxmilianhütte steel plant in Sulzbach-Rosenberg in cooperation with the Canadian company Air Liquide developed a method wherein flow of oxygen was blown through lances located in the bottom of a converter. This flow of oxygen was surrounded by a protective layer of hydrocarbons ensuring cooling of orifices of lances. So in 1967, the original patent of Bessemer was implemented - refining of pig iron with pure oxygen respectively with mixture oxygen/finely ground lime through lances located in the bottom of a converter (Fig. 5).
In Europe, this process is called **OBM process** (Oxygen Bottom Maxhütte), beyond Europe it is Q-BOP process (Quick Basic Oxygen Process). Either propane or cheaper natural gas, containing up to 98% of methane, are used for thermal protection of lances. French steelworks modified the OBM technology and used liquid fuel oils to protect lances in the bottom of a converter - this process is indicated as CLU process.

In the former Czechoslovakia, the first 130-ton LD converter was put into operation in the VSZ Kosice only in 1966 (that is 14 years after its world premiere), and only in 1983 LD process was implemented in an oxygen-converter steel plant of the Trinec Ironworks. The first bottom blown converter of a tonnage of 70 t was under the name OXYVIT put into operation in Vitkovice in 1981, so again, 14 years after its entry into service at the company Maximilianhütte.

1958 - Among the oxygen processes, which have historically shown to be unpromising ways of basic steel-making technologies, we include also **tandem process**. This process was implemented in the 60s in Japan, amid the stormy development of oxygen converters.

Development of the tandem production process was an attempt to fundamentally modernize structure and principle of SM furnaces. In doing so, auxiliary fuel of SM furnaces was completely eliminated and physical and chemical heat of carbon monoxide, generated in a hearth in tandem, was used for preheating of a solid charge.

From the perspective of the Czech steel industry, tandem process is interesting twice:

- steelworks in Vitkovice and in Nova hut Ostrava contributed significantly to the verification of this production process,
- currently, a tandem steel plant Arcelor-Mittal Ostrava is the largest steel producer in the Czech Republic and its share in the total steel production in our country is about 43%.
Schematic comparison of tandem process with SM process is shown in Fig. 6. To simplify, a tandem furnace is composed of two "Martin furnaces" - two hearths – and a connecting channel. In a refining hearth, oxidation reactions take place as a result of pure oxygen blowing through a lance positioned obliquely above the surface of bath, while in a preheating hearth combustion of CO to CO₂ leads to preheating of charged steel scrap.

After each tap, functions of hearths mutually change. That permitted to increase proportion of steel scrap in a charge compared to LD converter from 25 up to 33 - 35%.

Tandem furnace, with its manufacturing and economic parameters, does not reach the level of oxygen converters, so this manufacturing process is almost not used in the world.

Current level of development of converter processes is represented by technologies of combined blowing. They consist in combining blowing of oxygen and inert gas to reduce concentration and temperature gradient of bath and get closer to equilibrium state, especially in reactions taking place between slag and metal. Blowing of oxygen from above (as at LD process) and blowing of inert gas from the bottom of a converter is the most commonly used option.

Demonstrable assets of oxygen converters - high efficiency of these production methods - (refining takes about 16 minutes and time of melting including charging and tapping is about 45 minutes, regardless of size of a converter) caused that in the early 21st century, oxygen converters along with electric arc furnaces (particularly type of UHP and SUHP) almost displaced open-hearth (flame) furnaces.

- It is mentioned in the “Chapter Structuring”

- Historical and current methods of industrial production of steel and their characteristics.
3 CONDITIONS FOR TRANSITION OF ELEMENTS BETWEEN THE ATMOSPHERE, A MELT OF SLAG AND A MELT OF METAL DURING PRODUCTION OF STEEL

Chapter Structuring

✓ Characteristics of the parameters that determine behaviour of elements in steel production

Time for Study: individual

Target: Understanding the relation between technological execution of melting and theoretical principles of relevant processes is the target of this chapter.

- Basic terms compose the „Chapter Structuring“

Interpretation

Both thermodynamic parameters and technological parameters of melting determine, whether and in which quantity an element passes from a charge or from the furnace atmosphere into steel or into slag.

Thermodynamic parameters express behaviour of elements and their compounds in melts of steel, slag and atmosphere at temperatures of steelmaking processes. Among basic parameters we rank:

- affinity of an element for oxygen resp. stability of its oxides at temperatures of steelmaking processes,
- activity of an element in liquid steel, which is determined by content of the element and chemical composition of the steel,
- affinity of oxide of an element in slag for other components of slag, which depends on content of the oxide and chemical composition of a melt of the slag,
- temperature of steel and slag.

Technological parameters result from capabilities of a relevant production unit and from specific period of melting.

They will differ in converter technologies of steel production, in open-hearth furnaces, in production of steel in electric furnaces.
Among technological parameters we include e.g. intensity of oxygen blowing, distance of a lance from the surface of bath, blowing of inert gas into metal in converters:

- proportion of pig iron and steel scrap in a charge, heating of a charge in SM furnaces,
- heating of a charge by electric arc in EAF.

These parameters affect mainly direction and velocity of processes running between a metal charge, slag and atmosphere, i.e. kinetics of process.

Principle of behaviour of elements in production and refining of steel is contained in the subject “The theory of processes in production of pig iron and steel: Part II - The Theory of steel-making processes”.

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**Summary of Terms of the Chapter**

- It is mentioned in the “Chapter Structuring”

**Questions to the Taught Curriculum**

- Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”
4 PRODUCTION OF STEEL IN OXYGEN CONVERTERS BY MEANS OF LD PROCESS

Chapter Structuring

✓ Principle of LD process
✓ Charge of a converter
✓ Sequence of charging into a converter
✓ Heat balance of LD converter
✓ Construction of LD converter
   o Lining of LD converter
   o Oxygen lance
✓ Technology of oxygen blowing
✓ Course of oxidation of iron and impurities
   o Positioning of a lance above the surface of bath
   o Oxidation of carbon
   o Dephosphorization of pig iron in LD converter
   o Desulfurization of steel in LD converter
   o Gases in converter steel
   o Slag in LD converter

Time for Study: individual

Target: Familiarization with technology of execution of melting in LD converter, basic parameters of a converter and processes of refining of pig iron is the target of this chapter.

Basic terms compose the “Chapter Structuring”
Interpretation

Refining of pig iron with low phosphorus content by oxygen blowing through a lance, positioned in axis of the converter, beneath the surface of liquid metal is the principle of LD (Linz-Donawitz) process.

**Oxygen:**
- purity: min 99.5 % volume of O₂
- pressure: 0.6 to 1.5 MPa
- intensity of blowing: 2.0 to 3.5 Nm³.t⁻¹.min⁻¹

Oxygen jet flows out of a lance at supersonic velocity, penetrates into mass of metal and participates in mixing of the metal and slag phase (with approx. 10-15% of the energy of bath mixing; 85-90% of the energy of bath mixing is provided by carbon reaction - steel bubbling with carbon monoxide and blowing of argon into bath during combined blowing).

When penetrating into the mass of metal bath, oxygen creates the so called reaction zone, wherein the bath temperature reaches up to 2500°C. In this area, oxidation of iron and partially also accompanying elements (Translator Note: impurities) takes place. Emerging iron oxide carries oxygen into steel, partially reacts with impurities and partially passes into slag.

By changing position of a lance, it is possible to regulate position and volume of the reaction zone and hence content of FeO in slag, respectively proportion of FeO, which passes into metal bath.

Metal with emerging slag forms emulsion and together with high temperature in the reaction zone they ensure exceptional velocity of all reactions in progress. This causes that time of metal refining takes about 16 minutes, regardless of size of a converter. LD converters operate with the single-slag technology and therefore the total tap-to-tap melting time ranges between 45 - 60 minutes. From this perspective, it is the most efficient industrially used reactor.

### 4.1 Charge of a Converter

1) **Metal Charge.** Metal charge of a converter consists of liquid pig iron and steel scrap.

   - **Pig Iron** shall have the highest possible temperature for the optimum heat balance of melting, ensuring increased throughput of steel scrap and thus reducing costs of melting - e.g. from 1350 to 1400°C.
     - **Chemical Composition of Pig Iron**

       - **Silicon** 0.5 – 0.7 wt. % Silicon, on the one hand improves heat balance during its oxidation to SiO₂, on the other hand increased content of Si results in larger amount of emerging (SiO₂) and, to ensure required basicity of slag, also more charged lime and hence higher weight of slag - which worsens heat balance of melting.

       - **Manganese** 0.5 – 0.7 wt. % Manganese is during refining oxidized to MnO which is after completion of the process transferred as waste together with slag to a slag heap. Mn is not involved in the process of desulfurization due to high temperatures and its
low content in metal. In the end of melting, it may affect lower content of oxygen in metal (it appears in a bottom blown OBM converter).

**Carbon** 4.2 – 4.5 wt. % Due to high content of C in pig iron, carbon significantly contributes to heat balance, i.e. to heating of a charge during refining to the tapping temperature of steel (oxidation of carbon covers approx. 50% of total heat of exothermic reactions). During its oxidation, CO bubbles are formed and ensure homogenization of bath and course of reactions between metal and slag.

**Phosphorus** 0.12 – 0.17 wt. % (in the Czech Republic) Content of P in pig iron is limited (literature states max. 0.3 wt. % of P), since only oxidizing environment of a converter can provide its transition into slag and higher contents of phosphorus would require the double-slag melting technology.

Phosphorus content in pig iron is given by content of P in a charge of a blast furnace, particularly in iron ore, from which it is completely eliminated during the blast furnace process into metal.

**Sulfur** 0.020 – 0.025 wt. % Content of sulfur in pig iron is associated with melting process in a blast furnace - the lower content of sulfur, the higher manufacturing costs of pig iron. Oxidizing environment of a converter is not suitable environment for metal desulfurization. Production of steel with minimal contents of sulfur can be provided by the ladle metallurgy or by desulfurization of pig iron in a pouring ladle between a blast furnace and a converter. When producing steels with controlled sulfur content (SBQ: 0.03 to 0.06 wt. %; cutting steels: 0.1 to 0.2 wt. % of S), pig iron with increased sulfur content is used.

b) **Steel Scrap**

For oxygen converters unalloyed steel scrap is used, because alloyants (e.g. Cr, Ti, Mo, etc.) would deteriorate quality of slags. Lumpiness of waste should not damage lining of a converter during charging (heavy scrap) nor should increase duration of charging (too lightweight scrap).

2) **Slag-forming Materials (Fluxes)**

Quicklime is the main component of fluxes. Optimal lumpiness of lime is 3 to 5 cm, sometimes it is also used as lime powder pressed into “pellets”. Content of CaO in lime dedicated for steelworks should be min. 95.0 wt. %, MgO content max. 2 wt. %, SiO₂ content max. 1 wt. %, content of higher oxides R₂O₃ max. 1 wt. %, content of sulfur max. 0.05 wt. % and loss on ignition (CO₂ content + humidity) max. 3 - 4 wt. %.

The specific surface area of grains is an important property of lime. Soft burnt lime has final firing temperature of limestone approx. 1150°C. It is characterized by large specific surface area and higher rate of dissolution in slag, but also higher loss on ignition (higher content of CO₂). Hard burnt lime has final firing temperature approx. 1300°C, has smaller specific surface area and dissolves more slowly in slag. It is characterized by lower loss on ignition below 2 wt. %.
Reactivity of lime - lime quality test. It represents consumption of 4 molar HCl (in ml) used for neutralization of a defined sample of lime in aqueous solution at 40°C and that in the 2nd and 10th minute of the process. HCl is titrated with an indicator phenolphthalein. Consumption of HCl in the 2nd minute characterizes rate of dissolution (assimilation) of lime and consumption of HCl in the 10th minute characterizes content of CaO in lime.

**Dolomitic lime** obtained by firing dolomite comprises about 12 wt. % of MgO and 83 wt. % of CaO, and other components as normal lime. This lime increases MgO content in slag and reduces wear of magnesite linings. Content of MgO in slag should not exceed 7 wt. %, higher content of MgO increases density of slag and slows down processes between slag and steel.

Lime consumption per a melt varies between 33 to 40 kg of lime per 1 ton of pig iron. It is calculated from weight of pig iron, content of silicon and phosphorus and required basicity of slag.

**Fluxes** - their target is to adjust chemical composition of slag and hence its properties such as fluidity (viscosity), oxidation ability, to reduce wear of lining etc. Among fluxes we include dolomite and magnesite (MgO source), agglomerate (source of iron oxides), iron scales (source of FeO), sometimes bauxite (source of Al₂O₃), formerly also fluorspar (CaF₂ source).

Chemical composition of slag is affected also by **carbon materials**, added to a charge to improve heat balance of a converter, such as anthracite, coke, coal. These materials should not contain sulfur and phosphorus and minimum of ash - components that negatively affect the converter process.

### 4.2 Sequence of Charging a Converter

1) As first, steel scrap is charged by means of charging boxes (gutter).

2) Lime is charged in batches so as it is assimilated by emerging slag as fast as possible. First batch of lime is dropped onto scrap, second after beginning of oxygen blowing. Along with lime also agglomerate and carbon materials (anthracite, coal) are charged.

3) Molten pig iron is poured directly onto a solid charge, a converter is then rotated into operational (vertical) position, an oxygen lance is lowered into a converter and oxygen blowing begins.

4) When oxidation of carbon is finished, approximately in 13th minute of blowing a sample of metal is collected (by means of “sublance” at lowered intensity of blowing) and to finish dephosphorization, raw dolomite, magnesite or other lime is charged onto a charge. Oxygen blowing continues another 2 or 3 minutes.

5) On the bottom there is sometimes added so called steelworks agglomerate with a high content of MgO (~ 20 wt. %), which protects lining resp. prolongs its lifetime.

6) Preheating of scrap is often carried out to improve heat balance of melting. Anthracite, coal, coke are dropped onto steel scrap and oxygen is blown before pig iron pouring, carbon materials are burnt and so preheat the solid part of a charge.
4.3 Heat Balance of LD Converter

Heat balance of a converter must ensure enough heat to heat up steel scrap, pig iron and fluxes to the tapping temperature of steel. The tapping temperature depends on quality of produced steel, requirements for its refining in a ladle and especially casting temperature of steel, which is related to chemical composition of produced steel.

**Heat Sources:**
- heat accumulated in liquid pig iron (represents about 50% of heat sources),
- heat released from exothermic reactions during oxidation of impurities in pig iron (Si, Mn, C, P) incl. iron (represents approximately 48% of heat sources). The biggest portion of heat (about ½ of heat of exothermic reactions) results from oxidation of carbon, because its content in pig iron is about 4.5 wt. %,
- heat released from exothermic reactions in slag (represents about 2% of heat sources).

**Heat Losses:**
- heat accumulated in produced steel at the tapping temperature (about 70 to 75% of lost heat),
- heat accumulated in molten slag poured out of a converter after tapping (about 20% of lost heat),
- heat accumulated in fugitive emissions of gaseous and solid phase (about 2 to 5% of lost heat),
- heat losses by emission, piping, cooling water, etc. (about 2 to 4% of lost heat).

4.4 Construction of LD Converter

Oxygen converter consists of a converter vessel (reactor), a tilting mechanism, a lance and dedusting equipment (see Fig. 7). Among equipment necessary to ensure functionality of a converter, we include:
- charging box (gutter) for steel scrap
- pouring ladle for molten pig iron
- casting (refining) ladle for produced steel
- slag ladle (slag pot)
- flux bins including weighing equipment and a hopper
- flue for sucking exhaust gases away from converter
- taphole on the back side of a converter vessel.
Production of Steel in Oxygen Converters by means of LD Process

Figure 7. Arrangement of an oxygen converter and its basic accessories

Body of a converter vessel consists of a steel shell and lining. Middle part is cylindrical, upper part has a shape of truncated cone and lower part is usually spherical.

A steel shell of a converter is mounted by a trunnion ring and trunnion pins in bearings of a mount and it can be tilted up to 360°.

4.4.1 Lining of LD converter

To line oxygen converters, almost exclusively magnesia-carbon materials of different types, which are used for lining of particular zones of a converter vessel, are currently used. To increase lining life, zoned linings of various kinds of MgO-C building materials were implemented. Overall design of oxygen converter linings is shown in Fig. 8.
Production of Steel in Oxygen Converters by means of LD Process

Legend:

1 – upper cone lining
2 – wall lining – slag line during a tap
3 – bottom lining
4 – lower knuckle lining of MgO-C building materials with 15% of C
5 – charging side lining of MgO-C building materials with 10% of C
6 – upper cone lining around a taphole

Figure 8. Overall design of an oxygen converter

The lining touching a steel shell - the safety lining - is made of burnt magnesia with low content of Fe₂O₃, CaO, SiO₂ and Al₂O₃. The safety lining is bricked of magnesia bricks. Space between the safety and working lining is composed of an interlayer based on sintered magnesia with MgO content min 63 wt. %.

Lining of the cylindrical wall of a converter is exposed to various stresses, which require different types of refractories. In the area of a cone and pins, lining is not exposed to impact of slag - there are used MgO-C building materials with 10 to 14% of C with or without antioxidants. Slag line area is bricked of blocks of MgO-C, bound with antioxidants by pitch.

The bottom of an oxygen converter consists of a layer of insulating safety lining and working lining. Insulation lining is composed of lining from alkaline materials, on which blocks of hard fireclay or of ferrous MgO sinter are placed. Next layer is composed of magnesia blocks and a layer of melted MgO of about 250 mm. Working layer of lining is bricked of MgO-C blocks with antioxidants of thickness of about 750 mm. Thickness of the bottom of a converter is usually 1.5 m, the wall thickness of about 1 m.

4.4.2 Oxygen Lance

Lance for oxygen supply must enable oxygen blowing in required amount, pressure and distance from the surface of bath. Nozzle design significantly affects course of refining. Currently, multi-hole nozzles are mostly used.

Oxygen lance is constructed so that the blown oxygen jet, on the one hand creates optimum conditions with regard to FeO content in slag and during the course of oxidation of impurities in metal bath, and on the other hand positively affects formation of metal and slag emulsion and level of wear of lining.

Construction of a three-hole lance is schematically depicted in Fig. 9.
From Fig. 9 it is evident that a lance is triple-shell, oxygen flows through the central tube and two outer annuli are intended for inflow of cooling water (inner annulus) and outflow of cooling water (outer annulus). Steel lance is ended with a copper head with multiple Laval nozzles (see section B-B Fig. 9). Laval nozzles must ensure supercritical oxygen jet, i.e. velocity of the outflowing oxygen jet must be greater than velocity of sound in the given environment. The Mach number for outflowing oxygen is approx. 1.3. Axis of Laval nozzles is tilted by 5 to 8° compared to the vertical, which permits to increase FeO content in slag and to accelerate dissolution of lime. Supercritical velocity of oxygen outlet minimizes suction of furnace atmosphere and hence pollution of blown oxygen. Therefore length of the beam with the supercritical velocity of oxygen should extend from the orifice of a nozzle to the surface of bath.

Intensity of the blown oxygen is 2.5 to 3.5 m³.t⁻¹.min⁻¹. E.g. for 200 t converter at oxygen flow rate 600 m³.min⁻¹, intensity of blowing is 3.0 m³.t⁻¹.min⁻¹.

4.5 Technology of Oxygen Blowing

The total oxygen blowing period can be divided into several parts:

1. Preheating of furnace charge prior to pouring of pig iron. It is performed (but not always) to improve heat balance of a converter and to increase throughput of scrap. Proportion of scrap in a charge may be increased to 30 to 33%.
2. **Ignition of refining reactions** after pouring pig iron, lowering a lance to the surface of bath and beginning of intensive blowing. Time to ignition of silicon oxidation takes about 10 to 30 seconds. At that time, oxidation of iron oxides (FeO, Fe$_3$O$_4$, Fe$_2$O$_3$) occurs, followed by their melting, thereby oxygen content in metal increases, and also by increase in content of FeO in emerging slag.

Emerging red-brown iron oxide fumes can also be found in dry dusts exhausted from a converter. At the moment, when oxygen content in pig iron exceeds equilibrium content relative to silicon content, oxidation of silicon will start. At this point, coloured fumes disappear because all oxygen is consumed for the course of refining reactions.

3. **Main oxygen blowing** takes place after ignition of refining processes until the end of refining; it takes about 16 to 19 minutes. During the main blowing, oxidation of all impurities (Si, Mn, C, P) in pig iron and creation of active alkaline slag, ensuring mainly dephosphorization of a metal melt, occur. At the same time, emerging steel must be heated to the tapping temperature.

In the 13th minute of melting, intensity of O$_2$ blowing is briefly reduced (approx. 200 m$^3$.min$^{-1}$) and temperature measuring and sample of metal (sometimes also slag) collecting by so-called “sublance” to analyse are carried out. If analysis of steel and its temperature are in accordance with DTP, steel is tapped. It is done through a taphole on the back side of a converter. After completion of tapping, a converter tilts to charging side and slag is poured into a slag pot.

4. **Reblow** of oxygen is performed in case, that the analysis of steel (especially phosphorus content) is not in conformity with DTP. In that case, lime or magnesite and dolomite are added into the converter and oxygen is again shortly blown. Reblow is undesirable because it extends duration of a melt.

### 4.6 Course of Oxidation of Iron and Impurities

Oxidation of iron and impurities in pig iron is carried out in the following ways:

1) gaseous oxygen,
2) oxygen dissolved in mass of metal,
3) droplets of FeO inserted into mass of metal.

**ad 1) Oxidation of elements dissolved in pig iron with gaseous oxygen O$_2(g)$**

These reactions occur at the gas/metal interface

\[
[\text{Si}] + O_2(g) = (\text{SiO}_2) \quad \Delta H < 0 \quad (1)
\]

\[
[\text{Mn}] + \frac{1}{2}O_2(g) = (\text{MnO}) \quad \Delta H < 0 \quad (2)
\]

\[
[\text{C}] + \frac{1}{2}O_2(g) = \text{CO}(g) \quad \Delta H < 0 \quad (3)
\]

- Approx. 5% of elements dissolved in liquid pig iron are oxidized in this way.
ad 2) Oxidation of elements dissolved in pig iron with oxygen dissolved in mass of metal

At first, it is necessary to describe transition of gaseous oxygen into metal. Although affinity of iron for oxygen is lower than that of Si, C, Mn or P, it is oxidized according to reaction (4) as the first with oxygen gas, which penetrates into mass of metal. Probability of interaction of an oxygen molecule with an atom of iron is much higher than with atoms of dissolved impurities because pig iron contains about 95 wt. % of Fe(l). Temperatures within the reaction zone in mass of metal reach up to 2500°C and therefore velocity of reaction (4) is extremely high. Moreover, the zone of oxidation of iron, which is enclosed in mass of metal, does not come into contact with lining and that is not attacked by high temperature. This is also a principle of the LD process patent compared to a bottom blown converter.

Gaseous oxygen hence first oxidizes iron and only in the second stage, formed oxides dissolve in iron.

\[
\begin{align*}
\text{Fe(l)} + \frac{1}{2} \text{O}_2(g) &= (\text{FeO}) ; \quad (\text{Fe}_3\text{O}_4); (\text{Fe}_2\text{O}_3); \quad \Delta H << 0 \\
(\text{FeO}) &= \text{Fe(l)} + [O] \quad \Delta H > 0 \\
\frac{1}{2} \text{O}_2(g) &= + [O] \quad \Delta H < 0
\end{align*}
\]

Resultant reaction represents only a formal sum of previous reactions. When in contact with a melt of metal, higher iron oxides are reduced to FeO.

\[
\begin{align*}
(\text{Fe}_3\text{O}_4) + \text{Fe(l)} &= 4 (\text{FeO}) \\
(\text{Fe}_2\text{O}_3) + \text{Fe(l)} &= 3 (\text{FeO})
\end{align*}
\]

Proportion of oxygen, which in form of (FeO) remains in slag and which as atomically dissolved is transferred into metal, can be affected by distance of an oxygen lance above the surface of bath. During “soft blowing”, a lance is positioned above surface (e.g. 3 meters) and emerging FeO concentrates in slag, because droplets of FeO are carried only shallowly under the surface of metal. During “hard blowing”, a lance is low above bath (e.g. 1.5 m), emerging FeO is carried deep under the surface of metal and due to reaction (5), major part of oxygen dissolves in metal and FeO content in slag decreases.

Reactions of refining by dissolved oxygen occur in mass of metal

\[
\begin{align*}
[\text{Si}] + 2 [O] &= (\text{SiO}_2) \quad \Delta H << 0 \\
[\text{Mn}] + [O] &= (\text{MnO}) \quad \Delta H < 0 \\
[\text{C}] + [O] &= \text{CO}_2(g) \quad \Delta H < 0
\end{align*}
\]

Approx. 85 % of elements dissolved in pig iron are oxidized in this way.
Production of Steel in Oxygen Converters by means of LD Process

**ad 3)** Oxidation of elements in pig iron on the surface of droplets of formed FeO takes place subsequently (slag phase with a high FeO content is emulsified in pig iron)

$$[\text{Si}] + 2(\text{FeO}) = (\text{SiO}_2) + 2\text{Fe}_{(l)} \quad \Delta H < 0$$

$$[\text{Mn}] + (\text{FeO}) = (\text{MnO}) + \text{Fe}_{(l)} \quad \Delta H < 0$$

$$[\text{C}] + (\text{FeO}) = \text{CO}_{(g)} + \text{Fe}_{(l)} \quad \Delta H > 0$$

Relevant reactions can be obtained as a sum of exothermic processes (9), (10), (11) and endothermic reaction (5). Since the exothermic heat effect of oxidation of carbon (11) is in the absolute value smaller than the endothermic effect of dissolution of FeO in metal (5), reaction (14) is accompanied by heat consumption.

By this mechanism, approx. 10% of elements of pig iron are oxidized.

Course of changes in chemical composition of metal during the oxygen blowing is shown in the “refining diagram” - see Figure 10.

![Figure 10](image)  
*Figure 10. Course of changes in chemical composition of metal during refining in LD converter*

From the refining diagram it follows.

- Si content decreases to zero within 3 to 4 minutes of blowing.
- Manganese is oxidized in the end of oxidation of silicon. During refining its content may slightly increase when low FeO content in slag (see reaction 15), and in the end of refining it decreases again, because of increasing content of oxygen in metal and also FeO in slag.

$$(\text{MnO}) + \text{Fe}_{(l)} = (\text{FeO}) + [\text{Mn}]$$  

(15)
- Beginning of carbon oxidation occurs after completion of silicon oxidation, when oxygen content in metal increases to required level of supersaturation. When reached the critical carbon content, its content in metal already decreases gradually.

- Phosphorus is oxidized throughout refining, especially at the beginning (low temperature) and in the end, when slag is strongly alkaline (B ~ 3.5) and oxidizing (FeO 20 to 30 wt. %).

Reached levels of elements in steel before a tap:

<table>
<thead>
<tr>
<th>Element</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.001 wt. %</td>
</tr>
<tr>
<td>Mn</td>
<td>0.1 to 0.15 wt. %</td>
</tr>
<tr>
<td>C</td>
<td>0.04 to 0.07 wt. %</td>
</tr>
<tr>
<td>P</td>
<td>0.02 to 0.01 wt. %</td>
</tr>
</tbody>
</table>

4.6.1 Positioning of a Lance above the Surface of Bath

Intensity of oxygen blowing is in most converters constant throughout a melt (except for a period of metal samples collection by "a sublance"). Amount of blown oxygen relates to size of a converter, its shape and free space above bath. High intensity of blowing reduces refining time (and hence duration of melting) and on the other hand it is limited by danger of slag and steel slopping from a converter. Change in the intensity of oxygen blowing may be compensated to some extent by changing the distance of a nozzle orifice above the surface of bath. A typical diagram of nozzle positioning depending on the course of refining is for a 200 t converter shown in Fig. 11.

Figure 11. Scheme of nozzle positioning above the surface of bath in LD converter
Distance of a nozzle orifice from bath significantly affects transition of oxygen from the gas phase firstly into metal and secondly into slag. This way it affects also processes that take place in these phases during refining (see Fig. 11).

1st part of melting - beginning – soft blowing (about 3 m above bath). The main objective is to accelerate dissolution of lime and thereby increase alkalinity of slag in order to launch dephosphorization of pig iron. This requires high content of FeO in slag, which increases its liquidity.

2nd part of melting (approx. from 5th minute of blowing) – hard blowing. Silicon is completely oxidized to SiO₂, manganese partly to MnO. Hard blowing ensures increase in oxygen content in metal, rapid oxidation of carbon begins when all the oxygen in metal and slag is consumed by oxidation of carbon. Velocity of this reaction is limited by speed of transport of oxygen to the reaction zone, i.e. by intensity of oxygen blowing. Hard blowing is completed in approximately 13th minute of refining, when carbon content is so low - it reaches the critical value - when rate of its oxidation already limits transport (diffusion) of carbon into the reaction zone.

3rd part of melting (from 13th minute till the end of refining) – soft blowing (about 2 m above bath). At subcritical carbon content, the aim is to complete dephosphorization of steel. For this, repeated increase in FeO content in slag to about 25 to 30 wt. % and its high alkalinity (B = 3.5 to 4.5) is used, because lime is already completely dissolved in slag.

4.6.2 Oxidation of Carbon

Oxidation of carbon results in CO formation and is carried out mainly according to reaction

\[ [C] + O] = CO_{(g)} \] (11)

It is a slightly exothermic reaction, but due to high content of carbon in pig iron (about 4.5 wt. %) it significantly contributes to heating of a charge of a converter to the tapping temperature of steel. The only one of refining reactions which produces gaseous phase - CO bubbles mix metal bath and slag, and ensure course of reactions between slag and metal. In the end of melting, when the carbon reaction is almost finished, its mixing effect is replaced by blowing of argon into bath through the bottom of a converter. Carbon reaction runs intensively between 5th and 13th minute of refining, when critical carbon content in metal is reached (about 0.1 to 0.2 wt. %). That is the content of carbon when the slowest, i.e. limiting part of reactions changes - diffusion of dissolved oxygen in the supercritical area to limiting diffusion of carbon into the reaction zone in the subcritical area.

4.6.3 Dephosphorization of Pig Iron in LD Converter

In most cases, phosphorus is an undesirable element in manufactured steel. Its content in pig iron, intended for converter production of steel, is limited. High efficiency of converter process requires the single-slag technology of melting. Therefore phosphorus content in pig iron should not exceed 0.2 to 0.3 wt. %. In the Czech Republic, content of P ranges from
0.1 to 0.18 wt. % due to low-phosphorus ores. Limited phosphorus contents in produced steels:
- Common carbon steels below 0.02 wt. %
- Quality steels: below 0.01 wt. %
- Steels long-term stressed at high temperatures: 0.001 wt. %

4.6.3.1 Thermodynamics of Dephosphorization Process in LD Converter

Successful transition of phosphorus into oxidation slag is conditioned by several factors, mainly:
- Chemical composition of slag
- Chemical composition of metal
- Oxidation potential of slag and metal
- Temperature

In molten iron, phosphorus occurs in atomic form. Its oxidation and transition into slag take place at the slag/metal interface.

Dephosphorization of pig iron is a two-step process. At first, phosphorus is oxidized with present FeO at the interphase interface with slag and then formed P₂O₅ must be stabilized in slag by alkaline oxide CaO. These reactions can be described by following equations:

\[ 2[P] + 5(FeO) = (P₂O₅) + 5Fe(l) \quad \Delta H₁ << 0 \] (16)

\[ (P₂O₅) + 3(CaO) = (Ca₃(PO₄)₂) \quad \Delta H₂ < 0 \] (17)

\[ 2[P] + 5(FeO) + 3(CaO) = (Ca₃(PO₄)₂) + 5Fe(l) \quad \Delta H₃ << 0 \] (18)

Since oxidation of phosphorus (16) is strongly exothermic, also the resulting reaction (18) is again strongly exothermic.

Optimal conditions for dephosphorization of metal can be derived from the relation for equilibrium constant of reaction (18)

\[ K_p = \frac{a_{(Ca₃(PO₄)₂)}}{[\%P]^2 \cdot a_{(FeO)}^5 \cdot a_{(CaO)}^4 \cdot f_p} \] (19)

- high activity of FeO (content 18 - 25 wt. %) and CaO (content 45 - 55 wt. %) in slag
- low activity of Ca₃(PO₄)₂ in slag – content of Ca₃(PO₄)₂ can be reduced by slag skimming
- reduced temperature to approx. 1550 – 1600°C.

Excessive content of FeO in slag (over 30%) reduces activity of CaO due to presence of acidic oxide Fe₂O₃ and excessive content of CaO (above 60%) increases temperature of a slag liquidus, thus its viscosity, density and later also heterogeneity of slag, and the process of dephosphorization slows down.

The above analysis shows that dephosphorization of pig iron requires oxidation and alkaline slag. Under operational conditions for melting in LD converter, dephosphorization is carried out mainly in the first third of oxygen blowing (low temperature, high content of FeO in slag due to the soft blowing, relatively high initial phosphorus content in pig iron). In this stage of the process, content of CaO in slag which depends on the rate of assimilation of lime by slag, is limiting. In the second third of the process, when the carbon reaction initiated (approx. 5th minute of blowing), content of FeO in slag and also oxygen content in metal are significantly decreased. That causes decrease in the rate of dephosphorization. In the end of refining, phosphorus content must be reduced at least to a value limited by DTP. That is due to the fact that steel is deoxidized after a tap from a converter and also emerging ladle slag must be reductive (with a minimum content of FeO and MnO). In this environment, reduction of phosphorus from slag into metal takes place. Final slag in LD converter is strongly alkaline (all lime is already dissolved) and due to the raised position of a lance also content of FeO in slag increases. At the same time, content of Si (about 0.001 wt. %), C (about 0.05 wt. %) and Mn (about 0.10 wt. %) in metal is minimized. Thus iron oxides content in slag increases (up to 20 to 30 wt. %) and so does content of oxygen dissolved in metal (about 0.10 wt. % = 1000 ppm). Dephosphorization takes place again, even though the steel temperature was increased (to approx. 1630°C).

If the phosphorus content in steel before tapping is higher than limited, a dose of dolomite or magnesite or lime is added onto slag and a short reblow is performed. The reblow of oxygen is undesirable because it extends melting time.

4.6.4 Desulfurization of Steel in LD Converter

LD converter is not a device designed for desulfurization of steel. The reason lies in the fact that for a considerable part of melting, strongly oxidizing slag containing 10 to 30 wt. % of FeO participates in reactions with metal. This corresponds to high oxygen content in metal and thus equilibria of desulfurization reactions (20) and (21) are shifted to the side of initial substances

\[
(CaO) + [S] = (CaS) + [O] \quad (20)
\]

\[
(CaO) + [S] + Fe(l) = (CaS) + (FeO) \quad (21)
\]

Partial desulfurization can occur only at increased sulfur content in pig iron.

Because there was detected SO₂ in converter gases, it can be assumed that a small portion of sulfur in metal and slag (~ 10%) is oxidized to SO₂.

\[
[S] + O_{2(g)} = SO_{2(g)} \quad (22)
\]
or

\[(\text{CaS}) + \frac{3}{2} \text{O}_2(g) = (\text{CaSO}_3)\]  
(23)

\[(\text{CaSO}_3) = (\text{CaO}) + \text{SO}_2(g)\]  
(24)

These reactions assume direct oxidation of sulfur with oxygen gas or oxidation of CaS in slag to calcium sulfite, which at high temperatures dissociates to CaO + SO₂. Since also charged fluxes (e.g. lime) contain sulfur, it may happen that during tapping content of sulfur in steel is higher than in charged pig iron.

4.6.5 Gases in Converter Steel

**Hydrogen.** Source of hydrogen in manufactured steel may be found in charged materials - humidity of lime, coke, agglomerate, steel scrap, etc. Due to intensive formation of bubbles of CO during refining and high content of dissolved oxygen in the end of melting, there are good conditions for achieving low hydrogen content in steel in LD converter. Dehydrogenation of steel is supported also by blowing Ar through the bottom into a converter, especially in the end of melting when course of carbon reaction is limited. Reached levels of hydrogen in steel before a tap are even below 2 ppm.

**Nitrogen.** Porous charged materials (coke, lime, agglomerate, etc.) and also the atmosphere of a converter are sources of nitrogen in converter steel. Since pure oxygen is blown into a converter (above 99.5% of O₂), there is low nitrogen content (about 50 to 70 ppm) in manufactured steel. Its content is reduced both, by bubbles of CO and blown argon during melting.

**Oxygen.** Oxygen is a refining medium. All the blown oxygen passes firstly into slag in form of oxides, secondly into the atmosphere in form of CO and also remains dissolved in produced steel. As in the end of refining all impurities are oxidized to a minimum level, oxygen oxidizes iron in last minutes of melting and FeO is dissolved in metal. Therefore during tapping of a converter, steel evince high content of oxygen, namely 800 to 1200 ppm. This fact has a negative impact on high consumption of ferroalloys in subsequent deoxidation.

4.6.6 Slag in LD Converter

Development of chemical composition of slag during melting is determining for the final composition of steel, especially for minimization of phosphorus content. Chemical composition of the slag is affected by technological parameters of melting:

- proportion of charged pig iron and steel scrap
- composition of non-metallic charge, especially weight of lime
- intensity of blown oxygen and positioning of a lance
Chemical composition of slag changes during refining. Development of chemical composition of slag including reached final contents of oxides is depicted in Fig. 12.

When oxygen blowing initiated, iron oxides are formed as the first, mainly FeO. After beginning of refining reactions, especially carbon, its content in slag decreases and increases again when reached the critical carbon content.

SiO₂ content reaches its maximum in the end of oxidation of silicon and because of the growth of weight of slag, its content is being decreased until the end of refining. Manganese oxide is present in slag after beginning of oxidation of manganese, reaches its maximum and during the reaction of carbon its content decreases till the end of blowing.

CaO content continuously increases during refining as a result of dissolution of lime in slag. Consequently, also weight of slag increases continuously.

![Figure 12. Development of chemical composition of slag during refining in LD converter](image)

At the end of melting, weight of slag is about 10% of weight of steel. After a tap, the slag is poured from converter into a slag ladle (by tilting a converter vessel to the charging side). Sometimes a part of liquid slag is, after adding materials enriched with MgO, used to repair a lining of the bottom of a converter.

<table>
<thead>
<tr>
<th>Summary of Terms of the Chapter</th>
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<td>– Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”</td>
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5 PRODUCTION OF STEEL IN OXYGEN CONVERTERS BY OBM, RESP. Q-BOP PROCESS (OXYVIT IN THE CZECH REPUBLIC)

Chapter Structuring

- Tuyeres and their cooling
- Converter vessel
- Blown materials
- Charge of OBM converter
- Refining of pig iron in OBM converter
- Formation of slag in OBM converter
- Comparison of LD with OBM converter
- Converters with combined blowing

Time for Study: individual

Target: Familiarization with technology of execution of melting in an OBM converter, basic parameters of a converter and processes of refining of pig iron is the target of this chapter.

Basic terms compose the “Chapter Structuring”

Interpretation

Bottom blown converters could be placed in steelworks instead of Thomas converters. Unlike LD converters with a long lance placed above a converter, they do not require construction of a new steelworks building on a green-field land.

5.1 Tuyeres and Their Cooling

During bottom oxygen blowing through tuyeres located in the bottom of a converter, temperatures exceeding 2500°C occur in the vicinity of tuyeres. To prevent undesirable flame polishing of lining on the bottom of a converter, oxygen is injected into molten metal by means of double-shell tuyeres. Oxygen resp. oxygen together with powdered lime are injected through the central portion of a tuyere with diameter of about 2.5 to 3.5 cm and hydrocarbon
gas is injected through the annular section between the two concentric pipes of a thickness of about 1 mm (see Fig. 13).

Figure 13. Scheme of a tuyere of OBM converter

To cool the tip of a tuyere, natural gas (contains 98 wt. % of methane) or other hydrocarbons such as propane, resp. liquid hydrocarbons corresponding with diesel oil, are usually used (CLU – Creusol-Loire-Udelholm - process).

Due to high temperature of metal, in the tip of a tuyere there occurs thermal decomposition of concurrently blown hydrocarbon, which is a strongly endothermic reaction. Emerging carbon is dissolved in metal and again, it is a slightly endothermic reaction. Resulting process is therefore associated with intense heat consumption

\[
\begin{align*}
\text{CH}_4(g) &= C(s) + 2 \text{H}_2(g) & \Delta H_1 &\approx +93\,000 \text{ kJ.kmol}^{-1} \\
C(s) &= \text{[C]} & \Delta H_2 &\approx +22\,000 \text{ kJ.kmol}^{-1} \\
\text{CH}_4(g) &= \text{[C]} + 2 \text{H}_2(g) & \Delta H_3 &\approx +105\,000 \text{ kJ.kmol}^{-1}
\end{align*}
\]

On the other hand, it is necessary to reduce maximally oxidation of methane resp. dissociated carbon with blown oxygen, which are exothermic reactions (28, 29) and they would compensate cooling effect of reaction (25).

\[
\begin{align*}
\text{C(s)} + \frac{1}{2} \text{O}_2(g) &= \text{CO}(g) & \Delta H_4 &\approx -114\,000 \text{ kJ.kmol}^{-1} \\
\text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) &= \text{CO}(g) + 2\text{H}_2\text{C}(g) & \Delta H_5 &\approx -21\,000 \text{ kJ.kmol}^{-1}
\end{align*}
\]

It is closely related to the kinetics of process, i.e. with rate of thermal decomposition.
Example

Rate of thermal decomposition of methane can be described by the Arrhenius equation

$$k = A \cdot e^{-\frac{E}{RT}}$$

where:
- $A$ ... frequency factor, s$^{-1}$
- $E$ ... activation energy of dissociation of methane, J.mol$^{-1}$
- $k$ ... rate constant, s$^{-1}$

$$A_{CH_4} = 3.645 \cdot 10^7 \text{ s}^{-1}$$
$$E_{CH_4} = 271960 \text{ J.mol}^{-1}$$

Assuming that the thermal dissociation of methane is a reaction of the 1$^{st}$ order, it is valid

$$c = c_0 \cdot e^{-kt}$$

where
- $c$ ... concentration of methane in time $\tau$
- $c_0$ ... concentration of methane in time $\tau = 0$; $c_0 = 1$
- $\tau$ ... duration of dissociation, s

Proportion of dissociated methane in time $\tau$ as a percentage of its initial concentration may be expressed by the equation

$$\eta = \frac{c_0 - c}{c_0} \cdot 100 = \left(1 - \frac{c}{c_0}\right) \cdot 100 = (1 - e^{-k\tau}) \cdot 100$$

Assuming that in the tip of a tuyere there is, due to oxidation of molten iron, temperature of 2000°C (2273 K), then sufficient contact time of methane with metal is 0.2 s to dissociate the methane from 98.3% ($K_{2273K} = 20,497 \text{ s}^{-1}$). At higher temperature, complete decomposition of methane passes off in time shorter than 0.1 s. This means that under these conditions methane dissociates already in the tip of a tuyere, which is a prerequisite of its cooling. If dissociation was carried out more slowly, i.e. in larger distance from the tip of a tuyere, then consumed heat would not cool the tuyere but metal above.

Therefore amount of blown gas depends not only on dissociation heat of methane, but also on the rate of thermal dissociation, which is determined by stability of blown hydrocarbon and metal temperature in the tip of a tuyere. As a result of cooling of the tip of a tuyere, along its edge molten pig iron creates porous "mushroom" - see Fig. 14.

Velocity of natural gas flowing through pores of "mushroom" decreases, and thus conditions for cracking of methane are improved. This reduces possibility of mixing natural gas with oxygen and course of undesirable oxidation of CH$_4$, which is strongly exothermic.
Figure 14. Processes running in surroundings of a tuyere of OBM converter

**Number and layout** of tuyeres in the bottom of a converter relates to intensity and uniformity of bath mixing. By way of illustration, a 14-tuyeres layout of an ellipse shape or 9-tuyeres layout of an X shape.

5.2 **Converter vessel**

Converter vessel consists of a shell and interchangeable bottom. This is due to lower life of the bottom refractory of a converter, even with cooling by tuyeres, compared to walls of a vessel. Another difference consists in shape of a converter, which unlike LD converter has a smaller ratio of height to outer diameter ($H:D = 1.0$ to $1.1$; LD: $H:D \approx 1.2$). This relates to
generally stiller course of refining reactions when \( \text{O}_2 \) blown from the bottom. Thickness of the bottom lining is about 1.5 m; thickness of the shell lining is about 1.0 m.

### 5.3 Blown materials

Through inner portion of a tuyere of OBM converter, pure oxygen (above 99.5% of \( \text{O}_2 \)) mixed with powdered lime is blown. Their optimum ratio is ensured by mixer of oxygen and lime in front of a converter. Lime should be hard burnt to prevent clogging of nozzles. Total consumption of oxygen is about \( 55 \, \text{m}^3/\text{t} \) of steel, which corresponds with LD converter. Oxygen consumption on the one hand is increased by partial oxidation of methane, which cannot be avoided; on the other hand it is reduced by lower FeO content in slag of OBM converter.

If oxygen is not blown with lime, inert gas must be blown into a converter to prevent clogging of a nozzle with intruded liquid metal. Nitrogen, or sometimes also argon, is used as the inert gas. Inert is blown through inner tube and outer annulus of a tuyere. Exchange of blown oxygen and natural gas for inert gas is carried out by means of "momentary" valves to avoid pressure drop in a nozzle, intrusion of molten metal and clogging of a nozzle.

### 5.4 Charge of OBM converter

A charge consists of solid steel scrap and molten pig iron. Proportion of steel scrap is about 23 to 25% of a charge. This proportion is lower than for LD converter (25 - 30%) due to worse heat balance of OBM converter - lower FeO content in slag - about 10 wt. % (LD: 20 - 30 wt. %).

Required composition of steelmaking pig iron is the same as for LD process.

Temperature of pig iron depends on its tapping temperature and distance of a steel plant from blast furnaces, resp. on the time of transport to a steel plant.

We can improve heat balance of OBM process by:

- firstly, post-combustion of \( \text{CO} \) in converter gases in the upper cone of a converter vessel by means of a top lance,
- secondly, preheating of charged scrap by blowing natural gas and oxygen through tuyeres from the bottom prior to pouring of pig iron.

**Charging** of scrap and subsequently pig iron is carried out toward the front charging side, tapping of steel through a taphole by tilting a converter to the opposite side.

During charging and tapping, inert gas is blown through nozzles into a converter.

### 5.5 Refining of Pig Iron in OBM Converter

When charging completed, a converter is rotated to operational (vertical) position and substitution of blown inert for oxygen with powdered lime is carried out.
Order of oxidation of elements in pig iron is the same as for LD converter, i.e. silicon, manganese, carbon, and throughout refining phosphorus. Still refining process shows certain peculiarities.

1) Transition of gaseous oxygen into steel and slag. As for LD converter, oxygen gas initially oxidizes iron and formed FeO subsequently dissolves and carries oxygen into metal (see reactions (4) and (5)).

Nevertheless, bottom injecting of oxygen maximally extends time of contact of FeO with metal. Consequently, content of FeO in slag is low and does not exceed approx. 10 wt. %. At the same time, OBM converter (compared to LD converter) has higher yield of metal by up to 3 - 4%.

2) Oxidation of impurities in pig iron is carried out mainly with oxygen dissolved in metal, partly with oxygen gas. FeO oxide contributes to refining less than at LD process due to its low content.

3) SiO₂ oxide of oxidized silicon is on the surface of lime grains immediately neutralized to (Ca₂SiO₄). Therefore, during the first 3 minutes silicon content drops almost to zero.

4) Oxidation of manganese runs in parallel with oxidation of silicon, but more slowly. Mn content during melting and in manufactured steel is higher than at LD process. This is due to low FeO content in slag and shifting equilibrium of reaction (30) to the left.

\[
(\text{FeO}) + [\text{Mn}] = (\text{MnO}) + \text{Fe}_0
\]  

(30)

Increased content of Mn in steel prior to tapping (0.15 to 0.25 wt. %) corresponds to lower content of dissolved oxygen (500 - 800 ppm LD: 800 - 1200 ppm) and saving of deoxidizing ferroalloys.

5) Thermal decomposition of natural gas in a tip of a tuyere. Hydrogen gas is a product of cracking of methane. Hydrogen bubbles represent a surface on which oxidation of dissolved carbon runs without necessity of nucleation of a new phase - bubbles of CO.

Therefore, carbon reaction (11) may run almost simultaneously with oxidation of silicon and manganese. At the beginning, carbon reaction runs more slowly because it shares oxygen with oxidizing silicon. Oxidation of carbon is limited by intensity of blown oxygen throughout the course up to the critical carbon content.

6) Oxidation of phosphorus. Due to low content of FeO in slag, it is carried out with oxygen adsorbed on the surface of grains of injected lime according to reaction (31). Emerging P₂O₅ is then neutralized by calcium oxide according to reaction (32).

\[
2[\text{P}] + 5 [\text{O}]_{\text{ads}} = (\text{P}_2\text{O}_5)
\]  

(31)

\[
(\text{P}_2\text{O}_5) + 3 (\text{CaO}) = (\text{Ca}_3(\text{PO}_4)_2)
\]  

(32)

Dephosphorization runs successfully from beginning to end of blowing due to regular supply of oxygen together with lime. It may be reached less than 100 ppm of phosphorus in produced steel.
7) OBM converter like the other converters is not an aggregate designed for desulfurization. If during refining sulfur content in metal drops, then it happened due to e.g. increased sulfur content in pig iron, resp. also oxidation slag has specific sulfide capacity, i.e. ability to absorb sulfur. Certain proportion, about 15% of removed sulfur is oxidized to SO₂.

5.5.1 Changes in Chemical Composition of Metal during Oxygen Blowing

These changes are depicted in the refining diagram of OBM process. In the diagram, there are for comparison plotted together curves of decrease in elements in LD converter (black) and OBM converter (blue) - see Fig. 15.

![Chemical Composition Diagram](image)

Figure 15. Course of changes in chemical composition of metal during refining in OBM (blue) and LD (black) converter

From the diagram in Figure 15 it follows:

- all oxidation reactions (Si, Mn, C) run somewhat faster than in LD converter. This implies that refining time is slightly shorter namely about 15 to 16 minutes (LD: about 16 to 18 minutes).
- Throughout melting all reactions are closer to equilibrium. For this reason, the entire process is well controllable by a computer program. To do this, comparison of actual carbon content with the theoretically calculated one (from intensity of oxygen blowing and other parameters of melting) during refining, is used. Actual carbon content in metal is continuously calculated from measured CO content in exhaust gases.
- Greater intensity of bath mixing during blowing of gases through the bottom of a converter compared with top blowing, is the cause of the aforementioned differences.
5.6 Formation of Slag in OBM Converter

In a bottom blown converter, there are two types of slag.

1) **Microslag**, which forms on the surface of grains of injected lime from emerging oxides (Fe, Si, Mn, P). It is an active slag, which is involved in all reactions with metal. Particles (droplets) of slag are continuously recreated and float out to the surface of bath.

2) **Accumulation slag** on the surface of bath, which absorbs microslag. This slag is relatively cool, on the surface also gravelly and does not participate in reactions with metal. If we blow oxygen during the combined blowing also through a top nozzle, it may be partially involved in processes of refining.

5.7 Gases in Converter Steel

**Hydrogen** dissolves in metal throughout melting due to cracking of methane. At the same time, it also partially elutes into bubbles of carbon monoxide or bubbles of inert gas, blown into a converter before steel tapping. Still in refined steel there is 5 to 10 ppm of hydrogen, which is unacceptable for quality of most steels. We reduce hydrogen content in liquid steel by subsequent vacuum treatment, respectively in ingot by its long-term staying in a circle after stripping. At red-hot, hydrogen has time to diffuse from steel into the atmosphere.

**Nitrogen** When argon used as inert gas, nitrogen content in liquid refined steel is low, approximately 50 ppm. If nitrogen is blown into steel as inert gas, then its content in steel in the end of melting at high temperature will increase.

5.8 Comparison of LD with OBM Converter

Advantages of OBM converter:

- High homogeneity of bath throughout melting.
- Higher yield of metal due to lower content of FeO in slag.
- Lower oxygen content in steel prior to tapping and subsequent saving of deoxidizing ferroalloys.
- Almost no slopping from a converter and lower evaporation of iron is again reflected in increased yield.

Disadvantages of OBM converter:

- Higher consumption of refractories for often relining of the bottom of a converter.
- Higher nitrogen content in steel.
- Lower throughput of steel scrap.
- More complex technique of blowing (O₂ + lime, natural gas, inert gas) including valves preventing intrusion of liquid metal into tuyeres.
Despite some advantages of bottom blown converters, in the world there broke through LD converters, resp. LD converters in combination with injection of inert gas through the bottom. Simplicity of equipment associated with high productivity is the main reason for that.

5.9 Converters with Combined Blowing of Oxygen and Inert Gas

The aim of combined processes is to combine benefits of top and bottom blown converters. Among concrete targets we rank:

1) To increase yield of metal by reducing content of FeO in slag and thereby to reduce weight of slag.

2) To improve heat balance of the process and thus proportion of steel scrap in a charge.

3) To improve conditions for controlling of the process by minimizing deviations from equilibrium state at each moment of melting.

4) To create conditions for steelmaking with increased content of carbon.

Most commonly, a system is used in which oxygen is blown through a top lance and inert gas is supplied through porous bricks or other permeable elements of the bottom of a converter. This system is known as TBI (top-blown, inert-gas stirred).

In the first third to half of refining, cheap nitrogen is supplied through the bottom, then argon is necessary in order not to increase nitrogen content in steel. Bottom blown converters (OBM) are equipped with a top oxygen lance. Top blown oxygen is used for the post-combustion of CO in the cone of a converter (possibility to increase the share of charged scrap). Higher intensity of top blown oxygen can provide liquefaction of accumulation slag and improve dephosphorization of steel.

Summary of Terms of the Chapter

- It is mentioned in the “Chapter Structuring”

Questions to the Taught Curriculum

- Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”
6  PROCESSING OF PIG IRON WITH INCREASED PHOSPHORUS CONTENT

Chapter Structuring

✓ Principles of the process
✓ Kaldo converter

Time for Study: individual

Target: Familiarization with conditions for processing of pig iron with higher content of phosphorus in a converter is the aim of this chapter.

Basic terms compose the “Chapter Structuring”

Interpretation

Originally, LD process was developed for processing of pig iron with low phosphorus content (P < 0.3 wt. %). The single-slag technology of LD process is highly effective because it ensures maximum productivity of a converter. Duration of one melting cycle, i.e. charging, refining, tapping, takes about 60 minutes, regardless of size of a converter.

If pig iron with higher content of phosphorus (P ~ 0.4 to 0.6 wt. %) is to be processed in a converter, some further conditions, based on the theoretical nature of dephosphorization process, must be met.

1) Higher proportion of alkaline oxidation slag according to the weight of steel.
2) Accelerated formation of dephosphorizing slag:
   a) adding liquefying agents into a charge
   b) soft blowing of oxygen resp. blowing of O_{2(g)} through a multiple hole nozzle, which increases content of liquefying FeO in slag
   c) optimization of lime charging in batches
   d) keeping a rest of molten slag from a previous melt
3) By skimming of primary slag and creating a new one – the double-slag technology.
E.g.: OLP technology (Oxygen Lime Process) or LD-AC, when powdered lime is injected together with oxygen from above into a converter, or LDP process (LD-Pompey) using slag skimming.

### 6.1 Kaldo Converter

A converter, which was able both to dephosphorize and increase throughput of steel scrap, was Kaldo converter (Kalling – Domnarvet). Scheme of this converter is shown in Fig. 16.

![Kaldo Converter Scheme](image)

**Figure 16. Scheme of Kaldo converter**

Kaldo converter - characteristics:
- it rotates around its longitudinal axis at optional speed,
- when in operating position, the converter is tilted about 20 ° from the horizontal axis,
nozzle with the axis of the converter form an angle of about 5°,
oxygen is blown onto the bath surface at an angle of about 25°.

New possibilities of Kaldo process follow from different construction relative to LD converter.
1) Oblique oxygen blowing (as well as soft blowing) increases content of FeO in slag.
2) Slow rotation of a converter together with high content of FeO accelerates dissolution of lime and also dephosphorization at the slag/metal interface.
3) Fast rotation of a converter results in accumulation of slag at walls, exposure of bath and accelerating of carbon reaction.
4) Oblique oxygen blowing also enables post-combustion of CO to CO₂ above bath. As a result of better heat balance, proportion of scrap in a charge may be increased up to 45%.

Kaldo converter also enables skimming of slag when high content of phosphorus in pig iron.
Main advantages of this converter consist in a high level of flexibility to batch materials, in possibility to process up to twice as much steel scrap compared to LD converter.
Main disadvantages of Kaldo converter:
- high consumption of refractories
- high investment costs
- extension of duration of refining when slag skimmed to up to 40 minutes and thus low productivity of a device.

The disadvantages of Kaldo process were reflected primarily in higher costs of 1 ton of steel compared to LD process. Therefore, these converters for steel production did not break through.

Summary of Terms of the Chapter
- It is mentioned in the “Chapter Structuring”

Questions to the Taught Curriculum
- Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”
7 STEEL PRODUCTION IN TANDEM FURNACES (T-FURNACES)

Structuring

✓ Construction of a tandem furnace

✓ Stages of melting in production of steel in a T-furnace
  - Charging
  - Oxidation of impurities
  - Slag of a tandem process

Time for Study: individual

Target: Familiarization with technology of melting in a T-furnace, construction of a T-furnace and processes of refining of pig iron is the aim of this chapter.

Basic terms compose the “Chapter Structuring”

Interpretation

Tandem furnaces were developed from SM furnaces, and therefore they do not rank among converters. In the Czech Republic, they hold an important position because still in 2013, almost 50% of steel was produced in these furnaces. T-furnaces of Ostrava ironworks have a tonnage of 2 x 200 t of steel.

Principle of steelmaking in tandem furnaces lies in usage of physical heat of combustion products and chemical heat from the oxidation of CO to CO₂ for preheating of a metal and non-metallic charge.

7.1 Construction of a Tandem Furnace

Figure 17. Scheme of a tandem furnace
A tandem furnace comprises two hearths:

- preheating hearth
- refining hearth
- hearths are connected by a channel, which ensures a flow of combustion products from preheating to refining hearth
- each hearth is equipped with obliquely retractable refining lance, then top post-combustion lance (burns CO to CO\(_2\)) and sometimes top driving lance (secures flow of combustion products into a preheating hearth)

After each tapping, functions of each hearth mutually exchange. **Furnace itself comprises:**

- hearth
- walls of a furnace
- furnace crown

In the front wall there are charging holes provided with a door, in the back side there is a taphole including a downstream trough. The furnace is tiltable to the tap side (when tapping steel) as well as the charging side (when pouring slag of the furnace). On both sides of the furnace there are closable exhaust channels for combustion products and downstream slag chambers for accumulation of dust particles from products of combustion. A furnace crown is made up of panels for a rapid exchange of lining.

Figure 18. Cross section of a tandem furnace lining

Hearth lining:

- safety of magnesite bricks (500 to 600 mm)
- working of MgO-C materials (300 to 400 mm)
Refining tuyeres are extendable; they extend into a hearth at an angle of 30 - 65 °. Tuyeres are tipped with a copper head with several Laval nozzles; they are water-cooled. During refining, it is possible to adjust the distance of a nozzle from the surface of bath.

Oxygen having a purity of 99.5% of O\(_2\) is blown into bath with intensity of 0.5 to 1.5 m\(^3\).t\(^{-1}\).min\(^{-1}\). E.g. to melt 220 t at consumption of O\(_2\) 53 m\(^3\).t\(^{-1}\) and 68 minutes of melting, it is about 11660 m\(^3\) of O\(_2\) per melting. For post-combustion of carbon oxide, oxygen having a purity of 95 % or also air is used.

7.2 Stages of Melting in Production of Steel in a T-Furnace

Production process in T-furnace takes place concurrently in a preheating and refining hearth.

7.2.1 Charging

- steel scrap (33 to 35 % of a metal charge)
- lump lime (5 to 6 % of a metal charge; lumpiness 3 to 5 cm)
- liquid pig iron (chemical composition as of oxygen converters)

Stages of Charging and Melting Process

Course of melting in a tandem furnace can be divided into three periods.

**Period I** - preheating hearth (charging and warming up):
- furnace inspection and intermelt repair
- charging of steel scrap and its preheating
- charging of lime and further preheating until pig iron poured

**Period II** - refining hearth (melting):
- pouring of pig iron
- melting and refining of metal with primary oxygen
- skimming primary foamy slag in 1\(^{st}\) third of refining (approx. 23 minutes)

**Period III** - refining hearth (completion):
- creation of new slag of lime and diluents
- further refining
- collection of 1\(^{st}\) test of metal and measurement of metal temperature (approx. 50\(^{th}\) minute)
- treatment of slag by means of lime, solvents, nozzle position
- temperature measurement of metal before tapping
- completion of melting and a tap (approx. 68th minute)

7.2.2 Oxidation of Impurities

Progress and sequence of oxidation of impurities in pig iron is similar to LD converter. Differences result from structural configuration of the furnace and method of oxygen blowing.

1) Refining nozzle is obliquely retractable at an angle of 30 to 65° from the side into a hearth.
2) Oxygen is blown with lower intensity which can be adjusted during refining.
3) Position of a nozzle above the surface of bath is also adjusted during melting.

During refining, these differences manifest themselves as follows.

a) Obliquely positioned nozzle and lower intensity of oxygen blowing ensure higher content of FeO in slag both during and in the end of melting (similar to soft blowing of oxygen in LD converter).

b) Due to lower intensity of blowing also duration of refining is considerably longer - about 68 minutes.

c) Time of refining is also extended due to foamy slag skimming when oxidation of silicon completed.

d) Slag skimming and creation of a new one of charged lime (the double-slag technology) improves conditions for steel dephosphorization, on the other hand it deteriorates yield of metal.

Silicon Among impurities it oxidizes as first to almost zero in 1st third of refining. Primary slag containing up to 25 wt. % of SiO₂ is skimmed. Therefore a tandem furnace can process pig iron with up to 1 wt. % of silicon.

Manganese It oxidizes, though more slowly, from the beginning of refining. Rate of its oxidation is affected by position of a nozzle above bath. Greater distance of a nozzle (soft blowing) increases content of FeO in slag and hence the rate of oxidation of manganese (reaction: (FeO) + [Mn] = (MnO) + Fe(0)).

Hard oxygen blowing accelerates transition of oxygen from slag into metal. Present carbon is preferentially oxidized with this oxygen because it has much higher affinity for oxygen than manganese. In the end of refining at subcritical carbon content, the manganese content decreases rapidly.

Carbon Nature of decline in carbon content is the same as in LD converter, but much slower. In first 3 to 6 minutes, carbon oxidation is almost not carried out. With
declining content of Si and Mn and with increasing temperature, decarburization rate increases and after approximately 20 minutes refining is maximum, limited by intensity of oxygen blowing. When the critical carbon content reached (approx. 60th minute) decarburization rate of an element decreases. Produced steel contains 0.04 to 0.07 wt. % of C.

**Phosphorus** Phosphorus oxidation occurs at the slag/metal interface with present FeO oxide. Concurrently high basicity of slag (CaO: 45 to 50 wt. %) determines stabilization of P₂O₅ in slag. This oxidation and alkaline slag is created in a short time after beginning of oxygen blowing and therefore also dephosphorization occurs throughout melting.

In the first third of refining, dephosphorization is also supported by low bath temperature and initial P content in pig iron. In the second third of refining, carbon reaction significantly reduces the dephosphorization rate - causes decrease in (FeO) content below 15 wt. %. In the end of melting, dephosphorization ability of slag is again optimum. In tandem process, primary slag skimming and new slag creation affect dephosphorization of metal very favourably. Therefore, it is possible to achieve final content of phosphorus in metal even below 0.015 wt. %.

**Sulfur** Highly oxidizing slag throughout refining does not create conditions for desulfurization. It may be assumed that small proportion of sulfur (to 10%) is oxidized to SO₂. Final sulfur content in steel is determined by its content in pig iron and also mass of slag with certain, even though minimum sulfide capacity.

**Oxygen** Due to high content of iron oxides in the final slag of a T-furnace (∼ 28 wt. %), also oxygen content in refined steel is high 800 to 1200 ppm (0.08 to 0.12 wt.%).

### 7.2.3 Slag of a Tandem Process

Average chemical composition of slags during melting in a T-furnace (200 t) is mentioned in the table.

**Table 1** Average chemical composition of slags during melting in a 200 t T-furnace

<table>
<thead>
<tr>
<th>Melting Period</th>
<th>Chemical Composition %</th>
<th>( B = \frac{CaO}{SiO_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Foamy Slag Skimming</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>Collection of Test 1</td>
<td>39</td>
<td>18</td>
</tr>
<tr>
<td>Collection of Last Test Prior to a Tap</td>
<td>40</td>
<td>12</td>
</tr>
</tbody>
</table>

From the table of development of present components it follows:
CaO: CaO content continuously increases as charged lime gradually dissolves. In the end, slag alkalinity reaches the values of B = 3.33 and even higher.

SiO₂: By contrast, SiO₂ content declines after completed silicon oxidation. Presence of SiO₂ after foamy slag skimming is caused by only partial skimming of this slag and further decrease in its content relates to growth of slag mass during melting.

MgO: Furnace lining eventually charged dolomitic lime is a source of MgO.

MnO: Oxidized manganese in pig iron is its source.

Al₂O₃: Its origin is mainly from furnace lining.

FeO, Fe₂O₃: Throughout refining, slag is strongly oxidizing, only when carbon reaction is carried out, FeO content significantly declines. Lower intensity of blowing or soft oxygen blowing through a nozzle positioned obliquely to the surface of bath contributes to increase in content of iron oxides. When approx. 135 kg of slag per ton of steel present, weight of iron oxides in finished steel is about 7.5 tons.

It implies that it is necessary to separate iron oxides from cooled tandem slag and return them into production cycle. Present P₂O₅ is a limiting factor of this separation, which is with recycled slag carried back into a charge of a blast furnace and consequently its content in pig iron increases. High content of iron oxides in slag reduces also yield of metal to approx. 88 %.

P₂O₅: Content of P₂O₅ in slag is determined especially by phosphorus content in charged pig iron, then also by oxidation potential and alkalinity of slag.

Summary of Terms of the Chapter
- It is mentioned in the “Chapter Structuring”

Questions to the Taught Curriculum
- Formulation of questions to the curriculum corresponds to titles of partial chapters in the “Chapter Structuring”