Metals Production in The Future

Opportunities for Spinning Disc Technology

John van der Schaaf
Chemicals Production in The Future

Opportunities for Spinning Disc Technology

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Chemicals Production in the Future: Energy, Raw Materials, Capital & Risk

Highly variable supply
Distributed production
Storage/transport inefficient
Use for chemicals production
Highly variable production rate
Chemicals Production in the Future: Energy, Raw Materials, Capital & Risk

Highly variable resources
Biomass, recycle, waste
Distributed production
Safe, robust, efficient, versatile equipment + processes
Chemicals Production in the Future: Energy, Raw Materials, Capital & Risk

- Low CAPEX
- High ROI
- Multipurpose, Scalable
- Robust, Safe
- Millions vs. Billions

Source: MICA-ELU Political Risk Survey 2013
Multiphase Systems: Bottlenecks

\[
\frac{-r_A}{C_g} = \left( \frac{1}{k_g a_{gl}} + \frac{H}{k_l a_{gl}} + \frac{H}{k_s a_s} + \frac{H}{\eta k_r L_t \delta a_s} \right)^{-1}
\]

\[
-r_A \Delta H_R V_R = UA \Delta T_{lm}
\]
Rotor – Stator Spinning Disc Reactor

Von Karman

Inner core

Bödewadt

Rotor

Stator

r << R

Liquid flow only

\[ \text{Re}_h = 0.0025 \]

Liquid flow only

Gas inlet

Liquid inlet

Gas-liquid outlet

Stator

Gas inlet

Rotor

\( D = 13.2 \text{ cm} \)

Disk spacing

(1.3 mm)
Rotor – Stator Spinning Disc Reactor

Von Karman

- Inner core
- Bödewadit

$r << R$

- Gas inlet
- Liquid inlet
- Gas-liquid outlet
- Rotor

Rotational speed $\phi$

Disk spacing (1.3 mm)

35 rpm; slowed down factor 4

1000 rpm; slowed down factor 120
Rotor – Stator Spinning Disc Reactor

disc rotational speed: 1500 rpm; gas flow rate: 500 ml/min

1 gas inlet movies slowed down factor 120 8 gas inlets
Mass Transfer

Gas bubbles detach from gas inlet due to shear:
Increase in gas-liquid interfacial area $a_{GL}$

High rate of renewal of liquid at bubble interface:
Increase in mass transfer coefficient $k_L$
Mass Transfer

Bubble column: $k_L a_{GL} < 0.15 \text{ m}^3 \text{ m}^3 \text{ s}^{-1}$

Bubble column: $\frac{k_L a_{GL}}{\varepsilon_G} \approx 0.5 \text{ m}^3 \text{ m}_G^3 \text{ s}^{-1}$
Gas-Liquid Mass Transfer

Van Eeten et al., A theoretical study on gas-liquid mass transfer in the rotor stator spinning disc reactor, *CES* 129 2015
Multiple Spinning Discs Reactor

- Diameter disc 13.2 cm
- Maximum disc speed 4000 rpm
- Disc spacing 0.5 – 5 mm
- Cooled or heated discs
- Discs coated with catalyst
- Co- and countercurrent operation
Spinning Disc Technology

Technical characteristics:

- High mass transfer (GL ~ 10 1/s, LL ~ 300 1/s, LS ~ 1-300 1/s)
- High heat transfer (U·A ~ 40 MW/m³/K)
- Short micro mixing times (tₘ ~ 0.1 ms)
- Counter-current flow (100-1000 kg/hr)
- Plug flow (~ 4 tons/hr)
- Low volume (Vᵣ ~ 1 L)

Application areas:

- Extreme fast and exothermic reactions (nitrification)
- Multiphase reactions (sulfonation, halogenation)
- Extraction (LL, LS)
- Distillation (RPB), Absorption
- Crystallization
- Electrochemistry, Photochemistry
Intensification Chlor-alkali production

State-of-the-art operation (now)
15 kton/yr

High current operation

High pressure operation (~10 bar)

High temperature operation (~150 °C)

In the horizon
Vision

Dot on the horizon (10 kton/yr ~ 1 m³)

Back-of-a-truck production plant

Transported to clients

Plug ‘n’ Produce

Remote controlled

Transport NaCl from clients or...

recycle salt stream
Intensification Chlor-alkali production

\[ \text{Cl}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Cl}_2(l) + \text{H}_2\text{O}(l) \]

\[ \text{Cl}_2(l) + \text{Hydrate(s)} \]

\[ \text{Cl}_2(g) + \text{Hydrate(s)} \]

Source: A. T. Bozzo et al., 1975

\[ \text{H}_2\text{SO}_4 \]

Cl\(_2\)-H\(_2\)O phase diagram

Pressure [KPa]

Temperature [°C]

0.35 m\(^3\)/s

1 m\(^3\)/s

25 %

2 %
Intensification Chlor-alkali production

WP1: Brine Circuit
WP2: Electrolysis
WP3: Caustic Soda Processing
WP4: Hydrogen Processing

Inputs:
- Salt
- Water
- Energy

Outputs:
- H₂
- Cl₂
- NaOH
- NaOCl

Processes:
- ELECTROLYSIS
- CHLORINE PROCESSING
- HYDROGEN PROCESSING
- CAUSTIC SODA PROCESSING
Intensification Chlor-alkali production

- 0.03 kA/m², 2.33 V
- 0.12 kA/m², 3.03 V
- 0.21 kA/m², 3.59 V
- 0.30 kA/m², 4.32 V
- 0.39 kA/m², 4.60 V
- 1.40 kA/m², 9.92 V
Intensification Chlor-alkali production

Centrifugal force removes bubbles from electrode

Turbulence increases mass transfer
Intensification Chlor-alkali production

\[ Sh = 2.2 \text{Re}^{0.5} \text{Sc}^{0.33} \]

Disc: \( a_{LS} = 477 m_{e.a.}^2 / m_R^3 \)

Mesh: \( a_{LS} = 1322 m_{e.a.}^2 / m_R^3 \)
Intensification Chlor-alkali production

Paola Granados-Mendoza
Shohreh Moshtarikhah
Intensification Chlor-alkali production

- Voltage vs. current density
  - Electrocell
  - Spinning Disc Electrolyser

- Diagram of a chlor-alkali electrolysis cell with
  - Membrane
  - Rotor
  - Stator
  - Anode
  - Cathode
  - NaCl
  - H₂O
  - H₂(g)
  - NaOH
  - Cl₂(g)

- Graphs showing
  - Voltage vs. current density
  - Current density vs. rpm
  - Voltage vs. rpm
Intensification Chlor-alkali production

**Cl₂-H₂O phase diagram**

- **Cl₂(g) + H₂O(l)**
  - 300 ppm
  - 7.5 ⋅ 10⁻⁴ m³/s

- **Cl₂(l) + Hydrate(s)**
  - 1 m³/s
  - 25 %
  - 0.35 m³/s

- **Cl₂(l) + Hydrate(s)**
  - 1 %
  - 0.05 m³/s

- **Cl₂(g) + H₂O(l)**

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**Source:**

A. T. Bozzo et al., 1975

**H₂SO₄**
Intensification Chlor-alkali production

State-of-the-art operation (now)
15 kton/yr

High pressure operation (~10 bar)

High current density operation

High temperature operation (~150 ºC)

Dot on the horizon:

Electrolysis: 8 m², 100 kA/ m²
16 discs, 0.8 m ID, 0.08 m³
Chlorine drying: <0.5 m³
Evaporation: ~ 1 m³
Spinning Disc Zinc Production

Molten zinc metal can be easily transformed in small particles (µm range)
Zinc hydrogen production

1) Zinc + Concentrated sulfuric acid (10 mol/L)

\[ \text{Zn}(s) + 2 \text{H}^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + \text{H}_2 \text{(g)} \text{ (ambient, 0.9 mol}_\text{H}_2/\text{L, 0.36 mol}_\text{H}_2/\text{kg)} \]

2) Addition of catalytic amount of copper + Hot water

\[ \text{Zn}(s) + 2 \text{H}_2\text{O}(\ell) \rightarrow \text{Zn(OH)}_2(s) + \text{H}_2 \text{(g)} \text{ (~100 °C, 28 mol}_\text{H}_2/\text{L, 21 mol}_\text{H}_2/\text{kg)} \]

3) Molten zinc + steam

\[ \text{Zn}(l) + \text{H}_2\text{O(g)} \rightarrow \text{ZnO(s)} + \text{H}_2 \text{(g)} \text{ (~450 °C, 55 mol}_\text{H}_2/\text{L, 34 mol}_\text{H}_2/\text{kg)} \]

Exothermic!
Iron Fuel: gas phase oxidation/reduction

Cyclic operation packed bed

Energy production from heat of oxidation

\[ 2 \text{Fe} + \frac{3}{2} \text{O}_2 \rightarrow \ldots \rightarrow \text{Fe}_2\text{O}_3 \quad + \Delta H_R = -823 \text{kJ/mol}_\text{Fe} \]

\[ \text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightarrow \ldots \rightarrow \text{Fe} + 3 \text{H}_2\text{O} \quad + \Delta H_R = +196 \text{kJ/mol}_\text{Fe} \quad T>570 \, ^\circ\text{C} \]

1) Oxygen from air: high T leads to NO\textsubscript{x}

2) Oxygen and hydrogen from water electrolysis (recycle water)

3) Direct electrochemical reduction after dissolution \( \text{Fe}_2\text{O}_3 \) in sulfuric acid

\[ \text{Fe}^{2+}_{(aq)} + 2 \text{e}^- \rightarrow \text{Fe}_{(s)} \]

Solid iron poorly accessible for oxygen 😞
Use of oxygen from electrolysis

2 Fe + 3 O₂ → 2 Fe₂O₃

O₂ gas

liquid Xe
P < 1 bar

cryo O₂

14 MJ/kg, 58 MJ/L
41 hrs/tonne @ 100 kW

13 hrs @ 1 kW
Ragone Chart

\[ k_a a_g = 30 \text{ m/s} \]

\[ C_{O2} = 13 \text{ mol/m}^3 \]

\[ \sim 40 \text{ mol}_Fe/m_R^3/s \]

\[ \sim 32 \text{ MW} \]
Current & Future Work: Chemical Production Process

A(S) + B(g) \rightarrow C(S)

C(S) + B(g) \rightarrow D(S)
Current & Future Work: 
Chemical Production Process
Current & Future Work: Chemical Production Process
Current & Future Work: Chemical Production Process

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