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R&D status for the Cu-Cl thermochemical cycle

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UChicago Argonne LLC

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Overview

Time Line

- Start date: 10/07
- End date: ?
- % complete: 30%

Budget

- $98K for FY09
- Complementary program supported by DOE-EERE
  - $939K from FY06 to FY08

Barriers

- G. Capital Cost
- H. Efficiency
- AU. High temperature thermochemical technology

Partners

- International Nuclear Energy Research Initiative (INERI)
  - Atomic Energy of Canada Ltd and six Canadian universities
- Nuclear Energy Research Initiative-Consortium (NERI-C)
  - Three US universities

Relevance: objective and rationale for R&D

- Develop a commercially viable process for producing hydrogen based on a thermochemical cycle that meets DOE cost and efficiency targets
- Cu-Cl cycle chosen
  - Current Aspen flowsheet indicates possible to meet the targets if assumptions can be validated
- Features that promote meeting targets
  - The 550C maximum temperature reduces demands on materials
    - *Couples with various heat sources: solar power tower, Na-cooled fast reactor and supercritical water reactor*
  - Yields near 100% in hydrolysis and oxychloride decomposition without catalysts-no recycle streams in these reactions
  - Conceptual process design uses commercially practiced processes
  - Preliminary H2A analysis indicates H_2 production costs are within range of 2025 target if assumptions validated

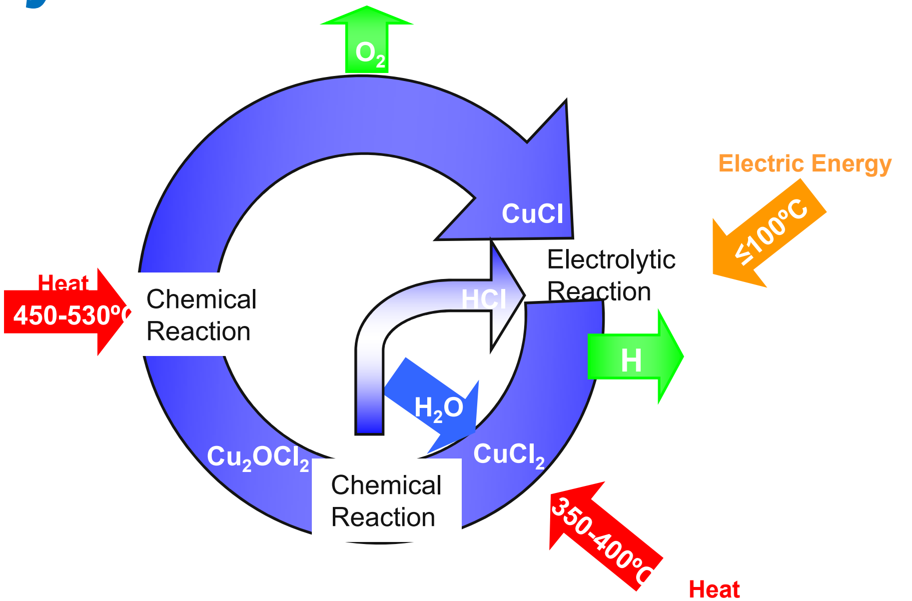
Approach/Milestones

- **Experimental program**
  - Focus on hydrolysis reaction
    - *Demonstrate high conversions and free flowing product powders*
  - Focus on advanced electrochemical technologies with NERI-C partners
- **Modeling program**
  - Develop flowsheet
    - *Estimate efficiency and capital costs*
  - Use H2A methodology for H_2 production costs

Project Milestones	Task Completion Date				Progress Notes
	Original Planned	Revised Planned	Actual	Percent Complete	
Define Optimum Conditions for Hydrolysis Reaction			12/20/2008	100%	Completed for given funding level
Define Optimum Conditions for Electrolysis Reaction	12/21/2007	08/10		20%	Higher operating temperatures, stirring, prevent Cu crossover; Work stopped
Verify Non-Int. Cycle in Lab	8/19/2008	08/11		5%	Work stopped
Complete cost analysis	4/15/2007	3/31/2008		75%	Optimization ongoing

Approach: Study individual reactions & complete preliminary economic analysis

- **Hydrolysis reaction**
  - **$2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$**
  - Optimize conditions for high yields and free flowing powders
- **Oxychloride decomposition**
  - **$Cu_2OCl_2 \Leftrightarrow 2CuCl + ½O_2$**
  - Maximum temperature reaction
- **Electrolysis (simplified)**
  - **$2CuCl + 2HCl \Leftrightarrow 2CuCl_2 + H_2$**
    - ***Anode: $2Cu^+ \Leftrightarrow 2Cu^{2+} + 2e^-$***
    - ***Cathode: $2H^+ \Leftrightarrow H_2$***

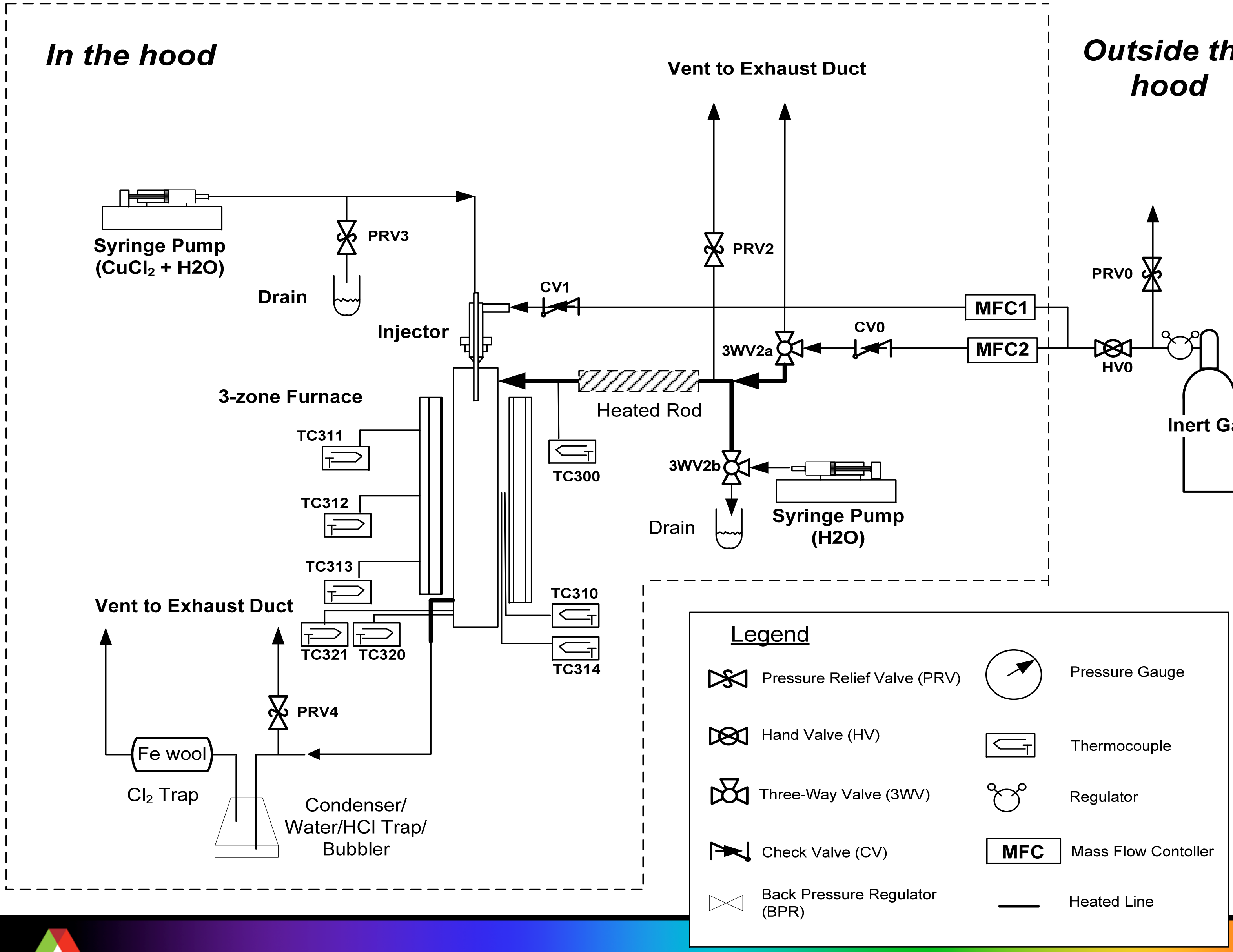


- **Separation methods to treat spent anolyte and catholyte**
  - *R&D just started*

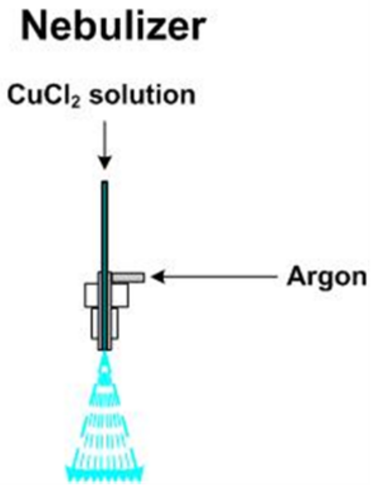
Hydrolysis rxn: $2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$

- **Early experimental results in fixed bed reactors showed up to 25 wt% CuCl and unreacted $CuCl_2$ in products, even with large excess of water**
- **For a cyclic process:**
  - Obtain high yields (~100%) of products, HCl and Cu_2OCl_2
  - Prevent competing reactions
    - *$CuCl_2$ can decompose to give chlorine but this reaction can be avoided by choice of operating conditions*
    - *Cu_2OCl_2 decomposes to give oxygen (not a showstopper)*
- **For an efficient and low capital cost process**
  - Reduce water consumption (very important)
    - *Aspen predicts that 100% yield can be obtained with S/Cu = 17 at 370C*
  - Use reactor design that provides best heat and mass transfer

Schematic of spray reactor (shown with nebulizer)



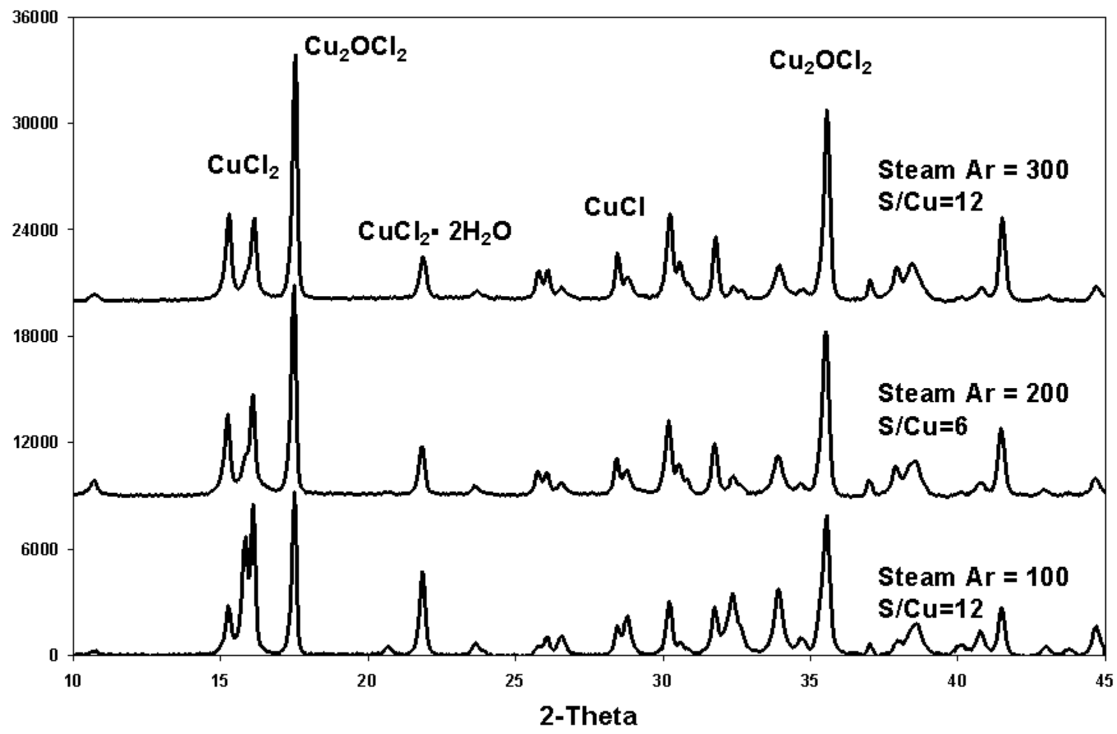
Spray reactors using ‘pneumatic’ nebulizer and ultrasonic nozzle tested



- Counter current operation with nebulizer gave good products after optimization of variables
  - Ar flowrate in nebulizer
  - Ar flowrate in superheated steam line
  - Flow rate of $CuCl_2$ solution
  - Temperature
- However, some unreacted $CuCl_2$ and some CuCl observed in x-ray diffraction patterns
- Co-current operation appears unlikely
  - Nebulizer clogs readily
    - *$CuCl_2$ solution dehydrates in capillary tube*
  - Low conversion to Cu_2OCl_2

Technical accomplishments

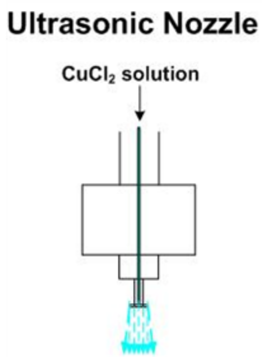
Experimental parameters, e.g., Ar flow rates affect yields



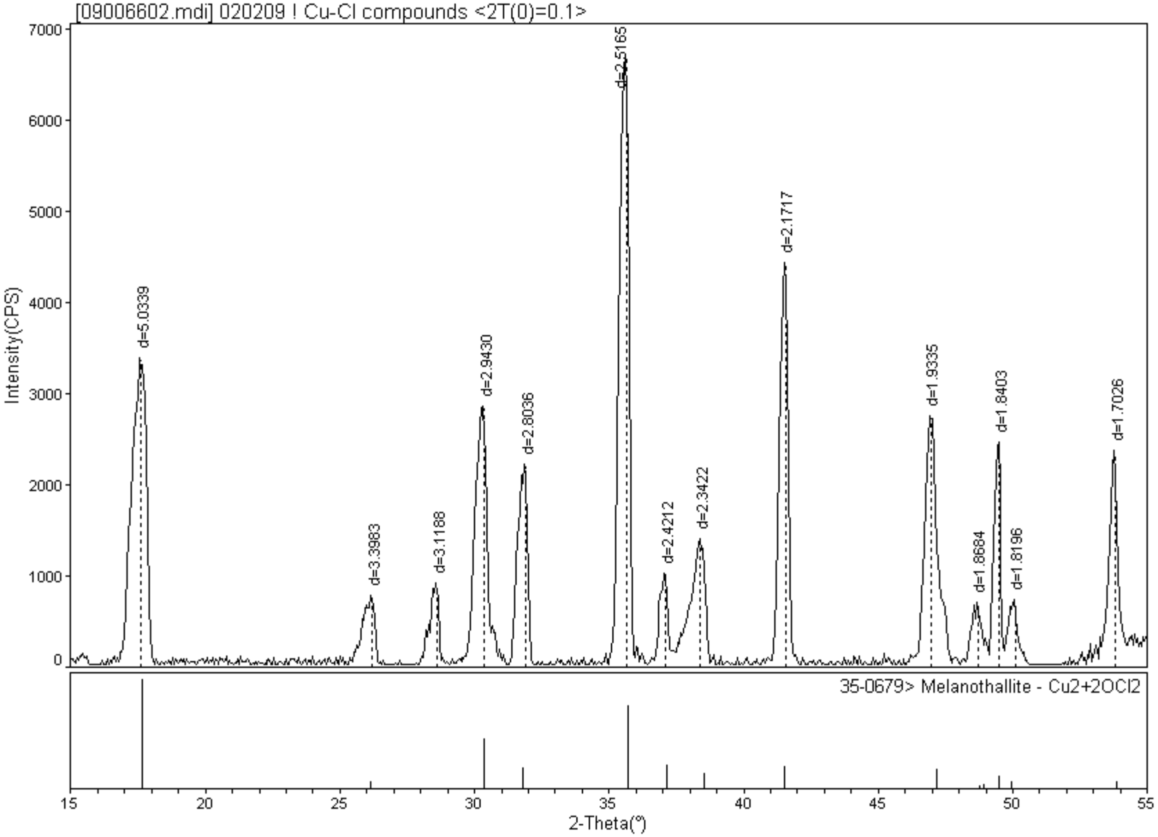
- Increasing Ar flow rates through the superheated steam line (or nebulizer) result in increasing yields of Cu_2OCl_2

Technical accomplishments

Ultrasonic nozzle is easier to use-no clogging and gives superior conversions

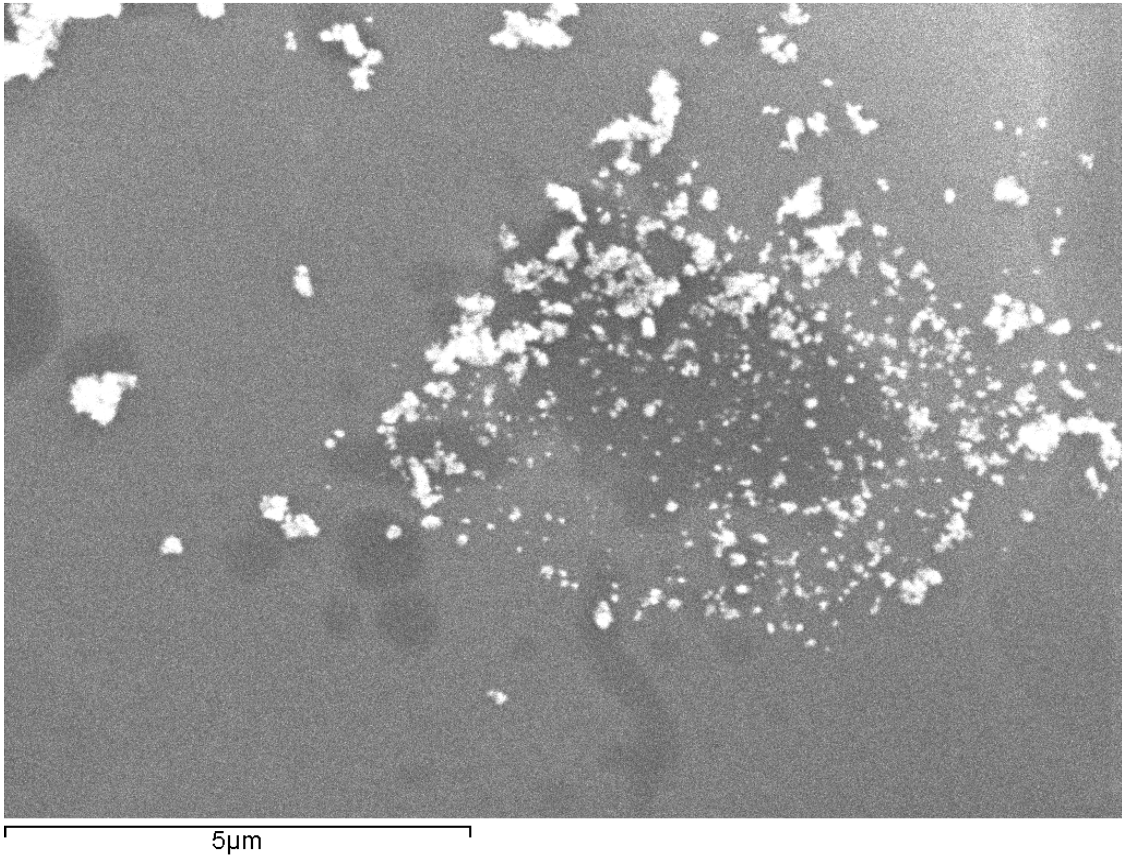


- Still some CuCl
  - Assume source is Cu_2OCl_2 decomposition
  - No Cl_2 in gas phase in experiments at CEA
- Thanks to Bob Evans for suggestion



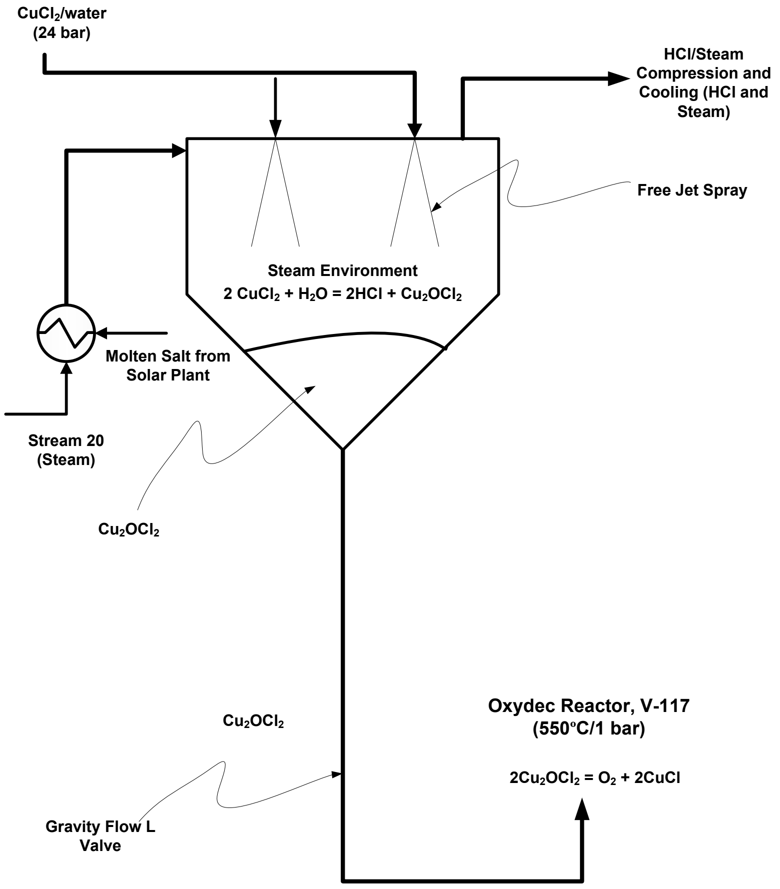
Technical accomplishment

Cu_2OCl_2 particles small, <100 nm to 30μm, & free flowing



Integration of lab results with modeling activities leads to conceptual process design

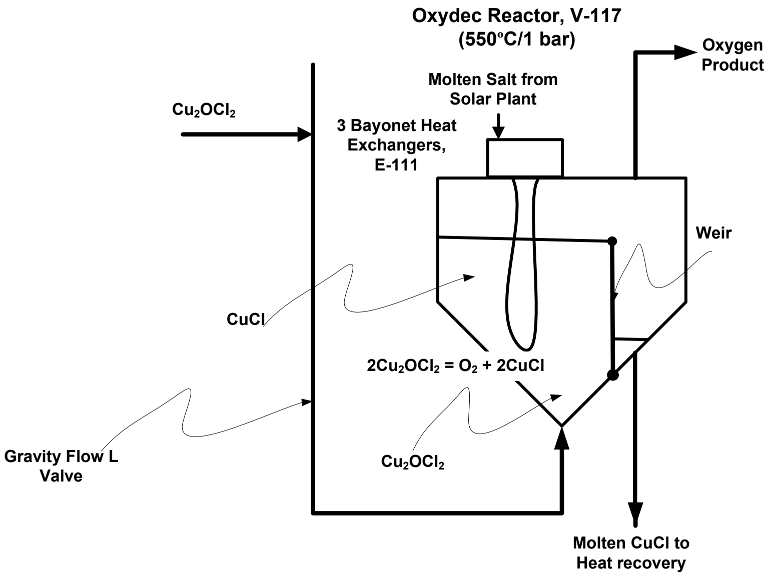
- Lab: Ultrasonic nozzle provides small droplets of $CuCl_2$*$2H_2O$ solution that are readily converted to Cu_2OCl_2
- Concept: Spray roaster
  - $CuCl_2$ slurry at 24 bar, injected into 400C steam environment at 0.25 bar
  - Drop in pressure causes slurry to be issued at supersonic velocity which promotes mass and heat transfer within the steam environment
    - *No Ar carrier gas needed*
  - Lower pressure (0.25 bar) results in a reduction of S/Cu & lower capital cost
    - *Vacuum provided by steam injector*
  - Similar to commercial operations in which HCl is recovered from spent pickling solutions



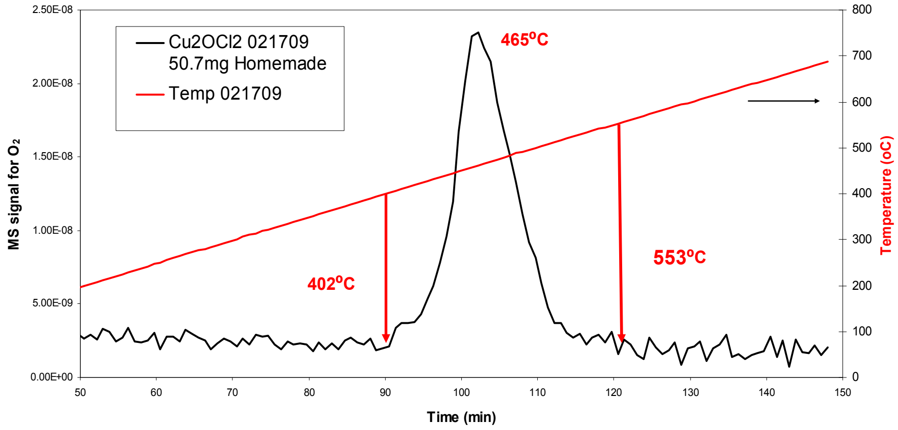
Technical accomplishment

Oxychloride decomposition reactor: concept and T(max)

- Cu_2OCl_2 is free flowing
  - Transferable by gravity from the hydrolysis to the Cu_2OCl_2 decomposition reactor
  - Injection position subject to change
- Oxychloride decomposition reactor's temperature is about 550C
- CuCl is discharged as a molten salt and oxygen is released



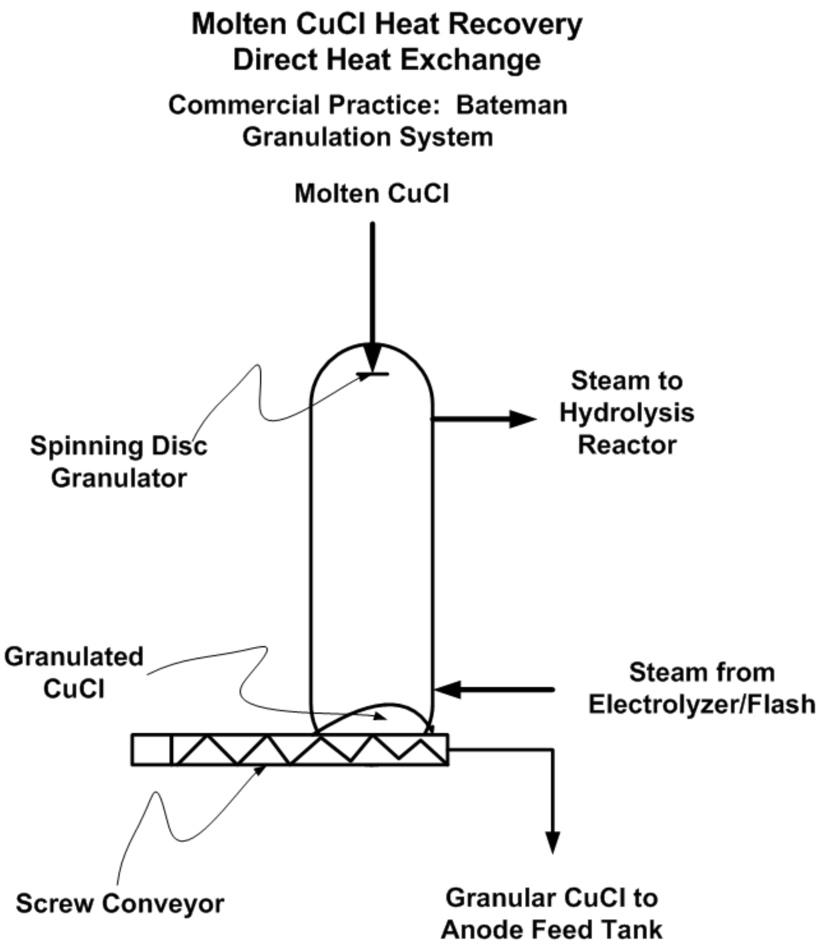
- Ultrasonically produced Cu_2OCl_2 decomposes between 400 to 550C



Technical accomplishment

Optimized heat recovery

- Direct contact heat recovery is proposed for recovering the molten CuCl salt's enthalpy
  - Heat low temperature steam to 400C steam for hydrolysis reactor
  - Highly efficient heat transfer
  - Idea by UOIT and USC staff



Results of H2A analysis: Estimated H_2 production costs and efficiencies for solar heat based on current Aspen flowsheet

Case	Capital Investment, $M, Solar/Chemical	Cell EMF, V	Electrical Cost, $/kw	$/kg	Sensitivity	Efficiency, % (LHV)
Solar 2015	208.3/136	0.7	0.068	4.53	3.78-5.31	39
Solar 2025	168.5/106.6	0.63	0.048	3.48	2.91-4.11	41

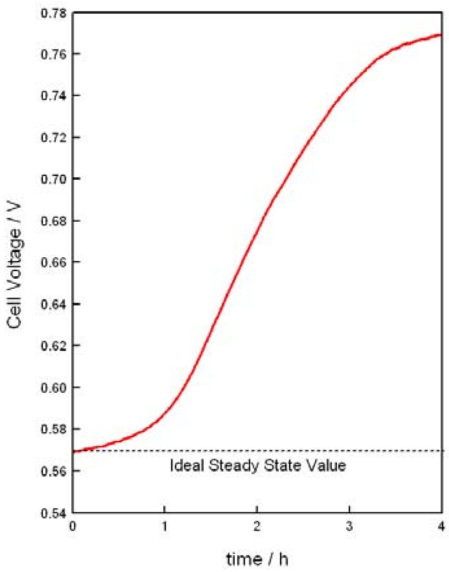
$$\text{Efficiency} = \frac{\text{Mol. of } H_2 \text{ Produced} * \text{LHV}}{(\text{Pinch Heat} + \text{Electrochemical work} + \text{Shaft work})}$$

Assumes electrolyzer and crystallizer operability meets specified targets

Develop membrane for electrolyzer to stop Cu crossover
Penn State (S. Lvov-PI)

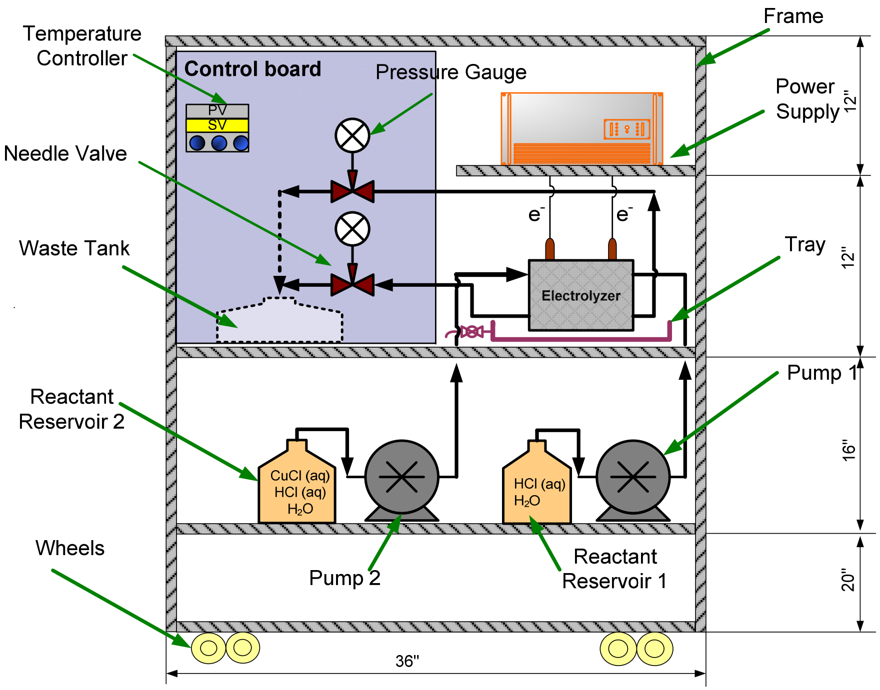
- Challenge: AECL's test results show that Cu crossover from the cathode to the anode causes an increase in cell voltage

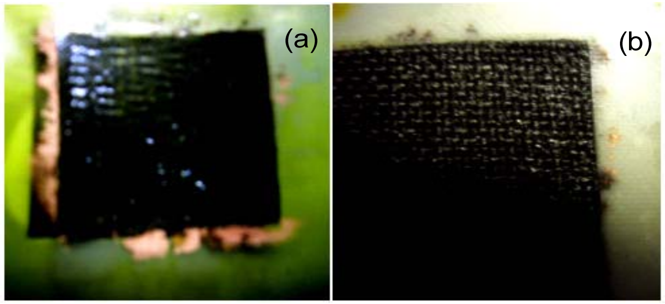
- Solutions:
  - Pennsylvania State University is developing new chlorine conductive materials, poly(ethylene-co-hexenylamine) (PEHA) random copolymers
    - *High chlorine conductivity*
    - *Good chlorine exchange membrane stability (chemical, thermal, and water-swelling).*
    - *Testing in electrolyzer to start shortly*
  - Cation exchange membranes are being investigated in Canada



Membrane development work at Penn State (S. Lvov-PI)

- Build and test electrolyzer and test commercial membranes as well as the promising new membranes
  - AHA, ACM, AMI, AMX, ACS, AM-3, and AHT tested in the Cu-Cl electrolyzer
  - No Cu crossover with AHT
  - The AHT system showed a significantly higher current efficiency in comparison with other systems.

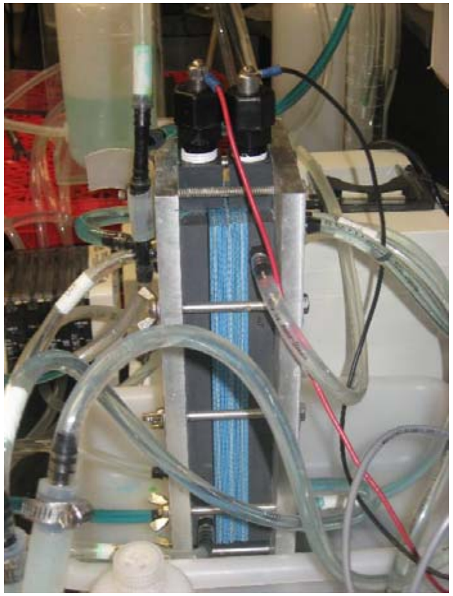




•*ACM (a) is more susceptible than AHA (b)*

Develop and evaluate different separation methods for processing spent anolyte and catholyte

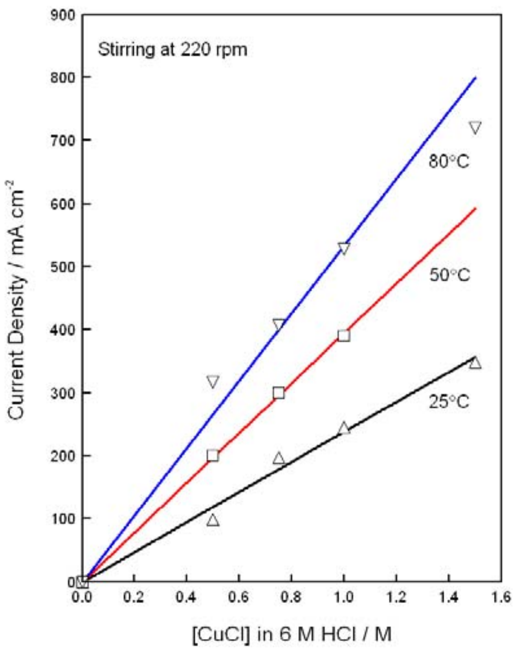
- Electrodialysis (requires 20-30 kWh/ton water for high salt solutions vs. 620 kWh/ton for distillation)
  - USC developed an analytical method for online analysis of copper compounds in highly concentrated aqueous solutions
  - [$CuCl_2$] in the diluate was reduced from 1.26% to 0.15% while the [$CuCl_2$] in the concentrated solution reached 23.13%
- Membrane distillation (uses waste heat)
- Evaporative crystallization
  - Solubilities needed for complicated system
    - *Literature search completed; additional data needed*



Electrodialysis unit at USC from Tom Davis

Expertise/contributions from INERI partner

- Atomic Energy of Canada Ltd. is developing the electrolyzer
  - Showed that higher temperatures and stirring increased current density at 0.8V cell potential
- AECL provided seed money to several Canadian universities who obtained $5M grant from Ontario Research Foundation
  - Build small pilot plant
  - Identify and test possible materials of construction
  - Measure thermodynamics properties of important species in the CuCl-$CuCl_2$-HCl-H_2O system



Summary

- Spray reactor provides necessary heat and mass transfer and product powders are free flowing
- Maximum process temperature of 550C confirmed with Cu_2OCl_2 powders produced with ultrasonic nozzle
- Based on current Aspen model and conceptual design, it should be possible to meet hydrogen production cost target for 2025
  - Assumptions on operability of crystallizer and electrolyzer to be proven
  - Commercially practiced operations incorporated to reduce development costs
- AECL has promising results for the electrolyzer's operation but further improvement is needed
- NERI-C partners are focused on advanced electrochemical technologies, e.g. membrane development, electrolyzer model development, etc

Future work

- Continue with model optimization and updates of efficiency and H_2 production costs
- Identify a membrane for the electrolysis cell that prevents Cu crossover
- Develop quantitative models for hydrolysis and electrolysis reactions
  - Measure solubility of CuCl-$CuCl_2$ solubility in aqueous HCl solutions as a function of temperature, pH and concentrations of copper species
- Demonstrate the separation methods for handling the spent anolyte
  - Consider different methods, e.g., membrane distillation, electrodialysis, and evaporative crystallization

Acknowledgements

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