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## *Evaluation of Alternative Thermochemical Cycles*

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## *Introduction*

- Program approach
- Alternative cycle identification
- University participation
- Summary of proposed new R&D at the universities

## Alternative Cycle Program Approach

2005	<p>Develop NHI methodology for evaluating alternate thermochemical cycles.</p> <p>Identify promising cycles from the literature.</p>
2006	<p>Identify promising alternate cycles from GA-A24972, current literature, and ongoing work at universities using NHI methodology.</p> <p>Invite university participation in cycle evaluation.</p> <p>Coordinate evaluation activities at the universities.</p>
2007	<p>Initiate R&amp;D activities at universities.</p> <ul style="list-style-type: none"><li>·Continue simulation work and review Aspen models.</li><li>·Complete proof-of-concept experiments for new approaches.</li></ul> <p>Down select to 4 cycles: February 15, 2007.</p> <p>Down select to 1 or 2 cycles: May 15, 2007.</p>

## *Metrics used for selecting cycles as promising from the literature in general and in GA-A24972 in particular*

### ■ Screening criteria.

- $\leq 850^{\circ}\text{C}$ , abundance,
- Completion of proof-of-concept experiments that indicate chemical viability and engineering feasibility.
- Promising efficiencies reported in the literature
- Promising efficiencies calculated using NHI methodology.
  - *Levels 1 and 2 efficiencies*

## Different definitions of efficiency

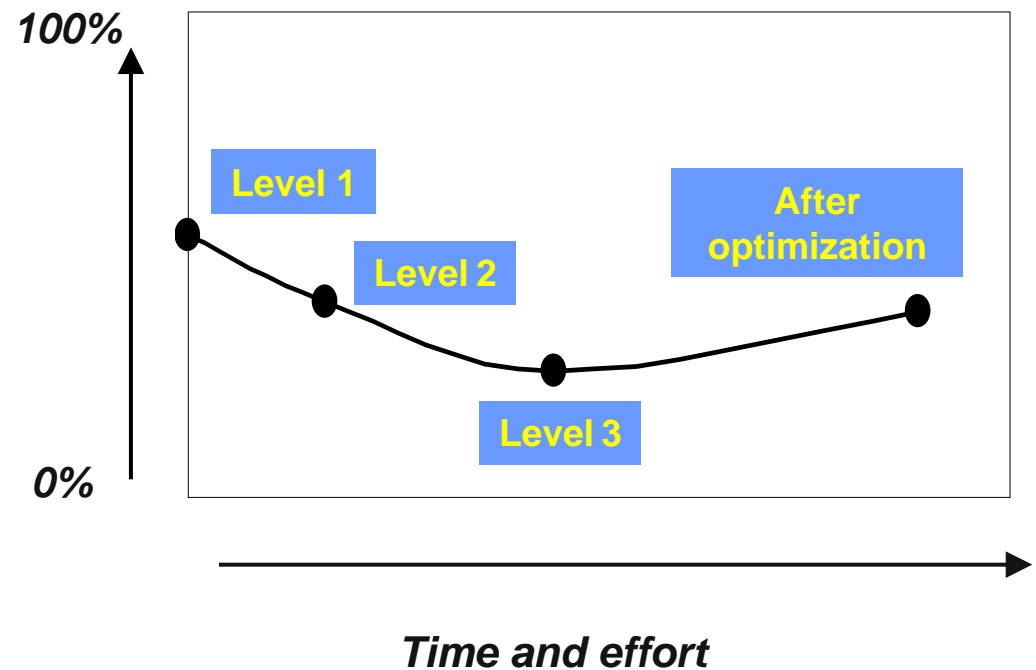
- Level 1: Use simplified reactions and data for enthalpy, free energy, and heat capacity.



- Level 2: Consider equilibrium data and vary operating conditions to increase yields and minimize competing reactions.



- Level 3: Use “real” chemistry and simulation software.



## *Cycles selected as promising*

- **‘Proven’ cycles reported in the literature indicate chemical viability, engineering feasibility and promising efficiencies:**
  - Mg-I
  - Hybrid Cu-Cl
  - Hybrid Cl
  - Hybrid Cu-SO<sub>4</sub>
  - Fe-Cl
  - V-Cl
  - Ce-Cl (studied at CEA)
  
- **New cycle (active-metal alloy)**

## Efficiency (LHV) results by ANL and others as shown

	<b>Level 1</b>	<b>Level 2</b>	<b>Flowsheet</b>
Ce-Cl	48%		
Fe-Cl	33.8%		40.6% [Carty]
Mg-I			36.4% [Fujii]
Hybrid Cu-Cl	48%	41.5%	39.6%
Active metal alloy	39%		
Hybrid Cu-SO4	43.8%	37.8%	30.7% [Carty]
V-Cl	53.4%		36% [Knoche]
Hybrid chlorine	34.3%	30.7%	

## *Additional justification for cycle selection*

<b>Cycle</b>	<b>Max. Temp.</b>	<b>Advantages</b>
Ce-Cl	850°C	Leverage R&D conducted at CEA.
Cu-Cl	550°C	Maximum temperature <550°C.
Cu-SO <sub>4</sub>	850°C	High projected efficiencies; leverage R&D from S-I to reduce CuSO <sub>4</sub> decomposition temperature.
Fe-Cl	925°C	Relatively inexpensive chemicals, well known chemistry.
Hybrid Cl <sub>2</sub>	850°C	Two unit operations; use of PEM fuel cell technology improves efficiency.
Mg-I	600°C	Maximum temperature <600°C; similar HI decomposition reaction in S-I cycle.
Hybrid Active-Metal Alloy	475-675°C	Relatively simple unit operations, minimal separations.
V-Cl	850°C	High projected efficiencies.

## *Universities invited to conduct in-depth evaluation*

- ANL sent a solicitation to all universities with Ph.D. programs in chemical engineering.
- 8 universities selected to continue evaluation of these thermochemical cycles during the summer of 2006.
- Evaluation followed an aggressive schedule
  - Interim report: results from a literature review and Levels 1 and 2 analyses.
  - Final report: Level 3 simulation and recommendations for future work.
- Work was expedited by ANL:
  - Methodology for Levels 1 and 2 provided.
  - Guidelines for Level 3 provided.

## Assignments

- Clemson University: Hybrid chlorine
- Tulane University: Hybrid Cu-SO<sub>4</sub>
- University of South Carolina: Mg-I
- Rensselaer Polytechnic Institute: Fe-Cl
- University of Illinois at Chicago: Hybrid Cu-Cl
- Howard University: Ce-Cl
- Massachusetts Institute of Technology: V-Cl
- Pennsylvania State University: Active metal alloy

## Efficiency (LHV) results by universities

	Level 1	Level 2	Flowsheet
Ce-Cl		16.8%	20.9%
Fe-Cl		18.5%	Not justified
<b>Mg-I</b>	<b>47%</b>	<b>45%</b>	<b>45% (31%)</b>
Hybrid Cu-Cl	48%	41.5%	39.6%
Hybrid Active-Metal	30-48%	No equilibrium data	No equilibrium data
<b>Hybrid Cu-SO<sub>4</sub></b>	<b>47.1%</b>	<b>25-40%</b>	<b>52.4% (with Tulane's approach)</b>
V-Cl	52.5%	48.9%	45.7% (2-stage separation with V <sub>2</sub> O)
			31.4% with reverse Deacon reaction
<b>Hybrid chlorine</b>	<b>34.3%</b>	<b>32.1%</b>	<b>35.1% with membrane reactor</b>

## Technical barriers noted by universities

Cycle	Challenges
Cu-Cl	Development of electrochemical reaction.
Cu-SO <sub>4</sub>	Electrochemical cell development, high temperature for CuSO <sub>4</sub> decomposition, .
Hybrid Cl <sub>2</sub>	High work costs for electrochemical reaction, separations and high temperature in the reverse-Deacon reaction.
Mg-I	HI decomposition in the presence of iodine, excess water handling, separations, azeotrope formation.
Active-metal alloy	No experimental work completed, unknown chemistry.
V-Cl	Separations and high temperature of the reverse-Deacon reaction, kinetics of the chlorination reaction.

## *Proof of principle (POP) work for Cu-SO<sub>4</sub> cycle completed*

■ Cu-SO<sub>4</sub> cycle was studied extensively at Gas Research Institute in the 1970's and at Tulane now

■ Four reactions:

- $\text{CuO} + x\text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{CuSO}_4 \cdot (x-1) \text{H}_2\text{O} + \text{H}_2(\text{g})$  25°C
- $\text{CuSO}_4 \cdot x\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + x\text{H}_2\text{O} (\text{g})$  225°C
- $\text{CuSO}_4 \rightleftharpoons \text{CuO} + \text{SO}_3 (\text{g})$  850°C
- $\text{SO}_3 (\text{g}) \rightleftharpoons \frac{1}{2}\text{O}_2 (\text{g}) + \text{SO}_2 (\text{g})$  850°C

■ Barriers

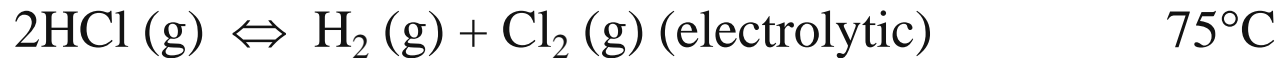
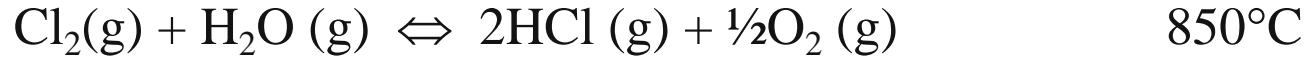
- Reaction to produce hydrogen is electrochemical
- Very high temperatures to dissociate CuSO<sub>4</sub>
  - *Leverage R&D from baseline sulfur cycles to lower temperatures*

## *Possible approach to reduce barriers in the Cu-SO<sub>4</sub> cycle addressed*

- Convert the electrochemical hydrogen generation reaction,  $\text{CuO} + x\text{H}_2\text{O} + \text{SO}_2 \Leftrightarrow \text{CuSO}_4 \cdot (x-1)\text{H}_2\text{O} + \text{H}_2(\text{g})$ , to a thermal one
  - Tulane will be testing their new approach shortly
- If successful, simplified Level 3 analysis predicts an efficiency of >50% (LHV)
- Lower the high temperature decomposition of CuSO<sub>4</sub> using results of R&D program in the baseline sulfur cycles to reduce the decomposition temperature for SO<sub>3</sub>

## Reactions in the hybrid chlorine cycle

- Hybrid chlorine cycle consists of two reactions:



- Electrolytic decomposition of HCl

- Electrolysis can be conducted with HCl in gas phase (PEMFC) or in aqueous phase (UHDE process)
  - *Aqueous electrolysis requires 770 kJ per 2 mol of HCl but gaseous electrolysis requires 580 kJ per 2 mol HCl*
  - *If the RDR was energy neutral, the Level 1 cycle efficiency would be 42% (LHV) efficient with gaseous electrolysis*
- PEMFC development is ‘nearly’ complete
  - *Further improvements unlikely in PEMFC design in near term*



***New R&D will focus only on reverse Deacon reaction (RDR):  
 $H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2 (g)$***

- Reaction does **NOT** go to completion at 850C
  - At 850C, equilibrium constant,  $K = 6.8$ , and equilibrium reached in a few seconds, while at 100 C,  $K = 2.3 \text{ E-}05$
  - No significant side reactions are known
  
- But
  - Gases not readily separable with current technology
  - Product gases have to be quenched or they recombine to reform reactants
  - Separation costs are therefore high
  
- If one of the product gases can be preferentially removed, separations may be easier and the reaction can be driven to completion at lower temperatures

## ***New R&D on the Reverse Deacon reaction, $H_2O + Cl_2 \rightarrow 2HCl + \frac{1}{2}O_2$ (g) at Clemson***

- New approach for increasing the conversion to HCl suggested in a patent application by Amendola
  - Results of simple proof-of-concept experiments (disclosed after non-disclosure agreement) by Amendola appear promising
    - *HCl reversibly sorbed and desorbed at lower temperatures*
  
- Experimental program to start shortly at Clemson
  - Clemson has a laboratory already equipped to handle HCl and chlorine gases
  
- Clemson also suggests the use of a dense oxygen permeable membrane reactor for RDR

## *Justification for continuing R&D on hybrid chlorine/RDR*

- Hybrid chlorine cycle is simple and may have low capital costs for producing hydrogen, even though its efficiency is relatively low
- If energy efficient, cost effective method for separating gas mixtures consisting of O<sub>2</sub>, HCl, Cl<sub>2</sub>, and H<sub>2</sub>O can be found, these improvements can be used in most cycles containing HCl and chlorine

## History of Mg-I cycle

- **Studied in Japan for several years**
- **Positive results from Japanese R&D**
  - Each reaction in cycle proceeds smoothly at a sufficient rate and yield
  - Products of reaction can be easily separated by filtration or solidification of iodine
  - Maximum operating temperature is <600C, thereby reducing demands on equipment and materials
- **Major technical barrier identified by Japanese is HI decomposition**
  - Separation of the mixed gases ( $H_2$ , HI,  $I_2$ , and  $H_2O$ ) in an energy efficient process is the most important process of the cycle
- **But technology developed for handling HI in the S-I cycle can be applied here**

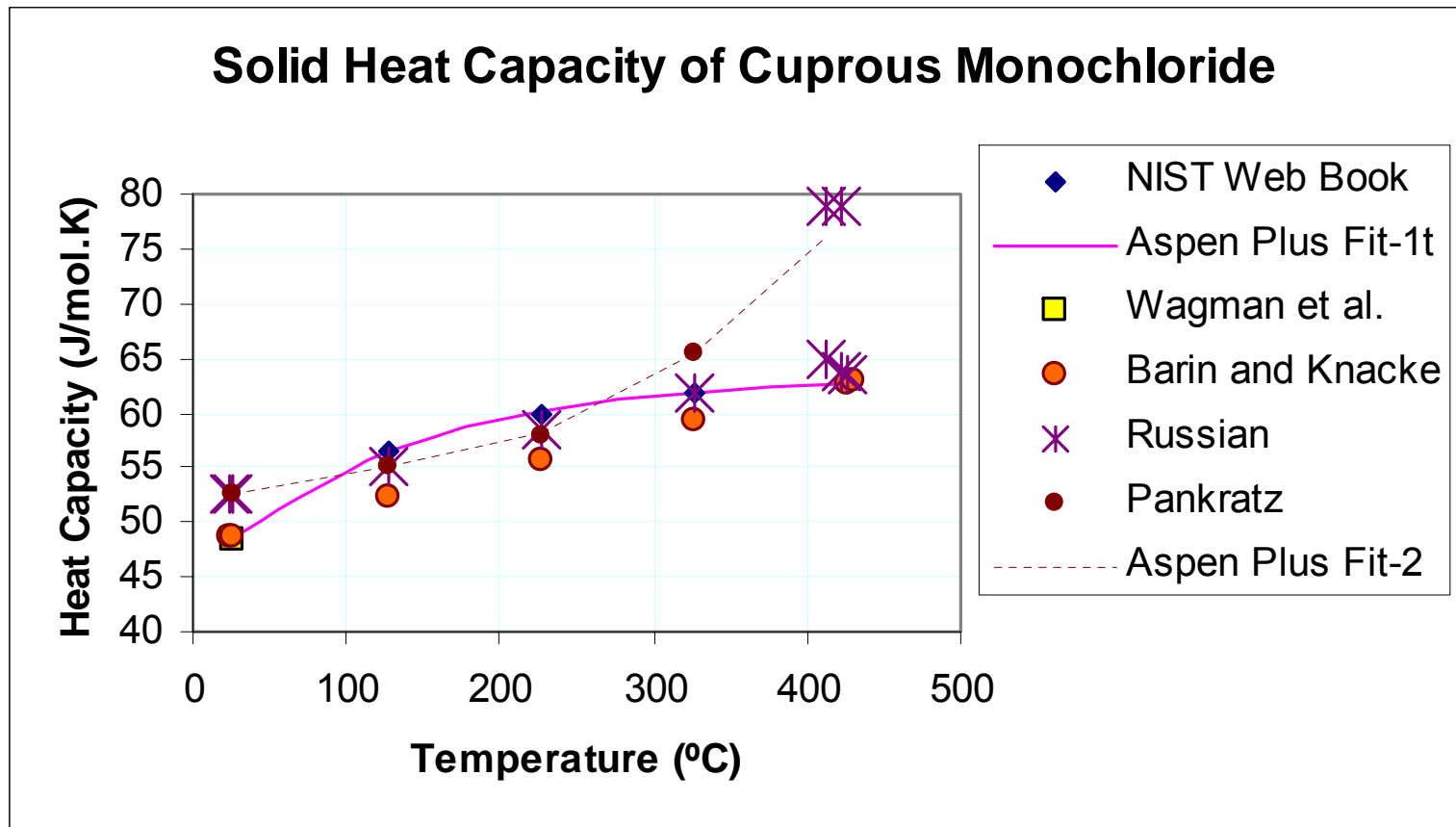
## Simplified reactions in the Mg-I cycle

- $6/5 \text{ MgO (s)} + 6/5 \text{ I}_2 \text{ (l)} \Leftrightarrow 1/5 \text{ Mg(IO}_3)_2 \text{ (s)} + \text{MgI}_2 \text{ (aq)}$   $T = 120^\circ\text{C}$
- $1/5 \text{ Mg(IO}_3)_2 \text{ (s)} \Leftrightarrow 1/5 \text{ MgO (s)} + 1/5 \text{ I}_2 \text{ (g)} + 1/2 \text{ O}_2 \text{ (g)}$   $T = 600^\circ\text{C}$
- $\text{MgI}_2 \cdot 6\text{H}_2\text{O (s)} \Leftrightarrow \text{MgO (s)} + 5 \text{ H}_2\text{O (g)} + 2 \text{ HI (g)}$   $T = 450^\circ\text{C}$
- $2 \text{ HI (g)} \Leftrightarrow \text{I}_2 \text{ (g)} + \text{H}_2 \text{ (g)}$   $T = 500^\circ\text{C}$
- Note that in this representation we do not have a cycle-the excess water is ignored.

## More realistic representation of two reactions in the Mg-I cycle

- $1.2 \text{ MgO(s)} + 8.2 \text{ I}_2 \text{ (l)} + 14 \text{ H}_2\text{O} \Leftrightarrow$   
 $0.2 \text{ Mg(IO}_3)_2 \text{ (s)} + \text{MgI}_2 \cdot 6\text{H}_2\text{O(aq)} + 8 \text{ H}_2\text{O} + 7 \text{ I}_2 \text{ (l)}$
- $\text{MgI}_2 \cdot 6\text{H}_2\text{O(s)} + 1 \text{ to } 3 \text{ I}_2 \text{ (l,s)} \Leftrightarrow \text{MgO} + 5 \text{ H}_2\text{O(g)} + 2 \text{ HI(g)} + 1 \text{ to } 3 \text{ I}_2 \text{ (g)}$
- This representation shows the following:
  - Excess water and excess iodine are required
  - Not all of the iodine is easily removed in the iodination reaction
  - The gas stream containing HI also contains steam and iodine
- Level 3 analysis was based on simplified chemistry with respect to HI

## Need for reliable thermodynamic data



## *Summary: Status of alternative cycle analysis*

- First Aspen simulation completed and critical barriers identified for each
- Preliminary Level 3 efficiency calculations completed, ranging from 34 to >50% (LHV)
- All have one or more of the following desirable features:
  - potentially low capital costs
  - ability to meet timeline established by DOE-NE
  - potentially high efficiencies
  - a broad temperature region
  - completion of most proof of principle work
  - ability to use R&D results from baseline sulfur program
- All have barriers, e.g. the need for energy efficient, cost effective methods for separations and removal of excess reagents

## *Acknowledgments*

- Financial support from DOE-Contract W-31-109 ENG-38
- Intellectual effort by all of the university participants

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1. go to <http://shgr.unlv.edu/stchNew/source/login.asp>
2. click on "new member registration"
3. follow the steps and a new account ID and password will send to you through email.

If all else fails, contact Sean Hsieht at [hsiehht@nscee.edu](mailto:hsiehht@nscee.edu)