THE SULFUR-IODINE AND OTHER THERMOCHEMICAL STUDIES AT CEA

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A CEA R&D Strategy

Concentrate efforts on a scientific approach
- data acquisition (development of specific analytical devices)
- modeling (physical models, flow-sheet analysis, systemic approach)

Develop expertise on thermochemical cycles assessments
Benefit from collaboration with international programs

Basic Research
- Thermodynamics
- Data acquisition
- Modeling
- Flow-sheet analysis
- Corrosion studies

Technological Assessments
- Laboratory loops
- Demonstrators
- Technological improvements
- Industrial viability

Collaboration with USA:
- GA, Sandia, Argonne, Idaho

Collaboration with Europe:
- HYTECH program

Collaboration with Japan:
- JAERI
CEA’s program for nuclear hydrogen

Hydrogen massive production using nuclear heat

Thermochemical cycles

Sulfur family

Other cycles

HTE

Assessment

Methodology

Flowsheet

Plant design

Reactor coupling

Economics

Sulfur-iodine

Hybrid sulfur

Flowsheet

Materials for membranes

Process breakthroughs

Bunsen: stoichiometry

H2SO4: high temperature part

H1: reactive distillation, membranes, catalysts

Modeling

Materials

Flowsheet

Technology

Modeling

Plant design

Reactor coupling

Economics

Modeling

Experiments

Lower priority →
Where are we today?

- 3 years work give an estimated efficiency of 35±5%
- A lot of key points are identified
- But will they come more and more?
- A R&D program was defined to get better and better

![Graph showing efficiency over time](image-url)
Main issues of Sulfur-Iodine cycle

SO₃ decomposition:
- catalyst
- coupling to reactor

HI separation
HI decomposition:
- catalyst (reactive distillation)
- incomplete reaction
Heat demand

Diagram:

- SO₃ decomposition
- HI decomposition
- Corrosion
- Iodine losses
Bunsen section: objectives

**Bunsen Reaction**

\[ xI_2 + SO_2 + (n+2)H_2O \rightleftharpoons [H_2SO_4 + (n-m)H_2O] + [2HI + (x-1)I_2 + mH_2O] \]

- **H_2SO_4(aq) phase**
- **HIx phase**

**Objectives:**

- Reduce excess of H_2O and I_2 while keeping phase separation
- Minimize side reactions

\[ H_2SO_4 + 6 HI \rightleftharpoons S + 3 I_2 + 4 H_2O \]

\[ H_2SO_4 + 8 HI \rightleftharpoons H_2S + 4I_2 + 4H_2O \]

- Minimize heat losses
## Bunsen section: experimental devices

<table>
<thead>
<tr>
<th>Device</th>
<th>Material</th>
<th>Operating temperature</th>
<th>Input chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>Glass</td>
<td>30-60°C</td>
<td>HI, H$_2$SO$_4$, I$_2$, H$_2$O</td>
</tr>
<tr>
<td>B1</td>
<td>Glass</td>
<td>100-120°C (limit 1,5 bar)</td>
<td>HI, H$_2$SO$_4$, I$_2$, H$_2$O</td>
</tr>
<tr>
<td>B2</td>
<td>Ta</td>
<td>100-150°C</td>
<td>I$_2$, H$_2$O, SO$_2$</td>
</tr>
<tr>
<td>B3</td>
<td></td>
<td></td>
<td><strong>Bunsen section of the I-NERI loop</strong></td>
</tr>
</tbody>
</table>

![Image of B0 device](image1)

![Image of B1 device](image2)

![Diagram of B2 device](image3)
**Bunsen section: analytical methods**

- **Objectives:**
  - Composition of the phases
  - Control of parasite reactions

- **Available methods (ex situ):**
  - $I$: UV-visible measurements after reduction of all ioded species
  - $S$: ICP-AES
  - $H^+$: potentiometric titration

- **Under development:**
  - Voltamperometry (ex situ)
  - $\gamma$-absorptiometry
  - ATR probe
  - Anti-Stokes Raman diffusion

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**CEA results**
Issues for the iodine section

- Exit of Bunsen section: HI/I2/H2O mixture (HIx)
- HI/H2O/I2 azeotrope: no simple separation
- Slow and incomplete decomposition of HI

Azeotrope composition as a function of temperature for the binary mixture HI-H2O (models)

No experimental data available up to now in relevant conditions: flow-sheet calculations based on assumptions, extrapolations, best estimates
Main options for the iodine section

Extractive distillation

- Add third body
  - $\text{HI}/(\text{H}_2\text{O}/\text{H}_3\text{PO}_4)$
  - Distillate

- Recycle
  - $\text{H}_2\text{O}$

- $\text{H}_3\text{PO}_4$

Electrodialysis

- Concentrate HIx
  - $\text{HI/}I_2/\text{H}_2\text{O}$
  - Distillate

- Decompose HI
  - $\text{HI/}I_2$/$I_2$

- Separate $\text{H}_2$

- Separate $\text{H}_2$

Reactive distillation

- Reactive distillation
  - $\text{H}_2\text{O}/H_2$

- $I_2$

- $\text{H}_2\text{O}$
## HI section: experimental devices

**Objective:** HIx liquid-vapor equilibrium data in process conditions

<table>
<thead>
<tr>
<th>Device</th>
<th>Material</th>
<th>Operating temperature</th>
<th>Pressure</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>Ta</td>
<td>100-300°C</td>
<td>1-100 bar</td>
<td>Total pressure</td>
</tr>
<tr>
<td>I2</td>
<td>Glass</td>
<td>up to 150°C</td>
<td>1,5 bar</td>
<td>Partial pressures</td>
</tr>
<tr>
<td>I3</td>
<td>Ta</td>
<td>100-300°C</td>
<td>1-100 bar</td>
<td>Partial pressures</td>
</tr>
</tbody>
</table>

### Total Pressure of the ternary HI-H2O-I2

![Graph showing total pressure vs. temperature](image)

Legend:
- **LSRM**
- **Littérature**
Corrosion of materials

- Bibliographic study
- Preliminary screening tests:
  - Bunsen section
  - HI section
- Study of associated mechanisms

Electrochemical tests in H₂SO₄

Tantalum, Zirconium: stable passive layer
Hastelloy B3: anodic dissolution
New devices for the study of corrosion

• Bunsen section: from 2006

A new device for longer tests in more representative conditions

– Ta Reactor
– Maximum temperature: 150°C
– Maximum pressure: 7 bars
– Volume: 1.5 L
– Possible sampling of the two liquid phases

• HI section: planned 2007

The CORBUN device
A long route to viability: efficiency and cost optimization

The challenges:
- R&D activities with no iterative process
  - flow-sheet assessment, heat distribution, materials, innovative concepts…
- Answer questions about strategy for the hydrogen economy
  - position vs. competitors (especially electrolysis), raw materials availability, safety, public acceptance, massive or dispersed production units…
### Experimental Tests

#### Volatility

<table>
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<tr>
<th>Reaction</th>
<th>Condition</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CaBr}_2 \Rightarrow \text{CaO}$</td>
<td>At 725°C/24h</td>
<td>Incomplete reaction, Particle collapse</td>
</tr>
<tr>
<td>$\text{CaBr}_2 \Rightarrow \text{CaO}$</td>
<td>At 750°C/24h</td>
<td>Just above melting point of CaBr2, Incomplete reaction, Hardened solid</td>
</tr>
<tr>
<td>$\text{FeBr}_2 \Rightarrow \text{Fe}_3\text{O}_4$</td>
<td>At 600°C/24h</td>
<td>Fe2O3 forms instead of Fe3O4, Incomplete reaction</td>
</tr>
<tr>
<td>$\text{FeBr}_2 \Rightarrow \text{Fe}_2\text{O}_3$</td>
<td>At 700°C/24h</td>
<td>Just above melting point of FeBr2, Fe2O3 forms instead of Fe3O4</td>
</tr>
</tbody>
</table>

#### The cycle is modified!
The Hybrid Sulfur Cycle

- Main issues: Electrolysis Section
  - Membrane (SO₂ permeation)
  - Cell over-voltage
The Cerium Chloride Cycle

- Membranes were suppressed
- High & rapid efficiency of reaction 2
- Viability of reaction 3

Lab tests:

- Cl₂ + H₂O
- 119 t/h
- Cl₂
- 95 t/h
- H₂O
- 24 t/h
- H₂O
- 24 t/h
- H₂ + H₂O + HCl
- 2.7 t/h + X t/h
- H₂
- 2.7 t/h
- HCl
- 295 t/h
- HCl
- 390 t/h
- H₂ + H₂O + HCl
- 2.7 t/h + X t/h + 287 t/h
- H₂O
- 73 t/h
- H₂O
- 24 t/h

- Membranes were suppressed
- High & rapid efficiency of reaction 2
- Viability of reaction 3
UT_3 cycle

CaO + Br₂ -> CaBr₂ + 1/2 O₂ (500-600°C)
CaBr₂ + H₂O -> CaO + 2 HBr (700-750°C)
Fe₃O₄ + 8 Hbr -> 3 FeBr₂ + 4 H₂O + Br₂ (200-300°C)
3 FeBr₂ + 4 H₂O -> Fe₃O₄ + 6 HBr + H₂ (550-650°C)

• Main advantage : max T° lower than for S-I
• A lot of unresolved difficulties + bromine toxicity

=> negative conclusion. We have given up this cycle

Sulfate cycles

Gas-solid reactions:
MO + H₂O + SO₂ → MSO₄ + H₂ exothermal - low T°
MSO₄ → MO + SO₂ + ½ O₂ endothermal - high T°
M could be Fe (T > 730°C), Ni, Co, Mn

Hybrid Sulfur cycle

SO₂ + 2H₂O → H₂SO₄ + 2H⁺ + 2e⁻ Low T° Electrolysis <120°C
H₂SO₄ → 4H₂O + SO₂ + ½ H₂ High T° Decomposition

• Advantage : 2 reactions cycles
• Difficulties : transfer of solid, parasites reactions (formation of MS, H₂S)

=> Tests underway

Cerium Chloride cycle

H₂O + Cl₂ → 2HCl + ½ O₂ ~ 650 °C
8HCl + 2 CeO₂ → 2CeCl₃ + Cl₂ + 4 H₂O ~ 100 °C
2CeCl₃ + 4H₂O → 2CeO₂ + 6HCl + H₂ ~ 750 °C

• Chloride and materials well none
• Medium toxicity

=> study underway