Converter processes in stainless steelmaking

477427A High temperature processes

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Contents

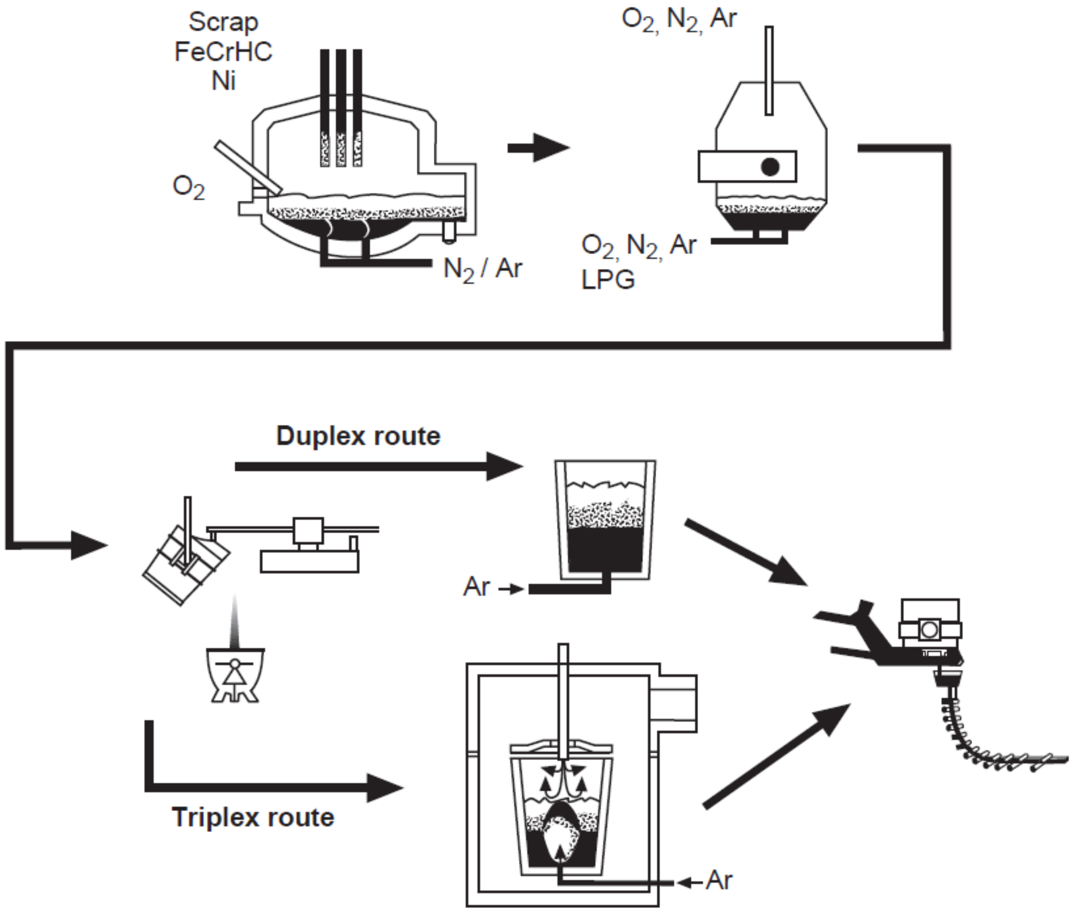
Learning aims

- The lecture focuses on the converter processes in stainless steelmaking.
- After the lecture, the student should
  1. be able to explain the purpose of AOD, VOD, and ferrochrome converter processes.
  2. understand their thermodynamic and kinetic fundamentals.
  3. know their typical operating practices.
  4. have an overview of future development needs.

Introduction

Production routes

- Modern stainless steelmaking is based on melting and refining of scrap alloyed with FeCr.
- The **duplex route** is constituted by an electric arc furnace (EAF) and a converter process.
  - The EAF serves the purpose of melting the scrap.
  - The refining of steel takes place in a separate converter process (e.g. AOD).
- The **triplex route** features also vacuum oxygen decarburisation (VOD) for removing dissolved gases.
- Outokumpu's meltshop on Tornio is the only stainless steel meltshop in Finland and is thus used as an example for contextualisation.



Comparison of duplex and triplex process route in stainless steelmaking.[1]

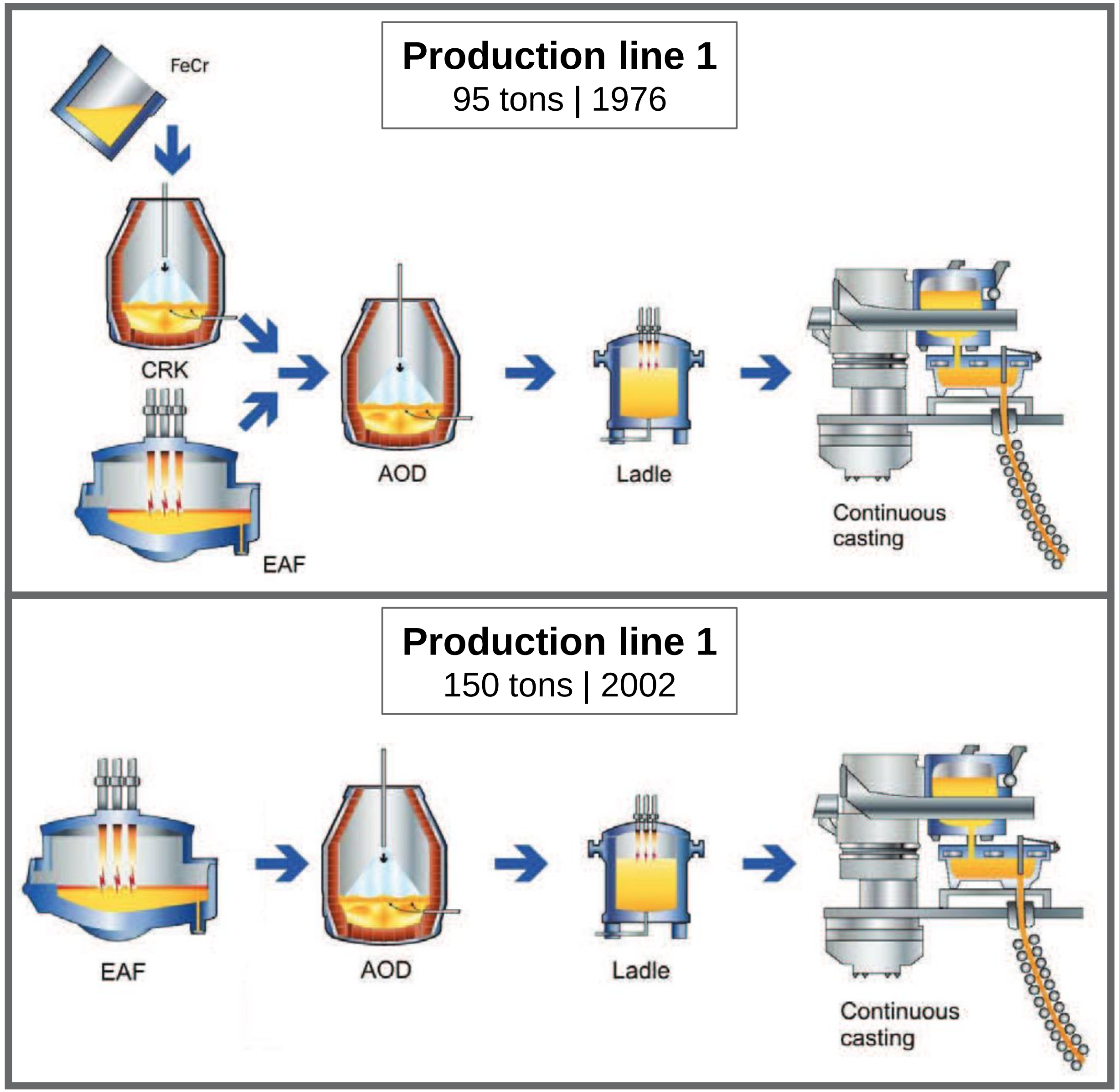
Reference

[1] B.V. Patil, A.H. Chan, and R.J. Choulet, in: *The Making, Shaping and Treating of Steel. 11th Edition Steel Making and Refining*, pp. 715–741, 1998.

Introduction

Tornio meltshop

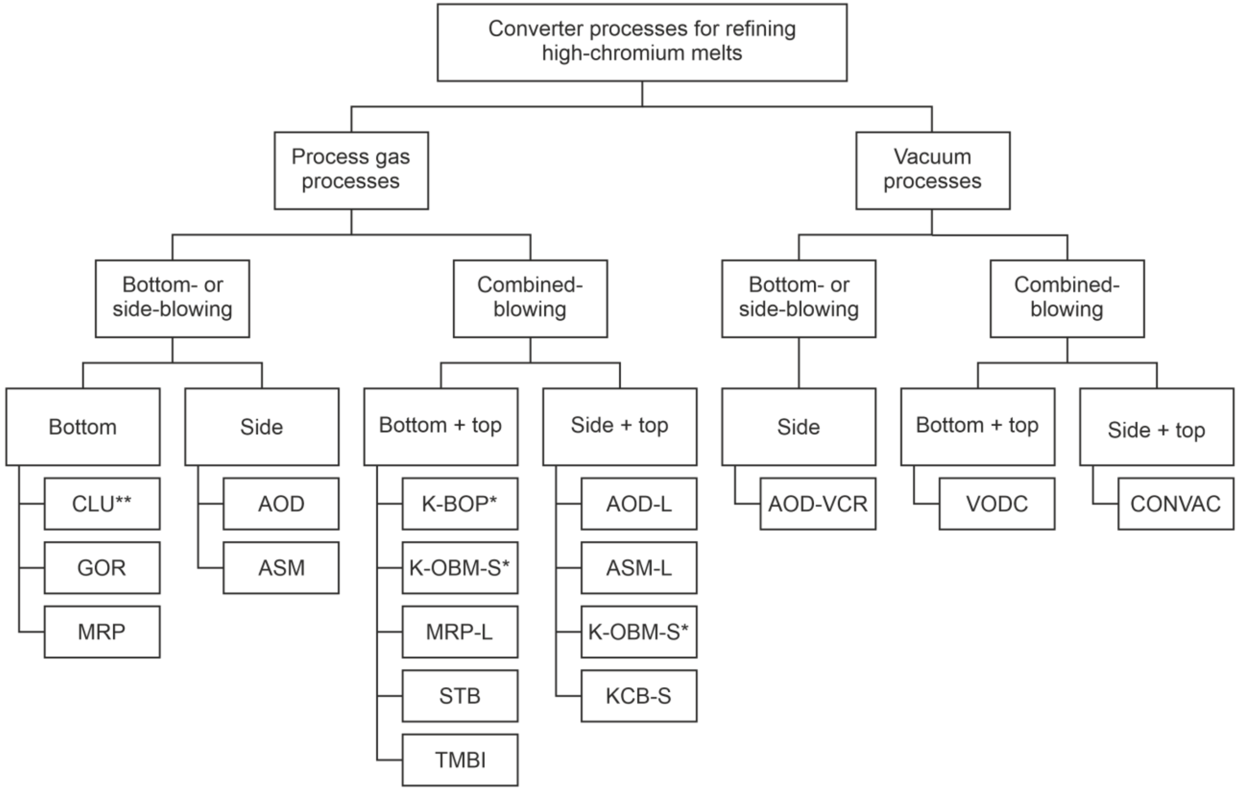
- The meltshop features two production lines based on the EAF-AOD duplex route.
- Production line 1 was commenced in 1976 and has a charge weight of 95 tons.
    - Features a 95-ton ferrochrome converter, which supplies refined ferrochrome and serves as a buffer.
    - The molten ferrochrome is mixed with the molten steel scrap from the EAF.
    - Decarburisation takes place in a 95-ton AOD.
- Production line 2 was commenced in 2002 and has a charge weight of 150 tons.
    - Operates a 150-ton AOD for decarburisation.



Introduction

Converter processes for stainless steels

- While the AOD process is the most common process for refining stainless steel, several other processes have also been developed.
- The converter processes for stainless steelmaking can be grouped based on the
  - **operating pressure** (atmosphere vs vacuum)
  - **mode of gas injection** (bottom, side, top or combinations)
- Some processes use hydrocarbons or steam alongside or instead of oxygen-inert mixtures.
- The competing processes have not become as widespread as the AOD process but have influenced its evolution.



- Converter processes for refining high-chromium melts
  - Process gas processes
    - Bottom- or side-blowing
      - Bottom
        - CLU**
        - GOR
        - MRP
      - Side
        - AOD
        - ASM
    - Combined-blowing
      - Bottom + top
        - K-BOP*
        - K-OBM-S*
        - MRP-L
        - STB
        - TMBI
      - Side + top
        - AOD-L
        - ASM-L
        - K-OBM-S*
        - KCB-S
  - Vacuum processes
    - Bottom- or side-blowing
      - Side
        - AOD-VCR
    - Combined-blowing
      - Bottom + top
        - VODC
      - Side + top
        - CONVAC

Categorisation of converter processes for refining high-chromium melts based on operating pressure and mode of gas injection.[1]
Processes involving the use of hydrocarbons (*) or steam (**) are also indicated.

Reference

[1] V.-V. Visuri & L. Holappa, Converter Steelmaking, Treatise in Process Metallurgy, forthcoming.

Introduction

Dilution and vacuum principles

- In the refining of stainless steel, oxygen is consumed primarily for the oxidation of carbon and chromium dissolved in the metal bath.
- The equilibrium of C and Cr can be described using the following endothermic overall reaction:

  $$3[\mathrm{C}] + (\mathrm{Cr_2O_3}) = 3\{\mathrm{CO}\} + 2[\mathrm{Cr}] \qquad (\Delta H^\circ > 0)$$

- At equilibrium, the reaction quotient is equal to the equilibrium constant:[1]

  $$\underbrace{\frac{p_{\mathrm{CO}}^3\left(a_{[\mathrm{Cr}]}^{\mathrm{H}}\right)^2}{\left(a_{[\mathrm{C}]}^{\mathrm{H}}\right)^3 a_{\mathrm{Cr_2O_3}}^{\mathrm{R}}}}_{\text{reaction quotient }(Q)} = \underset{\text{equilibrium constant }(K)}{\exp\left(-\frac{88704}{T} + 56.67\right)}$$

- The Henrian activity of carbon at equilibrium can be defined as follows:

  $$a_{[\mathrm{C}]}^{\mathrm{H}} = f_{[\mathrm{C}]}^{\mathrm{H}} \cdot [\%\mathrm{C}]_{\mathrm{eq}},$$

  where $f_{[\mathrm{C}]}^{\mathrm{H}}$ is the Henrian activity coefficient of carbon and $[\%\mathrm{C}]_{\mathrm{eq}}$ is the carbon content (in wt-%).
- Finally, the following expression can be derived for the equilibrium carbon content:

  $$[\%\mathrm{C}]_{\mathrm{eq}} = \left(\frac{p_{\mathrm{CO}}^3\left(a_{[\mathrm{Cr}]}^{\mathrm{H}}\right)^2}{\left(f_{[\mathrm{C}]}^{\mathrm{H}}\right)^3 a_{\mathrm{Cr_2O_3}}^{\mathrm{R}} \exp\left(-\frac{88704}{T} + 56.67\right)}\right)^{1/3}$$

Reference

[1] O. Wijk, in: T. A. Engh, *Principles of Metal Refining*, 1992, pp. 280–301.

Introduction

Dilution and vacuum principles (continued)

- The means to affect the equilibrium carbon content can be deduced from the equation given in the last slide:

$$[\%\mathrm{C}]_{\mathrm{eq}} = \left(\frac{p_{\mathrm{CO}}^{3} \left(a_{[\mathrm{Cr}]}^{\mathrm{H}}\right)^{2}}{\left(f_{[\mathrm{C}]}^{\mathrm{H}}\right)^{3} a_{\mathrm{Cr_2O_3}}^{\mathrm{R}} \exp\left(-\frac{88704}{T} + 56.67\right)} \right)^{1/3}$$

- Decarburisation is favoured by
  low p_{CO} and $a_{[\mathrm{Cr}]}^{\mathrm{H}}$
  high $f_{[\mathrm{C}]}^{\mathrm{H}}$, $a_{\mathrm{Cr_2O_3}}^{\mathrm{R}}$ and T
- The strongest effect is achieved by decreasing the partial pressure of CO.
  - **Dilution principle**: diluting the blowing mixture using inert gases.
  - **Vacuum principle**: using vacuum conditions.

Means to favour the decarburisation of stainless steels.

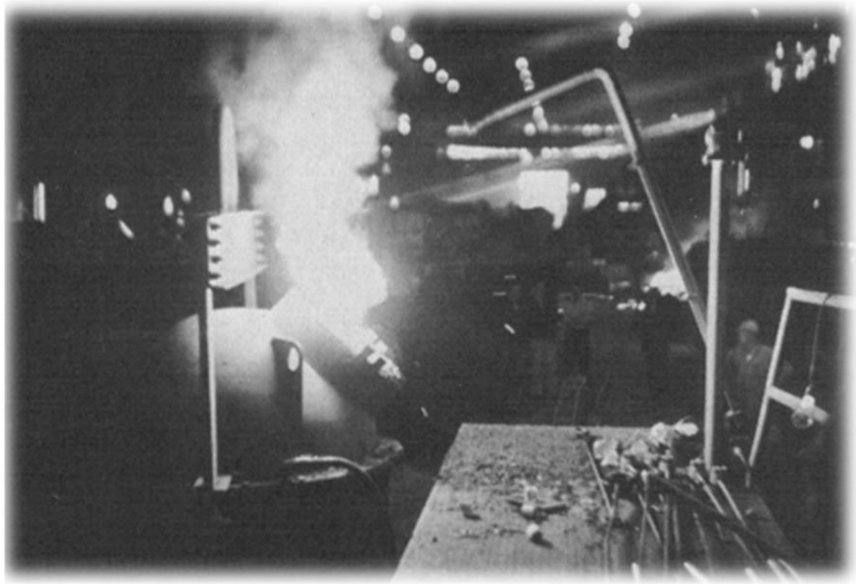
Contributing factor	Practical means to influence
Low partial pressure of CO	Dilution of blowing mixture with inert gases (*dilution principle*) Lowering of total gas pressure (*vacuum principle*)
Low activity of Cr	Limited
High activity coefficient of C	Limited
High activity of Cr_2O_3	Addition of lime to decrease the solubility of Cr_2O_3 in slag
High temperature	Increase operating temperature

AOD process

Dr. William A. Krivsky.[1]

Invention

- The basic principle of the argon-oxygen decarburisation (AOD) process was invented by Union Carbide in the 1950s.
- After substantial initial difficulties, the first full heat was produced at Joslyn Stainless Steel Company in 1967 with industrial operation starting in 1969.
- The main idea was to lower the partial pressure of CO with argon to reduce the oxidation of chromium and other alloying elements (*dilution principle*).
- The AOD process made the old practice of melting and refining in the EAF obsolete almost overnight and was adopted rapidly around the world from the 1970s onwards.



First 15-ton AOD vessel, which produced the first full heat at Joslyn Stainless Steel Company in 1967.[1]

Reference

[1] W. A. Krivsky, *Metall. Trans.*, 4(6): 439–1447, 1973.

AOD process

Benefits over the old EAF practice

- In comparison to refining in the EAF process, the AOD process enabled several advantages:[1]
  - higher refining rate
  - lower chromium losses, which eliminated the need to add low-C FeCr after refining
  - increased meltshop output due to the separation of melting and refining steps
  - higher predictability
  - high steel cleanliness
  - relatively low sulfur content
  - ability to use inexpensive charge materials.

Comparison of the EAF and AOD methods.[2]

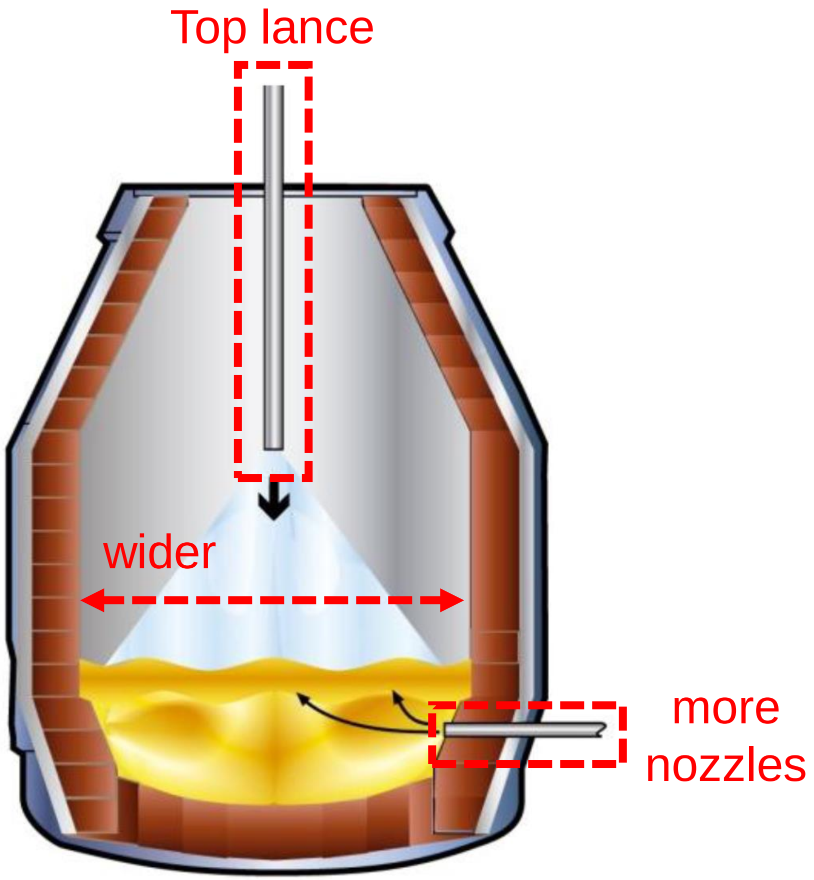
Step	"Conventional" EAF method	"New" AOD method
Charging	Melt charge in EAF 4 wt-% Cr charge normal; less Cr charged for extra low carbon (ELC) grades	Melt charge in EAF a) 18 wt-% Cr charged even for ELC grades b) deslag melted charge transfer charge; to AOD vessel
Decarburisation	Lance with oxygen; end point 3300 °F (1815 °C) 2 wt-% Cr 0.02 wt-% C	Blow with oxygen-argon mixture; end point 3100 °F (1705 °C) 17 wt-% Cr 0.03 wt-% C
Reduction	Recover ½ of Cr (1 wt-%) in slag with FeCrSi or FeSi addition.	Recover 0.75 wt-% Cr from slag. Pure argon injection.
Alloying	Add 15 to 17 wt-% Cr as low carbon FeCr to final specification Final composition 18.5 wt-% Cr 0.02 wt-% C	No low carbon FeCr addition necessary. Final composition 18.5 wt-% Cr 0.01 wt-% C

References
[1] V.-V. Visuri and L. Holappa, in *Treatise in Process Metallurgy*, forthcoming.
[2] W.A. Krivsky, *Metall. Trans.*, 4(6): 439–1447, 1973.

AOD process

Evolution of the AOD process

- Over the years, several improvements have been made to the original concept.
  - Increasing the number of nozzles in the sidewall.
  - Improved nozzle positioning.
  - Introduction of a top lance.
  - Wider vessel geometry.
  - Use of nitrogen as a cheap alternative for argon.
  - Single slag practice.
  - Vacuum lids.
  - Modern control methods.



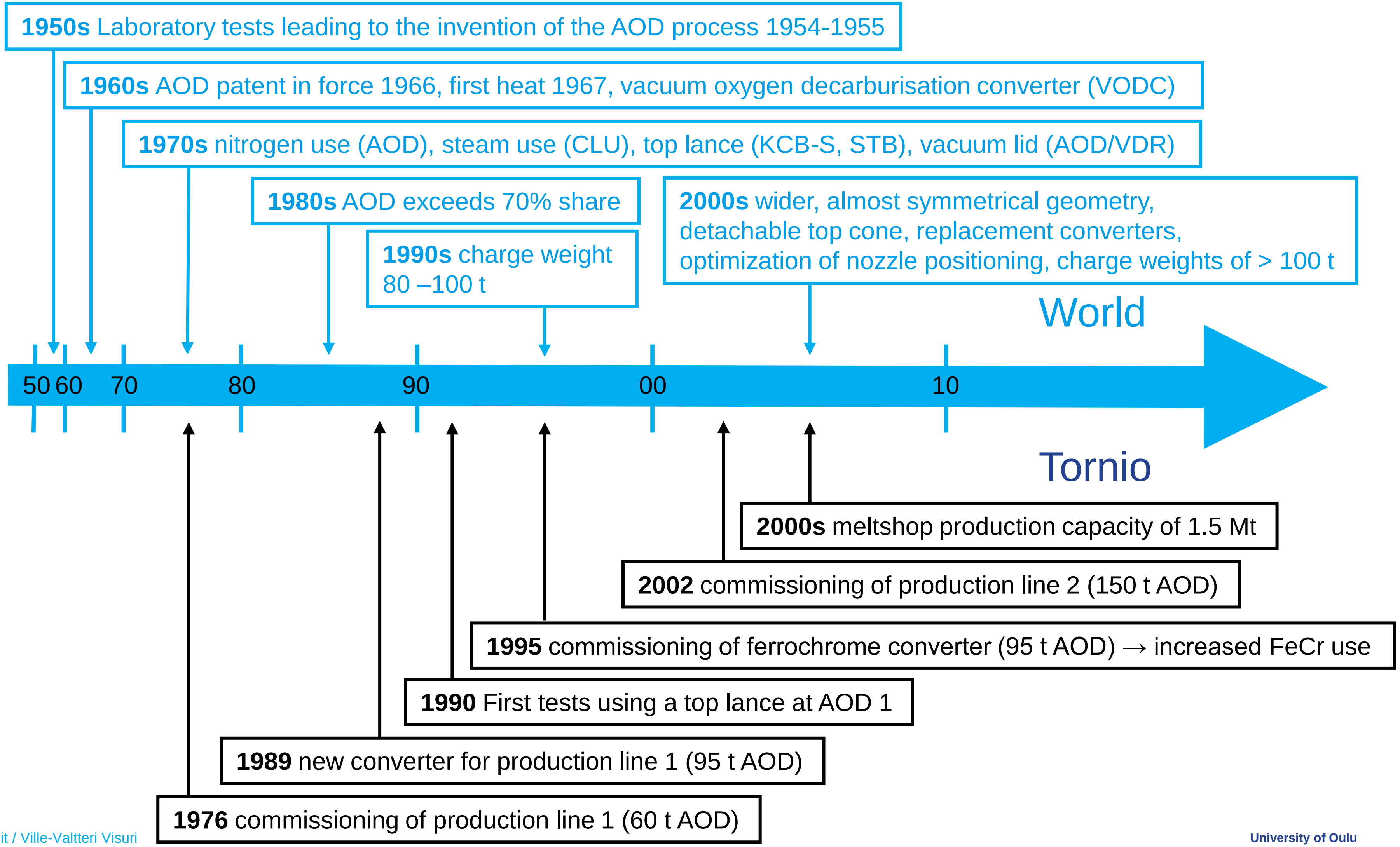
Schematic illustration of a modern AOD vessel.[1]

Reference
[1] Teräskirja

AOD process

Timeline of the AOD process at Tornio

- AOD was chosen as the basis for production line 1 commissioned in 1976.
- This turned out to be a very good decision as the AOD soon established itself as the dominating process for refining of stainless steel.
- A significant increase in production capacity was brought about by the commissioning of production line 2 in 2002.



1950s Laboratory tests leading to the invention of the AOD process 1954-1955

1960s AOD patent in force 1966, first heat 1967, vacuum oxygen decarburisation converter (VODC)

1970s nitrogen use (AOD), steam use (CLU), top lance (KCB-S, STB), vacuum lid (AOD/VDR)

1980s AOD exceeds 70% share

1990s charge weight 80 –100 t

2000s wider, almost symmetrical geometry, detachable top cone, replacement converters, optimization of nozzle positioning, charge weights of > 100 t

2000s meltshop production capacity of 1.5 Mt

2002 commissioning of production line 2 (150 t AOD)

1995 commissioning of ferrochrome converter (95 t AOD) → increased FeCr use

1990 First tests using a top lance at AOD 1

1989 new converter for production line 1 (95 t AOD)

1976 commissioning of production line 1 (60 t AOD)

AOD process

Production line 1: AOD 1

Supplier	MAN GHH
Charge weight	95 tons
Total weight	160 tons
Gas injection system	Five nozzles + supersonic top lance
Max. gas injection rate	170 Nm^3/min
Heats per day	20

Production line 2: AOD 2

Supplier	Voest-Alpine Industrieanlagenbau
Charge weight	150 tons
Total weight	250 tons
Gas injection system	Seven nozzles + supersonic top lance
Max. gas injection rate	300 Nm^3/min
Heats per day	20

AOD process

Charge materials and consumables

− Charge materials	EAF melt and slag
− Process gases	e.g. oxygen or argon
− Material additions	
▪ scrap	e.g. low carbon steel
▪ ferroalloys	e.g. FeMn, FeNi
▪ slag formers	e.g. lime, dolomitic lime
▪ fluxes	e.g. fluorspar
▪ reductants	e.g. FeSi or Al
− Refractories	e.g. doloma or MgO-C

Typically, the main cost factors are tap-to-tap time, chromium yield, refractory wear and argon use.

Typical consumptions of an 80-ton AOD making AISI 304.[1]

Material	Units	Typical	Best
Argon	Nm^3/ton	12	9
Nitrogen	Nm^3/ton	9–11	9
Oxygen	Nm^3/ton	25–32	NA
Lime	kg/ton	50–60	42
Fluorspar	kg/ton	3	2
Aluminum	kg/ton	2	1
Silicon (reduction)	kg/ton	8–9	6
Brick	kg/ton	5–9	2
Decarburisation metallics	kg/ton	135	NA
Charge to tap time	min	50–80	40
Total Cr yield	%EAF/AOD	96–97	99.5
Total Mn yield	%EAF/AOD	88	95
Total metallic yield	%EAF/AOD	95	97

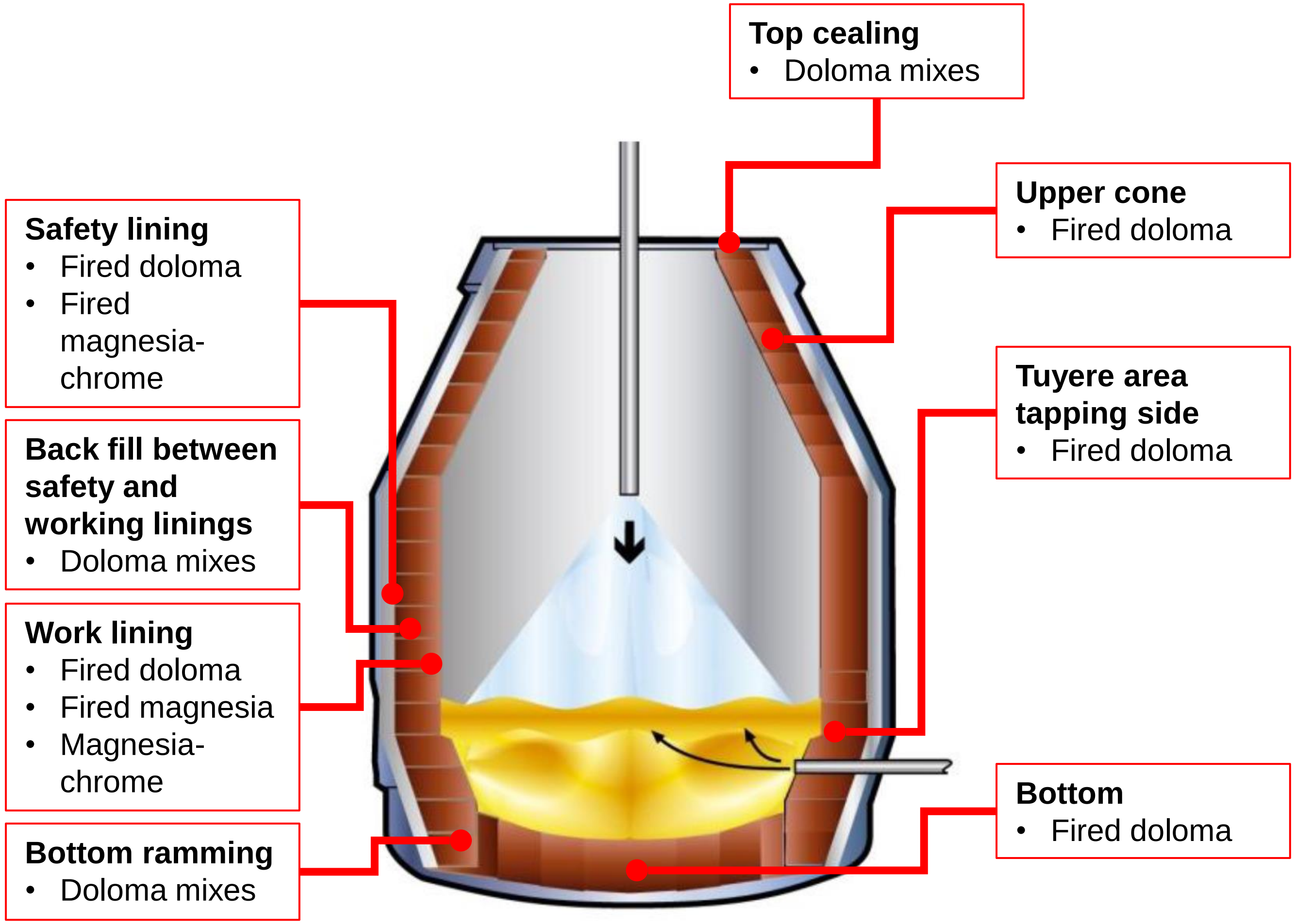
Reference

[1] B.V. Patil, A.H. Chan, and R.J. Choulet, in: *The Making, Shaping and Treating of Steel. 11th Edition Steel Making and Refining*, pp. 715–741, 1998.

AOD process

Refractories

- The AOD process is characterised by the high refractory wear caused by turbulent flows, thermal cycling and corrosive reduction slag.
- Typical refractory materials.[1]
  - Fired doloma bricks
  - Fired magnesia bricks
  - Fired magnesia-chrome bricks
- Higher quality materials are used for areas of highest wear (tuyere wall and slag line).[1]
- Typical lifetimes for doloma refractories are around 120–170 heats.[2]



Top cealing
- Doloma mixes

Upper cone
- Fired doloma

Tuyere area tapping side
- Fired doloma

Bottom
- Fired doloma

Safety lining
- Fired doloma
- Fired magnesia-chrome

Back fill between safety and working linings
- Doloma mixes

Work lining
- Fired doloma
- Fired magnesia
- Magnesia-chrome

Bottom ramming
- Doloma mixes

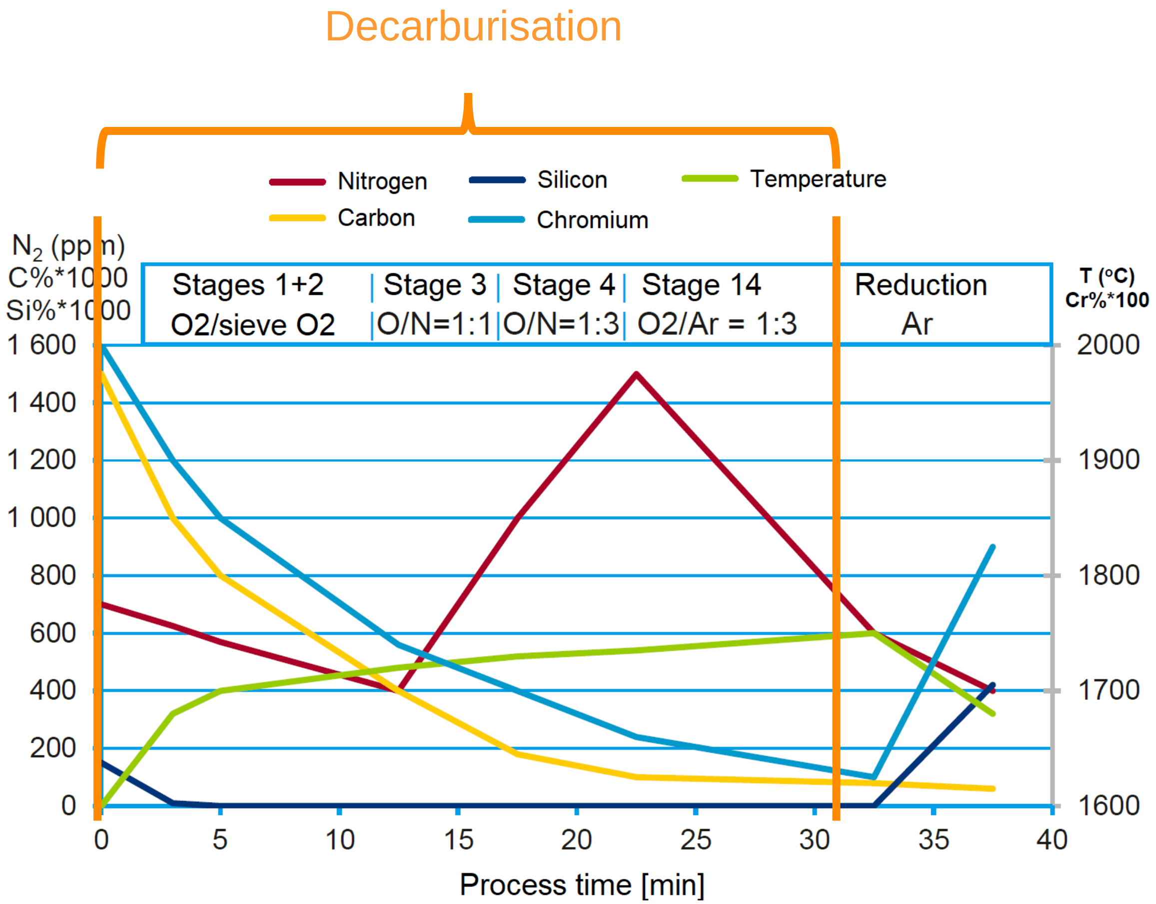
Schematic illustration refractory types based on Refs.[1,2]. AOD schematic taken from Ref.[3].

References
[1] M. Oberbach and G. Schmeiduch, in *Elektrostahlerzeugung*, pp. 115–162, 1997.
[2] G. Staudinger and S. Dimitrov, in: *Proceedings of the AISTech2007*, 2007.
[3] Teräskirja

AOD process

Process stages

- **In the decarburisation stage**, oxygen is blown into the melt to oxidise carbon down to specification.
  - Typical duration of 20 to 35 minutes.
  - Several stages with different oxygen-inert ratios.
  - In combined blowing vessels, the top lance is used typically only in the high carbon regime.
  - Si burns fast during the first minutes, after which the oxygen is consumed mainly by C and Cr.
  - By the end of the decarburisation, the bath temperature rises to 1750 °C.

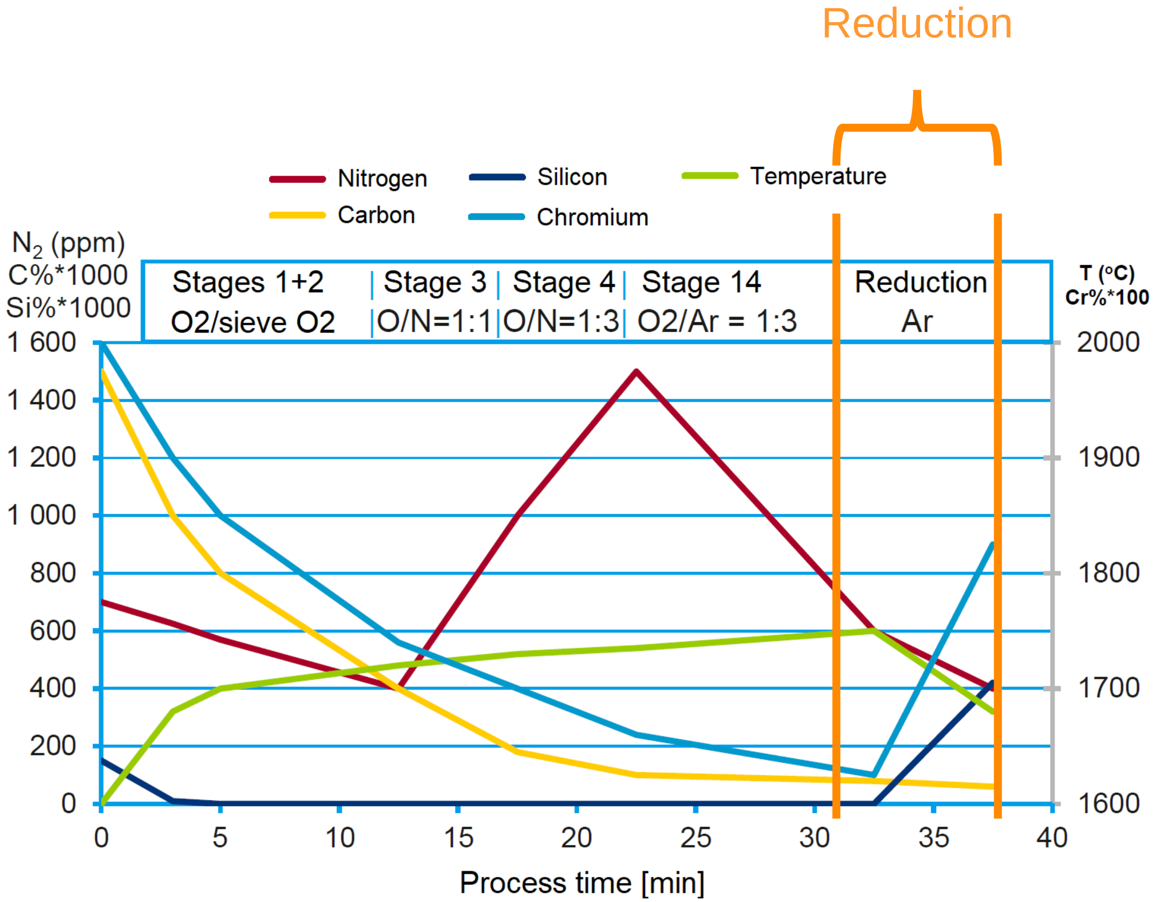


Typical evolution of bath composition in the production of austenitic grades at AOD 2.

AOD process

Process stages (continued)

- **In the reduction stage**, the oxidised alloying elements are reduced back to metal.
  - Typical duration of 5 to 8 minutes.
  - Typical reductants: FeSi and/or Al.
  - Slag formers are added to adjust the basicity of the slag.
  - Argon-stirring and fluxes are used to promote the metal-slag kinetics.



Typical evolution of bath composition in the production of austenitic grades at AOD 2.

AOD process

Decarburisation stage: chemical reactions

- Oxygen is used primarily for the oxidation of C and Cr, but Mn and Si are oxidised as well.
  - The main oxidation reactions are strongly exothermic.
  - The heat released by the oxidation of silicon is much stronger than that of other species.
- Scrap can be added to cool the metal bath.
- If necessary, it is possible to heat-up up the metal bath using FeSi additions in combination with oxygen blowing.

Heats of formation for various oxides.[1]

Reaction	Δ*H* [kJ/mol]	Δ*T* per 1% of oxidised element [°C]
$[\mathrm{C}] + \frac{1}{2}\{\mathrm{O_2}\} \rightleftharpoons \{\mathrm{CO}\}$	–139.8	109
$\mathrm{Fe_{(l)}} + \frac{1}{2}\{\mathrm{O_2}\} \rightleftharpoons (\mathrm{FeO})$	–256.3	46
$2[\mathrm{Cr}] + \frac{3}{2}\{\mathrm{O_2}\} \rightleftharpoons (\mathrm{Cr_2O_3})$	–1141.6	108
$[\mathrm{Mn}] + \frac{1}{2}\{\mathrm{O_2}\} \rightleftharpoons (\mathrm{MnO})$	–404.3	74
$[\mathrm{Si}] + \{\mathrm{O_2}\} \rightleftharpoons (\mathrm{SiO_2})$	–825.9	333

Reference

[1] O. Wijk, in: T. A. Engh, *Principles of Metal Refining*, 1992, pp. 280–301.

AOD process

Decarburisation stage: kinetics

- The direct oxidation of carbon takes place via

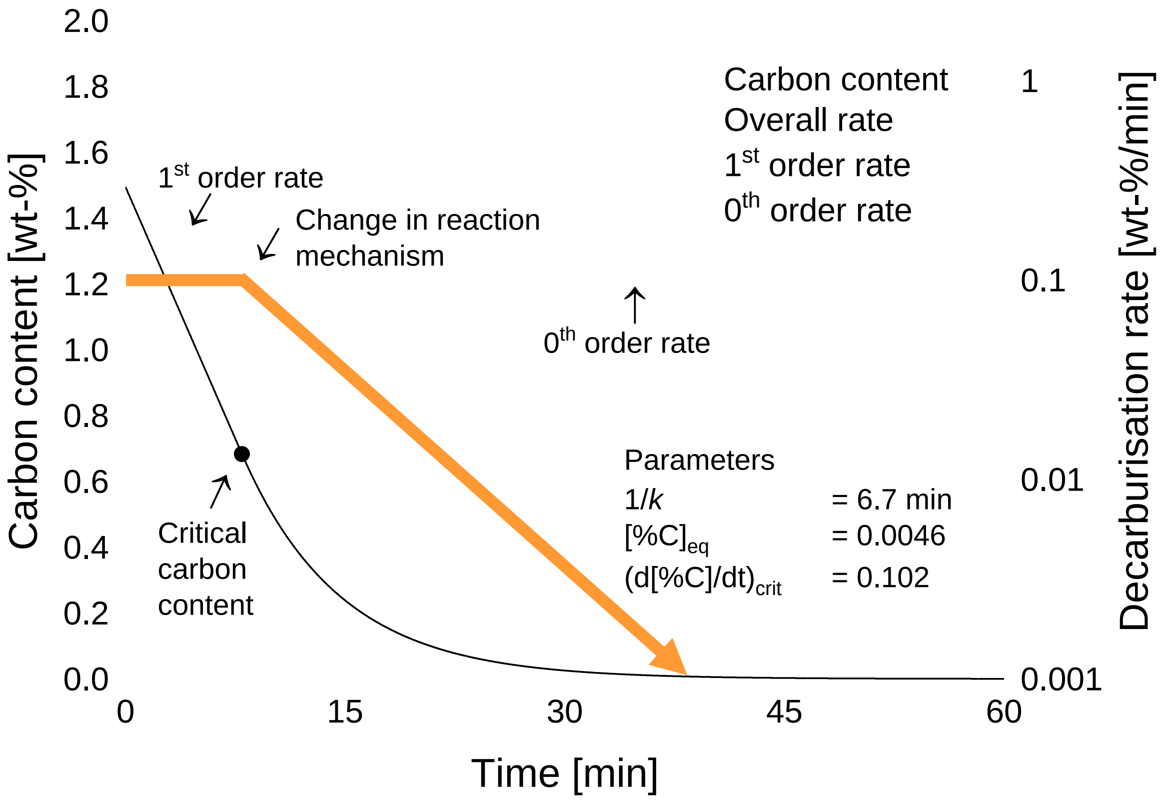
$$[\mathrm{C}] + \frac{1}{2}\{\mathrm{O}_2\} = \{\mathrm{CO}\}.$$

- At high carbon contents, the decarburisation rate is limited by the oxygen supply:

$$\frac{\mathrm{d}[\%\mathrm{C}]}{\mathrm{d}t} = -\alpha \cdot \underbrace{\left(\frac{100}{m_\mathrm{L}}\frac{2M_\mathrm{C}}{M_{\mathrm{O}_2}}\dot{m}_{\mathrm{O}_2}\right)}_{\substack{\text{stoichiometric}\\ \text{carbon removal}}} \qquad \text{(0th order).}$$

- At the **critical carbon content**, the decarburisation rate becomes limited by the mass transfer of carbon in the metal bath:

$$\frac{\mathrm{d}[\%\mathrm{C}]}{\mathrm{d}t} = -k\left([\%\mathrm{C}] - [\%\mathrm{C}]_\mathrm{eq}\right) \qquad \text{(1st order).}$$



An example of the decarburisation kinetics in the AOD process. Parameters from Reichel and Szekely[1].

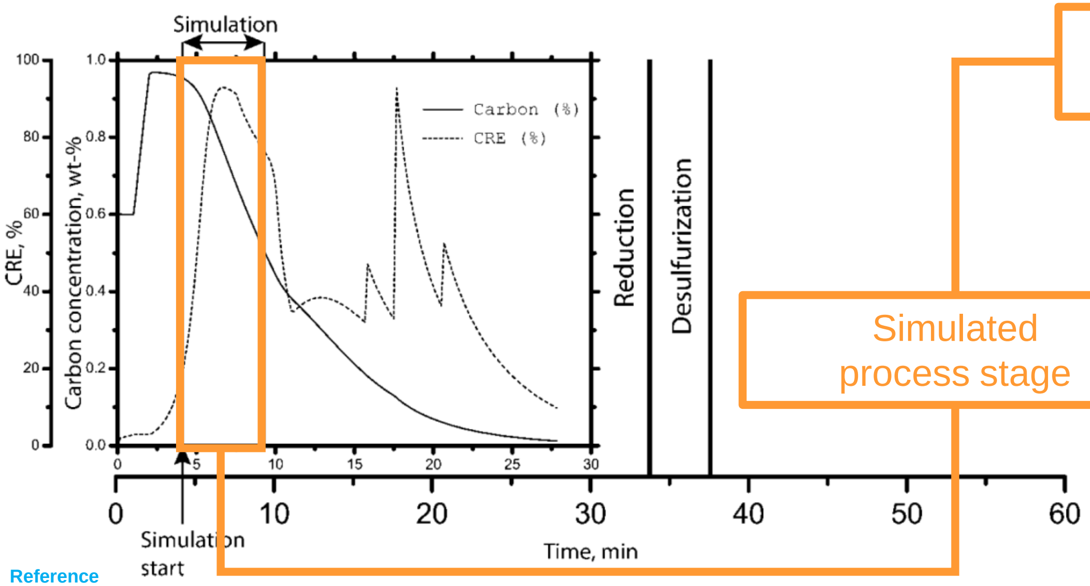
Reference

[1] J. Reichel and J. Szekely, *Iron Steelmaker*, 22(5): 41–48, 1995.

AOD process

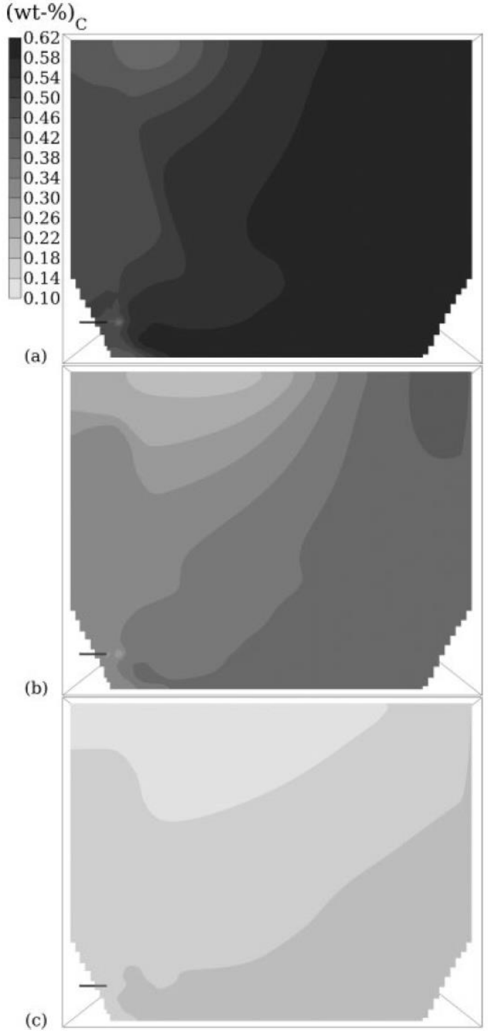
Decarburisation stage: kinetics

- In recent years, simulation tools have been developed to study the local decarburisation rates in the AOD process.
- **Example**: model by Andersson et al.[1].



Simulated process stage

Carbon content in the metal bath



1 min

3 min

6 min

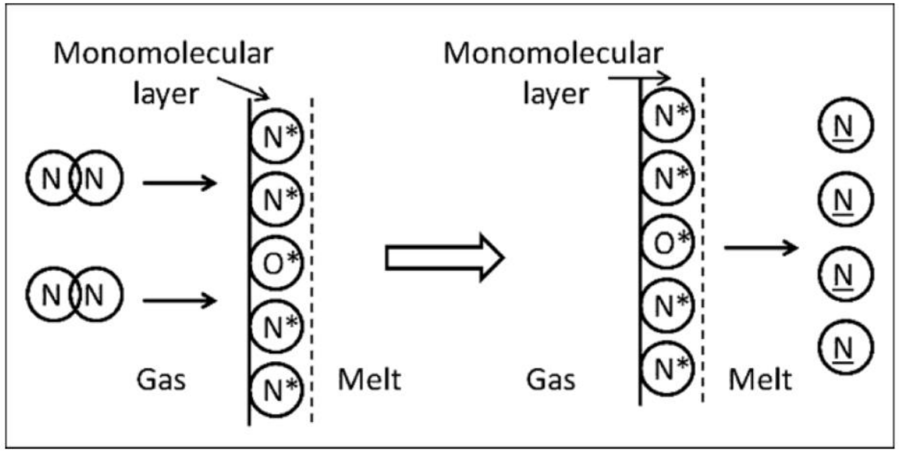
Reference

[1] N.Å.I. Andersson, A. Tilliander, L.T.I. Jonsson and P.G. Jönsson, *Ironmaking Steelmaking*, 40(5): 390–397, 2013

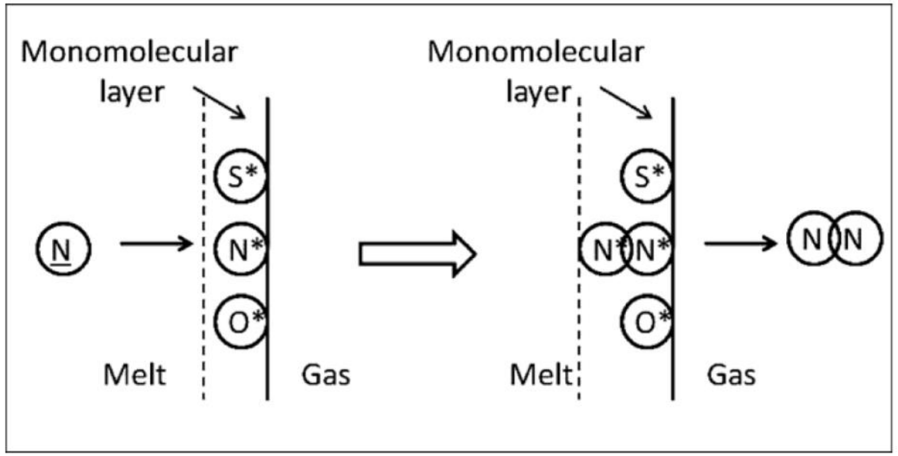
AOD process

Decarburisation stage: nitrification

- The use of nitrogen as an inexpensive substitute for argon is commonplace.
  - The downside is that some nitrogen inevitably dissolves into the steel and may deteriorate its properties.
  - Nitrogen control is thus important.
- Two nitrification mechanisms:[1]
  - First stages: dual-site mechanism (absorption)
  - Last stages: single-site mechanism (desorption)
- Generally, top-blown nitrogen induces much less nitrification than side-blown nitrogen.[2]
  - The differences can be attributed to the lower total pressure at the bath surface.



Absorption of nitrogen by dual-site mechanism.[1]



Desorption of nitrogen by single-site mechanism.[1]

References
[1] J. Riipi, T. Fabritius, E.-P. Heikkinen, P. Kupari, and A. Kärnä, *ISIJ Int.*, 49(10): 1468–1473, 2009.
[2] P.R. Scheller and F.-J. Wahlers, *ISIJ Int.*, 36(Supplement): S69–S72, 1996.

AOD process

Decarburisation stage: slag practice

- Main objectives of the slag practice during the decarburisation stage:
  - ensuring compatibility with employed refractory lining, and
  - minimising chromium oxide stability in the slag by using solid slag practice.
- The basicity is adjusted using basic slag formers, e.g. lime.
- The slag former additions amount typically to 3–7% of total bath weight.[1]

Basicity ratios for decarburisation slags. Adapted from Ref.[2]

Basic oxide addition	Minimum basicity ratios for refractory compatibility	Recommended basicity ratios for solid slag practice
Typical steel grades (low Al_2O_3 and Nb_2O_5)		
Lime addition only	$\frac{\%CaO}{\%SiO_2} \leq 1.6$	$\frac{\%CaO}{\%SiO_2} \leq 2.0$
Doloma or doloma/lime	$\frac{\%CaO + \%MgO}{\%SiO_2} \leq 2.0$	$\frac{\%CaO}{\%SiO_2} \leq 2.0$ or $\frac{\%CaO + \%MgO}{\%SiO_2} \leq 3.33$
Special steel grades (high Al_2O_3 and Nb_2O_5)		
Doloma or doloma/lime	$\frac{\%CaO + \%MgO)}{\%SiO_2 + \%Al_2O_3 + \%Nb_2O_5} \leq 2.0$	$\frac{\%CaO + \%MgO)}{\%SiO_2 + \%Al_2O_3 + \%Nb_2O_5} \leq 3.33$

Note: all contents are given in weight-percent.

References

[1] B.V. Patil, A.H. Chan, and R.J. Choulet, in: *The Making, Shaping and Treating of Steel. 11th Edition Steel Making and Refining*, pp. 715–741, 1998.

[2] E.B. Pretorius and R.C. Nunnington, *Ironmaking Steelmaking* 29(2): 133–139, 2002.

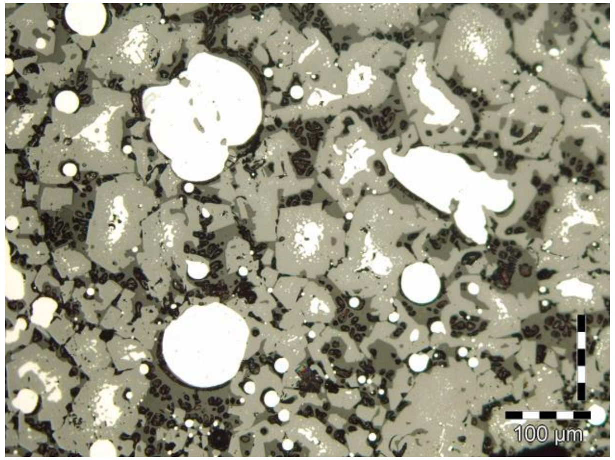
AOD process

Decarburisation stage: slag samples

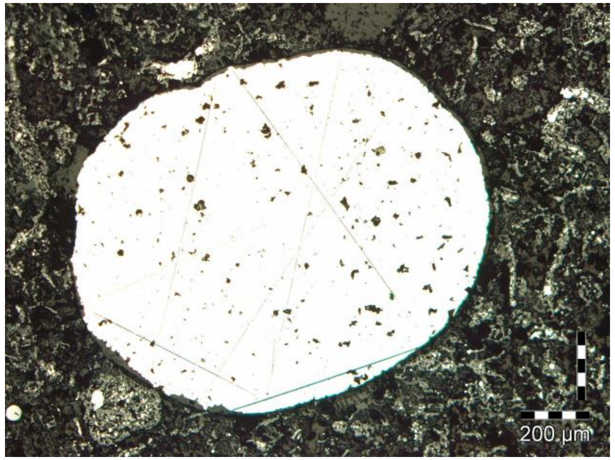
- Decarburisation slags are very stiff and difficult to take samples from.
- The slag samples typically contain a lot of entrapped metal droplets.[1]
  - These are roughly 0.1 to 5 mm in diameter.[1]
  - The carbon content of the metal droplets found from slag samples taken after the combined-blowing decarburisation stage is much lower than that of the metal bath.[2]
- The slag samples may also contain undissolved lime particles covered by a solid shell.
  - It has been suggested that the shell is calcium silicate.[2]


Decarburisation slag (stage 12)


Lime particle (stage 13).



Metal droplets in a cross-section of decarburisation slag sample.[1]



Close-up of a spherical droplet in a decarburisation slag samples.[3]

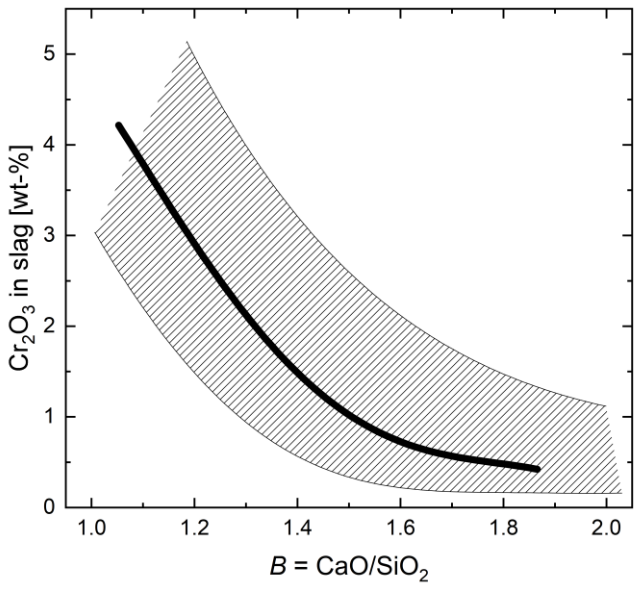
References

[1] V.-V. Visuri, *doctoral thesis*, University of Oulu, 2017.
[2] W. Rubens, *doctoral thesis*, Technical University of Clausthal, 1989.
[3] V.-V. Visuri, M. Järvinen, A. Kärnä, P. Sulasalmi, E.-P. Heikkinen, P. Kupari, and T. Fabritius, *Metall. Mater. Trans. B*, 48(3): 1850–1867, 2017.

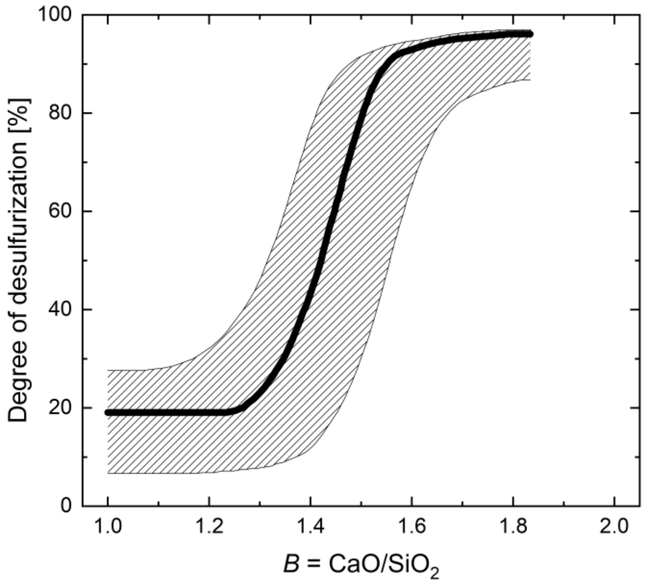
AOD process

Reduction stage: basicity of slag

- In the reduction stage, the slag practice aims to provide advantageous thermodynamic and kinetic conditions for metal-slag reactions.
- The basicity of the slag affects the efficiency of the reduction of slag and desulfurisation.
  - The basicity is adjusted primarily using lime and dolomite lime additions.
  - A residual Cr_2O_3 content of around 0.5 wt-% and a desulfurisation degree of >90% are achievable.[1]



Slag basicity vs. Cr_2O_3 content of the slag after the reduction stage.[1] Taken from Ref.[2].



Slag basicity vs. degree of desulfurisation after the reduction stage[1]. Taken from Ref.[2].

References

[1] K.-H. Heinen, B. Steffes, H. Zörcher, Sekundärmetallurgie, in: K.-H. Heinen (Ed.), Elektrostahlerzeugung, Verlag Stahleisen GmbH, Düsseldorf, Germany, pp. 513–571, 1997.

[2] V.-V. Visuri & L. Holappa, Converter Steelmaking, Treatise in Process Metallurgy, forthcoming

AOD process

Reduction stage: slag practice

- Nowadays, it is commonplace to use a **single-slag practice**.
  - Desulfurisation is conducted in conjunction with the reduction of slag.
  - Enables a faster tap-to-tap time.
  - Final sulfur contents in the range of 0.001–0.005 wt-% (10–50 ppm) are attainable.[1]
- The old **two-slag practice** is still used in the production of steel grades with low sulfur and oxygen aims.
  - Separate reduction and desulfurisation slags.
  - Suitable for grades that are susceptible to cracking.
  - Final sulfur contents of 0.001 wt-% (10 ppm) or less are achievable.[1]

Reference

[1] B.V. Patil, A.H. Chan, and R.J. Choulet, in: *The Making, Shaping and Treating of Steel. 11th Edition Steel Making and Refining*, pp. 715–741, 1998.

AOD process

Reduction stage: thermodynamics of FeSi reduction

- For FeSi-based reduction, the main reduction reaction is the reduction of Cr_2O_3 by Si:

$$(\mathrm{Cr_2O_3}) + \frac{3}{2}[\mathrm{Si}] \rightleftharpoons 2[\mathrm{Cr}] + \frac{3}{2}(\mathrm{SiO_2}) \qquad (\Delta H > 0)$$

- The corresponding equilibrium constant is given by:

$$K = \frac{\left(a^{\mathrm{H}}_{[\mathrm{Cr}]}\right)^2 \left(a^{\mathrm{R}}_{(\mathrm{SiO_2})}\right)^{3/2}}{a^{\mathrm{R}}_{(\mathrm{Cr_2O_3})} \left(a^{\mathrm{H}}_{[\mathrm{Si}]}\right)^{3/2}}$$

- The reduction is thus favoured by
  - a lower activity of SiO_2,
  - a higher activity of Si, and
  - a higher temperature.

Typical AOD slags at desulfurisation after FeSi and Al reduction.[1]

Type of reduction	Al_2O_3	CaO	Cr_2O_3	FeO	MgO	SiO_2
Al	30–35	50–55	0–2	0–1	5–10	5–8
FeSi	1–4	47–52	0–2	0–1	5–10	30–35

Reference

[1] M. Görnerup & P. Sjöberg, *Ironmaking Steelmaking*, 26(1): 58–63, 1999.

AOD process

Reduction stage: thermodynamics of desulfurisation

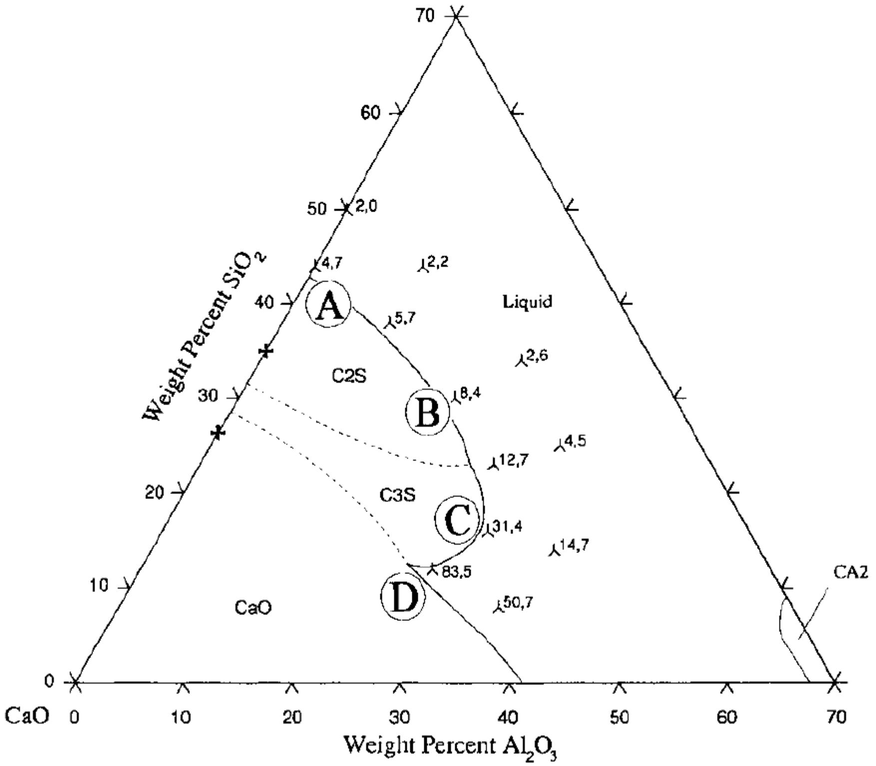
- Sulfur partition ratio describes the distribution of sulfur between slag and metal.[1]

$$L_S = \frac{(\%S)}{[\%S]} = \frac{\text{sulfur in slag (wt} - \%)}{\text{sulfur in metal (wt} - \%)}$$

$$\log_{10} L_S = -\frac{935}{T} + 1.375 + \log_{10} C_S + \log_{10} f^{H}_{[S]} - \log_{10} a^{H}_{[O]}$$

where T is the temperature, C_S is the sulfide capacity of the slag, $f^{H}_{[S]}$ is the Henrian activity coefficient of sulfur, and $a^{H}_{[O]}$ is the Henrian activity of oxygen.

- The activity of oxygen is lower for Al-based reduction than for FeSi-based reduction.
  - This is due to the higher oxygen affinity of Al in comparison to Si.



CaO corner of CaO–SiO$_2$–Al$_2$O$_3$ system with measured C_S values at 1600°C.[1]

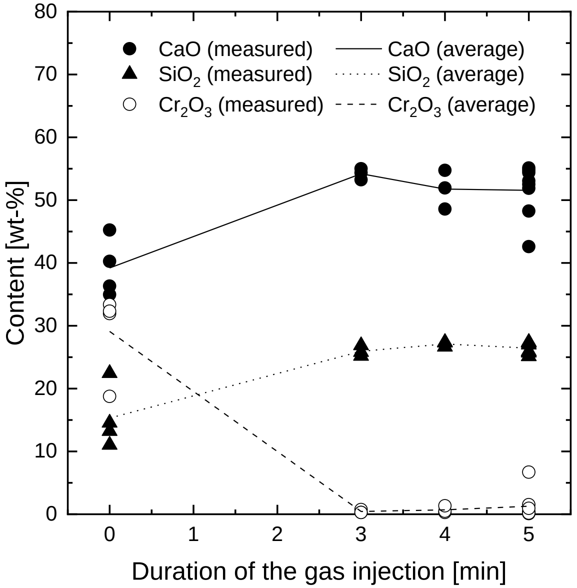
Reference

[1] M. Görnerup & P. Sjöberg, *Ironmaking Steelmaking*, 26(1): 58–63, 1999.

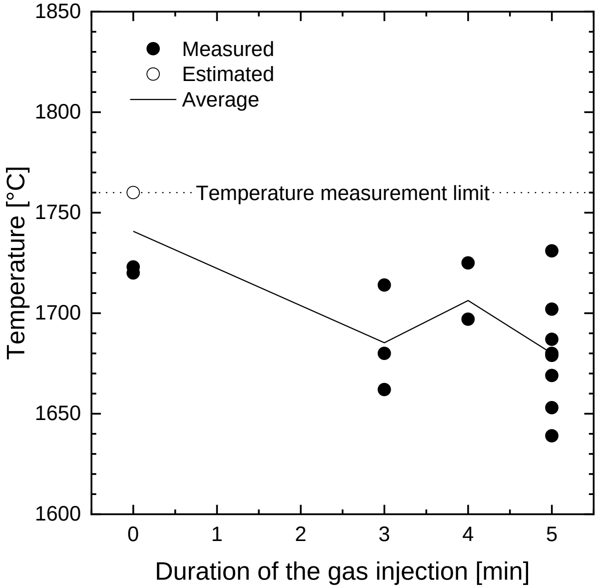
AOD process

Reduction stage: kinetics

- The reduction stage is characterised by a dramatic change of slag properties and composition in a short time.
  - The Cr_2O_3 content decreases from around 30–40 wt-% to around 1 wt-%.
  - The slag becomes visually fully liquid.
- It has been suggested that most of the reduction of Cr_2O_3 takes place within the three first minutes.[1]
  - Also sulphur is removed very fast.[1]
  - However, the nitrogen content decreases until the end of the reduction stage.[1]



Changes in slag composition.[1]



Changes in bath temperature.[1]

Reference

[1] V.-V. Visuri, E.-P. Heikkinen, and T. Fabritius, *Proc. 9th International Conference on Modeling and Simulation of Metallurgical Processes in Steelmaking*, 2021.

AOD process

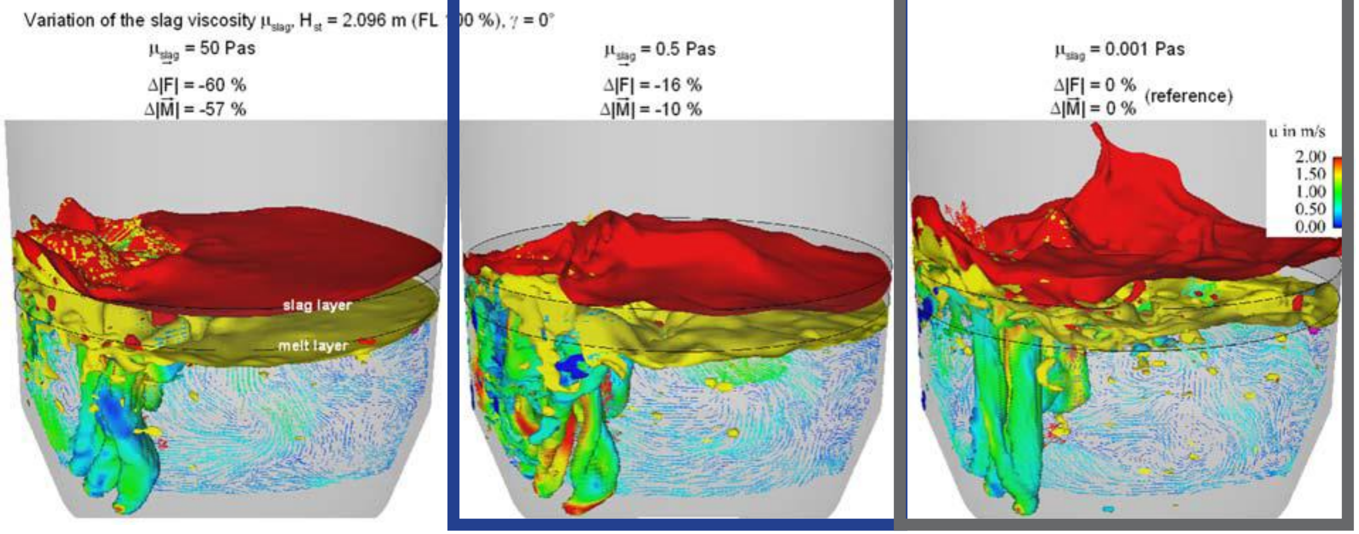
Reduction stage: fluid mechanics

- Reductants are charged into the vessel at the beginning of the reduction stage.
- The metal bath is stirred vigorously with argon throughout the reduction stage.
    - Provides a reducing atmosphere.
    - Causes emulsification of slag, thereby increasing the metal-slag interfacial area.
    - Helps to disperse reductants.
- Fluxes such as fluorspar (CaF_2) are added to lower the viscosity and increase the liquid fraction of slag.
    - The decrease in viscosity leads to more violent bath movements.

Expected conditions in the reduction stage

Beginning

End



Fluid flow field in the reduction stage of the AOD process.[1]

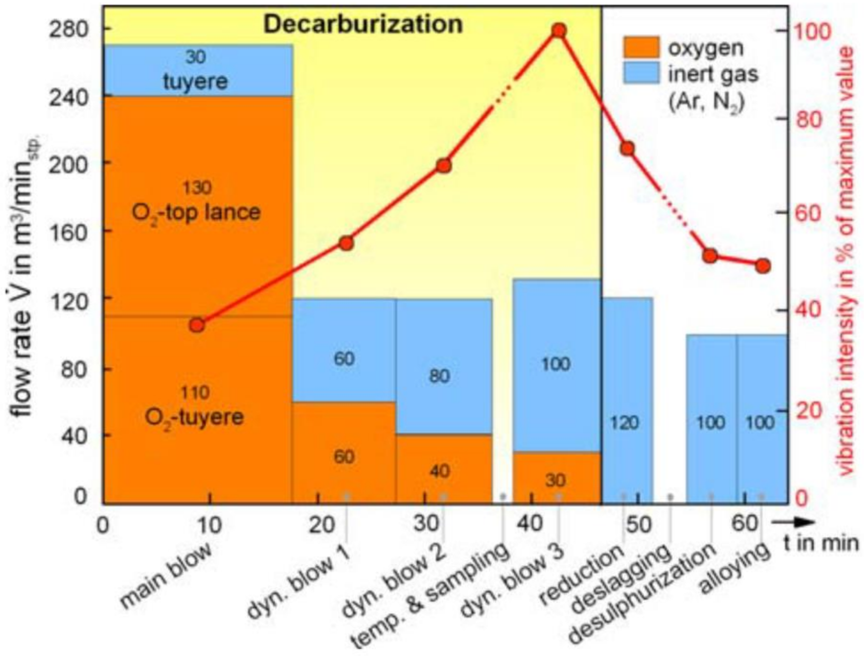
Reference

[1] H.-J. Odenthal, U. Thiedemann, U. Falkenreck, and J. Schlueter., *Metall. Mater. Trans. B*, 41(2): 396–413, 2010.

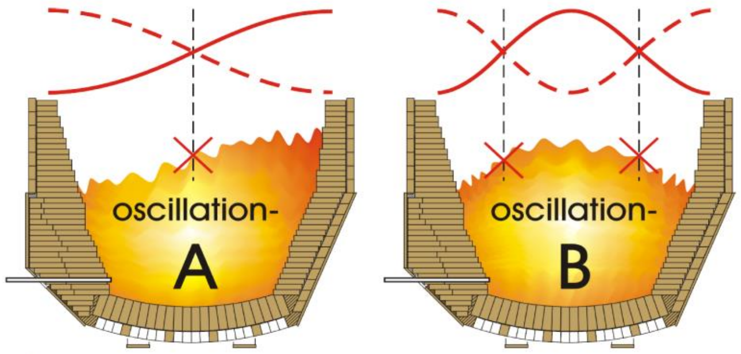
AOD process

Vessel vibration and bath oscillation

- The vibration of the vessel affects the wear of the tilting drive and support structure.
  - The highest vibration intensity is experienced at the end of the decarburisation stage.[1,2]
  - The vibration intensity in the reduction stage is also relatively high.[1,2]
- The wavelength of bath oscillation affects the vessel vibration and stresses.[2]
  - AOD converters have a natural bath oscillation frequency that depends mainly on the vessel geometry.[3]
  - Type A bath oscillation takes place at high gas injection rates typical for the AOD process.[2]



Blowing pattern of a 120-ton AOD converter with characteristic vibration intensity levels.[1]



Two types of bath oscillation in a 1:9 scale physical model of a 150-ton AOD converter.[2]

References

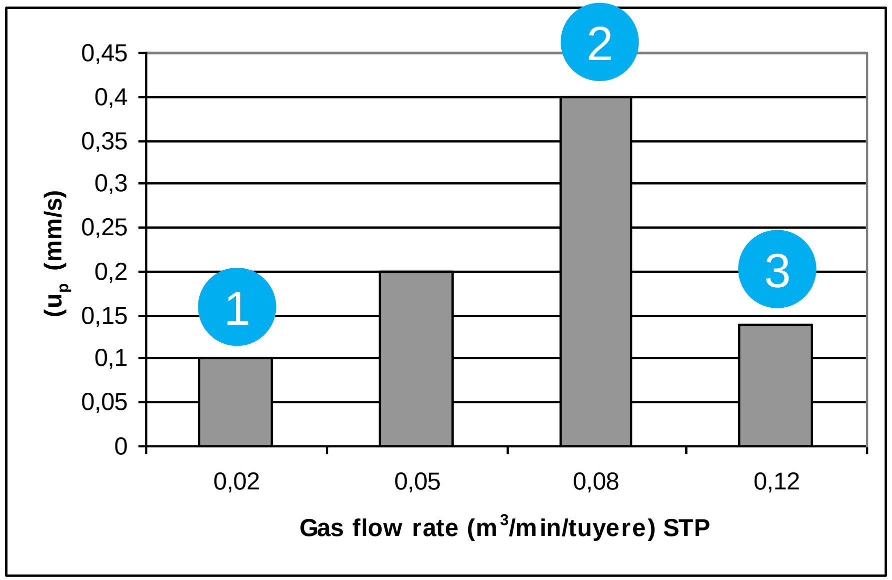
[1] H.-J. Odenthal, U. Thiedemann, U. Falkenrech, and J. Schlueter, *Metall. Mater. Trans. B*, 41(2): 396–413, 2010.

[2] T. Fabritius, P. Mure, and J. Härkki, *ISIJ Int.*, 43(8): 1177–1184, 2003.

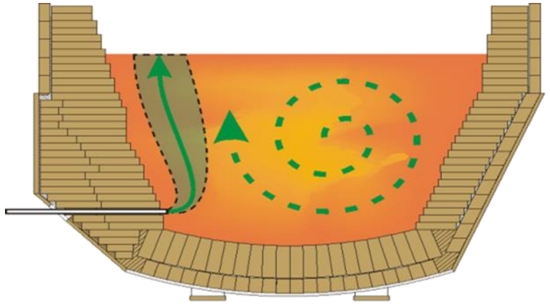
[3] T.M.J. Fabritius, P.T Kurkinen, P.T. Mure, *Ironmaking Steelmaking*, 32(2): 113–119, 2005.

AOD process

Penetration modes

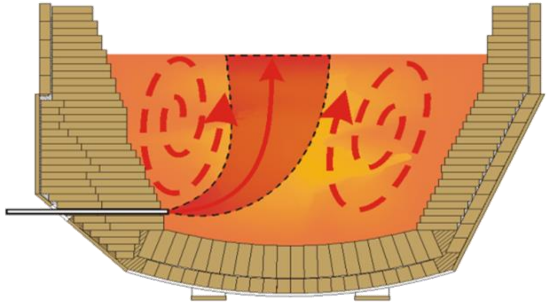


Vibration intensity with different gas flow rates in a 1:9 scale water model of a 150-ton AOD converter.[1]



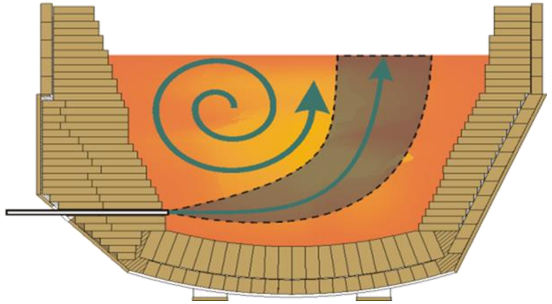
1. **Shallow penetration**

- Stable bath.
- Relatively slow circular motion of the bath.



2. **Penetration into the middle of the converter**

- Strongly oscillating bath.
- Two strong circulations.



3. **Deep penetration**

- Stable bath.
- Strong circular motion of the bath.

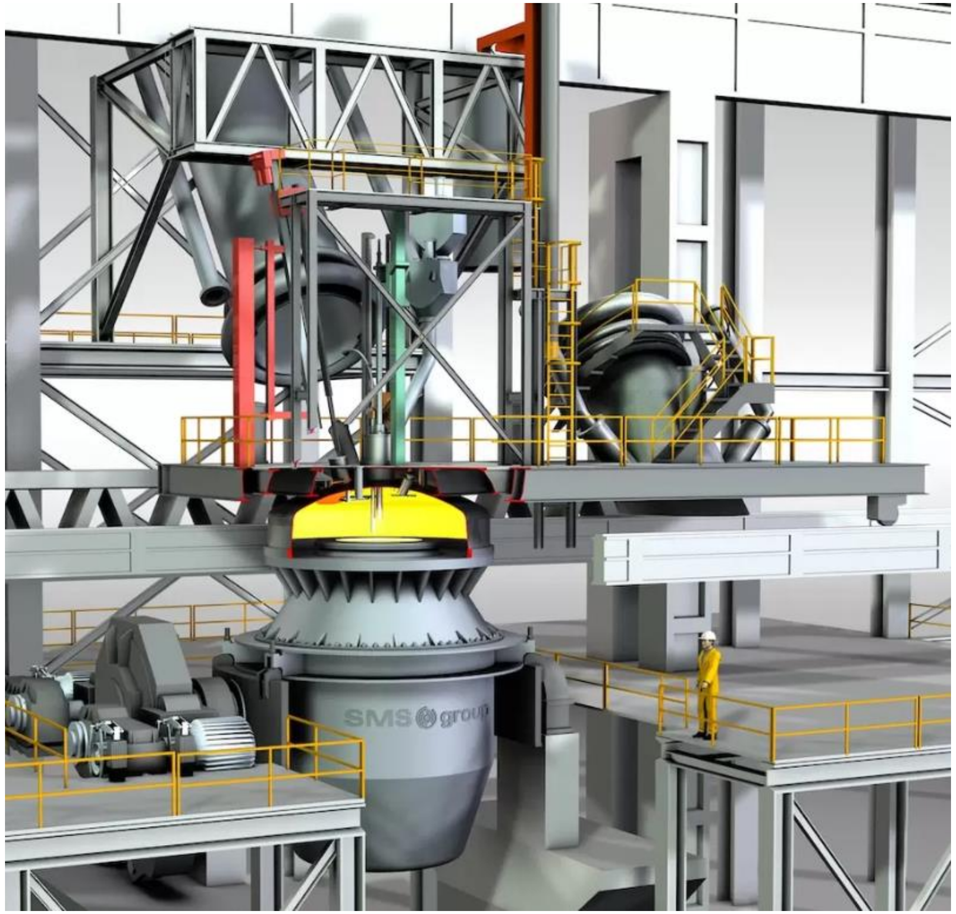
Reference

[1] T.M.J. Fabritius, P.T Kurkinen, P.T. Mure, *Ironmaking Steelmaking*, 32(2): 113–119, 2005.

AOD process

Vacuum lid technology: overview

- The vacuum lids can be seen either as a modification of the AOD or as a process of its own.
  - Commercial names include AOD-VCR, vacuum converter, VAOD and CONVAC.
- The vacuum lid technology aims to combine the benefits of the dilution and vacuum principles.
  - Fast decarburisation at high carbon contents.
  - Advantageous decarburisation conditions at lower carbon contents, enabling a lower use of argon and reductants.
  - However, vacuum converters have a higher investment cost and more complicated maintenance.



Vacuum cover and dedusting hood arrangement.[1]

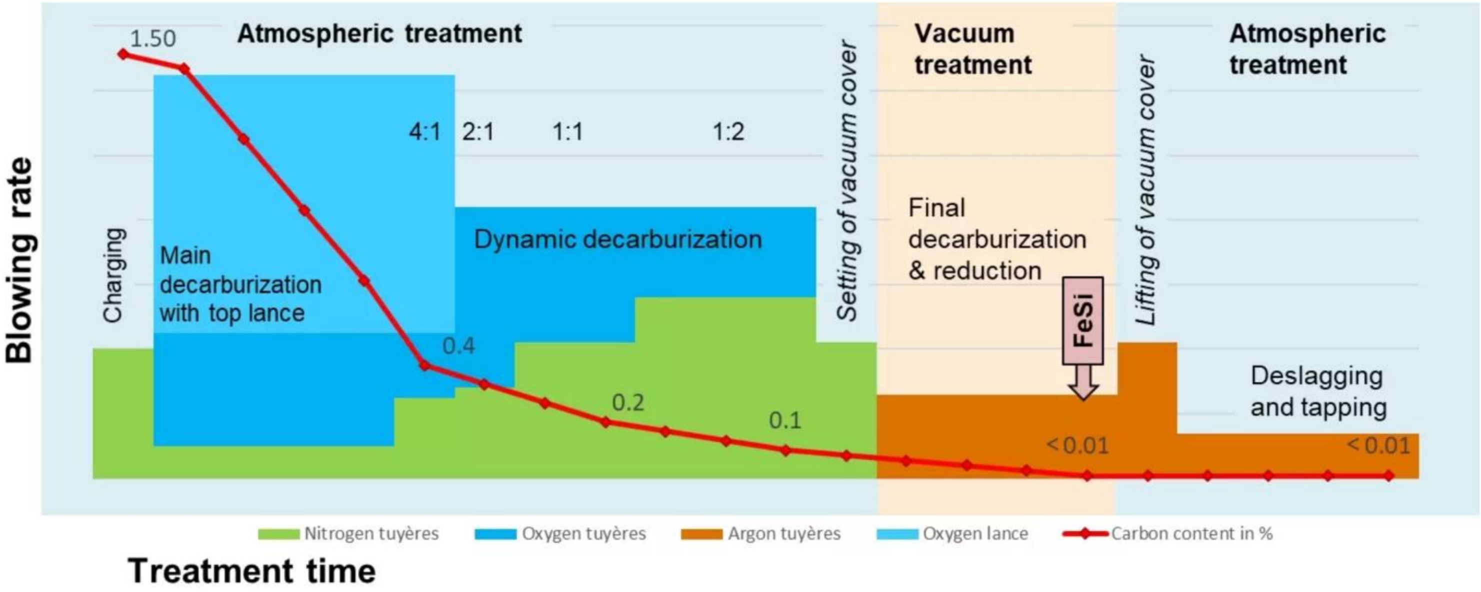
Reference

[1] SMS Group GmbH.

AOD process

Vacuum lid technology: operating practice

- The process is operated as an AOD process down to a carbon content of about 0.1 wt-%.[1]
- Thereafter, the refining is continued under a reduced pressure of 30–1000 mbar.[1]
  - Final decarburisation
  - Reduction of slag
- Deslagging and tapping takes place under atmospheric conditions.[1]
- The total treatment time is claimed to be 15% shorter than that of the AOD process.[1]



Typical vacuum converter treatment cycle.[2]

References

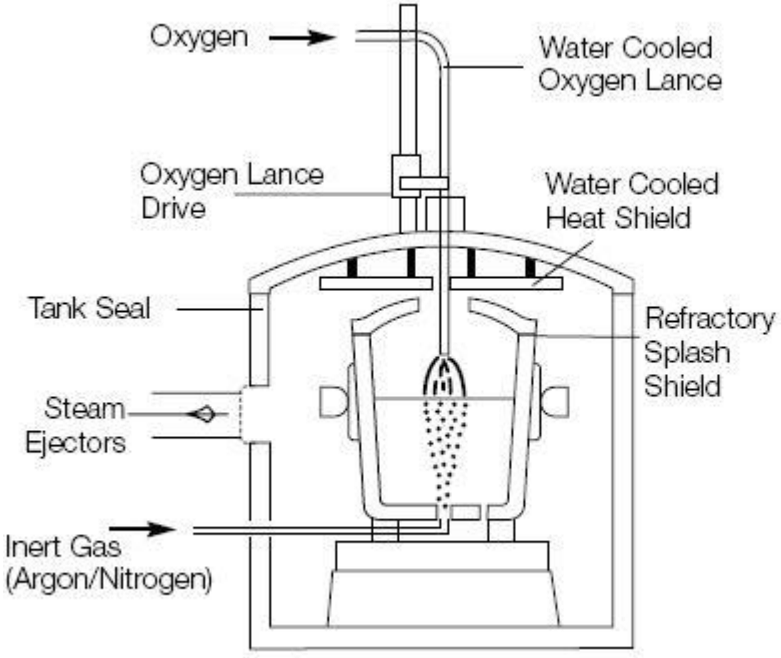
[1] U. Thiedemann, M. Paluszak and T. Kleier, in: *Proc. 4th European Steel Technology and Application Days*, 2019.

[2] SMS Group GmbH.

VOD process

Introduction

- The vacuum oxygen decarburisation (VOD) process was developed by Edelstahlwerk Witten AG in Germany between 1962 and 1967.
  - The partial pressure of CO is lowered by the use of vacuum conditions.
  - Argon-stirring is used to improve bath mixing.
- The VOD enables the production of steels with very low C contents with low Si and Ar consumption.
- The VOD is slower than converter processes based on the dilution principle.
- Further drawbacks are the higher refractory consumption and additional capital investment.



Vacuum-oxygen decarburisation unit.[1]

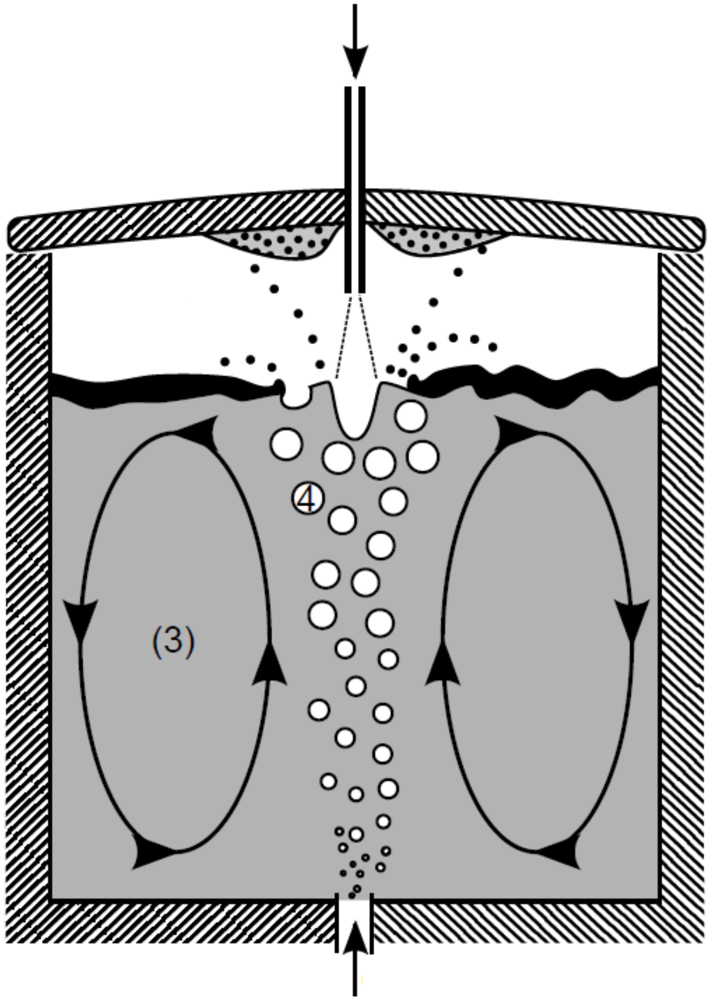
Reference

[1] Courtesy of totalmateria.com

VOD process

Process stages[1]

- Oxygen-blowing (30–60 minutes)
  - Vacuum pressure of 100–200 mbar.
  - Oxygen is blown for decarburisation.
  - Alloys and fluxes are added.
- Degassing (~10 minutes)
  - Vacuum pressure of 1–5 mbar.
  - The decarburisation continues due to the lower pressure.
- Reduction (~40 minutes)
  - Vacuum pressure of 1–5 mbar.
  - Reductants are added to recover Cr from the slag.
  - Fluxes and slag formers are added.
  - Final temperature in the range of 1640–1750 °C.



Schematic illustration of the fluid flow phenomena in the VOD.[2]

References

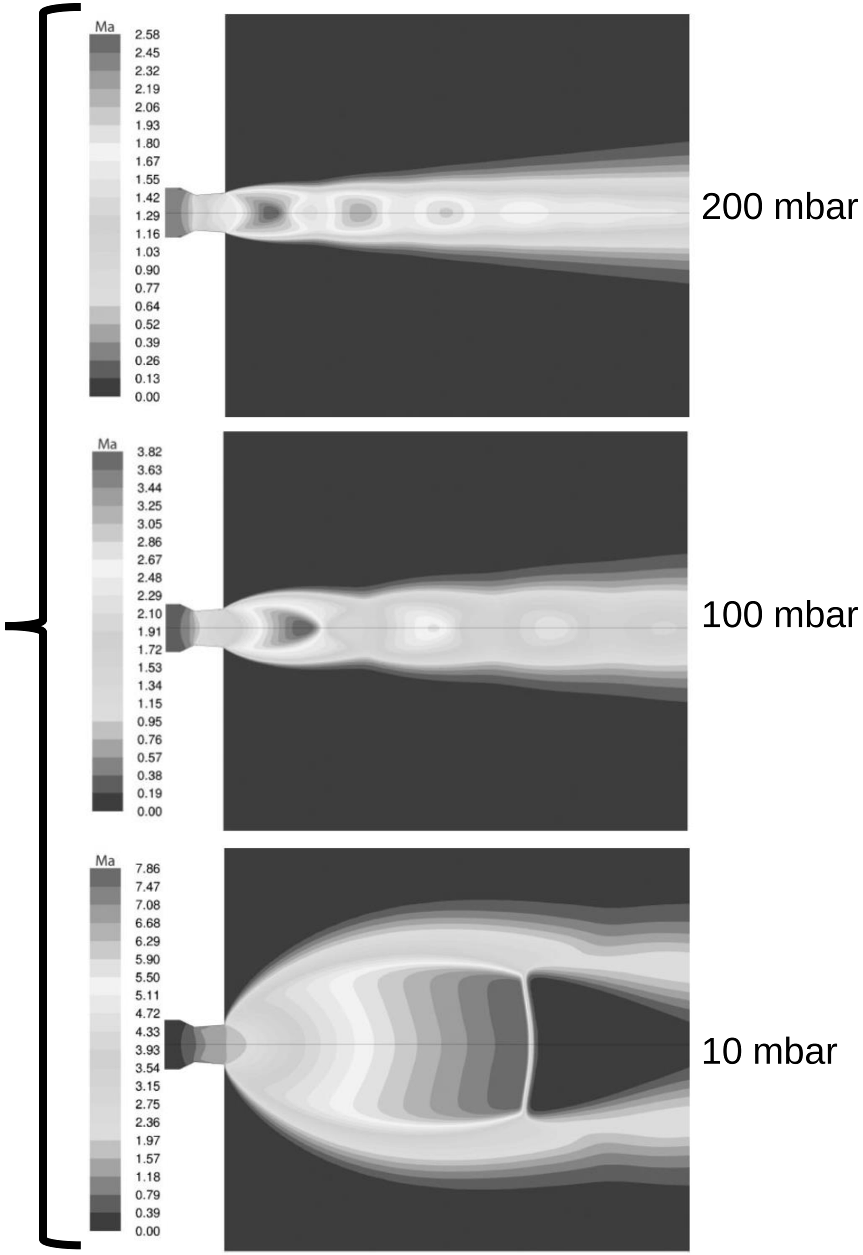
[1] R. Ding, B. Blanpain, P.T. Jones, and P. Wollants, *Metall. Mater. Trans. B*, 31(29): 197–206, 2000.

[2] D. Rhezak, *Doctoral thesis*, RTWH Aachen University, 2013.

VOD process

Behaviour of the gas jet under vacuum conditions

- The oxygen is supplied using a supersonic top lance.
- An increase in the ambient temperature lengthens the supersonic region because the ambient density is reduced.[1]
- In the VOD process, the gas jet is affected also by vacuum conditions.[2]
    - A decrease in ambient pressure increases the dynamic pressure and narrows the gas jet.
    - However, a too-low ambient pressure can cause acute fluctuation of the gas flow.



Mach number of the gas jet at 1600 °C at different ambient pressures.[2]

References

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

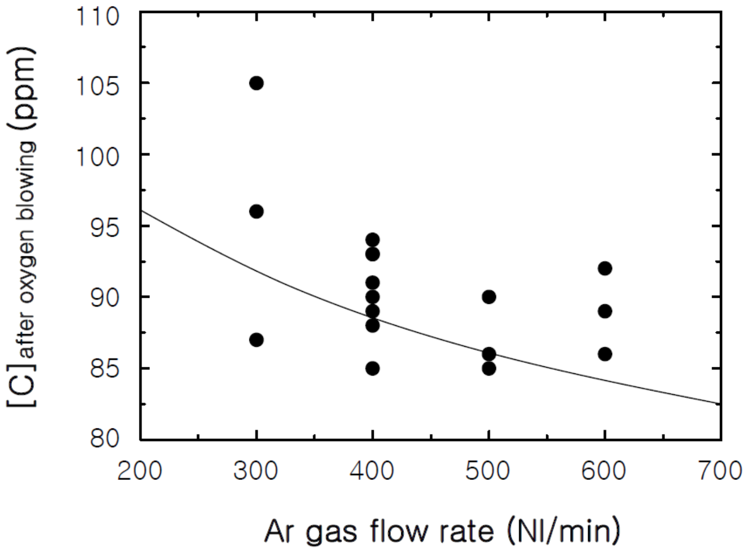
[2] Z. Song, M. Ersson, and P. Jönsson, *Steel Res. Int.*, 82(39: 249–259, 2011.

VOD process

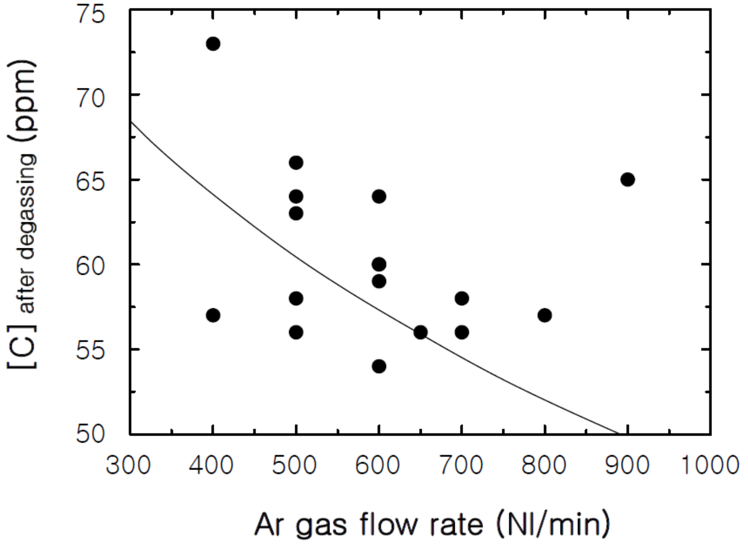
Gas stirring

- Typically, a higher stirring rate is employed in the degassing and reduction stages than in the oxygen-blowing stage.[1]
- The choice of stirring rate represents a trade-off between achieving a lower carbon content and the cost of argon.[2]

Carbon content vs. argon gas flow rate.[2]



After oxygen blowing



After degassing

References

[1] R. Ding, B. Blanpain, P.T. Jones, and P. Wollants, *Metall. Mater. Trans. B*, 31(29): 197–206, 2000.

[2] S. Lee, S.-M. Byun, J. Park, M.-O. Suk, J.A.T. Jones, and D.I. Walker, *Proc. 3rd International Conference on Process Development in Iron and Steelmaking*, pp. 131–140, 2008.

CRC process

Purpose

- Ferrochrome converter (CRC) process is a process for refining liquid ferrochrome.
- Serves to decrease the Si and C levels of liquid high-C ferrochrome.
  - The C content is roughly halved.
  - Around 90% of the Si is removed.
- The heat released by the exothermic reactions can be utilised for scrap melting.
- The partial decarburisation conducted in the ferrochrome converter reduces the treatment time at the AOD converter.

Typical changes in bath composition and temperature.

Parameter	Initial	Final	Unit
Cr content	53−55	33−36	wt-%
Si content	4−5	0.1−0.5	wt-%
C content	6.5−7.0	2.5−3.0	wt-%
Temperature	~1520	1600−1700	°C

CRC process

Ferrochrome converter at Tornio works

- At Tornio works, production line 1 operates a 95-ton ferrochrome converter.
- The vessel is geometrically similar to the AOD converter 1 operating in the same production line.
- The ferrochrome converter serves also as a buffer between ferrochrome production and the meltshop.
- The charge weight varies from 30 to 60 tons, while the final weight is 40 to 90 tons.[1]

Production line 1: CRC

Supplier	MAN GHH
Charge weight	95 tons
Total weight	180 tons
Gas injection system	Five nozzles + supersonic top lance
Max. O_2 injection rate	140 Nm^3/min
Heats per day	10

Reference

[1] J. Kaisto, *Master's thesis*, University of Oulu, 2018.

CRC process

Charge materials and consumables

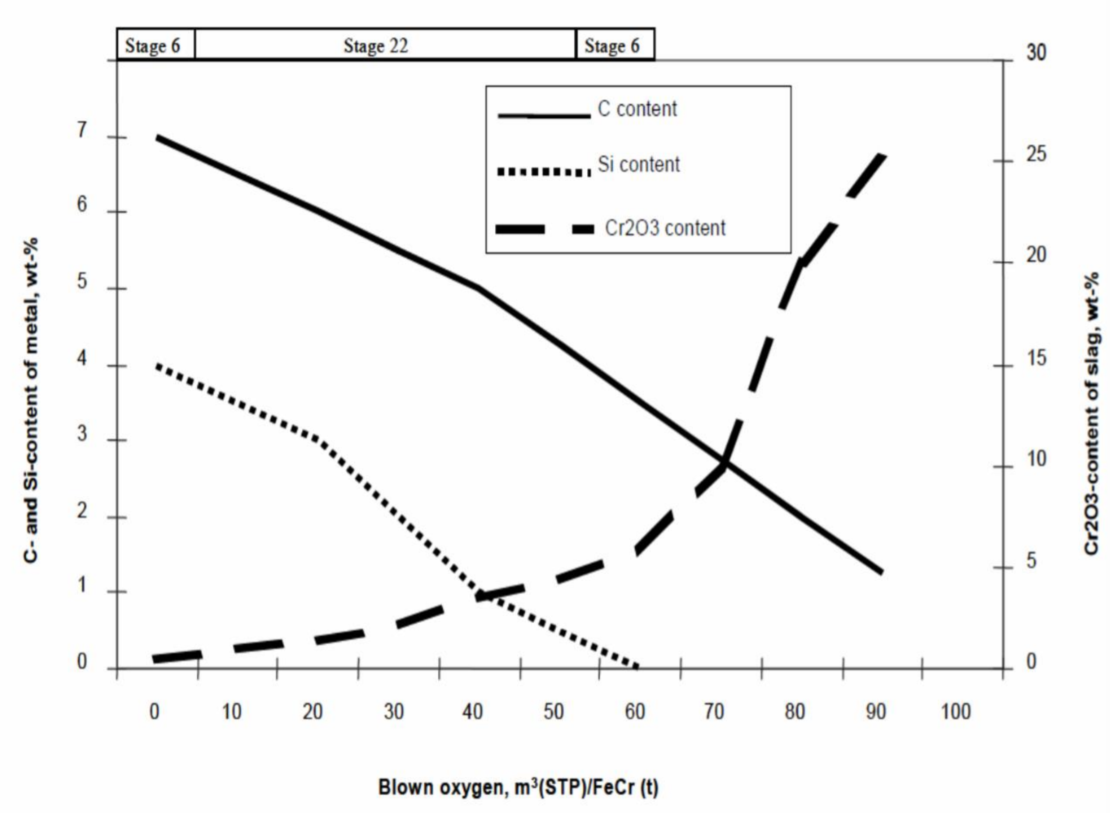
− Charge materials	High-Cr FeCr
− Process gases	e.g. O_2 and air
− Material additions (silos)	
▪ Slag formers	e.g. lime and dolomite lime
▪ Ni-containing materials	e.g. FeNi
▪ Silo scrap	
▪ Solid FeCr	
− Material additions (crane)	
▪ Fe briquettes	
▪ Scrap	
− Refractories	e.g. doloma

CRC process

Stage 6	60 Nm^3/min of O_2 via tuyeres
Stage 22	50 Nm^3/min of air via tuyeres 130 Nm^3/min of O_2 via top lance

Operating practice

- The silicon content decreases rapidly during the initial part of the process.
- The oxidation preference of species depends heavily on the C content:[1]
  - At high C contents, both Si and C are oxidized.
  - At lower C contents, Si and Cr oxidize more aggressively than C.
- Additions during the process:
  - Scrap: 550 kg/ton FeCr
  - Slag formers: 150 kg/ton FeCr



Evolution of bath and slag compositions during the ferrochrome converter process.[1]

Reference

[1] E.-P. Heikkinen, T. Ikäheimonen, O. Mattila, T. Fabritius, and V.-V. Visuri, *Proc. 6th European Oxygen Steelmaking Conference*, 2011.

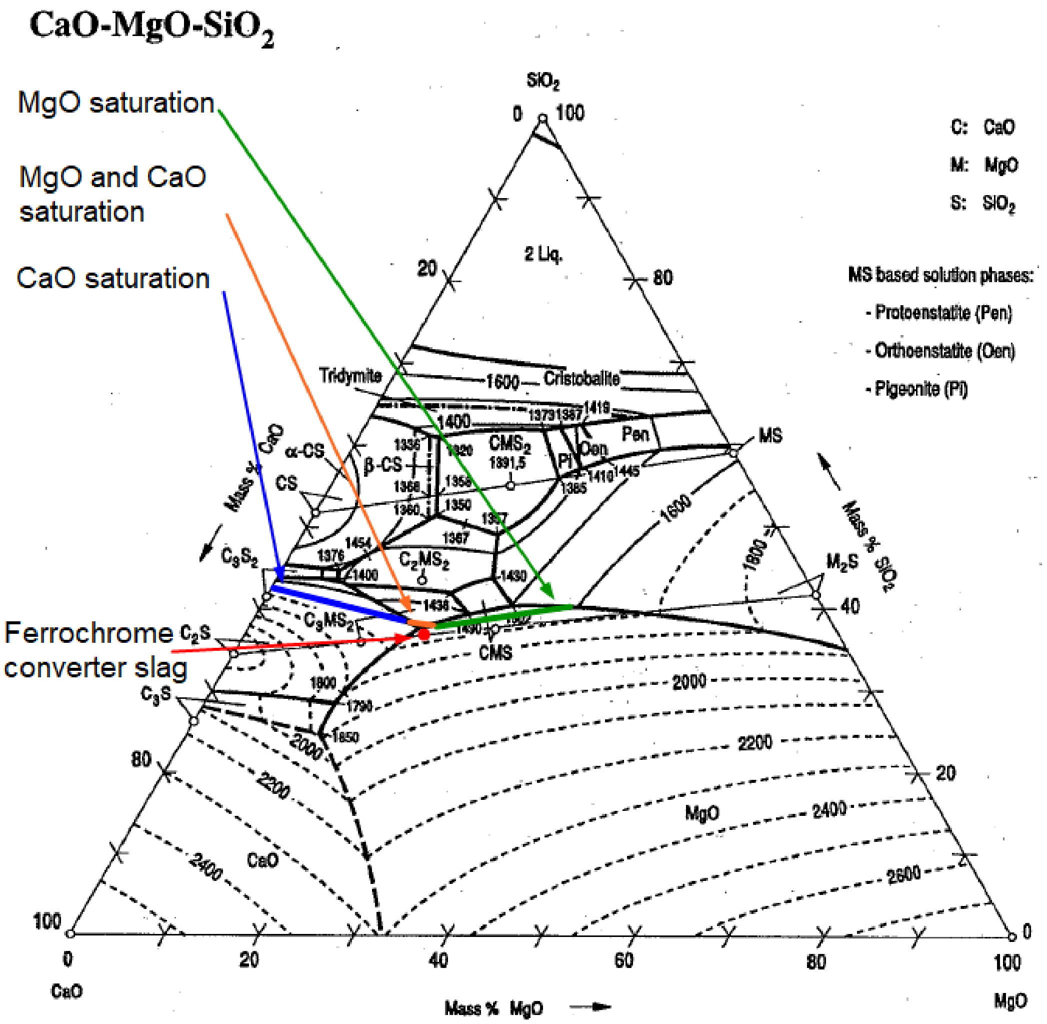
CRC process

Refractories and slag practice

- The main refractory materials are doloma and magnesia.
  - The refractory lifetime varies from 45 to 100 heats.[1]
- The CRC process is operated with an acid slag.
  - The target basicity is defined as follows:[1]

$$B = \frac{(\%\mathrm{CaO}) + (\%\mathrm{MgO})}{(\%\mathrm{SiO_2})} = 1.7$$

  - The slag composition is adjusted using slag formers, such as lime and dolomitic lime.
- The final slag composition is approximately in the MgO and CaO saturated area.[1]
  - This means that the slag does not dissolve MgO or CaO from the refractories.



CaO–MgO–SiO_2 system with the average composition of the ferrochrome converter slag.[1]

Reference

[1] J. Kaisto, *Master's thesis*, University of Oulu, 2018.

Future outlook

AOD process

- For the time being, the AOD process is likely to remain the most important process for refining stainless steels.
- New measurement technologies will be taken into use to enable better monitoring of the process.
- New mathematical models could allow a better offline optimisation of the blowing stages and slag practice.
- Model predictive control using fundamental models is starting to become feasible.[1]
  - This could help to reduce process variation.

Camera system for monitoring nozzle area.[2]

References

[1] V.-V. Visuri, P. Kupari, A. Hammervold, S. O. Wasbø, M. Schlautmann, and V. Peiss, *Proc. 9th International Conference on Modeling and Simulation of Metallurgical Processes in Steelmaking*, pp. 128–135, 2021.

[2] Sapotech Oy.

Future outlook

Vacuum technology

- As steel producers strive to achieve a higher impurity control, vacuum technology is likely to become more commonplace.
- Here, the vacuum lids compete against VOD.
- Aside from costs and metallurgical viewpoints, the space available in the meltshop also plays a role.

Future outlook

CRC process

- The production of ferrochrome takes place by reduction of chromite ore using coke.
- Carbon-free direct reduction methods for ferrochrome production are under development.
  - These methods would produce low-carbon ferrochrome, which is suitable for alloying as such.
  - Consequently, there would be no need for the ferrochrome converter process.
  - Nevertheless, the CO_2-free ferrochromium production technologies are still far away from commercial implementations.

Summary

- Modern stainless steel production is based on the duplex (EAF+AOD) and triplex (EAF+AOD+VOD) routes.
- The AOD process is the most common unit process for refining stainless steels.
  - Based on the dilution principle, i.e. on the use of inert gases to reduce the partial pressure of CO.
  - Two main stages: decarburisation and reduction.
- The VOD process is a process that is based on the vacuum principle, i.e. lowering the total pressure of the metal bath.
- The ferrochrome converter is a process for removing excess carbon and silicon from molten ferrochrome.

Thank you for your attention!

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