An overview of R&D activities for the Cu-Cl cycle with emphasis on the hydrolysis reaction

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Abstract

This paper describes the status of the development effort for the Cu-Cl thermochemical cycle. Most of the recent work has been focused on the hydrolysis reaction, which is challenging because of the need for excess steam to achieve high yields. Two types of spray reactors were tested and the ultrasonic nozzle gave excellent results. The conceptual process design for the overall process now includes a spray reactor. Engineering methods to increase efficiency are proposed. Preliminary values for the efficiency and capital costs for producing hydrogen using the Cu-Cl cycle have been calculated.

Introduction

The Cu-Cl thermochemical cycle has been under development for several years. The goal is to achieve a commercially viable method for producing hydrogen at a moderate temperature (~550°C). This chemical process, if successfully developed, could be coupled with several types of heat sources, *e.g.* the supercritical water reactor, the Na-cooled fast reactor or a solar heat source such as the solar power tower with molten salt heat storage. The use of lower temperature processes is expected to place less demand on materials of construction compared to higher (~850°C) temperature processes.

Besides the lower temperature requirement, other positive features of the cycle are the following:

- Proof-of-concept experiments have shown chemical viability and no showstoppers.

- No catalysts are required for the thermal reactions or for the anode reaction in the electrolysis step.

- The preliminary conceptual process design and the corresponding flow sheet have shown an efficiency of 39-41% (LHV). These values depend on assumptions regarding the operability of the electrolyser and the crystalliser, which separates components in the spent anolyte and catholyte.

The three reactions in the cycle are given in Table 1. This representation of the cycle is simplistic as 100% yields and stoichiometric quantities of reagents are assumed for all reactions. The challenge in developing any thermochemical cycle is to determine how to obtain these yields, while reducing the amount of any excess reagent used to drive the reaction as far to the right as possible. This paper will focus on laboratory and reactor design work for the hydrolysis reaction and will also describe the conceptual process design, with special emphasis on the hydrolysis reaction.

**Table 1: Reactions in the Cu-Cl thermochemical cycle**

	Reaction	Temperature, °C
Hydrolysis	$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2 (s) + 2HCl(g)$	340-400
Decomposition	$Cu_2OCl_2 (s) \rightarrow \frac{1}{2} O_2 (g) + 2CuCl(s)$	450-530
Electrolysis	$2CuCl(s) + 2HCl(g) \rightarrow 2CuCl_2 + H_2 (g)$	100

The hydrolysis reaction, $CuCl_2 + H_2O(g) \Leftrightarrow Cu_2OCl_2 + 2HCl(g)$, requires excess steam to obtain high yields. Theoretically, the steam to $CuCl_2$ molar ratio (S/Cu) required for ~100% yield is temperature and pressure dependent. At 375°C, the S/Cu is about 17 at atmospheric pressure. Most of our early fixed bed experiments confirmed that the S/Cu of 15-20 was needed to obtain 60-80% conversion to Cu_2OCl_2. However, the solid products contained up to 25 wt.% CuCl and, in some cases, large amounts of unreacted $CuCl_2$, found agglomerated in the middle of the fixed bed. It was concluded that fixed bed reactor designs provided poor heat and mass transfer. A spray reactor, which offers better mass and heat transfer, was therefore designed, built and tested. The conceptual process design has incorporated a spray reactor design and also includes engineering solutions that mitigate the costs associated with the need for a large excess of steam. These are described below.

Experimental

A schematic of the apparatus is shown in Figure 1. The dimensions of the glass reactor are 12.1 cm (4.75 in) OD, 3 mm wall thickness and 137.2 cm (54 in) long. Two types of injectors were tested: *i)* a "pneumatic" quartz nebuliser, typically used for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses (Glass Expansion); *ii)* an ultrasonic nozzle (Sono-Tek). The pneumatic one requires a sweep gas to create a fine mist of $CuCl_2$ solution while the ultrasonic nozzle uses mechanical vibrations to atomise the solution. The heated zone of the furnace is 91.4 cm (36 in) long. Superheated steam was used to assist heat transfer and was injected either co-currently or counter-currently with the $CuCl_2$ solution. The carrier gas was 99.999% Ar and its flow rate was controlled by mass flow controllers. The liquid flows were controlled by syringe pumps. The $CuCl_2$ solution was made by dissolving 5 g of 99.99% purity $CuCl_2 \cdot 2H_2O$ from Aldrich into 10 g of deionised water.

**Figure 1: Schematic of the nebuliser reactor for the Cu-Cl hydrolysis experiments.
The pneumatic nebuliser is represented at the top of the reactor.**

TC = thermocouple
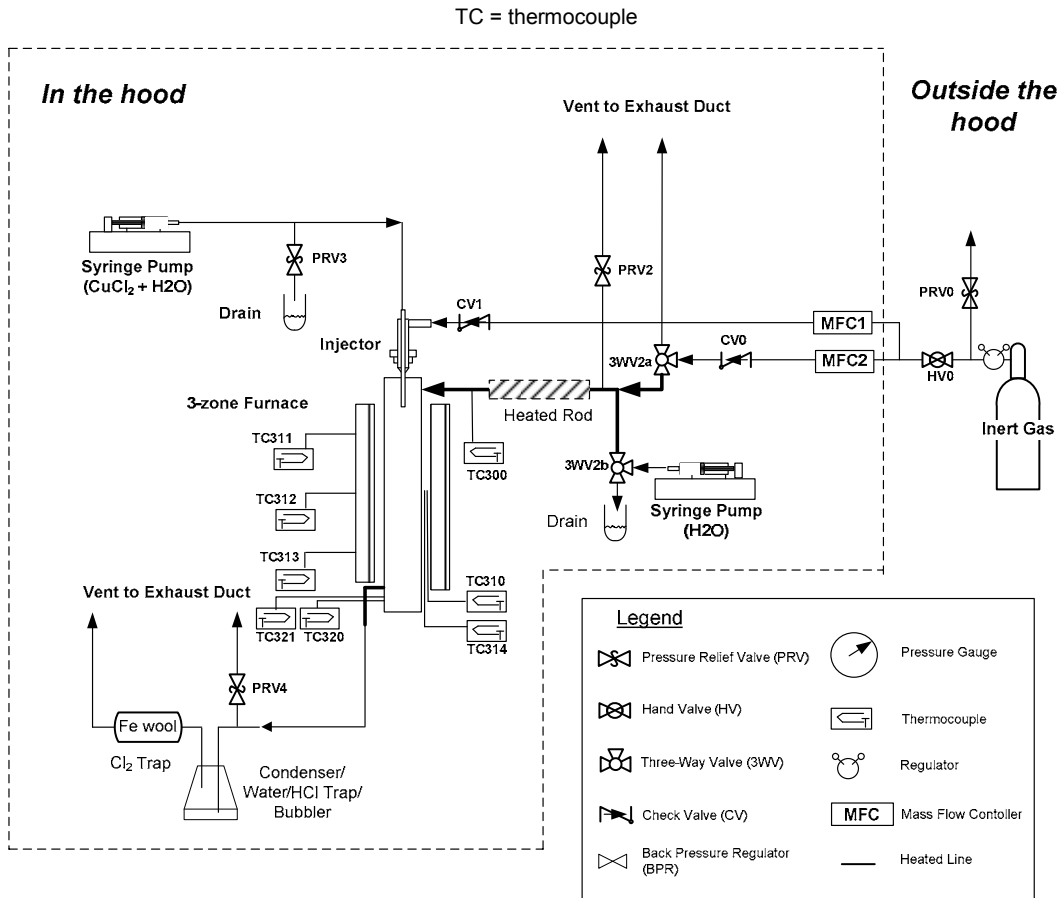
The furnace was preheated and the atmosphere conditioned by passing Ar (up to 300 mL/h) humidified with superheated steam for one hour prior to starting the test. The Ar was humidified by injecting water from a syringe pump into the Ar line, which was heated with an internal Kal-rod heater and is referred to as the superheated steam line (SHS). The temperature of the humidified Ar at the exit of the SHS was monitored with a thermocouple and was varied via a variac.

After the pretreatment, the ultrasonic nozzle or pneumatic nebuliser was placed at the top of the reactor and connected via a Teflon transfer line to a syringe containing $CuCl_2$ solution. A syringe pump delivered the $CuCl_2$ solution at a measured flow rate, typically 0.5 mL/h or 0.0083 mL/m, into the reactor. The runs varied from 48 to 96 minutes, longer times being used to prepare more product. The product gases were passed through a bubbler containing NaOH solution. At the completion of the run, the reactor temperature was reduced to 150°C and allowed to cool overnight with dry Ar flowing. Heating tapes maintained the bottom of the reactor at about 150°C. Besides quenching the hydrolysis reaction, maintaining 150°C prevents steam condensation during cool-down. If the steam was allowed to condense at the bottom of the reactor, any unreacted $CuCl_2$ would become hydrated and the Cu_2OCl_2 would be converted to a copper hydroxychloride, such as atacamite. When dry, the product consisted of free flowing powders, which were easily removed by tapping the reactor bottom. Some samples were analysed with X-ray diffraction and/or a wet chemical analysis. All X-ray diffraction patterns were obtained using a copper radiation source and scanned from 2θ = 10 to 50. Because the analyses were expensive, we used visual observations for a qualitative assessment of each product. For example, dry Cu_2OCl_2 is black, CuOHCl is dark brown, dehydrated $CuCl_2$ is medium brown, hydrated $CuCl_2$ ($CuCl_2 \cdot 2H_2O$) is blue, and CuCl is white. If the temperature of the run was too high or too much water was used, CuO, which is also black, is formed.

Some of these products can be distinguished by their behaviour in water. For example, CuO is insoluble while Cu_2OCl_2 forms a suspension of black particles, which subsequently precipitate as a blue-green copper hydroxychloride salt. The $CuCl_2$ is water soluble and forms a blue solution. CuCl is insoluble but is readily oxidised to $CuCl_2$ in air.

The decomposition temperature of Cu_2OCl_2 was measured by passing the effluent gas from the reactor to a mass spectrometer.

Results

Experiments were conducted with the pneumatic nebuliser in co-current mode, with and without superheated steam, at furnace temperatures of 300 to 400°C and Ar flow rates varying from 200 to 400 mL/min. Either very little or no Cu_2OCl_2 was detected in the X-ray patterns of these products. However, injecting superheated steam counter-currently resulted in a product that consisted mostly of Cu_2OCl_2. The X-ray diffraction pattern is shown in Figure 2. It contains lines identified as melanothallite, the mineral form of Cu_2OCl_2 and several lines identified as hydrated or dehydrated $CuCl_2$. There is one line that is characteristic of CuCl at a d-spacing of 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:

- superheated steam temperature of 450°C;
- Ar flow rate through both the nebuliser and SHS of 200 mL/min;
- furnace temperature of 370°C;
- flow rates of water to nebuliser and SHS line during preheat of 1 mL/h and 0.25 mL/h, respectively.

Figure 2: XRD pattern of sample produced in the nebuliser reactor, counter-current mode
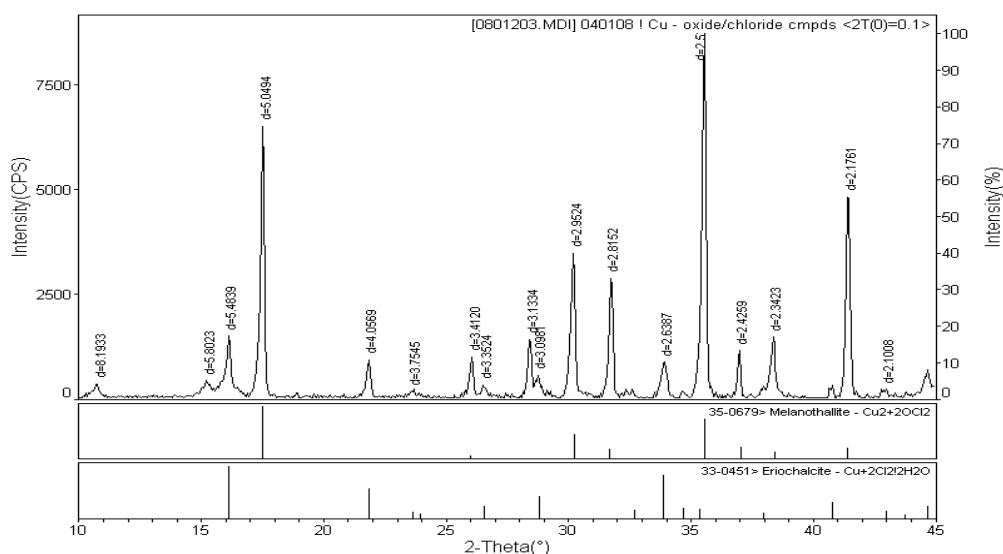
Several variables were changed to determine their effect on Cu_2OCl_2 yield when the experiments were run counter-currently. In Figure 3, the effect of varying Ar flow rates from 100 to 300 mL/h through the nebuliser is shown. There is less conversion when the Ar flow rate through the nebuliser is 100 mL/min compared to 300 mL/min. This suggests higher flow rates give finer droplets, which results in better heat and mass transfer and therefore greater conversion to Cu_2OCl_2. The flow rate of the Ar gas through the superheated steam line also affects the conversion to the oxychloride. As can be seen in Figure 4, there is more conversion to the oxychloride and less unreacted $CuCl_2$ as the Ar

Figure 3: Effect of different Ar flow rates through the pneumatic nebuliser
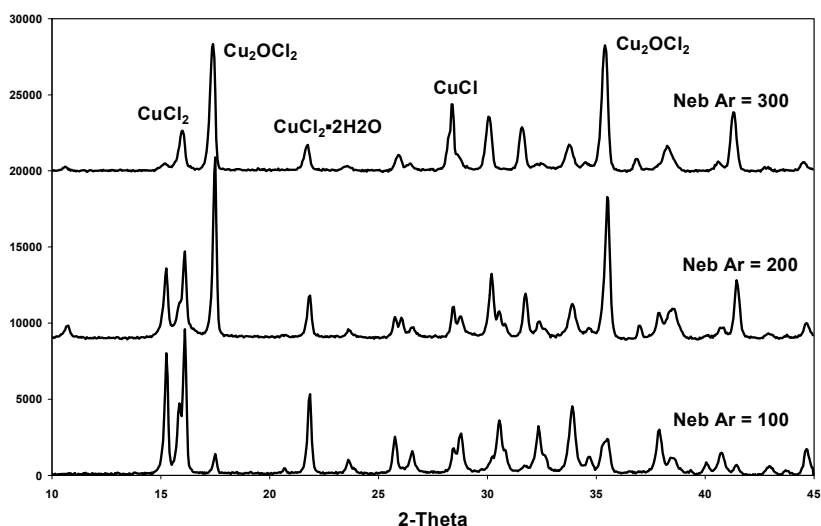
Figure 4: Effect of different Ar flow rates through the superheated steam line
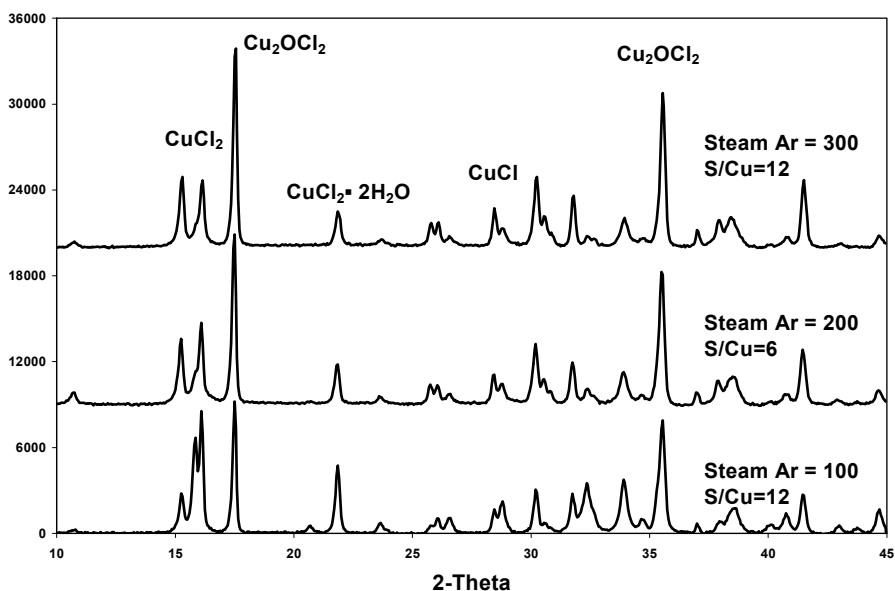
flow rate increases from 100 to 300 mL/h. We conclude that the higher flow rate of the Ar from the superheated steam provides more turbulence and better mixing. We do not believe that the difference in the steam to copper molar ratios (6 or 12) is as important as the differences in the Ar flow rate.

The $CuCl_2$ solution flow rate was also varied from 1 to 3 mL/h with a fixed Ar flow rate. There was less conversion at the higher $CuCl_2$ flow rate than at the lower flow rate. We concluded that the higher $CuCl_2$ solution flow rate results in larger droplets, hence less conversion.

While possible to obtain satisfactory products with the pneumatic nebuliser, the experimental difficulties due to clogging and the strong dependence on many interrelated variables indicated that another type of atomiser should be investigated. An ultrasonic nozzle, in which high frequency electrical energy is converted into vibratory mechanical motion at the same frequency, was therefore examined. The ultrasonic nozzle was chosen because the average droplet size was small, about 25 microns, and

because the inner bore could be constructed of Ti, which is corrosion resistant to $CuCl_2$ solutions. No clogging of the capillary tube occurred. Tests were conducted in the co-current mode. Excellent results were obtained. The product consisted of very fine, free-flowing black powders with little or no "chunks" after optimisation of the unit's power. (To use ultrasonic nozzles properly, the vibrational amplitude must be carefully controlled. If too high, the liquid breaks off in chunks and if too low, there is insufficient energy to produce atomisation.) The experiments were reproducible. The water wash of a small fraction of the powders showed no insoluble particles. No conversion was obtained when superheated steam was not present.

The X-ray diffraction patterns for samples prepared with the ultrasonic nozzle were similar to that shown in Figure 3 above except that there were no peaks for hydrated and dehydrated $CuCl_2$. A typical pattern is shown in Figure 5. All of the peaks were those of the mineral melanothallite or Cu_2OCl_2 except for weak lines assigned CuCl. Wet chemistry analysis showed that these samples contained 3-5 wt.% CuCl. We believe the source of the CuCl is the decomposition of Cu_2OCl_2 because hydrolysis experiments in which the effluent gas phase was analysed showed no chlorine evolution (Ferrandon, 2010). The absence of chlorine in the gas phase indicates that the $CuCl_2$ did not decompose to give CuCl and chlorine.

**Figure 5: X-ray diffraction pattern for hydrolysis
reaction products obtained with the ultrasonic nozzle**
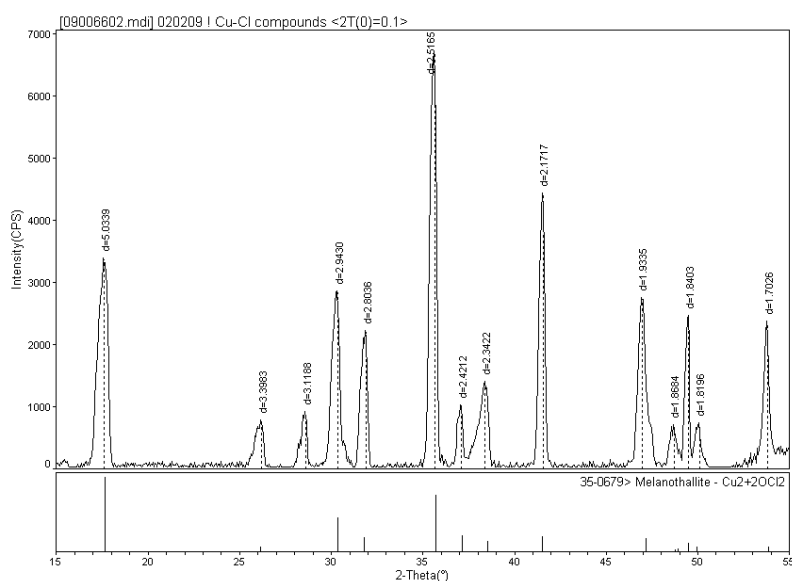
Scanning electron micrographs for particles of Cu_2OCl_2 obtained with the ultrasonic nozzle with an optimised power setting had an estimated size of 100 nanometers to 30 microns.

Solid Cu_2OCl_2 products formed by the ultrasonic nozzle were subsequently heated from room temperature to 700°C to investigate its decomposition behavior as a function of temperature. While several mass numbers were monitored as a function of time and reaction temperature, the oxygen peak at mass number 32 is shown in Figure 6. The peak area was determined and converted to an amount of oxygen via a calibration curve. As can be seen the oxygen signal started near 400°C and ended near 550°C. The calibration showed that the peak area corresponded to 100% of the theoretical amount.

Discussion

The spray reactor with the ultrasonic nozzle provided sufficient heat and mass transfer in the laboratory tests as essentially all of the $CuCl_2$ was converted to Cu_2OCl_2. The ultrasonic nozzle provided droplets with an estimated size of 25 microns. Mass and heat transfer was achieved by injecting these small droplets/dehydrated particles into an atmosphere of superheated, humidified Ar. These results provide

**Figure 6: Measurement of oxygen evolution from Cu$_2$OCl$_2$
as a function of temperature using mass spectrometry**
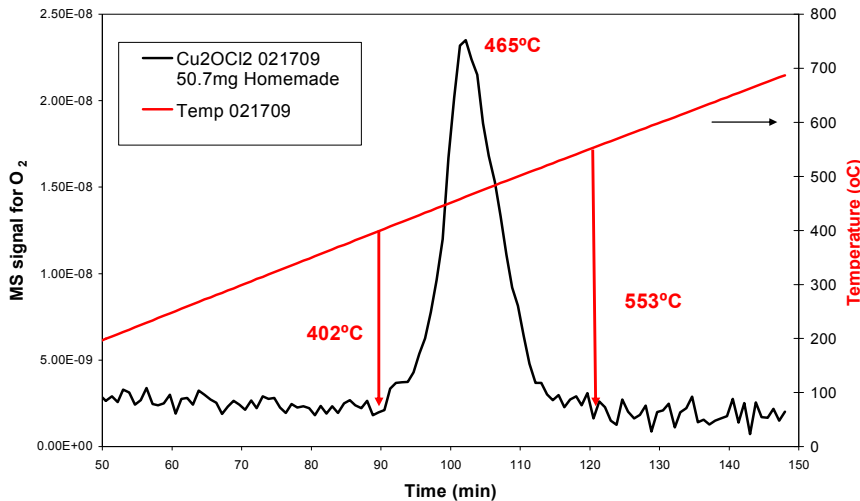
partial validation of our conceptual design for a commercial hydrolysis reactor. Critical to obtaining the high yields necessary for commercial operation is high mass and heat transfer. A spray reactor has thus proposed in the conceptual process design. In order to achieve the mass and heat transfer needed, the CuCl$_2$ slurry would be injected at 24 bar (obtained from a crystalliser unit) into a hydrolysis reactor containing superheated steam. The pressure in the reactor is to be about 0.25 bar. As the droplets enter the hot reactor, the pressure drop would cause the droplets/particles in the slurry to be injected at supersonic speed. Under these conditions, the slurry would form a free jet. As the CuCl$_2$ jet expands, it aspirates the superheated steam into the jet resulting in high mass and heat transfer between the CuCl$_2$ droplets/particles and the steam. Thus, the need for an Ar carrier gas, which was found to be critical in the laboratory, will be eliminated for commercial operation.

The test results with the ultrasonic nozzle were obtained with an estimated steam to copper (S/Cu) ratio of 23 and the humidified Ar was injected co-currently with the CuCl$_2$ solution. Several variables remain to be investigated, *i.e.* lower S/Cu ratios, counter-current instead of co-current operation, and subatmospheric pressures. LeChatelier's Principle predicts that reducing the pressure in the hydrolysis reactor should reduce the S/Cu ratio. The effect of a reduced pressure was quantified by the results of a sensitivity study using Aspen. Aspen predicts that a S/Cu ratio of 17 is needed for essentially complete conversion at 375°C and atmospheric pressure while a S/Cu ratio of 13 is required at 0.5 bar. The conceptual process design specifies that the hydrolysis reactor be run at 0.25 bar. The pressure drop in the reactor is achieved by adding a low temperature steam ejector after the condenser at the exit of the hydrolysis reactor in the conceptual design.

One of the most important characteristics of this cycle is the relatively low maximum process temperature required, about 550°C. Early tests showed that a temperature of 530-550°C was required for complete decomposition (Serban, 2004). The results of the decomposition studies with the Cu$_2$OCl$_2$ produced with the ultrasonic nozzle also showed that the maximum temperature is near 550°C.

The results of the energy and mass balance from the current Aspen flow sheet/ heat exchanger network optimised with pinch analysis gave an efficiency for the cycle of 39 to 41% (LHV), as shown in Table 2. This result is based on assumptions regarding the performance of the electrolyser and the crystalliser. In the electrolyser, 2H$^+$ is reduced to H$_2$ (g) and CuCl is oxidised to CuCl$_2$. For the purposes of the efficiency calculation, we have assumed cell operating parameters of 0.7 V and 500 mA/cm^2 for 2015. We have assumed technical improvements in membranes, electrocatalysts and electrode materials will allow a reduction in cell emf to 0.63 V and 500 mA/cm^2 for 2025. This calculation assumes a 40% factor for converting heat to electricity. In the crystalliser the spent anolyte is processed into a CuCl$_2$ slurry suitable for the feed for the hydrolysis reactor.

Table 2: Results of H2A cost analysis for hydrogen production costs using the Cu-Cl cycle

Case	Capital investment, $MM, solar/chemical	Cell EMF, V	Electrical cost, $/kw	$/kg of H2	Sensitivity range, $/kg	Efficiency, % (LHV)
Solar 2015	208.3/138	0.7	0.068	4.53	3.78-5.31	39
Solar 2025	168.5/110.6	0.63	0.048	3.48	2.91-4.11	41

H2A analysis was used to predict hydrogen production costs as shown in Table 2. These results are based on the use of solar power tower as the heat source and also include assumptions that have yet to be validated. Work is ongoing in these areas. Nevertheless, the preliminary hydrogen production costs as well as the preliminary efficiency numbers indicate that the Cu-Cl cycle has promise and that further R&D is justifiable.

Summary

The Cu-Cl cycle represents a promising technology for producing hydrogen efficiently and cost effectively. Work has focused on the most challenging aspects of the cycle, *i.e.* the hydrolysis and the electrolysis reactions. The hydrolysis reaction is challenging because of the need for the large excess of water/steam needed to achieve complete conversion of the $CuCl_2$ to Cu_2OCl_2. The present work describes a possible method to achieve the high yields required using a spray reactor design, which optimises heat and mass transfer and was very effective in the laboratory tests. Engineering solutions have been conceptualised to reduce the steam to copper chloride molar ratio (S/Cu) from 17 to <10 by using reduced pressure operation. In addition, the process of injecting the $CuCl_2$ slurry at 24 bar into a reactor operating at ~0.25 bar should provide sufficient turbulence to enhance mass and heat transfer without the use of a carrier gas.

Future work

The development of the Cu-Cl is still in its early stages. Work is progressing in several areas, *e.g.* membrane and electrocatalyst development, identification of the speciation of the copper species in the electrolyser, development of a thermodynamic model of the electrolyser, by researchers at Atomic Energy of Canada Limited, Pennsylvania State University, and University of South Carolina. Work at Argonne National Laboratory will focus on further development of the hydrolysis reactor, *e.g.* designing and testing a reactor that operates at 0.25 to 0.5 bar, determining the lowest minimum S/Cu ratio, and operating. The Aspen flow sheet and the H2A will be updated to reflect new data as it becomes available.

Reference

Ferrandon, M.S., *et al.* (2010), "Production of Cu_2OCl_2 Using a Spray Reactor and Formation of HCl and Cl_2 During the Hydrolysis of $CuCl_2$ in the Cu-Cl Thermochemical Cycle", *International Journal of Hydrogen Energy*, 35, 992-1000.

Serban, M., M.A. Lewis, J.K. Basco (2004), "Kinetic Study for the Hydrogen and Oxygen Production Reactions in the Copper-Chlorine Thermochemical Cycle", *Conference Proceedings, AIChE Spring National Meeting*, 2690-2698.