

Recent Canadian advances in the thermochemical Cu-Cl cycle for nuclear hydrogen production

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Abstract

This paper presents recent Canadian advances in nuclear-based production of hydrogen with the thermochemical copper-chlorine (Cu-Cl) cycle. Current collaboration between UOIT, Atomic Energy of Canada Limited, Argonne National Laboratory and partner institutions is focusing on enabling technologies for the Cu-Cl cycle, through the Generation IV International Forum. This paper presents the recent advances in the development of individual reactor designs, thermal efficiency, process developments, corrosion resistant materials and linkage between nuclear and hydrogen plants. The paper provides an overview of latest advances by a Canadian consortium that is collaborating on equipment scale-up for the Cu-Cl cycle.

Introduction

A key future challenge of the hydrogen economy will be sustainable large-scale production of hydrogen at low cost. This paper presents the latest Canadian research in sustainable hydrogen production from nuclear energy, for a carbon-free source of hydrogen. Currently, large quantities of hydrogen are needed by many industrial sectors, such as the Canadian oil sands (bitumen upgrading), agricultural (ammonia for fertilisers) and petroleum product industries. In the transportation sector, it is widely believed that hydrogen will eventually become a dominant energy carrier. Hydrogen is a desirable energy vector because it can be stored and used to generate electricity, either onboard vehicles or stationary power systems (Stevens, 2008).

Thermochemical water splitting is a promising technology for large-scale sustainable production of hydrogen. Using intermediate compounds, a sequence of chemical and physical processes decompose water into hydrogen and oxygen, without releasing any pollutants externally to the atmosphere. The intermediate compounds are recycled internally within a closed loop. Over 200 thermochemical cycles have been identified previously (Lewis, 2006; McQuillan, 2002). But very few have progressed beyond theoretical calculations to working experimental demonstrations that establish scientific and practical feasibility of the thermochemical processes.

The sulphur-iodine (S-I) cycle is a leading process where equipment has been scaled up to a pilot plant level. Active development is underway at General Atomics (USA), Sandia National Laboratory (USA), Japan Atomic Energy Agency (JAEA), CEA (France) and others (Sakurai, 2000; Schultz, 2003). Approximately 30 litres/hr of hydrogen were produced from an S-I pilot facility by JAEA (Sakurai, 2000). It aims to scale up the S-I cycle to much larger production capacities that could eventually support a significant volume of fuel cell vehicles. Korea (KAERI), China and Canada (Sadhankar, 2005) are also advancing towards large-scale production of hydrogen from nuclear energy. This paper provides an overview of Canada's latest advances in thermochemical hydrogen production, with particular focus on the copper-chlorine (Cu-Cl) cycle.

Current collaboration between UOIT, Atomic Energy of Canada Limited (AECL), Argonne National Laboratory and partner institutions, is focusing on enabling technologies for the Cu-Cl cycle, through the Generation IV International Forum (GIF) (Sadhankar, 2007). This paper focuses on recent Canadian developments to scale up these enabling technologies to larger capacities of hydrogen production with the Cu-Cl cycle. Thermal efficiency and individual process developments within the Cu-Cl cycle will be presented, as well as corrosion resistant materials and linkage between nuclear and hydrogen plants.

Overview of the Cu-Cl cycle

The Cu-Cl cycle uses a set of reactions to achieve the overall splitting of water into hydrogen and oxygen as follows: $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$. The Cu-Cl cycle decomposes water into hydrogen and oxygen through intermediate copper and chloride compounds. These chemical reactions form a closed internal loop that recycles all chemicals on a continuous basis, without emitting any greenhouse gases. Process steps in the Cu-Cl cycle are shown in Table 1.

Thermochemical process for hydrogen production

Step 1 in the Cu-Cl cycle is the H_2 production step, which occurs at 430-475°C, characterised by the reaction $2\text{Cu}(\text{s}) + 2\text{HCl}(\text{g}) \rightarrow \text{H}_2(\text{g}) + 2\text{CuCl}(\text{l})$ (see Table 1). Copper particles enter the reactor vessel and react with HCl gas to generate H_2 gas and molten CuCl. Scientific feasibility of this chemical reaction has been demonstrated experimentally by Serban, *et al.* (2004). The conversion of HCl to hydrogen was found to be a function of Cu particle size as shown in Figure 2 (Serban, 2004). The yields varied between 65 and 100%, with complete conversion in the case of 3- μm Cu particles. The 100- μm Cu particles were obtained in an electrolytic cell by disproportionating CuCl to Cu and CuCl_2 . The size and shape of electrolytic copper particles were affected by the operating parameters of the cell. To directly measure the kinetics of the reaction between HCl and Cu, the reaction rates were measured at four different temperatures (400, 425, 450 and 475°C).

Table 1: Steps and chemical reactions in the Cu-Cl cycle

Step	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: Electrolytic Cu + dry HCl + Q Output: $\text{H}_2 + \text{CuCl(l)}$ salt
2	$2\text{CuCl(s)} \rightarrow 2\text{CuCl(aq)} \rightarrow \text{CuCl}_2\text{(aq)} + \text{Cu(s)}$	Ambient (electrolysis)	Feed: Powder/granular CuCl and HCl + V Output: Electrolytic Cu and slurry containing HCl and CuCl_2
3	$\text{CuCl}_2\text{(aq)} \rightarrow \text{CuCl}_2\text{(s)}$	<100	Feed: Slurry containing HCl and $\text{CuCl}_2 + \text{Q}$ Output: Granular $\text{CuCl}_2 + \text{H}_2\text{O/HCl}$ vapours
4	$2\text{CuCl}_2\text{(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CuO}^*\text{CuCl}_2\text{(s)} + 2\text{HCl(g)}$	400	Feed: Powder/granular $\text{CuCl}_2 + \text{H}_2\text{O(g)} + \text{Q}$ Output: Powder/granular $\text{CuO}^*\text{CuCl}_2 + 2\text{HCl(g)}$
5	$\text{CuO}^*\text{CuCl}_2\text{(s)} \rightarrow 2\text{CuCl(l)} + 1/2\text{O}_2\text{(g)}$	500	Feed: Powder/granular $\text{CuO}^*\text{CuCl}_2\text{(s)} + \text{Q}$ Output: Molten CuCl salt + oxygen

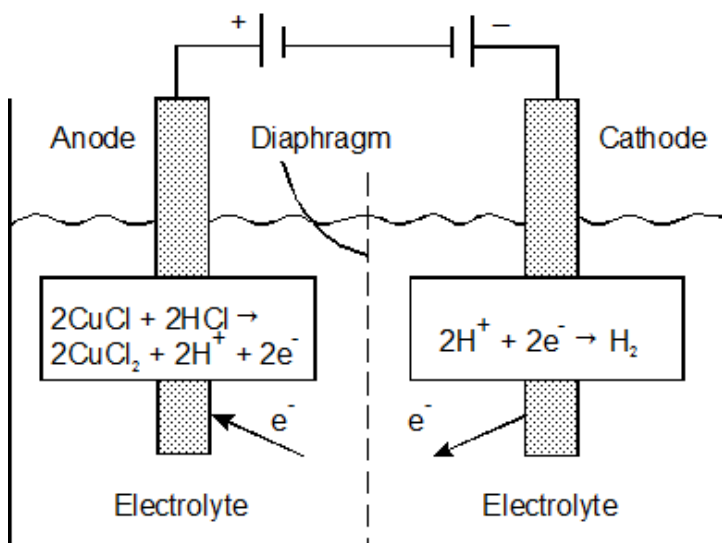
Notes: Alternative four-step cycle combines above Steps 1 and 2 to produce hydrogen directly as follows: $2\text{CuCl(aq)} + 2\text{HCl(aq)} \rightarrow \text{H}_2\text{(g)} + 2\text{CuCl}_2\text{(aq)}$.

Q = thermal energy, V = electrical energy.

Electrochemical process of hydrogen production (four-step Cu-Cl cycle)

An electrochemical process is required, either separately from the hydrogen reaction (separate Steps 1 and 2 in Table 1), or combining electrochemical and thermochemical processes together to produce hydrogen directly via electrolysis. Past studies demonstrate the scientific feasibility of the latter process of cuprous chloride/HCl electrolysis (Suppiah, 2008). Oxidation of cuprous chloride (CuCl) during an electrochemical reaction occurs in the presence of hydrochloric acid (HCl) to generate hydrogen. The cuprous ion is oxidised to cupric chloride at the anode, and the hydrogen ion is reduced at the cathode (see Figure 1).

AECL has demonstrated experimentally a CuCl electrolyser in which hydrogen is produced electrolytically at the cathode and Cu(I) is oxidised to Cu(II) at the anode (Suppiah, 2008).

Figure 1: Schematic of the electrochemical cell

Electrochemical process of copper production (five-step Cu-Cl cycle)

A fundamental investigation of the anode electrode materials has been undertaken by Easton and Santhanam (Suppiah, 2008) for the five-step cycle (see Table 1). Their experiments employed three-electrode cell measurements using various working electrode materials. A 1 mM solution of

CuCl in 1.5 M HCl, saturated calomel electrode (SCE) as the reference electrode, and Pt auxiliary electrode were used. The experiments focused on the influence of the electrode materials on the anode electrode kinetics. The primary goal was to determine if there is any performance gain by employing a noble metal based electrode material. Two materials were chosen: glassy carbon (GC) and Pt 5 mm diameter rotating disk electrodes (RDE). Cyclic voltammetry (CV) was performed with a stationary and rotating working electrode. No difference was observed in the potential requirements to drive the reaction on either a glassy carbon or Pt electrode surface. However, the limiting current densities with a Pt electrode surface were approximately three times larger than those achieved with a glassy carbon electrode. Voltammetric measurements at different electrode rotation rates showed the typical Levich behaviour (limiting current proportional to square root of rotation rate) for both Pt and GC.

Drying of aqueous cupric chloride

Step 3 of the Cu-Cl cycle is the drying step as expressed by: $2\text{CuCl}_2(\text{aq}) \rightarrow 2\text{CuCl}_2(\text{s})$ (see Table 1). An aqueous CuCl_2 stream exiting from the electrochemical cell is supplied to a spray dryer to produce solid $\text{CuCl}_2(\text{s})$, which is required for a subsequent hydrolysis step that produces copper oxychloride ($\text{CuO} \cdot \text{CuCl}_2$) and HCl gas. The apparatus must add sufficient heat to evaporate and remove the water. The process is an energy-intensive step within the Cu-Cl cycle. Although the amount of heat required for the drying step is much higher than other steps in the cycle, it occurs at a lower temperature (lower quality) and therefore with heat that is more readily available. Within the drying step, the energy requirement increases from one to five times higher for slurry feed to solution, respectively, depending on the CuCl_2 concentration. The overall cycle efficiency is higher with slurry feed in the drying step than drying of aqueous solution. Spray drying is an efficient method of water removal due to the relatively large surface area available for heat and mass transfer, provided the liquid atomises into sufficiently small droplets (order of a hundred microns). Experimental studies have been conducted to demonstrate the scientific feasibility of drying aqueous cupric chloride to produce solid CuCl_2 particles (Suppiah, 2008). Spray drying is a unique process that involves both particle formation and drying. The powder characteristics can be controlled and powder properties maintained constant throughout a continuous operation.

Hydrolysis reaction for copper oxychloride production

The following hydrolysis reaction occurs within the Cu-Cl cycle (see Table 1): $\text{H}_2\text{O}(\text{g}) + 2\text{CuCl}_2(\text{s}) \rightarrow \text{Cu}_2\text{OCl}_2(\text{s}) + 2\text{HCl}(\text{g})$. The reaction is an endothermic non-catalytic gas-solid reaction that operates between 350 and 400°C. The solid feed to the hydrolysis reaction is cupric chloride, which comes from the dried CuCl_2 product of Step 2 (electrolysis). Aqueous cupric chloride is dried to produce CuCl_2 solids, which are then transported to the hydrolysis chamber and reacted with superheated steam to produce copper oxychloride solid and hydrochloric gas. Recent developments have examined the transport phenomena of reactive spray drying (a combination of the hydrolysis and drying processes), as well as a non-catalytic gas-solid reaction that separates drying and chemical reaction processes during hydrolysis.

Ferrandon, *et al.* (2008) have demonstrated experimentally the scientific practicality of the hydrolysis reaction to produce HCl gas and solid copper oxychloride. In order to vary the particle sizes, the material was first dried in a dessicator, crushed and sieved to the desired particle sizes and then re-hydrated. During the hydrolysis experiments, the sample was heated rapidly (within 10 minutes) in humidified Ar to the reaction temperature, between 300 and 400°C, and then held at the test temperature for a fixed period.

Molten salt reactor for oxygen production

The oxygen production step (Step 5; see Table 1) receives solid feed of $\text{CuO} \cdot \text{CuCl}_2$ and produces O_2 gas and liquid cuprous chloride. The reaction is given by $\text{CuO} \cdot \text{CuCl}_2(\text{s}) = 2\text{CuCl}(\text{molten}) + 0.5\text{O}_2(\text{gas})$ at 530°C. Gas species leaving the oxygen reactor include oxygen gas and potentially impurities of products from side reactions, such as CuCl vapour, chlorine gas, HCl gas (trace amount) and H_2O vapour (trace amount). The substances exiting the reactor are molten CuCl, potentially solid CuCl_2 from the upstream

reaction (CuCl_2 hydrolysis step), due to the incomplete decomposition of CuCl_2 at a temperature lower than 750°C , as well as reactant particles entrained by the flow of molten CuCl . In the oxygen reactor, copper oxychloride particles decompose into molten salt and oxygen. The reactant particles absorb decomposition heat from the surrounding molten bath.

Serban, *et al.* (2004) have demonstrated experimentally the scientific practicality of the oxygen production reaction at a small test-tube scale. Recent efforts have focused on experimental work that scales up equipment beyond small test-tubes to much larger reactors. Several design issues must be addressed at these larger flow capacities (Naterer, 2008; Wang, 2008). For example, aggregation into blocks of $\text{CuO}\cdot\text{CuCl}_2$ particles may occur during the process of removing, conveying and feeding of particles. The aggregation may choke or clog the feeder and cause sudden spouting of particles.

Also, embedded particles of CuCl_2 from the upstream hydrolysis reactor may exist. The existence of CuCl_2 particles in $\text{CuO}\cdot\text{CuCl}_2$ would lead to undesirable products and side reactions, i.e. CuCl_2 may decompose to CuCl and Cl_2 gas. If particles enter the reactor at a temperature lower than 430°C , a difficulty with the presence of bubbles in the molten salt may occur. Some CuCl vapour might condense and molten CuCl might solidify around the $\text{CuO}\cdot\text{CuCl}_2$ particles. If an aggregation develops with particles, molten salt and bubbles, the contact area between a reactant particle and heating medium (molten CuCl) will decrease and the aggregations may float along the surface of the molten salt. This would deter the decomposition of reactant particles and potentially lead to choking of the reactor (a major safety concern).

Thermal and life cycle analyses of the Cu-Cl cycle

Water is decomposed into hydrogen and oxygen as the net result of the Cu-Cl thermochemical cycle. The cycle involves five steps, as listed in Table 1: 1) $\text{HCl}(\text{g})$ production using equipment such as a fluidised bed; 2) oxygen production; 3) copper (Cu) production; 4) drying; 5) hydrogen production. Recent studies by Chukwu, *et al.* (2008) and Orhan, *et al.* (2008) have analysed the overall thermal efficiency of the five-step Cu-Cl cycle. The efficiency of the cycle versus temperature was analysed for three cases: $x = 0.2, 0.3$ and 0.4 , where x refers to the fraction of heat loss to heat input to the cycle. The calculated efficiencies varied from 42 to 55% at 550°C .

A life-cycle analysis (LCA) was also conducted (Suppiah, 2008). One objective of the LCA was to identify environmental issues associated with nuclear-produced hydrogen and determine which are the most critical. The study focused on identifying energy, materials, and waste in/out of the system for the nuclear-hydrogen plant. Sensitivity analyses were performed to investigate what future improvements should be made, and identify specific areas where significant contributions would improve the overall environmental impact.

Thermochemical data for working fluids

Accurate self-consistent thermochemical data for the copper chlorides up to 200°C are required, in order to improve solubility calculations and electrochemical modelling capabilities for Aspen Plus and OLI software. Experimental work has been initiated at the University of Guelph, Canada and UOIT to determine a comprehensive thermochemical database, for solubility limits of OMIT, and aqueous cupric chloride versus chloride concentration and temperature using UV-VIS spectroscopy (Suppiah, 2008). The chloride ion is obtained by adding LiCl OMIT. The conditions of tests are primarily $25\text{-}200^\circ\text{C}$, up to 20 bars. Specialised equipment for this task is needed to reach elevated temperatures and pressures, because cupric chloride is chemically aggressive, and because changes in the solution concentrations must be made precisely. A titanium test cell has been custom made, including a UV-VIS spectrometer with sapphire windows, HPLC pumps and an automated injection system. The data acquired will be combined with past literature data for the cuprous chloride system to develop a self-consistent database for the copper (I) and copper (II) chloride-water systems.

Development of corrosion resistant materials

One of the challenging environments for materials to resist corrosion is the copper oxychloride decomposition reactor. In this reactor, a gaseous stream of pure oxygen is produced at temperatures

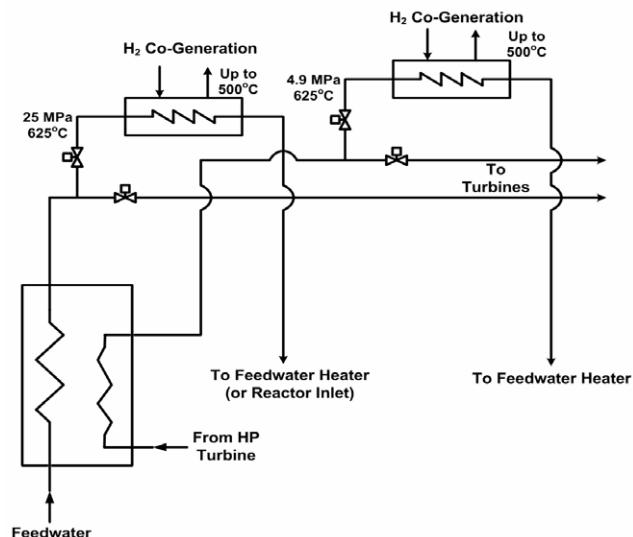
between 450 and 550°C. This stream may contain HCl or Cl₂ gas impurities and small quantities of entrained copper oxychloride. The impurity concentrations should be small because the hydrolysis reactor (feeding the decomposition reactor) will operate at negative pressures in order to enhance the performance of the hydrolysis reactor. High Ni-Cr alloys were identified as the most promising materials of construction for this environment because of their corrosion resistance in high temperature oxidising environments.

The FACTSage thermochemical database was used to identify the thermodynamically stable phases that could exist in a system comprised of a pure metal, oxygen, HCl and Cl₂ at 500°C (Suppiah, 2008). The predominant Fe, Ni, Cu and Cr phases in an O₂/HCl/Cl₂ environment were determined. The equilibrium reaction boundary was plotted as a function of the partial pressures of O₂ and HCl, for a constant Cl₂ partial pressure. The resulting predominance diagrams were plotted over an O₂ and HCl partial pressure range of 10⁻²⁰ to 1 atm for Cl₂ partial pressures between 10⁻⁶ and 1 atm. The predominant Ni and Cr species are solids, suggesting that a corrosion resistant protective layer could be formed on the metal.

Linkage of nuclear and hydrogen plants

The Generation IV nuclear reactor, Super-critical Water Reactor (SCWR) is being designed to operate at higher temperatures (550-625°C) that can facilitate co-generation of electricity and hydrogen. SCWR is expected to co-generate electricity and hydrogen uniformly throughout the year, independently of the electrical load. With an electrical load decrease, the SCWR could produce more hydrogen and vice versa. Using high temperature heat from a nuclear power plant to heat water in the hydrogen production loop is a promising option with SCWR. Heat exchangers of a recuperator-type would be used for this purpose (see Figure 2). Currently, UOIT is collaborating with AECL on various plant configurations for co-generation of electricity and hydrogen (Mokry, 2009).

Figure 2: Single-reheat cycle with co-generation of hydrogen in a nuclear power plant (Mokry, 2009)



Conclusions

This paper has presented the recent Canadian advances in nuclear-based hydrogen production. The Cu-Cl cycle was identified by Atomic Energy of Canada Limited, AECL [Chalk River Laboratories (CRL)], as the most promising cycle for thermochemical hydrogen production with the Generation IV nuclear reactor Super-critical Water Reactor (SCWR). Recent developments of enabling technologies for the Cu-Cl cycle were presented, particularly the individual reactor designs, thermochemical properties, advanced materials and linkage between nuclear and hydrogen plants.

Acknowledgements

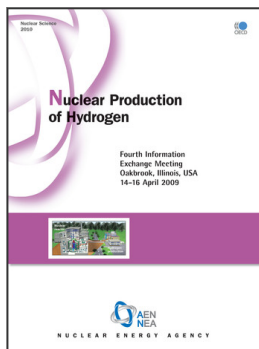
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