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# *Alternative Thermochemical Cycle Evaluation*

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U.S. Department  
of Energy

UChicago ►  
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PDP23

# Overview

## Time Line

- Start date: 10/04
- End date: 09/07
- % complete: 90%

## Barriers

- Unknown thermodynamic data
- Unknown chemistry
- Short timeline

## Budget

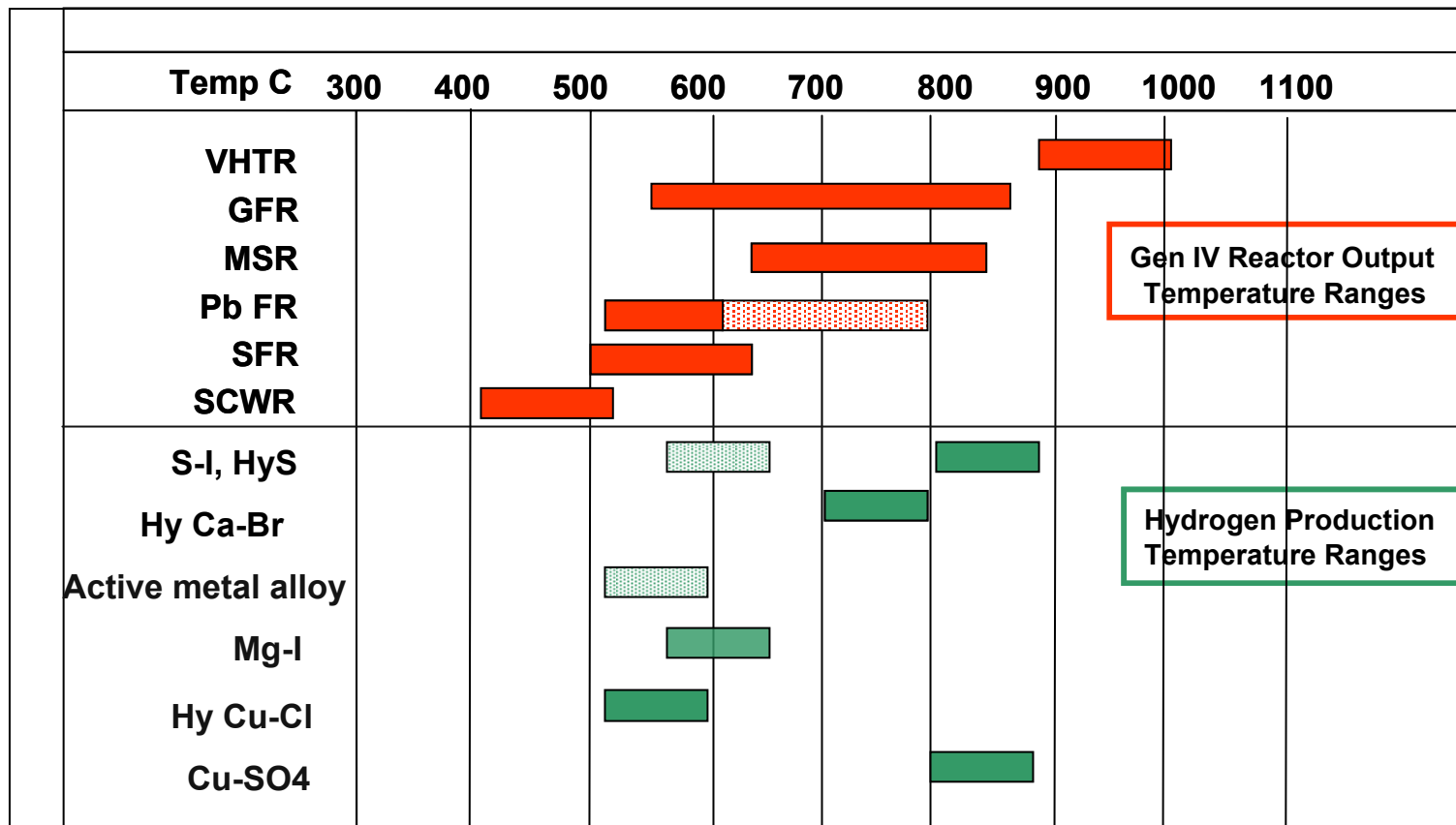
- FY 06 = \$1,043K
- Funds supported 8 universities
- Complementary program supported by DOE-EERE

## Partners

- Eight universities
- Information exchange
  - Atomic Energy of Canada, Ltd.
  - Commissariat à l'Énergie Atomique
  - Ontario Institute of Technology

# Objective: Balance temperature portfolio of nuclear heating sources with thermochemical cycles for H<sub>2</sub> generation

- Electrical generation - **Gen IV Energy Conversion Program**
- Hydrogen production - **Nuclear Hydrogen Initiative (NHI)**



# Approach

- **Identify promising cycles from the literature with various maximum temperatures to match heat output from different nuclear reactors**
- **Invite university participation to evaluate cycles using consistent methodology**
  - Clemson, Howard, MIT, Pennsylvania State University, Rensselaer Polytechnic Institute, Tulane, University of South Carolina, University of Illinois-Chicago (UIC)
  - NHI methodology consists of 3 levels of evaluation
    - *Level 1 based on stoichiometric reactions*
    - *Level 2 based on equilibrium considerations*
    - *Level 3 based on 'real' chemistry to the extent it is known*
    - *Pinch analysis used for heat management in all levels*
- **Determine critical R&D needs or recommend no further work**
- **Down select 1 or 2 of the most promising cycles for further R&D**

# What is a promising alternative thermochemical cycle?

## ■ Chemically viable

- Determined from literature or current experimental work
- No important competing reactions
- Fast kinetics and high yields

## ■ Thermodynamically feasible

- Free energies for all reactions are within  $\pm 15$  kcal or about 60 kJ
- Determined from thermodynamic databases

## ■ Thermally efficient

- Literature results used for initial assessment of promise
- Recalculated values from NHI methodology by the universities used for final assessment

## ■ R&D needs compatible with DOE timeline

## ■ Cost competitive with gasoline equivalent

- To be determined
  - Currently \$2.00-3.00/gge (*delivered, untaxed, 2005\$, by 2015*),  
*independent of the pathway used to produce and deliver hydrogen*

## Efficiency results from university evaluations

Cycle	Efficiency % (LHV)		
	Level 1	Level 2	Level 3
Active metal alloy	30-48	Insufficient data	
Ca-Br	46	In progress	Insufficient data
Ce-Cl	Not calculated	16.8	20.9 <sup>a</sup>
Cu-Cl	42-50	38-48	43
Cu-SO <sub>4</sub>	47.1	25-40	52.4
Fe-Cl	29	18.5	NA
Hybrid Cl <sub>2</sub>	34.3	32.1	34-35
Mg-I	47	45	46 <sup>a,b</sup>
V-Cl	52.5	48.9	46

<sup>a</sup> Level 3 calculated for H<sub>2</sub> final pressure of 1 bar

<sup>b</sup> Thermodynamic data in question; preliminary estimate

## Other positive attributes for these cycles

Cycle	Advantages
Active Metal Alloy (Hybrid)	Simple unit operations, minimal separations
Ca-Br (Hybrid)	Maximum temperature $\sim 750^{\circ}\text{C}$ , leverage R&D from UT-3 cycle and Ispra cycles
Cu-Cl (Hybrid)	Maximum temperature $\sim 550^{\circ}\text{C}$ ; completed proof-of-concept work
Cu-SO <sub>4</sub>	High projected efficiencies if electrochemical rxn. can be converted to a thermal one; less aggressive chemicals than in other sulfur cycles; leverage R&D from S-I cycle
Hybrid Cl <sub>2</sub>	Relatively simple, two unit operations
Mg-I	Maximum temperature $\sim 600^{\circ}\text{C}$ ; leverage R&D from S-I cycle to handle HI
V-Cl	High projected efficiencies; on hold pending results of reverse Deacon reaction study in the hybrid chlorine cycle

## Challenges for further development of these cycles

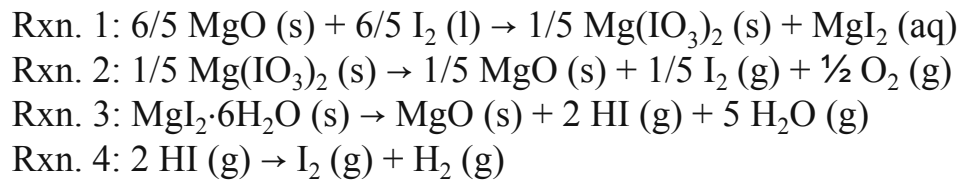
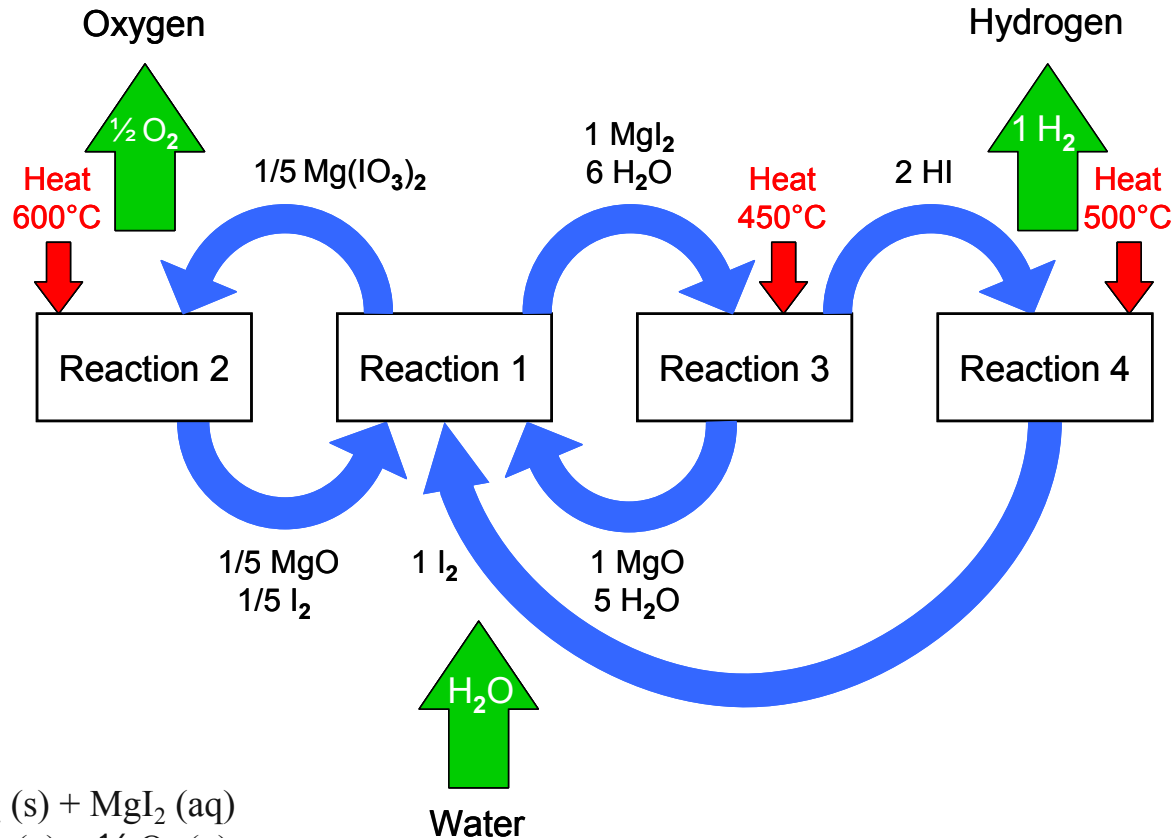
Cycle	Challenges
Active metal alloy	No proof of concept work, unknown chemistry, absence of thermodynamic data for most species
Ca-Br	No proof of concept work for bromination reaction, missing thermodynamic data
Cu-Cl	Development of the electrochemical reaction and optimization of conditions for hydrolysis reaction
Cu-SO <sub>4</sub>	High temperature for CuSO <sub>4</sub> decomposition, conversion of electrochemical reaction to thermal one
Hybrid Cl <sub>2</sub>	High electrical input for electrolysis of HCl, challenging separations and temperatures in reverse Deacon reaction (RDR)
Mg-I	HI-I <sub>2</sub> or HI <sub>x</sub> decomposition, excess water handling, azeotrope formation
V-Cl	Separations/high temperature of the reverse Deacon reaction, kinetics of the chlorination reaction



## Mg-I: $T_{max} = 600\text{ }^{\circ}\text{C}$

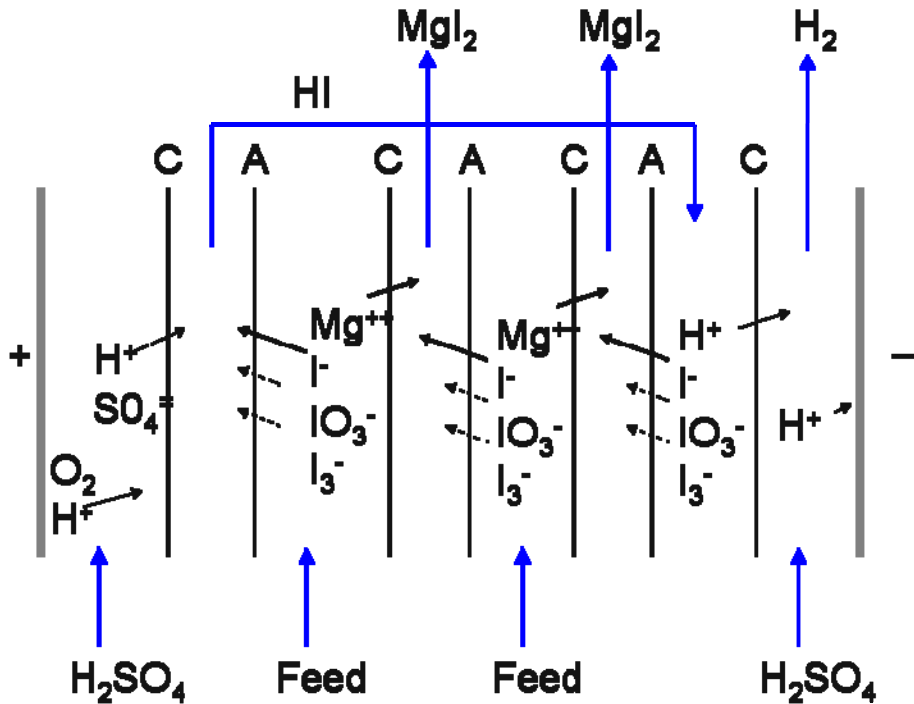
### Mg-I cycle was extensively studied in Japan

- Yields and reaction kinetics are sufficient
- Most separations relatively easy
- Most challenging aspect is HI decomposition
  - *Leverage R&D from S-I cycle*
- Excess water and iodine required



## Mg-I: $T_{max} = 600\text{ }^{\circ}\text{C}$ , Cont.

- Use electro dialysis to remove dissolved iodate in the  $\text{MgI}_2$  solution
- Electro dialysis costs are relatively low



Method	Energy (kWh/ton water)
Distillation	620
Multiple Effect	100
Reverse osmosis	7
Electrodialysis	3 to 8, low salt 15 to 25, high salt

# Hybrid chlorine: $T_{max} \leq 850^\circ\text{C}$

## R&D Emphasis on the reverse Deacon reaction (RDR)

### ■ Two reaction cycle

- RDR:  $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$   $850^\circ\text{C}$
- $2\text{HCl}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$  (electrolytic)  $75^\circ\text{C}$ 
  - *A small scale unit for electrolyzing HCl (g) is available*

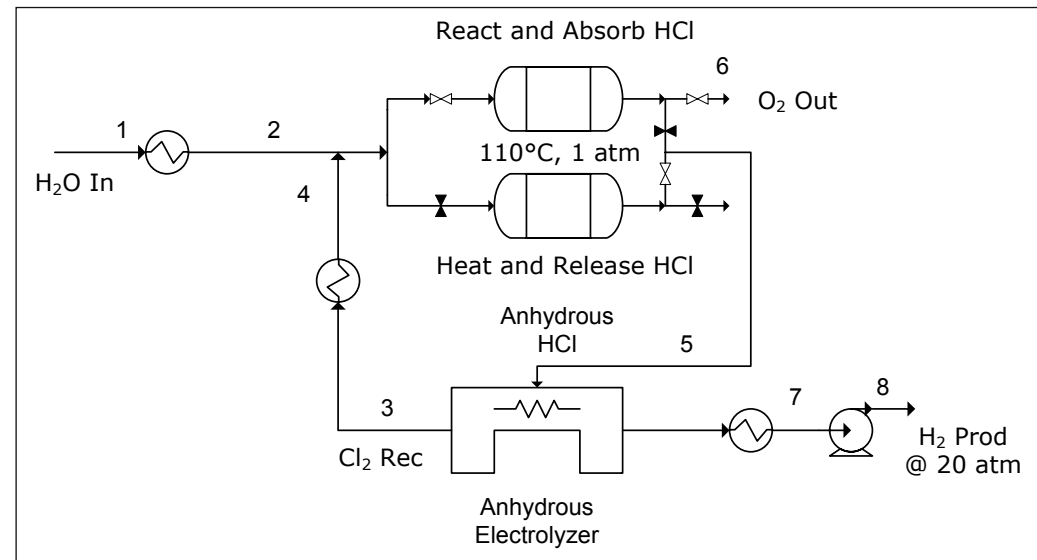
### ■ Challenge lies in the RDR

- 60% yield at  $850^\circ\text{C}$

### ■ Increase yield by removing HCl or $\text{O}_2$

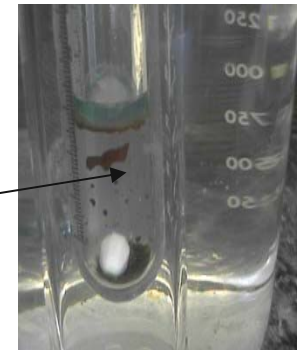
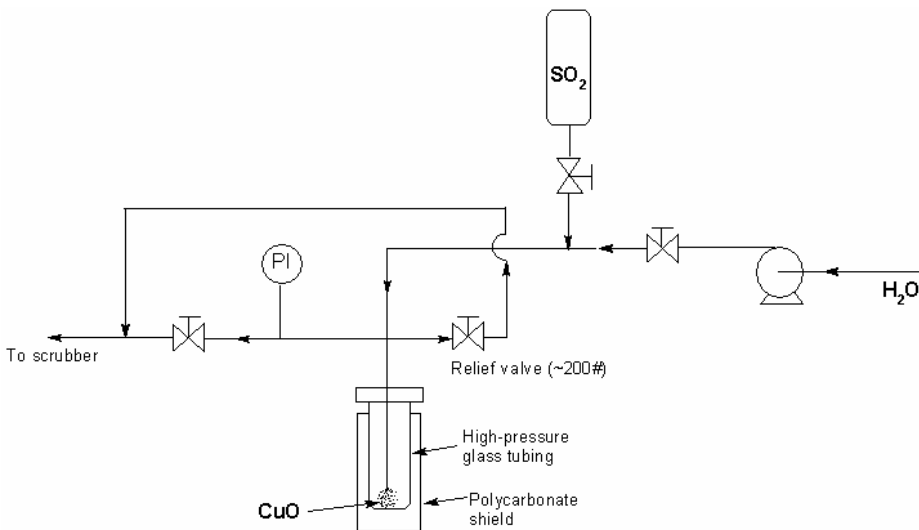
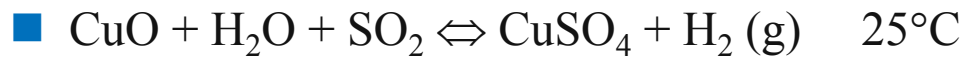
### ■ Clemson studied acidic sorbers

- Zeolite gave best results
  - *$\text{O}_2$  product observed*
  - *Proof-of-concept !!*



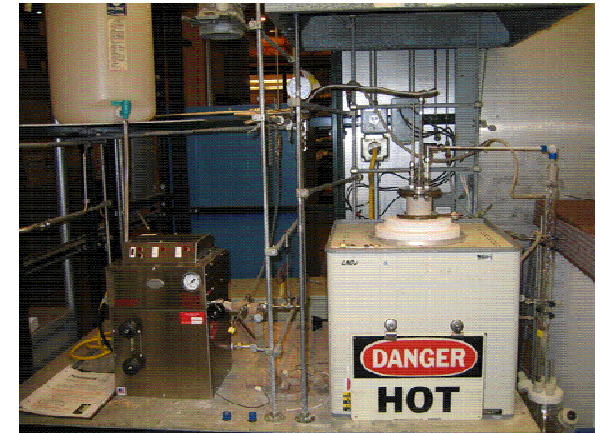
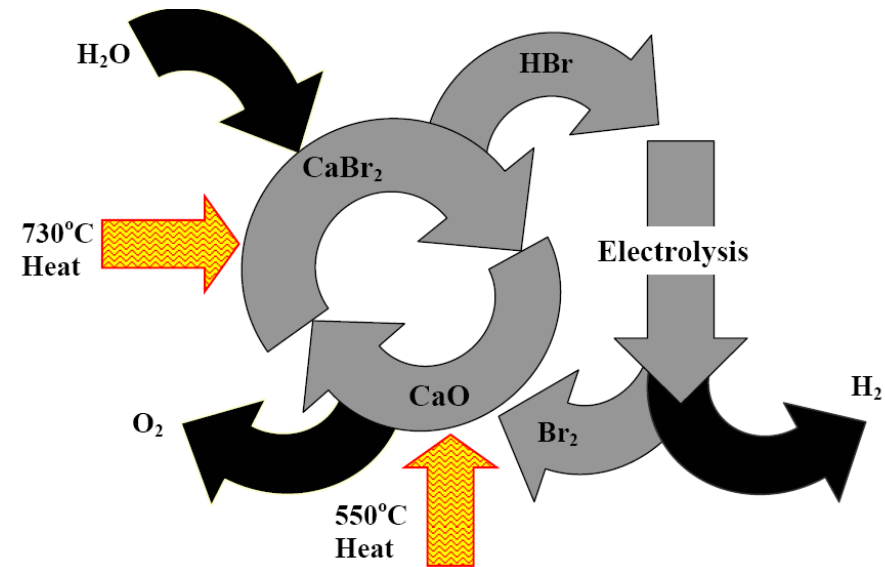
## Hybrid (?) $\text{CuSO}_4$ : $T_{\text{max}} \leq 850^\circ\text{C}$

- Tulane's concept was to convert hydrogen generation reaction from a proven electrochemical one to a thermal one by using liquid  $\text{SO}_2$  instead of gaseous  $\text{SO}_2$ 
  - Large increase in efficiency if successful but Chevrel's salt formed
  - Decrease temperature of  $\text{CuSO}_4$  decomposition by leveraging R&D in the S cycles
  - $\text{CuSO}_4$  is less aggressive than  $\text{H}_2\text{SO}_4$



## New ideas in the hybrid Ca-Br cycle: $T_{max} = 750^{\circ}\text{C}$

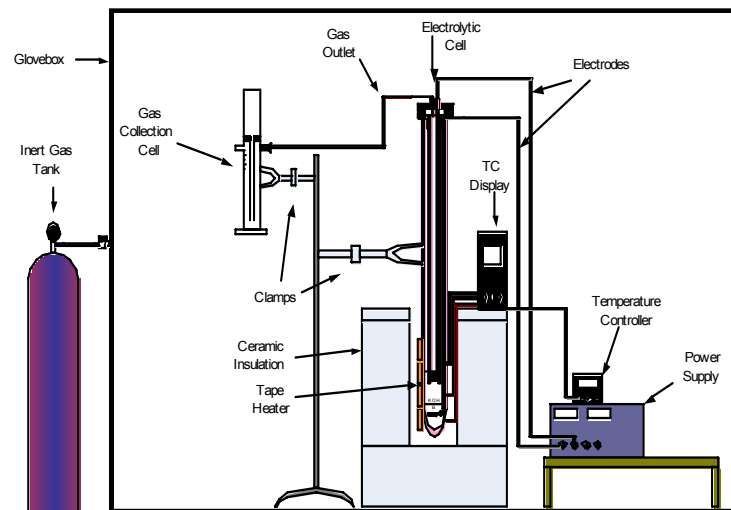
- UIC calculated Level 1 efficiency of 46% (LHV) and developed reactor sparging model
- Sparging of steam through molten  $\text{CaBr}_2$  successfully demonstrated at Argonne
  - High yields of HBr in the hydrolysis reaction
  - $\text{H}_2\text{O}$  droplets sparged into  $\text{CaBr}_2$  melt
  - $\text{CaO}$  dissolved in melt and complex formed
- HBr dissociation using PEM electrolyzer cell looks promising
- Experiments to regenerate melt by sparging  $\text{Br}_2$  into  $\text{CaO-CaBr}_2$  melt planned



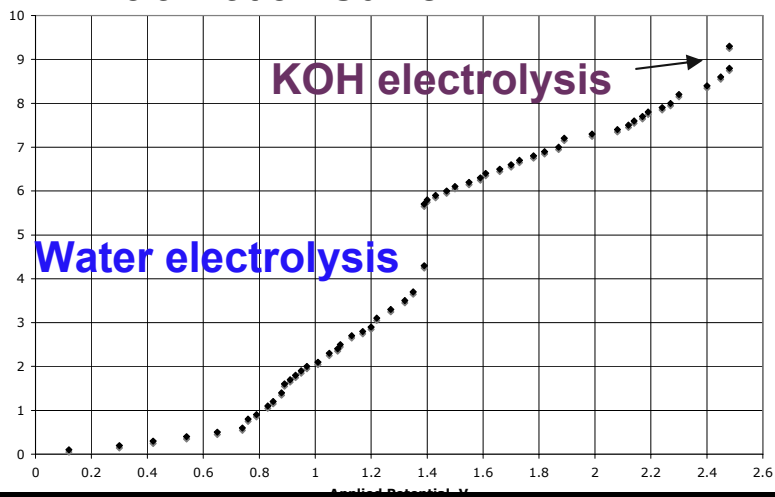
# Hybrid active metal alloy cycle: $T_{max} = 575\text{ }^{\circ}\text{C}$

Two reactions:

- $\text{KBi} + \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{H}_2 + \text{KOH(l)} + \text{Bi}$
- $\text{KOH(l)} + \text{Bi(l)} \leftrightarrow \frac{1}{4} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + \text{KBi(l)}$ 
  - Cathode:  $\text{K}^+ + \text{Bi(l)} + e^- \leftrightarrow \text{KBi(l)}$
  - Anode:  $\text{OH}^- \leftrightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + e^-$
  - $\text{OH}^- \leftrightarrow \frac{1}{2} \text{H}_2\text{O}(\text{g}) + \frac{1}{4} \text{O}_2(\text{g}) + e^-$
  - Anode reaction not known yet

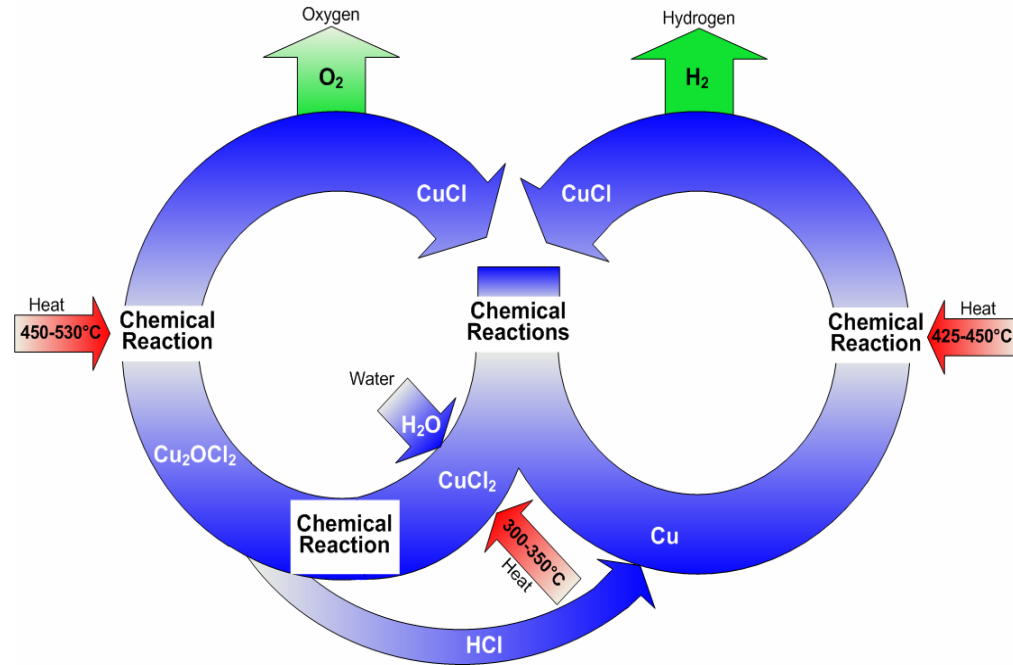


Polarization Curve





# Hybrid Cu-Cl cycle: $T_{max} = 550\text{ }^{\circ}\text{C}$



## ■ Proof of principle experiments completed for all reactions

- $2\text{Cu} + 2\text{HCl} \leftrightarrow 2\text{CuCl} + \text{H}_2$
- $4\text{CuCl} \leftrightarrow 2\text{CuCl}_2 + 2\text{Cu}$
- $\text{CuCl}_2 + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$
- $\text{Cu}_2\text{OCl}_2 \leftrightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2$

## ■ Reaction yields and kinetics indicate no showstoppers

## ■ Hydrolysis reaction being studied to minimize competing reaction

- $2\text{CuCl}_2 \leftrightarrow 2\text{CuCl} + \text{Cl}_2$

## ■ Study of electrochemical reactions to minimize capital costs and maximize overall cycle efficiency

- $2\text{CuCl} + 2\text{HCl} \leftrightarrow \text{H}_2 + \text{CuCl}_2$  or
- $2\text{Cu} + 2\text{HCl} \leftrightarrow 2\text{CuCl} + \text{H}_2$

## Summary of current evaluation results for alternative thermochemical cycles

- **All proof of principle work completed for Cu-Cl and Mg-I cycles**
  - Optimization work now ongoing
    - *Hydrolysis reaction and electrochemical cell development for Cu-Cl cycle*
    - *HI<sub>x</sub> decomposition (in R&D for S-I) and separations for Mg-I*
- **Proof of principle experiments almost complete for Ca-Br and hybrid Cl<sub>2</sub> cycles**
  - Two reactions demonstrated; oxidation of CaBr<sub>2</sub> to CaO via regeneration of bed in progress
  - Qualitative evidence for O<sub>2</sub> formation in the reverse Deacon reaction (RDR)
- **Possible show stoppers**
  - Experiments indicated formation of Chevrel's salt in the Cu-SO<sub>4</sub> study
  - Experiments showed no hydrogen formation in the active metal alloy cycle
- **V-Cl cycle on hold pending results of the RDR study but unlikely to meet DOE timeline**



## Future work

- **Down select one or two of the most promising cycles in June 2007 using the following metrics:**
  - Efficiency evaluations and results of ongoing experimental work
  - Assessment of critical needs for further development with respect to the DOE timeline and available technology
    - *Any potential showstoppers?*
  - Availability of heat sources
    - *For VHTR, GFR, MSR: All cycles*
      - Assumes current maximum temperatures for Cu-SO<sub>4</sub> and hybrid Cl<sub>2</sub> are lowered, which seems possible at this time
      - Use excess heat for electricity production for lower temperature cycles
    - *For Pb FR, SFR, and SCWR\*: Mg-I, hybrid Cu-Cl, hybrid active metal alloy if ongoing R&D is successful*

*\*Assumes that it is possible to adapt pressure tube technology to obtain higher maximum temperatures for the SCWR*

## Project summary

- **Relevance:** Needed to balance the thermochemical cycle portfolio with various heat sources
- **Approach:** Identify promising cycles from the literature and engage universities to reevaluate them using the Nuclear Hydrogen Initiative (NHI) consistent methodology and to start experimental work for critical R&D
- **Technical Accomplishments and Progress:** Eight cycles evaluated and six chosen for further R&D. Experimental work in progress. Down selection to 1 or 2 cycles in June 2007
- **Technology Transfer/Collaborations:** Active partnership with Atomic Energy of Canada, Ltd., University of Ontario Institute of Technology, and Commissariat à l'Energie Atomique, University of Nevada-Las Vegas, Sandia National Laboratory, and the universities involved in the program
- **Proposed Future Research:** Continue R&D for the most promising one or two alternative cycles
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