

# ***Alternative Thermochemical Cycle Evaluation***

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This presentation does not contain any proprietary information

***Argonne National Laboratory***

PD29



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# Overview

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## Time Line

- **Start date: 10/04**
- **End date: 9/05**
- **% complete: 40%**

## Barriers

- **Unknown thermodynamic data**
- **Unknown chemistry**

## Budget

- **FY 05 = \$150K**
- **Complementary program supported by internal LDRD funds**

## Partners

- **INERI with CEA**
- **INERI with AECL**
- **Primarily information exchange**

# ***Objectives/Deliverables***

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- **Review candidate alternative thermochemical cycles, characterize potential advantages and disadvantages**
- **Report – *Candidate Alternative Cycles for NHI Flowsheet Analysis (2-1-05)***
- **Report - *Alternative Thermochemical Cycles for Nuclear Hydrogen Production (9-1-05)***
  - Use updated assessments and downselect the most promising

# ***Other Objectives***

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- **Support two International Nuclear Energy Research Initiative (INERI) projects:**
  - Thermochemical Hydrogen Production Process Analysis (CEA)
    - *Collaborate on developing a standard, consistent methodology for quantifying cycle efficiency*
    - *Evaluate the S-I and an alternative cycle*
  - Lower-Temperature Thermochemical Hydrogen Production (AECL)
    - *Collaborate on assessing the use of lower-temperature cycles with nuclear reactor options*
      - Candu SCWR has an outlet temperature of 625C

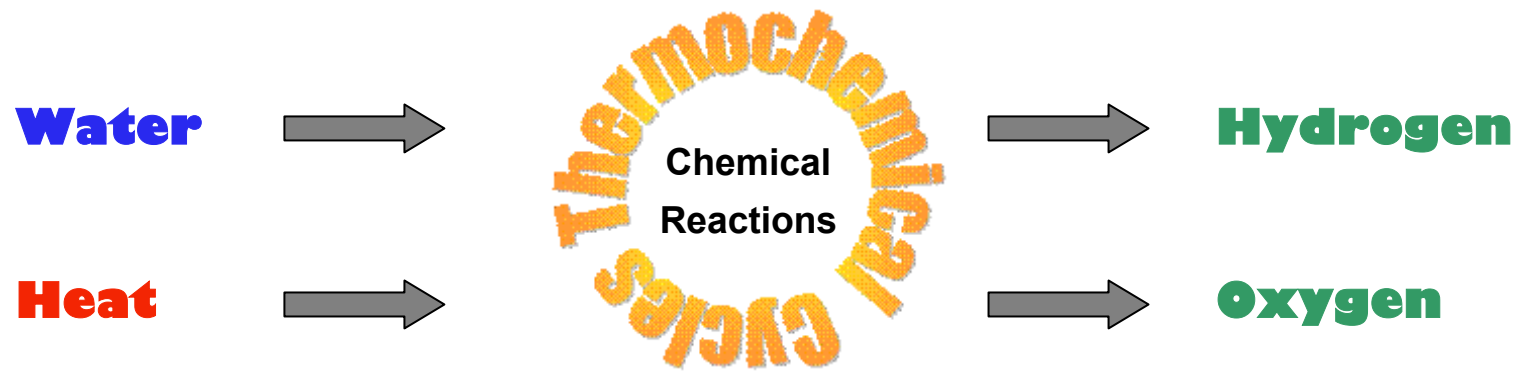
# Approach

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- **Identify potentially promising cycles (2-1-05)**
  - Review literature, NE-R&D Plan, EERE programs, R&D at national labs and foreign research labs such as CEA
  - Determine benchmarks for assessing potential
    - *Reported idealized efficiencies*
    - *Reported evaluations of chemical viability*
- **Coordinate process for downselecting most promising cycles**
  - Perform scoping flowsheet analysis
  - Identify critical R&D needs for selected cycles
- **Select most promising cycles from updated assessments (9-1-05)**

# Definition

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# Literature Sources

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- **Review articles that contain lists of cycles:**
  - Yalcin, Baumberger, Williams, Beghi (Ispra)
- **Individual papers within various journals:**
  - International Journal of Hydrogen Energy
  - Hydrogen Energy
  - Hydrogen Energy Progress
  - Alternate Energy Sources
  - More obscure journal articles by authors of interest

# ***Literature Sources, Cont.***

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- **Two great summary reports available:**
  - GRI-80/0023.1 by McCarty, et al.
    - *Funded by The Gas Supply Research Division of the Gas Research Institute from 1972-1980*
    - *Contains efficiency and summary of experimental results*
    - *11 of 131 cycles selected as promising*
  - Solar Thermochemical Hydrogen Generation Report (STHGR) (to be published)
    - *Sponsored by DOE-EERE (Paster)*
    - *Contains a summary of 200+ cycles with efficiency for selected cycles*
    - *14 of 200+ cycles selected as promising*



# Promising cycles from summary reports

- **GRI's Cycles**

- Hybrid Cu-SO<sub>4</sub> (1100K)
- Hybrid Cu-SO<sub>4</sub> (1363K)
- Hybrid Zn-SO<sub>4</sub> (1150K)
- Hybrid Cu-Cl (805K)
- Hybrid Cd (1500K)
- Cr-Cl (1475-1525K)
- Fe-Cl (875-975K)
- Fe-Cl (1175-1275)
- NH<sub>3</sub>-CO<sub>3</sub>-Hg (875-975K)

- **STHGR's Cycles**

- Cd-SO<sub>4</sub> (1475K)
- BaMo-SO<sub>4</sub> (1275K)
- Mn-SO<sub>4</sub> (1275K)
- Hybrid Cu-Cl (825K)
- Hybrid Cd (1475K)
- Cd-CO<sub>3</sub> (1475K)
- Multivalent sulfur (1845K)
- Zn (2475K)
- NiMnFe (1075K)
- ZnMnFe (1475K)
- NaMn-3 (1735K)
- ?

# ***Results: Rationale for Selection***

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- **Identify cycles with high idealized efficiency in both GRI and STHGR reports**
- **Eliminate cycles with maximum temperatures incompatible with the VTGR (<1150 K)**
  - Fe-Cl (875-975K)
  - NH<sub>3</sub>-CO<sub>3</sub>-Hg (875-975K)
  - Hybrid Cu-Cl (805K)
  - Hybrid Cu-SO<sub>4</sub> (1100K)
  - Hybrid Zn-SO<sub>4</sub> (1150K)
  - NiMnFe (1075K)

# ***Results: Rationale for Selection-Cont.***

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- **Assess chemical viability**
  - Proof of principle work, if available
  - General chemical knowledge
    - *GRI provides useful experimental data for some cycles*
  - Cycles with Se, Hg, and Cd eliminated based on release rates for RICA metals

# Results of literature search: 4 Cycles Selected

- **Hybrid metal sulfate, ‘proven’ chemistry:**
  - Cu: idealized efficiency of 69-73% (HHV);  $T_{\max} = 1100$  K
  - Zn: idealized efficiency of 55-61% (HHV);  $T_{\max} = 1150$  K
- **Hybrid Cu-Cl, ‘proven’ chemistry:**
  - Idealized efficiency = 49% (HHV);  $T_{\max} = 805$  K
- **Hybrid K-Bi cycle; general chemical knowledge:**
  - Idealized efficiency = 57% (HHV);  $T_{\max} = 850$  K

# ***Other sources, other cycles?***

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- **Untapped sources**
  - Universities
  - Foreign institutions, companies such as GE, other national labs
- **Ongoing work is considered proprietary**
  - This presents a challenge in identification and assessment
- **Still open to new cycles**
  - Questions remain on Fe-Cl and on NiMnFe

# Definitions

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$$E = -\frac{\Delta H^\circ(H_2O(g))(25^\circ C)}{\Sigma Q}$$

- **Efficiency (LHV) with work inputs**
  - $-\Delta H^\circ(H_2O(g)) = 57.8 \text{ kcal/mol}$
  - $\Sigma Q = \Sigma q_i + \Sigma W_i/\eta$
  - **W = the sum of the work inputs**
  - $\eta =$  efficiency of converting heat to electricity
- **Electrochemical work from Faraday's law,  $\Delta G = nFE$**
- **Energy for shaft work is based on typical engineering assumptions**

# ***A Caution on Reported Efficiencies***

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- **Idealized efficiencies reported by various authors appear to use different assumptions**

	<b>Efficiency from GRI (HHV)</b>	<b>Efficiency from STHGR (HHV)</b>
<b>Fe-Cl</b>	<b>47 – 49%</b>	<b>20%</b>
<b>Hy-S</b>	<b>41.5 – 49.2%</b>	<b>51%</b>

# ***A Caution on Reported Efficiencies-Cont.***

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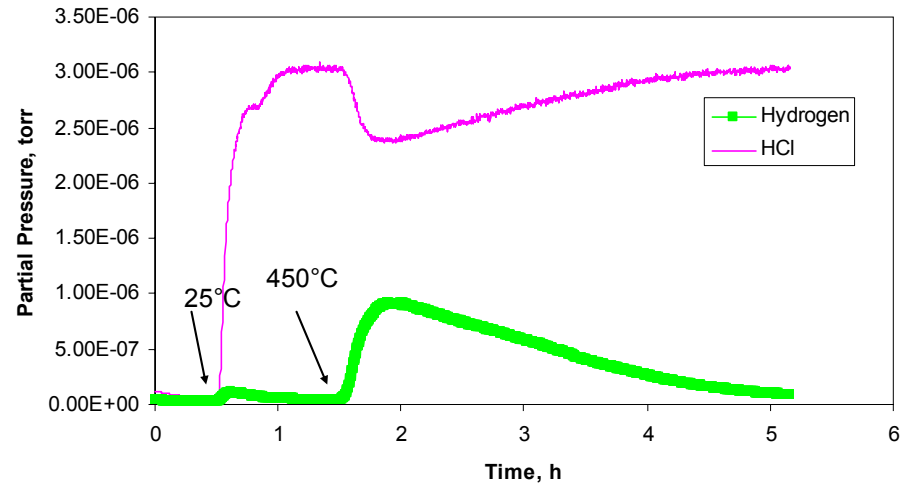
- **Unknown thermodynamic data**
  - No thermodynamic available for  $\text{Cu}_2\text{Cl}_2\text{O}$
  - Incomplete thermodynamic data for HI-I<sub>2</sub>-H<sub>2</sub>O ternary
- **Inconsistencies in various thermodynamic databases**
- **Unknown assumptions in idealized efficiency calculations**
- **Unknowns in assessing chemical viability**
  - Yields, kinetics, separations, separation techniques, and amount of water in cycle
    - *Water removal is energy intensive*
  - Viability of reverse Deacon reaction- $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2$



# Kinetics vs. thermodynamics

- Realizable thermodynamics: necessary but not sufficient

Temp., C	( $\Delta G$ ), kcal/mol
25	-11.8
425	-0.5



- Kinetics trumps thermo at 25C

# Ongoing Work - FY2005

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- **Perform scoping flowsheet analyses on promising alternative cycles**
  - Make assumptions transparent
    - *Unknown thermodynamic data specified and estimation method clearly defined*
  - Use Excel format for new users (if possible)
  - Compare with other reported analyses
- **Develop critical guidelines for assessing chemical viability and identify most critical R&D needs for 4 cycles selected and provide guidance for new cycles**
- **Identify ‘best’ alternative cycles**

# Possible guidelines for assessing chemical viability

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- **When proof of principle is absent**
- **Check spontaneity ( $\Delta G$ ) of reactions**
  - Check  $\Delta G$  for each reaction:  $< \pm 10\text{-}15$  kcal/mol
    - $\Delta G > -15$  kcal/mol implies a very stable product
    - $\Delta G < +15$  kcal/mol implies a reaction that does not go
- **Check abundance and cost**
  - Cycles with Hg, Se, and Cd eliminated on the basis of EPA release rates for RCRA wastes; Ag cycles, on cost basis
- **Check number of elements and reactions**
  - No more than 2 other than O, and H
  - Relatively small number of reactions; how to define?

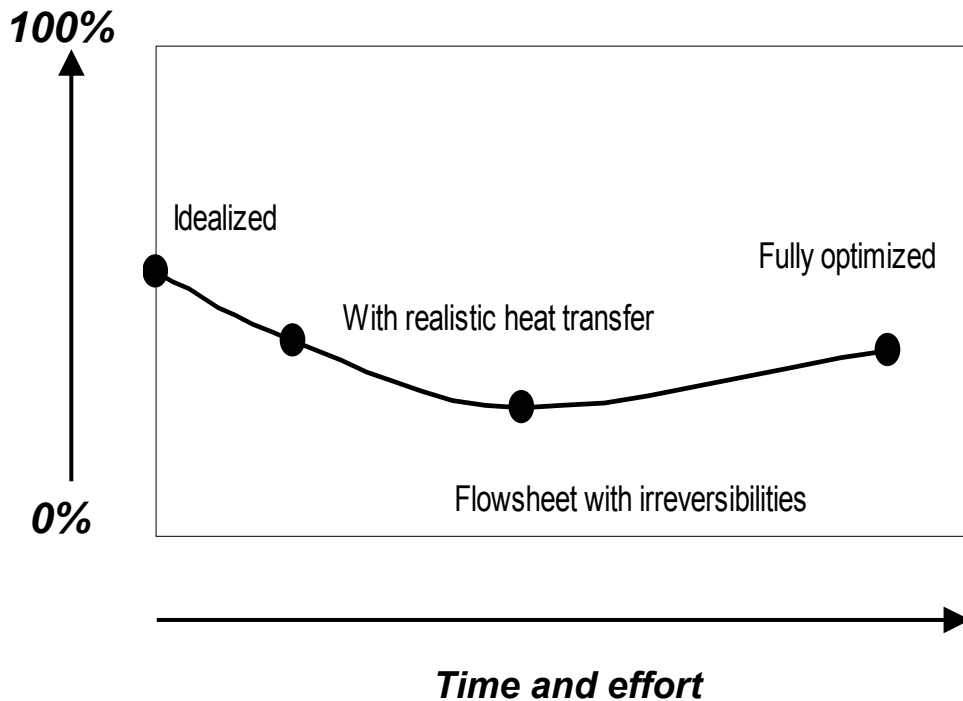
# ANL-CEA Collaboration

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- **Objectives of ANL-CEA INERI**
  - Develop a standard method for assessing thermochemical hydrogen production cycle efficiencies
  - Use methodology to compare leading technologies
- **Information exchange meeting**
  - ANL meeting on Feb. 3 and 4, 2005, with Pascal Anziew, Jean-Marc Borgard, and Philippe Carles of CEA
  - Agreed on general approach and noted that efficiency values change with knowledge of cycle
    - *CEA to define various levels of knowledge in cycle development*

# ***High idealized efficiencies are necessary but not sufficient for assessment***

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Graph from CEA (Pascal Anziew)

# ***Future Work: ANL/CEA Collaboration***

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- **Critical review of the NHI scoping methodology**
- **Define levels of cycle development and appropriate methodologies for calculating efficiency**
  - Different methods required for different levels of chemical and engineering knowledge
- **Define common parameters for simulations**
  - Engineering parameters
  - Guidelines for common unit operations for all thermochemical cycles
- **Joint authorship of several proposed papers**

# ***Future Work: ANL/CEA Collaborations***

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- **Quantify Go/No-Go Criteria (part of chemical viability assessment)**
  - Consider cost/availability of raw materials at required level of purity
  - Assess environmental impact based on probable release rates
  - Determine impact of competing reactions
  - Determine consensus on maximum number of elements and maximum number of reactions
- **Energy usage optimization**
  - Balance process heat needs with heat source
  - Determine impact of transients
  - Determine effect of cogeneration

# ***Future Work-ANL/AECL Collaborations***

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- **Collaborate on assessing the use of lower-temperature cycles with nuclear reactor options**
- **With funding**
  - Development of electrochemical cell for hybrid Cu-Cl cycle
  - An integrated demonstration by 2007
  - An economic assessment



# Summary

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- **Selected 4 cycles as promising alternative cycles for nuclear hydrogen production but still open**
- **Ongoing work includes scoping flowsheet analysis and identification of critical R&D needs**
  - Identify the most challenging reaction in a cycle
    - *Measurement of thermodynamic data, kinetic studies, proof of principle for reactions with high  $\Delta G$ , determination of amount of water, or challenges in electrochemical cell configuration such as electrode material, catalysts, etc.*
- **Select most promising alternative cycles by 9-05**