R&D Status for the Cu-Cl thermochemical cycle-2010

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Overview

Time Line
- Start date: 10/06
- End date: TBD
- % complete: 30%

Budget
- $100 K for FY09
- $550 K for FY10

Barriers
- U. High temperature thermochemical technology
- V. Robust materials
- W. Cost

Partners
- Atomic Energy of Canada Ltd
- Five Canadian universities
- Penn State & Univ. of S. Carolina
- Commissariat à l’Energie Atomique
Relevance to DOE Mission

- **Objective**: Develop a commercially viable process for producing hydrogen that meets **DOE cost and efficiency targets** using the Cu-Cl thermochemical cycle.

- **3 major reactions in cycle**
  - **Hydrolysis**
    - $2\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$
  - **Oxychloride decomposition**
    - $\text{Cu}_2\text{OCl}_2 \rightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2$
  - **Electrolysis**
    - $2\text{CuCl} + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2$
      - Anode: $2\text{Cu}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{e}^-$
      - Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Relevance to DOE Mission-2

- Features of cycle that promote meeting targets and overcoming barriers
  - The 550°C maximum temperature allows coupling with the solar power tower, which is near commercialization
  - Conceptual design uses commercially practiced processes
  - High yields in thermal reactions; no catalysts required
  - Preliminary Aspen flowsheet indicates it is possible to meet the efficiency and cost targets
  - Key challenges

  • Electrolyzer:
    - Inhibit copper crossover
    - Achieve stable cell performance

  • Identify and cost materials of construction

  • Reduce steam demand for hydrolyser
Approach - critical path

- Electrolysis reaction: $2\text{CuCl} + 2\text{HCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2$
  - Potential showstopper: Copper crossover in the electrolyzer causes cell potential to increase and eventually destroys the cell
  - Continue collaboration with our partners in Canada and Penn State
    - Investigate other designs for electrolyzers
  - Initiate new program on membrane development
    - Test available membranes that show high conductivity and low selectivity for all species except the proton
    - Tune selected membranes to obtain desired characteristics
    - Test various coatings on a Nafion® substrate to obtain size selectivity
  - Meet targets:
    - 0.70 V, 500 mA/cm² by 2015
    - 0.63 V, 500 mA/cm² by 2025
Approach - critical path

- Materials of construction
  - CuCl$_2$ solutions and HCl solutions are extremely corrosive
    - Contact vendors, get coupons for testing and cost estimates
    - Work with collaborators in Canada who are studying corrosion of possible materials

- Hydrolysis reaction: $2\text{CuCl}_2 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$
  - Large amount of excess water is required for high yields
  - Drives capital costs up because of the number/size of reactors and the efficiency down because of the high heat of vaporization of water
    - Optimize process conditions to reduce steam demand
Previous Technical Accomplishments - FY09

- New hydrolysis reactors designed and tested
  - Yields obtained with fixed bed reactors were too low to be practical
  - More realistic spray reactors using nebulizer and ultrasonic nozzle were tested
    - Ultrasonic nozzle preferred
      - Easier to use (no clogging, no inert gas needed)
      - Higher yields of Cu$_2$OCl$_2$ (at H$_2$O/CuCl$_2$ ratios of 20-23)
      - Smaller and free-flowing Cu$_2$OCl$_2$ particles (<100 nm to 30 μm)
        » Important because process design uses gravity feed for transfer
- In-house Cu$_2$OCl$_2$ decomposed between 400 and 550°C. CuCl was discharged as a molten salt and oxygen was released
  - Measured yield of O$_2$ was nearly 100% of theoretical
- Preliminary Aspen flowsheet prepared and H2A cost analyses completed
Technical Accomplishments
Sub-atmospheric hydrolysis reactor built and tested

- Ultrasonic nozzle for spray formation of Cu₂OCl₂
- Aspirator (Venturi effect) which allows operation at reduced pressure
- Qualitative (X-ray diffraction) and quantitative analyses of solid products

Conceptual Hydrolysis Reactor

- Low Pressure Steam
- Ejector
- CuCl₂/water to Electrolyzer Feed Tank
- Free Jet Spray
- Cu₂OCl₂ to decomposer
- 400°C/0.25 bar

Steam Environment
2CuCl₂ + H₂O = 2HCl + Cu₂OCl₂

Steam
CuCl₂/water (400°C, 24 bar)

Power supply
CuCl₂ aqueous solution
Syringe Pump

Superheated steam 450°C
Atomizer
Solid Products
Heating Tape @150°C

Syringe Pump
Mass Flow Controller
Heated Rod
Water

Reactors
Temperature Controller
3-zone Furnace
Gaseous Products
HCl Trap
Regulator
Aspirator Pump
Vent

Ar

Sub-atmospheric hydrolysis reactor built and tested

 Aspirator (Venturi effect) which allows operation at reduced pressure
Steam-to-CuCl₂ ratio can be decreased at reduced pressure

- Aspen sensitivity studies show that complete conversion is shifted to lower H₂O/CuCl₂ (20 to 13) when pressure is decreased from 1 to 0.5 bar

- Similar results from lab: maximum yield of Cu₂OCl₂ at H₂O:CuCl₂=15 and 0.4 bar
  - In addition, CuCl yield lower at 0.4 bar than at 1 bar
  - Two paths for CuCl formation:
    - 2CuCl₂ → 2CuCl + Cl₂
    - Cu₂OCl₂ → 2CuCl + 0.5 O₂
No Cl$_2$ observed below 400°C

Cumulative formation of HCl (a) and Cl$_2$ (b) as a function of time and temperature during the hydrolysis reaction of CuCl$_2$ in a fixed bed

Tests conducted at CEA*

Conditions: Ar flowrate = 5L/h, H$_2$O/CuCl$_2$=15.

*CEA = Commissariat à l’Energie Atomique
The CuCl electrolyzer is under development

- Copper crossover from anode to cathode was observed with all tested membranes (anion and cation exchange membranes)
  - Cell performance degrades

- New work focuses on cation exchange membranes
  - High selectivity for H\(^+\) & negligible transport of all copper complexes
  - Low electrical resistance
  - Good mechanical strength and long term stability

\[
\begin{align*}
\text{Cathode} & : \quad 2\text{H}^+ \rightarrow \text{H}_2 \\
\text{Anode} & : \quad \text{Cu(I)} \rightarrow \text{Cu(II)}
\end{align*}
\]
Electrolyzer development at Penn State University looks promising

- Experimental set up is now complete

- Best performance: current density of 300 mA/cm² at 0.7 V at 30ºC (expect higher current density at 80ºC)
- Anolyte: 0.2m CuCl in 2m HCl
- Catholyte: water
- 5 h duration
Longer term test conducted at Atomic Energy of Canada Limited

- Copper crossover observed in all early 25°C tests; cell potential started to increase after 20 min in first set of tests
- More concentrated anolyte and longer (95 h) cell stability in most recent tests

Anolyte: 0.5 M CuCl, 10 M HCl
Catholyte 10 M HCl

- Higher temperatures/stirring improve kinetics and increase achievable current density for a given voltage
Summary of the Technical Accomplishments - FY10

- Promising results at AECL and Penn State for improving the electrolyzer performance and inhibiting copper crossover
  - AECL has extended the stability of the cell’s potential from 20 min to 95 h
  - PSU’s design was stable for 5 h using a liquid water catholyte

- A decrease in the reactor pressure (with aspirator) reduces the amount of steam required for high yields (>90%) of the desired Cu$_2$OCl$_2$ product
  - H$_2$O/CuCl$_2$ ratio reduced from 20-23 to 11-15

- Tests conducted at CEA with a H$_2$O/CuCl$_2$ ratio of 15 showed that only HCl was formed at temperatures \( \leq 390^\circ C \), some Cl$_2$ above 400$^\circ$C.

- University of Ontario Institute of Technology has just finished outfitting a building for a large scale integrated demonstration; large scale reactors are in place and are being cold tested.
Future work

- Continue development/testing of new membrane materials and electrolyzer designs to inhibit copper crossover and obtain stable cell performance
  - Mechanism for copper crossover to be investigated
  - Test performance over a wide range of HCl/CuCl$_2$ concentrations and temperatures up to 80ºC
- Identify materials of construction
- Complete revisions of Aspen flowsheet and cost analysis
- Optimize performance of hydrolyser operating at sub-atmospheric pressure to further reduce the steam demand
  - Model assumes a H$_2$O/CuCl$_2$ ratio of less than 10
  - Determine mechanisms for CuCl$_2$ hydrolysis and CuCl formation; measure kinetics for hydrolysis and decomposition reactions using synchrotron radiation at the Advanced Photon Source (General Users Proposal submitted)
Collaboration - Acknowledgements

- Industry: Atomic Energy of Canada Ltd (AECL)
- Universities:
  - University of Ontario Institute of Technology (UOIT), Guelph University, McMaster University, Western Ontario University, University of Toronto, Pennsylvania State University and University of South Carolina
- Federal: Commissariat à l’Energie Atomique (CEA), France
- Consultant: Orion Consulting
- DOE-EERE for their financial support and encouragement
Supplemental Slides
Speciation studies at PSU

- Speciation is determined by pH, concentrations of Cu species and Eh as shown by the speciation diagrams for Cu(I) conversion to Cu(II) for two sets of relatively dilute conditions:
  - a. 0.2 m CuCl + 2 m HCl(aq)
  - b. 1 m CuCl + 6 m HCl(aq)
Decomposition of \( \text{Cu}_2\text{OCl}_2 \) accelerated in steam

- In dry Ar, \( \text{Cu}_2\text{OCl}_2 \) decomposes between 400 and 550\(^\circ\)C:
  - \( \text{Cu}_2\text{OCl}_2 \rightarrow 2 \text{CuCl} + \frac{1}{2} \text{O}_2 \)

- In humid Ar, \( \text{Cu}_2\text{OCl}_2 \) starts to decompose already at 350\(^\circ\)C
- Need to investigate mechanism of decomposition with and without steam

MS signal for \( \text{O}_2 \)