

Nuclear-Based Hydrogen Production with a Thermochemical Copper-Chlorine Cycle and Supercritical Water Reactor

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Abstract

Efficient and sustainable methods of clean fuel production are needed in Ontario (and elsewhere) in the face of depleting oil reserves and the need to reduce carbon dioxide emissions. With commitments for a hydrogen village, a hydrogen airport and a hydrogen corridor, Ontario has already begun to move toward a hydrogen-fueled economy. However, a key missing element is a large-scale method of hydrogen production. As a carbon-based technology, the predominant existing process (steam-methane reforming (SMR)) is unsuitable. The two main alternatives are electrolysis and thermochemical decomposition of water. This article describes a thermochemical cycle driven by nuclear heat from Canada's Generation IV reactor (SCWR), which is a CANDU derivative using Super-Critical Water cooling. The copper-chlorine (Cu-Cl) cycle has been identified by AECL as the most promising cycle for thermochemical hydrogen production with SCWR. Water is decomposed into hydrogen and oxygen through intermediate Cu-Cl compounds. This paper outlines the primary challenges, design issues and current status of hydrogen production with a Cu-Cl cycle coupled to Canada's nuclear reactors.

Introduction

Hydrogen demand is expected to rise dramatically over the next few decades. Hydrogen for development has been reviewed by Bertel [1], Duffey and Miller [2-4]. Kloosterman [5] has predicted that hydrogen demand from the chemical, fertilizer and petrochemical industries alone will rise by a factor of four over the next decade. This is very rapid growth, even by oil-industry standards, especially since it precedes an expected phase of far higher growth in the emerging hydrogen economy for the transportation sector with automotive fuel cells.

In Alberta, oil sands development is requiring huge quantities of hydrogen to upgrade bitumen to synthetic crude. Dincer [6] has outlined many of the key technical and environmental concerns of hydrogen production. Unlike SMR technology [7], nuclear-based hydrogen production does not emit greenhouse gases. Furthermore, the recent rise in oil prices and the need to sequester CO₂ has tilted the economic balance away from the traditional SMR. A comprehensive overview of various hydrogen production schemes was presented by Yildiz and Kazimi [8]. Rosen [9-10] has evaluated the thermodynamic efficiency of electrolytic hydrogen production from nuclear energy and other sources. Operating temperatures are key factors, both for electrolytic and thermochemical methods of hydrogen production. Thus, optimization of heat flows is important for high energy conversion efficiency (Naterer [11]).

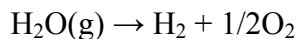
Electrolysis is a proven, commercial technology that separates water into hydrogen and oxygen using electricity. Net electrolysis efficiencies are typically about 24%. In contrast, thermochemical reactions to produce hydrogen using nuclear heat can achieve heat-to-hydrogen efficiencies up to about 50% [12, 13]. Nuclear-based “water splitting” requires an intermediate heat exchanger between the nuclear reactor and hydrogen plant, which transfers heat from the reactor coolant to the thermochemical cycle [14]. An intermediate loop prevents exposure to radiation from the reactor coolant in the hydrogen plant, as well as corrosive fluids in the thermochemical cycle entering the nuclear plant.

This paper focuses on a copper-chlorine (Cu-Cl) cycle, which has been identified by Atomic Energy of Canada Ltd. (AECL) [15, 16] at its Chalk River Laboratories (CRL) as a highly promising cycle for thermochemical hydrogen production. Water is decomposed into hydrogen and oxygen through intermediate Cu-Cl compounds. Past studies at Argonne National Laboratory (ANL) have developed enabling technologies for the Cu-Cl thermochemical cycle, through an International Nuclear Energy Research Initiative (I-NERI), as reported by Lewis et al. [17]. The Cu-Cl cycle is well matched to Canada’s nuclear reactors, since its heat requirement for high temperatures is adaptable to the Super-Critical Water Reactor (SCWR), one of which is Canada’s Generation IV nuclear reactor. Other advantages of this proposed process are reduced demands on materials of construction, inexpensive chemical agents, insignificant solids handling and reactions going to completion without side reactions.

Other countries (Japan, U.S. and France) are currently advancing nuclear technology for thermochemical hydrogen production [18-20]. The Sandia National Laboratory in the U.S. and CEA in France are developing a hydrogen pilot plant with a sulfur-iodine (S-I) cycle [21]. The Korean KAERI Institute is collaborating with China to produce hydrogen with their HTR-10 reactor. The Japan Atomic Energy Agency (JAEA) aims to complete a large S-I plant to produce 60,000 m³/hr of hydrogen by 2020, which will be sufficient for about 1 million fuel cell vehicles [22]. This article focuses on current Canadian technologies of thermochemical hydrogen production coupled with Canada’s nuclear reactors.

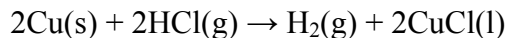
2. Copper-Chlorine (Cu-Cl) Cycle

The Cu-Cl thermochemical cycle uses a series of reactions to achieve the overall splitting of water into hydrogen and oxygen:



Steps in the Cu-Cl cycle and a possible realization of the cycle are shown in Table 1 and Fig. 1.

A possible realization of the Cu-Cl cycle is shown in Fig. 1. The primary components of the cycle are five interconnected reaction vessels, with intermediate heat exchangers (see schematic). Step 1 in the Cu-Cl cycle is the H₂ production step, which occurs at 430–475°C, characterized by the reaction



In the reactor unit, copper particles enter the mixing chamber, descend along an inclined bed and melt to produce CuCl(l) at the exit. Simultaneously, HCl(g) enters and passes through the chamber to generate H₂(g) in a second exit stream. The reaction process involves three distinct phases and turbulent gas mixing. Some key current technological challenges involve more efficient performance of the mixing chamber and better detailed understanding of particle mixing with co-current liquid and solid particle streams within the chamber, which are both needed to improve the reactor yield of hydrogen.

Table 1. Steps in the Cu-Cl Thermochemical Cycle for Hydrogen Production

Equation	Reaction	Temp. Range (°C)	Feed/Output*	
1	$2\text{Cu(s)} + 2\text{HCl(g)} \rightarrow 2\text{CuCl(l)} + \text{H}_2\text{(g)}$	430 - 475	Feed: Output:	Electrolytic Cu + dry HCl + Q H ₂ + CuCl(l) salt
2	$2\text{CuCl(s)} \rightarrow 2\text{CuCl(aq)} \rightarrow \text{CuCl}_2\text{(aq)} + \text{Cu(s)}$	Ambient (electrolysis)	Feed: Output:	Powder/granular CuCl and HCl + V Electrolytic Cu and slurry containing HCl and CuCl ₂
3	$\text{CuCl}_2\text{(aq)} \rightarrow \text{CuCl}_2\text{(s)}$	>100	Feed: Output:	Slurry containing HCl and CuCl ₂ + Q Powder/granular CuCl ₂ + H ₂ O/HCl vapours
4	$2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CuO*CuCl}_2\text{(s)} + 2\text{HCl(g)}$	400	Feed: Output:	Powder/granular CuCl ₂ + H ₂ O(g) + Q Powder/granular CuO*CuCl ₂ + 2HCl (g)
5	$\text{CuO*CuCl}_2\text{(s)} \rightarrow 2\text{CuCl(l)} + 1/2\text{O}_2\text{(g)}$	500	Feed: Output:	Powder/granular CuO* CuCl ₂ (s) + Q Molten CuCl salt + oxygen

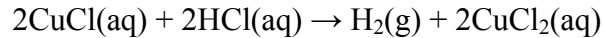
* Q denotes thermal energy, and V electrical energy.

Step 2 of the Cu-Cl cycle may be implemented by means of an electrochemical cell, which produces solid copper particles as input for Step 1 via the process



CuCl(s) enters the unit and copper particles exit on a conveyer. Important parameters include the chemical kinetics in the electrochemical cell, as a function of temperature, pressure and compositions. Incoming solid CuCl streams from Steps 1 and 5 pass through heat exchangers, before entering the electrochemical cell under ambient conditions. Due to the high temperature and corrosive fluids, new innovations in conventional heat exchanger technologies are needed to permit fluid processing in the extreme operating conditions. Extensions of conventional heat exchangers to relevant operating conditions are needed, including appropriate heat transfer correlations, and pressure drop and friction coefficients of working fluids in the Cu-Cl pilot plant.

In the electrochemical step, an aqueous CuCl solution reacts in an electrochemical cell to produce solid copper and aqueous CuCl₂. Solid particles exiting from the base are collected and transported by a copper conveyor or screw propeller to the hydrogen production chamber. As an adaptation of silver-refining technology, a current concept of an electrochemical device (based on a Moebius cell) would be prohibitively expensive, excessively large, and too energy intensive. Production of copper particles is substantially different from a Moebius cell developed originally for the silver refining industry. However, the existing Moebius technology serves as a useful basis upon which research can develop new equipment with better performance. AECL [15, 23] is investigating modification of the Cu-Cl cycle, in order to reduce the challenges involved in solid handling by direct electrolysis of CuCl(aq) and HCl(aq) to produce hydrogen, as per the following reaction:



The above reaction, if successful, will replace steps 1 and 2 of the Cu-Cl cycle.

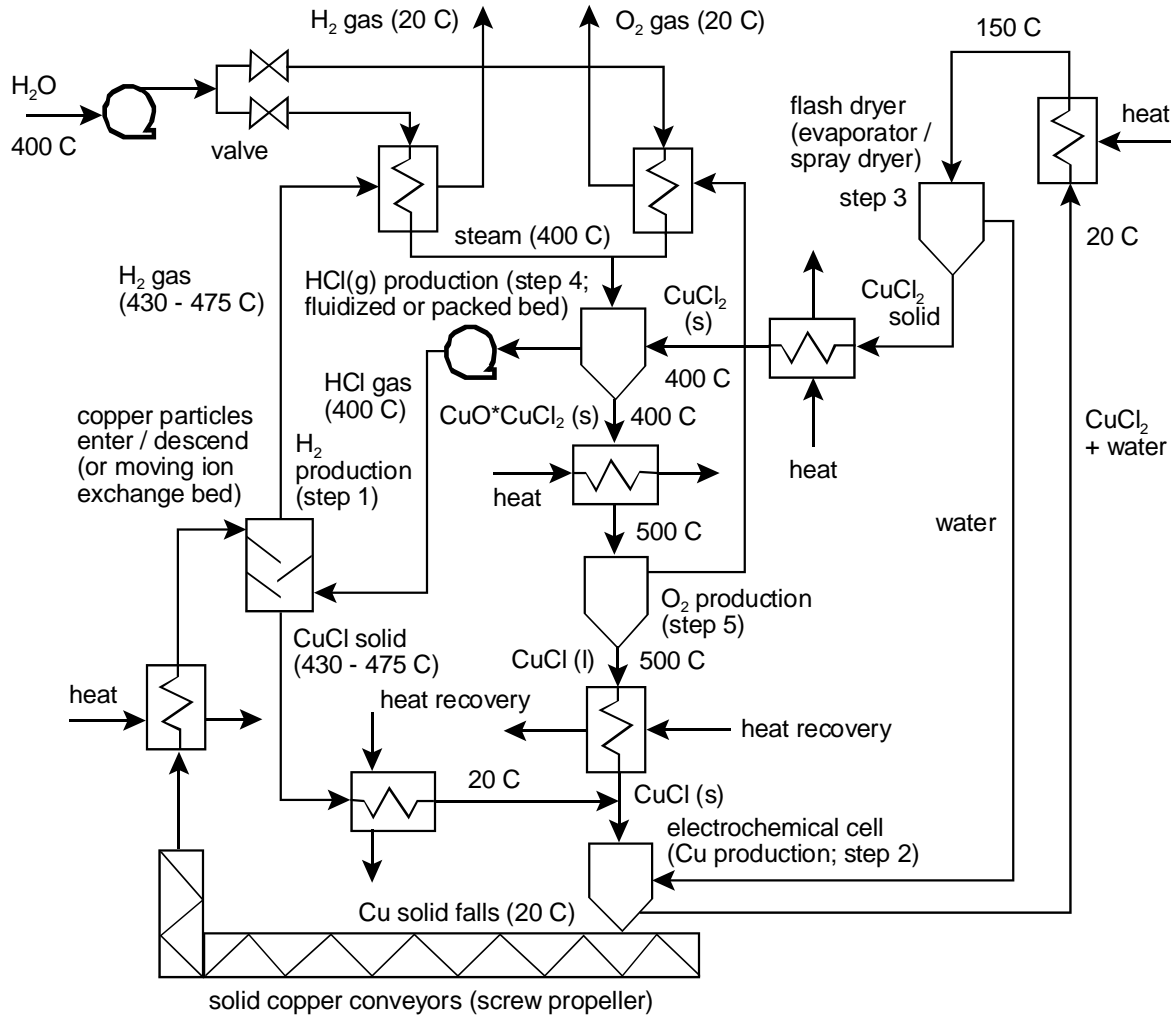


Figure 1 – Conceptual layout of a copper-chlorine (Cu-Cl) cycle.

In Step 3 (flash dryer) of the Cu-Cl cycle, an aqueous CuCl_2 stream exiting from the electrochemical cell is preheated to 150°C , before entering the flash dryer to produce solid $\text{CuCl}_2(\text{s})$, which is required for Step 4. The device must add sufficient heat to remove the water and recover solid CuCl_2 . New innovations can develop alternatives to reduce costs and improve efficiency of the evaporation process for CuCl_2 particle production. For example, a new method to pressurize the liquid stream sufficiently to atomize droplets through a pressure-reducing nozzle in the spray system would enhance the device's performance. The liquid phase flashes due to a sudden pressure drop.

Step 4 in the cycle produces $\text{HCl}(\text{g})$ at 430°C in a fluidized bed reactor, via the process



In this step, high temperature steam and solid CuCl_2 particles mix to produce the two exit streams. Steam enters a bed of $\text{CuCl}_2(\text{s})$ particles supplied from Step 3 (flash dryer). $\text{HCl}(\text{g})$ and $\text{CuO} \cdot \text{CuCl}_2$ solid particles leave the reactor. The $\text{HCl}(\text{g})$ supplies the hydrogen production step (Step 1), while the exiting particles supply an oxygen production reactor (Step 5), which implements the process:



Since $\text{CuCl}_2(\text{s})$ and $\text{CuO} \cdot \text{CuCl}_2(\text{s})$ are sparingly soluble in dense supercritical steam, which may cause poisoning of catalyst surfaces, further studies are needed to determine the solubilities of these components in a mixture of steam and $\text{HCl}(\text{g})$.

Heat exchangers represent an important component within the Cu-Cl cycle. Between each step of the Cu-Cl plant, heat exchangers are needed for heat input or heat recovery and fluid transport to different portions of the thermochemical cycle. The oxygen production step has the highest temperature requirement (500°C) in the cycle. Since temperature drops are experienced across each heat exchanger, the inflow stream to the oxygen reactor unit must exceed 500°C . Furthermore, multiple heat exchangers are needed between the heat source and the oxygen reactor (Step 5), through an intermediate loop. Heat supply is required at various temperatures throughout the cycle, so new innovations are needed to develop an effective series arrangement of heat exchangers to minimize heat losses. In particular, an intermediate loop with several heat exchangers in series is needed to give progressively higher temperatures. Further research is needed to determine how flow rates, temperatures and fluid streams should be most effectively partitioned for each step of the Cu-Cl cycle. Also, heat losses must be identified and evaluated throughout the piping network, with new methods developed for heat recovery.

Several types of fluid devices are used throughout the hydrogen plant, including the electrochemical cell, heat exchangers, pumps, valves, pipes and blowers (for gases). Certain components require substantial modifications of existing technologies with new materials to become economically viable in extreme operating conditions of high-temperature corrosive fluids. For example, common refractory materials for heat exchangers have poor thermal conductivity.

Also, high performance metal alloys cannot withstand corrosive fluids over a long duration. High temperature alloys with coatings of silicone based ceramics appear promising in this regard, but their thermal behavior and surface interactions in high-temperature multiphase conditions must be studied. Further data is needed to better understand the functionality of these materials with the working fluids in the Cu-Cl cycle. This includes thermal behavior, mechanical stresses, fracture toughness, strength and corrosion resistance over time. Improvements to existing equipment can then be achieved through new materials developed specifically for operating conditions in the Cu-Cl cycle.

Exergy analysis can be used to identify efficiencies and thermodynamic losses in the overall process and its steps. Exergy losses occur through both waste exergy emissions and internal exergy destructions. Exergy destruction is a valuable parameter for identifying locations and magnitudes of efficiency losses. For instance, one of the authors (Rosen) carried out a thermodynamic analysis of hydrogen production with thermochemical water decomposition using the Ispra Mark-10 Cycle [24]. Although that process differs from the one considered here, the insights gained via exergy analysis were clearly illustrated.

3. Discussion and Conclusions

Worldwide demand for oil will soon outpace worldwide production capabilities. This critical turning point in modern civilization (called the global “Peak Oil”) could have analogous implications as gradual dehydration of a human body. Since the human body is about 70 percent water and water is so crucial to human life, even a small loss of water can be fatal. In a similar way, modern society will not need to deplete its entire reserve of oil before it begins to suffer drastically. In addition to transportation, nearly every step of modern food production is fossil fuel and petroleum powered. Modern society has developed an extreme dependence on petroleum, which is an increasingly scarce commodity. Also, burning of fossil fuels emits harmful greenhouse gases that contribute to climate change. As a result, it is well known that modern society’s dependence on petroleum is unsustainable, both economically and environmentally. Unlike fossil fuels, hydrogen is a sustainable and clean energy carrier, which is widely believed to be the world’s next-generation fuel. Ontario and other provinces have already begun to move towards a hydrogen-fueled economy. For example, the HyLYZER refueling station at Exhibition Place in Toronto is part of Toronto’s Hydrogen Village. The station produces about 65 kg of hydrogen per day using wind energy, which can supply the daily hydrogen needs for about 20 vehicles.

The predominant existing process for larger scale hydrogen production is steam-methane reforming (SMR). Unfortunately, SMR is a carbon-based technology that emits a primary greenhouse gas (carbon dioxide). In contrast, nuclear-based hydrogen production does not emit greenhouse gases. Nuclear heat can be supplied abundantly for large-scale capacities of hydrogen production. Adoption of fuel cell vehicles is expected to be an important driving force for large-scale hydrogen consumption in the near future. Although it is difficult to predict when fuel cell vehicles will achieve a significant market share, it is widely believed that hydrogen will become the primary fuel in the future transportation sector. This paradigm shift will require large-scale production of hydrogen, which can be achieved with nuclear energy. The 2010s decade could well mark the beginning of the “Hydrogen Age”.

Unlike other sustainable energy resources (such as wind power), nuclear energy provides a consistent large-scale capacity for hydrogen production. Nuclear energy for hydrogen production is an innovative “green” idea that can take a significant step towards saving modern society from climate change, irreversible damage to worldwide ecosystems and possibly our planet itself.

Acknowledgements

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Author Biographies

Marc A. Rosen is Professor and founding Dean of the Faculty of Engineering and Applied Science at the University of Ontario Institute of Technology (UOIT) in Oshawa, Canada. Prior to this appointment, he was a professor in the Department of Mechanical, Aerospace and Industrial Engineering at Ryerson University in Toronto, where he served as department Chair and Director of Aerospace Engineering. He has also worked for such organizations as Imatra Power Company in Finland, Argonne National Laboratory near Chicago, and the Institute for Hydrogen Systems, near Toronto. He is President-elect of the Engineering Institute of Canada, and has served as President of the Canadian Society for Mechanical Engineering. Dr. Rosen has received numerous honours, including an Award of Excellence in Research and Technology Development from the Ontario Ministry of Environment and Energy.

Greg F. Naterer is Professor and Director of Research, Graduate Studies and Development in the Faculty of Engineering and Applied Science at UOIT in Oshawa, Canada. Prior to this appointment, he was a Professor in the Department of Mechanical and Manufacturing Engineering at the University of Manitoba in Winnipeg. His research interests include hydrogen production, energy conversion, heat transfer and microfluidics. His background includes past collaborative work and consulting for projects with Honeywell Aerospace, Manitoba Hydro, NB Power, Westland Helicopters, Bombardier, United Space Alliance, U.S. Air Force Research Laboratory and others. He has co-developed 2 patents and supervised numerous M.Sc. and Ph.D. students. Dr. Naterer is a Fellow of the Canadian Society for Mechanical Engineering and an Associate Fellow of the American Institute of Aeronautics and Astronautics.

Ramesh Sadhankar is Manager of Hydrogen Isotopes Technology at AECL. He has published extensively on nuclear/hydrogen topics, including heavy water production from hydrogen sources, electrolysis and hydrogen production for heavy oil recovery. He made key contributions to integration of water vapour electrolysis with an advanced CANDU reactor for hydrogen production. Under Dr. Sadhankar's leadership, AECL has become widely recognized around the world for its expertise in separating hydrogen isotopes. For example, special "wet-proofed" catalysts have been developed for water/hydrogen exchange.

Sam Suppiah is Senior Scientist/Engineer at AECL, Chalk River Laboratories. He has numerous widely-referenced publications and conference presentations, particularly involving chemical engineering of catalytic reactions, hydrogen and related technologies. Effective catalysis in certain thermochemical reactions of the Cu-Cl cycle (discussed in this paper) is a key issue in the overall energy efficiency of nuclear-based hydrogen production from water decomposition. In addition to catalysis, Dr. Suppiah has made significant contributions to advances in heavy water production and fuel cell technologies