

II.G.1 R&D Status for the Cu-Cl Thermochemical Cycle

Michele A. Lewis (Primary Contact),
Magali Ferrandon, and David Tatterson
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
Phone: (630) 252-6603; Fax: (630) 252-5246
E-mail: lewism@cmt.anl.gov

DOE Program Manager, Nuclear Hydrogen Research: Carl Sink
Phone: (301) 903-5131
E-mail: Carl.Sink@nuclear.energy.gov

DOE Program Manager, Energy Efficiency and Renewable Energy: Rick Farmer
Phone: (202) 586-1623; Fax: (202) 586-2373
E-mail: Richard.Farmer@ee.doe.gov

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Objective

The strategic objective is to develop a robust process for producing hydrogen that meets DOE's targets for cost and energy usage; the tactical objective is to conduct experimental and modeling programs that will facilitate the development of an integrated laboratory scale demonstration for the Cu-Cl cycle that can operate with heat sources that provide process heat near 550°C.

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

- Developed a method/reactor design for obtaining high yields (near 100%) of the desired products in the hydrolysis reaction.
- Verified that 550°C was the maximum process temperature and showed that no catalysts were required for the thermal reactions.
- Completed a conceptual process design and Aspen flowsheet for the Cu-Cl cycle.
- Completed an estimate of the efficiency and cost of producing hydrogen based on the conceptual process design.
- Continued participation in an International Nuclear Energy Research Initiative (INERI) with the Atomic Energy of Canada Ltd. (AECL) and six Canadian universities and an informal information exchange with Commissariat à l'Énergie Atomique (CEA) in France.
- Continued participation in a Nuclear Energy Research Initiative-Consortium (NERI-C) with three U.S. universities.
- Identified promising membrane materials for the electrolyzer through the INERI and NERI-C programs; these have the potential to eliminate the copper crossover observed experimentally.



Introduction

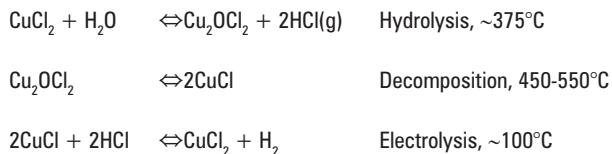
The focus of the Nuclear Hydrogen Initiative (NHI) of the U.S. Department of Energy's Office of Nuclear Energy (DOE-NE) is to identify and ultimately commercialize hydrogen production technologies that are compatible with nuclear energy systems and that do not produce greenhouse gases. The NHI objective 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 as well as the Cu-Cl cycle because of its lower temperature and potentially simpler unit operations. The U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) is also supporting the development of thermochemical cycles that use solar heat. Their focus is to identify thermochemical cycles that operate with solar heat and meet efficiency and cost targets as described in the following. The lower temperature option is also attractive to DOE-EERE because the solar power tower provides heat near 550°C and is near commercialization.

Based on preliminary experimental and modeling work, the Cu-Cl thermochemical cycle was chosen for further development for the following reasons:

- A maximum temperature of about 550°C was verified.
- All reactions were demonstrated at laboratory scale.
- No catalysts were needed for thermal reactions; no catalyst needed for the anode in the electrolyzer.
- The conceptual process design is based on commercially practiced technologies.
- The mass and energy balanced flowsheet showed promising efficiency.
- The H2A analysis showed potential to meet hydrogen production cost target.

Approach

The basic chemistry in the Cu-Cl cycle can be represented by the following three reactions:



This representation is simplistic and does not include any separations or phase changes and is useful for describing the cycle at a high level.

The approach has been to demonstrate the chemistry of the reactions and to optimize the operating parameters to prove the assumptions made in the modeling program. The overall focus has been to develop a process that can meet DOE's targets. The preliminary efficiency and costs are based on proving several assumptions, e.g., obtaining high yields of the desired products in the hydrolysis reaction with the minimum amount of excess water, developing a membrane that prevents copper crossover from the anode to the cathode with the electrolyzer operating at 0.7 V (2015 target) and 0.63 V (2025 target), and demonstrating that the copper oxychloride formed in the hydrolysis reactor was free flowing and decomposed over a range of temperatures. At Argonne National Laboratory, we have focused on meeting the challenges associated with the hydrolysis reaction and measured the temperature range over which the oxychloride decomposes. Partners in the INERI and NERI-C programs are focused on developing and optimizing the performance of the electrolyzer and developing methods to obtain a CuCl₂ stream suitable for the hydrolysis reactor, i.e., one that is nearly free of HCl and CuCl and contains minimal water.

The challenges in the hydrolysis reaction are the need for excess water to drive the reaction to the right

and the elimination of the parasitic reaction in which CuCl₂ decomposes to give CuCl and chlorine. In early fixed bed experiments much of the CuCl₂ remained unreacted and the amount of CuCl formed was high, in some cases greater than 20 wt%. Conditions that promoted mass transfer resulted in improved yields, about 80-90%, of the desired copper oxychloride, Cu₂OCl₂. Smaller amounts of CuCl₂ remain unreacted and some CuCl was still observed. The results were not reproducible and a very high flow rate of a carrier gas was needed for the 80-90% yields. Therefore the primary task was to design, build and test a reactor that would provide better heat and mass transfer.

Results

In order to obtain better heat and mass transfer, we designed a spray reactor with a glass 'pneumatic' nebulizer as described in the 2008 report. Many variables, e.g. the Ar flow rates used for atomization and to deliver superheated steam, the CuCl₂ solution concentration and flowrate and the steam to copper chloride molar ratio, were optimized. While the nebulizer worked reasonably well in counter-current operation, it was difficult to use. The capillary tube in the nebulizer frequently clogged, especially in co-current operation, and the solution droplets/particles expanded in a large cone, causing deposits to form on the wall of the reactor. The nebulizer also required the use of an atomizing gas, which would not be practical commercially.

It was suggested that an ultrasonic nozzle would eliminate these difficulties [2]. After optimization of the experimental variables, very favorable results were obtained. Products consisting of ≥95% Cu₂OCl₂ were reproducibly produced with the ultrasonic nozzle. A typical X-ray diffraction pattern is shown in Figure 1. Also shown is the standard pattern for melanotallite, the crystalline form of copper oxychloride. Comparison of the standard pattern and our product's pattern shows a one-to-one correspondence for all of the peaks except the one at d-spacing of 3.14 Å, which was assigned to CuCl. Wet chemistry analysis of the product powders showed that the CuCl was present at 3-5 wt% of the product. In addition, the product powders were very fine and free flowing. The morphology of the Cu₂OCl₂ is important because our current conceptual process design uses gravity to feed the Cu₂OCl₂ to the decomposition reactor.

The Cu₂OCl₂ powders produced with the ultrasonic nozzle were subsequently decomposed by heating them to higher temperatures. The effluent gas from the decomposition reactor was analyzed with a mass spectrometer. Figure 2 shows the evolution of oxygen as a function of temperature. The maximum temperature was 700°C. As can be seen, the oxygen signal appears from 400-550°C. Using a calibration curve, the peak

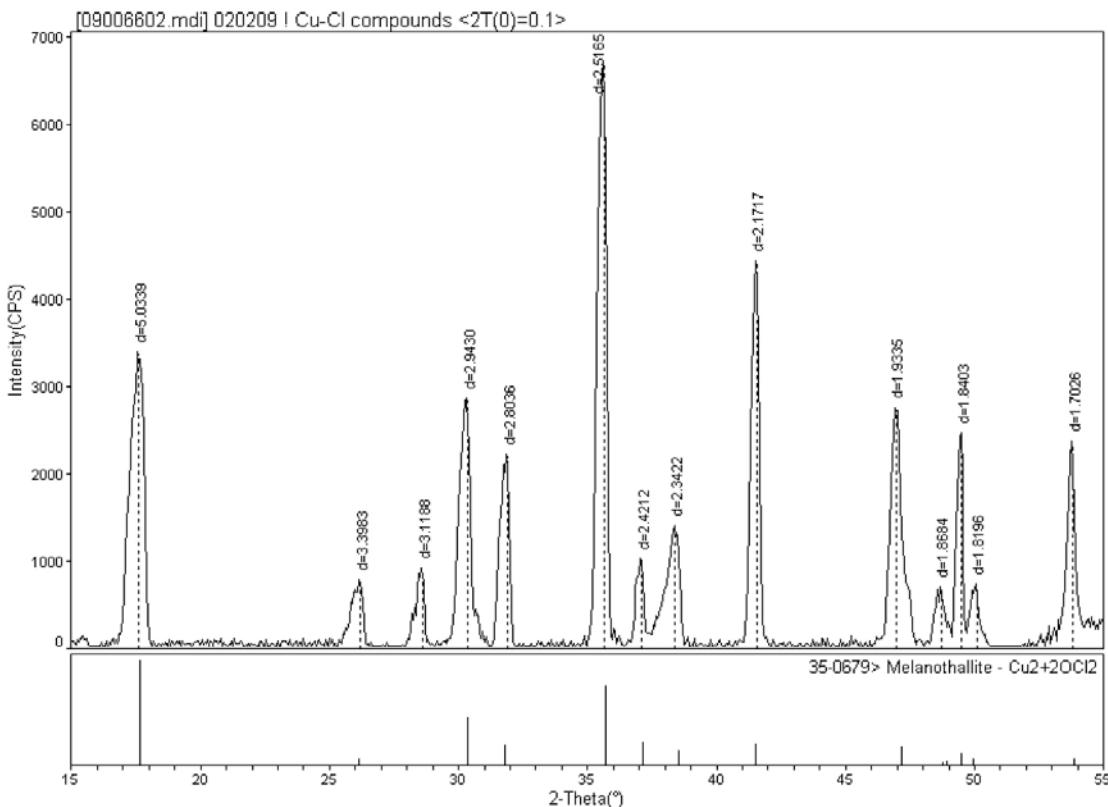


FIGURE 1. X-ray Diffraction Pattern for a Product of the Hydrolysis Reaction

area corresponded to 100% of the theoretical amount of oxygen in the starting Cu_2OCl_2 powders. No chlorine was observed in the mass spectrum.

The modeling program is focused on identifying the path forward for meeting DOE's targets for cost and efficiency. An Aspen flowsheet and a conceptual process design have been completed. The flowsheet was used to calculate the efficiency of the cycle and the conceptual process design with the H2A methodology was used to

calculate the cost of hydrogen production. The results are shown in Table 1. The conceptual process design is based on unit operations that are commercially practiced. Where a choice is available, operations are selected on the basis of low cost and high efficiency with respect to energy usage.

The results of the experimental work with the spray reactor indicated that the conceptual process design for the hydrolysis reactor was viable. A search of the literature indicated that spray reactors are in commercial operation. For example, spray reactors are used in pyrohydrolysis, a commercial process for converting MgCl_2 solutions to MgO , and in HCl recovery processes. A schematic of the hydrolysis reactor in the conceptual process design is shown in Figure 3. The feed for the hydrolysis reactor is the spent anolyte, a mixture of CuCl_2 and unreacted CuCl in an HCl aqueous solution at 24 bar and near 100°C. These parameters follow from the conditions used in the electrolysis. The electrolyzer is to be run at 24 bar (350 psi) pressure and near 100°C. The pressure is fixed at 24 bar to obtain the hydrogen gas product at DOE's target of 300 psi. A temperature near 100°C is used to minimize the cell voltage. (Proprietary work has shown that the cell voltage decreases with increasing temperature for a given current density.) The spent anolyte must be processed to remove most of the HCl and water from the

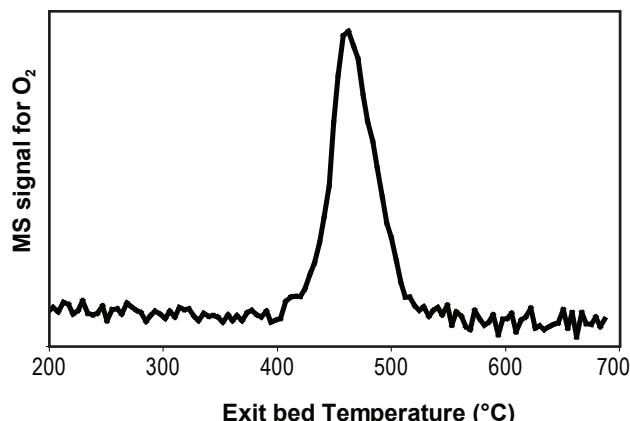


FIGURE 2. Hydrolysis Reactor in the Conceptual Process Design

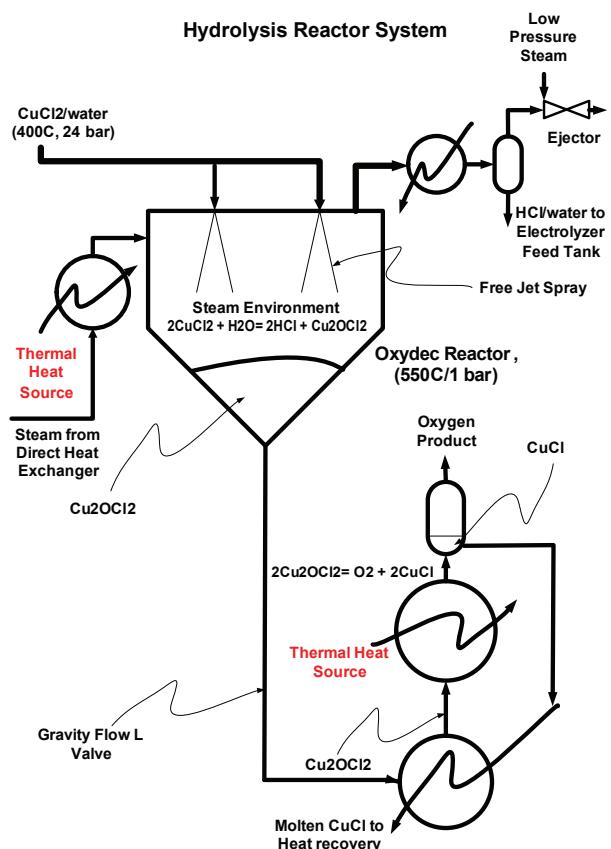
TABLE 1. Results of the Calculations for Efficiency and Hydrogen Production Cost¹

Case	Capital Investment, \$M, Solar/Chemical	Cell EMF, V	Electricity Cost, \$/kW	\$/kg	Sensitivity	Efficiency, % (LHV) ²
20152	208.3/136	0.7	0.068	4.53	3.78-5.31	39
2025	168.5/106.6	0.63	0.048	3.48	2.91-4.11	41

¹The assumptions in the cost analysis are as follows:

1. Electrolyzer operates at a current density of 500 mA/cm² at above voltages.
2. Electrolysis cell area is 1.5 m² for 2015 and 3.0 m² for 2025.
3. Corrosion issues can be solved by coating with porcelain coating at a cost of 6% above carbon steel.
4. Residence times in the hydrolysis reactor are 5 sec (2015) and 2.5 sec (2025).
5. Crystallizer operates as a cooler followed by a hydroclone at 55°C.
6. Bulk HCl cost is \$241/metric ton; Bulk CuCl cost is \$7,200/metric ton
7. Cost of heliostat field can be reduced from \$127/m² in 2015 to \$90/m² in 2025.
8. Conversion factor for converting work to heat is 40%.

²Efficiency is defined as the LHV of the moles of H₂ produced divided by the sum of the heat and work. Work is converted to the thermal equivalent [1]. EMF - electromotive force

**FIGURE 3.** The Evolution of Oxygen from Cu₂OCl₂ as a Function of Temperature

CuCl₂. The current flowsheet specifies a crystallization process but other methods, e.g. electrodialysis, membrane distillation, and evaporative crystallization are being considered. The resulting slurry of CuCl₂ will be injected near 24 bar into the reactor. Superheated steam is injected into radial ports. The pressure of the reactor is about 0.25 bar, which is obtained by placing

an injector near the exit. As the droplets enter the hot reactor, the pressure drop should cause the slurry to form a free jet. As the CuCl₂ jet expands, it aspirates the superheated steam into the jet resulting in high mass and heat transfer between the CuCl₂ and the steam. Thus, the need for the carrier gas found to be critical in the laboratory can be eliminated in a commercial operation.

The NERI-C and the INERI members have made progress in their tasks. After the first year of these programs, it was recognized by the group that it was critical to identify a membrane material that minimizes or preferably eliminates copper crossover. Copper crossover degrades the electrolyzer's performance and prevents operation of the electrolyzer at the cell voltage and current density targets on which the current values for efficiency and cost of hydrogen production are based. Therefore, Pennsylvania State University (PSU) and AECL are both working on this task. PSU is characterizing commercial anion exchange membranes as well as developing novel chloride exchange membranes specifically designed for use in the Cu-Cl electrolyzer while AECL is examining cation exchange membranes. PSU recently reported that one of their new anion exchange membranes was stable for a relatively long period of time in conductivity tests. AECL recently reported that a new membrane material and a modified electrolyzer design resulted in a stable cell voltage for 19.5 hours in contrast to previous work in which the voltage was stable for less than 0.5 hours. Other work that is ongoing at PSU is modeling of the electrolysis reaction. The University of South Carolina (USC) is investigating electrodialysis as a means to separate Cu(II) from Cu(I) as might be found in the spent anolyte, reviewing the current Aspen flowsheet, and testing various electrolyzer designs. USC recently found that Cu(I) and Cu(II) are separable via electrodialysis. However HCl did not separate. Tulane University is developing an alternate Aspen flowsheet and conceptual process design. Its efficiency is lower than that of the current flowsheet.

Conclusions

The experimental project for the development of the hydrolysis reaction has shown that the spray reactor design provides sufficient mass and heat transfer to effectively convert all of the CuCl₂ to Cu₂OCl₂. Tests with an ultrasonic nozzle led to improved results compared to those with a ‘pneumatic’ nebulizer. The modeling program has produced an Aspen flow sheet and a conceptual process design, which were used to calculate the efficiency and cost of hydrogen production. These results are based on meeting assumed values or targets for the cell voltage and current density for the electrolysis reaction and for crystallization as a method to separate CuCl and HCl from CuCl₂ in the spent anolyte.

Future Directions

- Continue experimental and modeling projects to further develop the Cu-Cl cycle.
- Continue optimization work for the hydrolysis reactor design; tests to be completed include the following: (1) determination of the minimum ratio of steam to copper for complete conversion, (2) the use of counter-current operation instead of co-current as currently used, and (3) determination of the viability of using reduced pressure to reduce the ratio of steam to copper.
- Measure the solubility of CuCl and CuCl₂ in aqueous HCl solutions as a function of temperature.

FY 2009 Publications/Presentations

Publications

1. M.A. Lewis, M.S. Ferrandon, D.F. Tatterson, An overview of R&D activities for the Cu-Cl cycle with emphasis on the hydrolysis reaction, Fourth Information Exchange Meeting on the Nuclear Production of Hydrogen, Chicago, IL, April 13–15, 2009, to be published.
2. M.A. Lewis, J.G. Masin, and P.A. O'Hare, Evaluation of alternative thermochemical cycles-Part I The methodology. Int. J. Hydrogen Energy 34 (2009) 4115-4124.
3. M.A. Lewis and J.G. Masin, Evaluation of alternative thermochemical cycles-Part II The down selection methodology. Int. J. Hydrogen Energy 34 (2009) 4125-4135.
4. 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 34(2009) 4136-4145.
5. M.S. Ferrandon, M.A. Lewis, and D.F. Tatterson, A. Gross, D. Doizi, L. Croizé, V. Dauvois, J.L. Roujou, Y. Zanella, P. Carles, Production of Cu₂OCl₂ using a spray reactor and formation of HCl and Cl₂ during the hydrolysis of CuCl₂ in the Cu-Cl thermochemical cycle, to be submitted to the Int. J. Hydrogen Energy.

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, January, 2009.

7. 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, 2009.

8. 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.

9. 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.

10. 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.

11. 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.

12. 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.

13. 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.

Presentations

1. M.A. Lewis, M.S. Ferrandon, D.F. Tatterson, An overview of R&D activities for the Cu-Cl cycle with emphasis on the hydrolysis reaction, Fourth Information Exchange Meeting on the Nuclear Production of Hydrogen, Chicago, IL, April 13-15, 2009.
2. M.A. Lewis, An overview of the R&D activities for the Cu-Cl cycle, International Conference on Hydrogen Production (ICH2P), Oshawa, CA, May 3-6, 2009.
3. M.A. Lewis, An overview of R&D activities for the Cu-Cl cycle with emphasis on the hydrolysis reaction, ORF Workshop, Oshawa, CA, May 2, 2009.
4. M.A. Lewis, R&D Status for the Cu-Cl Thermochemical Cycle, Annual Merit Review, Crystal City, VA, May 18-21, 2009.
5. M.A. Lewis, R&D Status for the Cu-Cl Thermochemical Cycle, HPTT Review, Las Vegas, NV, January 22-23, 2009.
6. M.A. Lewis, Status of the R&D effort for the Cu-Cl cycle, NERI-C Consortium Technical Progress Meeting, Argonne National Laboratory, Chicago, IL, September, 2009.

7. 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.
8. 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*, NHA Annual Hydrogen Conference 2008, Sacramento, CA, March 31 – April 4 2008.

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2. Evans, R. Personal communication, Argonne National Laboratory, September 2008.