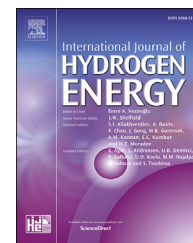


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Advances in unit operations and materials for the Cu–Cl cycle of hydrogen production



G.F. Naterer ^{a,*}, S. Suppiah ^b, M.A. Rosen ^c, K. Gabriel ^c, I. Dincer ^c,
O.A. Jianu ^c, Z. Wang ^e, E.B. Easton ^h, B.M. Ikeda ^d, G. Rizvi ^c, I. Piro ^d,
K. Pope ^a, J. Mostaghimi ^f, S.N. Lvov ^g

^a Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5, Canada

^b Hydrogen Isotopes Technology Branch, Canadian Nuclear Laboratories, Chalk River, Ontario, K0J 1J0, Canada

^c Faculty of Engineering and Applied Science, University of Ontario Institute of Technology (UOIT), 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada

^d Faculty of Energy Systems and Nuclear Science, University of Ontario Institute of Technology (UOIT), 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada

^e College of Energy, Xiamen University, Xiamen City, Fujian Province, 361102, China

^f Centre for Advanced Coatings Technologies, University of Toronto, Toronto, Ontario, M5S 3E5, Canada

^g Pennsylvania State University, 207 Hosler Building, University Park, PA, 16802, USA

^h Faculty of Science, University of Ontario Institute of Technology (UOIT), 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada

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ABSTRACT

This paper presents recent advances by an international team of five countries – Canada, U.S., China, Slovenia and Romania – on the development and scale-up of the copper–chlorine (Cu–Cl) cycle for thermochemical hydrogen production using nuclear or solar energy. Electrochemical cell analysis and membrane characterization for the CuCl/HCl electrolysis process are presented. Constituent solubility in the ternary CuCl/HCl/H₂O system and XRD measurements are reported in regards to the CuCl₂ crystallization process. Materials corrosion in high temperature copper chloride salts and performance of coatings of reactor surface alloys are examined. Finally, system integration is examined, with respect to scale-up of unit operations, cascaded heat pumps for heat upgrading, and linkage of heat exchangers with solar and nuclear plants.

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* Corresponding author. Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5, Canada.

E-mail address: gnaterer@mun.ca (G.F. Naterer).

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Introduction

The copper–chlorine (Cu–Cl) cycle of thermochemical water splitting is a promising method for large-scale hydrogen production from nuclear, solar or other thermal energy sources [1,2]. It offers significant advantages over other thermochemical cycles such as lower temperature operating requirements (below 550 °C) and the ability to effectively utilize low-grade waste heat for endothermic processes. It consists of four main steps: 1) hydrolysis, 2) thermolysis, 3) electrolysis, and 4) water separation (e.g. crystallization) [3–5] – which together split water into hydrogen and oxygen through intermediate copper and chlorine compounds. Other thermochemical cycles have been identified in a Nuclear Hydrogen Initiative [6], and this includes the sulfur-iodine [7], cerium-chlorine [8] and iron-chlorine [9] cycles. Funk [10] and Naterer et al. [11] presented comprehensive reviews of hydrogen production by thermochemical water decomposition.

In the CuCl/HCl electrolysis step, oxidation of copper (I) chloride (CuCl) during an electrochemical reaction occurs in the presence of hydrochloric acid (HCl) to generate hydrogen. The Cu(I) ion is oxidized to Cu(II) at the anode, and the hydrogen ion is reduced at the cathode. This CuCl/HCl electrolysis process was first demonstrated for a long duration by Canadian Nuclear Laboratories (CNL) [12,13]. Continuous electrolysis for 1600 h was demonstrated in a cell operating at a voltage of about 0.7 V at 45 °C [3]. Significant developments in CuCl/HCl electrolysis have also been demonstrated experimentally at Pennsylvania State University [14] and the University of Ontario Institute of Technology [15]. Various membranes have been investigated to mitigate the adverse effects of copper crossover [16]. Nafion-based and porous polyethylene (PPE) membranes have been found to inhibit copper transport with HCl as a catholyte [17,18]. It was shown that the current efficiency is more than 95% when the cell potential is stable at 0.7 V, and the current density is 0.5 A cm⁻² for a 36 h test using a Nafion-based membrane.

Early studies of the Cu–Cl cycle used a spray drying process to extract solid CuCl₂ from the aqueous solution exiting the electrochemical cell. However, this was subsequently determined to be energy intensive, and led to undesirable vaporization of other compounds; so alternatives such as crystallization were explored. Wang et al. [19] reported on the integration of electrolysis and hydrolysis steps using crystallization of CuCl₂ particles from the electrochemical cell. Leray [20] and Abdel [21] had previously examined the growth kinetics of hydrated copper (II) chloride (CuCl₂ · n_hH₂O, where n_h is the number of hydrated water molecules) and the recovery of cupric chloride from spent solutions. Crystallization of CuCl₂ is normally less energy intensive than spray drying because ambient air and cooling water can be sufficient for cooling the solution to ambient temperature.

Copper (II) chloride is the oxidation product of copper (I) chloride, hence copper (II) and copper (I) chlorides coexist in the aqueous solution of HCl. The solubility of copper (I) chloride (CuCl) in aqueous hydrochloric acid (HCl) at different molarities and temperatures [22–25] affects the crystallization process. The solubility of solid CuCl in aqueous HCl is much larger than in water [25]. The crystal sizes of the chloro-

complexes and the conversion rates from CuCl to CuCl₂ have been reported by O'Connor et al. [26]. Experiments were performed by Fritz [27] to determine the solubility of copper (I) chloride in various aqueous chlorides and their associated equilibrium constants of formation. A set of virial parameters expressing the activity coefficients of the ions formed by dissolution were found. These past studies found that the solubility of CuCl is increased by the presence of a relatively low concentration of HCl compared to the solubility in water.

The hydrolysis reaction is an endothermic non-catalytic gas–solid reaction at temperatures between 350 °C and 400 °C where CuCl₂ particles from the crystallization process are reacted with superheated steam to produce copper oxychloride solid (CuOCuCl₂, often denoted as Cu₂OCl₂) and hydrogen chloride (HCl). Extensive experimental studies with a spray reactor heated by a mixture of argon/steam [28,29] were conducted at the Argonne National Laboratory (ANL) to determine the mass flow rate of steam required to produce Cu₂OCl₂. Results indicated that 100% yields of Cu₂OCl₂ could be achieved with an ultrasonic nozzle to inject the reactants into the reactor at about 375 °C. The excess steam required for the heat supply reduces the overall cycle efficiency of the system. Pope et al. [30] examined the use of nitrogen to reduce the steam requirement of the hydrolysis reaction in a fluidized bed reactor. Equilibrium conversion rates, thermophysical properties of compounds, and a gas film layer around the solid CuCl₂ particles are significant factors that influence the hydrolysis reaction [31,32].

Materials of construction are major issues in the Cu–Cl cycle development. Limited data exists in past literature on the corrosion resistance of materials in molten CuCl. The most suitable materials for high temperature and corrosive environments are ceramics, refractory metals, molybdenum and nickel based alloys, graphite based materials, and Hastelloy C. Xie et al. [33] examined the corrosion of carbide/nitride materials in 2.5 mol/L HCl solutions at elevated temperatures. Wu et al. [34] tested mullite specimens in a 10 wt.% NaOH solution at 105 °C and examined a sol–gel coating to improve corrosion resistance. They have identified that the process of forming mullite has a significant impact on its ability to resist corrosion. Sure et al. [35] reported the performance of partially stabilized zirconia (PSZ) with graphite coatings at 600 °C and found that PSZ corroded by adding oxygen to the surface. Experimental findings of the corrosion of graphite in molten LiCl, and graphite powder mixed with 46 wt.% LiCl that were melted to change the molten salt structure, were reported by Kamali and Fray [36]. The corrosion behavior of Hastelloy C276, C-22 and N were examined at 250 and 500 °C in dry molten salt with a composition of 13.4 mol% NaCl, 33.7 mol% KCl and 52.9 mol% ZnCl₂ (Vignaroban et al. [37]). Sellers et al. [38] investigated the corrosion rates of Hastelloy N and 316 stainless Steel immersed for 100 h at 850 °C in a molten salt consisting of 46.5 mol% LiF, 11.5 mol % NaF and 42 mol% KF. Siantar [39] conducted experiments to examine the performance of metallic and ceramic coatings on a base metal exposed to molten CuCl at 500 °C.

A number of other related studies associated with the Cu–Cl cycle were conducted by the international team including exergo-economics using exergy-cost-energy-mass (EXCEM) analysis [40,41], life cycle analysis [42], environmental impacts

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