Global Research and Development

Massive production of primary iron metal by electrolysis



PRAXISforum "Electrolysis in Industry"

$$\frac{\partial f_{i,j}(\vec{x},\vec{c})}{\partial x^{i}} = \sum_{k \neq i} c_{k,i}$$

The right formula for the steels of the future





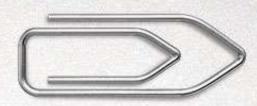
Outlook

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- Steel production and its environmental significance
 - Main figures
 - Steel Energy coupling
- 2. New steel process for low CO₂ emissions
 - Primary steel production by electricity
 - Chemical route to solve multivalencies of iron
- 3. Electrolysis processing route
 - Design by thermodynamic optimisation
 - SIDERWIN project



Lightweight, ...



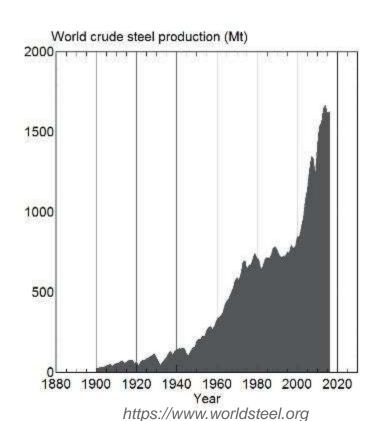
sustainable design



Our constant goal



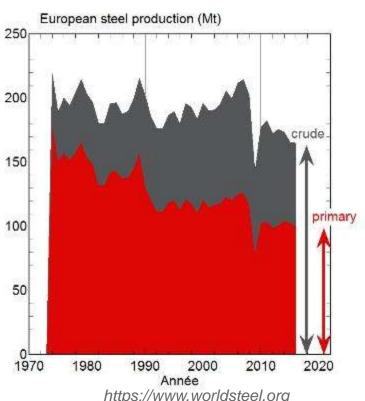
World steel production (2016)



- 1 628 Mt crude steel.
- 75% primary steel.
- 1000 G\$ turnover.
- BAU scenarios predict 2.0 à 2.5 Gt in 2050.
- Accounts for 6.7% GHG emissions.



European steel production (2016)



- 162 Mt crude steel (2016).
- 60% primary steel.
- 320 000 employees.
- 170 G\$ turnover.
- 1.4% GDP.
- Second world largest productor.
- 236 Mt expected in 2050.
- Accounts for 5.3% GHG emissions.



Steel stock per capita

orMittal Canada 12-Iron stocks (Vcap) 2000 ▼ 1975 1950 1900 10,000 15,000 20,000 5,000 25,000 30,000 GDP (1990 Intl\$/cap)

Steel consumption per capita



D. Müller et al. Patterns of Iron Use in Societal Evolution

20 Gt of steel in use worldwide

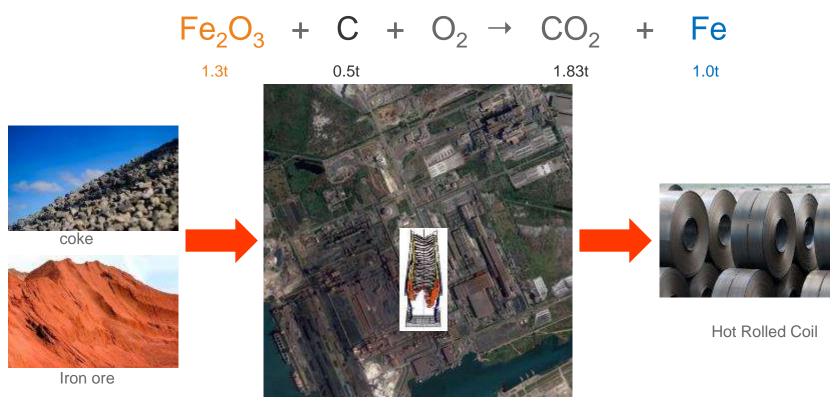
https://www.worldsteel.org

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Steel production process: Blast Furnace Route



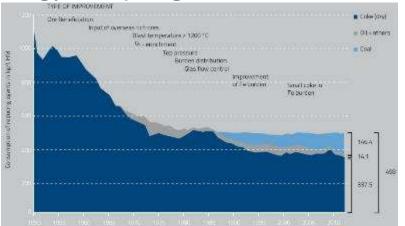
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Steel – Energy coupling:

No steel without energy

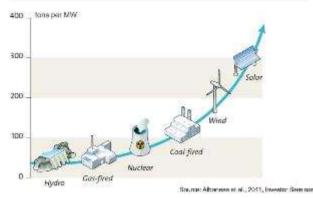


EUROFER - The European Steel Association

No energy
without
steel

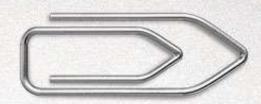


	Blast Furnace
Energy	18.6 GJ.t ⁻¹ steel
	5.2 MWh.t ⁻¹ steel
CO_2	1.83 t.t ⁻¹ steel





Lightweight, ...



sustainable design

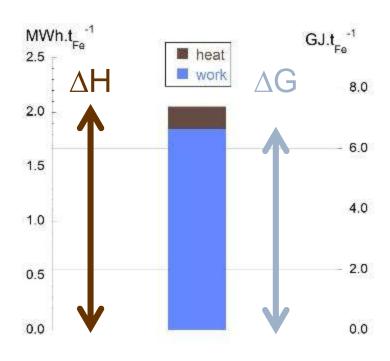


Our constant goal



Primary steel production: energy need.

$$\frac{1}{2}\text{Fe}_{2}\text{O}_{3} \text{ (s, 25°C)} + \frac{3}{4}\text{O}_{2} \text{ (g, 1atm, 25°C)}$$



- Total energy need :
- $\Delta H = 2.1 \text{ MWh.t}_{\text{Fe}}^{-1} \text{ or } 7.4 \text{ GJ.t}_{\text{Fe}}^{-1}$
 - Heat need 10% of total energy :

$$\Delta H$$
- $\Delta G = 0.2 \text{ MWh.t}_{\text{Fe}}^{-1} \text{ or } 0.7 \text{ GJ.t}_{\text{Fe}}^{-1}$

heat is taken by cooling atmosphere

Work need 90% of total energy :

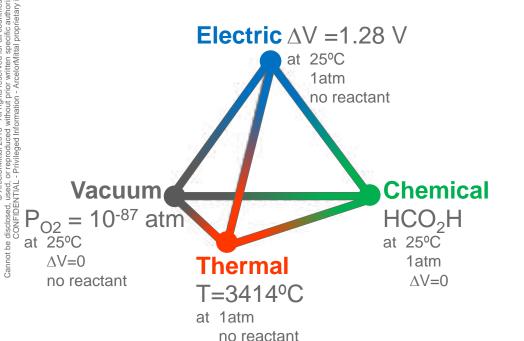
$$\Delta G = 1.9 \text{ MWh.t}_{Fe}^{-1} \text{ or } 6.7 \text{ GJ.t}_{Fe}^{-1}$$

what source for work?



Primary steel production: choice of an energy form.

$$\frac{1}{2}\text{Fe}_{2}\text{O}_{3} \text{ (s, 25°C)} + \frac{3}{4}\text{O}_{2} \text{ (g, 1atm, 25°C)}$$



 $\Lambda V=0$

Electrical seems particularly appropriate.

Which medium to separate ions?

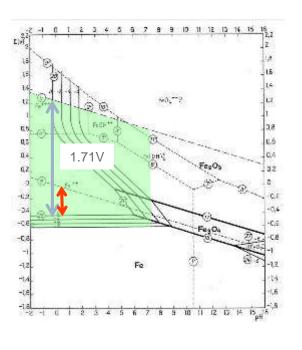
cathode Pe² anode

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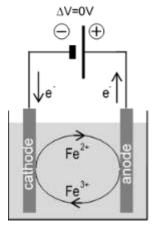


Acid chemical route: problem of iron multivalent ions



Pourbaix diagram

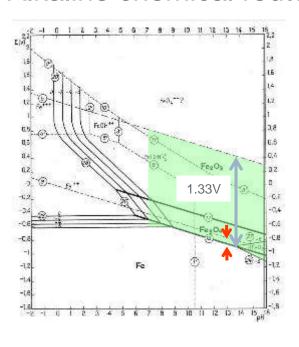
- Decomposition voltage is higher than thermodynamic minimum due to cation solvatation.
- Both Fe(II) and Fe(III) are soluble.



Chemical looping prevent iron metal production.



Alkaline chemical route solve multivalencies of iron.



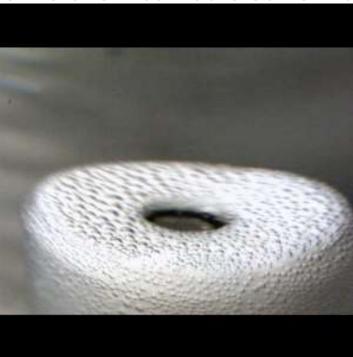
Pourbaix diagram

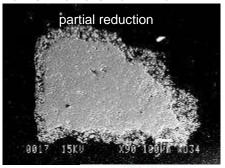
- Decomposition voltage corresponds to magnetite.
- Fe(III) is insoluble.
- Fe(II) soluble in reductive conditions.
- Magnetite is electronically conductive.

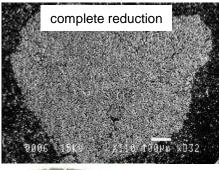
Is electrolysis at low solubility possible?



Alkaline chemical route solve multivalencies of iron







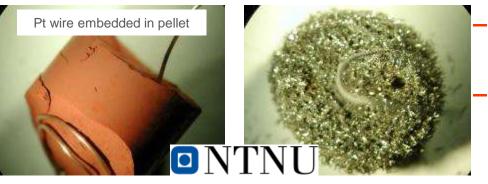




Solid particles of hematite are electrochemically reduced



Alkaline chemical route solve multivalencies of iron



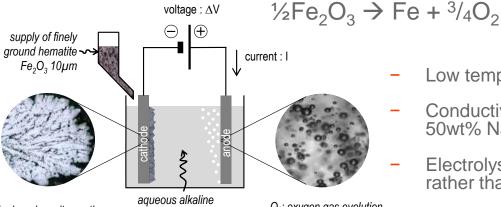


ParisTech

- Reaction progresses inward the particle.
- Magnetite is produced as an intermediate compound on hematite.
- Iron metal is produced as a separated solid phase.
- There is conservation of crystallographic orientations between the three phases.



Chemical route to solve multivalencies of iron



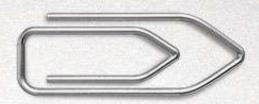
Fe: iron deposit growth solution with suspended particles

O₂: oxygen gas evolution

- Low temperature electrolysis: 110°C.
- Conductive aqueous alkaline electrolyte medium 50wt% NaOH - H2O.
- Electrolysis is applied to 10 µm hematite solid particles rather than dissolved ions.
- High reaction rate with current density 1000 A.m⁻².
- Anodic gaseous O_2 production.
- Non-consumable anode.
- Cathodic Iron grown as solid state deposit.
- Non critical elements in electrode materials, Ni anodes.



Lightweight, ...



sustainable design



Our constant goal



- Design by "thermodynamic optimization":
 - 1. Supply energy accurately in terms of amount, of form and intensity.
 - Operation close to thermodynamic reversibility with a ratchet effect to give an orientation to progress.
 - 3. Operation as close as possible to surrounding conditions, minimise heat and pressure losses.
 - 4. Straight, once through flow, energy change of form, no loop, no internal recirculation, not stable intermediates.
 - 5. No chemical mixing, dissolution, dispersion.
 - 6. Minimised transfer resistances, low ohmic and viscous "frictions".
 - 7. Uniformity in space of intensity parameters: no hot spots, not dead zones.
 - 8. Uniformity in time of intensity parameters: steady state, no transient.



Design by thermodynamic optimisation

The condition of simultaneous uniform potential and current density is constant curvature electrodes.

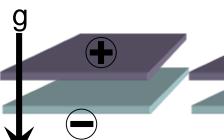
Separation of reaction products by proper orientation towards gravity. Ratchet effect by gravity separation of oxygen from iron.

Uniform and non accumulating supply of solid particles to the cathode surface by moderate electrolyte flow rate.

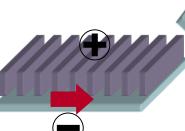
Anode is a gaselectricity exchanger: maximum openness to gas upward flow, minimum inter electrodes gap distance.

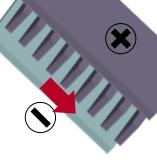
Full collection and minimum residence time of gas by a 45° electrodes inclination and counter flowing gas.











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 Technological development of iron metal production by electrolysis:





- Steady operation: thermal, hydraulic, electric.
- No separator as membrane, diaphragm between electrodes.
- Distance between electrodes 1cm.
- Productivity x3 compared to Ni et Co.
- Self-standing, stiff, compact and conveyable metal plates.
- Low voltage $\Delta V=1.6V$.
- Full recovery of oxygen gas.
- Cheap construction materials.





SIDERWIN project



- 5 years project 2017-2022
- Budget: 6.8 M€ includes 2.2 M€ for pilot.
- 7 different countries.
- 12 partners : 4 Companies + 4 SMEs + 4 RTO
- Multisectorial: steel, non-ferrous and power.
- Coordinated by ArcelorMittal.









 SIDERWIN project: addressing primary steel production in the its simplest chemical route.

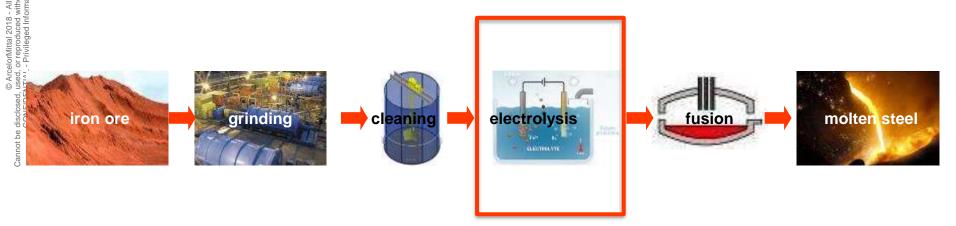
$$\frac{1}{2}\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \frac{3}{4}\text{O}_2$$

- Production of iron metal.
- Energy supplied as electricity.
- Treatment of naturally occurring oxides.
- Breakthrough compared to conventional routes.

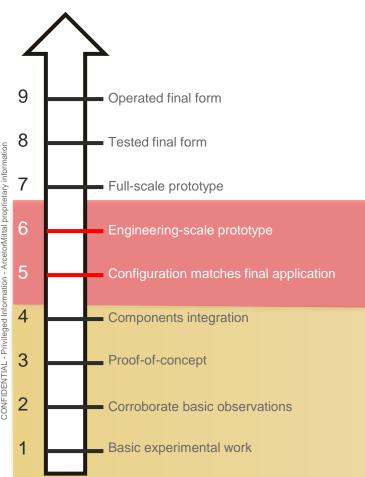




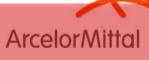
- SIDERWIN project: objectives
- A new processing route for steel.
- 2. Overall energy consumption 3.6 MWh.t⁻¹_{Fe} or 13 GJ.t⁻¹_{Fe}.
- 3. Reduction by 31% of the direct energy use.
- 4. Reduction by 87% of the direct CO₂ emissions.



SIDERWIN project







2017-2022 6.8M€









IERO



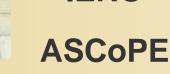


2007

2006

2005















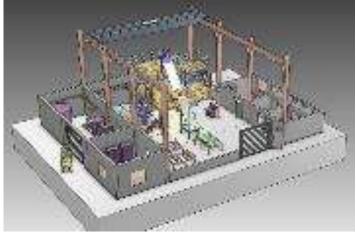
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SIDERWIN project: development of key components to achieve



- Continuous and automated iron ore supply.
- Gas oxygen collection.
- Metal harvesting system.
- Vertical extension for low footprint.





SIDERWIN project: operation in a relevant environment TRL6



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Flexible metal production:

- Contribute to integration of RES.
- Integration to power grid.

Enlarge iron oxide sources:

- Non-conventional feedstock.
- Residues from Al, Ni and Zn metallurgies.

Develop new business models:

- New service as residue treatment.
- New service as Demand Side Response.

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SIDERWIN project

https://www.siderwin-spire.eu/content/home







Bibliography

- A. Allanore, H. Lavelaine, G. Valentin, J. P. Birat, and F. Lapicque, « Iron Metal Production by Bulk Electrolysis of Iron Ore Particles in Aqueous Media », Journal of The Electrochemical Society, 155 (9) E125-E129 (2008)
- Boyan Yuan and G.-M. Haarberg, Electrowinning of Iron in Aqueous Alkaline Solution Using Rotating Disk Electrode, Volume 106, Issue 10 October 2009, pp. 455-459, DOI: https://doi.org/10.1051/metal/2009078
- H. Lavelaine and A. Allanore, "Optimized Design of an Iron Electrowinning Cell", Rev. Met. Paris, N°10 (October 2009), pp. 460-471, http://dx.doi.org/10.1051/metal/2009079
- A. Allanore, H. Lavelaine and Wen Xuan, "Application of Modeling to the Development of an Electrochemical Pilot Cell", Rev. Met. Paris, N°10 (October 2009), pp. 440-454
- A. Allanore, J. Feng, H. Lavelaine and K. Ogle, « The adsorption of hematite particles on steel in strongly alkaline electrolyte», Journal of The Electrochemical Society, 157 (3) E24-E30 (2010)
- A. Allanore, H. Lavelaine, G. Valentin, J.P. Birat, P. Delcroix, F. Lapicque, « Observation and modelling of the reduction of hematite particles to metal in alkaline solution by electrolysis », Electrochimica Acta 55 (2010) 4007–4013
- Antoine Allanore, H. Lavelaine, J. P. Birat, G. Valentin, F. Lapicque, Experimental investigation of cell design for the electrolysis of iron oxide suspensions in alkaline electrolyte J Appl Electrochem DOI 10.1007/s10800-010-0172-0
- Herve Lavelaine de Maubeuge, Influence of geometric variables on the current distribution uniformity at the edge of parallel plate electrodes, Electrochimica Acta 56 (2011) 10603–10611
- Yu. A. Ivanova, J. F. Monteiro, A. L. Horovistiz, D. K. Ivanou, D. Mata, R. F. Silva, J. R. Frade, Electrochemical deposition of Fe and Fe/CNTs composites, from strongly alkaline hematite suspensions, J Appl Electrochem, DOI 10.1007/s10800-015-0803-6
- IERO project: Iron production by electrochemical reduction of its oxide for high CO2 mitigation, Grant Agreement RFSR-CT-2010-00002, 1 July 2010 – 30 June 2014
- J.F. Monteiro, Yu. A. Ivanova, A.V. Kovalevskya, D.K. Ivanou, J.R. Frade, Reduction of magnetite to metallic iron in strong alkaline medium, Electrochimica Acta, Volume 193, 1 March 2016, Pages 284–292, http://www.sciencedirect.com/science/article/pii/S0013468616303371
- Feynerol, V & Lavelaine, H & Marlier, P & Pons, M.-N & Lapicque, F. (2017). Reactivity of suspended iron oxide particles in low temperature alkaline electrolysis. Journal of Applied Electrochemistry. 47. 1-12. 10.1007/s10800-017-1127-5.



High temperature electrolysis

