Study of the Hybrid Cu-Cl Cycle for Nuclear Hydrogen Production

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GenIV Reactor Systems

- Six Reactor Systems:
  - Gas-Cooled Fast Reactor (GFR)
  - Lead-Cooled Fast Reactor (LFR)
  - Molten Salt Reactor (MSR)
  - Sodium-Cooled Fast Reactor (SFR)
  - Supercritical-Water-cooled Reactor (SCWR)
  - Very-High-Temperature Reactor (VHTR)

Main interest for Canada
CANDU Technology
Evolutionary Development for 60 Years
1940’s – Heavy Water Moderated Research Reactors (Gen-0)
1950’s – CANDU Prototype (Gen-I)
1960’s – Large CANDU Commercial Plants (Gen-I+)
1970’s – Multi-Unit CANDU Plants (Gen-II)
1980’s – CANDU-6 (Gen-II+)
1990’s – CANDU-9 (Gen-III)
2000’s – ACR (Gen-III+)
2010’s – SCWR (Gen-IV)

Evolutionary product innovation strategy
SCWR makes sense for utilities

- Nuclear: 20%
- Supercritical coal: 20%
- Other: 2%
- Subcritical coal + gas + hydro: 58%

Nuclear + SC Fossil = SCWR
SCWR Objectives

- Major economic advantage
- High level of safety
- Flexible fuel cycle system(s)
- Direct and Indirect Production of H$_2$
- Direct SCW cycle (no steam generators)
- Higher efficiency (>44%)
- Turbine technology available
- Operating conditions:
  - Pressure: ~25 MPa.
  - Outlet Temperature: 500°C-650°C
Also channel design option with multi-stream products
As you would have guessed from Alistair Miller’s presentation yesterday, AECL is “vigorously” promoting the Hydrogen Economy
Low (Moderate?) Temperature Thermochemical Hydrogen Production

- CANDU Mark 2 SCWR meets temperature criterion of the ALTC (minimum 530 °C for the highest temperature reaction)
- The waste heat dump following the expansion of reactor coolant to 300 kPa will be very useful
- High quality waste heat for the thermal drying requirements in the copper-chlorine cycle
Step (1): \(2\text{CuCl (l)} + \text{H}_2 \text{(g)} <= 2\text{Cu} + 2\text{HCl (g)}\)

Step (2): \(4\text{CuCl (aq)} => 2\text{CuCl}_2 (\text{aq}) + 2\text{Cu}\)

Step (3): \(2\text{CuCl}_2 (\text{s}) <= 2\text{CuCl}_2 (\text{aq})\)

Step (4): \(2\text{CuCl}_2 (\text{s}) + \text{H}_2\text{O(g)} \Rightarrow \text{CuO*CuCl}_2 (\text{s}) + 2\text{HCl (g)}\)

Step (5): \(2\text{Cu} \text{(l)} + \frac{1}{2} \text{O}_2 \Rightarrow \text{CuO*CuCl}_2 (\text{s})\)

Heat

Electricity

Waste Heat

\(430 - 475°C\)

\(400°C\)

\(500°C\)

\(100°C\)

\(30-70°C \text{ T (electrolysis)}\)
# Thermochemical Process Steps in ALTC – 1 Cycle

<table>
<thead>
<tr>
<th>Equ#</th>
<th>Reaction</th>
<th>Temp. Range (°C)</th>
<th>Feed/Output</th>
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<tbody>
<tr>
<td>1</td>
<td>2Cu(s) + 2HCl(g) = 2CuCl(l) + H2(g)</td>
<td>430–475</td>
<td>Feed: Electrolytic Cu + dry HCl + Q  &lt;br&gt;Output: H2 + CuCl(l) salt</td>
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<td>2</td>
<td>4CuCl(s) = 4CuCl (aq) = 2CuCl2(aq) + 2Cu(s)  &lt;br&gt;(electrolysis)</td>
<td>30–70</td>
<td>Feed: Powder/granular CuCl and HCl + V  &lt;br&gt;Output: Electrolytic Cu and slurry containing HCl and CuCl2</td>
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<tr>
<td>3</td>
<td>2CuCl2(aq) = 2CuCl2(s)</td>
<td>&gt;100</td>
<td>Feed: Slurry containing HCl and CuCl2 + Q  &lt;br&gt;Output: Powder/granular CuCl2 + H2O/HCl vapours</td>
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<tr>
<td>4</td>
<td>2CuCl2(s) + H2O(g) = CuO*CuCl2(s) + 2HCl(g)</td>
<td>400</td>
<td>Feed: Powder/granular CuCl2 + H2O(g) + Q  &lt;br&gt;Output: Powder/granular CuO*CuCl2 + 2HCl (g)</td>
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<tr>
<td>5</td>
<td>CuO*CuCl2(s) = 2CuCl(l) + 1/2O2(g)</td>
<td>500</td>
<td>Feed: Powder/granular CuO* CuCl2(s) + Q  &lt;br&gt;Output: Molten CuCl salt + oxygen</td>
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</tbody>
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Q - Thermal energy, V - Electrical energy.
Attractiveness of ALTC-1

- High efficiency (from Scoping Flowsheet Methodology) - 41%
- Electrical energy - 39% of total energy consumption
- Low temperature requirement for heat source <530°C
- Temperature requirement for heat source met by currently existing power plant technology (e.g. thermal stations using supercritical water cycles)
- Potentially suitable to couple with AECL’s SCWR reactor
- Materials-of-construction and corrosion issues more tractable at 530°C than at higher temperatures required by other cycles
- Inexpensive raw materials as recycle agents (for example, compared to iodine for S-I cycles)
- No requirement for catalyst in thermal reactions
- No significant side reactions (?)
- Complete conversions to desired products in thermal reactions (?)
ANL (Michele Lewis et al) have shown:

- Thermodynamic viability of all reactions
- Experimental proof of principle for hydrogen generation and measurements of reaction rate
  - \[ 2\text{Cu} + 2\text{HCl}(g) = \text{H}_2(g) + 2\text{CuCl} \]
- Proof of principle for HCl and Oxygen generation
  - \[ 2\text{CuCl}_2 + \text{H}_2\text{O}(g) = \text{CuCl}_2\cdot\text{CuO} + 2\text{HCl} \]
  - \[ \text{CuCl}_2\cdot\text{CuO} = 2\text{CuCl} + \frac{1}{2}\text{O}_2 \]
- Electrochemical disproportionation of CuCl in aqueous system
  - Details follow
AECL’s focus on ANL’s Cycles

- Argonne’s Low Temperature Cycle 1 (ALTC-1)
  - Aqueous electrochemical step to produce copper metal
- ALTC-3
  - Aqueous electrochemical step to produce hydrogen

\[ 2\text{CuCl} + 2\text{HCl} = \text{H}_2 + \text{CuCl}_2 \]

Note:
Oxygen generation at 500°C is common to ALTC-1 & 3
HCl generation reaction at 400°C is also common
Electrochemical Disproportionation of CuCl in Aqueous System (ALTC-1)

- **Dissolution**: $4\text{CuCl} + 4\text{Cl}^- = 4\text{CuCl}_2^-$
  - Dissolution necessary for aqueous process
    - CuCl is insoluble in water but dissolves in HCl
      - $\text{CuCl} + \text{HCl(aq)} = \text{CuCl}_2^-(\text{aq}) + \text{H}^+(\text{aq})$

- **Electrochemical**: $4\text{CuCl}_2^- = 2\text{Cu} + 2\text{CuCl}_2 + 4\text{Cl}^-$

- **Drying**: $2\text{CuCl}_2(\text{aq}) = 2\text{CuCl}_2(\text{s})$

- **ANL’s e-cell experimental experience**
  - **Temp**: 20-80 °C
  - 0-4M HCl, 0.01-0.3M CuCl, 0-0.1M CuCl$_2$
  - **Anode Current Density**: ~21 mA/cm$^2$ @ 0.4 V
    - ~135 mA/cm$^2$ @ 0.6 V
CuCl Electrolysis

GTI’s development:  
- Voltage as low as 0.4V (unknown current density)  
- CuCl₂ concentrations as high as 5N  
- Proprietary anion exchange membrane  
- Graphite plates with channel as electrodes
Preliminary AECL Experimental Results

- Graphite Electrodes
  - 0.3 M CuCl in 4M HCl
  - 0.4 to 0.8 V
  - 29 to 37 mA·cm$^{-2}$

- Copper Cathode and Platinum Anode
  - 0.3 M CuCl in 4M HCl
  - 0.5 to 0.8 V
  - 14 to 86 mA·cm$^{-2}$
Key Issues

- Optimum Operating Voltage: ALTC-1 efficiency depends on this
- CuCl₂ Concentration should be high: minimize thermal load required for water removal
- CuCl₂ separation from HCl
- Selection of the Type of E-cell – Current expertise at AECL from conventional water electrolysis, material selections for high temperature and corrosive conditions of ALTC-1 and fuel cell developments
- Cell Characteristics: concentration polarization, ionic conductivity of electrolyte, membrane etc. Current expertise at AECL

AECL would like to participate in the development of the e-cell because of its background in water electrolysis, fuel cell expertise and the new collaboration arrangement with University of Ontario Institute of Technology
ALTC-3: electrochemical step

- Cycle proposed by M. Dokiya and Y. Kotera
- Relatively simple engineering
- Higher voltage leading to higher electrical energy requirements
  - Dokiya and Kotera reported >250 mA/cm² @ 0.6 to 1.0 V
  - ANL experience:
    - Room T
    - Celemion membrane
    - 0-5M HCl, 0.01-1 M CuCl, 0-0.5 M CuCl₂
    - Anode current density ~50 mA/cm² @ 1.0 V

- **ANL did not see any H₂ produced**
- **AECL would like to explore**
Modifications to existing e-cell test facilities
Reverse Deacon Cycle (ARDC)

*Michael Simpson et al.*

**Hallet Air Products Cycle**

\[ \text{H}_2\text{O}_{(g)} + \text{Cl}_2_{(g)} = 2\text{HCl} + 0.5\text{O}_2_{(g)} \]

800 °C

(Reverse Deacon Reaction)

\[ 2\text{HCl}_{(aq)} = \text{H}_2_{(g)} + \text{Cl}_2_{(g)} \]

25 °C, E= 2.0 V @ 4 kV/m²

(Aqueous HCl electrolysis)

**ARDC Cycle**

\[ \text{MgCl}_2_{(s)} + \text{H}_2\text{O}_{(g)} = \text{MgO}_{(s)} + 2\text{HCl}_{(g)} \]

450 - 550 °C

\[ 2\text{HCl}_{(g)} = \text{H}_2_{(g)} + \text{Cl}_2_{(g)} \]

25 °C, E= 1.6V @ 8kV/m²

\[ \text{MgO}_{(s)} + \text{Cl}_2_{(g)} = \text{MgCl}_2_{(s)} + 0.5\text{O}_2_{(g)} \]

**Issues:**
- High T Chemical reaction
- Aqueous HCl electrolysis requiring high electrical input
- At high T, HCl & O₂ recombine

**Improvements:**
- Lower T, suitable for SCWRs
- Prevent recombination of HCl & O₂
- Simple separation of gaseous products
Status of ARDC

- Proof of principle tests have been done (by Michael Simpson et.al.) on:
  - supporting MgCl₂ on Silicalite
  - MgCl₂ hydrolysis reaction
  - sufficient reactivity of MgCl₂ with steam
  - stability of Silicalite with acid/steam at ~500 °C
- DuPont’s CREG (Chlorine REGeneration) cell for for anhydrous HCl electrolysis:
  - 12kA/m² @ 1.7V (59% efficiency) -→ proposing to increase efficiency by operating @ 1.5V for a current density of 8 kA/m² (~66.7% efficiency)
- Need to demonstrate:
  - chlorination step
  - sufficient reactivity for chlorination step
  - repeatability of hydrolysis reaction without severe attrition
  - process optimization
  - equipment design
- According to Mike Simpson’s cycle efficiency analysis the ARDC in theory utilizes energy from a nuclear reactor more efficiently than water electrolysis by about 15%
Summary

- ANL’s ALTC-1 appealing to AECL for development work on the electrochemical step
- Significant hurdles to overcome even with ALTC-1
- AECL would explore the electrochemical step in ALTC-3
- AECL would like to explore the merits of ARDC