FS 2024/25

MSE-422 – Advanced Metallurgy

12-Metals processing – primary metallurgy

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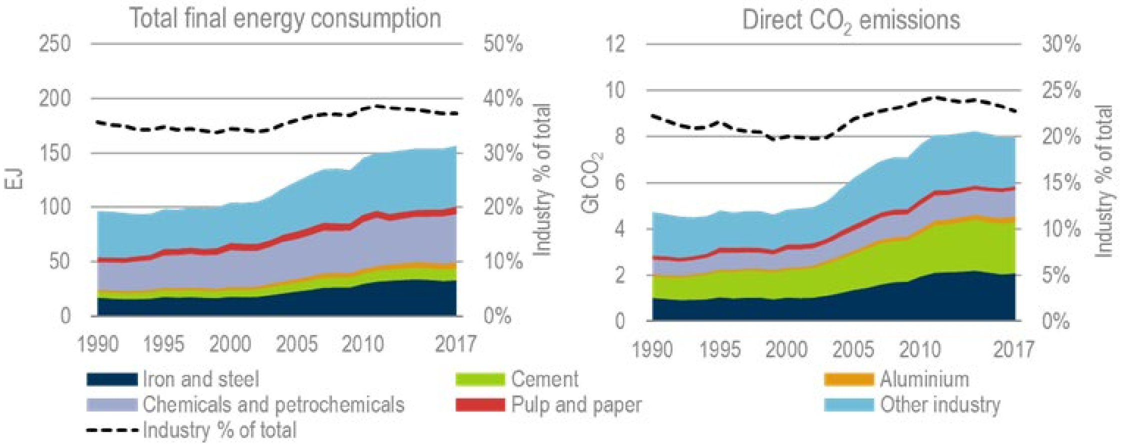
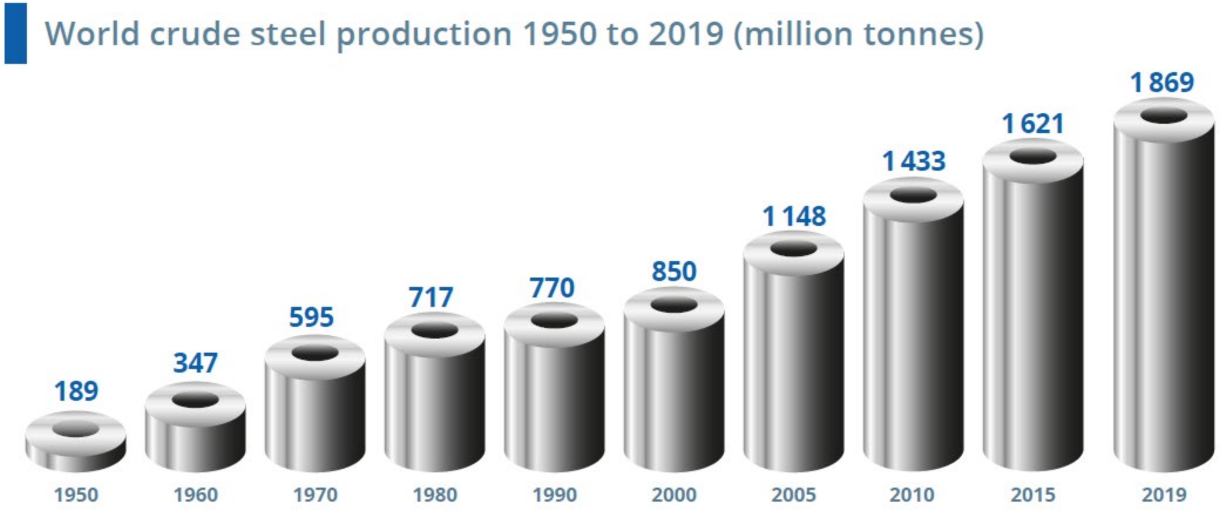
Industry energy and CO_2 footprint

- In 2017, industrial sector emitted 13 GT CO_2 (1/4 of all CO_2 eq. emissions)
  - 8.5 GT/y directly
  - 4.5 GT/y, from electricity, heating, processing and water.
- **Materials processing** accounts for most industrial emissions:
  metals : ~25%, cement: ~25%, plastics + paper: ~25%



https://www.iea.org

The problems with steel making



/www.worldsteel.org/

- Every ton of steel produced in 2018 emitted on average 1.85 tons of carbon dioxide, equating to about 8 percent of global carbon dioxide emissions.
- Are there ways for a more sustainable steel production?
- What is the picture for other metals?

Metal oxide stability

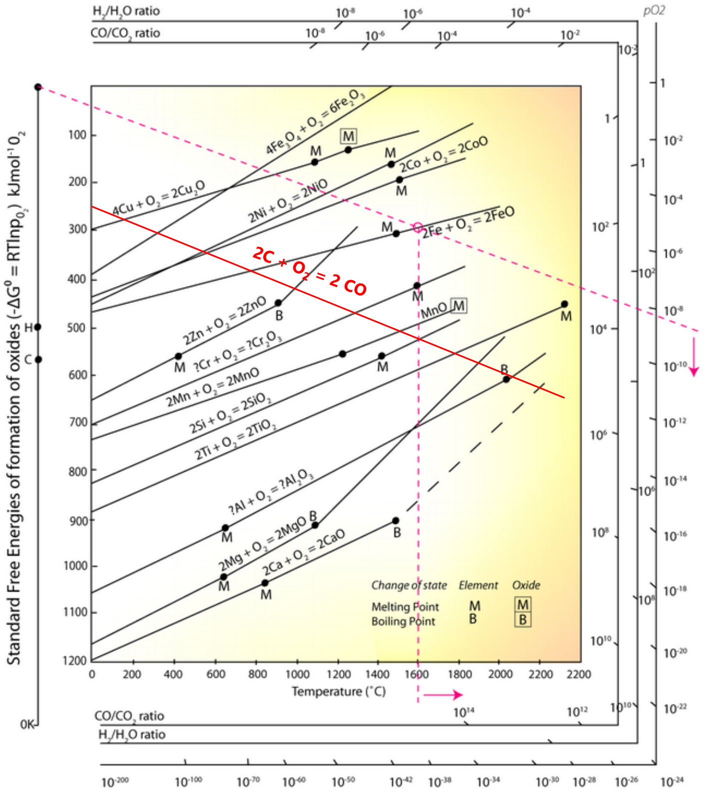
Ellingham diagram

- Graph represents the thermodynamic driving force $\Delta G_0 = RT\ln(p_{02})$ for an equilibrium reaction to occur:

  $x\,M + O_2 = M_xO_2$
- Equilibrium constant: $K=1/p_{02}$

  Thus $K=\exp(-DG_0/RT)$
- Use *top point* and p_{O2} right scale to solve equation graphically (slopes are $-\Delta S_0$
  - For lower pressure, oxide decomposes
  - For higher pressure, metal oxidizes
- Carbon reduces many oxides

  $2C + O_2 = 2CO$



http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/printall.php

Reduction of metal oxide

The oxygen liberated by oxide dissociation does not need to form oxygen gas. Instead, it can oxidize CO:

$$2CO + O_2 = 2CO_2$$

Reduction of metal oxide is then:

$$MeO + CO = Me + CO_2$$

A gas ratio p_{CO2}/ p_{CO} is established which is a unique function of temperature when Me and MeO coexist – use *point C* in Ellingham diagram.

If solid carbon is present

$$C + CO_2 = 2\ CO \quad \text{(endothermic)}$$

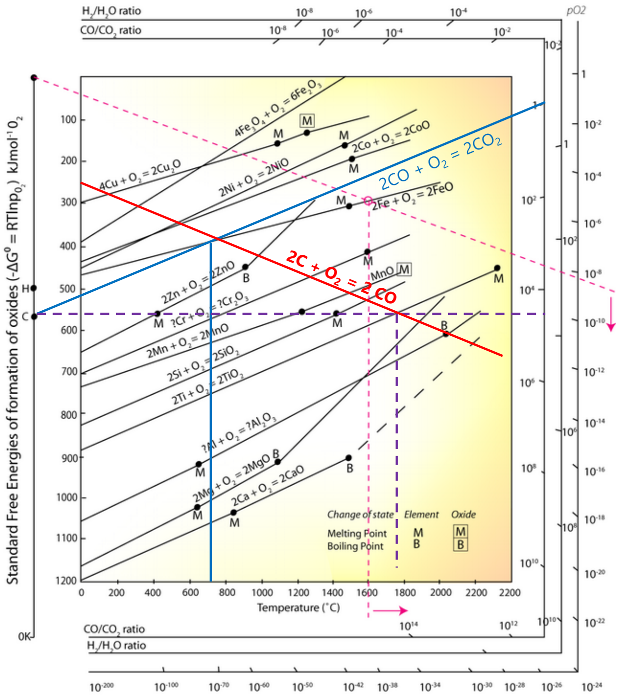
occurs simultaneously

Equilibrium for Me, MeO and C occurs at a unique T and p_{CO2}/ p_{CO}

Reduction with C occurs above that temperature

Fe_3O_4 reduced to FeO at (and above) 650 °C	$p_{CO2}/ p_{CO} = 2$
FeO reduced to Fe at 700 °C	$p_{CO2}/ p_{CO} = 1$
TiO_2 reduced to Ti at 1750 °C	$p_{CO2}/ p_{CO} = 3 \times 10^{-5}$

reduction with CO is endothermic for less noble metals, needs heat to go forward.



Reduction of metal oxide

- Reduction can occur with H_2

  $H_2 + ½\ O_2 = H_2O$ (use point H)

  Metal reduction with H_2 is more endothermic than with CO

- Reduction can occur with mixed CO and H_2

  Use natural gas, which is unstable above 500 °C

  $CH_4 = C + 2H_2$

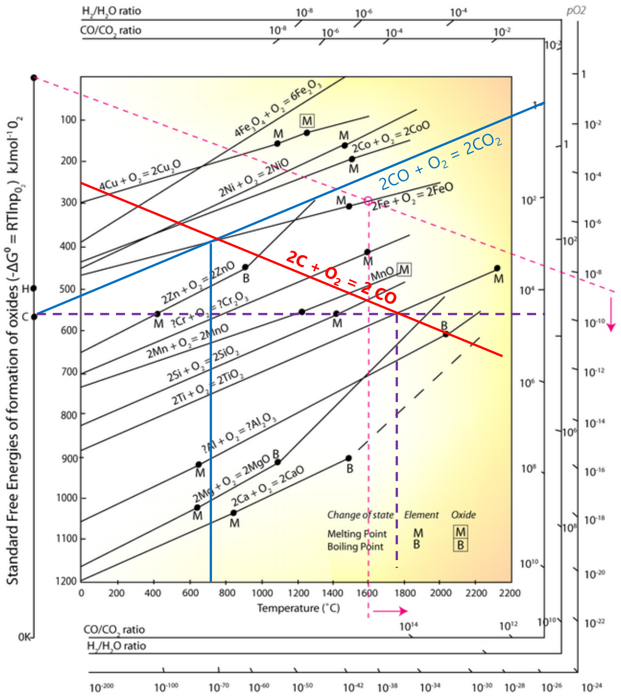
  Then reduce the metal:

  $2\ MeO + ½\ C + H_2 = 2\ Me + ½\ CO_2 + H_2O$

  (but beware MeC formation)

- Also possible: metallothermic reaction:

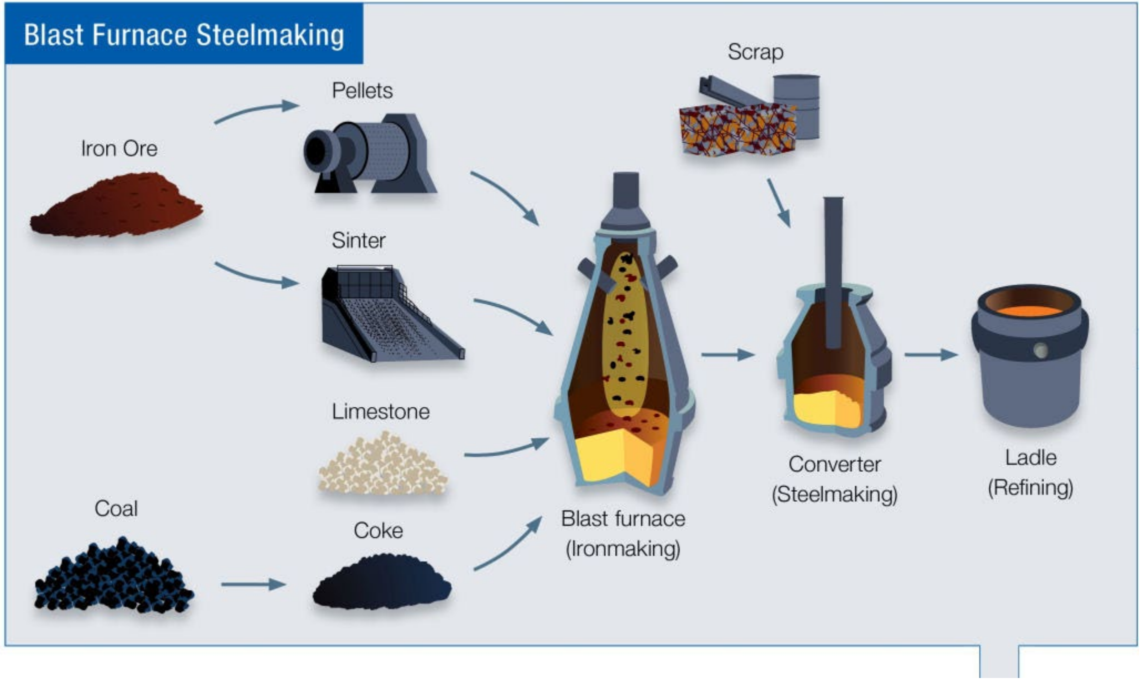
  $2\ FeO + Si = 2\ Fe + SiO_2$ (or use Al or Mg)



Overview of the steelmaking process

/www.worldsteel.org/

The blast furnace process



The blast furnace process

- Upper Part of the Furnace
  - Free moisture is removed from the burden materials.
  - Decomposition of hydrates and carbonates occurs.
- Lower Part of the Blast Furnace Shaft
  - Indirect reduction of iron oxides takes place, driven by carbon monoxide (CO) and hydrogen (H_2).
  - Temperature range: 700–1,000°C.
- Bosh Area (Softening and Melting Zone)
  - Iron oxides are reduced directly, and carbonization occurs through contact with coke.
  - Burden materials begin to soften and melt.
  - Molten iron and slag drip down to the hearth.
  - Temperature range: 1,000–1,600°C.
- Tuyeres and the Combustion Zone
  - Tuyeres: Water-cooled copper nozzles introduce preheated combustion air (900–1,300°C) into the furnace. This air is often enriched with oxygen.
  - Combustion Zone (Hottest Zone):
    - Temperature: 1,850–2,200°C.
    - Coke reacts with oxygen and steam in the blast, producing carbon monoxide (CO), hydrogen (H_2), heat, and completely melting iron and slag.

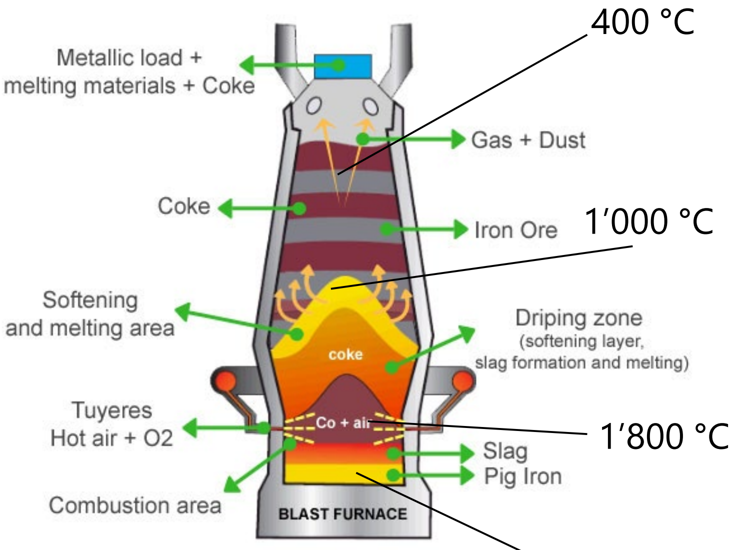


Figure 1 - Blast Furnace Operation

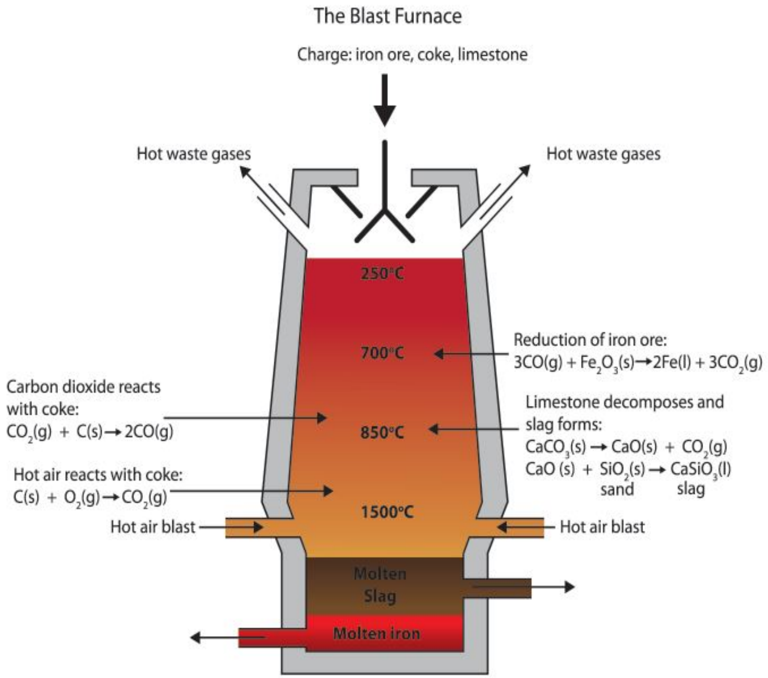
The blast furnace process

- Inputs
  - Air (O_2 + N_2)
  - Coke: for reduction and heating:
    $2C + O_2 = 2CO$ (0.5 ton coke per ton Fe)
  - Ore: Fe_2O_3
  - Flux: lime CaO or limestone $CaCO_3$ reacts with silica impurities to make calcium silicate slag
- Outputs
  - Pig iron (molten), slag (molten), CO_2 + N_2
- Reactions

$$3\,Fe_2O_3 + CO = 2\,Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO = 3\,FeO + CO_2$$
$$FeO + CO = Fe + CO_2$$

total: $Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2$

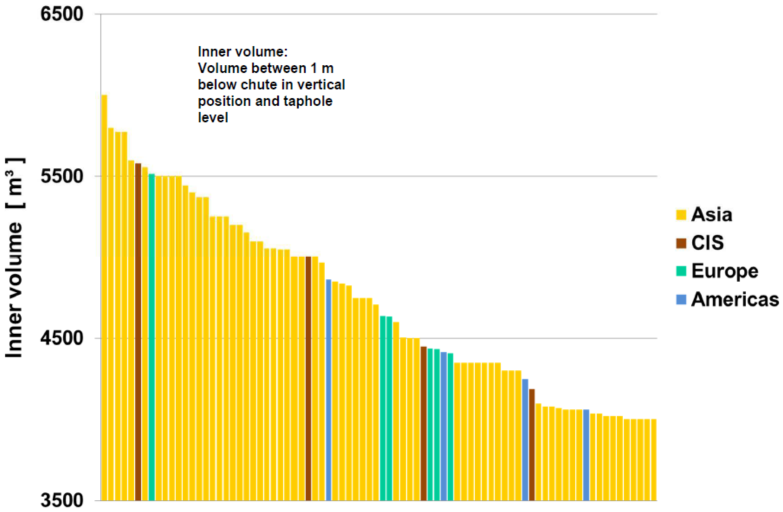
(→ 1.3 ton CO_2 per ton Fe)



Primary steel metallurgy

Blast furnace

- The number of blast furnaces in the world has decreased over the last 20 years, while their volumes have significantly increased
- The largest blast furnace in the world is in South Korea, with a volume around 6,000 m3 It can produce around 5’650’000 t of iron per year.



Converting raw iron into steel

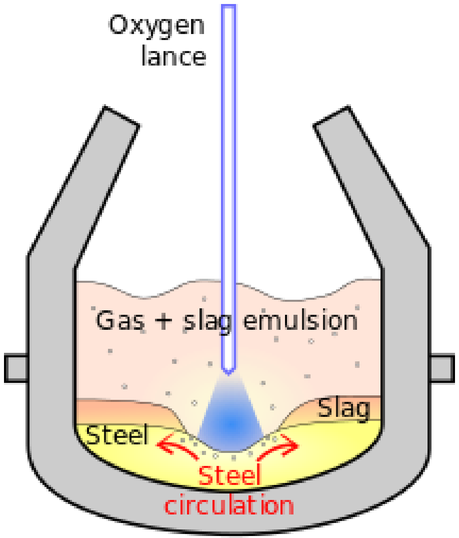
Oxygen converter process

- Basic Oxygen Steelmaking (BOS), also known as BOP, BOF, or OSM (oxygen converter process), is a primary steelmaking method where carbon-rich molten pig iron is refined into low-carbon steel by blowing oxygen through the molten metal.
- Blowing high-purity oxygen reduces the carbon content of pig iron, transforming it into steel while removing other impurities.
- Invented in 1948 by Swiss engineer Robert Durrer.
- Commercialized in 1952–1953 by the Austrian companies VOEST and ÖAMG in Linz and Donawitz (LD process).
- Contemporary BOS furnaces can handle up to 400 tons of molten iron, converting it into steel in less than 40 minutes.

Converting raw iron into steel

Oxygen converter process

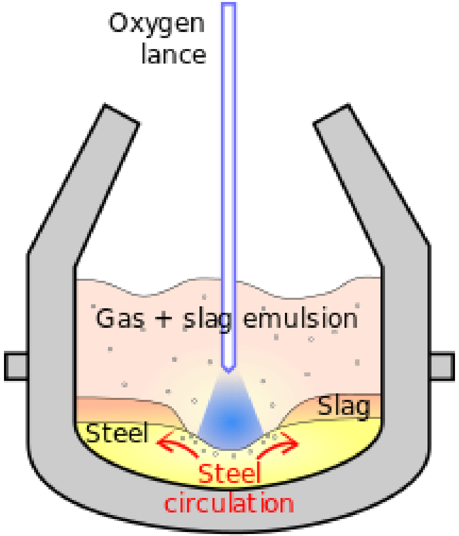
- Molten Crude Iron Handling
  - Molten crude iron ("hot metal") from the blast furnace is poured into a refractory-lined container called a ladle.
  - The ladle is used to transfer the metal directly to the basic oxygen steelmaking (BOS) vessel or to an external pretreatment stage.
- Pretreatment of Hot Metal
  - External pretreatment reduces impurities such as sulfur (S), silicon (Si), and phosphorus (P) before the hot metal is charged into the BOS converter.
- Charging the BOS Vessel
  - The BOS vessel is charged with 25%–30% scrap steel or iron, depending on the charge balance requirements
  - Molten iron from the ladle is added as needed to balance the charge. Maintaining the correct ratio of hot metal to cold scrap is critical for process efficiency and control.
- Oxygen Blowing
  - The vessel is set upright, and a water-cooled, copper-tipped lance with 3–7 nozzles is lowered into it.
  - High-purity oxygen is injected at supersonic speed and at a pressure of 700–1,000 kPa, initiating the steelmaking reactions.



Converting raw iron into steel

Oxygen converter process

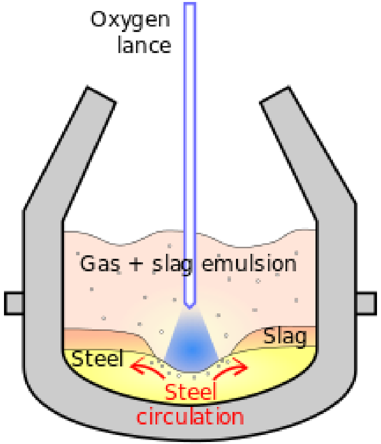
- Oxygen Blowing
  - 99% pure oxygen is blown over the molten iron using a lance.
  - The oxygen reacts with dissolved carbon, forming CO and CO_2, raising the temperature to approximately 1,700°C.
- Refining the Molten Iron
  - The increased temperature melts the scrap, reduces the carbon content, and removes unwanted chemical elements.
- Addition of Fluxes
  - Fluxes (burnt lime or dolomite) are added to the vessel to form slag, which absorbs impurities during the steelmaking process.
- Tapping the Steel
  - The BOS vessel is tilted toward the slagging side, and the refined steel is poured through a tap hole into a refractory-lined steel ladle ("tapping").
- Final Refinement in the Ladle Furnace
  - Alloying materials are added in the ladle furnace to impart specific properties required by the customer.



Converting raw iron into steel

Oxygen converter process

- Burning of the impurities in pig iron:
  - $\{O2\} \rightarrow 2[O]$ oxygen dissociates and dissolves in iron
  - $[Si] + 2[O] \rightarrow SiO_2$ at the beginning of the O_2 inblow
  - $[Fe] + [O] \rightarrow FeO$ (partial) iron slagging
  - $[Mn] + [O] \rightarrow (MnO)$ manganese slagging
  - $2[P] + 5[O] \rightarrow (P_2O_5)$ phosphorous burn
  - $2(FeO) + [O] \rightarrow (Fe_2O_3)$ (oxygen rich slag)
  - $3(CaO) + (P_2O_5) \rightarrow (CaO)_3(P_2O_5)$ removal of phosphorous with limestone
- Gas reactions
  - $[C] + [O] \rightarrow \{CO\}$ decarbonization
  - $\{CO\} + [O] \rightarrow \{CO_2\}$

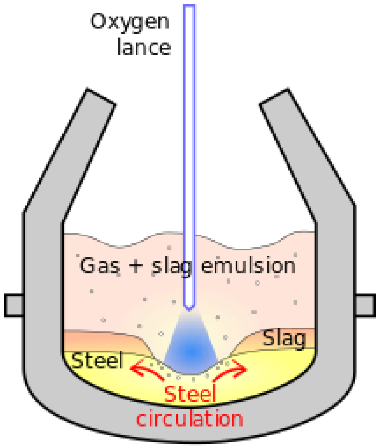


Converting raw iron into steel

Oxygen converter process

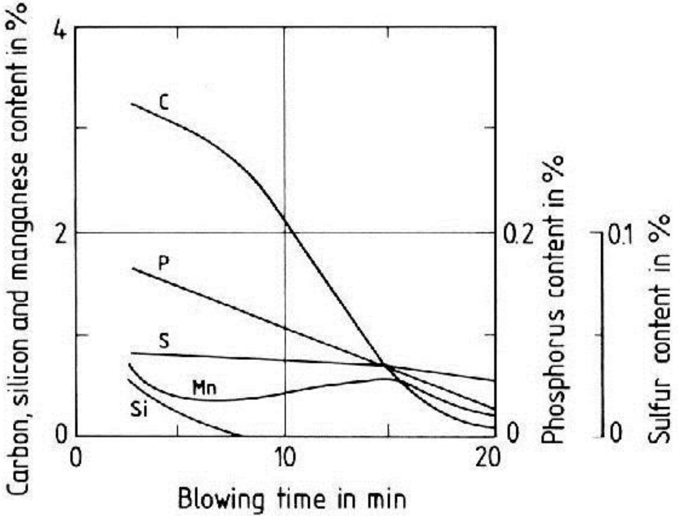
Composition

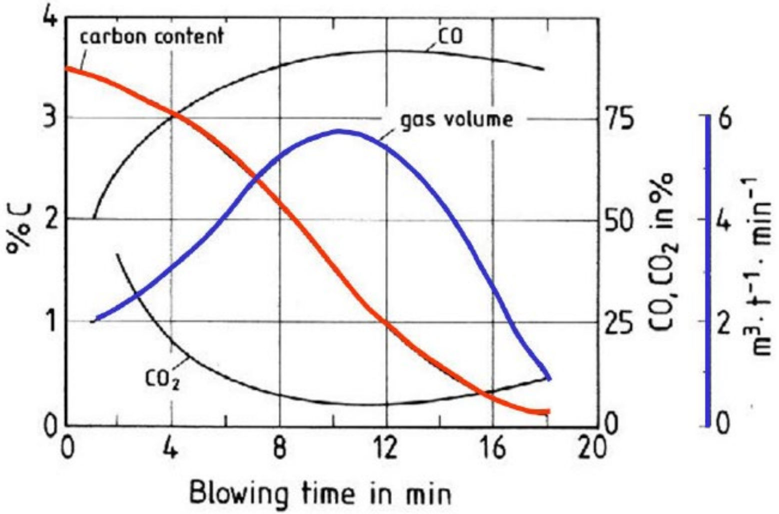
at charging	after OCP
[C] = 3.8-5 ma.%	[C] = 0.03 ma.%
[Si] = 0.5-0.8 ma.%	[Si] = 0.05 ma.%
[Mn] = 0.3-1.0 ma.%	[Mn] = 0.3 ma.%
[P] = 0.2 ma.% max.	[P] = 0.008 ma.% max.
[S] = 0.04 ma.% max.	[S] = 0.08 ma.% max
[Fe] = 94-95 ma.%	[Fe] = 99.6 ma.%
T_{charge} = 1’400°C	T_{out} = 1’700°C



Converting raw iron into steel

Oxygen converter process



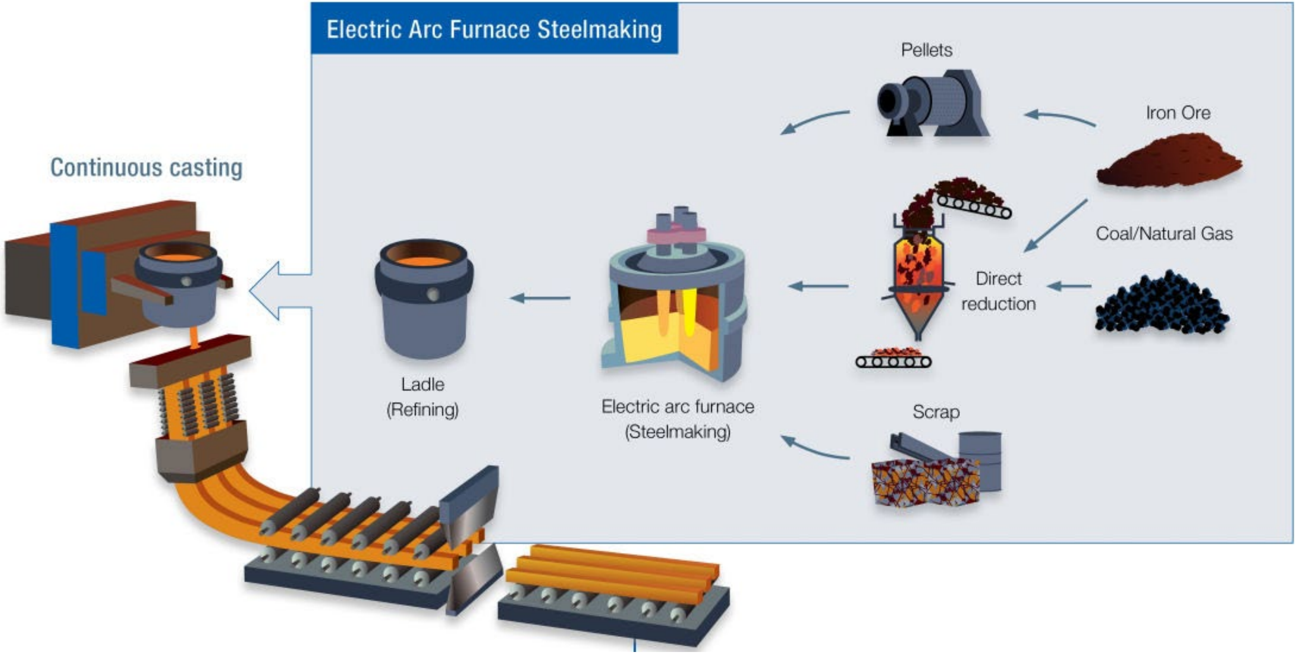


Converting raw iron into steel

Oxygen converter process

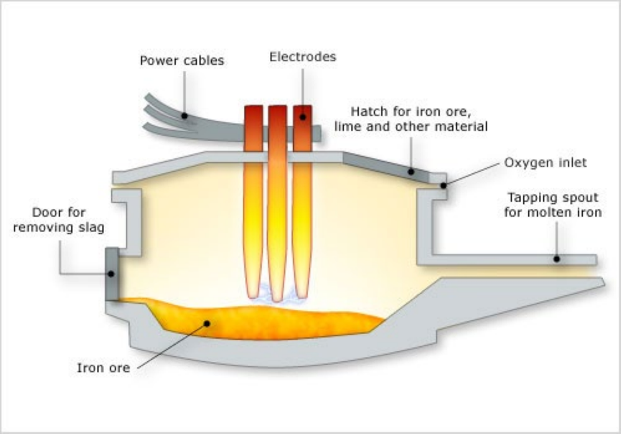
https://www.youtube.com/watch?v=iRss4r0f7Hk

Electric arc furnace steelmaking



Electric arc furnace steelmaking

- Electric Arc Furnace (EAF) is a steel making furnace, in which steel scrap is heated and melted by heat of electric arcs striking between the furnace electrodes and the metal bath.
- In steel making, three-phase AC EAFs with graphite electrodes are commonly used.
- The main advantage of the EAF over the Basic Oxygen Furnaces is their capability to treat charges containing up to 100% of scrap.
- About 33% of the crude steel in the world is made in the EAF
- Modern EAFs have a capacity of up to 400t



Electric arc furnace steelmaking

Steel scrap


Car body scrap


Mixed scrap


Sheet scrap


Blocks


<30mm


<60mm

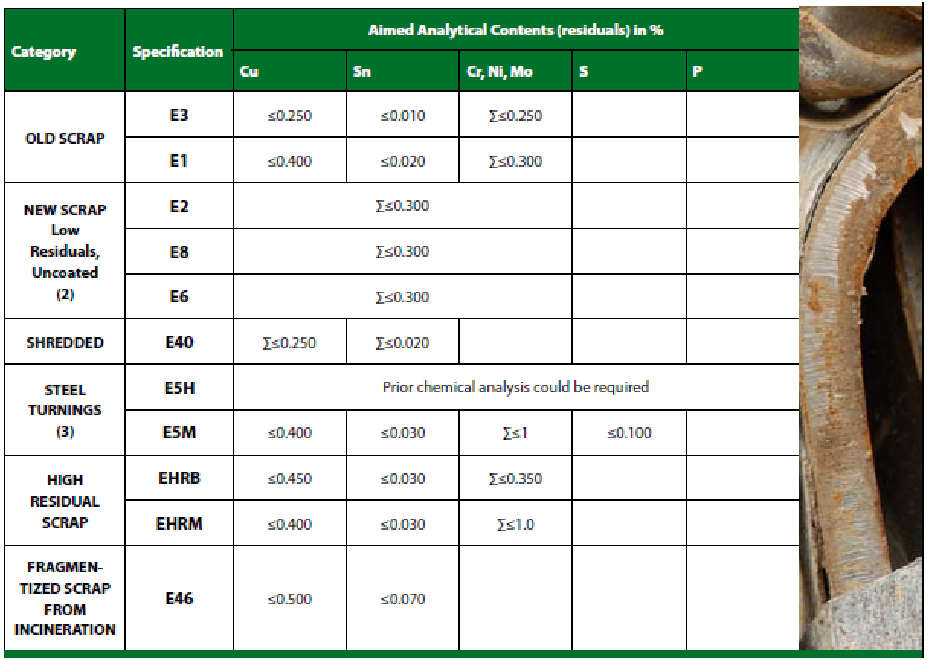

>60mm

- 85-90% of steel products are recovered at the end of their lifetime
- Steel scrap is important as
  - Chilling material in BOF
  - Main material in EAF
- Scrap is available in different shapes and sizes
- Strict regulations ensure
  - Safety (no dangerous or explosive materials); no pressurized components
  - Cleanliness (free of non-ferrous/non-metallic materials
  - Environmental quality

/www.euric-aisbl.eu/facts-figures/standards-specifications/

Steel scrap

- According to the EU-27 steel scrap specification, scrap is classified into 6 main categories
  - Old scrap
  - Low residual new scrap (new production)
  - Shredded scrap
  - High residual scrap
  - Fragmentized scrap
- The categories are divided into several specifications

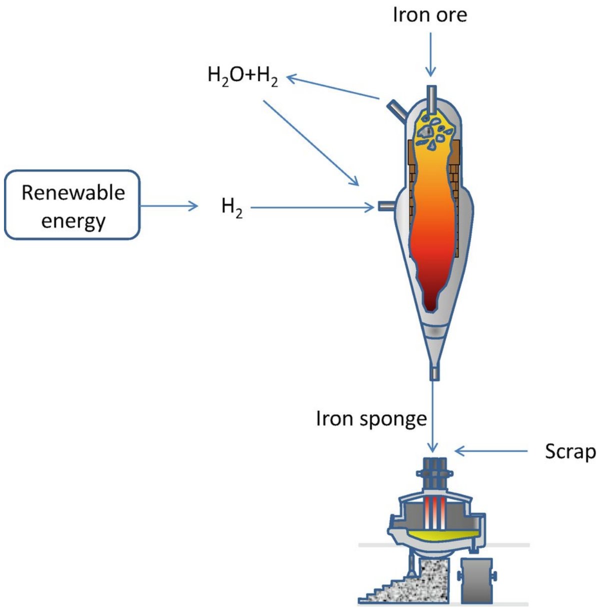


Category	Specification	Aimed Analytical Contents (residuals) in %				
		Cu	Sn	Cr, Ni, Mo	S	P
OLD SCRAP	E3	≤0.250	≤0.010	∑≤0.250		
	E1	≤0.400	≤0.020	∑≤0.300		
NEW SCRAP Low Residuals, Uncoated (2)	E2	∑≤0.300				
	E8	∑≤0.300				
	E6	∑≤0.300				
SHREDDED	E40	∑≤0.250	∑≤0.020			
STEEL TURNINGS (3)	E5H	Prior chemical analysis could be required				
	E5M	≤0.400	≤0.030	∑≤1	≤0.100	
HIGH RESIDUAL SCRAP	EHRB	≤0.450	≤0.030	∑≤0.350		
	EHRM	≤0.400	≤0.030	∑≤1.0		
FRAGMEN-TIZED SCRAP FROM INCINERATION	E46	≤0.500	≤0.070			

/www.euric-aisbl.eu/facts-figures/standards-specifications/

Direct reduction processes

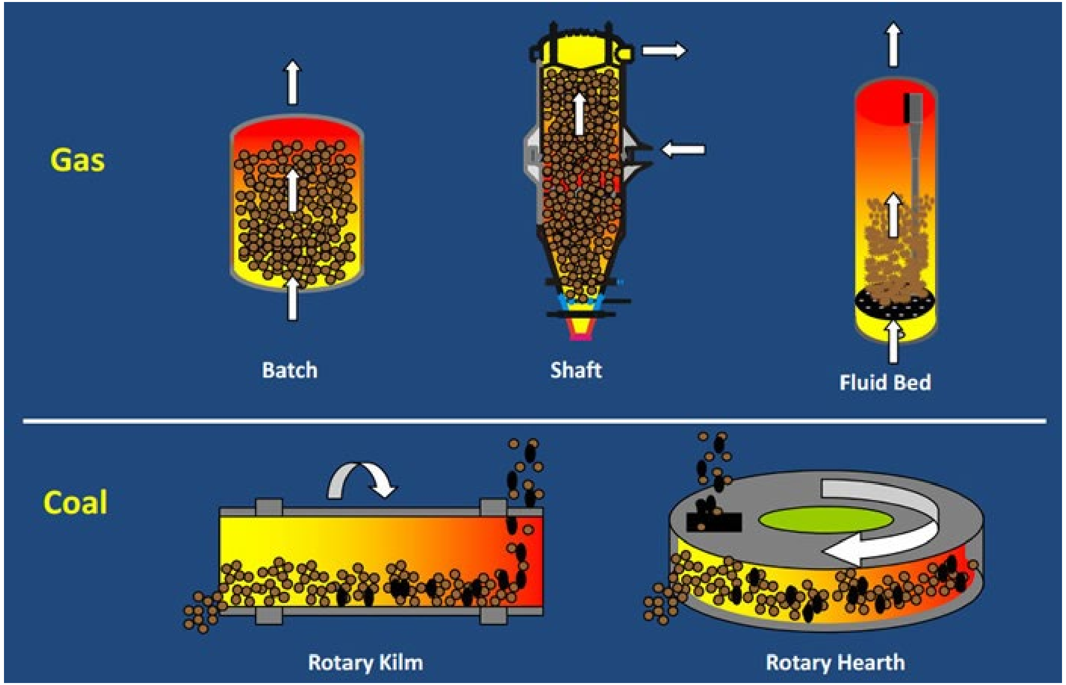
- Direct reduction refers to solid-state processes which reduce iron oxides to metallic iron at temperatures below the melting point of iron (at ~1’200°C)
- Direct reduced iron (DRI) is produced from the direct reduction of iron ore (in the form of lumps, pellets, or fines) into iron by a reducing gas or elemental carbon produced from natural gas or coal
- Direct reduction processes can be divided into two categories
  - gas-based by carbon monoxide and hydrogen derived from natural gas
  - coal-based



Direct reduction processes

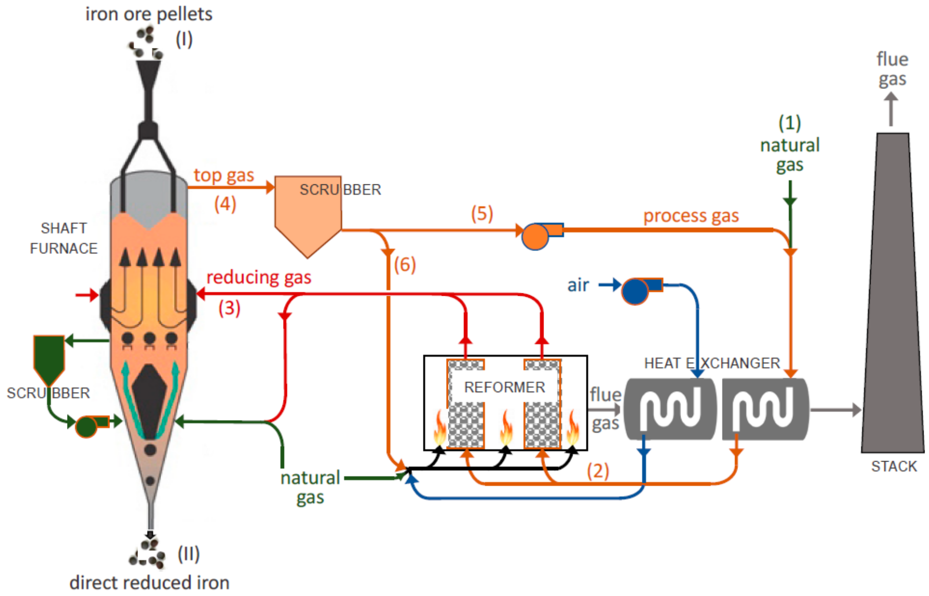
- The following reactions take place
  1) Conversion of hematite into magnetite
     $3Fe_2O_3 + CO/H_2 \rightarrow 2\ Fe_3O_4 + CO_2/H_2O$
  2) Conversion of magneitite into ferrous oxide
     $Fe_3O_4 + CO/H_2 \rightarrow 3\ FeO + CO_2/H_2O$
  3) Conversion of ferrous oxide into iron
     $FeO + CO/H_2 \rightarrow Fe + CO_2/H_2O$
- The resulting iron sponge is highly susceptible to oxidation and rusting if left unprotected and it is thus quickly processed further to steel
- Iron sponge can be protected by carburization and the formation of cementite
  - $3Fe + CH_4/2CO \rightarrow Fe_3C + 2H_2/CO_2$

Direct reduction processes



Direct reduction processes

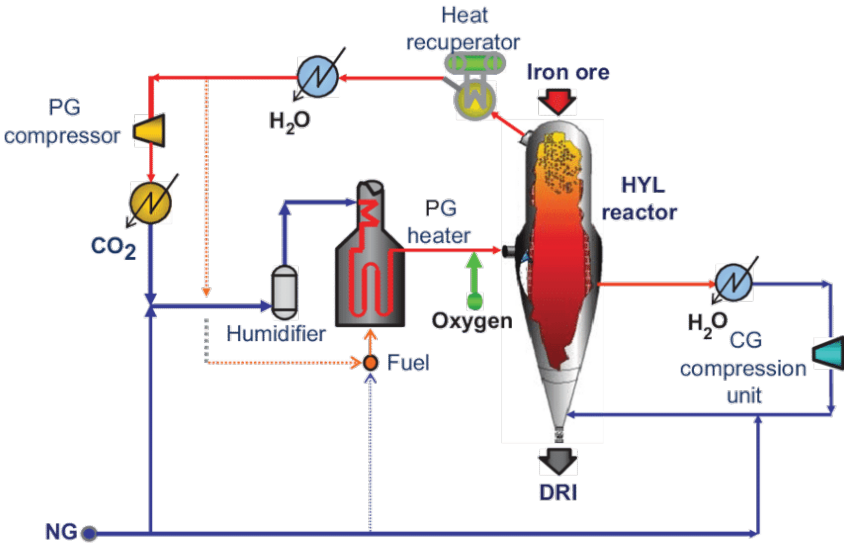
The MIDREX process



- Gas Production:
  - Natural gas (1) is heated and transformed into reducing gas (3) in the reformer (2).
- Reduction in Shaft Furnace:
  - The reducing gas is used to convert iron oxide pellets (I) into Direct Reduced Iron (DRI) (II) in the shaft furnace.
  - The gas is oxidized during this process and exits as top gas (4).
- Gas Recycling:
  - Top gas is scrubbed and split into two streams: One sent to the reformer (5) for reprocessing. The other sent to the burner (6) to provide heat for reforming and other applications.
- Gas Composition:
  - The reducing gas is a mixture primarily composed of CO and H_2, with smaller amounts of CO_2, H_2O, CH_4, and N_2.

Direct reduction processes

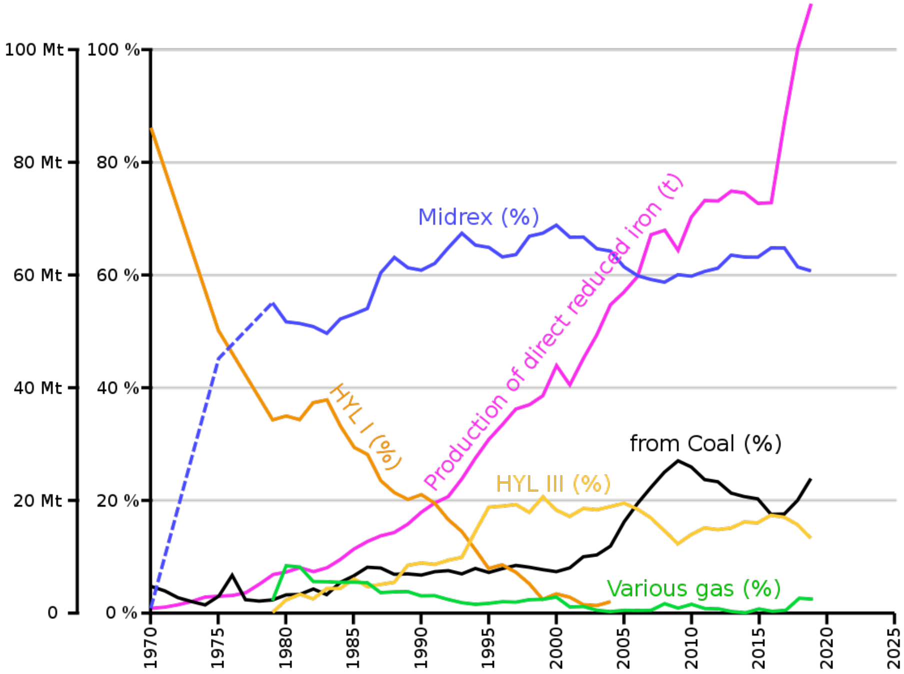
The HYL process



- Overview
  - Removes oxygen from iron ore pellets and lump ore using reducing gases in a moving bed shaft furnace.
  - Operates at ~930°C and pressures up to 6 bars.
- Main Sections
  - Reducing Gas Generation: Produces H_2 and CO using a natural gas-steam reformer.
  - Reduction Circuit: Removes oxygen from iron ore using hot reducing gases.
- Key Components
  - Gas Heater: Raises reducing gas temperature to ~925°C.
  - Scrubbing Unit: Removes dust, H_2O, and cools top gases.
  - Recycle Gas Compressor and CO_2 Removal Unit: Recycle and purify reducing gases.

Direct reduction processes

- Comparison of main direct reduction processes over the last 50 years



Direct reduction processes

- Benefits
  - The direct reduction process is comparatively energy efficient. Steel made using DRI requires significantly less fuel, in that a traditional blast furnace is not needed
  - DRI plants need not be part of an integrated steel plant, as is characteristic of blast furnaces.
  - The initial capital investment and operating costs of direct reduction plants are lower than integrated steel plants and are more suitable for developing countries where supplies of high grade coking coal are limited, but where steel scrap is generally available for recycling

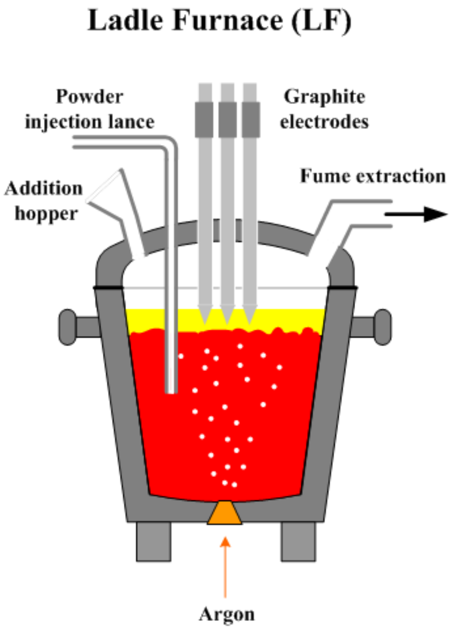
- Problems
  - DRI is highly susceptible to oxidation and rusting if left unprotected, and is normally quickly processed further to steel
  - The bulk iron can catch fire since it is pyrophoric
  - Unlike blast furnace pig iron, which is almost pure metal, DRI contains some siliceous gangue (if made from scrap, not from new iron from direct reduced iron with natural gas), which needs to be removed in the steel-making process.

Secondary steel metallurgy

- After the converter process the steel contains approx. 99.6 ma.% Fe plus some C, Mn, Si
- Before the continuous casting/block casting process, the target steel composition has to be adjusted in the so-called secondary metallurgy process
- Chemical
  - De-gassing – removal of nitrogen, hydrogen
  - De-oxidation
  - De-sulfurazition
  - Secondary de-carburization (for steels with extra-low C content)
  - Precision alloying – addition of Cr, Ni, Mn, Si etc. depending on target composition
- Physical
  - Adjustment of casting temperature
  - Purification of steel / removal of non-metallic inclusions via slag
  - Homogenization of the melt by stirring

Secondary steel metallurgy

- Secondary metallurgy furnace (ladle furnace) technology
  - In general vacuum furnaces
  - Heating: electric (inductive, arc, radiation), chemical (oxidation of Al and/or Si)
  - Cooling: with steel scrap; gas;
  - Stirring: with gas stream, inductive (scarcely mechanical stirring
- Reactions in the melt
  - Gas reactions: reactions between inserted gases like O2 and N2 and dissolved elements like [H] and [C]
  - Precipitation reactions: reactions with elements that form solid compounds
  - Controlled reactions between melt and slag
  - Melting and dissolution of alloying elements; addition as pellets, wire or powder



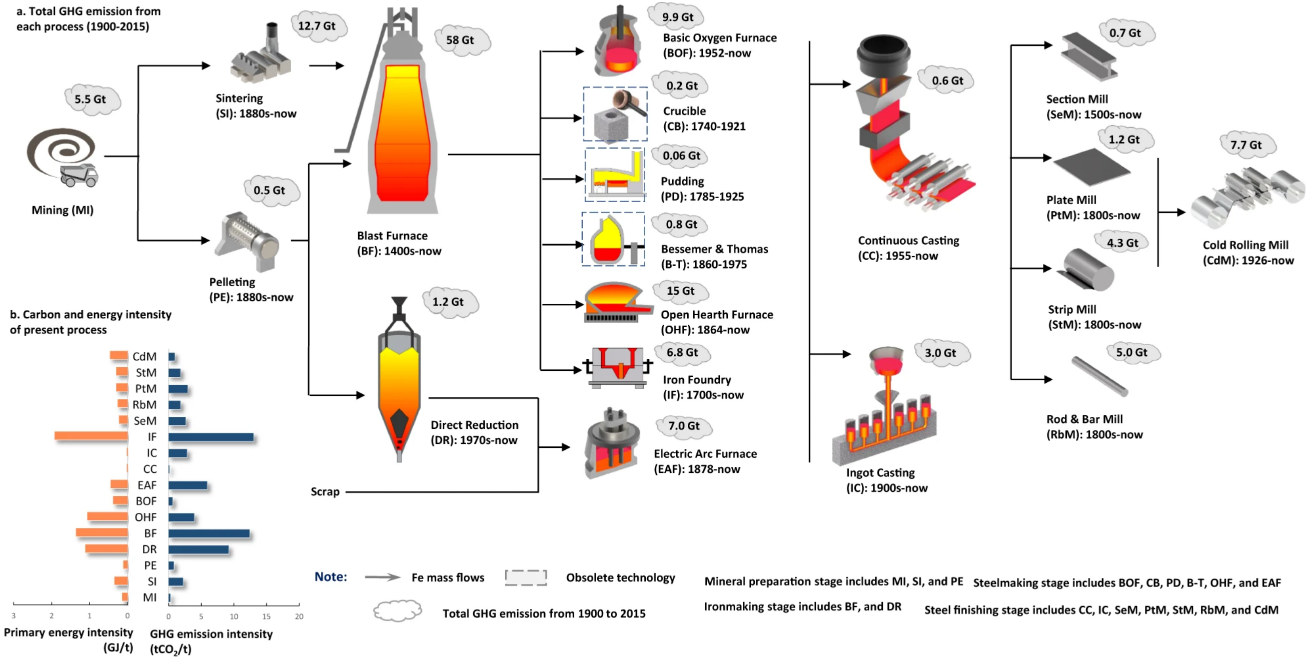
Environmental aspects of steelmaking

Comparison of different processes

- Energy consumption
  - Blast furnace + basic oxygen converter: 5’500-8’500 kWh/t_{LS} (waste
  - Direct reduction processes: 2’500-3’000 kWh/t_{LS}
  - Electric arc furnace (EAF) melting of steel scrap (100%): 340-390 kWh/t_{LS}
  - Electric arc furnace (EAF) melting of scrap + DRI: 530-680 kWh/t_{LS}
- CO_2 emission (direct)
  - Blast furnace + basic oxygen converter: 1.6-2.2 t_{CO2}/t_{LS}
  - Direct reduction processes: 0.5-0.7 t_{CO2}/t_{LS}
  - Melting of steel scrap (100%) in the electric arc furnace (EAF): 0.25-1.1 t_{CO2}/t_{LS}
  - Electric arc furnace (EAF) melting of scrap + DRI: 0.9-1.8 t_{CO2}/t_{LS}

Environmental aspects of steelmaking

Total emissions 1900-2015



a The connection of 19 dominating processes with their representative production technologies, application period and total carbon emissions from 1900 to 2015. **b** Energy intensity and carbon intensity level for each process (for details see Supplementary Information 1 Section S2.2). Abbreviations for steel production flows are: MI mining, SI sintering, PE pelleting, BF blast furnace, DR direct reduction, BOF basic oxygen furnace, CB crucible, PD puddling, B-T Bessemer & Thomas, OHF open-hearth furnace, IF iron foundry, EAF electric arc furnace, CC continuous casting, IC ingot casting, SeM section mill, PtM Plate Mill, StM strip mill, RbM rod bar mill, CdM Cold rolling mill.

/P. Wang et al., Nature Communications 12 (2021) 2066/

Environmental aspects of steelmaking

- Significant inprovements in process efficiency are offset by the much more pronounced increase in annual steel production, resulting in a 17-fold net increase in annual emissions

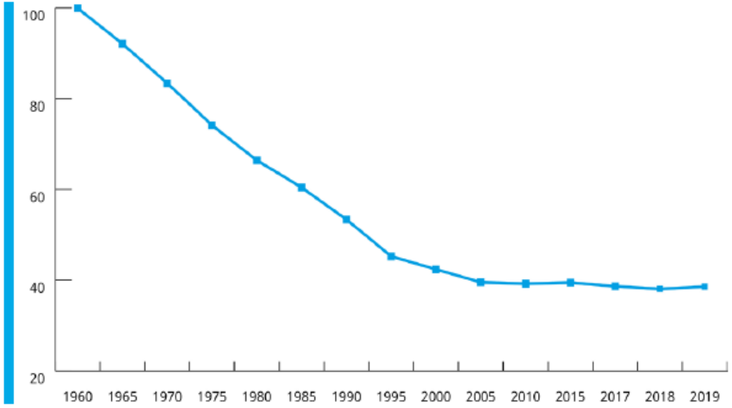
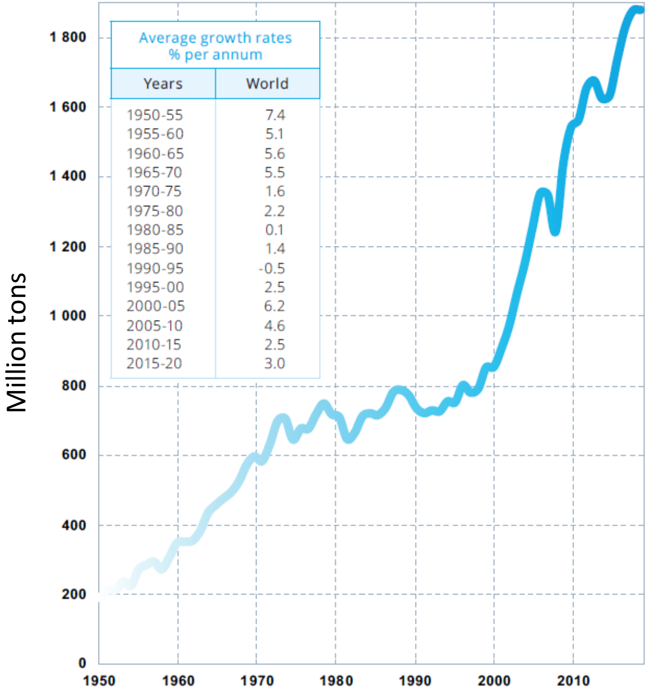


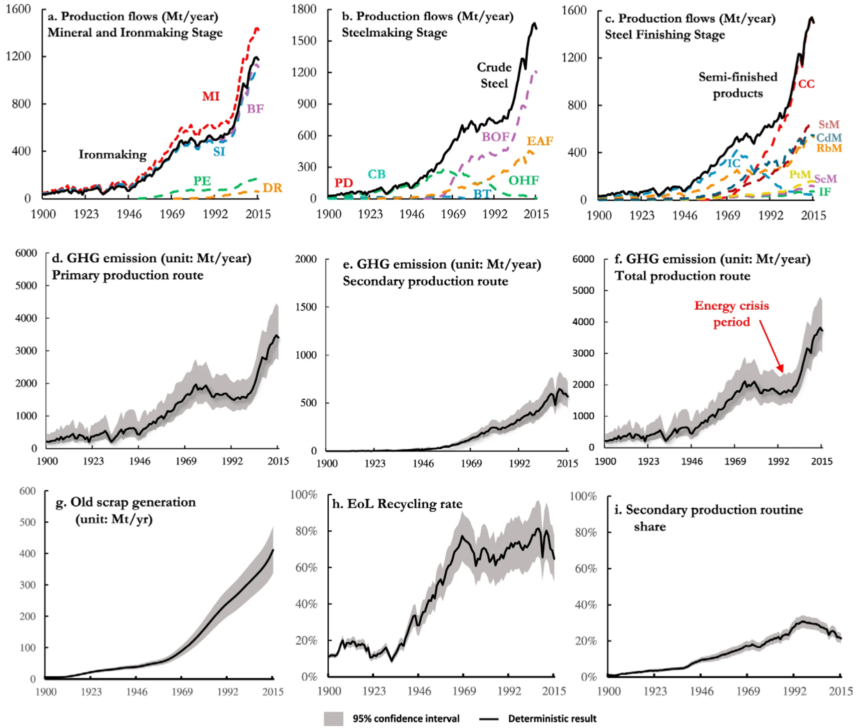
Figure 1: Indexed global energy consumption/tonne of crude steel production



Average growth rates
% per annum

Years	World
1950-55	7.4
1955-60	5.1
1960-65	5.6
1965-70	5.5
1970-75	1.6
1975-80	2.2
1980-85	0.1
1985-90	1.4
1990-95	-0.5
1995-00	2.5
2000-05	6.2
2005-10	4.6
2010-15	2.5
2015-20	3.0

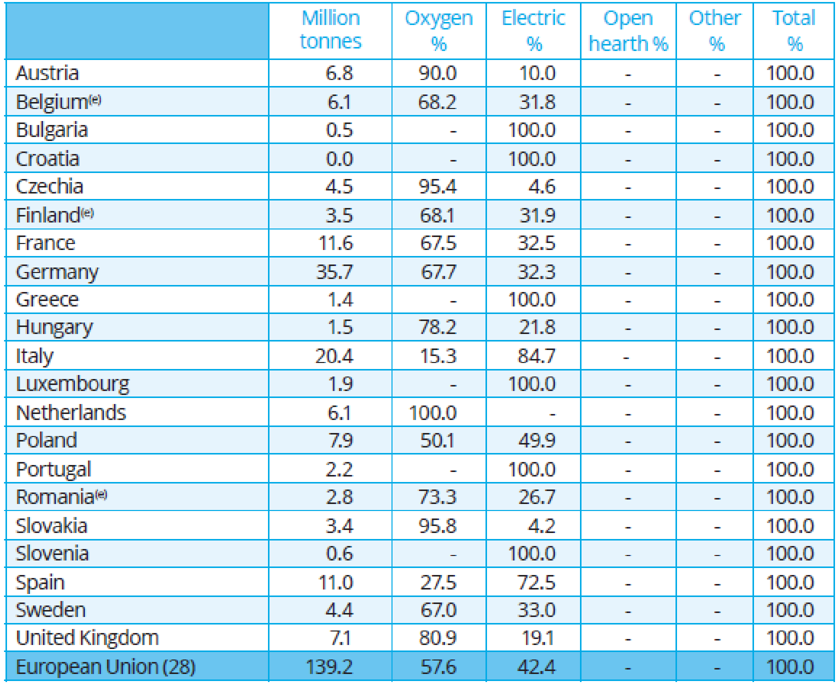
Environmental aspects of steelmaking



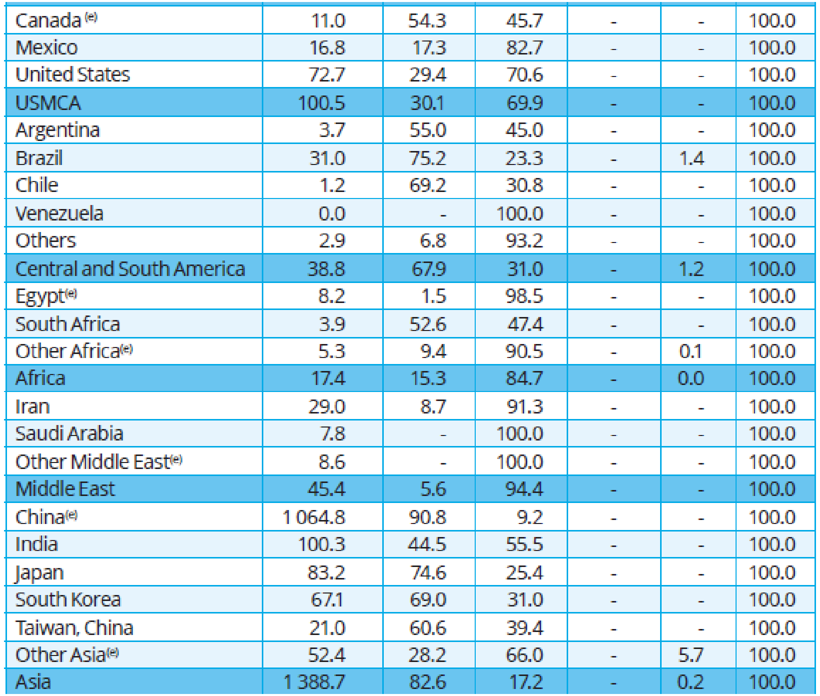
/P. Wang et al., Nature Communications 12 (2021) 2066/

MI mining, SI sintering, PE pelleting, BF blast furnace, DR direct reduction, BOF blast oxygen furnace, CB crucible, PD puddling, BT Bessemer & Thomas, OHF open-hearth furnace, IF iron foundry, EAF electric arc furnace, CC continuous casting, IC ingot casting, SeM section mill, PtM plate mill, StM strip mill, RbM rod bar mill, CdM cold rolling mill.

Environmental aspects of steelmaking

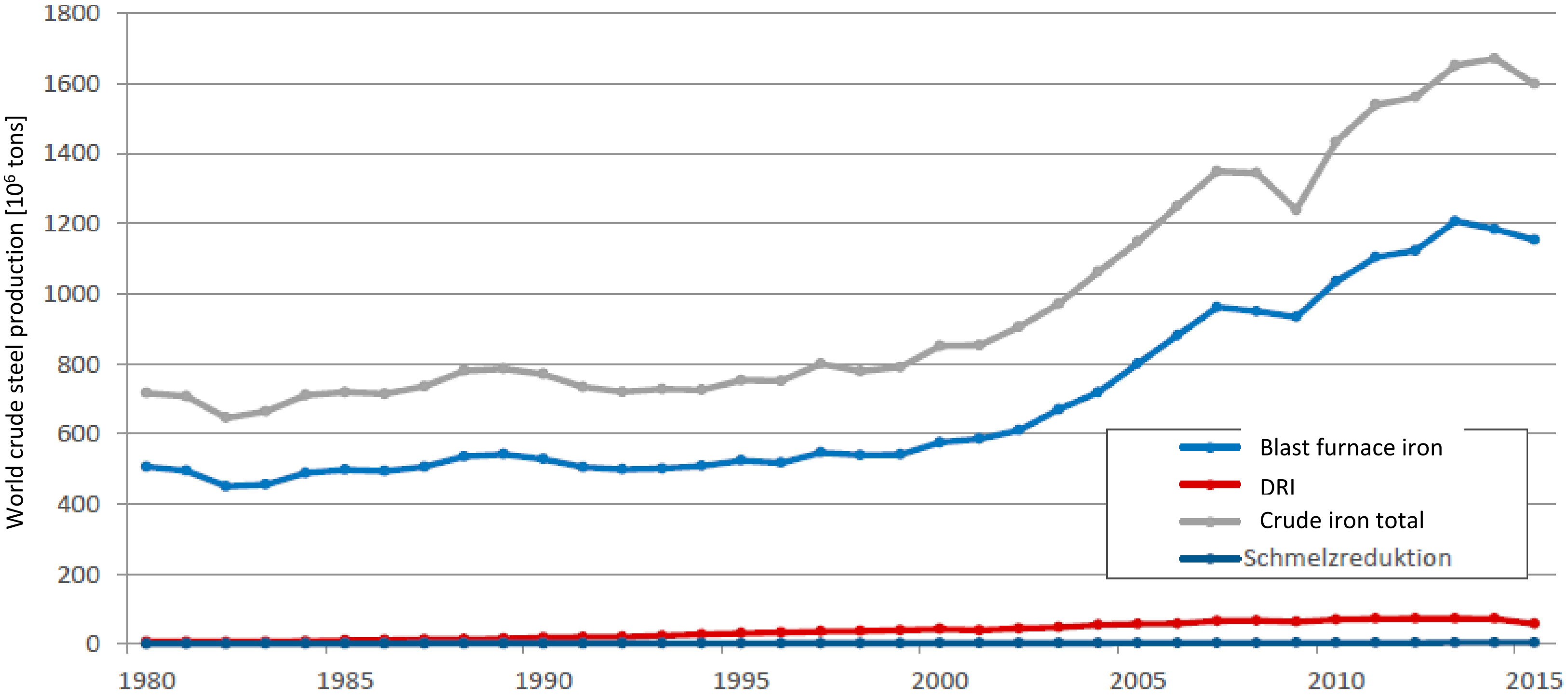


	Million tonnes	Oxygen %	Electric %	Open hearth %	Other %	Total %
Austria	6.8	90.0	10.0	-	-	100.0
Belgium[(e)]	6.1	68.2	31.8	-	-	100.0
Bulgaria	0.5	-	100.0	-	-	100.0
Croatia	0.0	-	100.0	-	-	100.0
Czechia	4.5	95.4	4.6	-	-	100.0
Finland[(e)]	3.5	68.1	31.9	-	-	100.0
France	11.6	67.5	32.5	-	-	100.0
Germany	35.7	67.7	32.3	-	-	100.0
Greece	1.4	-	100.0	-	-	100.0
Hungary	1.5	78.2	21.8	-	-	100.0
Italy	20.4	15.3	84.7	-	-	100.0
Luxembourg	1.9	-	100.0	-	-	100.0
Netherlands	6.1	100.0	-	-	-	100.0
Poland	7.9	50.1	49.9	-	-	100.0
Portugal	2.2	-	100.0	-	-	100.0
Romania[(e)]	2.8	73.3	26.7	-	-	100.0
Slovakia	3.4	95.8	4.2	-	-	100.0
Slovenia	0.6	-	100.0	-	-	100.0
Spain	11.0	27.5	72.5	-	-	100.0
Sweden	4.4	67.0	33.0	-	-	100.0
United Kingdom	7.1	80.9	19.1	-	-	100.0
European Union (28)	139.2	57.6	42.4	-	-	100.0



Canada [(e)]	11.0	54.3	45.7	-	-	100.0
Mexico	16.8	17.3	82.7	-	-	100.0
United States	72.7	29.4	70.6	-	-	100.0
USMCA	100.5	30.1	69.9	-	-	100.0
Argentina	3.7	55.0	45.0	-	-	100.0
Brazil	31.0	75.2	23.3	-	1.4	100.0
Chile	1.2	69.2	30.8	-	-	100.0
Venezuela	0.0	-	100.0	-	-	100.0
Others	2.9	6.8	93.2	-	-	100.0
Central and South America	38.8	67.9	31.0	-	1.2	100.0
Egypt[(e)]	8.2	1.5	98.5	-	-	100.0
South Africa	3.9	52.6	47.4	-	-	100.0
Other Africa[(e)]	5.3	9.4	90.5	-	0.1	100.0
Africa	17.4	15.3	84.7	-	0.0	100.0
Iran	29.0	8.7	91.3	-	-	100.0
Saudi Arabia	7.8	-	100.0	-	-	100.0
Other Middle East[(e)]	8.6	-	100.0	-	-	100.0
Middle East	45.4	5.6	94.4	-	-	100.0
China[(e)]	1 064.8	90.8	9.2	-	-	100.0
India	100.3	44.5	55.5	-	-	100.0
Japan	83.2	74.6	25.4	-	-	100.0
South Korea	67.1	69.0	31.0	-	-	100.0
Taiwan, China	21.0	60.6	39.4	-	-	100.0
Other Asia[(e)]	52.4	28.2	66.0	-	5.7	100.0
Asia	1 388.7	82.6	17.2	-	0.2	100.0

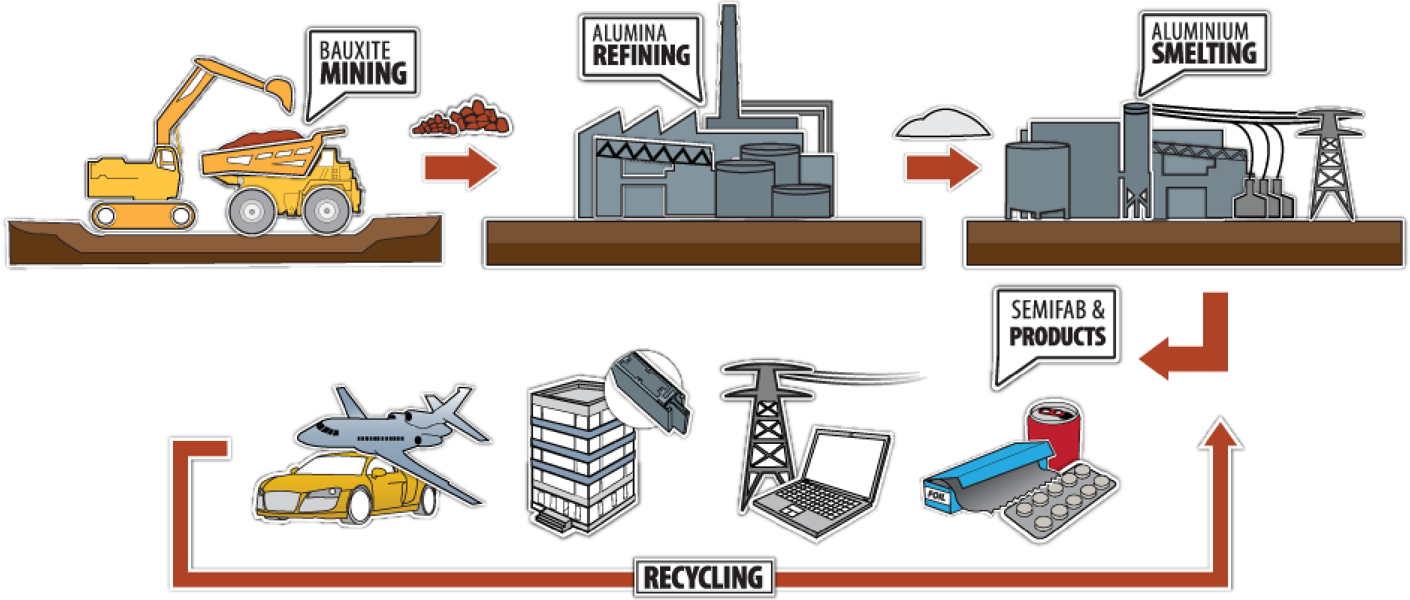
Environmental aspects of steelmaking



Direct reduction processes

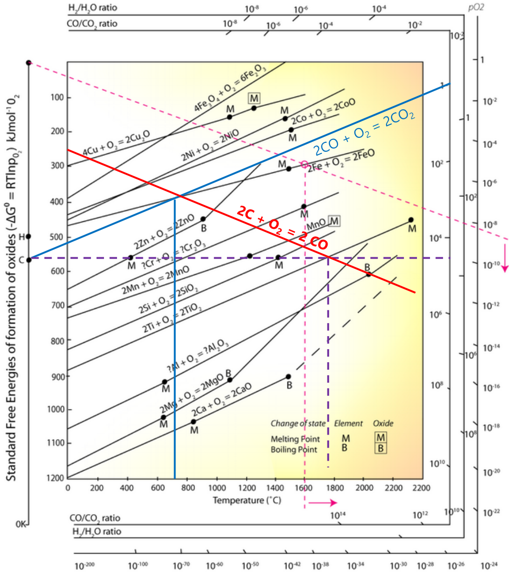
- Factors that help make DRI economical and ecological:
  - DRI has about the same iron content as pig iron, typically 90–94% total iron (depending on the quality of the raw ore) so it is an excellent feedstock for the electric furnaces used by mini mills, allowing them to use lower grades of scrap for the rest of the charge or to produce higher grades of steel.
  - Hot-briquetted iron (HBI) is a compacted form of DRI designed for ease of shipping, handling, and storage; hot direct reduced iron (HDRI) is DRI that is transported hot, directly from the reduction furnace, into an electric arc furnace, thereby saving energy.
  - The direct reduction process uses pelletized iron ore or natural "lump" ore. One exception is the fluidized bed process which requires sized iron ore particles.
  - The direct reduction process can use natural gas contaminated with inert gases, avoiding the need to remove these gases for other use. However, any inert gas contamination of the reducing gas lowers the effect (quality) of that gas stream and the thermal efficiency of the process.
  - In most cases the DRI plant is located near a natural gas source as it is more cost effective to ship the ore rather than the gas.
  - To eliminate fossil fuel use in iron and steel making, renewable hydrogen gas can be used in place of syngas to produce DRI.

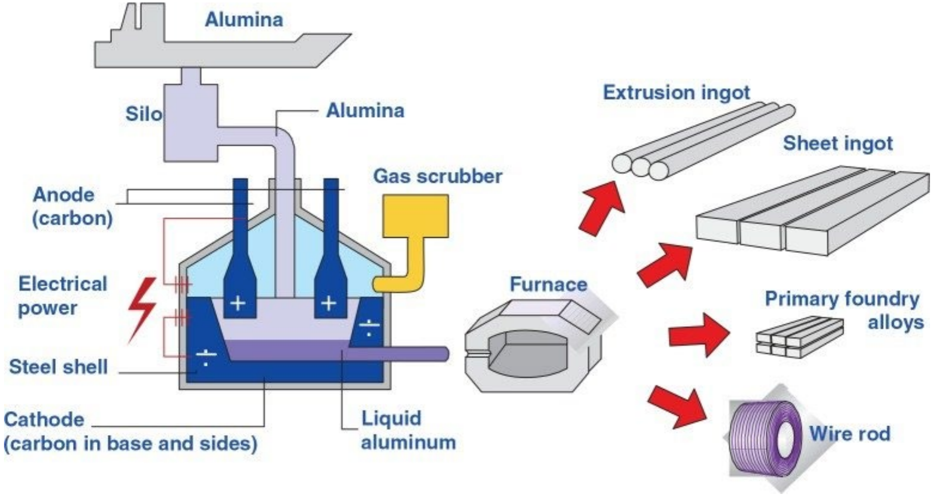
Overview of the Al making process



Reduction of Aluminia

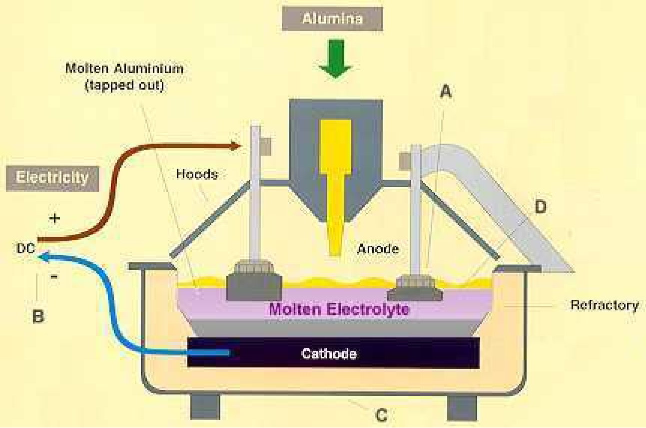
- Al_2O_3 has a melting point of 2050°C and is thermodynamically very stable, thus a reduction is very difficult
- The common process for the production of Al from Al_2O_3 is the Hall-Héroult electrolysis process



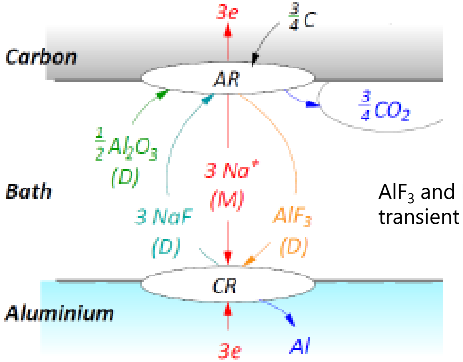


Reduction of Alumina

- Fused salt electrolysis (Hall-Heroult process)
  - Cathode (permanent), anode (graphite, consumed)
  - electrolyte is a eutectic of 81.5% cryolite Na_3AlF_6 and 18.5% Al_2O_3
- Reactions
  - Electrolysis: $Al_2O_3 = 2\ Al^{3+}\ 3\ O^{2-}$
    $Al^{3+} + 3\ e^- = Al$
  - Reaction with anode $C + 2\ O^{2-} = CO_2 + 4\ e^-$
  - Overall reaction: $2\ Al_2O_3 + 3\ C = 4\ Al + 3\ CO_2$
    (1.5 ton CO_2 per ton Al – carbon reduces voltage)
- Current efficiency is 80-95%
  - some losses due to Al dissolved in electrolyte, transferred to anode where it is reoxidized : $2Al + 3\ CO_2 = Al_2O_3 + 3\ CO$
  - Also ohmic resistance in electrolyte

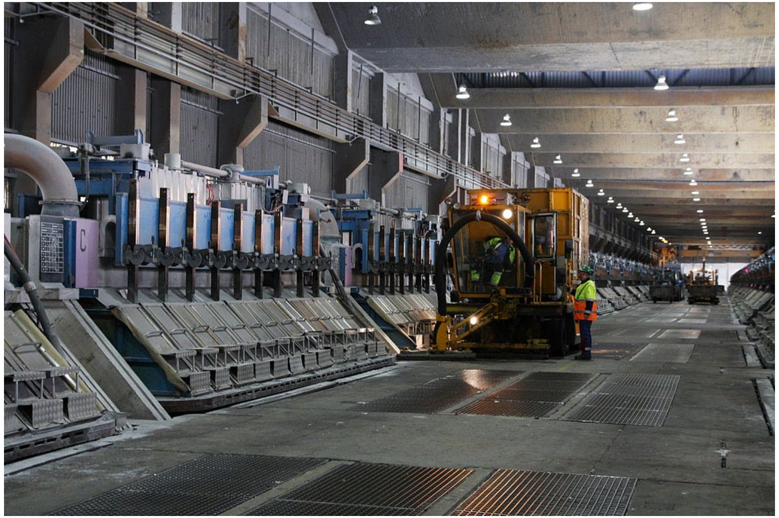


http://www.energymanagertraining.com/aluminium/Al_how.htm



AlF_3 and NaF are transient products

The Hall-Héroult process



/www.youtube.com/watch?v=4a1ptfTItXA/

Environmental aspects of the Al production

- Compared with other metallurgical processes, the Hall-Héroult process has a low productivity and consumes significant amounts of energy (13-15 kWh/kg_{Al})
- The production of each kg of Al consumes between 0.4 and 0.5 kg carbon in the form of anodes → Al production contributes to 2-5% of the world man-made CO_2 equivalent emissions
- The process also generates greenhouse gasses such as CF_4 and C_2F_6 or perfluorocarbons (PFCs) from the carbon electrode and reactions with liquid cryolite
- Possibilities for improving the environmental efficiency
  - Use of inert anodes instead of C
  - Alternative Al production methods
  - Al recycling

Inert anodes

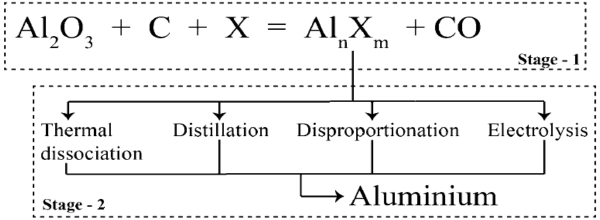
- Inert (i.e. non-reactive) anodes as a replacement of graphite have been investigated for >30years
- Their successful adoption to the electrolysis cell is expected to eliminate the emission of CO2
- Among the anode materials (cermets, ceramics and metals), metallic anodes are preferred as they possess high electrical conductivity, mechanical robustness, easy fabrication, good thermal resistance and ease in electrically connecting to current leads
- The metallic anode is protected by an oxide scale which grows once the anode is immersed into the melt, which is supposed to improve the anode's chemical resistance.
- Reactions:
  - Electrolysis: $Al_2O_3 = 2\,Al^{3+}\ 3\,O^{2-}$
    $Al^{3+} + 3\,e^- = Al$
  - Reaction with anode $M_{(s)} + x\,O_{(c)}^{2-} = Mo_{x(s)} + 2x\,e^-$
    $2\,O_{(c)}^{2-} = O_{2(g)} + 4\,e^-$

Inert anodes

- Materials investigated
    - Fe(50-80)-Ni(50-20) alloys
    - Fe(55-60)-Ni(35-40)-Al(5) alloys
    - Cu(45-65)-Fe-Ni (Ni/Fe = 1.33) alloys
    - Cu(85-90)-Al(10-15) alloys
    - Cermets
- All materials form complex oxide layer structures at the surface upon exposure to liquid cryolite
- Pronounced corrosion of anodes; pre-oxidizing the anode materials can improve the corrosion resistance.
- The use of low-temperature electrolytes can improve the stability of the anode oxide scale
- No industry has successfully launched an inert anode for the Al electrolysis yet.

Alternative Al production methods

- The Direct carbothermal reaction (DCR) aims at
  - $Al_2O_3(s) + 3C(s) = 2Al(s) + 3CO(g)$
  - $Al_2O_3(s) + 3CH_4(g) = 2Al(s) + 3CO(g) + 6H_2(g)$
  - These two reactions are thermodynamically favored above 2057°C and 1497°C, respectively
- Indirect carbothermal reaction (IDCR) involves two or more steps where in the first step (stage 1) alumina or Al ores are converted to intermediate Al compounds. The ntermediate Al compounds are then further reduced to Al in subsequent steps (stage 2)
  - Carbochlorination route
  - Extraction of Al from Al trichloride
  - Extraction of Al from Al sulphides
  - Extraction of Al from Al nitride

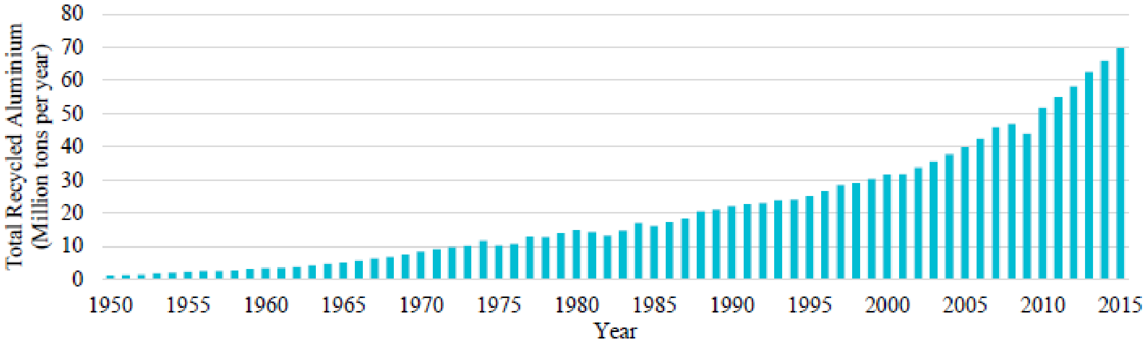


$Al_2O_3 + C + X = Al_nX_m + CO$

- DCR has not been commercialised because of problems with extreme operating conditions and yield
- stage indirect carbothermic reduction using Cl, S and N sources to form intermediates have been investigated but still require significant developments

Al recycling

- Al has a high recycling potential and the amount of recycled Al has continuously increased over the years
- The high reactivity of Al and the stability of Al-based IMCs lead to the presence of e.g. Cu or Fe within the different types of Al alloys which is a major limitation to achieve high quality secondary Al
- Aluminium is an infinitely recyclable material, and it takes up to 95 percent less energy to recycle it than to produce primary aluminum, which also limits emissions, including greenhouse gases.
- Today, about 75 percent of all aluminum produced in history, nearly a billion tons, is still in use.



Al recycling

- Aluminium beverage cans are usually recycled by the following method:
  - Cans are first divided from municipal waste, usually through an eddy current separator, and cut into small, equally sized pieces to lessen the volume and make it easier for the machines that separate them.
  - Pieces are cleaned chemically/mechanically and blocked to minimize oxidation losses when melted.
  - Blocks are loaded into a furnace and heated to 750 °C ± 100 °C to produce molten aluminium.
  - Slag is removed, and any dissolved hydrogen is degassed. (This is typically done with chlorine and nitrogen gas)
  - Samples are taken for spectroscopic analysis. Depending on the final product desired, high-purity aluminium, copper, zinc, manganese, silicon, and/or magnesium is added to alter the molten composition to the proper alloy specification.
  - The furnace is tapped, the molten Al poured out, and the process is repeated again for the next batch. Depending on the end product, it may be cast into ingots, billets, or rods, formed into large slabs for rolling, atomized into powder, sent to an extruder, or transported in its molten state to manufacturing facilities for further processing.

Learning objectives

- Primary metallurgy basics
    - Explore the key principles of extracting and refining metals from ores.
    - Study the thermodynamic and kinetic factors influencing metal production.
    - Use Ellingham Diagrams and process modeling tools to predict reactions.
- Steelmaking processes
    - Compare the Blast Furnace and Direct Reduction methods.
    - Understand the Basic Oxygen Converter Process and its role in steel refinement.
- Environmental Aspects
    - Examine the CO_2 emissions and energy consumption of primary metallurgy.
    - Discuss potential strategies for sustainable steel and aluminum production.
    - Investigate the role of advanced technologies in improving efficiency.
    - Assess the significance of recycling and alternative raw materials in reducing waste.