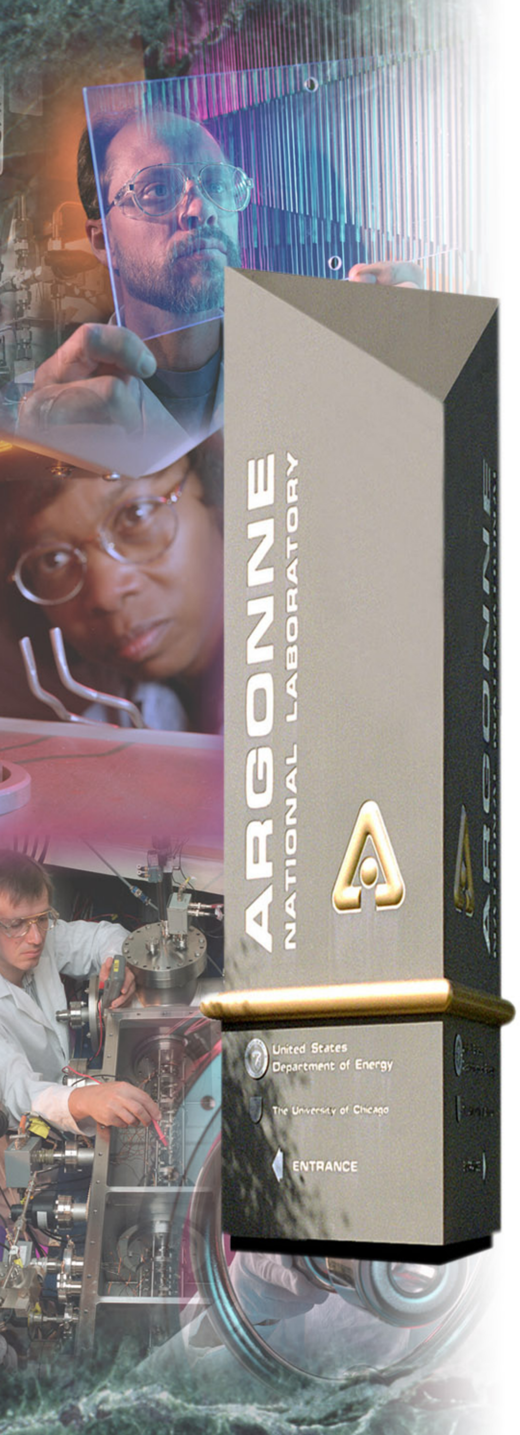

Alternative Thermochemical Cycle Evaluation

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This presentation does not contain any proprietary information

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Argonne National Laboratory

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Overview

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

- **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

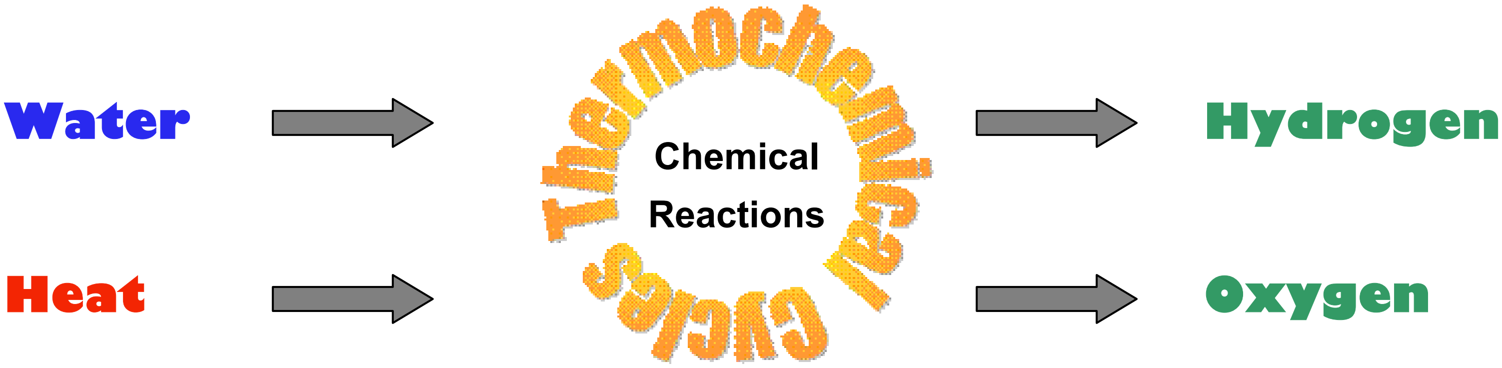
Other Objectives

- **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

- **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


Water
Heat
Thermochemical Cycles
Chemical
Reactions
Hydrogen
Oxygen

Literature Sources

- **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.

- **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_4 (1100K)
  - Hybrid Cu-SO_4 (1363K)
  - Hybrid Zn-SO_4 (1150K)
  - Hybrid Cu-Cl (805K)
  - Hybrid Cd (1500K)
  - Cr-Cl (1475-1525K)
  - Fe-Cl (875-975K)
  - Fe-Cl (1175-1275)
  - NH_3-CO_3-Hg (875-975K)
- **STHGR's Cycles**
  - Cd-SO_4 (1475K)
  - BaMo-SO_4 (1275K)
  - Mn-SO_4 (1275K)
  - Hybrid Cu-Cl (825K)
  - Hybrid Cd (1475K)
  - Cd-CO_3 (1475K)
  - Multivalent sulfur (1845K)
  - Zn (2475K)
  - NiMnFe (1075K)
  - ZnMnFe (1475K)
  - NaMn-3 (1735K)
  - ?

Results: Rationale for Selection

- **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_3-CO_3-Hg (875-975K)
  - Hybrid Cu-Cl (805K)
  - Hybrid Cu-SO_4 (1100K)
  - Hybrid Zn-SO_4 (1150K)
  - NiMnFe (1075K)

Results: Rationale for Selection-Cont.

- **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: <u>idealized</u> efficiency of 69-73% (HHV); T_{max} = 1100 K
  - Zn: <u>idealized</u> efficiency of 55-61% (HHV); T_{max} = 1150 K

- **Hybrid Cu-Cl, ‘proven’ chemistry:**
  - <u>Idealized</u> efficiency = 49% (HHV); T_{max} = 805 K

- **Hybrid K-Bi cycle; general chemical knowledge:**
  - <u>Idealized</u> efficiency = 57% (HHV); T_{max} = 850 K

Other sources, other cycles?

- **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

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

- Efficiency (LHV) with work inputs
  - $-\Delta H^\circ(H_2O(g)) = 57.8$ kcal/mol
  - $\Sigma Q = \Sigma q_i + \Sigma W_i/\eta$
  - W = the sum of the work inputs
  - η = 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

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

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

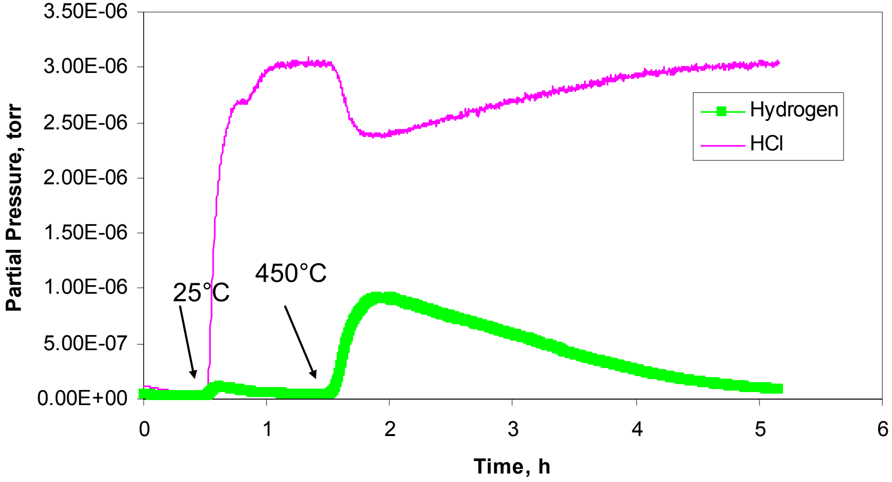
A Caution on Reported Efficiencies-Cont.

- **Unknown thermodynamic data**
  - No thermodynamic available for Cu_2Cl_2O
  - Incomplete thermodynamic data for $HI\text{-}I_2\text{-}H_2O$ 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-$Cl_2 + H_2O = 2HCl(g) + \frac{1}{2}O_2$

Kinetics vs. thermodynamics

- **Realizable thermodynamics: necessary but not sufficient**

Temp., C	(ΔG), kcal/mol
25	-11.8
425	-0.5



- **Kinetics trumps thermo at 25C**

Ongoing Work - FY2005

- **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

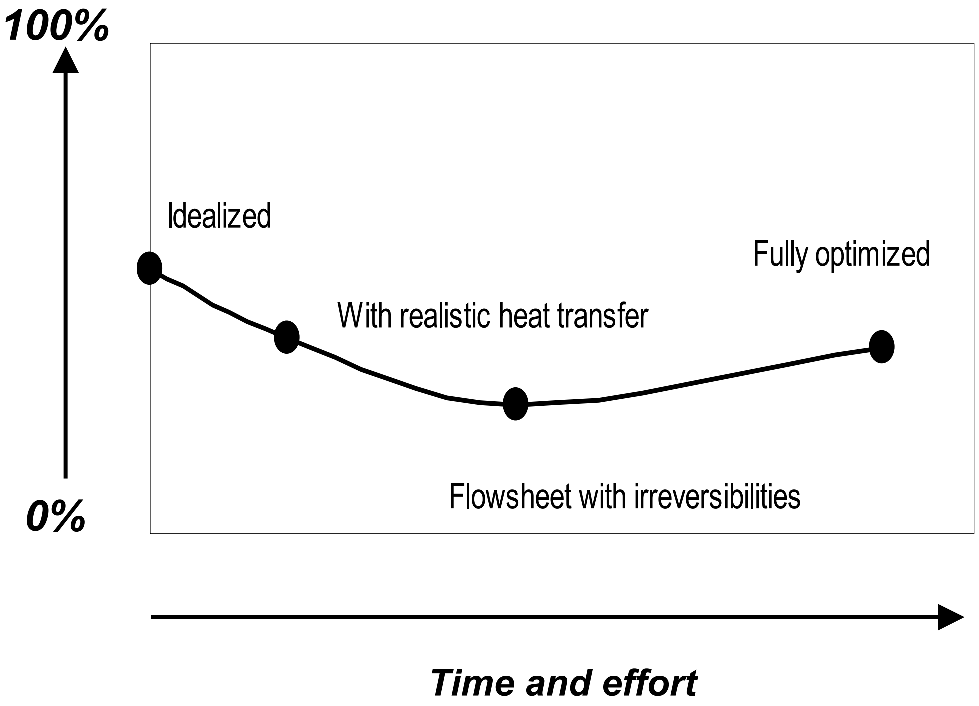
- **When proof of principle is absent**
- **Check spontaneity (ΔG) of reactions**
  - Check ΔG for each reaction: < ± 10-15 kcal/mol
    - *$\Delta G > -15$ kcal/mol implies a very stable product*
    - *$\Delta G < +15$ kcal/mol implies a reaction that does not go*
- **Check abundance and cost**
  - 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

- **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



Graph from CEA (Pascal Anziew)

Future Work: ANL/CEA Collaboration

- **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

- **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

- **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

- **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* ΔG*, 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**