Status of the Development Effort for the Thermochemical Cu-Cl Cycle

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1. Introduction

The hybrid copper-chlorine (Cu-Cl) cycle is one of the most promising thermochemical cycles for hydrogen production using nuclear or solar heat. The advantage of the hybrid CuCl cycle relative to other cycles is the relatively lower temperature heat (550ºC) source required which should mitigate some of the demands on the materials of construction. Several types of nuclear reactors can be used as a heat source, such as the supercritical water reactor being developed in Canada, CANDU Mark 2, the lead cooled reactor, or the high temperature gas reactor. Solar heat can be provided using the commercially proven tower technology. All these provide heat near or above 600ºC, the maximum temperature required for the cycle.

The copper-chlorine cycle consists of the three major reactions shown in Table 1. The electrolysis reaction *(1)* in which cupric chloride ($CuCl_2$) is produced at the anode and H_2 is released at the cathode. The $CuCl_2$(a) from *(1)* is hydrolyzed to copper oxychloride (Cu_2OCl_2) according to the hydrolysis reaction *(2)*. Molten cuprous chloride (CuCl) is then produced from the decomposition reaction *(3)*.

Table 1. Reactions in the Copper-Chlorine Cycle

Reaction	Conditions
(1) $2CuCl(a) + 2HCl(a) + 2H_2O \rightarrow CuCl_2 \cdot 2H_2O(a) + H_2(g)$	100ºC, 24 bar
(2) $2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$	400ºC, 1 bar
(3) $Cu_2OCl_2(s) \rightarrow \frac{1}{2} O_2(g) + 2CuCl(s)$	540ºC, 1 bar

All reactions have been experimentally demonstrated. The two thermal reactions, the hydrolysis of $CuCl_2$ *(2)*, and the decomposition of Cu_2OCl_2 *(3)* have been proven at ANL. In bench scale experiments, all of the oxygen was recovered at 530ºC from reaction *(3)*. The early experiments indicated technical challenges in the hydrolysis *(2)* and electrolysis reactions *(1)*. The electrolytic reaction *(1)* was demonstrated at the Atomic Energy of Canada, Ltd. (AECL) at Chalk River recently. Meeting performance of 500 mA/cm^2 at 0.7V is the primary challenge for the electrolysis reactor.

We consider the hydrolysis reaction to be the most challenging reaction because of two factors: (i) a competing reaction of $CuCl_2$ and (ii). the need for excess water The competing reaction is the thermal decomposition of $CuCl_2$:

$2CuCl_2 (s) \Leftrightarrow 2CuCl (s) + Cl_2 (g)$. *(4)*

Because CuCl is a product of the subsequent reaction, this competing reaction is not a showstopper, provided the chlorine can be scavenged and the amount of chlorine formed is minimal. We also believe that this competing reaction can be minimized by the choice of operating conditions and the reactor design. A sensitivity study and the experimental results indicate that the steam must be in excess for high yields of the desired Cu_2OCl_2 and HCl. The excess steam increases capital costs significantly because of the larger number of vessels required and the high energy usage for vaporizing the water.

The paper is divided into two sections. The first section describes the current conceptual design. In order to determine the potential of the Cu-Cl cycle, an Aspen Plus™ flowsheet was developed using this process design and the cycle's efficiency was calculated. The energy and mass balances, the heat exchanger duties and shaft work were calculated, and heat recovery was optimized with pinch analysis. The hydrogen production cost was estimated using the hydrogen analysis (H2A) methodology [1]. Capital costs for the thermal processes were estimated using Capcost software [2]. Operating costs (thermal and electrical energy, cooling water, etc.) were set to be consistent with the H2A analysis.

In the second section of this paper, experimental operating parameters were varied to see which had the greatest impact on the Cu_2OCl_2 formation during the hydrolysis reaction. The goal is to inhibit $CuCl_2$ thermal decomposition while minimizing the steam-to-copper molar ratio (S/Cu). The latter is critical for high efficiency since vaporizing the water is energy intensive. The reactor used is a engineering-scale continuous spray reactor, similar to the industrial spray roasters.

2. Experimental

Past work has shown that the previous fixed bed reactor design was not optimal [3]. Inefficiencies in heat and mass transfer inhibited the desired reaction. Unreacted $CuCl_2$ was observed and this material tended to be agglomerated in the middle of the fixed bed.

A spray reactor was used for the new series of tests, as shown in Figure 1. In this concept, a solution of $CuCl_2$ is injected into the reactor using one of two types of atomizers. The first one is a pneumatic quartz nebulizer used for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses (Glass Expansion) and the other one is an ultrasonic nozzle (Sono-Tek). The pneumatic one requires Ar as a sweep gas to create a fine mist of $CuCl_2$ solution while the ultrasonic nozzle uses ultrasonic vibrations to atomize the solution. When the mist enters the heated zone, mass transfer is enhanced relative to the fixed bed because the droplets are dispersed and very small. Superheated steam with or without Ar was used to improve heat transfer. Steam can be added from the top (co-current flow design) or at the bottom (counter-current flow design). Solid products are collected at the bottom of the reactor where the temperature is kept at 150ºC for quenching the reaction while keeping the material dry.

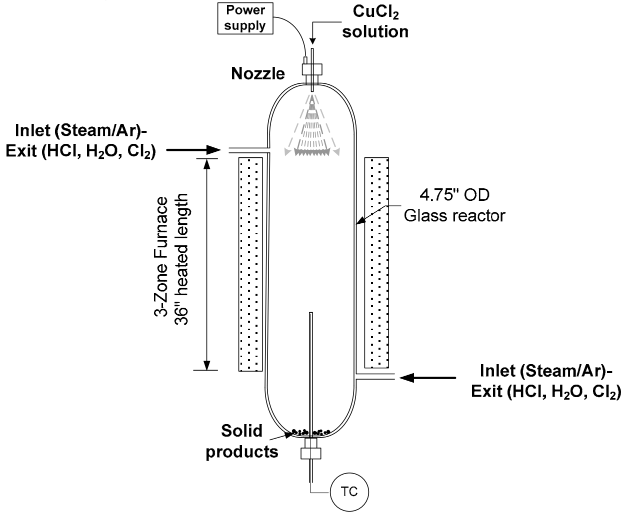

Figure 1. Schematic of the nebulizer reactor for the Cu-Cl hydrolysis experiments. TC=thermocouple.

This design is a continuous reactor, similar to that in the conceptual process design (described below) except for the presence of Ar and the pressure/temperature (1 atm/room temperature vs 24 bar/400ºC) at which $CuCl_2$ stream enters the reactor.

3. Results

3.1. Conceptual Process

Aspen Plus [4] was used to develop mass and energy balances for a process based on these 3 reactions. Little is known about the electrolysis reaction and in the calculations, we have assumed the electrolyzer operates at 0.7 V and 500 mA/cm^2. The Aspen simulation provided stream flows and properties as well as heat exchanger duties and work requirements for pumps. The overall process flow sheet is shown in Figure 2.

A CuCl cycle plant producing 125 MT H_2/day requires 191 MW of thermal energy and 100.5 MW of electrical energy. The energy efficiency of the process is defined as energy out divided by energy in. Based on the low heating value for hydrogen, the efficiency of this process is:

$$\text{Efficiency} = \frac{\text{Mol. of } H_2 \text{ Produced} * \text{LHV}}{(\text{Shaft work} + \text{Electrochemical work} + \text{Pinch Heat})}$$

$$\text{Efficiency} = 125{,}000 \times 33.3/\ (24(3000/0.4+97{,}500/0.4 +191{,}000) = 39\%\ (\text{LHV})$$

In this equation it is assumed that the efficiency of converting thermal energy into electrical power is 0.4.

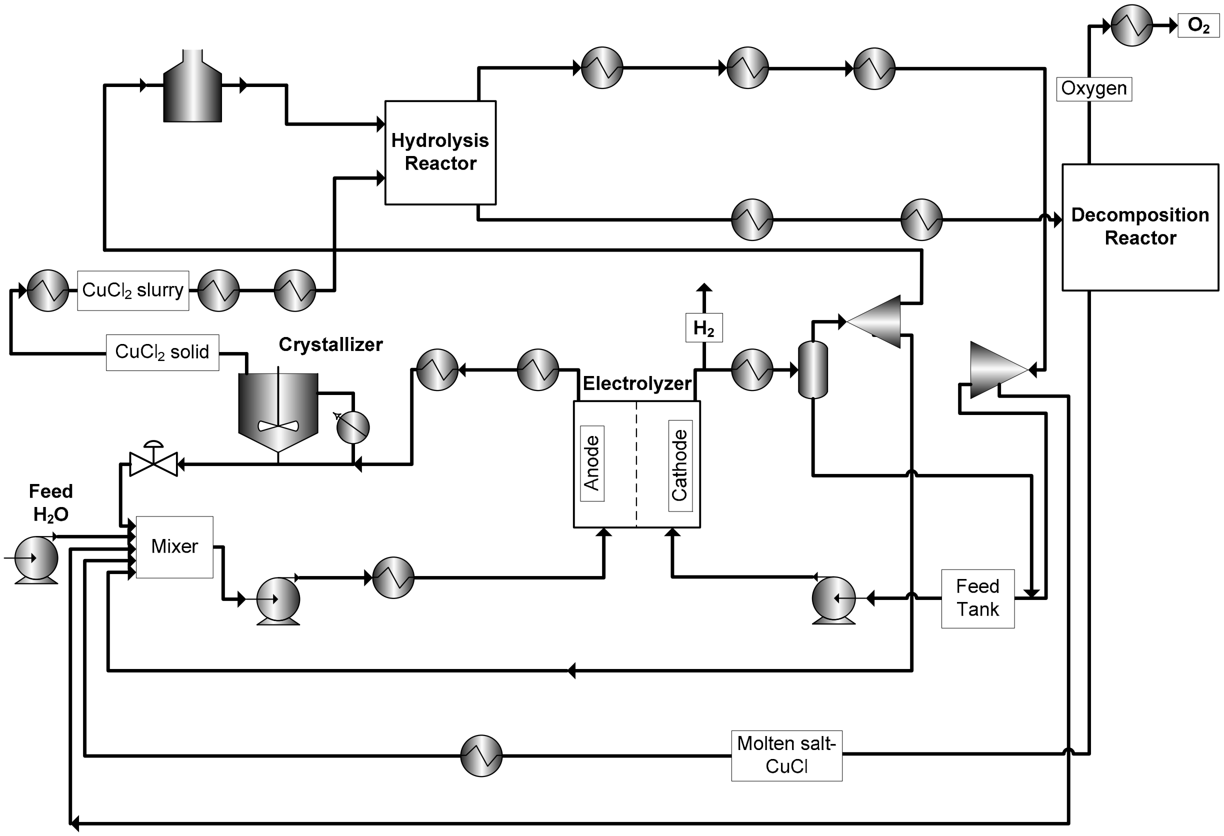

Figure 2. Aspen flow sheet of the CuCl cycle.

The conceptual process design for the CuCl cycle is divided into 4 sections:

1. The electrolyzer
2. The crystallizer
3. The hydrolysis/oxychloride decomposition reactors
4. The CuCl heat recovery system

We have assumed that the electrolyzer will operate near 100ºC at 24 bar in order to produce hydrogen at 300 psi. A conceptual design for the electrolyzer has been developed and is discussed below. Many of the process steps are similar to commercially practiced technologies. These technologies are pointed out where appropriated.

Electrolyzer /Crystallizer

Anode and Crystallizer Section: Feed water, recycled granulated CuCl, any make up HCl and crystallizer recycle is added to the anode feed tank. The solution containing dissolved CuCl, HCl and residual $CuCl_2$ is then pressurized to 24 bar and transferred to the anode section of the electrolyzer. Chloride ion migrates from the cathode across the electrolyzer membrane and reacts at the anode with the CuCl to form $CuCl_2$.

The anolyte solution is then cooled to 55ºC in the crystallizer cooler and most of the $CuCl_2$ crystallizes. This cooler could be similar to the scrapped surface crystallizer manufactured by Armstrong Engineering. After exiting the cooler, the solid $CuCl_2$ is collected in the bottom of a hydroclone. The solid $CuCl_2$ is then fed to the hydrolysis reactor. The overflow of the hydroclone is recycled back to the anode feed tank through a pressure let down valve.

Cathode and Hydrogen Generation Section: Aqueous HCl is pumped (24 bar) from the cathode feed tank to the cathode. At the cathode the H^+ ion is reduced to H_2. The chloride ion migrates across the electrolyzer membrane as described above. Water and unreacted HCl are then heated to 106ºC and flashed to atmospheric pressure. The vapor from the flash (which contains less than 1mole % HCl) is then sent to the direct heat exchanger and superheated to 400ºC. It is then sent to the hydrolysis reactor. The liquid stream from the flash is recycled back to the cathode feed tank.

Hydrolysis/Oxychloride Decomposition

The solid product from the hydrolysis reactor (*2*) goes to the oxychloride decomposition reactor (*3*). Thermal energy is used as the final preheat agent of all streams to the hydrolysis reactor and to decompose the Cu_2OCl_2 in the oxychloride decomposition reactor. The reactors are sized using residence times observed in the laboratory. The effluent from the oxychloride decomposition reactor is a molten salt. The heat from the molten salt is recovered in a direct heat exchanger (see below).

Hydrolysis reactor: The hot, pressurized (24 bar) $CuCl_2$ is sprayed into a superheated (400ºC) steam environment at 0.25 bar where it forms a free jet. As the jet expands it aspirates the superheated steam into the jet resulting in high mass and heat transfer between the $CuCl_2$ in the jet and the steam. The $CuCl_2$ is converted to Cu_2OCl_2 and HCl.

The HCl and unreacted steam exit the hydrolysis reactor to be cooled in feed pre-heaters and fed to the cathode of the electrolyzer. A steam ejector and the volume contraction of the hydrolysis steam/HCl effluent pulls the vacuum on the hydrolysis reactor as it condenses. Dry, free flowing solid Cu_2OCl_2 accumulates at the bottom of the hydrolysis reactors. The solid copper oxychloride flows by gravity through an L valve to the oxychloride decomposition reactor. The hydrolysis reactor is elevated relative to the oxychloride decomposition reactor. The static head of the solids in the L valve provide the driving force to move the solids from the hydrolysis reactor to the oxychloride reactor.

The hydrolysis reactor is very similar to a spray roaster used in the steel industry to recover HCl from $FeCl_2$ generated by the steel pickling process. The flow of solid Cu_2OCl_2 from the hydrolysis reactor to the oxychloride decomposition reactor is similar to the flow of cracking catalyst in a fluid bed catalytic reactor in a refinery.

Oxychloride decomposition reactor. In the oxychloride decomposition reactor, the Cu_2OCl_2 is heated to 550ºC. Between 450 and 550ºC, the Cu_2OCl_2 decomposes to oxygen and molten CuCl. The oxygen leaves the oxychloride decomposition reactor as a gas and the molten CuCl spills over the weir. The stand pipe below the oxychloride decomposition reactor can be fluidized with air if required to assure smooth flow into the oxy-decomposition reactor. Air is aspirated into the oxygen stream using a venturi valve to cool and dilute the oxygen.

The Direct Heat Exchanger. The heat in the molten CuCl stream is recovered in a heat exchanger followed by a direct heat exchanger. The molten CuCl enters the direct heat exchanger at 440ºC (after it cooled down in a shell and tube heat exchanger from 550 to 440ºC) and is atomized by a spinning disc. As the molten CuCl cools it heats the vapor stream from the cathode flash. The vapor stream is then fed to the hydrolysis reactor. During the cooling the CuCl is granulated. The granulated CuCl is fed back to the anode feed tank via a screw feeder or via gravity flow. The direct heat exchanger is very similar to the Bateman Granulation system which is used to make granulated steel or slag.

Electrolyzer Design

The proposed electrolyzer combines individual electrolyzer cells consisting of a membrane and anodic/cathodic compartments using a modular design of stacks and modules to attain the necessary hydrogen production throughput. The ion-exchange membrane is located in the middle of the cell and is sandwiched between the two electrodes, the anode and the cathode. Both the anode and cathode are porous, carbon/carbon-felt electrodes typically used in PEM fuel cell design. In the CuCl electrolyzer, the cathode has an electrocatalyst layer to promote the hydrogen generation reaction whereas the anode does not need this layer. Moving outwards from the electrode is the bipolar plate, also called a flowplate, which acts as a channel for gas and electrolyte flow into and out of the anodic and cathodic compartments. In a multiple-cell configuration, the bipolar plate would have flow channels on each side.

In the proposed modular electrolyzer design, multiple cells are combined to make an electrolyzer stack. The stacks are then arranged into core modules of 2 or more stacks each in order to optimize the reactant/product flow, power, and operational and maintenance requirements. For the CuCl hybrid thermal process, three electrolyte flow trains have been proposed. Thus, the electrolyzer stacks should be grouped in such a way to make three core modules with a single input and output stream each for the anode and cathode electrolyte flows and with the proper amount of stacks per module to generate the hydrogen throughput. For a single cell area of 3 m^2, 300 cells/stack and 10 stacks/module, 6 modules (2 per process train) are required to achieve the 27,000 m^2 to produce 125,000kg of hydrogen/day. The 6 modules are contained in 9 pressure vessels.

3.1.1. H2A Economic Results

DOE has developed the H2A spread sheet [1] to evaluate potential hydrogen production projects. The H2A is a discounted cash flow analysis. It calculates the cost of producing hydrogen if a 10% return on equity is required.

The capital investment in the electrolyzer was estimated separately at $38.4 MM. Using Capcost software, the total capital investment (including offsites) for the CuCl plant is $105 MM. The number of operators required to operate the plant is 80. This number is high because of the 3 (crystallizer, hydrolysis and oxy-decomposition reactor) process steps which involve solids. The cost of energy from a nuclear source is estimated at $20/ MW-hr (thermal) and $60/MW hr (electrical). All estimates are in 2005 dollars.

When this investment, labor force and cost for energy (both thermal and electrical) are plugged into the H2A spread sheet, the estimated cost of hydrogen is $3.07/kg. A number of sensitivities were run on the economics. Depending on the sensitivity tested, the cost of hydrogen can range from $3.60 to 2.80/kg. As would be expected the cost is most sensitive to the plant capital cost, the operating factor and the cost of energy (both electrical and thermal). The cost is relatively insensitive to the size of the labor force.

3.2. Model of the Hydrolysis Reaction

The hydrolysis reactor was modeled with Aspen Plus with a feed of 100 kmol/hr of $CuCl_2$ and various amounts of water. Figure 3a shows the effect of temperature on the Cu_2OCl_2 yield as a function of the steam-to-copper (S/Cu) ratio as calculated by Aspen Plus™ model. An excess of steam is required for achieving high yields of Cu_2OCl_2. For instance, to achieve the maximum yield of 50 mol of Cu_2OCl_2 below 400ºC, a steam-to-copper ratio greater than 17 is needed. Below 400ºC, the model also predicts that the thermal decomposition reaction of $CuCl_2$ to CuCl occurs to a small extent, as seen in Figure 3b.

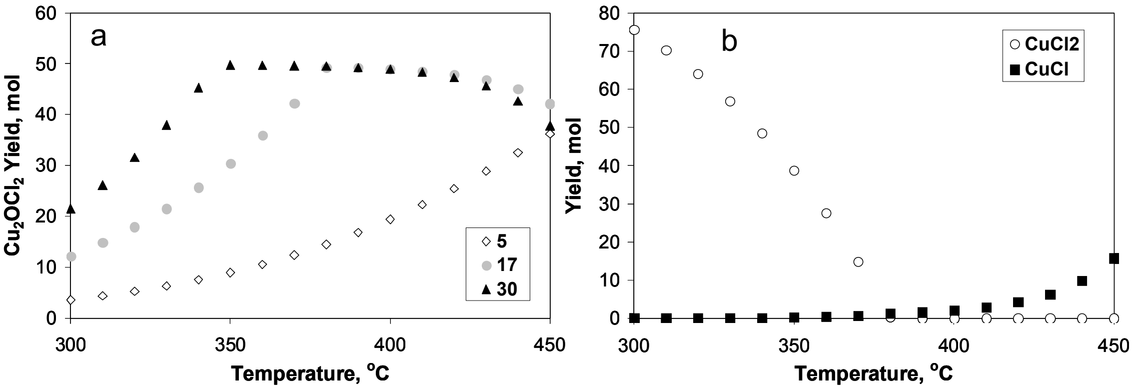

Figure 3. Effect of temperature on the Cu_2OCl_2 yield as a function of S/Cu ratio (a) and CuCl and $CuCl_2$ yields as a function of temperature (S/Cu=17) (b), calculated by Aspen Plus model (Ar=0).

3.3. Results from the Hydrolysis Experiments

The conditions varied were the following: flow rate of argon through the pneumatic nebulizer, the types of flow designs (co-current versus counter-current) and the types of atomizers. Scanning electron microscope (SEM) was used to measure the particles size of the solid product obtained. X-ray diffraction technique (XRD) was performed for identification of CuCl, Cu_2OCl_2 and $CuCl_2$. Analyses of CuCl were performed using a wet chemistry method by the Analytical Chemistry Laboratory at Argonne.

In Figure 4a, the effect of varying Ar flowrates from 200 to 400 mL/h through the nebulizer at *co-current* design is shown. Most of the reaction product is unreacted $CuCl_2$. We attribute this result to poor mixing and poor mass transfer. The amount of CuCl is small but increases with the Ar flowrate, as expected due to Le Chatelier's Principle. All flowrates show very little conversion into Cu_2OCl_2. All the peak intensities attributed to $CuCl_2$ and $CuCl_2{\cdot}2H_2O$ were lower at higher Ar flowrates. This suggests that at higher Ar flowrate the droplets are finer and hence the size of the solid particles is smaller.

In Figure 4b, the results are shown for the same type of experiments as in 2a but the flow is *counter-current*. These results suggest that counter-current flow gives more turbulence and better mixing. Very fine particles of black color, which is the color of Cu_2OCl_2, were found at the bottom of the reactor. Further, more Cu_2OCl_2 is formed relative to the amount of unreacted $CuCl_2$ in 4b. As the Ar flow increases, the solution droplets become finer and there is greater dispersion. We attribute the larger conversion to improved mass transfer.

Figures 5a and 5b show XRD patterns obtained from the nebulizer and the ultrasonic nozzle for the same conditions. The XRD pattern of the solid product obtained using the ultrasonic nozzle shows mostly Cu_2OCl_2, little unconverted $CuCl_2$ and much less CuCl compared to the pneumatic nebulizer. Analyses of the product showed less than 4 wt% of the undesired CuCl obtained using the ultrasonic nozzle. The difference in the results obtained with the two types of nozzle may come from: *(i)* the droplet size and *(ii)* the velocity at the tip of the atomizer. SEM pictures reveal the solid particles after reaction using the ultrasonic nozzle to be in the range of 2-3 μm with a homogeneous size distribution (Figure 6), which also corresponds to the mean size of liquid droplets (25 μm) according to the manufacturer.

The velocity of the gas/liquid at the tip of the ultrasonic nozzle is smaller than that of the pneumatic nebulizer because it does not use an inert gas and the orifice diameter is larger (510 µm versus 190 µm for the pneumatic nebulizer). Thus the terminal velocity is reached at a shorter distance in the reaction zone from the atomizer and the residence time is longer with the ultrasonic nozzle, resulting in a better heat and mass transfer.

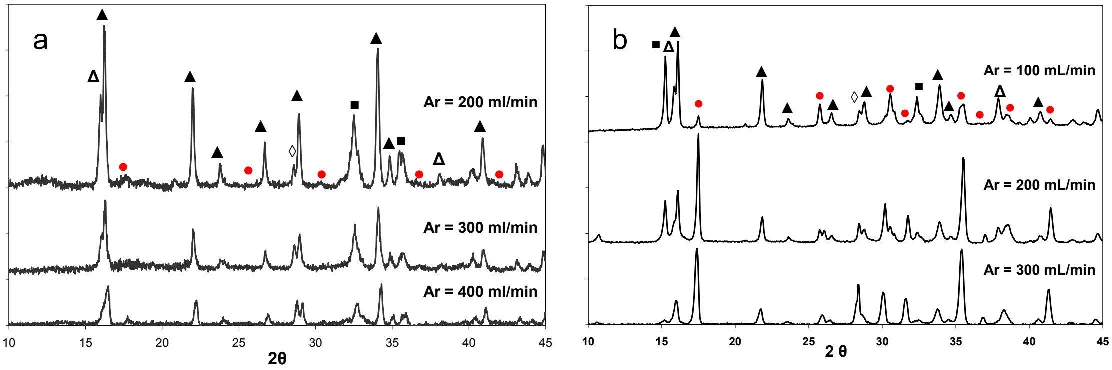

Figure 4. XRD pattern of solid products. Effect of different Ar flow rates using co-current (a) and counter-current (b) flow designs. Cu_2OCl_2 (●), $CuCl_2 \cdot 2H_2O$ (▲), $CuCl_2$ (Δ), CuCl (◊), Cu(OH)Cl (■).

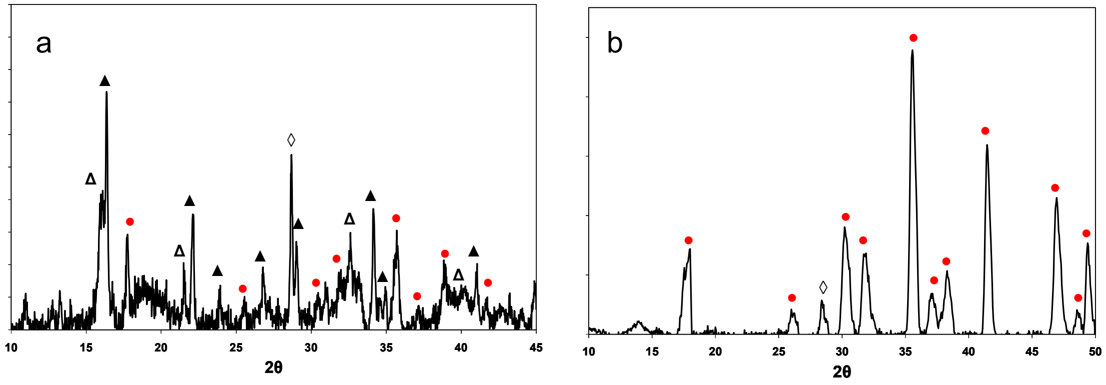

Figure 5. XRD pattern of solid products. Effect of different atomizers: pneumatic nebulizer (a) and ultrasonic nozzle (b). Cu_2OCl_2 (●), $CuCl_2 \cdot 2H_2O$ (▲), $CuCl_2$ (Δ), CuCl (◊), Cu(OH)Cl (■).

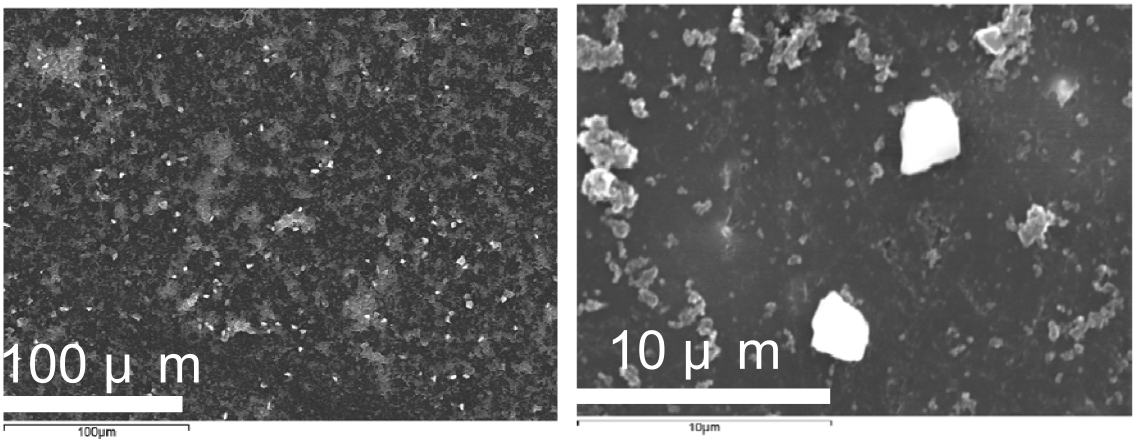

Figure 6. SEM pictures of particles of solid products (white) embedded in epoxy after hydrolysis reaction using the ultrasonic nozzle

4. Conclusions

A conceptual process design based on the 3 reaction Cu-Cl cycle has been developed to produce 125 MT of hydrogen /day. The process is based on an Aspen Plus simulation which provides mass and energy balances for the process. An integrated heat exchange network for the conceptual process captures process heat. External heat and utility requirements are 191MWt and 100.5 MWe respectively. Defining efficiency as energy out divided by energy in results in estimated efficiency of around 39%. The voltage assumed for the electrolyzer is 0.7V which is for ambient conditions. We plan to plan to run the electrolyzer at 80ºC, so the voltage could be lowered [5], thus the efficiency should go up. Capital requirements for the conceptual process were estimated using Capcost software. The chemical plant investment including the electrolyzer is $105MM (2005$). Operating costs were also estimated and an H2A analysis was preformed. The estimated cost of producing hydrogen is $3.07 with a range from $3.60 to 2.80/kg depending capital investment, amount of equity financing, and the cost of thermal and electrical energy. The results of the economic analysis are guiding the further development efforts, both experimental and modeling. Efforts are being focused in areas which will improve process efficiency and reduce capital investment.

During the hydrolysis of $CuCl_2$ with the pneumatic nebulizer, counter-current flow designs gave higher yields of Cu_2OCl_2 than co-current design. However, the latest results indicate that the best results are obtained when using an ultrasonic nozzle in the co-current design. Very fine and homogenous particles result, thereby providing good mass and heat transfer.

5. Acknowledgments

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