Canadian Advances in Thermochemical H₂ Production in the Context of Conventional Electrolysis

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Outline

The market for hydrogen

SMR vs LTE

The GIF context

AECL work on sulphur thermochemical cycles

Collaboration with USDOE on copper chloride cycles
Where will the demand be?

- Fuel for road vehicles?
  - Later perhaps but uncertain
    - Depends on battery vs fuel cell development
- More likely for larger vehicles (trains, ships)
- Big market is for upgrading petroleum
  - Exists and is growing rapidly
    - Especially in the oil sands developments in northern Alberta
  - Needs 3 to 5 kg $\text{H}_2$/bbl
  - Expect over 2 million bbl/d by 2015
  - 1 GWe = 160 000 bbl/d
How will $H_2$ be made?

- Conventionally come from natural gas by SMR
  - Cost has risen fast
    - Realistic to base on oil:gas at 6:1
    - Add 70 $/t CO_2$
    - Add 3% leakage of CH$_4$ from well to end use
  - Supply of natural gas is uncertain
    - All Mackenzie pipeline output could go to oil sands upgrading

- Need a new way
  - High-temperature thermochemical?
  - High-temperature electrolysis?
  - Conventional low-temperature electrolysis?
LTE will be available much sooner

- Make it using Generation III+ reactors
  - Could be deployed by 2015
- Key is to produce $H_2$ with off-peak electricity
  - Preferably with variable-current cells
  - Needs large-scale storage
    - In salt caverns

⇒ Alberta case
- 550 $/kW cells
- 5000 $/t storage
- Applying real-time Alberta power prices
And later?
Within the GenIV, Canada focuses on SCWR with crosslink to VHTR

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Spectrum</th>
<th>Fuel cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFR  Sodium Cooled Fast Reactor</td>
<td>Fast</td>
<td>Closed</td>
</tr>
<tr>
<td>LFR  Lead Alloy Cooled Reactor</td>
<td>Fast</td>
<td>Closed</td>
</tr>
<tr>
<td>GFR  Gas Cooled Fast Reactor</td>
<td>Fast</td>
<td>Closed</td>
</tr>
<tr>
<td>VHTR  Very High Temperature Reactor</td>
<td>Thermal</td>
<td>Once-through</td>
</tr>
<tr>
<td>SCWR  Supercritical Water Cooled Reactor</td>
<td>Th. &amp; F.</td>
<td>Once-t. &amp; Closed</td>
</tr>
<tr>
<td>MSR  Molten Salt Reactor</td>
<td>Thermal</td>
<td>Closed</td>
</tr>
</tbody>
</table>
CANDU Evolution

Current Generation CANDU

• Operating Feedback
• Market Pull
• Technology Push

Advanced CANDU Reactor

• Improved Economics
• Enhanced Safety
• Enhanced Operability

<5 years

Product Evolution

CANDU X (SCWR)

20+ years

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CANDU SCWR Concept

• Started in 1994 as Candu X Program
• Establish the design limits and ultimate potential
• Main CANDU features are retained.
  • Horizontal modular channels.
  • Heavy water moderator.
• Supercritical light water coolant (higher efficiency).
• Advanced fuel channel design (internal insulation without calandria tube).
• Options systematically studied
  • Mark 1: indirect cycle $T_{\text{out}} \sim 400^\circ \text{C}$ set by existing Zr
  • Mark 2: direct cycle $T_{\text{out}} \sim 600^\circ \text{C}$ set by existing turbine
  • Mark3: multiple cycle $T_{\text{out}} > 850^\circ \text{C}$ set by known materials
Thermochemical Work in Canada
In collaboration within the GIF and through I-NERI agreements with the USDOE
The $\text{H}_2\text{SO}_4$ Side of I/S and other S Cycles

- $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$
  - Majority of energy; lower temperature ($< 500^\circ\text{C}$)

- $\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2$
  - Minority of energy; higher temperature ($> 700^\circ\text{C}$)
  - Could avoid a high temperature reactor by providing direct electric heating of a substrate on which catalyst deposited
  - Work so far on selecting catalysts
Assessing catalysts for SO₂ decomp.

Fe catalyst

Pt catalyst

A metal (textured Inconel 800) sheet coated with catalyst for SO₃ decomposition
Copper chloride cycles

- Work led by USDOE at Argonne (Michelle Lewis)
- AECL is currently focused on the electrochemical step

<table>
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<tr>
<th>#</th>
<th>Reaction Stoichiometry</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2Cu + 2HCl(g) → 2 CuCl(l) + H₂(g)</td>
<td>425-450</td>
</tr>
<tr>
<td>2</td>
<td>4CuCl(s) → 2CuCl₂(a) + 2Cu</td>
<td>&lt;100</td>
</tr>
<tr>
<td>3</td>
<td>2CuCl₂(s) + H₂O(g) → Cu₂OCl₂ (s) + 2HCl(g)</td>
<td>300-375</td>
</tr>
<tr>
<td>4</td>
<td>Cu₂OCl₂ (s) → 2CuCl(l) + ½O₂(g)</td>
<td>450-530</td>
</tr>
</tbody>
</table>

- Or a variant on reaction #2: 2 CuCl + 2 HCl → 2 CuCl₂ + H₂
  - Avoids solid phase
  - Preliminary testing yields H₂ from both reactions at ~ 0.65 V
NRTEE + large nuclear deployment: 75% reduction ⇒

+9 GW(e) = +450 GW worldwide

As in NRTEE: ⇐ 50% reduction

+60 GW(e) = +5000 GW worldwide