Part I. Summary of Alternative Cycle Evaluation and Down Selection

Part II. R&D Status for the Cu-Cl Thermochemical Cycle

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PD28

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Overview

Time Line

- Start date: 6/06 (Part 1)
- Start date: 10/07 (Part 2)
- End date: 09/10
- % complete: 30%

Budget

- $1.3M for Phase 1
  - Mostly university support
- $250K for FY08 for Part 2
- Complementary program supported by DOE-EERE
  - $939K from FY06 to FY09

Barriers

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

Partners

- International Nuclear Energy Research Initiative (INERI)
- Nuclear Energy Research Initiative-Consortium (NERI-C)

Objectives

- Develop a commercially viable process for producing hydrogen based on a thermochemical cycle that meets DOE cost and efficiency targets

- Coordinate university evaluation of alternative cycles considered in the literature as promising and down select to most promising cycle
  - Selection criteria were chemical viability, engineering feasibility, projected efficiency and hydrogen production cost, and DOE-NE's time line for an integrated laboratory-scale demonstration (ILS)

Cu-Cl Cycle down selected based on knowledge in 8-07

Cycle	Chemical Viability	Engineering Feasibility	Cost and/or Efficiency	DOE's Timeline
Hybrid Cu-SO_4	No —competing product forms	?	?	No
Mg-I	No—HI_x decomposition/ separations	No—too complex	?	No
Active Metal Alloy	?	Yes— simple	Low efficiency, but low cost	?
Hybrid Cl_2	?	?	Possible	No
V-Cl	No—slow kinetics	?	?	No
Hybrid Ca-Br	?	Yes	?	No
Hybrid Cu-Cl	Yes	Yes	Yes	Yes

Some cycles have significant merit but insufficient data available when down selection occurred.

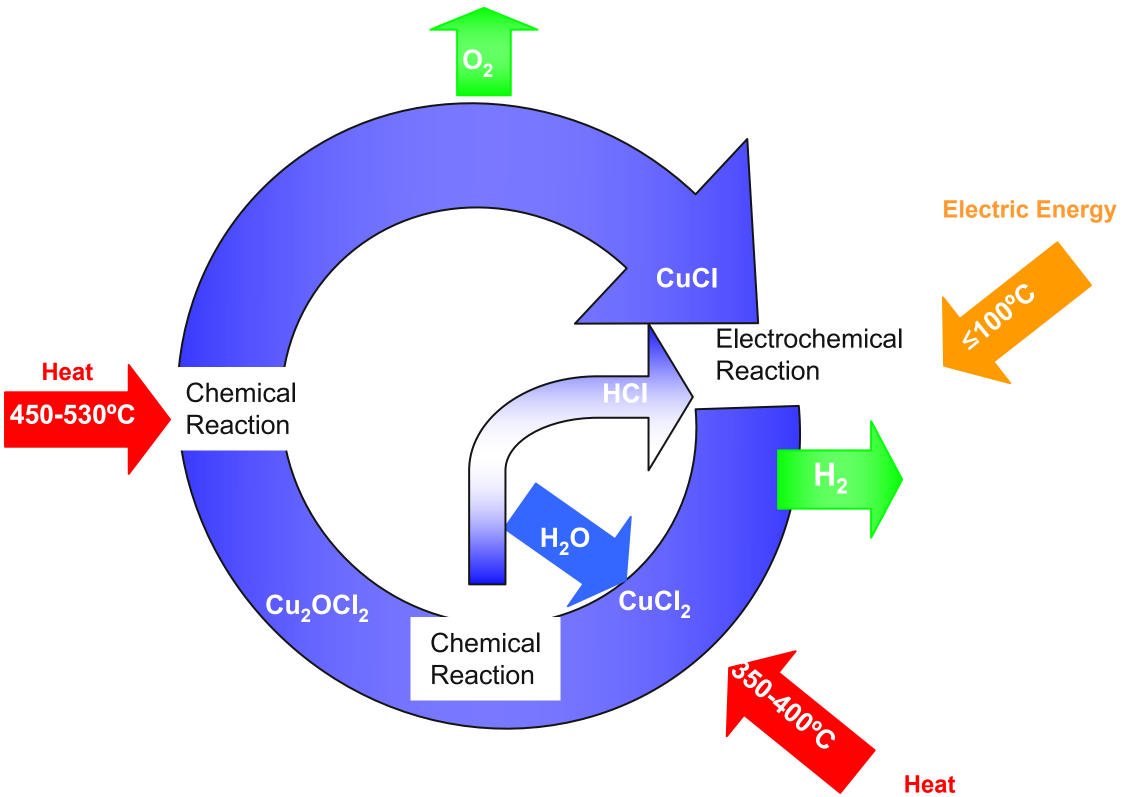
Milestones due 9/30/08

- Complete down selection process
  - CuCl selected for the following reasons:
    - *Proof of principle complete, no showstoppers identified*
    - *Low maximum temperature, 550C in lab-scale tests*
    - *Projected efficiency and H_2 production costs within DOE targets*
    - *International support*
  - K-Bi cycle selected as part of NERI-C
    - *Proof-of-concept work ongoing*

- Define optimum operating conditions and reactor designs for Cu-Cl thermochemical cycle but focus on an engineering lab-scale reactor for the <u>hydrolysis</u> reaction

- Coordinate activities with partners in INERI and NERI-C to develop robust hydrogen production process

Approach



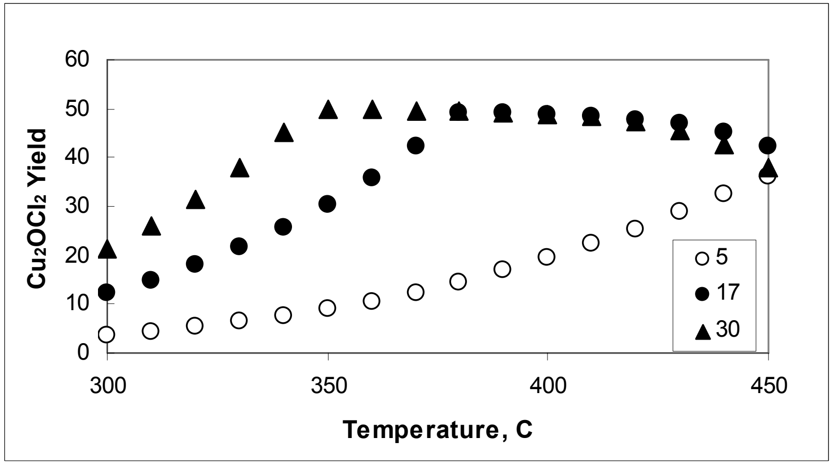
- **Experimental program**
  - Focus on hydrolysis reaction
  - Scale-up to an engineering lab-scale reactor
  - Feed results to model
- **Modeling program**
  - Supported by DOE-EERE
    - *Developed flowsheet*
    - *Estimated efficiency and capital costs*
    - *Used H2A analysis for H_2 production costs*
    - *Optimization ongoing*
  - Guide expt. program

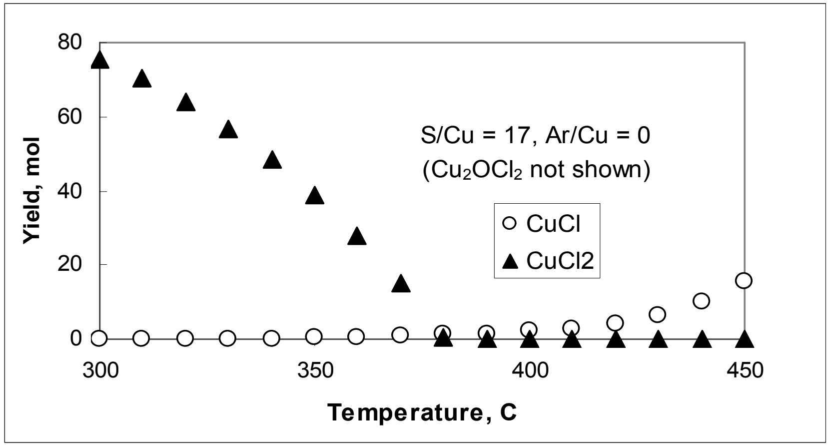
Three major reactions in the Cu-Cl cycle

- **Hydrolysis reactor**
- **$2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$**
  - Tested 4 reactor designs
    - ***Fixed bed***
    - ***Fluidized bed***
    - ***Rotary***
    - ***Nebulizer***
- **Oxychloride decomposer**
- **$Cu_2OCl_2 \Leftrightarrow 2CuCl + ½O_2$**
  - Completed proof-of-concept work shows reaction is a relatively simple thermal decomposition
- **Electrolysis**
- **$2CuCl + 2HCl \Leftrightarrow 2CuCl_2 + H_2$**
  - **2Cu(+1) ⇔ 2Cu(+2) + 2e(-)**
  - **2H(+1) ⇔ H_2**
    - *Proof-of-concept work completed at AECL*
    - *Optimization ongoing*

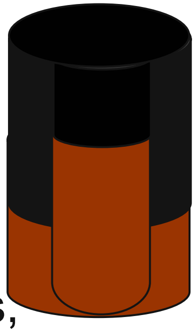
Hydrolysis reaction, $2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$, is primary focus

- Two challenges identified
  - Need for excess water shown by model and in experiments
    - *Steam to $CuCl_2$ ratio required is >14, not ½ as shown by stoichiometry*
  - Expensive to handle and heat
  - Parasitic reaction, $2CuCl_2 \Leftrightarrow 2CuCl + 2Cl_2$, observed in experiments but predicted to a lesser extent by model
    - *8-27% wt % CuCl in products experimentally*
    - *1-2 wt% predicted in model*





Fixed bed reactor provides poor mass and heat transfer



- Desired product formed at top and along the edge of the fixed bed
- High GHSV* provides needed mass transfer to obtain high yields of desired Cu_2OCl_2 and high steam to copper provides sufficient moisture
- CuCl formation increases with higher temperatures, longer test durations, higher carrier gas flow rates and lower steam to copper molar ratios

Steam/Cu Molar ratio	Time (min)	GHSV* (h^{-1})	H_2O vapor (%)	Cu_2OCl_2 (wt%)	CuCl (wt%)
28	60	43327	8	87	12
52	30	43135	26	89	8
17	60	8900	26	48	27
17	60	26000	8	66	17

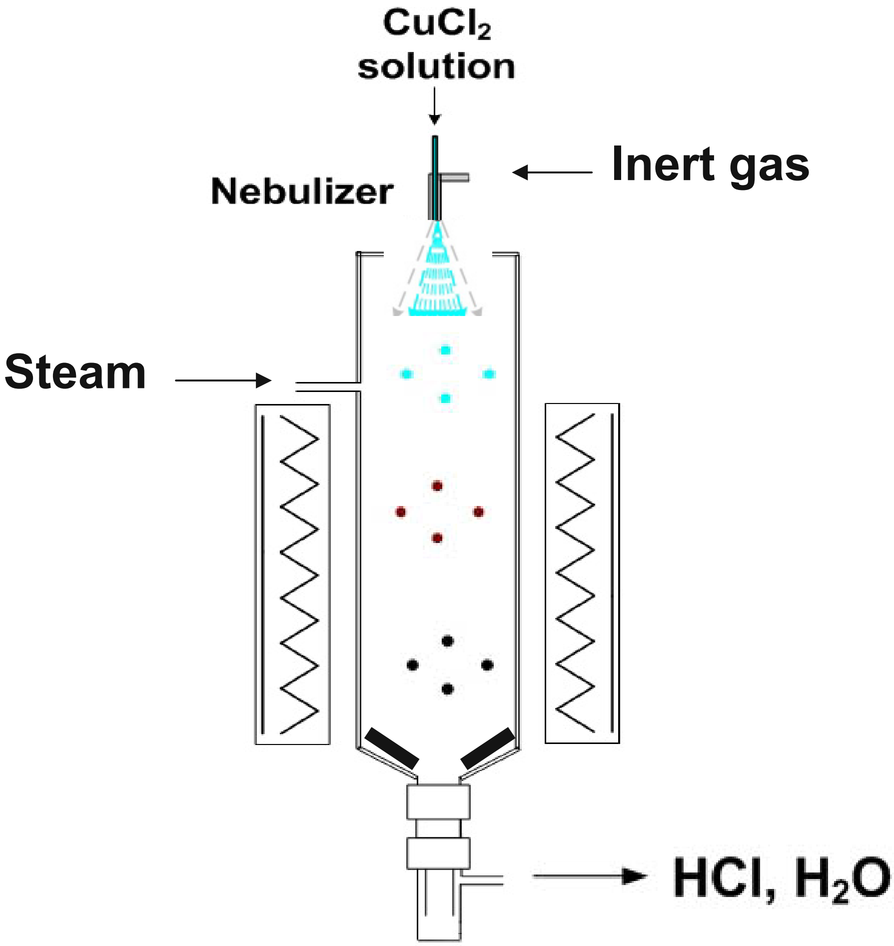
*GHSV = gas hourly space velocity

Fluidized bed reactor favors parasitic reaction, $2CuCl_2 \Leftrightarrow 2CuCl + 2Cl_2$

- High flow rate for carrier gas required for fluidization
- CuCl formed to a greater extent with high carrier (fluidization) gas flow rates
- Products were not fluidized

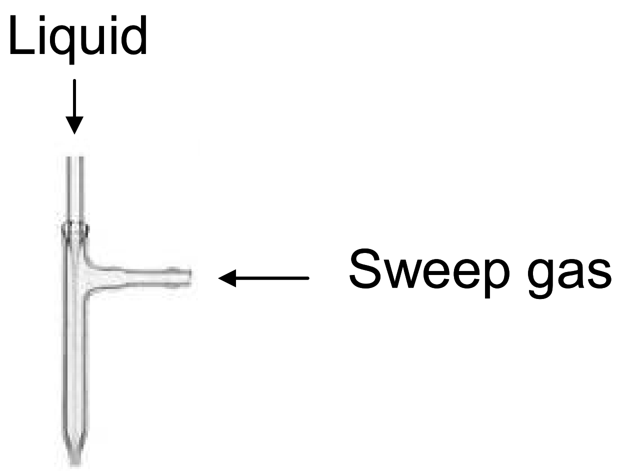
New reactor design needed to provide high mass and heat transfer and short residence times

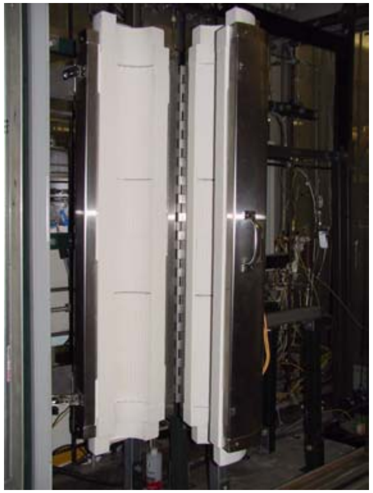
- Nebulizer reactor offers improved mass and heat transfer compared to fixed bed
- Small droplets of $CuCl_2$ (blue) solution are dehydrated
- Very small particles of $CuCl_2$ (brown) react with steam
- Very fine particles of Cu_2OCl_2 (black) are formed and fall to the bottom of the reactor to an unheated zone

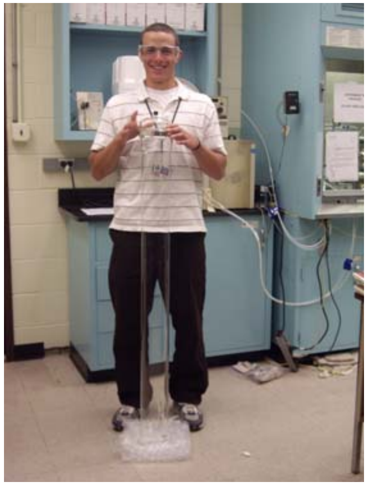


Nebulizer reactor

- Similar to spray reactor adapted for use in the laboratory
- Use nebulizer to obtain spray
  - Finest capillary in commercially available nebulizer gives 3 inch diameter cone about 3 inch from tip of nebulizer
  - Nebulizer must be kept ‘cool’ to prevent dehydration of solution in capillary
    - *Solid $CuCl_2$ plugs capillary*
- New furnace has a 5 inch ID and contains 3-12 inch heating zones
- New reactor is glass and is 5 feet long

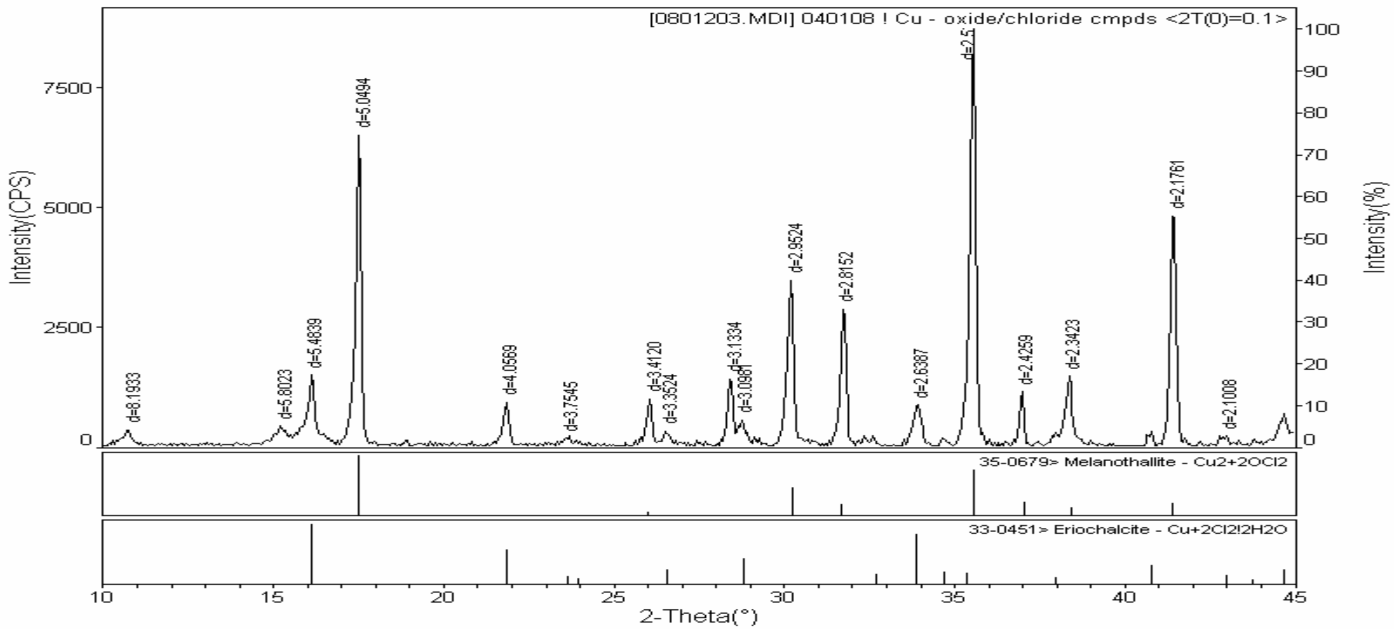






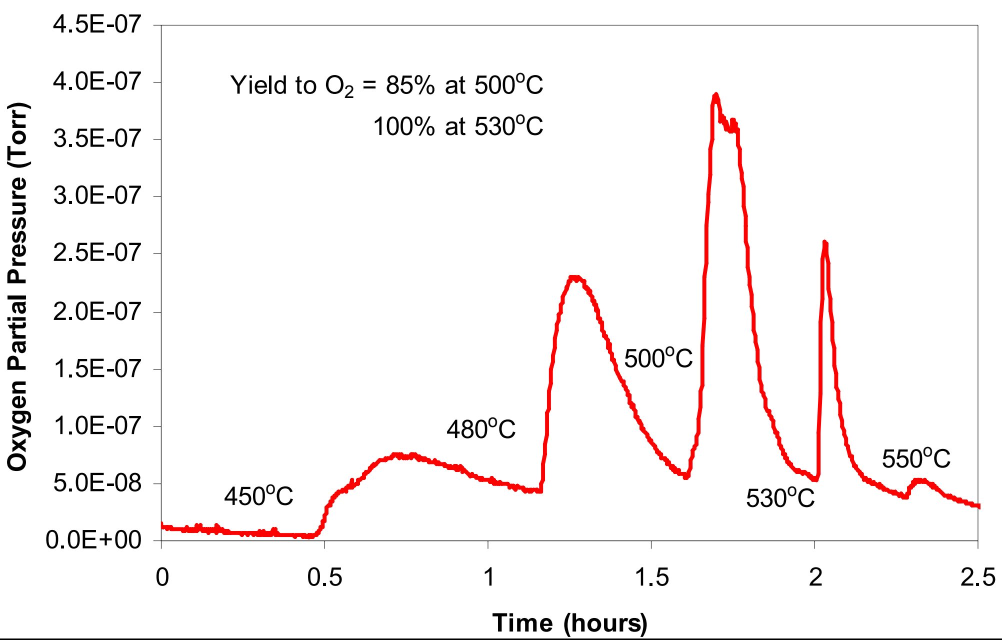
Key hydrolysis reaction just demonstrated at engineering lab-scale: $CuCl_2 + H_2O = Cu_2OCl_2 + HCl$

- Cu_2OCl_2 and minor amounts of unreacted $CuCl_2$ identified from XRD
- Experimental variables being optimized for highest yields of Cu_2OCl_2
- Question remains on whether CuCl was formed

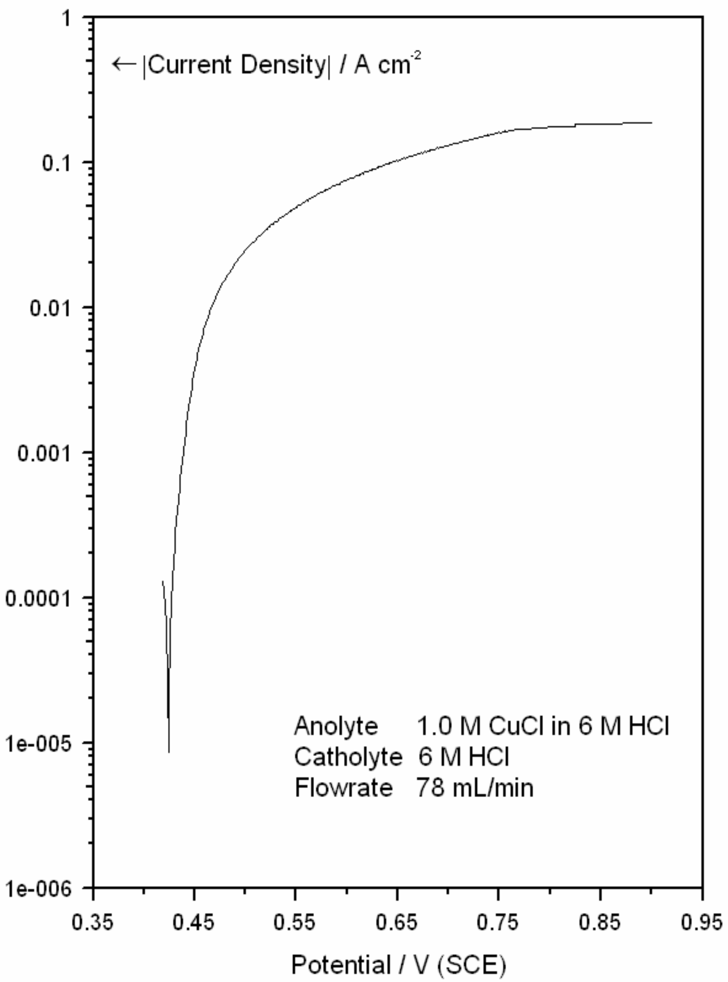


Oxychloride decomposer: Cu_2OCl_2 = 2CuCl + ½O_2

- The reaction has been validated with off-the-shelf and recycled (Cu_2OCl_2) materials (Supported by LDRD funds)
- O_2 yield 100% at 530°C; only O_2 detected on the mass spec - no apparent side reactions
- Kinetic data measured



Single-Cell CuCl/HCl Electrolysis



- At 20ºC and a cell voltage of 0.645 V a current density of 100 mA/cm^2 is observed
  - Goal is 0.5 V and 500 mA/cm^2
- The current density is limited by mass transfer effects
- Current densities of 300 mA/cm^2 should be achievable
  - Once mass transfer effects are eliminated through careful cell design
  - At higher temperatures

Expertise/contributions from NERI-C partners

- NERI-C partners: Penn State, University of South Carolina, and Tulane University: $2.4 M over 3 years
  - Develop characterization methods for Cl^- conductive membranes
  - Develop new Cl^- conductive membranes
  - Develop electrocatalysts for the electrodes for the Cu-Cl electrolyzer
  - Determine speciation and thermodynamic properties of important species in the $CuCl$-$CuCl_2$-HCl-H_2O electrolysis cell
  - Determine concepts to improve the operability of the process
    - *Utilize years of engineering know-how*
  - Develop separation methods as needed
    - *Electrodialysis*
    - *Breaking HCl azeotrope*

Expertise/contributions from INERI partner

- INERI partner (Atomic Energy of Canada Limited)
- AECL provided seed money to 4 Canadian universities who obtained $5M grant to study Cu-Cl cycle
  - Develop concepts to improve the operability of the process and other modeling activities
    - *Direct cooling of molten salt*
  - Measure needed thermodynamics properties of important species in the $CuCl$-$CuCl_2$-HCl-H_2O electrolysis cell
  - Develop membrane electrode assemblies
    - *Complementary to NERI-C work*
  - Develop lab-scale engineering equipment
  - Develop control systems and risk analysis
  - Identify and test possible materials of construction

Preliminary capital cost and H2A analysis results

125,000 kg of hydrogen /day

	2015	2025
Capital, $MM -Solar (Sandia) -Chemical Plant	 223.4 134.2	 183.2 77.3
Utilities, MW	92	82
Efficiency, % (LHV)	40	42
Cost of Hydrogen, $/kg	4.38	3.01

2017 Target
> 35
3.00

Assumptions:

2005 $, CEPCI = 468

Electrolyzer performance: 0.5 volts and 500 mA/cm^2

Electrode cost -- $2500/m^2

Porcelain coated carbon steel at a 6% cost increase

Crystallizer operability

Future work

- **FY08**
- Continue development of hydrolysis reactor
  - Understand effect of experimental parameters
  - Optimize performance
  - Measure kinetics of hydrolysis reaction using HCl formation

- **FY09**
- Couple hydrolysis and oxychloride decomposition reactors for integrated laboratory demonstration (ILS)
- Determine need for separations using both experimental and modeling approaches

Summary

- Engineering lab-scale hydrolysis reactor demonstrated—spray-type reactor provides necessary heat and mass transfer

- AECL has promising results for the electrolyzer's operation but further improvement is needed

- NERI-C and INERI partners are providing new concepts for improving operability of the process, increasing efficiency, and decreasing capital costs
  - Development and characterization of chloride ion conductive membranes, measurement of needed thermodynamic parameters to optimize electrolyzer performance

- Projected H_2 production cost and process efficiency meet DOE targets