Converter processes in carbon steelmaking

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477427A High temperature processes



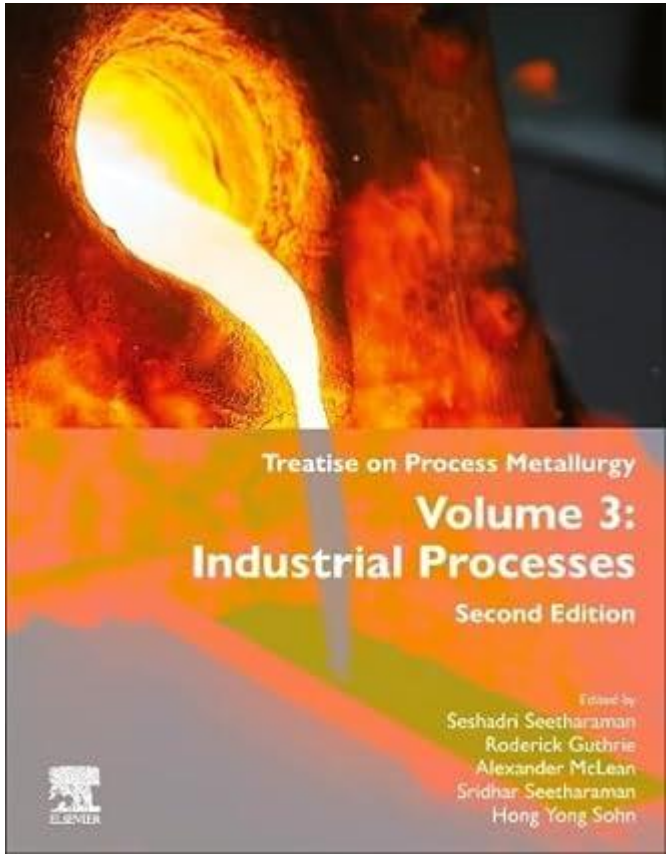
Contents

1. Learning aims
2. Introduction
3. Historical development
4. Modern basic oxygen furnace
5. Outlook
6. Summary



Learning aims

- After the lecture, the student should
  1. know the role of basic oxygen furnace in carbon steelmaking,
  2. understand its thermodynamic and kinetic fundamentals,
  3. know its typical operating practices, and
  4. have an overview of future development needs.
- The lecture is based loosely on a book chapter **Converter Steelmaking** written by myself and Professor Emeritus Lauri Holappa.[1]



Reference
[1] V.-V. Visuri, L. Holappa, in *Treatise on Process Metallurgy*, *Volume 3: Industrial Processes, 2nd Edition*, 2024.

Introduction

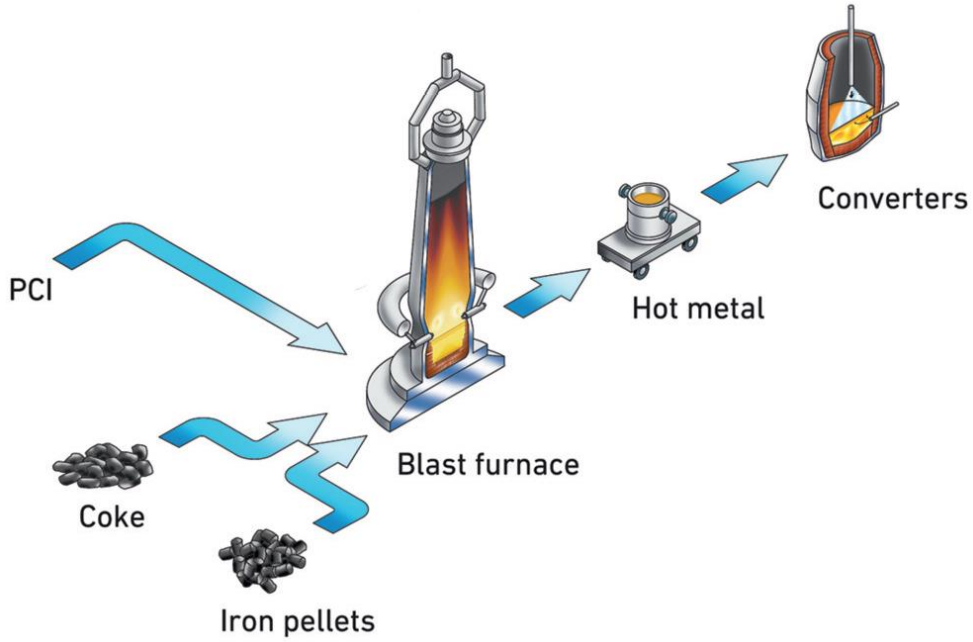


Stig-Göran Nilsson (2002) Jernkontoret's Picture Collection

Introduction

Blast furnace – converter route

- Contemporary iron-ore based steelmaking is based predominantly on the blast furnace – converter route.
- Converter steelmaking serves as the main refining stage.
  - The main objective is to lower the carbon content from approximately 4.5 wt-% to the target level of the steel grade.
  - The converter is also the main process for dephosphorisation of steel.
  - However, converters have only a limited capability for desulfurisation.



Contemporary blast furnace – converter route.[1]

Typical changes in bath composition and temperature in the BOF process.

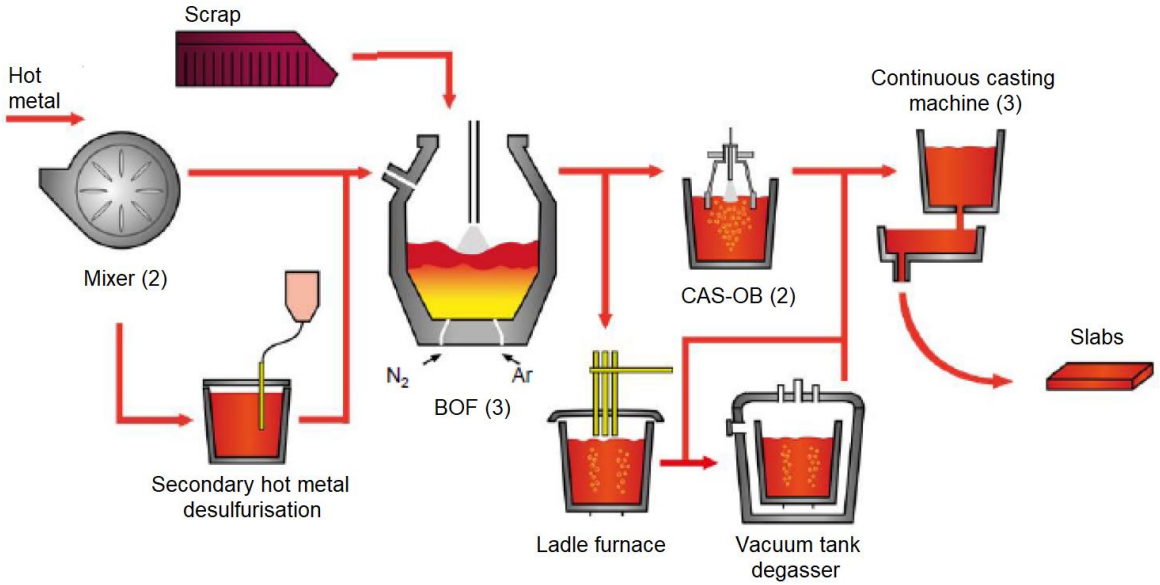
Parameter	Initial	Final	Unit
C content	~4.5	0.01–2.0	wt-%
P content	0.08–0.18	0.005–0.03	wt-%
Temperature	1300–1400	1600–1700	°C

Reference
[1] DIMECC Oy, *Flexible and adaptive operations in metal production*, final report, 2018.

Introduction

Example: Raahe meltshop

- The only meltshop operating BOFs in Finland is the Raahe meltshop of SSAB Europe Oy.
- The hot metal is supplied using transport ladles to two 1300-ton mixers.
- A secondary hot metal desulfurisation may be conducted using calcium carbide.
- The converter operation consists of three 125-ton LD-KG type combined-blowing BOFs.
- The secondary metallurgy and casting area feature a twin CAS-OB station, a ladle furnace, a vacuum tank degasser and three continuous casting machines.



Layout of the Raahe meltshop.[1]

Reference

[1] Rautaruukki Oyj.

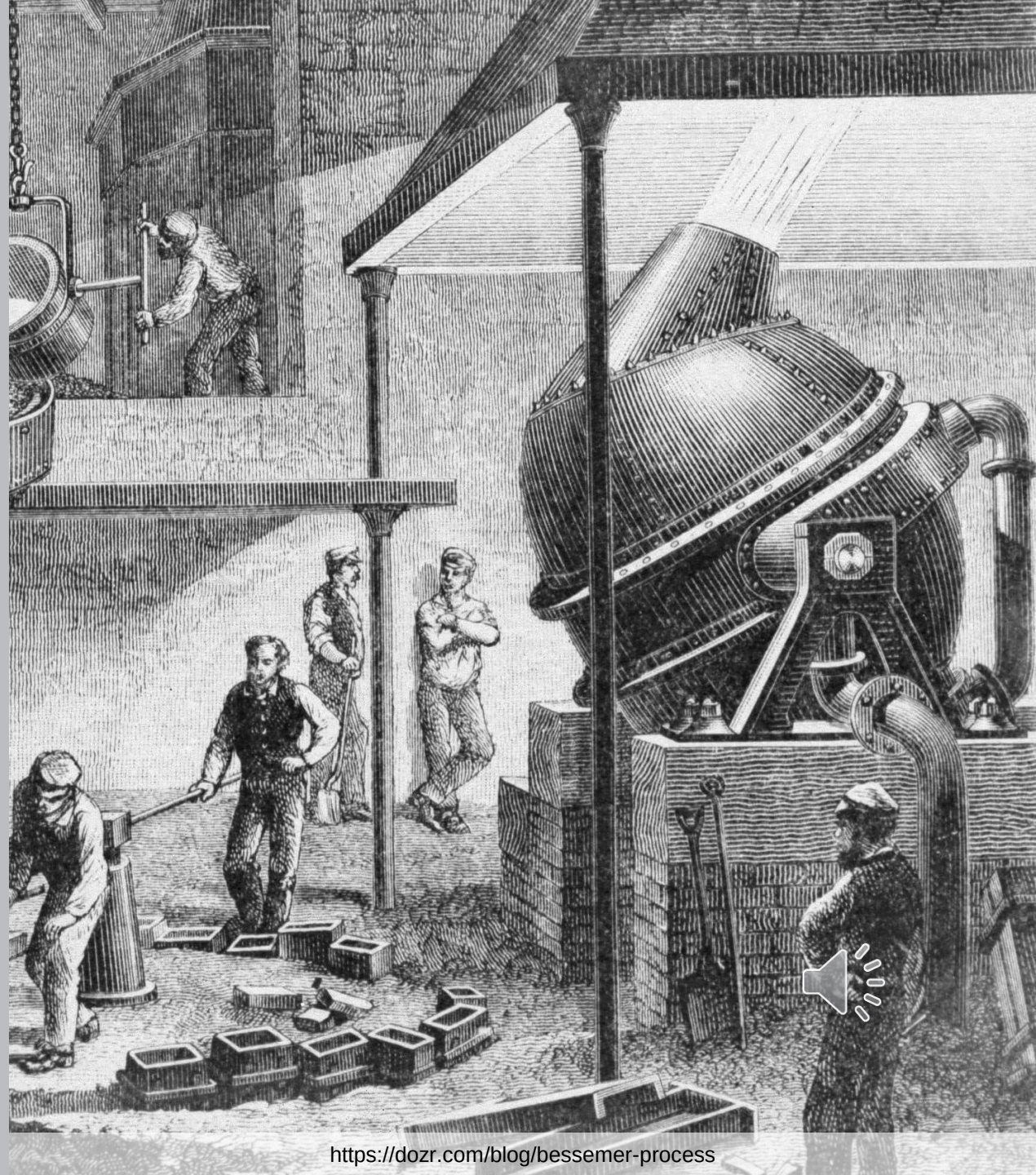
By now, you should know the answers to these questions

1. What are the main processes in contemporary ore-based steel production?
2. Which hot metal pretreatment is usually performed before the basic oxygen furnace?
3. What are the downstream processes after the basic oxygen furnace?



Stig-Göran Nilsson (2002) Jernkontoret's Picture Collection

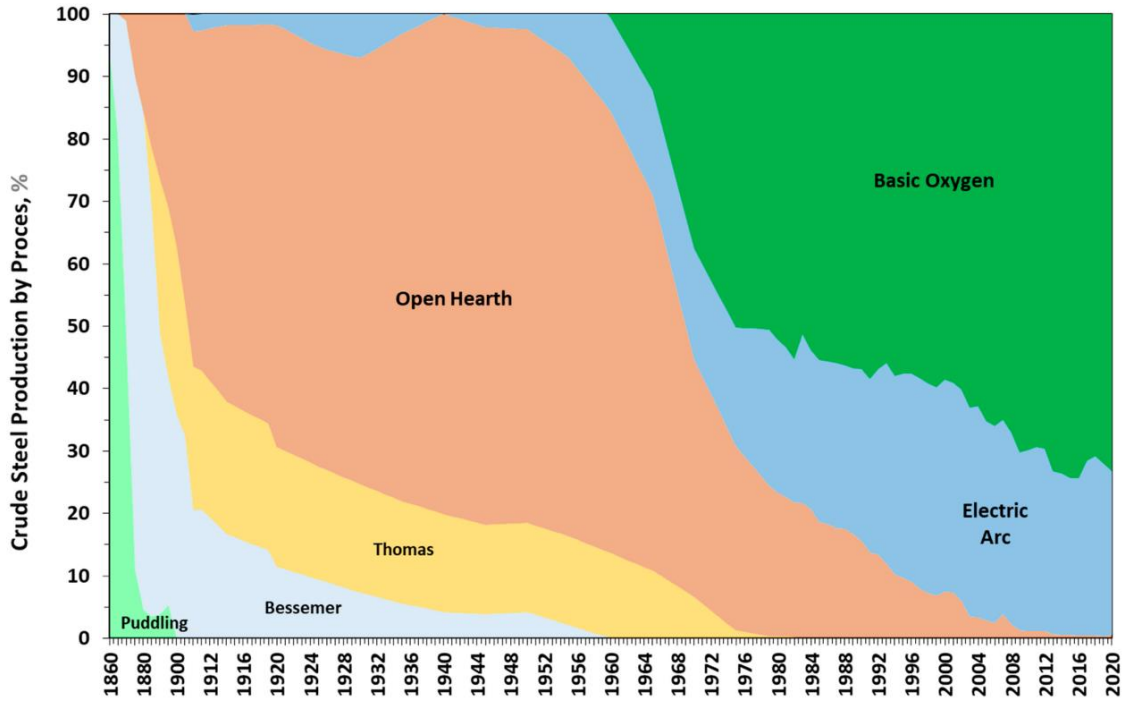
Historical development



https://dozr.com/blog/bessemer-process

Evolution of steelmaking technologies

- Converter metallurgy was started by the invention of the Bessemer process, which quickly surpassed puddling as the main steelmaking technology.
- The open hearth furnace was the dominant process in the period from 1900 to 1970.
- However, the open hearth furnace did not replace but instead complemented the Bessemer and Thomas converters.
- The invention of the basic oxygen furnace in the 1950s rendered the Bessemer and Thomas converters obsolete.
- Later, the electric arc furnace became the main process for scrap-based steelmaking.



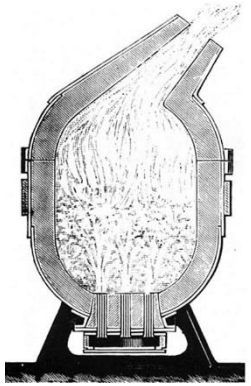
Development of the world steel production and the share of steelmaking technologies since 1860.[1]

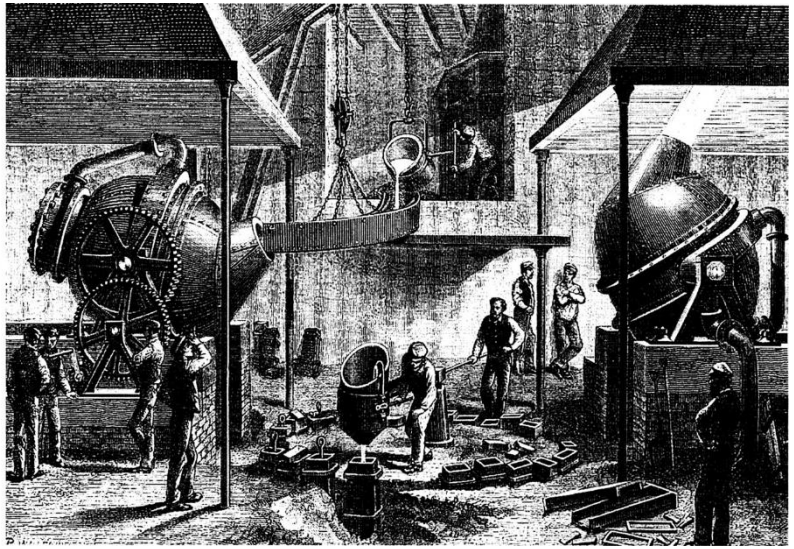
Reference

[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.

Bessemer converter

- Invented by Henry Bessemer in 1855 and patented in the following year.
- Marked the beginning of converter metallurgy.
- The decarburisation of hot metal took only 10 to 20 minutes and was achieved by bottom-blowing of air.
- Due to air-blowing, the exothermic reactions released enough heat to maintain the steel in liquid state, but did not allow the use of scrap.
- The use of air to refine the hot metal led to the relatively high N content of the produced steel.
- The process was designed for acid refractory practice.





Bessemer converter.[1]

Reference

[1] H. Bessemer, *Sir Henry Bessemer, F.R.S. An autobiography*, 1905.

Thomas converter

- Invented by Carlyle Gilchrist and Sidney Gilchrist Thomas; presented to the broad public in 1878.
- Essentially a Bessemer converter lined with basic refractories (dolomite fired with tar) and operated with a basic slag.
- Solved the problem of refining high-P ores, which were abundant in Europe, e.g., Minette ores in France.
- Was also better-suited for desulfurisation than the Bessemer converter.
- Owing to its high calcium phosphate content, the Thomas slag could be used as fertilizer and was thus a valuable by-product.

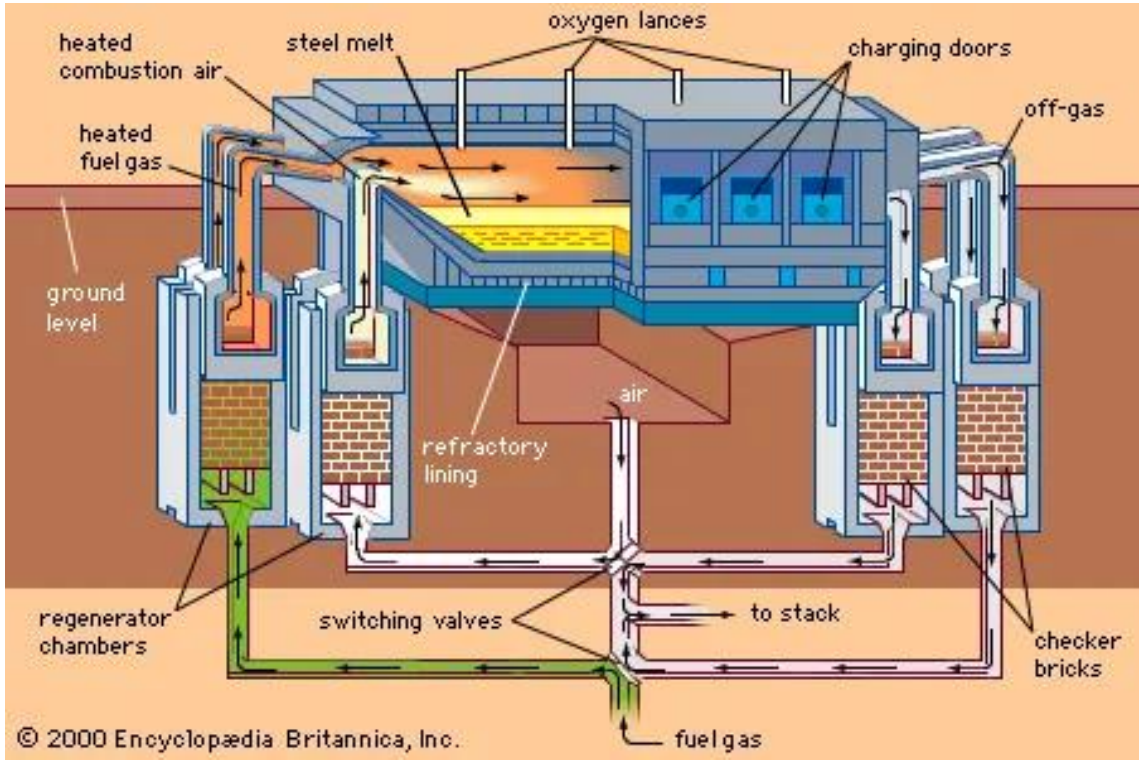


Thomas converter.[1]

Reference
[1] Wikipedia.

Open hearth furnace

- Developed by Pierre-Émile Martin in 1864 based on the regenerative furnace of Carl Wilhelm Siemens.
- Also known as the *Siemens-Martin process*.
- The heat required is brought by the combustion of heated air and fuel introduced into the furnace.
- The oxygen in iron oxide and other impurities decarburise the pig iron.
- Originally designed to have acid refractories, but later basic refractories became more commonplace.
- Key advantages:
  - Slow but easy to control.
  - Hot metal and scrap can used in any ratio.
  - Enables construction of large furnaces suitable for mass production of steel.



Open-hearth process.[1]

Reference
[1] Encyclopedia Britannica.

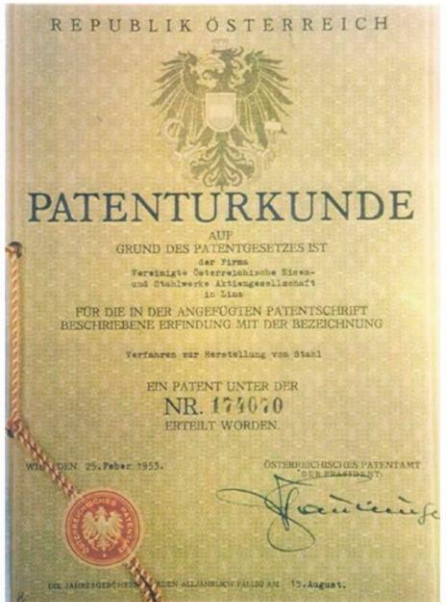
Basic oxygen furnace

LD converter

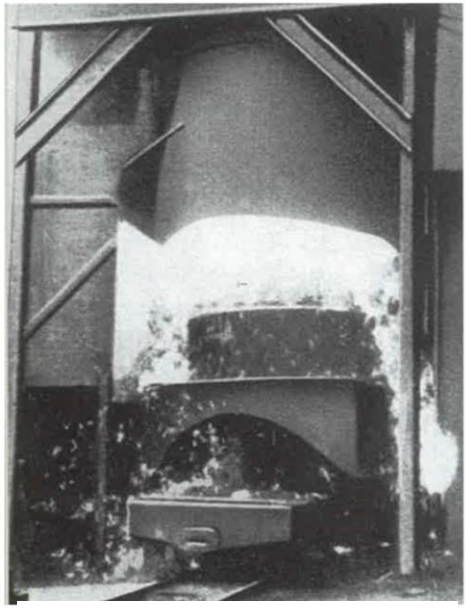
- Following tests on oxygen injection in the 1930s and 1940s, the principle of basic oxygen furnace (BOF) was invented by Robert Dürrer in 1948.
- The first furnaces were commissioned by VÖEST in Linz (1952) and ÖAMG in Donawitz (1953); this top-blowing type became to be known as the *LD converter*.
- The defining characteristics were the use of oxygen-blowing and basic refractories.
- The process enabled excellent steel quality and fast decarburisation.
- The higher heat release meant that the vessel had also some scrap melting capability.



First blowing trials with 15-ton vessel in Linz.[1]



LD-Patent from February 1953.[1]



Blowing trials with 10-ton ladle in Donawitz.[1]

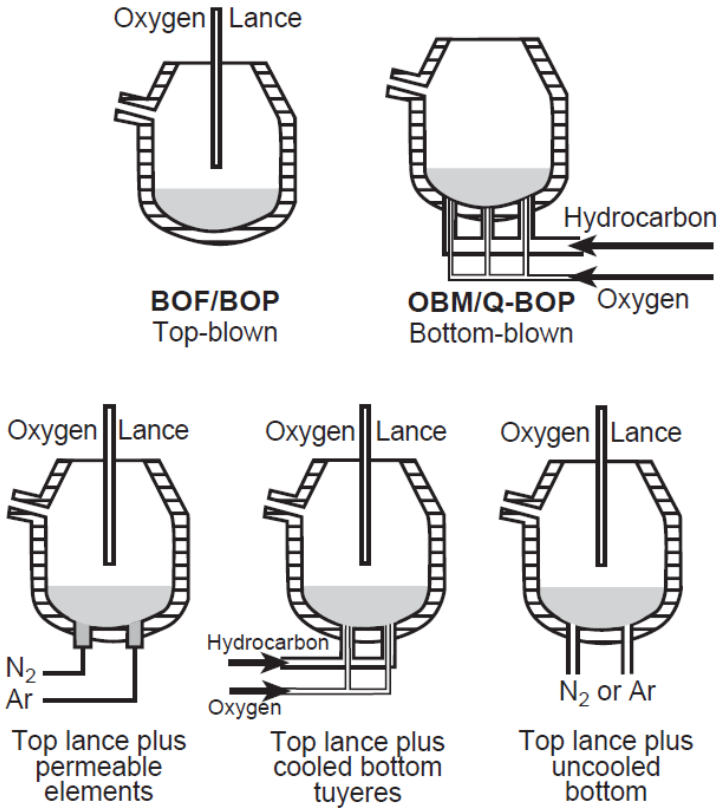
Reference

[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, and J. Schenk, *Metals*, 12(6): 912, 2022.

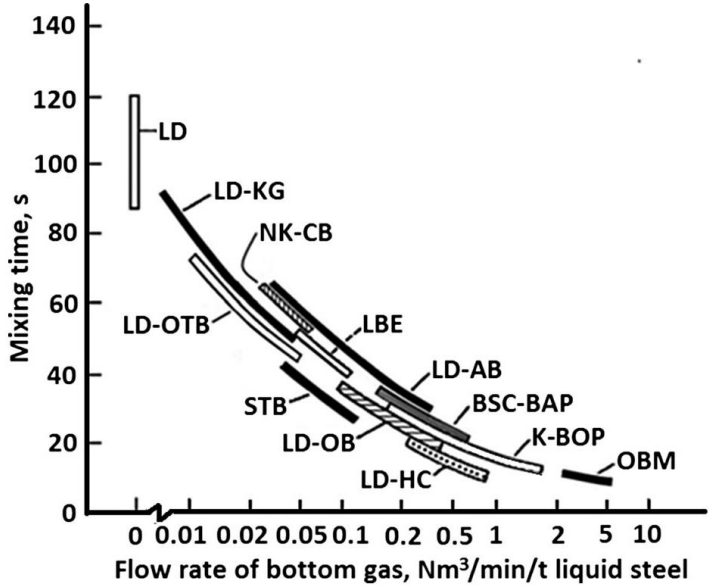
Basic oxygen furnace

Towards combined-blowing

- Different configurations for the gas injection were soon studied.
- The OBM process developed in the late 1960s uses the bottom-blowing of oxygen along with hydrocarbons for cooling.
- It had more efficient bath mixing but was technically more complex.
- Numerous combined blowing processes emerged; the most popular variants are based on the LD converter and combine oxygen top-blowing with inert bottom-blowing.



Methods of introducing oxygen and other gases into the steelmaking converter.[1]



Bottom gas flow rate vs. mixing time in different converter processes.[2] Reproduced from Ref.[3].

References

[1] L. Holappa, *Miner. Process. Extr. Metall.*, 128(1-2): 3–16, 2019.
[2] T. W. Miller, J. Jimenez, A. Sharan, D. A. Goldstein, in *The Making, Shaping and Treating of Steel. 11th Edition Steel Making and Refining*, 475–524, 1998.
[3] A. Chatterjee, C. Marique, P. Nilles, *Ironmaking Steelmaking*, 11(3): 117–131, 1984.

Basic oxygen furnace

Converter processes for carbon steelmaking.[1]

			Top blowing		Bottom blowing								
Main category	Process	Developer	O_2	O_2 + CaO	O_2	O_2 + CaO	Gaseous C_mH_n	Liquid C_mH_n	N_2 +/or Ar	CO_2	Coke	Coal	Steam
Top blowing	LD	Vöest-Alpine	X										
	LD-AC	Arbed – CNRM	X	X									
	AOB	Inland-Steel – Union Carbide	X	O_2 + Ar									
Top + bottom blowing I	LD-S	Vöest-Alpine	X						X				
	LD-KG	Kawasaki	X						X				
	LD-AB	Nippon-Kokan	X						X				
	LD-BC	CRM	X						X				
	TBM	Thyssen	X						X				
	M-TBI	Mannesmann	X						X				
	LBE	Arbed	X						X				
	NK-CB	Nippon-Kokan	X						X				
	LD-CL	Nippon-Kokan	X						X				

Original LD

Reference

[1] L. Holappa, *Miner. Process. Extr. Metall.*, 128(1-2): 3–16, 2019.

Basic oxygen furnace

Converter processes for carbon steelmaking.[1]

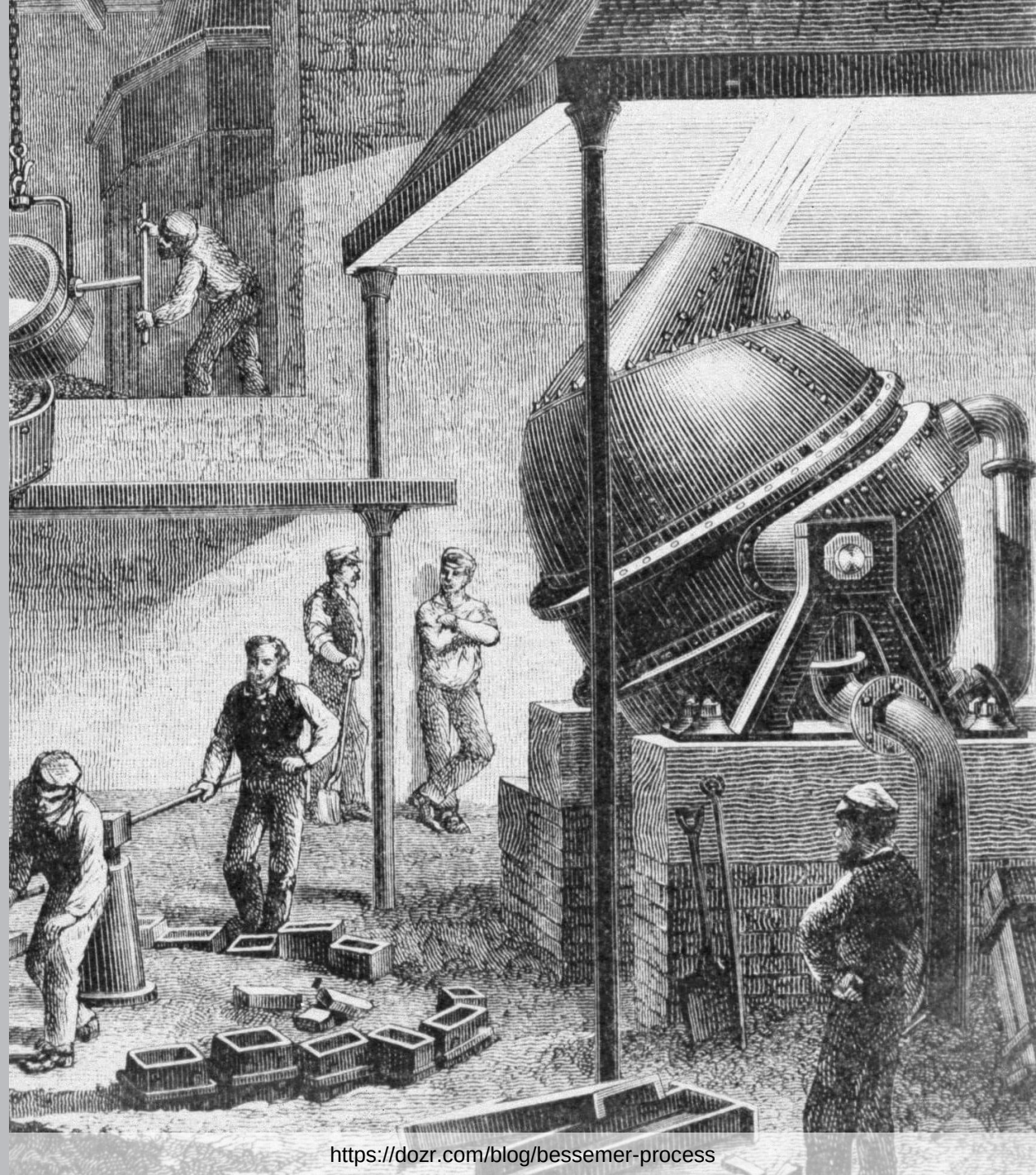
			Top blowing		Bottom blowing								
Main category	Process	Developer	O_2	O_2 + CaO	O_2	O_2 + CaO	Gaseous C_mH_n	Liquid C_mH_n	N_2 +/or Ar	CO_2	Coke	Coal	Steam
Top + bottom blowing II	LD-OTB	Kobe	X		(X)				X	X			
	LD-CB	Nippon-Kokan	X		X				X	X			
	LD-STB	Sumitomo	X		X				X	X			
Top + bottom blowing III	LD-OB	Nippon Steel	X		X		X		X				
	LD-HC	Maxhütte	X	X	X		X		X				
	K-OBM	Klöckner-Maxhütte	X		X		X	X	X				
	K-BOP	Kawasaki	X			X	X	X	X				
Bottom blowing	OBM/Q-BOP	Maxhütte/US Steel			X	X	X	X	X				
	LWS	Creusot-Loire				X	X	X	X				
Allothermal	KMS	Klöckner-Maxhütte			X	X	X	X			X	X	
	KS	Klöckner-Maxhütte			X	X	X	X			X	X	
	Z-BOP	Zapsib	X								X	X	

Reference

[1] L. Holappa, *Miner. Process. Extr. Metall.*, 128(1-2): 3–16, 2019.

By now, you should know the answers to these questions

1. What is the main difference between the Bessemer and Thomas converters?
2. What gas is used as the main oxidant in the BOF process?
3. What type of refractories and slag are used in the BOF?
4. How does the gas injection in modern BOFs differ from the original LD-type BOF?



https://dozr.com/blog/bessemer-process

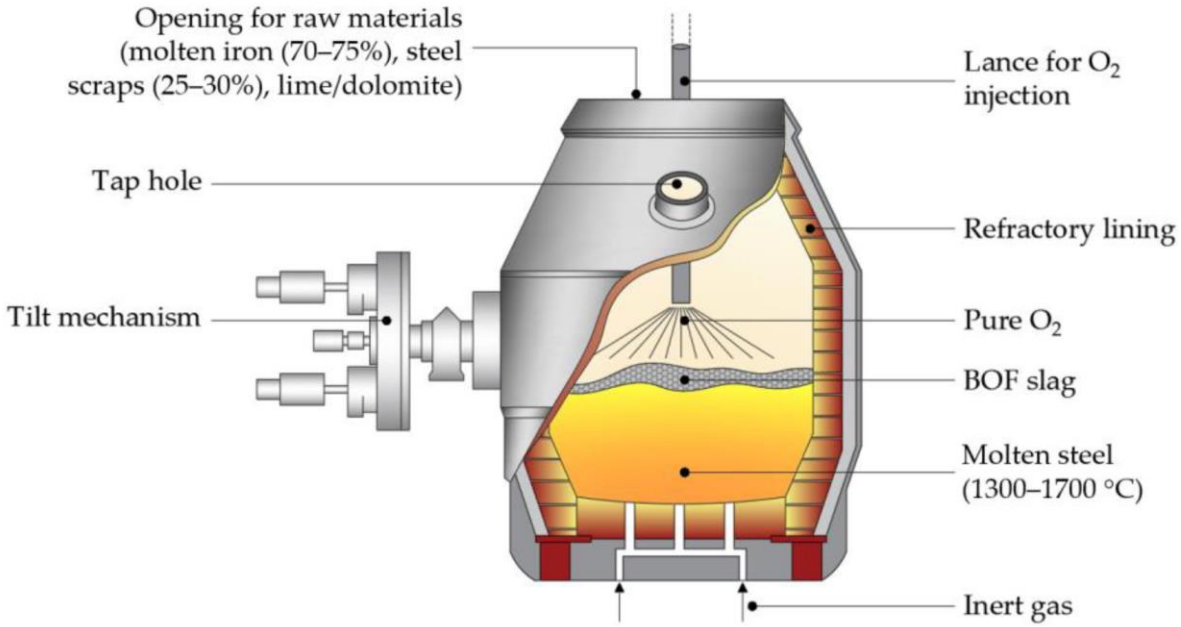
Modern basic oxygen furnace



Heat and mass balance

Main charge materials and consumables

- Charge materials
  - Hot metal (~ 70–75 wt-%)
  - Recycled scrap (~ 25–30 wt-%)
- Process gases
  - Oxygen, inert gases (N_2 or Ar)
- Material additions
  - Slag formers and fluxes: lime, dolomite, fluorspar
  - Ferroalloys, e.g., FeSi, SiMn, FeMn
  - Direct-reduced iron (DRI) lumps or briquettes
- Refractory materials
  - Examples: doloma, magnesia-carbon



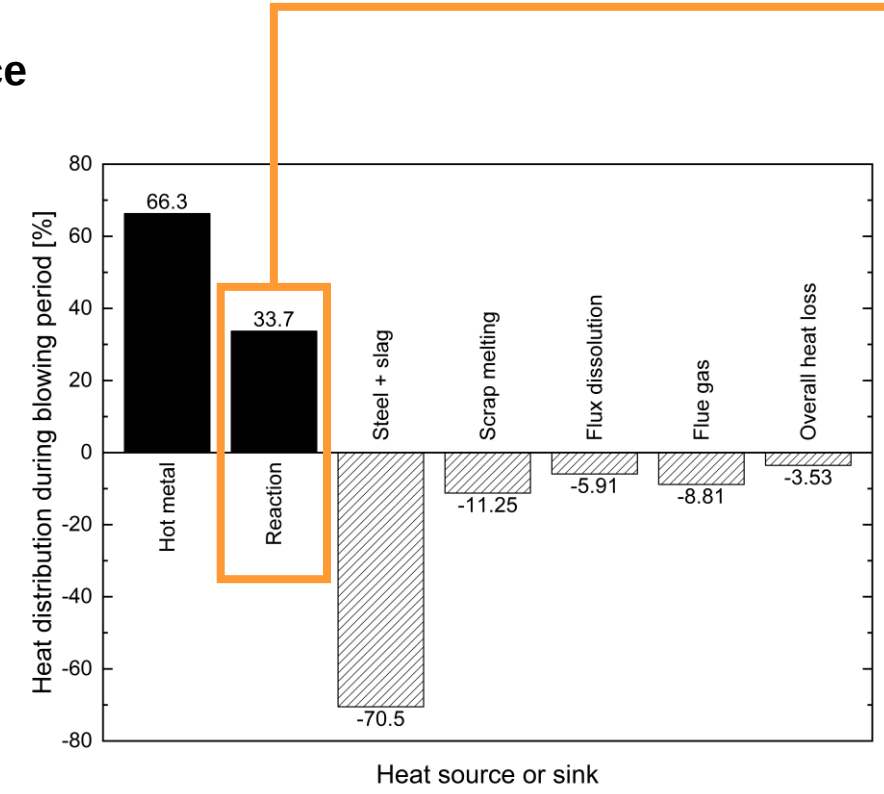
Schematic illustration of a BOF converter.[1]

Reference

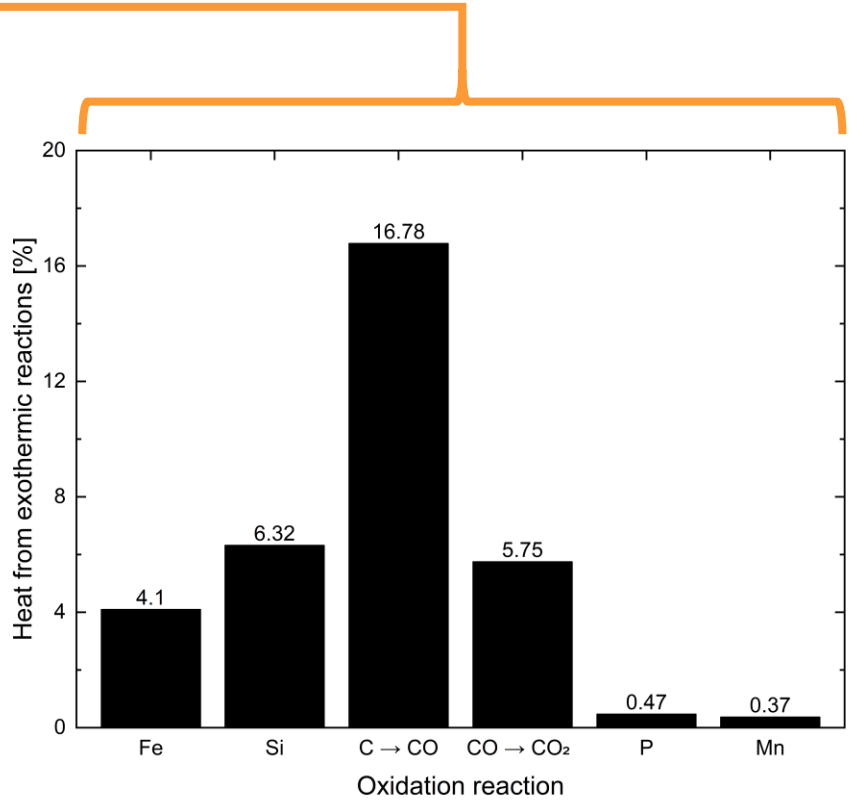
[1] A. Piemonti, A. Conforti, L. Cominoli, S. Sorlini, A. Luciano, G. Plizzari, *Sustainability*, 13(2): 556, 2021.

Heat and mass balance

Heat balance



Calculated heat distribution for a 350-ton BOF. Redrawn after Ref.[1].



Heat contribution of reactions in a 350-ton BOF. Redrawn after Ref.[1].

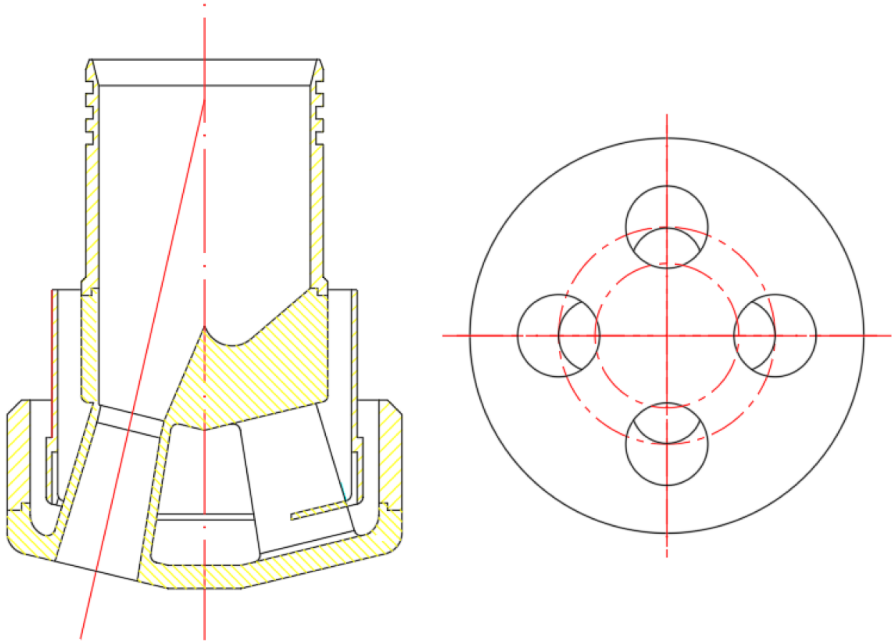
Reference

[1] N. Madhavan, G.A. Brooks, M. A. Rhamdhani, B. K. Rout, A. Overbosch, *J. Iron Steel Res.*, 28(5): 538–551, 2021.

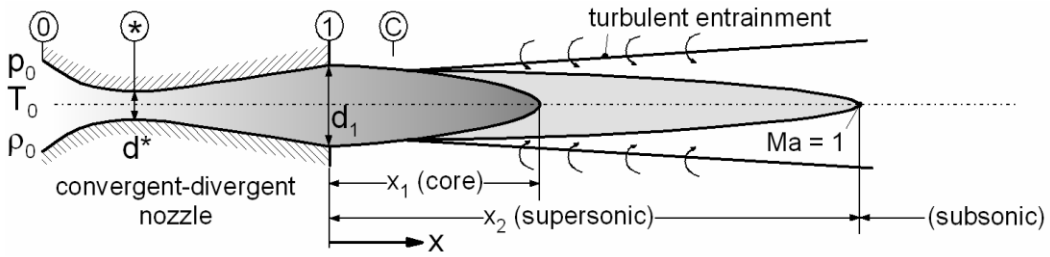
Equipment

Top lance

- The lance head is water-cooled and made from high conductivity cast copper alloy.
- Typical lance heads have four to six exit ports, each of which is fitted with a convergent-divergent nozzle (*de Laval nozzle*) for producing a supersonic gas jet.
- The top lance is designed for a specific gas flow rate to obtain optimal jet behaviour.
  - The length of the supersonic core is roughly 6 times the nozzle exit diameter.[1]
  - At 1650 °C, the supersonic region is 20–35 times the nozzle exit diameter.[1]
- The lance height from the bath surface is varied during the BOF process to control slag foaming.



A convergent-divergent lance head with four exit ports.[2]



Flow regimes in a supersonic jet.[1]

References

[1] H.-J. Odenthal, U. Falkenreck, J. Schlüter, *Proc. European Conference on Computational Fluid Dynamics*, 2006.

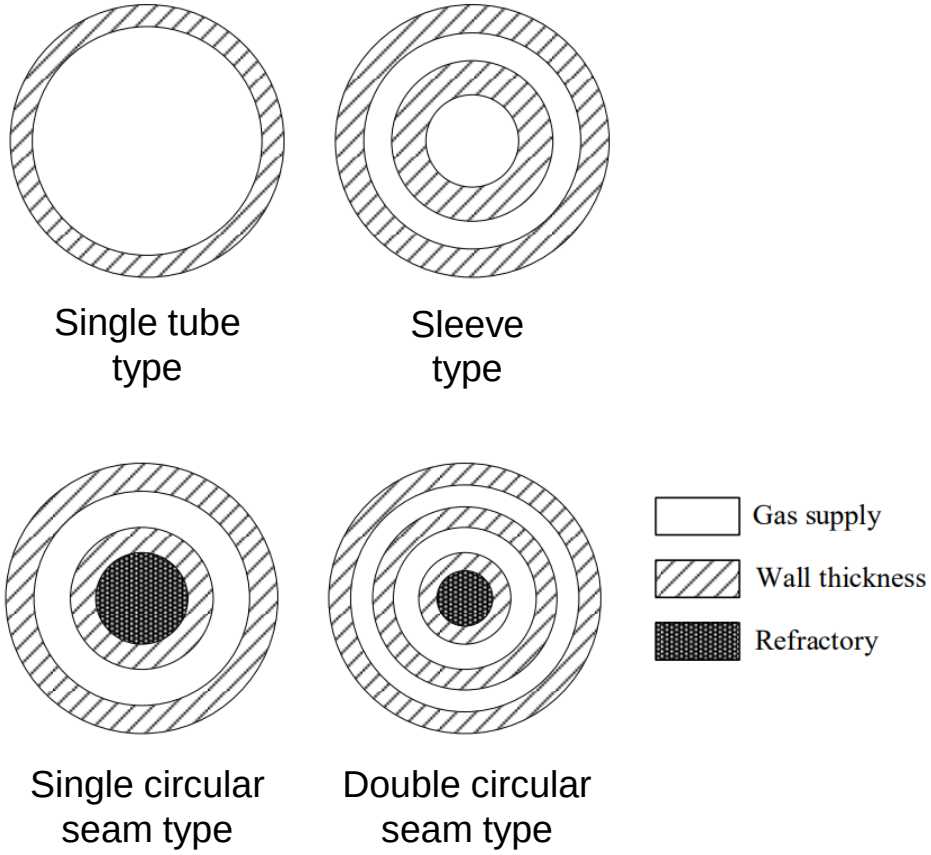
[2] M. Lv, S. Chen, L. Yang, G. Wei, *Metals*, 12(11): 1918, 2022.

Equipment

Bottom-blowing elements

Structural characteristics and performance of bottom blowing elements.[1]

Name	Dispersion-type breathable brick	Single tube type	Sleeve type	Circular seam type
Structural features	Multiple metal capillary tubes buried in refractories	A large diameter metal tube buried in refractories	Hollow straight circular tube and outer ring seam tube buried in refractories	Center tube filled with refractories, outer ring seam tube buried in refractories
Blockage condition	Easily blocked	Extremely easy to block	The central tube is easily clogged	Not easy to block
Element life (heats)	2000–2500	100–200	2000	More than 10000
Flowrate adjustment range	2–3 times	2–3 times	10 times	More than 10 times
Mushroom head cooling capacity	Weak	Weaker	Stronger	Strong



Schematic illustration of bottom blowing elements.[1]

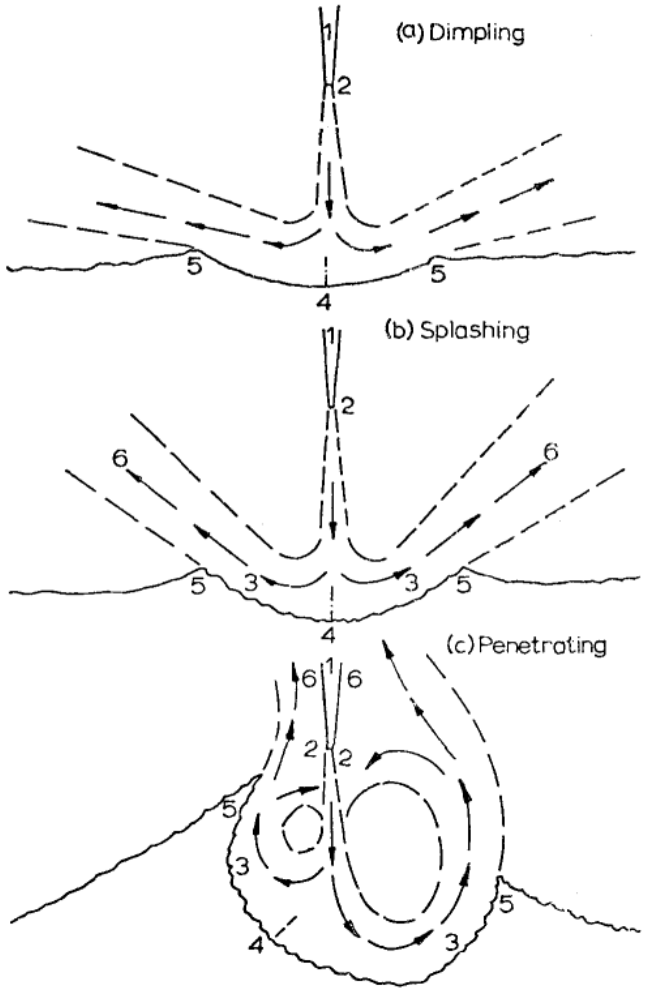
Reference

[1] M. Lv, S. Chen, L. Yang, G. Wei, *Metals*, 12(11): 1918, 2022.

Physical phenomena

Interaction of gas jet and metal bath

- The gas jet penetrates the metal bath, inducing an oscillating cavity.
- Three cavity modes can be distinguished:[1]
  1. dimpling,
  2. splashing, and
  3. penetrating.
- In the case of multi-hole lances, the cavities formed by individual jets may merge.
- The geometry of a single cavity can be approximated as a paraboloid of revolution.
- There are numerous correlations for the cavity dimensions.[2]



Cavity modes proposed by Molloy[1].

- Slight surface depression.
- No splashing.

- Shallow cavity.
- Splashing of small outwardly directed droplets.

- Deep penetration.
- Splashing of large inwardly directed droplets

References

[1] N. Molloy, *J. Iron Steel Inst.*, 2016(10): 943–950, 1970.

[2] A. Nordquist, N. Kumbhat, L. Jonsson, P. Jönsson, *Steel Res. Int.*, 76(2): 82–90, 2006.

Physical phenomena

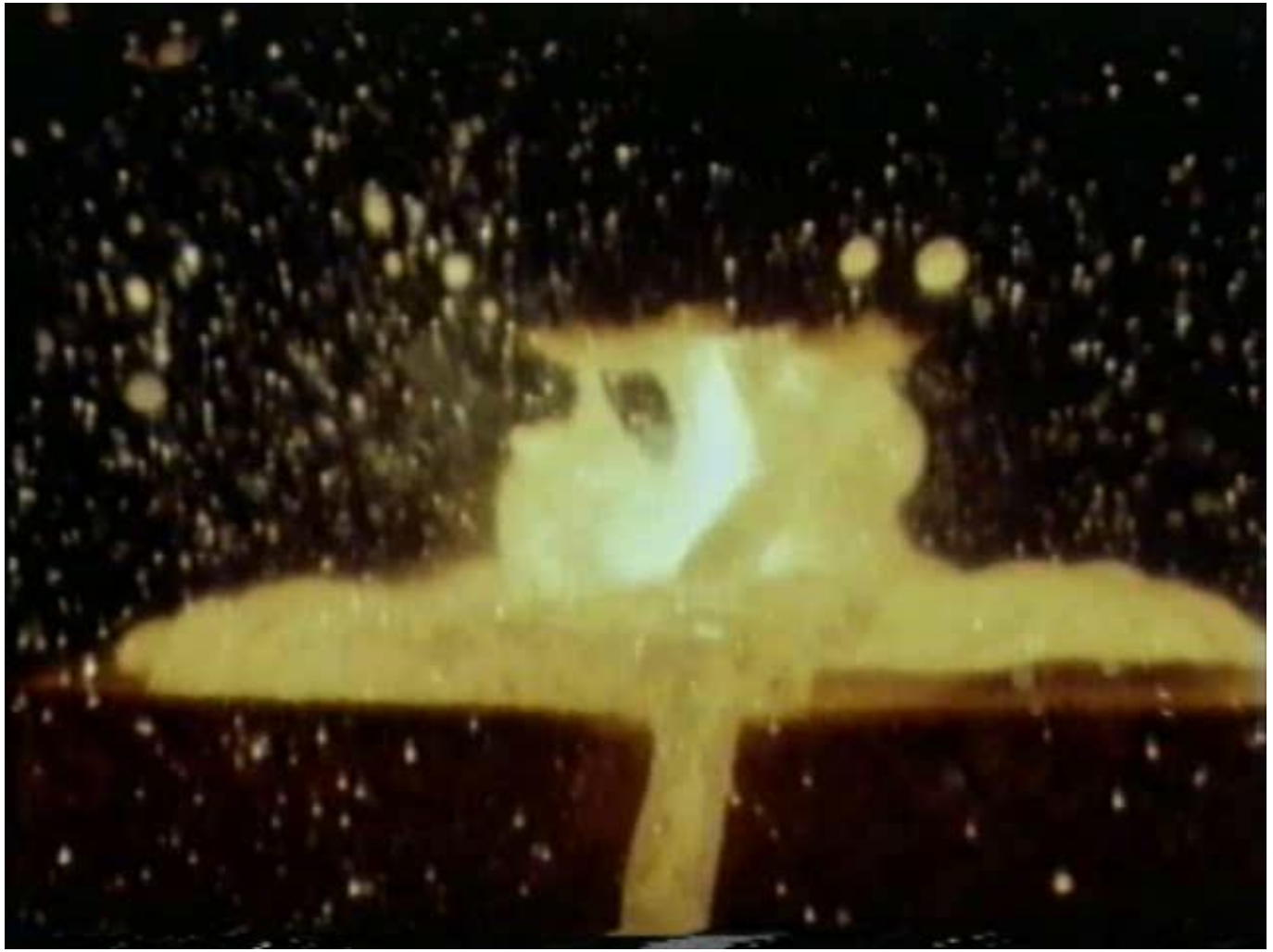
Generation of metal droplets

- The shear force of the gas jet detaches metal droplets at the periphery of the cavity.
- The size distribution of the generated droplets follows the modified **Rosin-Rammler-Sperling** distribution function:[1]

$$R = 100 \cdot 0.001^{\left(\frac{d}{d_{\text{limit}}}\right)^n},$$

where R is the cumulative weight [%], d is the droplet diameter, d_{limit} is the limiting droplet diameter (R = 0.1%), and n is the distribution exponent.

- Droplets found from slag samples are generally quite small, as large droplets may disintegrate and have short residence times.



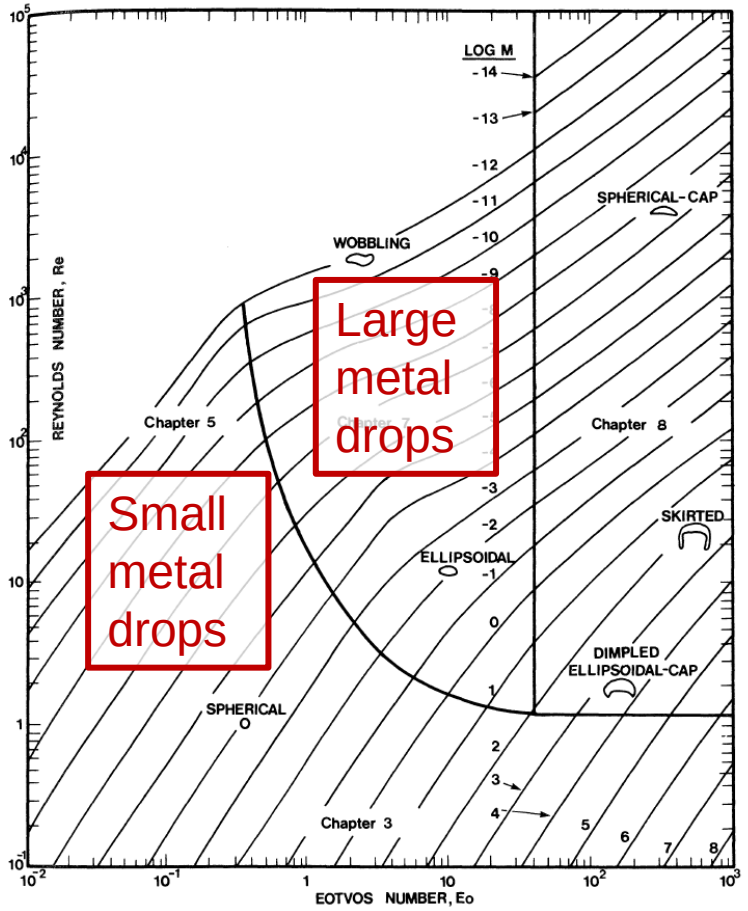
Splashing during top-blowing in a crucible experiment.[2]
Film clip courtesy of Prof. Dr.-Ing. Hans-Jürgen Odenthal.

References
[1] S. C. Koria, K. W. Lange, *Metall. Trans. B*, 15(1): 109–116, 1984.
[2] K. W. Lange, S. C. Koria, *Publ. Wiss. Film. Techn. Wiss./Naturw.*, Ser. 8, No. 9, Film D 1386, 1983.

Physical phenomena

Shape regime of metal droplets in slag

- The shape regimes of the metal droplets in slag depends on their Reynolds and Eotvos numbers.
  - Large droplets deform and exhibit turbulent internal circulation.
  - Small droplets have only internal diffusion and retain their shape.
- The shape regime of the metal droplets affects the selection of appropriate mass transfer correlations for predicting metal–slag reactions.



Shape regimes of bubbles and drops.[1]

Reference

[1] R. Clift, J. R. Grace, M. E. Weber, *Bubbles, Drops, and Particles*, 1978.

Thermodynamics

Nomenclature

T = temperature of the metal bath

p_{O_2} = oxygen partial pressure

B_2 = short basicity, $B_2 = \frac{(\text{wt}-\%\ \text{CaO})}{(\text{wt}-\%\ \text{SiO}_2)}$

Overview of thermodynamic preconditions for impurity removal

Aspect	Decarburisation		Dephosphorisation	Desulphurisation
Reaction	Metal–gas	Metal–slag	Metal–slag (minor removal to gas phase)	Metal–slag (minor removal to gas phase)
Reaction type	Oxidation	Oxidation	Ion exchange	Ion exchange
Stoichiometry	$[\text{C}] + \frac{1}{2}\{\text{O}_2\} = \{\text{CO}\}$	$x[\text{C}] + (\text{Me}_y\text{O}_x) = x\{\text{CO}\} + y[\text{Me}]$	$[\text{P}] + \frac{5}{2}[\text{O}] + \frac{3}{2}(\text{O}^{2-}) = (\text{PO}_4^{3-})$	$[\text{S}] + (\text{O}^{2-}) = (\text{S})^{2-} + [\text{O}]$
Heat generation	Exothermic	Endothermic	Exothermic	Endothermic
Favoured by	**Low T** **High p_{O_2}**	**High T** **High p_{O_2}**	**Low T** **High p_{O_2}** **High B_2**	**High T** **Low p_{O_2}** **High B_2**
Means to affect in the BOF	Temperature control Oxygen injection	Temperature control Oxygen injection	Temperature control Oxygen injection Basic slag formers	Temperature control Inert gas purging Basic slag formers
Removal efficiency in the BOF	Excellent		Good	Limited

Thermodynamics

Thermodynamics of decarburisation (1/3)

- The direct oxidation of carbon by the oxygen jet takes place according to the following exothermic reaction

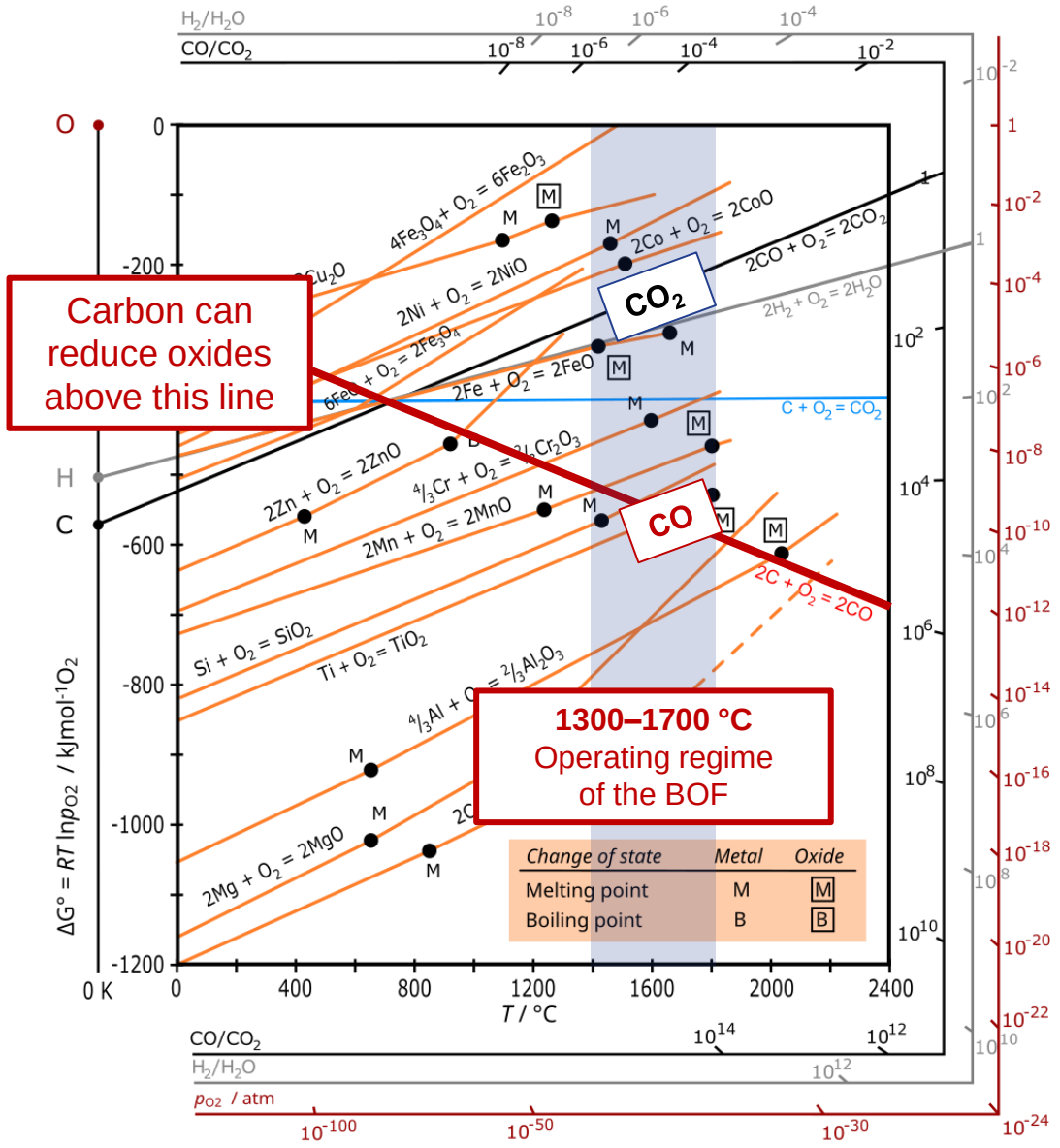
$$[\mathrm{C}] + \frac{1}{2}\{\mathrm{O_2}\} = \{\mathrm{CO}\} \qquad (\Delta H^\circ < 0)$$

- CO_2 is formed alongside CO according to

$$[\mathrm{C}] + \{\mathrm{O_2}\} = \{\mathrm{CO_2}\} \qquad (\Delta H^\circ < 0)$$

- Thermodynamically, the formation of CO is strongly preferred over that of CO_2. For [C] = 0.1 wt-%, p = 1 bar and T = 1600 °C, the equilibrium CO_2 content is only 1.2%.[1]
- Locally, the CO_2 can oxidise carbon according to the endothermic Boudouard reaction.

$$[\mathrm{C}] + \{\mathrm{CO_2}\} = 2\{\mathrm{CO}\} \qquad (\Delta H^\circ > 0)$$



Ellingham diagram.[2]

References

[1] F. Oeters, *Metallurgie der Stahlherstellung*, 1989.

[2] Wikipedia.

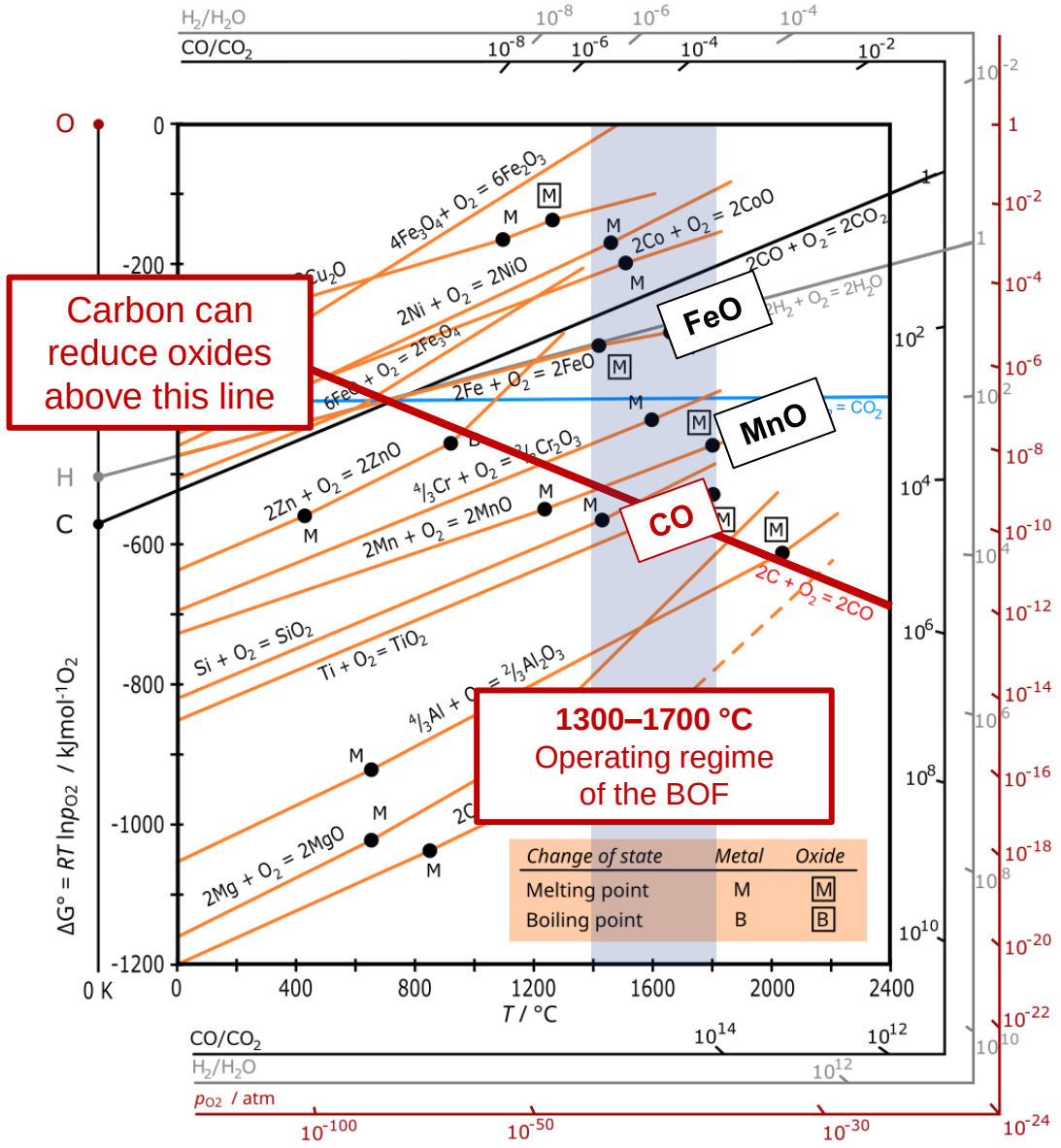
Thermodynamics

Thermodynamics of decarburisation (2/3)

- Decarburisation takes place also via metal–slag reactions.
- Thermodynamically this means that carbon reduces oxides with lower oxygen affinity than that of CO.
- At steelmaking temperatures, this means that carbon can reduce, e.g., FeO and MnO.
- The most important of the metal–slag reactions is the endothermic reduction of FeO by dissolved carbon:

$$[\mathrm{C}] + (\mathrm{FeO}) = \{\mathrm{CO}\} + [\mathrm{Fe}] \qquad (\Delta H > 0)$$

- This reaction is favoured by a high temperature and oxidative conditions.



Ellingham diagram.[1]

Reference

[1] Wikipedia.

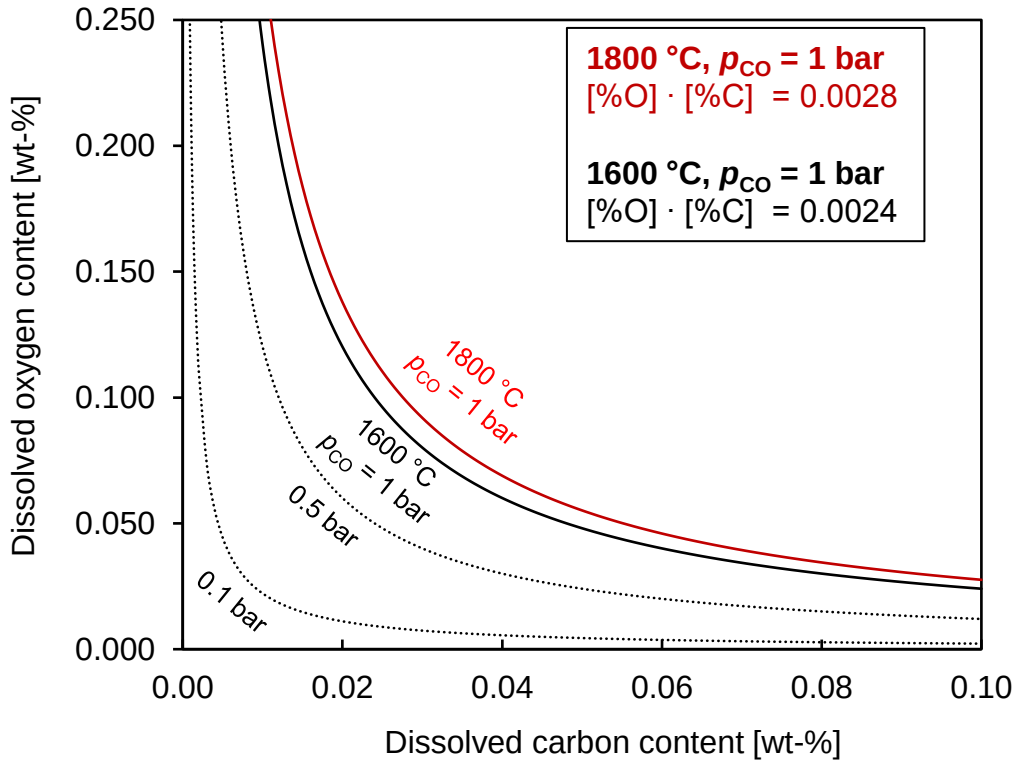
Thermodynamics

Thermodynamics of decarburisation (3/3)

- The carbon–oxygen equilibrium is given by:[1]

$$\log_{10}\left(\frac{a^{\mathrm{H}}_{[\mathrm{C}]}a^{\mathrm{H}}_{[\mathrm{O}]}}{p_{\mathrm{CO}}}\right) = -\frac{1160}{T} - 2.00$$

  where $a^{\mathrm{H}}_{[\mathrm{C}]}$ is the Henrian activity of dissolved carbon, $a^{\mathrm{H}}_{[\mathrm{O}]}$ is the Henrian activity of dissolved oxygen, p_{CO} is the partial pressure of oxygen (in bar) and T is the temperature (in K).
- At dilute concentrations, we may assume that $a^{\mathrm{H}}_{[\mathrm{C}]}$ = [%C] and $a^{\mathrm{H}}_{[\mathrm{O}]}$ = [%O].
- For a given temperature and pressure, the product [%C]·[%O] is constant. A decrease in [C] content thus leads to an increase in the [O] content.
- The effect of temperature on [%C]·[%O] is quite low.



Reference

[1] F. Oeters, *Metallurgie der Stahlherstellung*, 1989.

Thermodynamics

Thermodynamics of dephosphorisation

- The removal of phosphorus from metal to slag can be expressed according to the following reaction:[1]

$$[\mathrm{P}] + \frac{5}{2}[\mathrm{O}] + \frac{3}{2}(\mathrm{O}^{2-}) = (\mathrm{PO}_4^{3-})$$

- The phosphorus partition ratio is given by

$$L_\mathrm{P} = \frac{(\%\mathrm{P})}{[\%\mathrm{P}]} = \frac{\mathrm{P\ in\ slag\ (wt{-}\%)}}{\mathrm{P\ in\ metal\ (wt{-}\%)}}$$

- Various correlations have been proposed for linking the partition ratio L_P to temperature and slag composition.

Approach by Turkdogan[1]

- For low [P] and [O] contents, the activity coefficients of P and O are close to 1.
- Therefore, the equilibrium relation k_PO can be formulated as follows:

$$k_\mathrm{PO} = \frac{(\%\mathrm{P})}{[\%\mathrm{P}]}[\%\mathrm{O}]^{-2.5}$$

$$\rightarrow\ L_\mathrm{P} = \frac{(\%\mathrm{P})}{[\%\mathrm{P}]} = k_\mathrm{PO}[\%\mathrm{O}]^{2.5}$$

- The effect of temperature and slag composition on k_PO can be expressed as follows:

$$\log_{10} k_\mathrm{PO} = \frac{21740}{T} - 9.87 + 0.071 \cdot BO$$

$$BO = (\%\mathrm{CaO}) + (\%\mathrm{CaF_2}) + 0.3 \cdot (\%\mathrm{MgO})$$

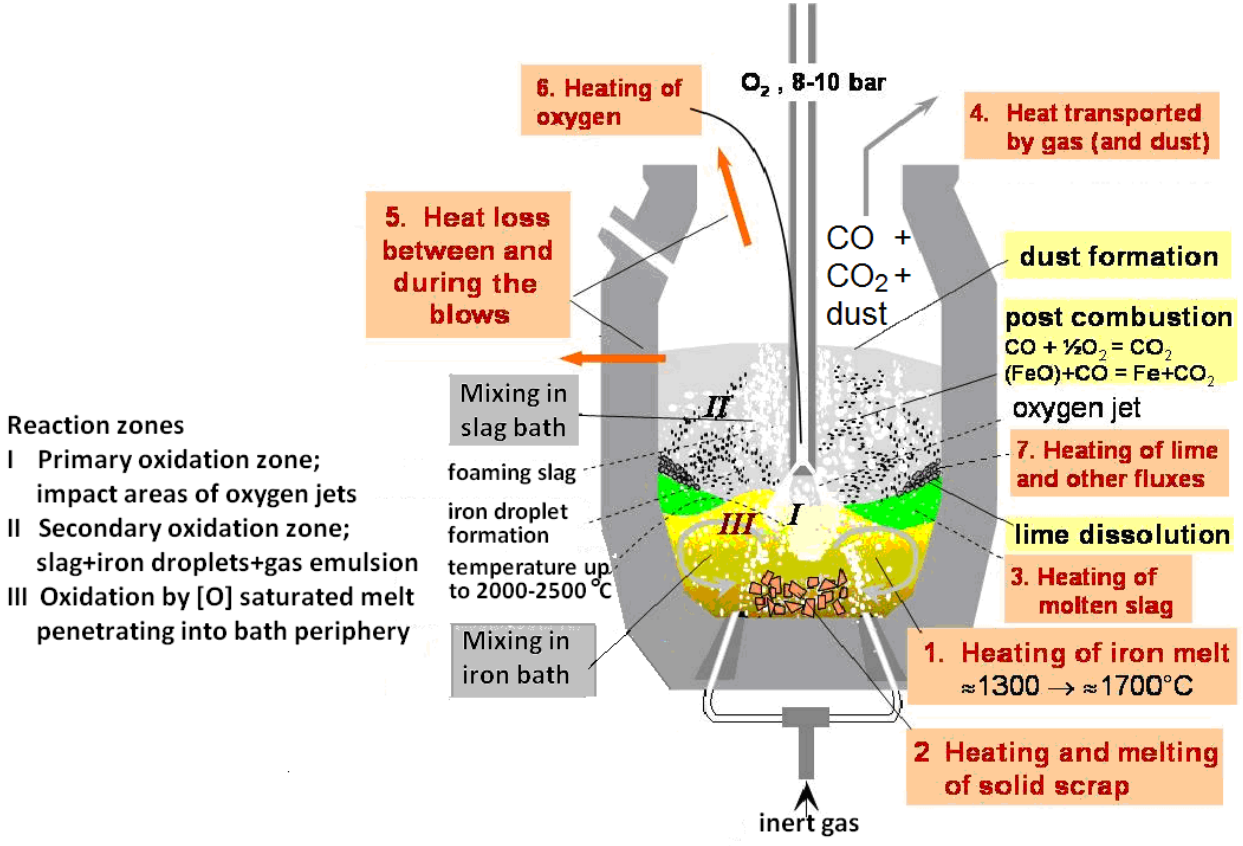
Reference

[1] E. T. Turkdogan, *Fundamentals of Steelmaking*, The Institute of Materials, 1996.

Kinetics

Reaction areas

- The main reaction areas are the impact zone (*hot spot*), metal-slag-gas foam (*emulsion*), and metal bath.
- The foaming is caused by the violent splashing of metal droplets and their subsequent decarburisation by the oxides in the slag.
- The foam provides an enormous interface for metal-slag reactions, which is highly advantageous for the refining rate.
- However, the ejection of the foam out of the furnace (*slopping*) must be avoided.
- Slag foaming can be controlled by adjusting the lance height and slag chemistry.



Schematic representation of the reaction zones in the BOF.[1]

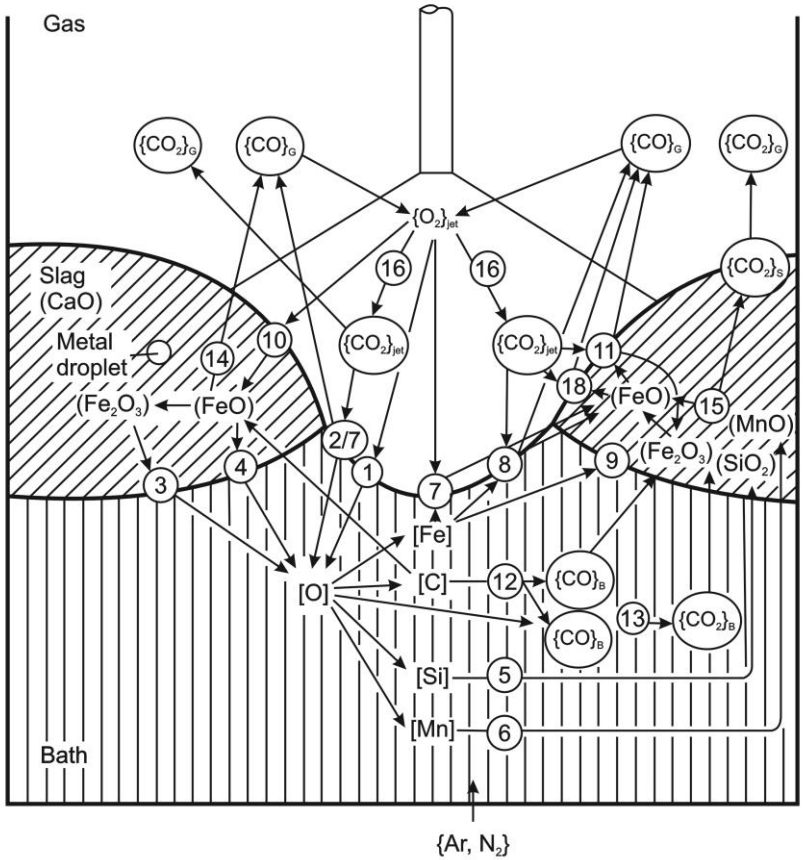
Reference

[1] H. Jalkanen, L. Holappa, in *Treatise on Process Metallurgy, Volume 3: Industrial Processes*, 223-270, 2014.

Kinetics

Reaction areas (continued)

- Oxidation and reduction reactions take place simultaneously at different sites.
- FeO and CO_2 are important intermediate products that oxidise carbon.



Schematic illustration of reaction areas and material flows during oxygen top-blowing. Redrawn after Ref.[1]

Reaction area		Reaction
[O] pickup by bath		
$\{O_2\}$ in hot spot	$½\{O_2\}_{jet} = [O]$	1
$\{CO_2\}$ in hot spot	$\{CO_2\}_{jet} = [O] + \{CO\}_G$	2
(Fe_2O_3) of slag	$(Fe_2O_3) = [O] + 2(FeO)$	3
(FeO) of slag	$(FeO) = [O] + [Fe]$	4
Removal into slag phase		
[Si] through [O] in bath	$[Si] + 2[O] = (SiO_2)$	5
[Mn] through [O] in bath	$[Mn] + [O] = (MnO)$	6
Fe through $\{O_2\}$ in hot spot	$[Fe] + ½\{O_2\}_{jet} = (FeO)$	7
Fe through $\{CO_2\}$ in hot spot	$[Fe] + \{CO_2\}_{jet} = (FeO) + \{CO\}_G$	8
Fe through (Fe_2O_3) in slag	$[Fe] + (Fe_2O_3) = 3(FeO)$	9
(O) pickup by slag		
$\{O_2\}$ in hot spot	$2(FeO) + ½\{O_2\} = (Fe_2O_3)$	10
$\{CO_2\}$ in hot spot	$2(FeO) + (CO_2)_{jet} = (Fe_2O_3) + \{CO\}_G$	11
Oxidation of [C] to {CO} and $\{CO_2\}$		
in bath	$[C] + [O] = \{CO\}_B$	12
in bath	$\{CO\}_B + [O] = \{CO_2\}_B$	13
in slag (metal droplets)	$[C] + (FeO) = \{CO\}_S + [Fe]$	14
in slag	$\{CO\}_S + (Fe_2O_3) = \{CO_2\}_S + (FeO)$	15
Post-combustion of {CO} to $\{CO_2\}$		
through O_2 jet	$\{CO\} + ½\{O_2\}_{jet} = \{CO_2\}_{jet}$	16
Decomposition of $\{CO_2\}$ obtained from post-combustion:		
in hot spot	$\{CO_2\}_{jet} = \{CO\} + [O]$	17
in slag	$\{CO_2\}_{jet} + 2(FeO) = \{CO\} + (Fe_2O_3)$	18
Summary of the sites of various reactions		
$\{CO_2\}$ formation	13, 15, 16	
$\{CO_2\}$ consumption	8, 17, 18	
[O] pickup by bath	1, 2, 3, 4	
[O] consumption	5, 6, 12, 13	
(O) pickup by slag	10, 11	
(O) given by slag	3, 4, 14, 15	

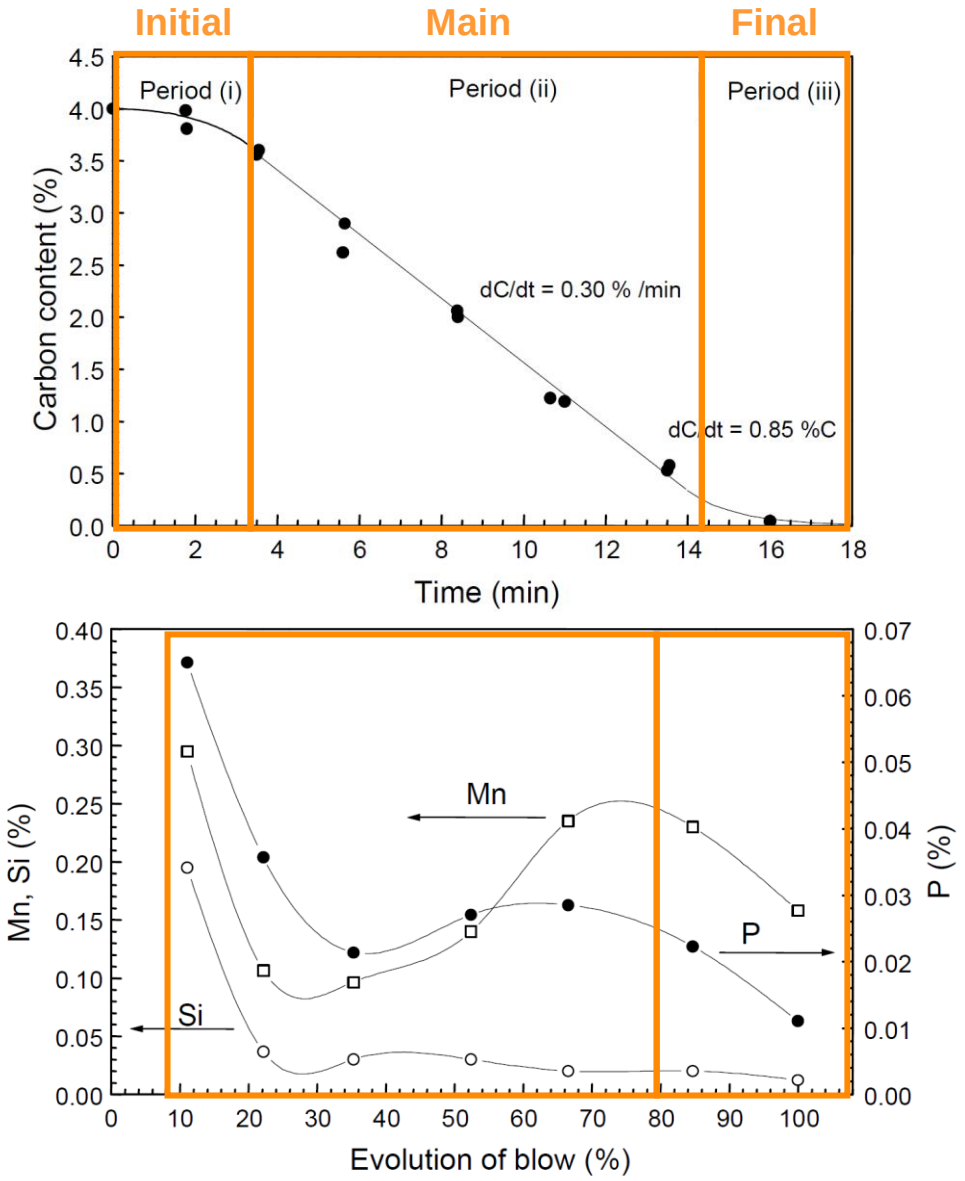
Reference

[1] E. Schürmann, H. Sperl, R. Hammer, A. Ender, *Stahl Eisen*, 106(23): 1267–1272, 1986.

Kinetics

Decarburisation kinetics

- The decarburisation kinetics exhibit three distinct periods:
  1. **Initial period**: the decarburisation rate increases with time.
  2. **Main period**: the decarburisation rate is approximately constant (0th order kinetics).
  3. **Final period**: the decarburisation rate decreases with time (1st order kinetics).
- Si, P and Mn oxidise rapidly in the initial period, but part of the MnO formed is reduced by carbon in the main period.
- As the C content diminishes in the final period, Fe and Mn start to oxidise rapidly.



Evolution of bath composition in the BOF process.[1]

Reference

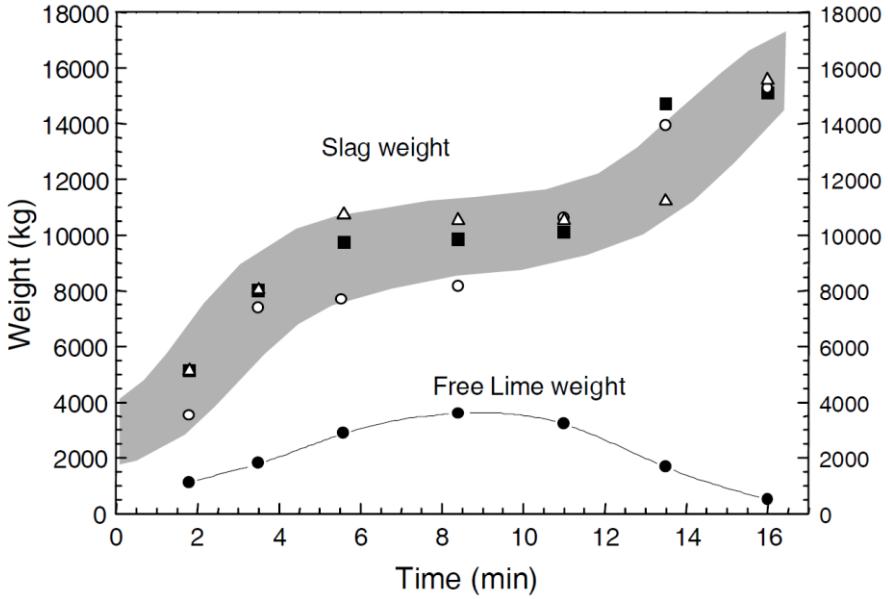
[1] C. Cicutti, M. Valdez, T. Pérez, J. Petroni, A. Gómez, R. Donayo, L. Ferro, *Proc. 6th International Conference on Molten Slags, Fluxes and Salts*, 2000.

Kinetics

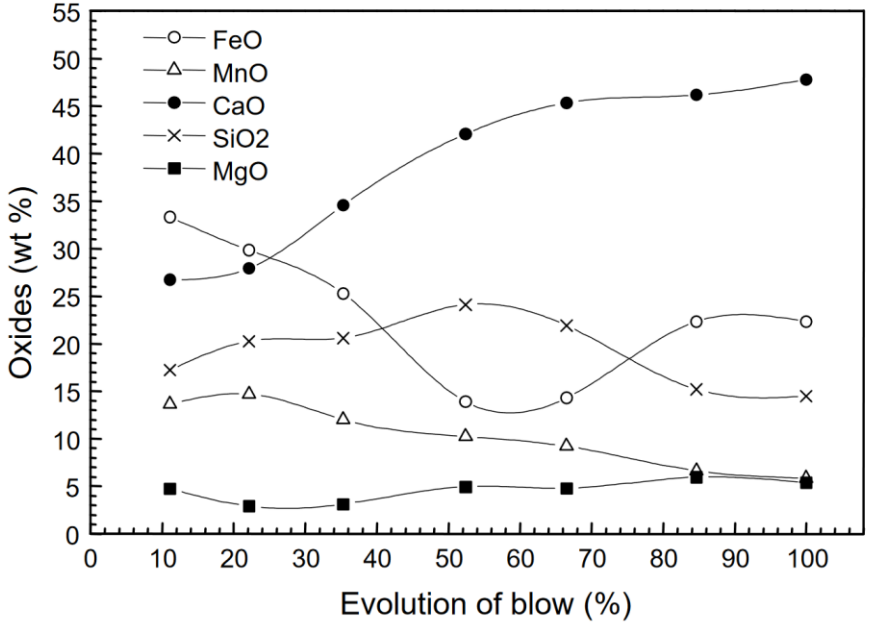
Evolution of slag composition

- The slag weight increases strongly during the beginning and final part of the BOF process.
- The oxidation and reduction of alloying elements is reflected in the composition of the slag.
- To maintain a basic slag, the slag basicity is controlled with lime and dolomite additions.
- However, the dissolution of the lime and dolomite particles is rather slow.
- Consequently, the BOF slag can contain a significant fraction of “free lime”.

Evolution of slag weight and free lime content in an LBE-type BOF.[1]



Evolution of slag composition in an LBE-type BOF.[2]



References

[1] C. Cicutti, M. Valdez, T. Pérez, R. Donayo, J. Petroni, *Lat. Am. Appl. Res.*, 32(3): 237–240, 2002.

[2] C. Cicutti, M. Valdez, T. Pérez, J. Petroni, A. Gómez, R. Donayo, L. Ferro, *Proc. 6th International Conference on Molten Slags, Fluxes and Salts*, 2000.

Kinetics

Modelling of dephosphorisation kinetics (1/4)

- The dephosphorisation reaction takes place between metal droplets and slag.
- At high temperatures, metal–slag reactions are generally limited by mass transfer and thus the interfacial reaction rate can be neglected.[1]
- The first-order rate of phosphorus in the metal phase can be expressed as follows:[1]

$$\frac{\mathrm{d}[\%\mathrm{P}]}{\mathrm{d}t} = -k_{\mathrm{tot}}([\%\mathrm{P}] - [\%\mathrm{P}]_{\mathrm{eq}})$$

- The overall time constant is obtained by summation of the contributions of individual size classes:[1]

$$k_{\mathrm{tot}} = \underbrace{\int \frac{V_{\mathrm{d}}(d)}{V_{\mathrm{L}}\, t_{\mathrm{res}}(d)} \eta_{\mathrm{M}}(d)\, \mathrm{d}d}_{\text{integral form}} \approx \underbrace{\lim_{\Delta d \to 0} \sum_{i} \frac{V_{\mathrm{d},i}}{V_{\mathrm{L}}\, t_{\mathrm{res},i}} \eta_{\mathrm{M},i}}_{\text{discrete form}}$$

Variables

$[\%\mathrm{P}]$	Phophorus in the metal phase [wt-%]
$[\%\mathrm{P}]_{\mathrm{eq}}$	Phophorus in the metal phase at equilibrium [wt-%]
k_{tot}	Overall time constant [1/s]
$V_{\mathrm{d},i}$	volume of size class i [m^3]
V_{L}	volume of the metal bath [m^3]
$t_{\mathrm{res},i}$	residence time of size class i [s]
$\eta_{\mathrm{M},i}$	microkinetic efficiency of size class i

Reference

[1] F. Oeters, *Metallurgie der Stahlherstellung*, 1989.

Kinetics

Modelling of dephosphorisation kinetics (2/4)

- The dephosphorisation rate of a single droplet can be predicted based on the *two-film theory.*[1]
- The microkinetic efficiency of a single size class is given by:[2]

$$\eta_{\mathrm{M}} = \frac{[\%\mathrm{P}] - [\%\mathrm{P}]_{\mathrm{d}}}{[\%\mathrm{P}] - [\%\mathrm{P}]_{\mathrm{eq}}} = 1 - \exp\left[-\beta_{\mathrm{tot,L}}\left(\frac{6}{d}\right)t_{\mathrm{res}}\right]$$

- Continuity condition: the mass flux of phosphorus must be the same in metal and slag phases.
- For wt-% units, the overall mass transfer coefficient can be expressed as follows:[2]

$$\beta_{\mathrm{L,tot}} = \frac{1}{\frac{1}{\beta_{\mathrm{L}}} + \frac{\rho_{\mathrm{L}}}{\beta_{\mathrm{S}}\rho_{\mathrm{S}}L_{\mathrm{P}}}}$$

Variables

η_{M}	microkinetic efficiency
$[\%\mathrm{P}]_{\mathrm{d}}$	P content in the metal droplets after t_{res} [wt-%]
$\beta_{\mathrm{tot,L}}$	total mass transfer coefficient of the metal phase [m/s]
d	droplet diameter [m]
t_{res}	residence time [s]
β_{L}	mass transfer coefficient of the metal phase [m/s]
β_{S}	mass transfer coefficient of the slag phase [m/s]
ρ_{L}	density of metal [kg/m^3]
ρ_{S}	density of slag [kg/m^3]
L_{P}	phosphorus partition ratio

References

[1] W. K. Lewis, W. G. Whitman, *Indust. Eng. Chem.*,16(12): 1215–1220, 1924.

[2] F. Oeters, *Metallurgie der Stahlherstellung,* 1989.

Kinetics

Modelling of dephosphorisation kinetics (3/4)

- Small metal droplets in slag can be modelled as a rigid sphere in creeping flow.
- The mass transfer in the metal droplet can be calculated using the Newman solution:[1]

$$\mathrm{Sh_L} = \frac{\beta_\mathrm{L} d}{D_\mathrm{L}} = \frac{2\pi^2}{3} \frac{\sum_{i=1}^{\infty}[\exp(-i^2\pi^2 \mathrm{Fo_M})]}{\sum_{i=1}^{\infty}\left[\frac{1}{i^2}\exp(-i^2\pi^2 \mathrm{Fo_M})\right]}$$

Steady-state
$\lim_{\mathrm{Fo_M}\to\infty} \mathrm{Sh_L} \approx 6.58$

- The mass transfer in the slag surrounding the metal droplet can be calculated using the Ranz-Marschall correlation:[2,3]

$$\mathrm{Sh_S} = \frac{\beta_\mathrm{S} d}{D_\mathrm{S}} = 2 + 0.6\mathrm{Re_S}^{1/2}\mathrm{Sc_S}^{1/3}$$

Stagnant flow
$\lim_{\mathrm{Re_S}\to 0} \mathrm{Sh_S} = 2$

Variables for metal

$\mathrm{Sh_L}$	Sherwood number
β_L	mass transfer coefficient [m/s]
d	droplet diameter [m]
D_L	mass diffusivity [m²/s]
$\mathrm{Fo_M}$	Fourier number for mass transfer; defined here as $\mathrm{Fo_M} = \frac{4D_\mathrm{L}t_\mathrm{res}}{d^2}$

Variables for slag

$\mathrm{Sh_S}$	Sherwood number
β_S	mass transfer coefficient [m/s]
D_S	mass diffusivity [m²/s]
$\mathrm{Re_S}$	Reynolds number
$\mathrm{Sc_S}$	Schmidt number

References
[1] A. B. Newman, *Trans. Am. Inst. Chem. Eng., 27:* 203–220, 1931.
[2] W. E. Ranz, W. R. Marschall, *Chem. Eng. Prog.*, 48(3): 141–146, 1952.
[3] W. E. Ranz, W. R. Marschall, *Chem. Eng. Prog. Prog.*, 48(3): 173–180, 1952.

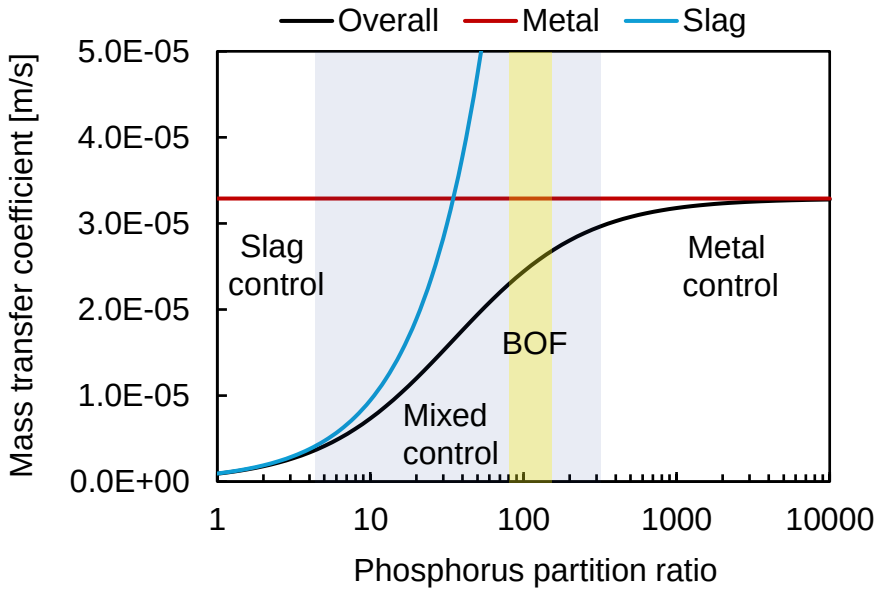
Kinetics

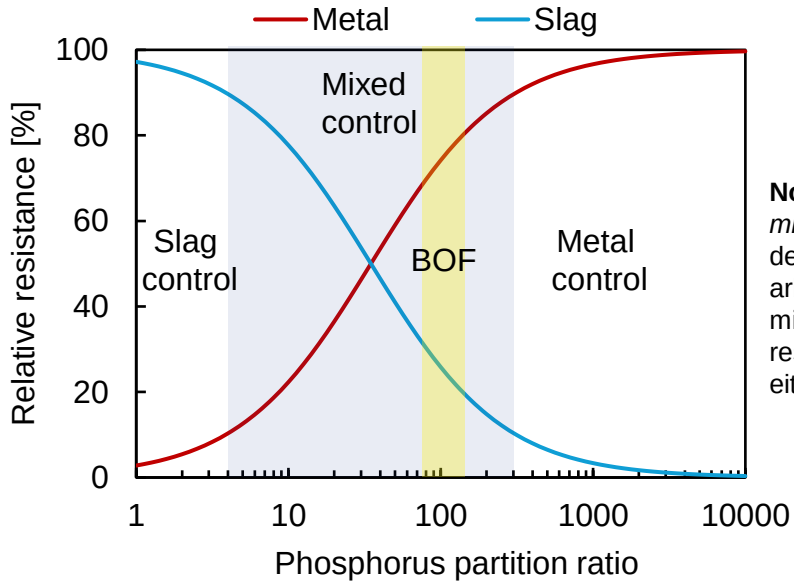
Modelling of dephosphorisation kinetics (4/4)

- The controlling steps are exemplified for a **1 mm droplet** by varying the phosphorus partition ratio (L_P).
- Assumptions:

Parameter	Metal	Slag
Fluid flow regime	Rigid sphere	Creeping flow
Sh correlation	Newman[1]	Ranz-Marschall[2,3]
Droplet diameter [m]	0.001 m	
Velocity [m/s]	0.1 m/s	
Density [kg/m^3]	7000	3000
Mass diffusivity [m^2/s]	$5 \cdot 10^{-9}$	$5 \cdot 10^{-10}$

- The phosphorus partition ratios reported for combined-blowing BOFs (L_P = ~75–150) in Ref.[4] coincide with the mixed control region.





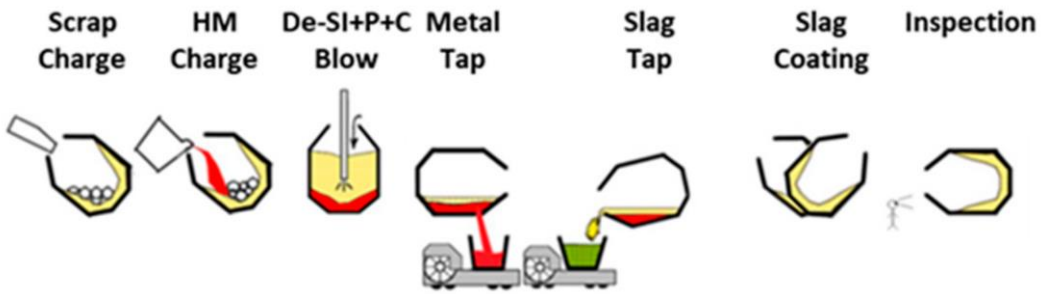
Note:
mixed control is defined here arbitrarily as min. 10% resistance in either phase.

References
[1] A. B. Newman, *Trans. Am. Inst. Chem. Eng., 27:* 203–220, 1931.
[2] W. E. Ranz, W. R. Marschall, *Chem. Eng. Prog.*, 48(3): 141–146, 1952.
[3] W. E. Ranz, W. R. Marschall, *Chem. Eng. Prog. Prog.*, 48(3): 173–180, 1952.
[4] W. Urban, M. Weinberg, J. Cappel, *Iron Steel Technol.*, 134(8): 27–39, 2014.

Operating practices

Straight blow practice[1]

- Emerged in the late 1960s as European steelmakers began operating with low-P ores.
- Intended for hot metal with
  low P (0.050–0.090 wt-%)
  low Si (0.30–0.60 wt-%)
- The process starts with the charging of scrap and is followed by charging of hot metal (in liquid state).
- Simultaneous oxidation of Si, P and C takes place during the blow.
- After the blow, the metal is tapped.



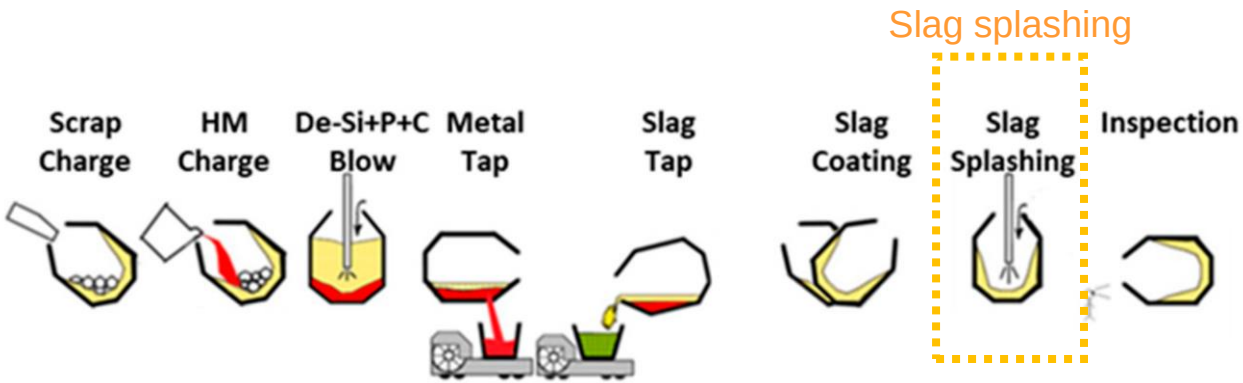
Straight blow practice.[1]

Reference
[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.

Operating practices

Blow-splash practice[1]

- Developed in North America in the 1980s.
- The refining is conducted similar to straight blow practice.
- The slag is splashed after tapping and slag coating using top-blowing of nitrogen.
- The splashed slag serves as protective layer for the refractory lining, thus increasing its lifetime.
- Drawbacks include higher MgO use, skulling, larger slag volumes, and poor slag properties for de-P.



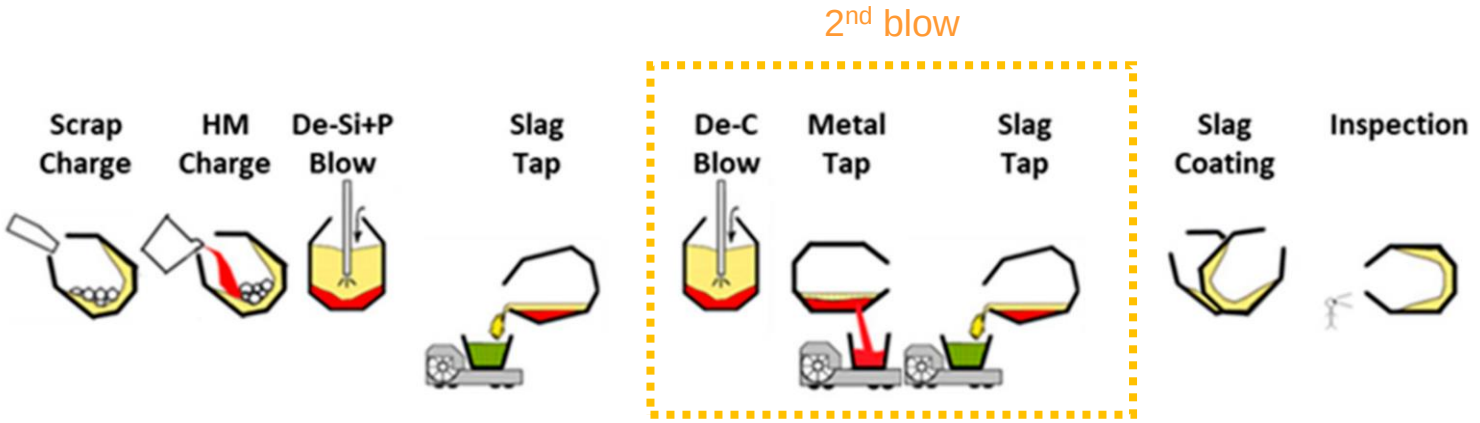
Blow-splash practice.[1]

Reference
[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.

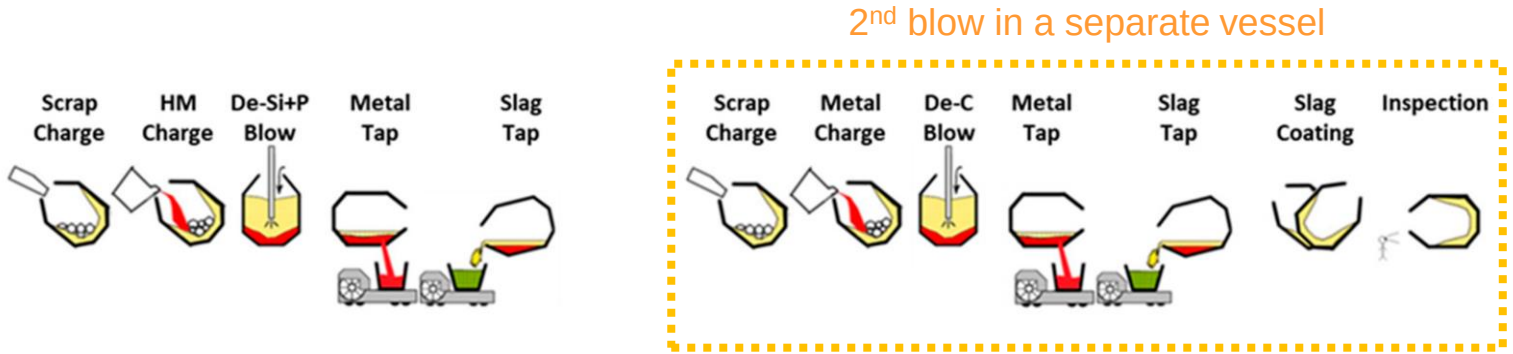
Operating practices

Double slag practice[1]

- Developed for achieving ultra-low phosphorus (ULP) conditions.
- Two blowing stages:
  - The first blow makes use of the low temperature for desiliconization and dephosphorization.
  - The second blow is conducted with a new lime flux, which allows for a fast decarburisation without slopping risk.
- The two blows can also be conducted in separate vessels.



Double slag practice in a single vessel.[1]



Double slag practice in two vessels.[1]

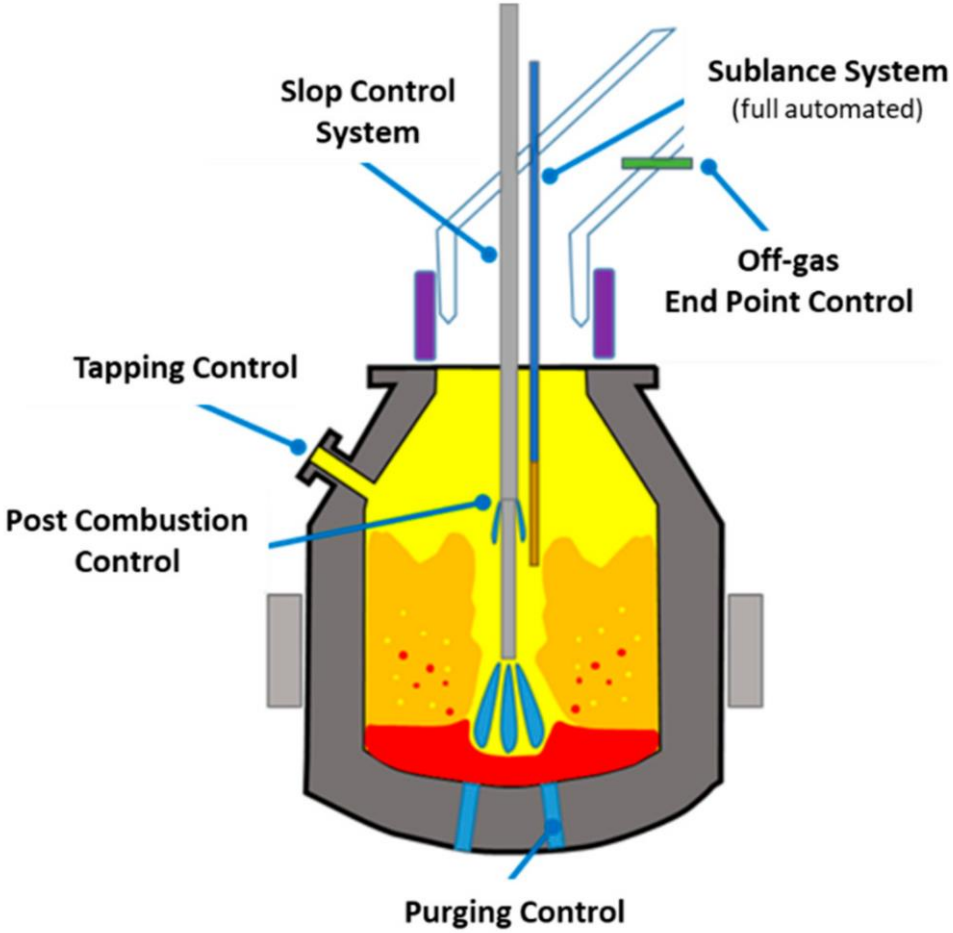
Reference

[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.

State-of-the-art technology

Gas injection[1]

- Purging control
  - Removable converter bottoms.
  - Multihole purging blocks.
  - Separate control of individual plugs.
- Post combustion control
  - Post-combustion distributors: injecting part of the oxygen through ring channels in the upper part of the lance.
- Slopping control system
  - Vibration-based monitoring.[2,3]
  - Acoustic monitoring.[2,3,4]



Overview of the technological innovations in the LD converter.[1]

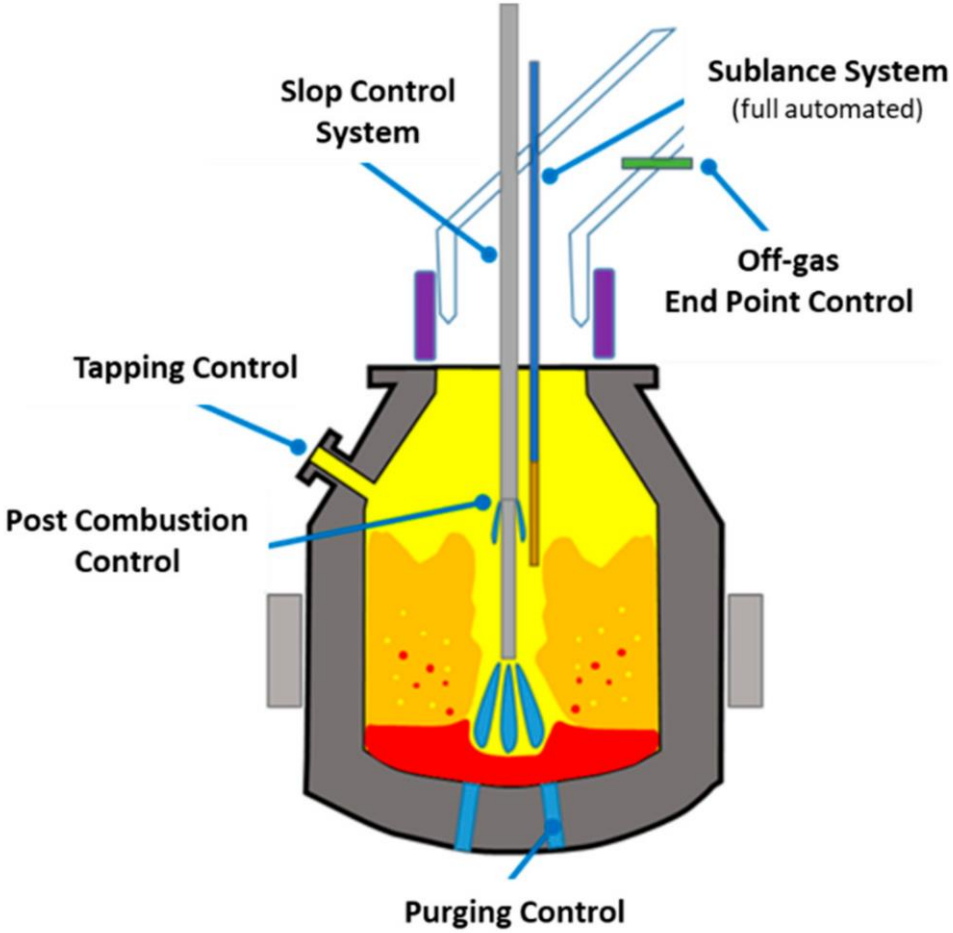
References

[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.
[2] M. Brämming, G. Parker, S. Millman, A. Kapilashrami, D. Malmberg, B. Björkman, *Steel Res. Int.*, 82(6): 683–692, 2011.
[3] J. Nissilä, M. Pylvänäinen, V.-V. Visuri, P. Ruotsalainen, J. Laurila, A. Rankinen, T. Palovaara, T. Liedes, *Metall. Mater. Trans. B*, 54(6): 2929–2950, 2023.
[4] J. Heenatimulla, G.A. Brooks, M. Dunn, D. Sly, R. Snashall, W. Leung, *Metals,* 12(7): 1142, 2022.

State-of-the-art technology

Sampling and tapping[1]

- Sublance system
  - Composition analysis during processing.
- Off-gas end point control
  - Process models coupled with flue gas analysis systems.
- Tapping control:
  - Pneumatic closure devices are replacing ball and dart systems.
  - IR-camera systems have replaced electromagnetic detectors.
  - Automatic/semi-automatic tapping.



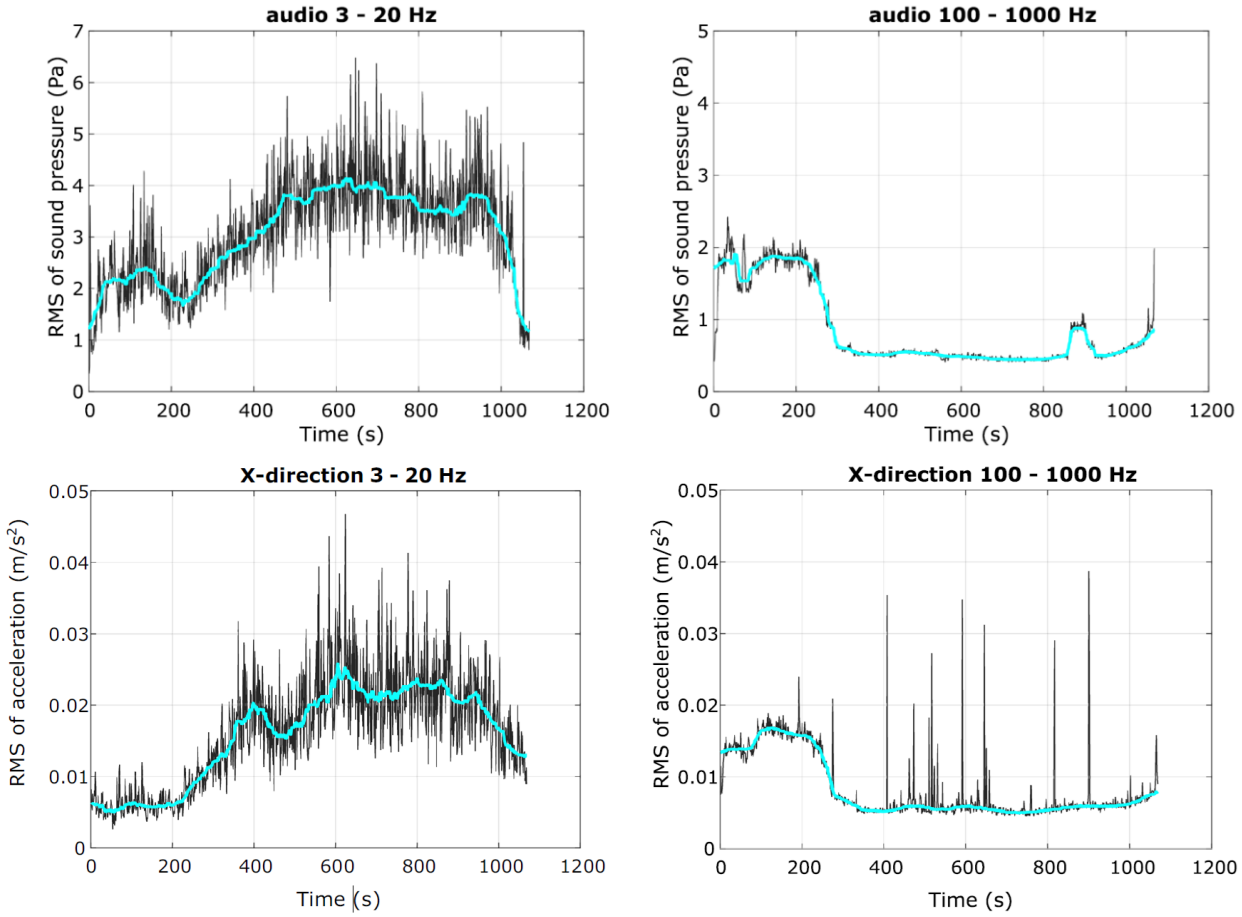
Overview of the technological innovations in the LD converter.[1]

Reference
[1] J. Cappel, F. Ahrenhold, M. W. Egger, H. Hiebler, J. Schenk, *Metals*, 12(6): 912, 2022.

State-of-the-art technology

Example: vibration- and audio-based monitoring

- Nissilä et al.[1] collected and analysed vibration and audio data from nearly 300 heats.
- The accelerometers were mounted on the tilting axis, while the microphone was placed above the converter.
- The off-gas temperature correlated with low-frequency (3–20 Hz) audio and RMS acceleration data from horizontal directions (X and Z).
- The lance height correlated with mid-frequency (100–1000 Hz) audio and RMS acceleration data from all directions.
- Audio and vibration measurements could serve as a basis for a monitoring system for foaming and even for slopping.



RMS signals for the audio and X-direction accelerometer measurements (X = tilting direction).[1]

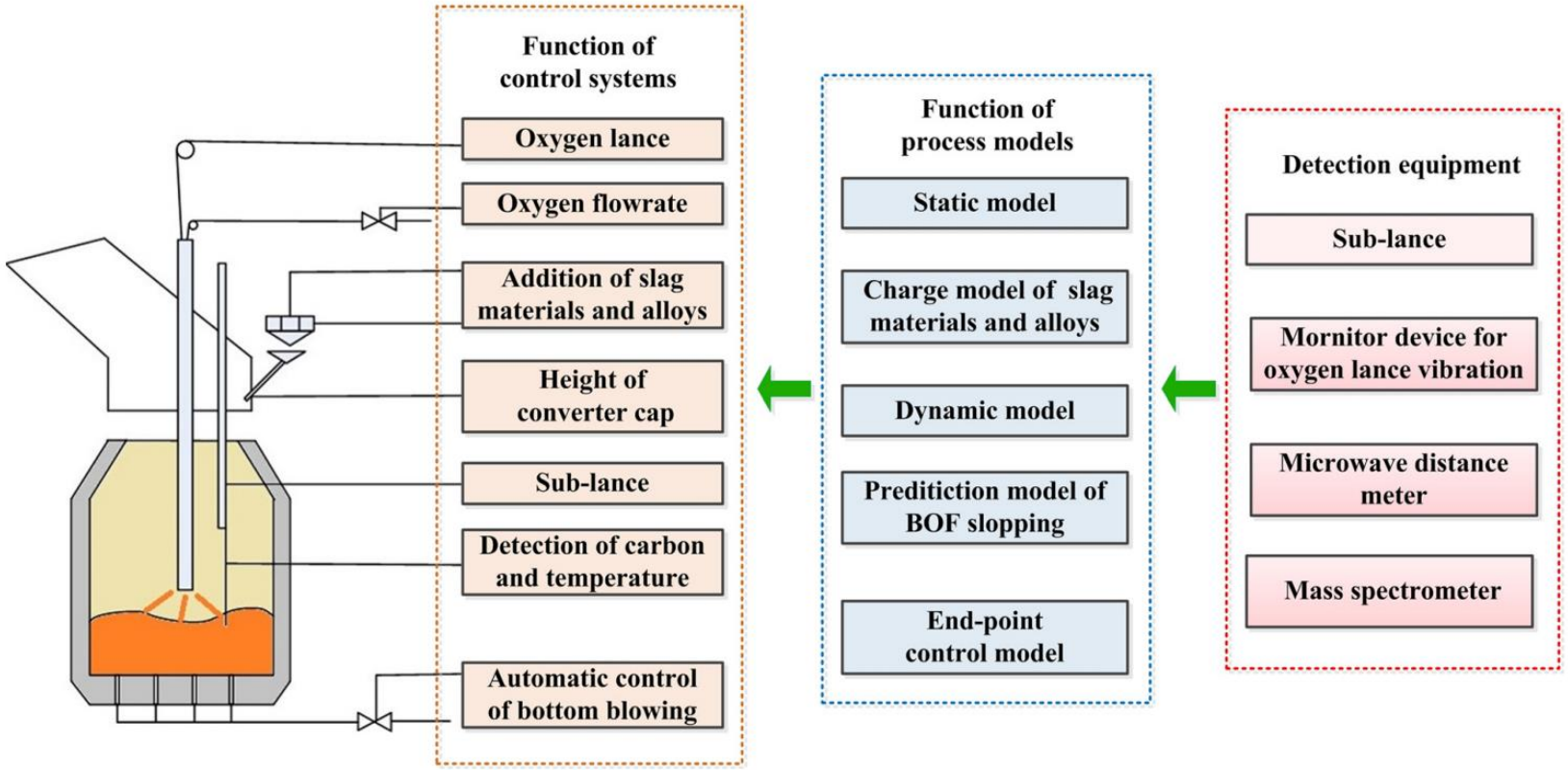
Reference

[1] J. Nissilä, M. Pylvänäinen, V.-V. Visuri, P. Ruotsalainen, J. Laurila, A. Rankinen, T. Palovaara, T. Liedes, *Metall. Mater. Trans. B*, 54(6): 2929–2950, 2023.

State-of-the-art technology

Process control

- Modern BOF control is based on the coupling of measurement information with predictive models.
- The predictive models range from deterministic thermodynamic-kinetic models to purely statistical or machine learning models.
- Indirect indicators such as vibration, light or sound can be used as soft sensors.



Example of an automatic BOF steelmaking system (Nippon Steel Corporation).[1]

Reference

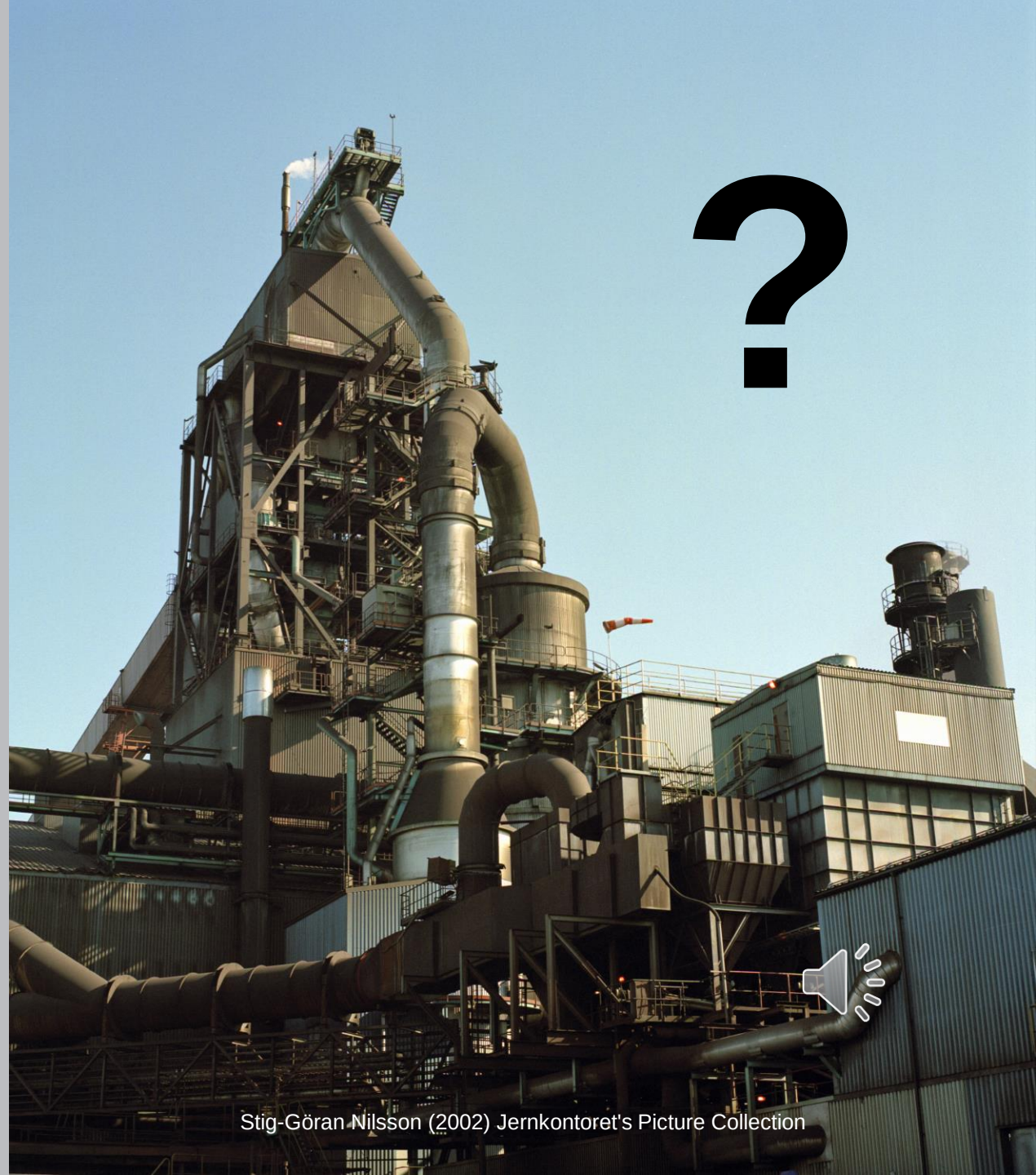
[1] Z. Wang, Q. Liu, H. Liu, S. Wei, *High Temp. Mater. Process.*, 39(1): 653-662, 2020.

By now, you should know the answers to these questions

1. What are the main charge materials and consumables of the BOF?
2. What causes the splashing of metal droplets and how do the metal droplets contribute to refining in the BOF?
3. What are the three regimes of decarburisation kinetics?
4. What is the course of the straight blow practice?



Outlook

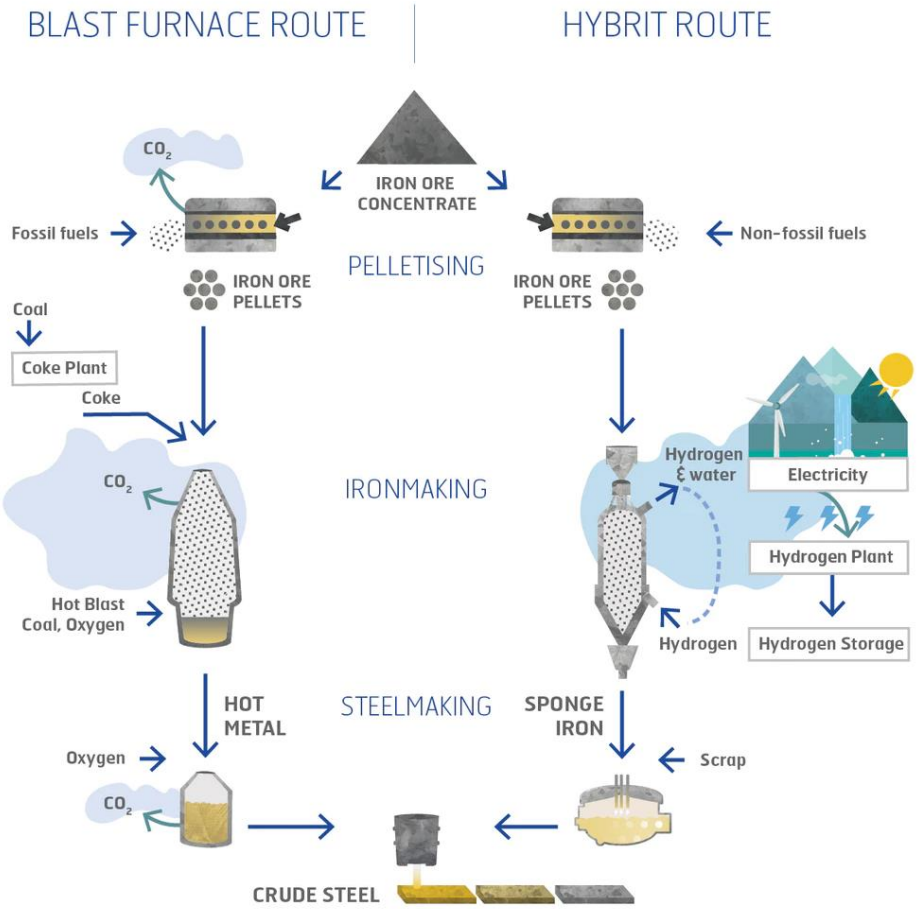


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Outlook

Hydrogen-reduction

- Development of fossil-free direct reduction processes using hydrogen is advancing at a rapid pace.
- The hydrogen direct reduction (H-DR) can be conducted in a shaft furnace or in a fluidised bed.
- As the direct reduced iron (DRI) contains no carbon, decarburisation in the BOF process is no longer needed.
- Owing to the high demand of hydrogen and electricity, is difficult to scale the production up to the level of the largest contemporary integrated steel plants (> 5 Mt).



Hydrogen reduction according to the HYBRIT concept.[1]

Reference
[1] HYBRIT AB.

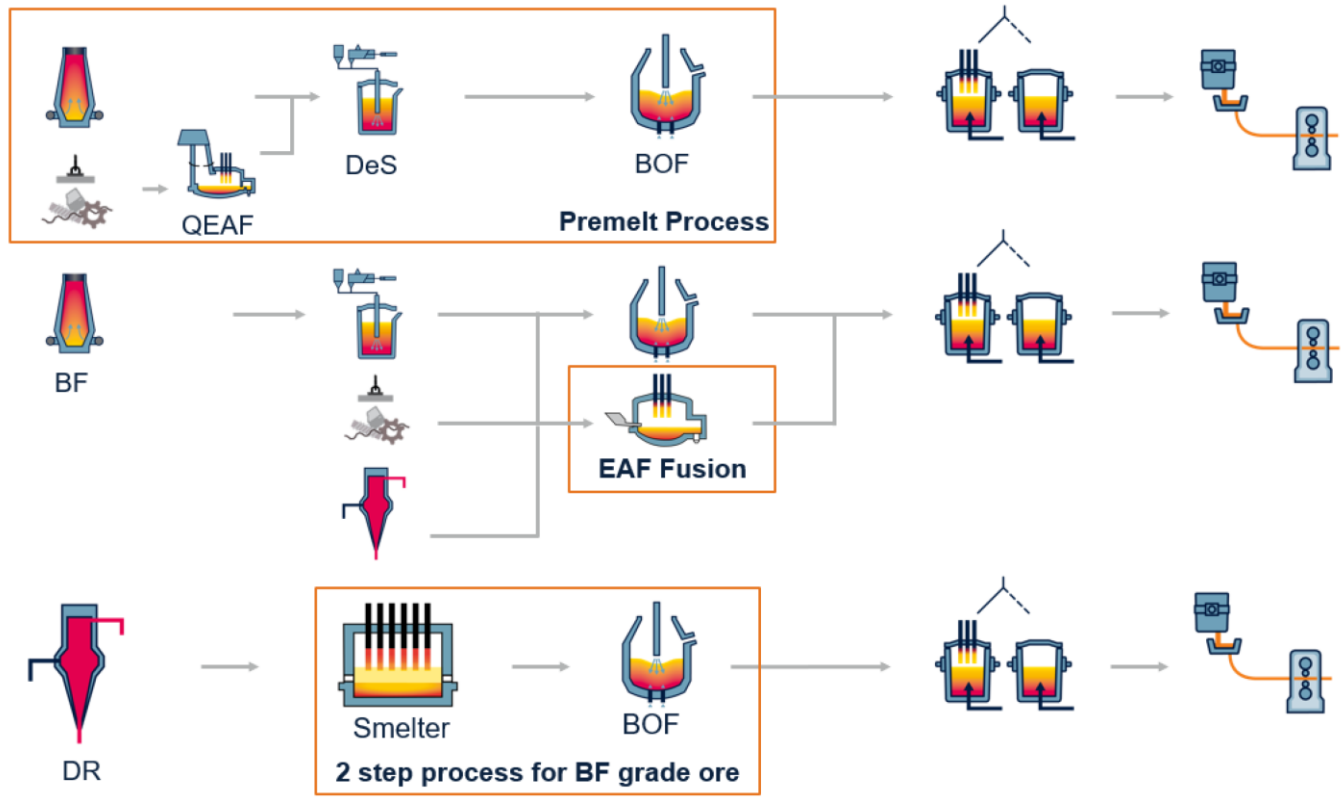
Outlook

Hybrid EAF–BOF plants

- **Premelt process**
  Scrap premelting in an EAF or induction furnace before the BOF.

- **EAF fusion**
  Mixing scrap melted using an EAF to crude steel produced with the BOF.

- **2-step process for BF grade ore**
  Processing low grade direct-reduced iron in a smelter before the BOF.



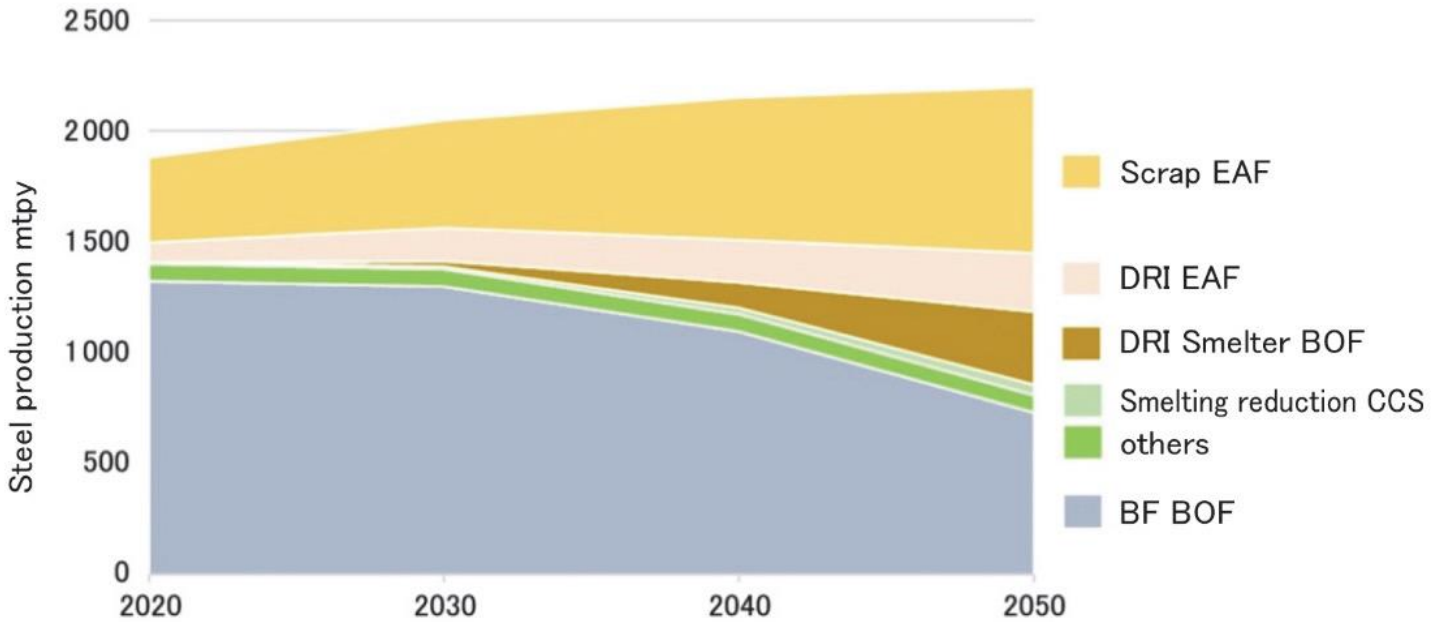
Hybrid EAF–BOF plants and possible routes for the transformation of BF grade ore based integrated steelmaking.[1]

Reference
[1] B. Voraberger, G. Wimmer, U. D. Salgado, E. Wimmer, K. Pastucha, A. Fleischanderl, *Metals*, 12(3): 466, 2022.

Outlook

Estimates for steel production

- Steel production is expected to grow beyond 2000 Mt/pa in the upcoming decades.
- The share of scrap-based steelmaking is expected to increase significantly.
- Ore-based steelmaking will remain dominant due to limited scrap supply.
- Process routes based on processing of hydrogen-reduced DRI are expected to account for about 40% of ore-based production by 2050.



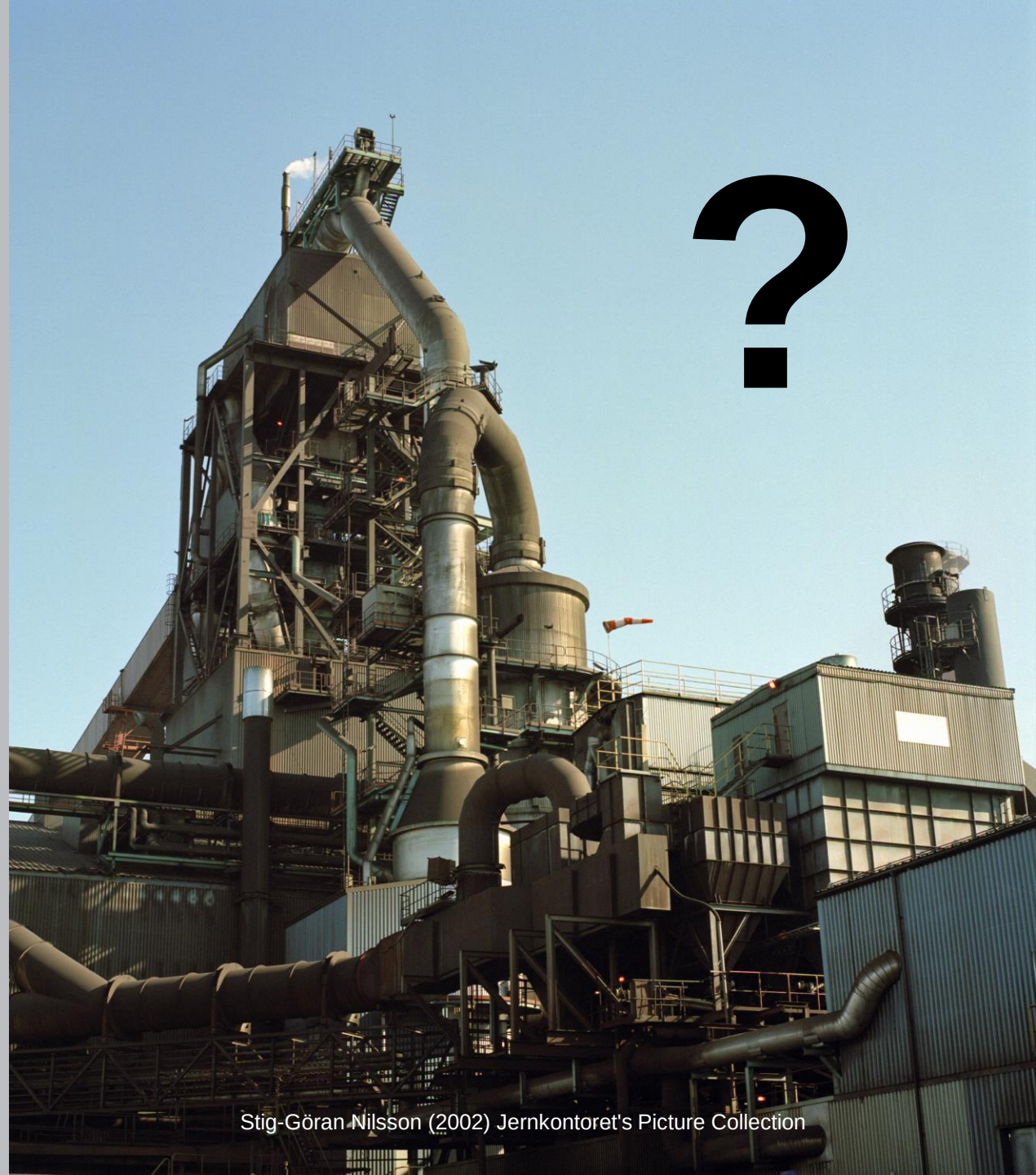
Estimated future share of steel production routes until 2050.[1]

Reference

[1] G. Wimmer, B. Voraberger, B. Kradel, A. Fleischanderl, *Mitsubishi Heavy Industries Technical Review,* 59(4): 1–7, 2022.

By now, you should know the answers to these questions

1. What reductant has been envisaged for replacing coke in reducing iron ore?
2. How can the BOF be employed in DRI-based steelmaking?
3. What is the outlook for the integrated blast furnace – basic oxygen furnace route in terms of production volume?



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Summary



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Summary

- The converter metallurgy of carbon steelmaking evolved from refining with air to oxygen steelmaking processes featuring basic refractories.
- Modern BOF converters are predominantly combined-blowing variants of the LD converter introduced.
- The oxygen is supplied with a top lance, while bottom-blowing is used for improving bath mixing.
  - The high refining rate is attributable to the formation of a metal-slag-gas foam.
  - The foaming of the slag is controlled primarily by adjusting the lance height and slag chemistry.
- The relative importance of the BOF process is likely to decrease in the future with increased scrap use and processing of hydrogen-reduction of iron ores, which could make the BOF redundant.

Thank you for your attention!

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