2006 DOE Hydrogen Program
Evaluation of Alternative Thermochemical Cycles

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This presentation does not contain any proprietary information

PDP 21

A U.S. Department of Energy laboratory
managed by The University of Chicago

Overview

Time Line

- Start: 10/06
- End: 9/07
- % complete 30%

Barriers

- Unknown chemistry
- Unknown thermodynamic data
- Engineering challenges

Budget

- FY 06 = $300 K
- $400 K to universities

Partners

- 8 Universities
- INERI* with CEA
- INERI* with AECL

*INERI =International Nuclear Energy Research Initiative

Objectives

2005	■ Develop consistent methodology for evaluating alternative thermochemical cycles ■ Identify promising cycles from the literature
2006	■ Identify promising alternative cycles from GA-A24972 (cycles evaluated for application with solar heat sources), current literature, and ongoing work at universities ■ Invite university participation in finalizing metrics in consistent methodology ■ Invite university participation in evaluating alternative cycles ■ Coordinate evaluation activities at the universities and determine the most promising of the alternative cycles

Approach for identifying promising cycles identified in Solar Hydrogen Program

Screen
202 cycles

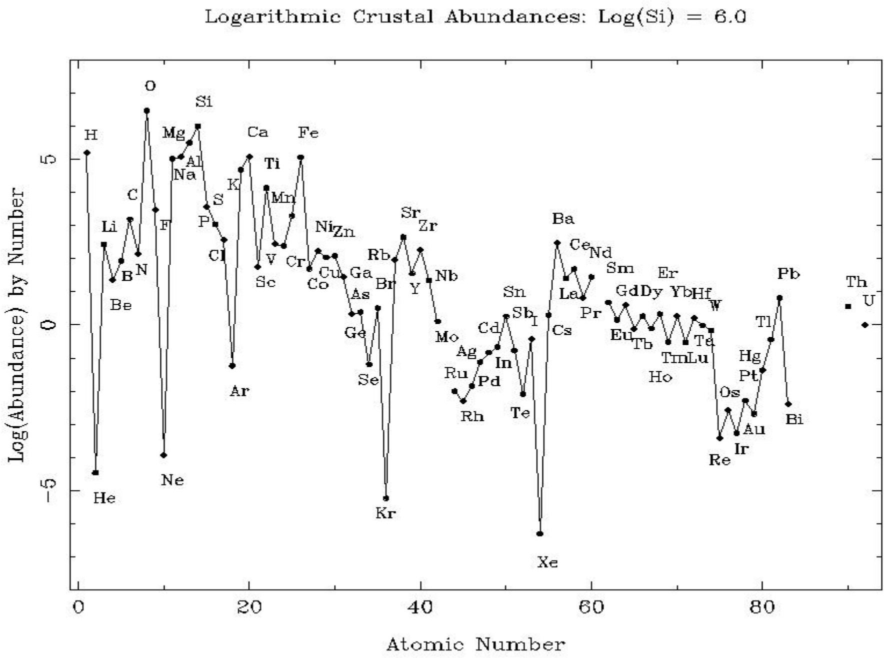
- Temperature requirement < 850C

Screen
65 cycles

- Abundance
- Toxicity
- Chemical viability
- Thermodynamic feasibility

Screening criteria

Abundance



- Ag, Au, Rh, etc are less abundant than others-capital costs high
- U is strategically important

Toxicity

- Elements with lowest allowable RICA releases are Hg, Se, and Cd

Thermodynamic feasibility

- ΔG < ± 15 kcal

Chemical viability

- Reactions proceed to the right with high yields and reasonable kinetics
  - Proof of principle experiments
  - General chemical knowledge

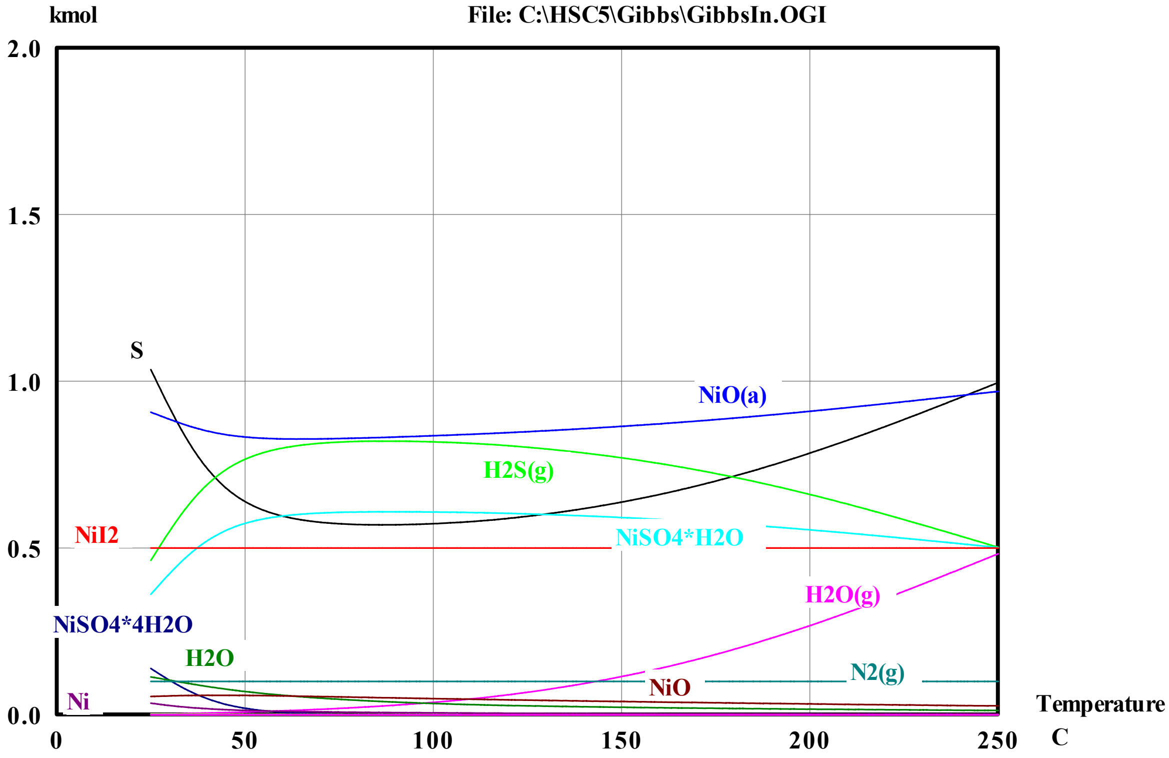
Screening process illustrated

- H_2SeO_3 (aq) + H_2O (l) → H_2SeO_4 (a) + H_2 (T= 80°C)
- H_2SeO_4(aq) → SeO_3 (s) + H_2O(l) (T= 250°C)
- SeO_3(s) → SeO_2 (s) + ½ O_2 (T= 50°C)

- *Eliminated because*
  - *Se is toxic and has very low release rates*
  - *Not chemically viable; H_2Se formed instead of H_2*
  - *Not thermodynamically viable*

H2SeO3(a) + H2O = H2SeO4(a) + H2(g)			
T	Delta H	Delta S	Delta G
C	kcal	cal/K	kcal
0	47.01	-19.76	52.41
50	43.20	-33.06	53.88
100	41.08	-39.15	55.69
150	38.90	-44.64	57.78
200	36.48	-50.03	60.15

Use HSC equilibrium data to screen for chemical viability
$2HI(a) + H_2SO_4(a) + 2Ni = NiI_2(a) + NiSO_4 + 2H_2$ (non-viable)



- Reaction is not chemically viable. No H_2 produced; other species, such as H_2S, are more likely to form*

*Data from thermodynamic (HSC) database

Sample results of evaluations completed for 65 cycles

Elements	PID # GA-A24972	Max Temp, °C	Comments
Fe-Cl-1	4	650	Low efficiency per GA-A24972
Fe-Cl-2	10	739	Low efficiency per GA-A24972
V-OCl	16	610	Not thermodynamically feasible (NTF); 2 rxns. : $\Delta G > 0$ up to 900C
Fe-Cl-S	17	800	Not chemically viable (NCV), $H_2S = H_2 + S$ has very low yields
Cr-Fe-Cl	19	700	NCV; Low yields of $CrCl_2$
Cr-Cu-Fe-Cl	20	800	NCV; Low yields of $CrCl_2$, $FeCl_3$ preferentially dimerizes; 5 reactions, complicated chemistry

Cycles selected as promising and the rationale for their selection

- **Promising proof-of-principle work**
  - V-Cl
  - Ce-Cl
  - Hybrid chlorine
  - Hybrid Cu-SO4
  - Hybrid Cu-Cl
  - Hybrid Mg-I
  - Fe-Cl

- **Lower capital costs**
  - Hybrid proprietary cycle
  - Hybrid chlorine
  - Fe-Cl (cheaper elements)

- **Fewer materials issues**
  - Cu-SO4

- **Lower maximum temperature**
  - Hybrid Cu-Cl
  - Hybrid Mg-I
  - Proprietary cycle

- **All require significant effort for further development**

Question: what cycle offers the most promise?

Use efficiency to ‘quantify’ promise

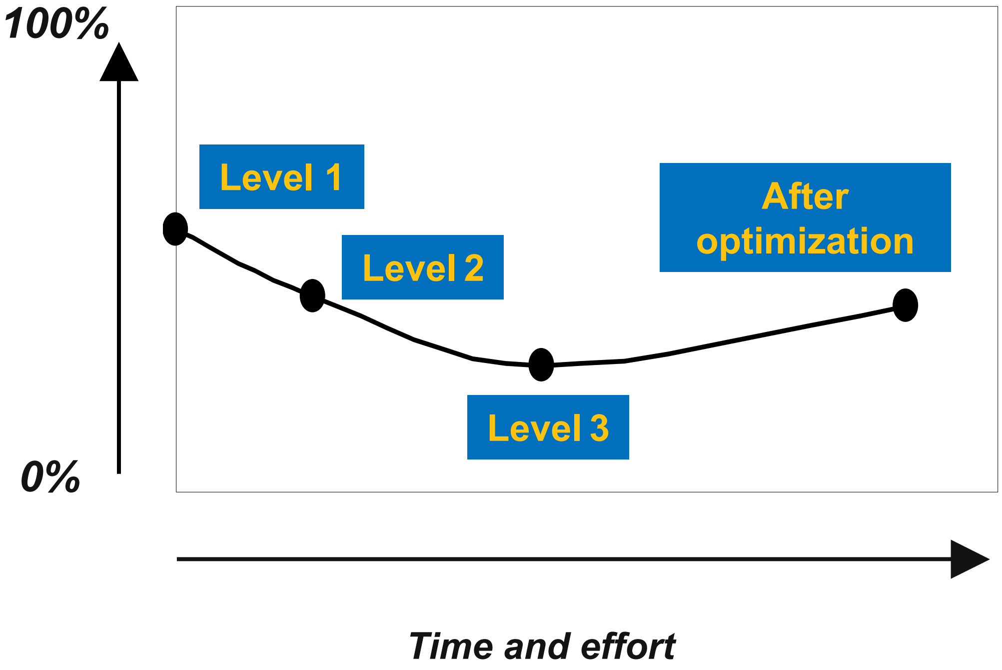
- Evaluate using consistent methodology
- Engage universities to complete more detailed evaluations

Use efficiency to "quantify" promise and recognize that efficiency varies with effort

- Level 1: For stoichiometric rxns.
  - Use Excel, HSC database, and pinch analysis for heat management
  - Gives ball-park type of analysis

- Level 2: For rxns. at equilibrium
  - Vary operating conditions to increase yields and minimize competing reactions
  - Use Excel, HSC database, and pinch analysis

- Level 3: For "real" reactions
  - Use simulation package
  - Use heat exchanger network



Efficiency defined as heat out/heat in

$$E = \frac{-\Delta H^{\circ}_{25^{\circ}C}(H_2O)}{Q + \frac{W}{0.5}}$$

- Q is the sum of the heat inputs:
  - Heat of reaction
  - Sensible
  - Latent heat
  - Pinch heat

- W is the sum of the work inputs:
  - Electrochemical
    - *Same as in GA-A24972*
  - Chemical
    - *Positive free energy*
  - Work of separation
    - $\Delta G_{sep} = -RT\ \Sigma_i y_i \ln y_i,$
    - *R is the gas constant, T is the absolute temperature, and y is the mole fraction of each component*
  - Shaft work ignored

- Work is converted to heat equivalent by appropriate conversion factor (0.5 here)

Efficiency (LHV) results

	Level 1	Level 2	Flowsheet *
Ce-Cl	48%	Competing rxns.	
Fe-Cl (PID# 200)	33.8%	Heat management	20% [Ispra];
			40% [Carty]
Mg-I (PID# 169)	Thermodynamic feasibility in question		36.4% [Fujii]
Hybrid Cu-Cl (PID# 191)	48%	41.5%	39.6% [Lewis]
Proprietary Hybrid	39%		
Hybrid Cu-SO4	43.8%	37.8%	30.7% [Carty]
V-Cl (PID# 32)	53.4%		0% [McQuillan]
			36.0 % [Knoche]
Hybrid chlorine (PID# 53)	34.3%	30.7%	

*Flowsheet efficiencies are based on published values and may contain assumptions that significantly affect the result reported; results are based on incomplete knowledge in all cases

Work in progress

- Several universities are now engaged in alternative cycle evaluation

- Tasks for new work at universities
  - Critique NHI methodology and obtain consensus on methodology
    - *Complete Levels 1 and 2 efficiency calculations*
  - Bring process design up to current technology standards
  - Complete Level 3 efficiency calculations and identify critical barriers to further development

- Many specialized skills are available for this effort
    - *Cycle design, property estimation methods, materials work, corrosion issues, reactor design for use with solids and pressurized aqueous solutions, uncertainty analysis, electrodialysis, solids handling, separations, and significant process design experience for the baseline cycles*

Teaming and communications

- Communicate results to SHGR team, other universities, and national laboratories for feedback
- Communicate with international partners
  - International Nuclear Energy Research Initiatives (INERI) with Commissariat à L'Energie Atomique (CEA) and with Atomic Energy of Canada, Limited (AECL)
  - CEA currently considering variations of Ce-Cl, Cu-Mg-Cl, and Mg-I cycles based on information provided by Argonne
    - *CEA's current efforts on the Cu-Mg-Cl offer significant promise if successful*
  - AECL currently investigating Cu-Cl cycle
- Engage industrial partners
  - R&D is high risk but several companies are interested
  - Communication is ongoing

Cu-Mg-Cl cycle (PID # 26)—another possibility if new ligand found at CEA

- 1. $CuCl(s) \rightarrow CuCl_2(aq) + Cu(s)$ (T=25°C)
  2. $CuCl_2(s) \rightarrow CuCl(s) + Cl_2(g)$ (T=550°C)
  3. $2\ Cu(s) + 2\ HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$ (T=450°C)
  4. $MgCl_2\ (s) + 2\ H_2O(l) \rightarrow 2\ HCl(g) + Mg(OH)(s)$ (T=285°, P = ?)
  5. $2Cl_2(g) + 2\ Mg(OH)_2(s) \rightarrow 2\ MgCl_2(s) + 2\ H_2O(g)$ (T= 140°C)

- Advantages : inexpensive materials, low temperature cycle

- Main issues :
  - reaction (1) common with CuCl cycle
  - impact of possible MgOHCl formation

- Proposed work:
  - Reaction (1) : use of a ‘new’ ligand (PhD proposal) gives a thermal pathway rather than an electrochemical pathway -
  - Advanced flow sheet optimization

Summary

- Alternative cycle identification and evaluation ongoing at
  - Universities
  - National laboratories
  - International laboratories
  - Solar Hydrogen Generation Research (SHGR) team

- Effort is coordinated and will lead to improved communications

- Results
  - Robust evaluation methodology
  - Transparent and defensible values for the efficiencies of promising alternative cycles
  - Critical evaluation of each cycle and decision for future R&D

Response to reviewers' comments

- ***Engage industry and universities***
  - Eight universities now involved
  - Robust teams to be formed with specialized, complementary skills for issues such as electrochemistry, materials, economic analysis, property estimation, reactor design
  - Industries marginally interested

- ***Improve communications with other workers in field***
  - Participate in conferences and expand effort at universities
  - Participate in SHGR meetings
  - Proprietary cycles being developed at universities now recognized

- ***Economic aspects not addressed***
  - Too early in development

Acknowledgements

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