Massive production of primary iron metal by electrolysis

PRAXISforum "Electrolysis in Industry"

The right formula for the steels of the future
Outlook

1. 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
Steel production

Lightweight, ...

sustainable design

Our constant goal

November 23th 2018

Frankfurt – DECHEMA - PRAXISforum “Electrolysis in Industry”
Steel production

- 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.

https://www.worldsteel.org
Steel production

• European steel production (2016)

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

https://www.worldsteel.org
Steel production

Steel stock per capita  
Steel consumption per capita

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

• 20 Gt of steel in use worldwide

November 23th 2018

https://www.worldsteel.org

Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"
Steel production

- Steel production process: Blast Furnace Route

\[ \text{Fe}_2\text{O}_3 + C + \text{O}_2 \rightarrow \text{CO}_2 + \text{Fe} \]

1.3t \quad 0.5t \quad 1.83t \quad 1.0t

Iron ore \quad coke \quad \text{Hot Rolled Coil}

November 23th 2018
Steel production

- Steel – Energy coupling:

  No steel without energy
  
  No energy without steel

<table>
<thead>
<tr>
<th>Blast Furnace</th>
<th>Energy</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.6 GJ.t⁻¹ steel</td>
<td>1.83 t.t⁻¹ steel</td>
</tr>
</tbody>
</table>

EUROFER - The European Steel Association
New steel process for low CO$_2$ emissions
New steel process for low CO₂ emissions

- Primary steel production: energy need.

\[ \frac{1}{2} \text{Fe}_2\text{O}_3 \text{ (s, 25°C)} \rightleftharpoons \text{Fe} \text{ (s, 25°C)} + \frac{3}{4} \text{O}_2 \text{ (g, 1atm, 25°C)} \]

- Total energy need:
  \[ \Delta H = 2.1 \text{ MWh.t}_\text{Fe}^{-1} \text{ or 7.4 GJ.t}_\text{Fe}^{-1} \]

- Heat need 10% of total energy:
  \[ \Delta H - \Delta G = 0.2 \text{ MWh.t}_\text{Fe}^{-1} \text{ or 0.7 GJ.t}_\text{Fe}^{-1} \]
  heat is taken by cooling atmosphere

- Work need 90% of total energy:
  \[ \Delta G = 1.9 \text{ MWh.t}_\text{Fe}^{-1} \text{ or 6.7 GJ.t}_\text{Fe}^{-1} \]

what source for work?
New steel process for low CO₂ emissions

- Primary steel production: choice of an energy form.

\[
\frac{1}{2} \text{Fe}_2\text{O}_3 (s, 25^\circ\text{C}) \rightleftharpoons \text{Fe} (s, 25^\circ\text{C}) + \frac{3}{4}\text{O}_2 (g, 1\text{atm}, 25^\circ\text{C})
\]

- Electrical seems particularly appropriate.

Which medium to separate ions?

Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"
New steel process for low CO$_2$ emissions

- Acid chemical route: problem of iron multivalent ions
  - Decomposition voltage is higher than thermodynamic minimum due to cation solvatation.
  - Both Fe(II) and Fe(III) are soluble.

Pourbaix diagram

Chemical looping prevent iron metal production.
New steel process for low CO$_2$ emissions

- Alkaline chemical route solve multivalencies of iron.
  - 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?

Pourbaix diagram
New steel process for low CO$_2$ emissions

- Alkaline chemical route solve multivalencies of iron

- Solid particles of hematite are electrochemically reduced
New steel process for low CO$_2$ emissions

- Alkaline chemical route solve multivalencies of iron

- 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.
New steel process for low CO$_2$ emissions

- Chemical route to solve multivalencies of iron

\[
\frac{1}{2}Fe_2O_3 \rightarrow Fe + \frac{3}{4}O_2
\]

- Low temperature electrolysis: 110°C.
- Conductive aqueous alkaline electrolyte medium 50wt% NaOH - H$_2$O.
- 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.
Electrolysis processing route

Lightweight, ...

sustainable design

Our constant goal

November 23th 2018

Frankfurt – DEHEMA - PRAXISforum “Electrolysis in Industry”
Electrolysis processing route

- Design by “thermodynamic optimization”:
  1. Supply energy accurately in terms of amount, of form and intensity.
  2. 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.
Electrolysis processing route

- 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 gas-electricity 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.
Electrolysis processing route

• 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.
Electrolysis processing route

• 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.

November 23th 2018
Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"
Electrolysis processing route

- SIDERWIN project: addressing primary steel production in its simplest chemical route.
  
  \[ \frac{1}{2} \text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \frac{3}{4}\text{O}_2 \]

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

November 23rd 2018

Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"
Electrolysis processing route

- SIDERWIN project: objectives
  1. 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 CO\(_2\) emissions.
SIDERWIN project

- Basic experimental work
- Corroborate basic observations
- Proof-of-concept
- Components integration
- Configuration matches final application
- Engineering-scale prototype
- Full-scale prototype
- Tested final form
- Operated final form

2005
2006
2007
2009
2017
2018

November 23th 2018
Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"
Electrolysis processing route

- SIDERWIN project: development of key components to achieve TRL5
  - Continuous and automated iron ore supply.
  - Gas oxygen collection.
  - Metal harvesting system.
  - Vertical extension for low footprint.
Electrolysis processing route

- SIDERWIN project: operation in a relevant environment TRL6

  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.
SIDERWIN project

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

- 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
- 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
High temperature electrolysis

iron ore

molten steel


Pt-Rh cathodic connection

Alumina tube

Pt anode

Alumina crucible

Refractory cement

1550°C, 3 V, Ar-Atmosphere

Molten oxide

Fe deposit

Cathode wire

Alumina Cement

1 cm

November 23th 2018

Frankfurt – DECHEMA - PRAXISforum "Electrolysis in Industry"