

II.J.3 High Temperature Thermochemical Processes

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Start Date: June 2006

Projected End Date: September 2007

- Experimental tasks for the Ca-Br cycle are:
(1) study of the rebromination reaction and
(2) further optimization of the HBr electrolysis
reaction; modeling tasks are: (1) development
and optimization of an Aspen Plus™ flowsheet
and (2) measurement of critically needed physical
properties.
- Experimental tasks for the Cu-Cl cycle are:
(1) scale-up studies for the hydrolysis reaction
and (2) development of the electrolytic cell for
producing hydrogen and CuCl₂. The latter task
will be completed in collaboration with Atomic
Energy of Canada, Ltd. and the University of
Ontario Institute of Technology. Modeling activities
include: (1) optimization of the process design after
simulation of the electrolytic cell is completed and
(2) cost analysis.

Objective

Coordinate and lead the efforts of several universities and Argonne National Laboratory to select the two most promising cycles from the initial list of nine alternative cycles.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (G) Capital Cost
- (H) System Efficiency

Near-term challenges:

- Critical but unknown thermodynamic data and chemistries.
- Short time line for down selection decision.

Accomplishments

- Conducted experiments to determine proof-of-concept.
- Completed uncertainty analyses.
- Collaborated with Atomic Energy of Canada, Ltd.
- Down selected two cycles and justified decision for further R&D.

Future Directions

- Continue experimental and modeling projects to develop the Ca-Br and the Cu-Cl cycles.



Introduction

The focus of the Nuclear Hydrogen Initiative (NHI) of the U.S. Department of Energy's Office of Nuclear Energy (DOE-NE) is to identify and ultimately commercialize hydrogen production technologies that are compatible with nuclear energy systems and that do not produce greenhouse gases. The NHI objective is to operate a nuclear hydrogen production plant at a cost competitive with other alternative transportation fuels by 2019. The NHI is currently supporting development of two sulfur cycles and high temperature steam electrolysis. The NHI is also supporting the alternative thermochemical cycle program and there is special interest in cycles that can provide lower temperature operation, simpler unit operations, and/or higher efficiency.

The NHI is supporting research into such alternative cycles at the following universities: Clemson University, Howard University, Massachusetts Institute of Technology, Pennsylvania State University, Rensselaer Polytechnic Institute, Tulane University, University of Illinois-Chicago, and the University of South Carolina. The corresponding cycles studied by these universities are the hybrid chlorine, the cerium chloride (Ce-Cl), the vanadium chloride (V-Cl), the K-Bi or active metal alloy, the iron chloride (Fe-Cl), the copper sulfate (Cu-SO₄), the hybrid copper chloride (Cu-Cl) and the calcium bromide (Ca-Br), and the magnesium iodide (Mg-I), respectively. All were identified in the literature as very promising [1-5]. The Cu-Cl and the Ca-Br cycles have been studied for several years at Argonne National Laboratory. Each university was responsible for the following tasks: (1) calculating the efficiency for their

assigned cycle, (2) recommending future work, and (3) down selecting the two most promising cycles. The universities were tasked with evaluating these cycles in light of today's technology. The goal is to determine which alternative cycles have sufficient merit to justify additional R&D today and whose development can meet the timeline established by the NHI.

Approach

The literature was examined for alternative cycles that were identified as promising, i.e., the efficiency was greater than 40% (lower heating value [LHV] basis). Because the methods and calculations used in this early work were obscure and inconsistent, a new methodology was developed. This methodology was then applied to all of the promising cycles by the universities. After the efficiency calculations were completed, the universities recommended critically needed work to assist in the down selection. DOE-NE provided funds for proof-of-concept work at the universities. Showstoppers and metrics to be used in the selection process were identified and used by the universities and Argonne National Laboratory to select the two most promising cycles for the NHI.

Results

The efficiencies of each cycle were calculated for three levels of complexity, as shown in Table 1. The first considers that all of the reactions in a cycle are stoichiometric, i.e., all of the reactions go to completion and no competing products are formed. The second level is based on equilibrium data where reactions may be only partially complete and competing products are allowed. Reaction conditions are set to maximize yields. These calculations are relatively simple and use

TABLE 1. Efficiencies for Levels 1-3 Calculated with the NHI Methodology

Cycle	Efficiency % (LHV)		
	Level 1	Level 2	Level 3
Active metal alloy	30-48	Insufficient data	
Ca-Br			
Ce-Cl		16.8	20.9
Cu-Cl	42-50	38-48	43
Cu-SO ₄	47.1	25-40	52.4
Fe-Cl	29	18.5	Not justified
Hybrid Cl ₂	34.3	32.1	34-35
Mg-I	47	45	31-46
V-Cl	52.5	48.9	46

a spreadsheet for calculation purposes. Separations and chemical work are considered ideal. Pinch analysis is used for heat management. For the third level, a process flow diagram is prepared using Aspen Plus™ or other chemical process simulator. The physical properties for the various chemical species are added into the database for the simulation program. A heat exchanger network may be used for heat management. From this efficiency study, two cycles, the Fe-Cl and the Ce-Cl, were eliminated. The advantages of the remaining cycles are described in Table 2 and specific challenges are described in Table 3.

The universities identified possible solutions to the challenges associated with each cycle. Projects were

TABLE 2. Advantageous Features for Alternative Thermochemical Cycles

Cycle	Advantages
Active Metal Alloy	Extremely simple unit operations, minimal separations
Ca-Br	Maximum temperature ~780°C, leverage R&D from UT-3 cycle
Cu-Cl	Maximum temperature <550°C; completed proof-of-concept work
Cu-SO ₄	High projected efficiencies; less corrosive materials; leverage R&D from S-I to reduce CuSO ₄ decomposition temperature
Hybrid Cl ₂	Relatively simple, two unit operations
Mg-I	Maximum temperature <600°C; leverage R&D from S-I cycle to handle HI _x decomposition
V-Cl	High projected efficiencies

TABLE 3. Challenges for Further Development of the Alternative Cycles

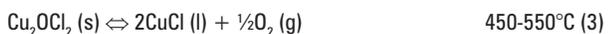
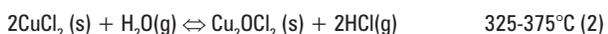
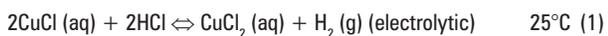
Cycle	Challenges
Active metal alloy	Incomplete proof-of-concept, unknown chemistry, no measured thermodynamic data for most species
Cu-Cl	Development of the electrochemical reaction and optimization of the hydrolysis reaction
Cu-SO ₄	High temperature for CuSO ₄ decomposition, conversion of the electrochemical reaction to a thermal one
Hybrid Cl ₂	High energy requirements for electrolysis of HCl, challenging separations and high temperature in the reverse Deacon reaction
Mg-I	HI-I ₂ or HI _x decomposition, excess water handling, azeotrope formation
V-Cl	Separations/high temperature for the reverse Deacon reaction; slow kinetics of the chlorination reaction, unknown thermodynamic data for vanadium oxides

designed to exploit expertise and available equipment. For example, Clemson had facilities to handle HCl-containing materials in place. The team at Clemson studied the functionality of acidic sorbers that could potentially shift the equilibrium of the reverse Deacon reaction, $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HCl} + \frac{1}{2}\text{O}_2$ to the right, while facilitating the separation of the various species. Tulane studied the hydrogen generation reaction in the Cu-SO₄ cycle, $\text{CuO} + \text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{CuSO}_4 + \text{H}_2$. This reaction is defined in the literature as an electrochemical one. Tulane found that the thermodynamics were favorable for running this reaction thermally when the SO₂ was in the liquid phase. The active metal alloy cycle was studied at Penn State. The reaction of interest was the electrolysis of molten KOH to produce hydrogen and oxygen. In all of these studies and others not mentioned here, significant progress was made but more work was required to establish proof-of-concept for the critical reactions in the active metal alloy, the Mg-I, the V-Cl and the hybrid chlorine cycles. The Ca-Br and Cu-Cl cycles were down-selected for further study for reasons described below. Detailed results of the experimental and modeling work conducted by the universities will be reported elsewhere.

Copper-Chloride (Cu-Cl) Cycle

The recommendation for down selecting the Cu-Cl cycle was based on the following: (1) completed proof-of-concept experiments for all of the reactions, (2) a maximum temperature requirement of about 550°C, (3) measurement of thermodynamic data for Cu₂OCl₂, which was identified as a critical need in a sensitivity analysis of an Aspen Plus™ flowsheet, (4) completion of the physical properties database for the Aspen Plus™ simulation, (5) relatively high efficiency, and (6) ongoing R&D at Argonne National Laboratory, Atomic Energy of Canada, Ltd., and the University of Ontario Institute of Technology.

Proof-of-concept work was completed for all reactions [6,7]. The results of the studies of the thermal reactions show high yields and reasonable kinetics. Most of the separations involve gases and either liquid or solids, which are relatively easy. The simplified representation of the reactions in the Cu-Cl cycle are as shown below. The reaction temperatures shown below for the thermal reactions (#s 2, 3) were determined experimentally. The electrolyzer's optimum temperature is unknown.



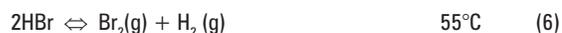
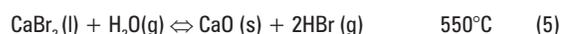
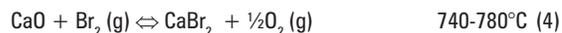
Challenges in this cycle are the following: (1) water management, (2) the development of an energy efficient electrolysis cell, and (3) the development of a method

to eliminate a parasitic reaction, $\text{CuCl}_2 \rightleftharpoons 2\text{CuCl} + \text{Cl}_2$, that accompanies the hydrolysis reaction (#2). Planned work includes a mechanistic study of the hydrolysis and the CuCl₂ decomposition reactions, further study of electrode and membrane materials for the electrolysis cell, and Aspen Plus™ simulations, which will guide the experimental project while identifying the drivers for maximizing efficiency and minimizing capital costs.

Calcium-Bromine (Ca-Br) Cycle

The recommendation for down selecting the Ca-Br cycle was based on the following: (1) its maximum temperature is 740-780°C, (2) proof-of-concept work has been completed for two of the three reactions, and (3) extensive R&D has been conducted on various aspects of the chemistry in the Ca-Br cycle in the UT-3 process [2] and in an ISPRA (location of the European Joint Research Centre) cycle [8], e.g., identification of materials of construction and of a complex formed. In addition, the results of new studies have shown that some of the engineering challenges associated with this cycle can be overcome [9].

The simplified representation of the reactions and their recommended process temperatures are as follows:



Recent experimental work at Argonne showed that CaBr₂ could be hydrolyzed by sparging steam through a molten bed of CaBr₂ to produce HBr. Yields of HBr were high. In addition, anhydrous HBr was successfully electrolyzed using polymer electrolyte membrane fuel cell (PEMFC) technology [10]. Most of the separations involve gases and molten salts and are therefore relatively easy to accomplish - no show stoppers have been identified.

The results of recent work indicated that the hydrolysis reaction (#6) involves a complex, (CaBr₂)₂·CaO, rather than CaO. The next step is to determine if the complex can be rebrominated when Br₂ is sparged into a molten bed containing the complex and unreacted CaBr₂. Steam sparging analysis with COMSOL and process design with Aspen Plus™ software are planned as well.

Conclusions

The university project successfully reevaluated nine promising thermochemical cycles using a consistent methodology for calculating efficiencies. Two cycles were eliminated on the basis of these results. It appears that the calculations used in the past to calculate efficiency did not include heat management issues.

New ideas/technologies were proposed as a means for meeting the challenges associated with the remaining cycles. Experimental and modeling programs were started and/or continued. The down selection to two cycles was based on the maturity of each cycle's development as well as an evaluation of the technical challenges.

FY 2007 Publications/Presentations

1. M. A. Lewis, J. G. Masin, and A. Taylor, A standardized method for evaluating the potential of alternative thermochemical cycles, Proceedings of the AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006.
2. J. G. Masin and M. A. Lewis, Efficiency calculations for the hybrid copper-chloride thermochemical cycle, Proceedings of the AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006.
3. M. A. Lewis and J. G. Masin, Cu-Cl Cycle R&D at Argonne National Laboratory, University of Ontario Institute of Technology, Oshawa, Canada, Dec. 8, 2006.
4. M. A. Lewis, Status of the R&D effort for the Cu-Cl cycle, University of Ontario Institute of Technology, Oshawa, Canada, May 28, 2007.

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10. J. W. Weidner, personal communication, Argonne National Laboratory, Argonne, IL 60439 (February 2006).