II.G.3 High Temperature Thermochemical Processes

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Objectives

- Identify promising cycles in the literature and in the recently published summary report, "High Efficiency Generation of Hydrogen Fuels using Solar Thermochemical Splitting of Water."
- Establish a working group comprised of several universities and Argonne National Laboratory whose purpose is to identify the most promising alternative thermochemical cycles for nuclear hydrogen production.
- Review other pertinent chemical and engineering literature to facilitate the evaluation process.
- Support the universities in their evaluation of various cycles using the Nuclear Hydrogen Initiative (NHI) methodology.
- Select the most promising cycles for further development for the NHI based on updated assessment.

Technical Barriers

- Critical but unknown thermodynamic data and chemistries.
- Difficult and expensive experiments required for proof of principle.
- Breakthroughs in membrane technologies for separations, electrochemical applications, water removal, etc.
- Corrosion resistant materials for reactors, transfer lines, etc. to handle very aggressive chemicals.

Accomplishments

- Identified seven cycles as promising alternative cycles.
- Established a working group comprising eight universities to evaluate the methodology and the various cycles through three levels of efficiency calculations.

Introduction

The objective of the first phase of the 2006 work was to identify the most promising thermochemical cycles from the current literature, with emphasis on a report entitled "High Efficiency Generation of Hydrogen Fuels using Solar Thermochemical Splitting of Water" by McQuillan et al.[1]. More than 200 cycles were identified in this report and evaluated for hydrogen production using various solar heating sources (trough, tower, dish, or advanced tower). A survey of the open literature from 2000 through 2005 did not reveal any new cycles.

The primary reasons for reexamining these cycles for the Nuclear Hydrogen Initiative (NHI) were the following: (1) to determine which cycles held promise for efficient hydrogen production using nuclear heat sources, (2) to consider if current technologies might overcome the barriers identified in the 1970's for cycles for which extensive R&D effort was completed, and (3) to take a second look at proposed cycles that were not fully assessed. The expected temperature for process heat from a high-temperature gas reactor is about 800-850°C, which is lower than that expected from most solar heat sources. One word of caution about the temperature requirement specified in the literature for process heat is the wide range of values reported for some reactions. For example, the reverse Deacon reaction, $Cl_2 + H_2O \rightarrow 2HCl\ (g) + 0.5O_2\ (g)$, is reported with temperature requirements of 610 to 1450°C in the McQuillan report. When such variability was noted, the temperature requirement was determined from equilibrium considerations.

Approach

The criteria that were used in the general screening process for the NHI effort were abundance, simplicity, chemical viability, thermodynamic feasibility, and safety issues. Cycles were eliminated from further consideration if they had one or more of the following characteristics:

1. Required process heat greater than 850°C.
2. Contained elements with low abundances. (See Figure 1)

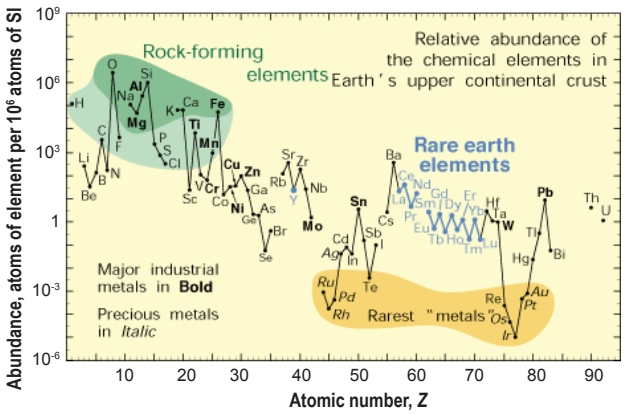

FIGURE 1. Crustal Abundance of the Elements

3. Specified more than four elements (including hydrogen and oxygen) and more than five reactions.
4. Contained Hg, Se, or Cd (because of the low releases allowed under Resource Conservation and Recovery Act standards) or reactions that were explosive.
5. Consisted of one or more reactions characterized with competing reactions, slow kinetics, or low yields, i.e., non-chemically viable reactions.
6. Contained reactions for which the free energy change exceeded ± 63 kJ (all other factors being equal), i.e., not thermodynamically feasible reactions.

The next phase of the evaluation was a calculation of the efficiency for various levels of development. Thermal efficiency, E, was defined by Beghi as

$$E = \frac{-\Delta H^{\circ}_{25^{\circ}C}(H_2O)}{Q_{hot} + \frac{W}{0.5}} \qquad [2]$$

The numerator is the standard enthalpy of the formation of water at 25°C, 285.83 kJ/mol for high heating value (HHV), or of steam at 25°C, 241.83 kJ/mol for low heating value (LHV). The denominator includes thermal heat, Q, supplied externally, and different types of work (chemical, electrochemical, mechanical, electrical, separation, etc.) converted to the thermal equivalent (assuming a 50% efficiency factor). Electrochemical work is defined by the Nernst equation, or $\Delta G = nFE$, where E is the cell potential in volts, F is Faraday's Constant, 96,493 coulombs. (ΔG is in Joules and the concentration term is not considered because of the unavailability of sufficient information.) Work of separation is defined by the equation $\Delta G_{sep} = -RT\,\Sigma_i n_i \ln y_i$, where R is the gas constant, T is the absolute temperature, n_i is the flow of each component, and y_i is the mole fraction. Chemical work is given by positive free energy for the reaction. A Level 1 efficiency calculation represents an idealized efficiency where all reactions are assumed to go to 100% completion. Pinch analysis is used for optimizing energy usage–that is, exothermic heat is recovered and used for endothermic processes only when temperatures can be matched. Shaft or mechanical work is not included. The calculations are normalized to one mole of water. For cycles that appear promising after the Level 1 analysis, a more detailed Level 2 efficiency is calculated. Level 2 includes consideration of competing reactions and the magnitude of the yields using equilibrium data. Such calculations are easily done with a spreadsheet and readily available thermodynamic databases. Methods for accomplishing the separations or chemical work are generally undefined for Levels 1 and 2. More advanced calculations, e.g., Level 3 and above, are based on "real" chemistry and consider azeotrope formation, solvation effects, etc., and use a process design simulator and heat exchange network for heat management.

Results

Information on elemental abundance can be found on various websites, e.g., http://en.wikipedia.org/wiki/Image:Relative_abundance_of_elements.png#file and http://www.seafriends.org.nz/oceano/abund.htm. These sources provide information on crustal and marine abundances. In general, elements with high abundances are preferred over those with low abundances. Figure 1 shows elemental abundance for the various elements. Two cycles that appeared promising were eliminated because they contained Bi or Ag whose abundances are low. After considering abundance and the other criteria listed above, the following seven cycles were identified as promising:

- Cerium-chlorine (Ce-Cl) [3]
- Iron-chlorine (Fe-Cl [3]
- Magnesium-iodine (Mg-I) [4]
- Vanadium-chlorine (V-Cl) [5, 6]
- Copper-chlorine (Cu-Cl) [7, 8]
- Copper-sulfate (Cu-SO4) [3]
- Hybrid chlorine [3, 9]

Proof-of-principle work has been completed for all of these cycles and chemical viability has been proven [3, 4, 5, 6, 7, 8 and references therein]. Most of these cycles require 850°C process heat. However, two of the cycles, the hybrid Cu-Cl and the Mg-I require process temperatures of 600°C or less.

The initial plan was to calculate Level 1 and 2 efficiencies for these cycles with the NHI scoping flowsheet methodology and the HSC thermodynamic database [10]. However, data for several species were not available in the HSC database and efficiency values reported in the literature were used for this preliminary assessment. The calculated and reported efficiencies for the seven cycles are shown in Table 1.

TABLE 1. Summary of the Efficiency Calculations

Cycle	Efficiency (LHV)		
	Level 1	Level 2	Flowsheet
Ce-Cl	48%		
Fe-Cl	33.8%		
Mg-I			36.4% [4]
Hybrid Cu-Cl	48.0%	41.5%	39.6% [7]
Hybrid Cu-SO4	43.8%	37.8%	30.7% [3]
V-Cl	53.4%		36% [5,6]
Hybrid chlorine	34.3%	30.7%	

Further developmental work for some of these cycles can be leveraged. For example, the Ce-Cl, Fe-Cl, V-Cl, and the hybrid chlorine cycles have a common reaction, the reverse Deacon. Any effort expended on this single reaction can be applied to all four cycles and possibly others. Some of the challenges associated with the further development of the hybrid chlorine cycle are discussed below. The Cu-SO_4 cycle has the same high-temperature SO_3 decomposition reaction of the baseline sulfur cycles but it involves less aggressive chemicals because no water is present when $CuSO_4$ decomposes. The Mg-I cycle and the baseline sulfur-iodine cycles have a common reaction. In both cycles, hydrogen iodide (HI) is decomposed to hydrogen and iodine.

The method for evaluating these cycles and identifying potential improvements is summarized for the hybrid chlorine cycle. The hybrid chlorine cycle is very simple, consisting of two reactions, (1) the reverse Deacon reaction and (2) the hydrochoric acid (HCl) decomposition, shown below. The analysis of this cycle at Levels 1 and 2 provides information on the challenges that must be meet if this cycle can be used to produce hydrogen efficiently.

1. $Cl_2(g) + H_2O\ (g) = 2HCl\ (g) + ½O_2\ (g)$ 850°C
2. $2HCl\ (g) = H_2\ (g) + Cl_2\ (g)$ 75°C

This cycle's efficiency was calculated to be 25.5% by McQuillan et al. when the Udhe process was used for electrolyzing aqueous HCl. However, a new electrolyzer design based on polymer electrolyzer membrane fuel cell (PEMFC) technology, which uses anhydrous HCl, may offer some advantages over the Udhe process for this application. Currently, the PEM cell prototypes require 1.65 V for a current density of 6 kA/m^2. Further optimization may lead to a reduction to 1.5 V or possibly less [9]. A cell EMF of 1.5 V has a heat equivalent of 577.4 kJ when the source efficiency is 50%. If there are no other heat requirements, the efficiency corresponding to the cycle with this amount of electrochemical work alone is 42% (LHV). With other heat and work demands, the efficiency is considerably less, 34.3% (LHV), as shown in Table 2. The energy inputs for the Level 2 calculation are higher. At 850°C, the equilibrium conversion is only 60%. By increasing the water to Cl_2 ratio to 3 to 1, the conversion is increased to 90% but was assumed to be 100% to simplify the calculation here. The pinch heat increased from 1.3 kJ to nearly 84 kJ to account for the condensation and reboiling of the excess water. The Levels 1 and 2 analyses show where R&D efforts should be focused to improve the efficiency of the hybrid chlorine cycle. These areas include the HCl electrolyzer, an oxygen separation membrane to drive the reverse Deacon reaction to the right, and optimized heat management.

This approach is being used for the other six cycles. The current work at the universities and ANL is structured to identify the challenges for each cycle and to use process design and engineering expertise to meet these challenges. The result will be a consistent evaluation of the seven cycles and the downselection of the most promising cycle(s) for producing hydrogen from nuclear heat sources.

TABLE 2. Efficiency Calculation for the Level 1 Analysis

	Energy, kJ/mol H_2	Heat Equivalent, kJ/mol H_2
Heat in (Reaction, Latent, and Sensible)	102.5	
Pinch heat	1.2	
Chemical potential work	0	0
Separation work	11.7	23.4
Electrochemical work	289.5	579.1
Sum of heat and work inputs		706.2
Enthalpy of formation, H_2	241.8	
Efficiency		34.3

Future Directions

- Guide universities in their evaluation process to ensure consistency.
- Identify critical data needs for further evaluation of the most promising cycles.
- Establish R&D activities at the university level to facilitate more detailed evaluations.
- Continue development of methodology to reflect the different levels of maturity for various cycles so that cycles' performance can be compared consistently.

FY 2006 Publications/Presentations

1. *M. Lewis, "Evaluation of Alternative Thermochemical Cycles,"* 2006 DOE Hydrogen Program Review, May 16-19, 2006, Crystal City, VA.

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