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

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PD013

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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

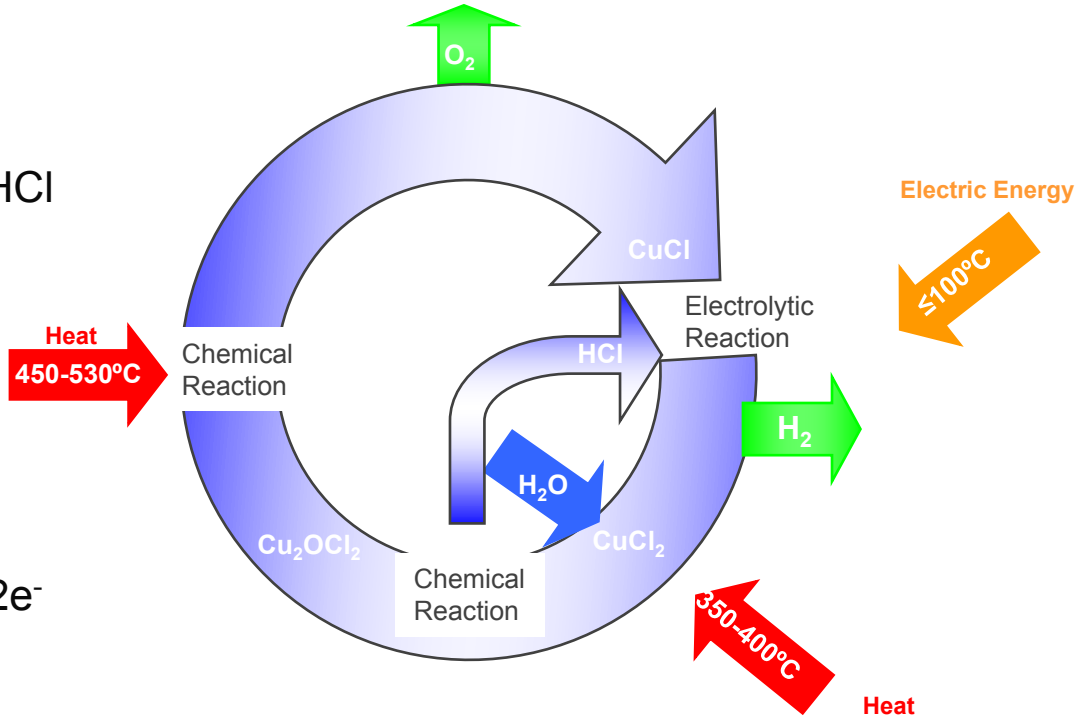
Partners

- 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***
    - $2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl$
  - ***Oxychloride decomposition***
    - $Cu_2OCl_2 \rightarrow 2CuCl + \frac{1}{2}O_2$
  - ***Electrolysis***
    - $2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2$
      - Anode: $2Cu^{+} \rightarrow 2Cu^{2+} + 2e^{-}$
      - Cathode: $2H^{+} + 2e^{-} \rightarrow H_2$



Relevance to DOE Mission-2

- Features of cycle that promote meeting targets and overcoming barriers
  - The 550ºC 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: $2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2$
  - 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/cm^2 by 2015
    - 0.63 V, 500 mA/cm^2 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: $2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl$
  - 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

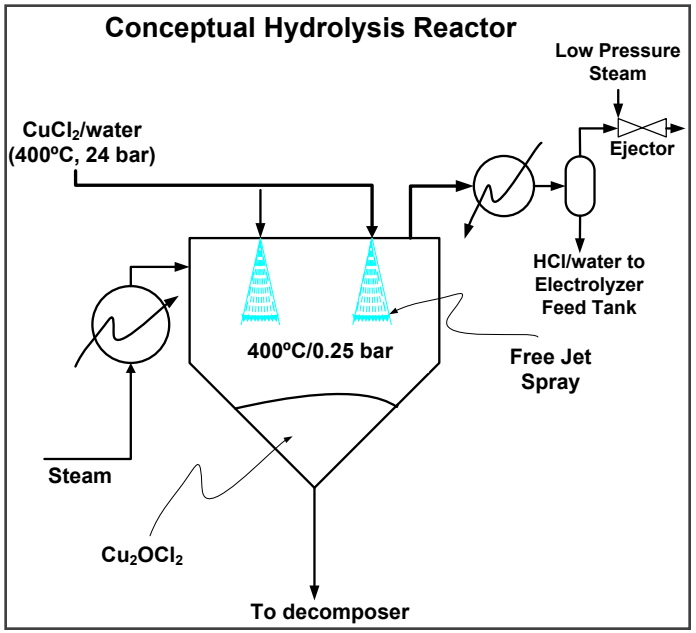
Previous Technical Accomplishments – FY09

- 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_2OCl_2 (at $H_2O/CuCl_2$ ratios of 20-23)
      - Smaller and free-flowing Cu_2OCl_2 particles (<100 nm to 30 μm)
        - » Important because process design uses gravity feed for transfer
- In-house Cu_2OCl_2 decomposed between 400 and 550ºC. 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

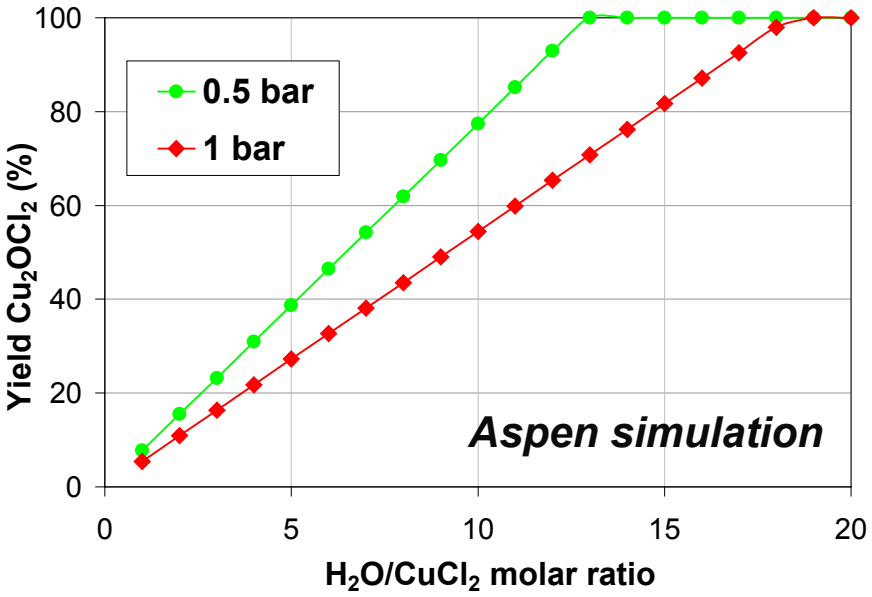
- Ultrasonic nozzle for spray formation of Cu_2OCl_2

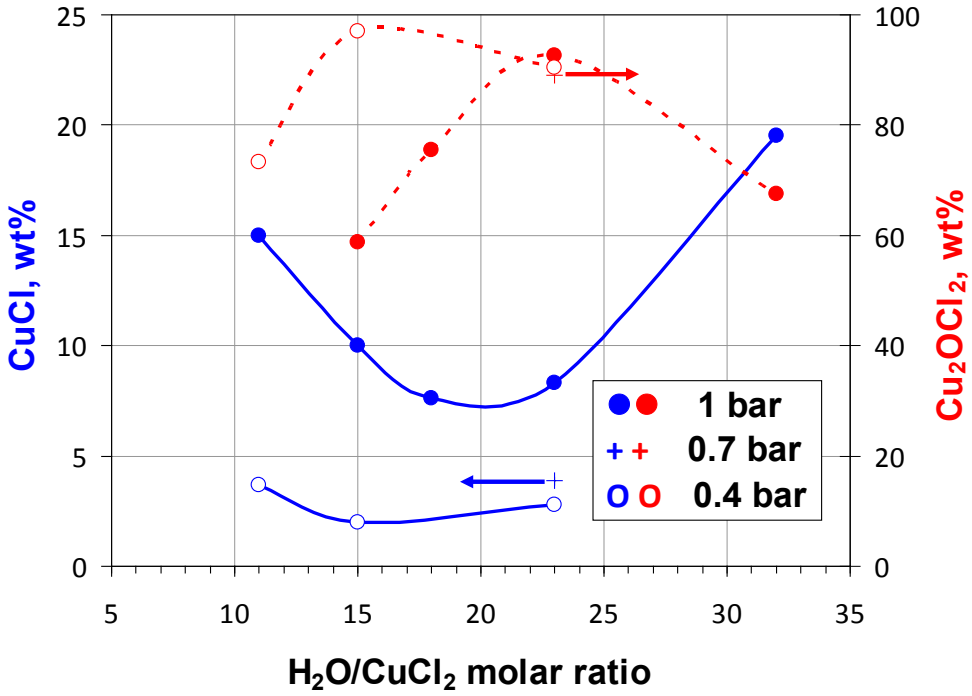


- Qualitative (X-ray diffraction) and quantitative analyses of solid products

- Aspirator (Venturi effect) which allows operation at reduced pressure

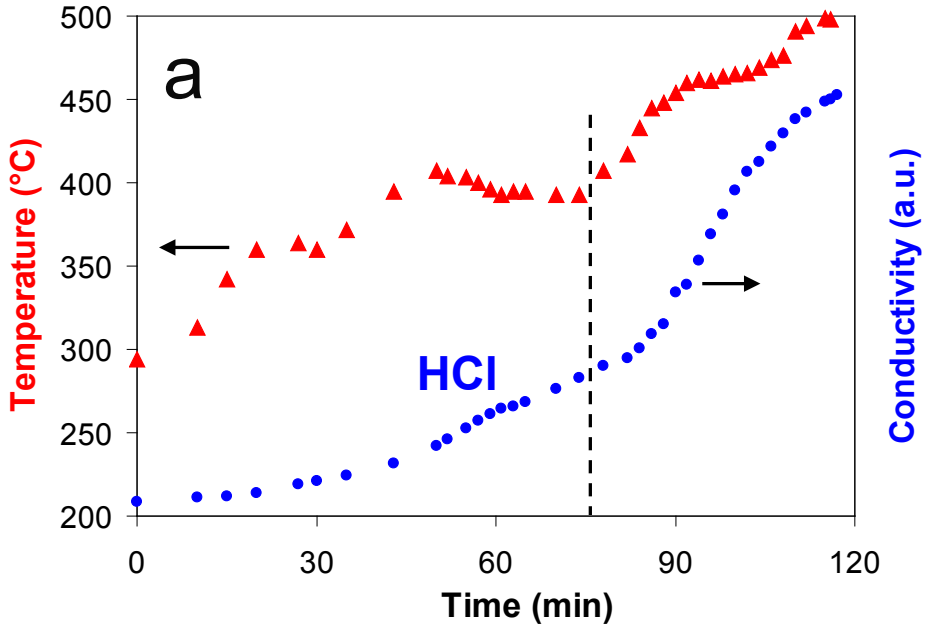
Steam-to-$CuCl_2$ ratio can be decreased at reduced pressure





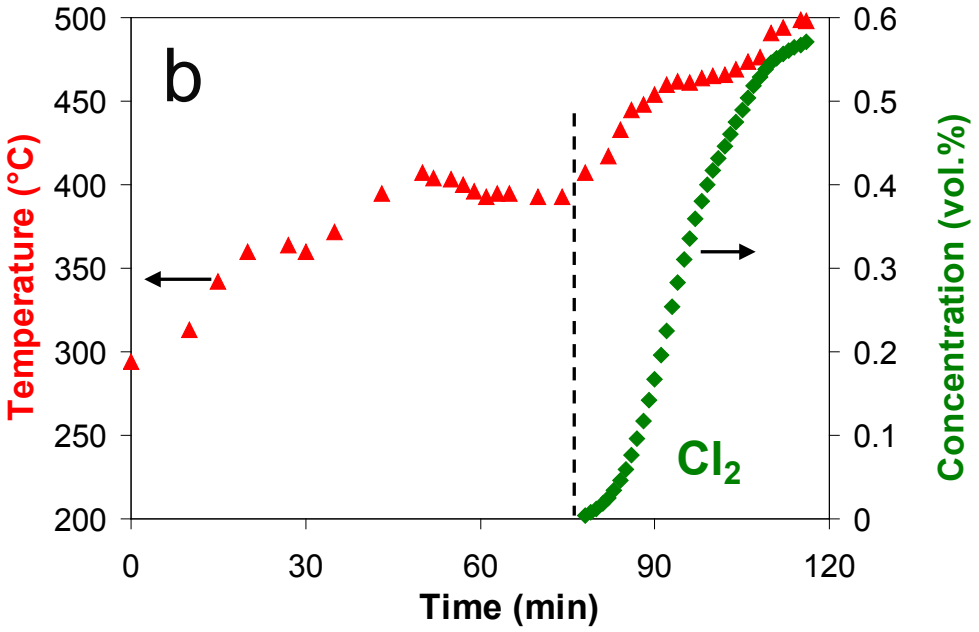
- Aspen sensitivity studies show that complete conversion is shifted to lower $H_2O/CuCl_2$ (20 to 13) when pressure is decreased from 1 to 0.5 bar
- Similar results from lab: maximum yield of Cu_2OCl_2 at $H_2O:CuCl_2$=15 and 0.4 bar
  - In addition, CuCl yield lower at 0.4 bar than at 1 bar
  - Two paths for CuCl formation:
    - $2CuCl_2 \rightarrow 2CuCl + Cl_2$
    - $Cu_2OCl_2 \rightarrow 2CuCl + 0.5\ O_2$

No Cl_2 observed below 400°C



a) Below 390°C, only HCl was observed

b) Above 400°C, Cl_2 was observed



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

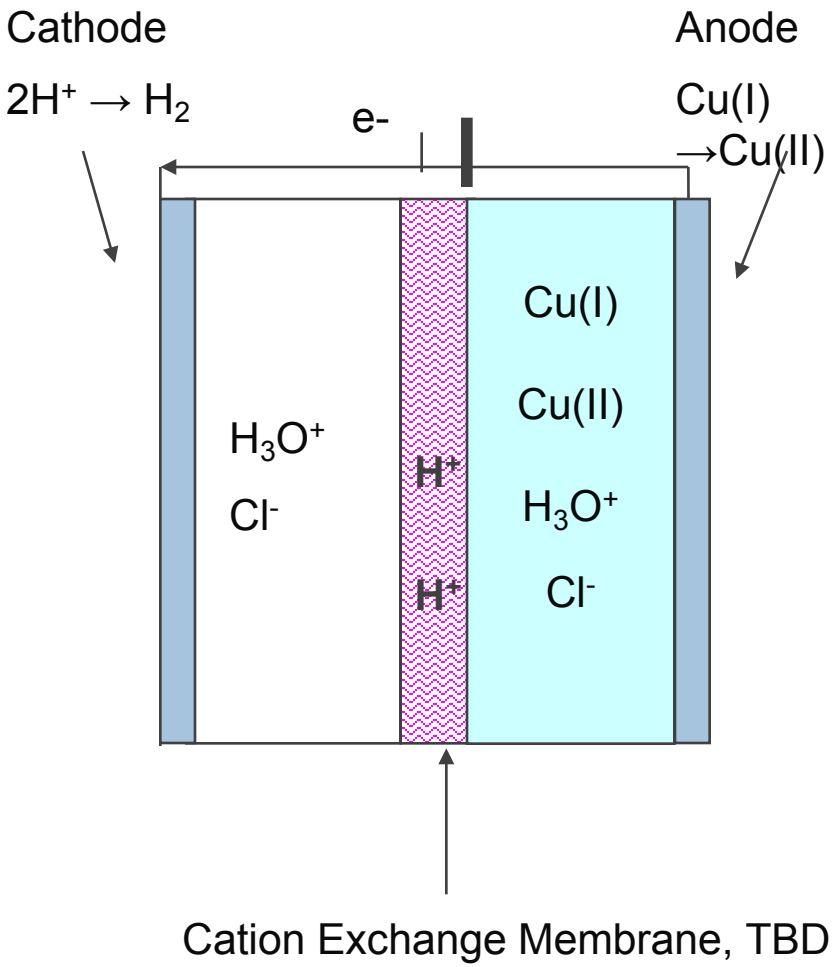
Tests conducted at CEA*

Conditions: Ar flowrate = 5L/h, $H_2O/CuCl_2$=15.

*CEA = Commissariat à l'Energie Atomique

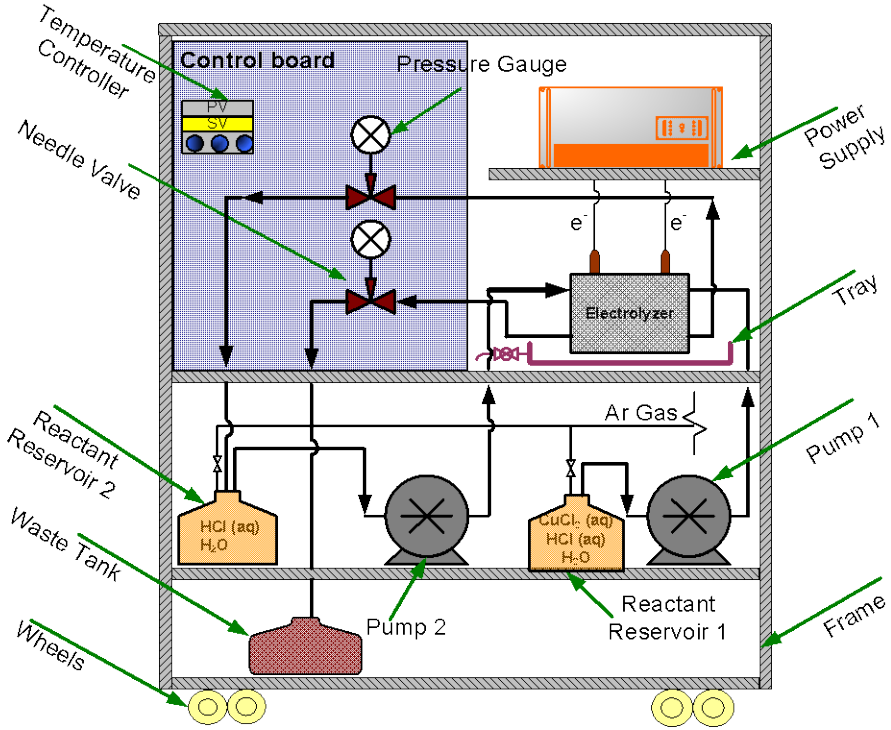
The CuCl electrolyzer is under development

- 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

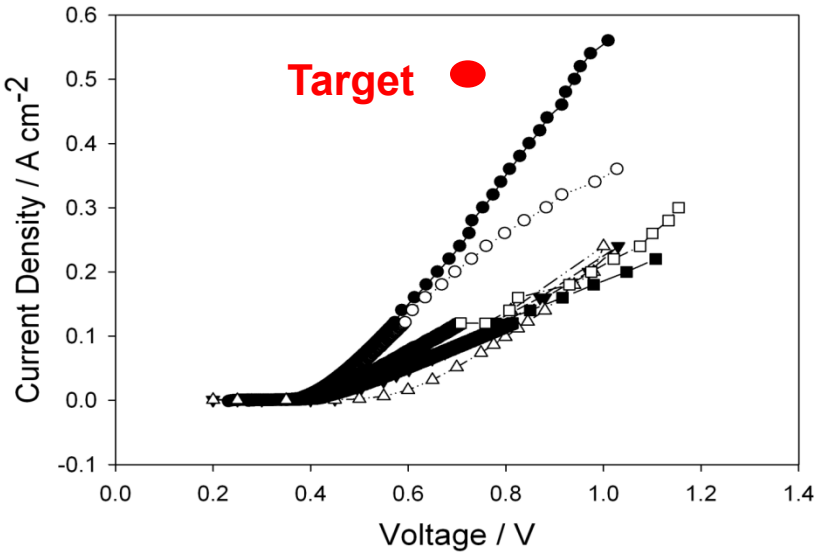


Electrolyzer development at Penn State University looks promising

- Experimental set up is now complete



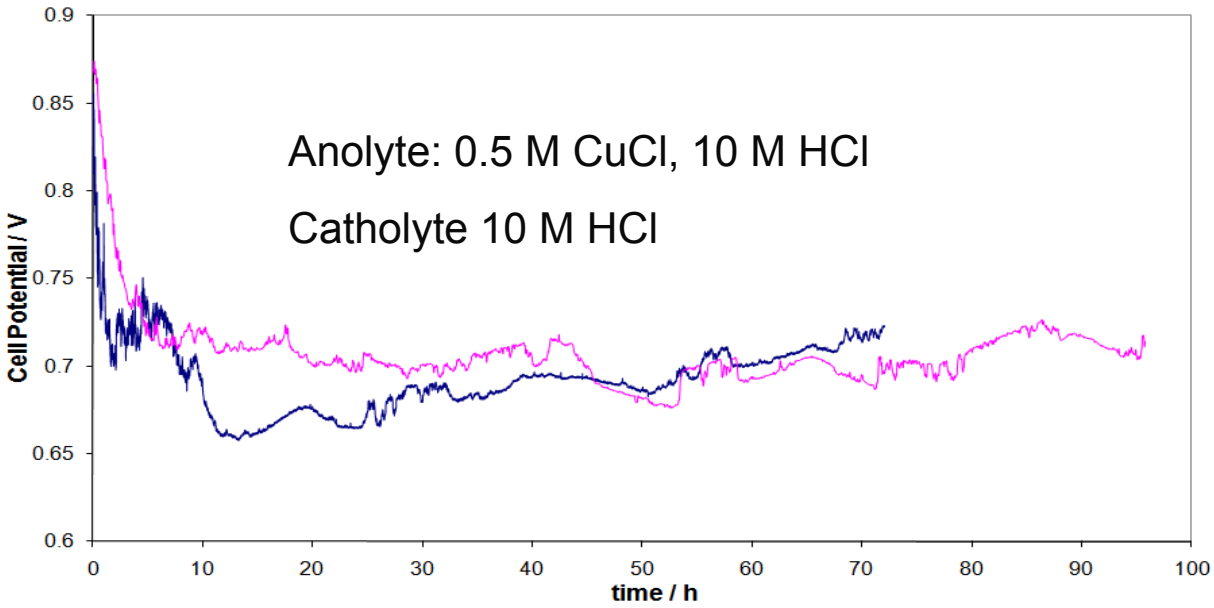
- Best performance: current density of 300 mA/cm^2 at 0.7 V at 30ºC (expect higher current density at 80ºC)
- Anolyte: 0.2m CuCl in 2m HCl
- Catholyte: water
- 5 h duration

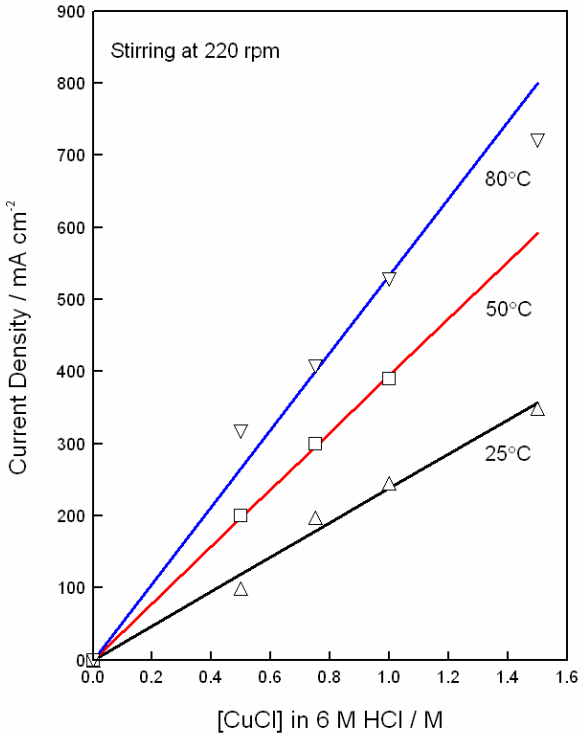


PENNSTATE

Longer term test conducted at Atomic Energy of Canada Limited

- Copper crossover observed in all early 25ºC 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





- 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_2OCl_2 product
    - $H_2O/CuCl_2$ ratio reduced from 20-23 to 11-15
- Tests conducted at CEA with a $H_2O/CuCl_2$ ratio of 15 showed that only HCl was formed at temperatures $\leq$390ºC, some Cl_2 above 400ºC.
- 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 $H_2O/CuCl_2$ 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)

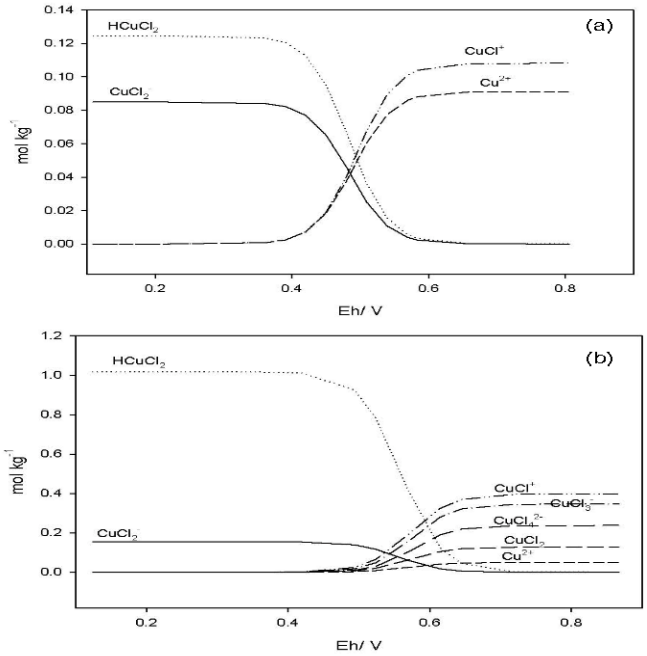
Collaboration - Acknowledgements

- Industry: Atomic Energy of Canada Ltd (AECL)
- Universities:
  - University of Ontario Institute of Technology (UOIT), Guelph University, McMasters University, Western Ontario University, University of Toronto, Pennylvania 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

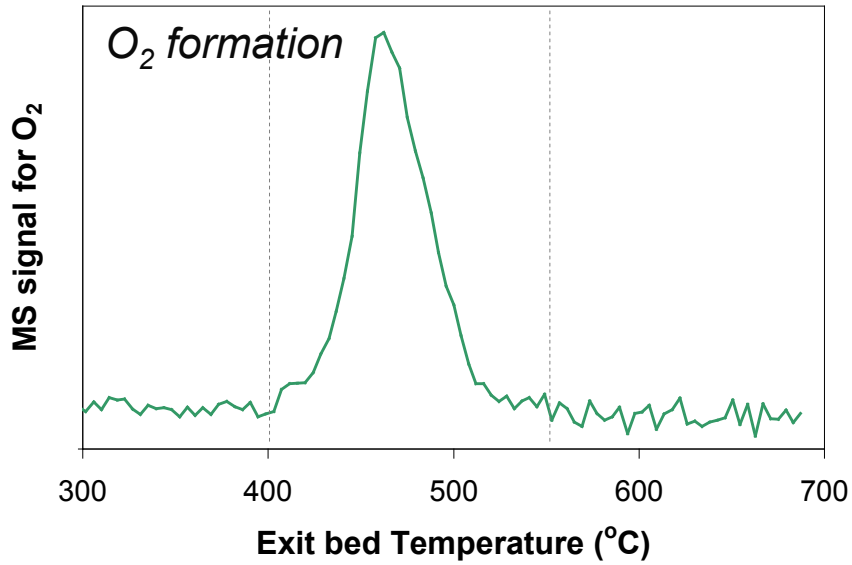
Supplemental Slides

Speciation studies at PSU

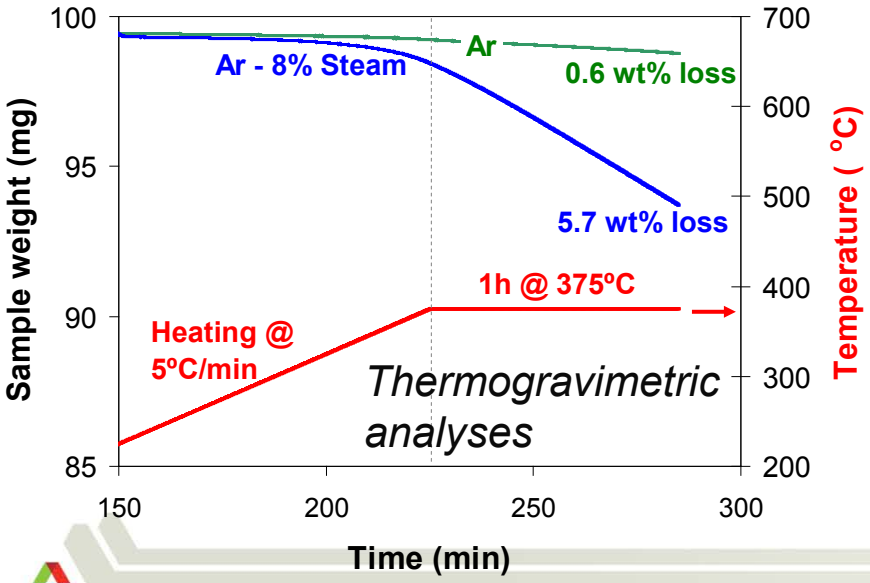
- Speciation is determined by pH, concentrations of Cu species and Eh as shown by the speciation diagrams for Cu(I) conversion to Cu(II) for two sets of relatively dilute conditions:
  - a. 0.2 m CuCl + 2 m HCl(aq)
  - b. 1 m CuCl + 6 m HCl(aq)



Decomposition of Cu_2OCl_2 accelerated in steam



- In dry Ar, Cu_2OCl_2 decomposes between 400 and 550ºC:
- $Cu_2OCl_2 \rightarrow 2\ CuCl + ½\ O_2$



- In humid Ar, Cu_2OCl_2 starts to decompose already at 350ºC
- Need to investigate mechanism of decomposition with and without steam