

II.H.4 High Temperature Thermochemical Processes

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- Designed, fabricated and successfully tested the nebulizer hydrolysis reactor.
- Completed a conceptual process design for the three reaction Cu-Cl cycle.
- Participated in an International Nuclear Energy Research Initiative with the Atomic Energy of Canada Ltd. and four Canadian universities and an informal information exchange with Commissariat à l'Énergie Atomique in France.
- Participated in a Nuclear Energy Research Initiative-Consortium (NERI-C) with three U.S. universities engaged in research and development (R&D) for the Cu-Cl, Ca-Br, and the K-Bi cycles.



Objective

The strategic objective is to develop a robust commercial process for producing hydrogen that meets DOE's targets for cost and energy usage; the tactical objective is to run experimental and modeling programs that will facilitate the development of an integrated laboratory-scale demonstration for the Cu-Cl cycle. This cycle was selected as the most promising cycle from the initial list of nine alternative cycles evaluated in the university program.

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:

- (U) High-temperature Thermochemical Technology
- (V) High-temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost

Technical Targets

The technical targets are the cost of hydrogen production and the process energy efficiency.

- For 2017, these are \$3.00 per gasoline gallon equivalent (gge) H₂ and >35% (lower heating value, LHV), respectively.

Accomplishments

- Selected the Cu-Cl cycle as the most promising alternative cycle.

Introduction

The focus of the Nuclear Hydrogen Initiative (NHI) of the U.S. Department of Energy's Office of Nuclear Energy 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 because there is special interest in cycles that use lower temperatures or involve simpler unit operations. DOE-Energy Efficiency and Renewable Energy is also supporting the development of thermochemical cycles that use solar heat.

The NHI alternative cycle evaluation project consisted of three phases: (1) identification of promising cycles from the literature, (2) reevaluation with the help of eight universities, and (3) selection and further development of the most promising cycle(s). Research was then focused on specific aspects of the selected cycles.

Approach

The university program for alternative cycle evaluation was completed. The Cu-Cl and Ca-Br cycles were identified as the most promising [1-3]. The primary reason these cycles were selected was that no showstoppers were identified by the universities and their development was in progress and/or an extensive data base of past work was available. Three cycles, the active metal alloy, the Mg-I, and the hybrid chlorine, were identified as promising but addressing the technical challenges was judged to be more difficult, requiring

a longer timeline. Showstoppers were identified for the other cycles. The results are summarized below and more detailed information can be found in various references [1-6 and references therein].

Selected as the Most Promising for Further R&D

- Hybrid Cu-Cl
 - A maximum temperature of <math><550^{\circ}\text{C}</math>
 - All reactions demonstrated at laboratory-scale
 - No catalysts needed for thermal reactions
 - Completed conceptual process design based on commercially practiced technologies
 - Mass and energy balanced flowsheet
 - Preliminary efficiency and hydrogen production costs within DOE targets
- Hybrid Ca-Br
 - New concepts proven for the HBr electrolyzer and the sparge hydrolysis reactor
 - Intermediate maximum temperature (about 770°C)
 - Large database of information from the UT-3 and the European Joint Research Centre research programs

Selected for Additional Study

- Active Metal Alloy
 - Lower maximum temperature ($<600^{\circ}\text{C}$) and potential for one ‘pot’ operation; however proof-of-concept was not demonstrated

Promising

- Mg-I
 - Reactions demonstrated and maximum temperature of about 600°C but it is more complex due to number of reactions and incomplete separations
- Hybrid Cl_2
 - New technology required to improve yield in reverse Deacon reaction

Non-Selected

- Fe-Cl
 - Low efficiency
 - Competing product formation
- Ce-Cl
 - Slow kinetics
- Hybrid CuSO_4
 - Competing product formation

- V-Cl
 - Slow kinetics

Funding continued for the Cu-Cl cycle’s development of the hydrolysis reactor. The NERI-C program provides some support for the active metal alloy cycle and the Ca-Br cycle.

Further development of the Cu-Cl cycle was focused on improving the yields in the hydrolysis reaction, $2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{Cu}_2\text{OCl}_2(\text{s}) + 2\text{HCl}(\text{g})$, a gas-solid reaction. These are notorious for poor mass and heat transfer, leading to low yields of products. The hydrolysis reaction is also complicated by two factors: (1) a competing reaction of CuCl_2 and (2) the need for excess water. The competing reaction is the decomposition of CuCl_2 , $2\text{CuCl}_2(\text{s}) \rightleftharpoons 2\text{CuCl}(\text{s}) + \text{Cl}_2(\text{g})$. The current model indicates that the above stoichiometry is not realized and that a steam to CuCl_2 molar ratio (S/Cu) of about 14 is required for high yields.

Tests with fixed bed reactors showed that high yields of the desired products could be obtained with fixed beds. However, very high flow rates of the carrier gas (as measured by the gas hourly space velocity, GHSV) and high steam to copper molar ratios were required, as shown in Table 1. In two of the fixed bed tests, the yield of Cu_2OCl_2 was low and there were significant amounts of CuCl_2 remaining for the experiments with S/Cu of 17 and GHSVs of 8,900 and 26,000 h^{-1} . In the tests with GHSV of 43,000 h^{-1} , conversion was higher at 87 and 89% for two quite different steam concentrations of 8 and 26%. The amount of unreacted CuCl_2 decreased as the GHSV increased. The higher GHSV provides for higher mass transfer.

TABLE 1. Some Results from Fixed Bed Experiments

S/Cu	GHSV ^a (h^{-1})	H ₂ O (%)	Cu ₂ OCl ₂ (wt%)	CuCl (wt%)	CuCl ₂ (wt%)
28	43,000	8	87	12	1
52 ^b	43,000	26	89	8	3
17	8,900	26	48	27	25
17	26,000	8	66	17	17

^aGHSV = Gas hourly space velocity, which is calculated by dividing the Ar flow rate by the sample volume

^bThis experiment was run for 30 minutes. The others were run for 60 minutes.

Thus, our approach was to design a reactor that provides better mass transfer compared to a fixed bed, and which should help to minimize CuCl_2 decomposition. Spray reactors offer improved heat and mass transfer but commercially available ones are not readily adaptable to laboratory-scale work. Consequently, a new hydrolysis reactor based on injecting the CuCl_2 solution with a nebulizer was

designed, built and tested. The nebulizer produces a very fine mist when the CuCl_2 solution is injected along with an inert gas with a flow rate of 100-300 mL/min through the nebulizer. The reactor, shown in Figure 1, has an inside diameter of 4.75 inches so that it can accommodate the cone of mist formed by nebulizer. There are two ports on the side of the reactor, which are used for injecting steam (which may be superheated) and/or a carrier gas. This flow can be either co-current (from the top) or counter-current from the bottom. The configuration in Figure 1 is for counter-current flow. The CuCl_2 solution is injected into the reactor using a syringe pump. If additional water is required, it is injected into the superheated steam line along with any Ar with a second syringe pump. The carrier gas flow rates are controlled by mass flow controllers.

Results

The preliminary test results for counter-current flow are encouraging. Very fine black particles are found at the bottom of the reactor after successful runs. Figure 2 is an X-ray diffraction (XRD) pattern of a sample that contains lines identified as melanothallite, the mineral form of Cu_2OCl_2 , and lines identified as CuCl_2 . There is one line that is characteristic of CuCl at d-spacing

3.14 Å. The relative intensities of the lines for CuCl_2 and CuCl are small compared to those for Cu_2OCl_2 . This sample was obtained under the following conditions:

- CuCl_2 concentration of 1.2 M
- Test duration of 75 min
- Superheated steam temperature of 450°C
- Ar flow rate through nebulizer of 200 ml/min
- Ar flow rate through superheated steam line of 200 ml/min
- Furnace temperature of 370°C with an internal temperature of 400°C
- Flowrate of water to nebulizer during preheat of 1 ml/h
- Flowrate of water through superheated steam line during preheat of 0.25 ml/h

The steam to copper molar ratio can not be precisely determined in the counter-current experiments because some water is removed at the exit near the top of the reactor before the reaction occurs.

The XRD pattern in Figure 3 shows the effect of different flow rates of Ar through the nebulizer. The lines for Cu_2OCl_2 are more intense when the Ar flow rate is 300 mL/min than when the Ar flow rate is

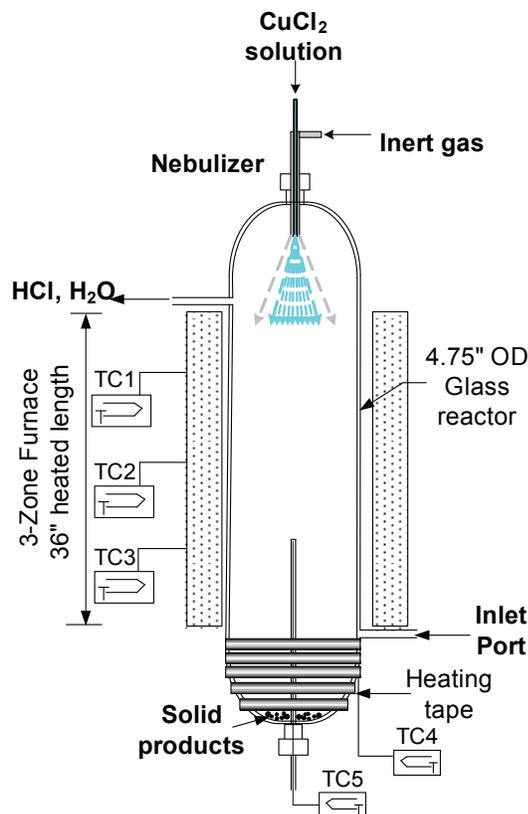


FIGURE 1. Schematic of the Nebulizer Reactor for the Cu-Cl Hydrolysis Experiments

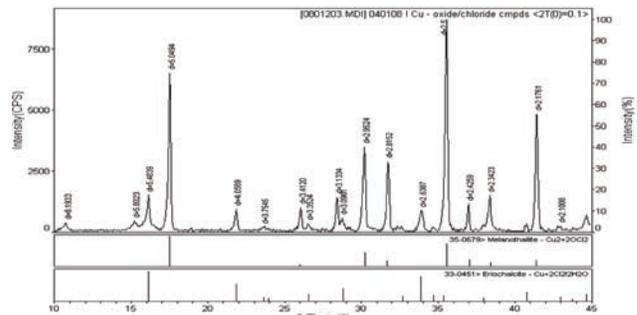


FIGURE 2. XRD Pattern of Sample Produced in the Nebulizer Reactor

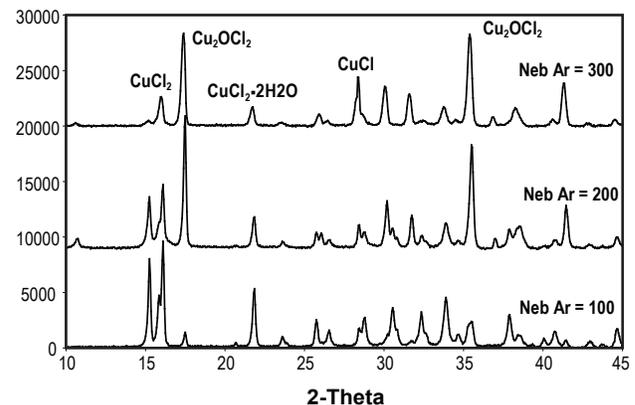


FIGURE 3. Effect of Different Ar Flow Rates through the Nebulizer

100 ml/min. The intensity of the lines for unreacted CuCl_2 follow the opposite trend, being larger when the Ar flow rate is smaller. We concluded that the higher the flowrate, the smaller the droplet/particle, the better the heat and mass transfer, and therefore, the greater conversion to the oxychloride. Other experiments showed that when CuCl_2 solution flowrate is increased from 1 to 3 ml/h, the relative intensity of the Cu_2OCl_2 lines decreases while that for unreacted CuCl_2 increases. We concluded that the higher CuCl_2 solution flowrate results in larger droplets, hence less conversion. In another series of tests, the flowrate of the Ar gas through the superheated steam line was varied. The result was that there was more conversion to the oxychloride and less unreacted CuCl_2 as the Ar flowrate increased from 100 to 300 ml/h. We concluded that the higher flowrate of the Ar from the superheated steam provides more turbulence and hence more mixing of the steam and the CuCl_2 droplets, hence more conversion. These results along with others are allowing a better understanding of how to improve the yield in the hydrolysis reaction in the Cu-Cl cycle.

Conclusions

The university program reevaluated nine thermochemical cycles identified in the literature as promising. The Cu-Cl was selected for further R&D because it was chemically viable and feasible with respect to engineering. A preliminary Aspen flowsheet was mass and energy balanced. The corresponding H₂A cost analysis was completed. The efficiency and hydrogen production costs are expected to meet DOE targets. However, much work remains to facilitate the development of an integrated laboratory scale experiment. An experimental program was designed to study the hydrolysis reaction. Past work showed that the yield of the desired products for this gas-solid reaction depended on good heat and mass transfer. New reactor concepts are now being tested that should improve contact between the CuCl_2 solid and the steam. The results of our tests with a nebulizer-type reactor showed improved heat and mass transfer. However, further improvements are necessary and we plan to test an ultrasonic nebulizer next.

Future Directions

- Continue experimental and modeling programs to further develop the Cu-Cl cycle and determine if the smaller-scale effort for the K-Bi cycle should continue.
- Continue optimization work for the hydrolysis reactor design; the current nebulizer will be replaced with an ultrasonic nozzle.
- Scale-up the design for the oxychloride decomposition reactor.

FY 2008 Publications/Presentations

Publications

1. M. A. Lewis, J. G. Masin, and P.A. O'Hare, Evaluation of alternative thermochemical cycles-Part I The methodology. Int. J. Hydrogen Energy, to be published (2008).
2. M. A. Lewis and J. G. Masin, Evaluation of alternative thermochemical cycles-Part II The down selection methodology, Int. J. Hydrogen Energy, submitted (2008).
3. M. A. Lewis, M. S. Ferrandon, D. F. Tatterson, and P. M. Mathias, Evaluation of alternative thermochemical cycles-Part III Further development of the Cu-Cl cycle, Int. J. Hydrogen Energy, submitted (2008).
4. M. A. Lewis, Quarterly Report for the Solar Hydrogen Generation Research Program-Status of the R&D Effort for the Cu-Cl Thermochemical Cycle for Hydrogen Production, January 10, 2008.
5. M. A. Lewis, Quarterly Report for the Solar Hydrogen Generation Research Program -Status of the R&D Effort for the Cu-Cl Thermochemical Cycle for Hydrogen Production, April 10, 2008.
6. M. A. Lewis, Quarterly Report for the Solar Hydrogen Generation Research Program -Status of the R&D Effort for the Cu-Cl Thermochemical Cycle for Hydrogen Production, July 14, 2008.
7. M. A. Lewis, Quarterly Report for the NHI Program-Development of the hydrolysis reactor for the Cu-Cl thermochemical cycle for hydrogen production, December, 2008.
8. M. A. Lewis, Quarterly Report for the NHI Program-Development of the hydrolysis reactor for the Cu-Cl thermochemical cycle for hydrogen production, March, 2008.
9. M. A. Lewis, Quarterly Report for the NHI Program - Development of the hydrolysis reactor for the Cu-Cl thermochemical cycle for hydrogen production, July 10, 2008.
10. M. S. Ferrandon, M., Lewis, M.A., Tatterson, D.F., Nankani, R.V., Kumar, M., Wedgewood, L.E., Nitsche, L.C., The hybrid Cu-Cl thermochemical cycle. I. Conceptual process design and H₂A cost analysis. II. Limiting the formation of CuCl during hydrolysis, Extended Abstract submitted for the NHA Annual Hydrogen Conference 2008, Sacramento, CA, March 31 – April 4, 2008.

Presentations

1. M. A. Lewis, Status of the R&D effort for the Cu-Cl cycle, NERI-C Consortium Technical Progress Meeting, Tulane University, New Orleans, LA, April 10-11, 2008.
2. M. A. Lewis, The conceptual process design and cost analysis for the Cu-Cl cycle, Oshawa, CA, Dec. 19-20, 2007.
3. M. A. Lewis, NERI-C Kickoff Meeting, Review of the R&D effort for the Cu-Cl cycle, University Park, PA, Nov. 30, 2007.

References

1. M.A. Lewis, J.G. Masin, and P.A. O'Hare, Evaluation of alternative thermochemical cycles-Part I The methodology, *Int. J. Hydrogen Energy*, To be published (2008).
2. M.A. Lewis and J.G. Masin, Evaluation of alternative thermochemical cycles-Part II The down selection methodology, *Int. J. Hydrogen Energy*, submitted (2008).
3. M.A. Lewis, M.S. Ferrandon, D.F. Tatterson, and P.M. Mathias, Evaluation of alternative thermochemical cycles-Part III Further development of the Cu-Cl cycle, *Int. J. Hydrogen Energy*, submitted (2008).
4. R.H. Carty, M.M. Mazumder, J.D. Schreider, and J.B. Pangborn, *Thermochemical Hydrogen Production*, Vols. 1-4, Gas Research Institute for the Institute of Gas Technology, GRI-80/0023, Chicago, IL 60616 (1981).
5. R.D. Doctor, J. Yang, C.B. Panchal, S.A. Lottes, and R.W. Lyczkowski, Optimization of CaBr₂ hydrolysis reaction in a Direct Steam Sparging Contactor, N-AN07TC0401 Report (March, 2007).
6. J.W. Weidner, personal communication, Argonne National Laboratory, Argonne, IL 60439 (February 2006).