

Development of the Low Temperature Hybrid Cu-Cl Thermochemical Cycle

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Introduction

Argonne National Laboratory (ANL) is developing low temperature thermochemical cycles designed to split water and produce hydrogen at 550°C or less. The rationale for this R&D effort is to identify new technologies that can produce hydrogen cost effectively without greenhouse gas emissions. Over three hundred thermochemical cycles have been reported in the literature. Most of these cycles use aggressive chemicals and require high temperatures, 850 °C and above. Engineering and materials issues are, therefore, extremely challenging. Lower temperature cycles may reduce the thermal burden and mitigate demands on materials as well as on potential heat sources. ANL has identified the copper-chlorine (Cu-Cl) cycle as one of the most promising cycles for the lower temperature region on the basis of successful proof-of-principle work. A simplified representation of the cycle is shown in Table 1, along with the reaction temperatures used in the proof-of-principle work. Experimental confirmation of the thermal reactions was completed in the laboratory. The kinetics of the reactions were reasonable. The maximum temperature of the cycle was 530°C and experimental yields for the three thermal reactions (#1, 3, and 4 in Table 1) were high. Competing reactions were not observed in the hydrogen and oxygen generation reactions (#1 and 4, respectively). However, examination of the products of the hydrolysis reaction of CuCl₂ (#3) showed evidence of a competing reaction, i.e., the decomposition of CuCl₂. CuCl was observed in the solid phase and chlorine gas, in the gas phase. The electrochemical reaction has not been extensively studied but copper deposition was observed with cell potentials between 0.4 and 0.6 V. This voltage is consistent with the free energy for the reaction.

Table 1. Reactions in the ANL Cu-Cl Cycle.

#	Reaction Stoichiometry	Temperature (°C)
1	$2\text{Cu} + 2\text{HCl}(\text{g}) \rightarrow 2\text{CuCl}(\text{l}) + \text{H}_2(\text{g})$	425-450
2	$4\text{CuCl}(\text{s}) \rightarrow 2\text{CuCl}_2(\text{a}) + 2\text{Cu}$	<100
3	$2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CuO}\cdot\text{CuCl}_2(\text{s}) + 2\text{HCl}(\text{g})$	300-375
4	$\text{CuO}\cdot\text{CuCl}_2(\text{s}) \rightarrow 2\text{CuCl}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$	450-530

Process Simulation Using Aspen Plus

In addition to the experimental work, a simulation was prepared for the three thermal reactions (#1, 3, and 4) using Aspen Plus. Low temperature reaction #2 was modeled as if being driven electrochemically. This used first a stoichiometric reactor to give the reaction #2 products, and then a component separator to allocate the compounds in the stream into anode and cathode product streams. The Aspen Plus model included all heat exchangers, pumps, and separation vessels as needed for the process, as shown in Figure 1. Drums were used to separate gases from solid/liquid streams. Filters were used to separate solids generated in the reactions from the liquid streams in the simulation, although the particle size distribution is not known. Therefore, more experimental work will be needed in order to specify the design parameters for those filters.

The Aspen model used reaction blocks modeled with stoichiometric reactors in order to increase the stability of the simulation with recycle streams present. However, conversions could be less than stoichiometric, as shown in Table 1. In addition, by-product formation was allowed – for example, chlorine gas was allowed to form from reaction #3. A simulation with parallel equilibrium reactors was used to determine yields, and then the reactions in the stoichiometric reactors were adjusted to substantially match the equilibrium concentrations for hydrogen and oxygen generation. This required setting the conversion levels for the intended and by-product formation reactions. Excess water was needed, compared to the reactions presented in Table 1, in order to have total solubility of the salts for aqueous reactions, and to drive some reactions to completion at reasonable temperatures. CuCl_2 is very soluble in water. CuCl is slightly soluble in water, but is soluble in HCl solution. An important part of the design is to allocate HCl to where it is needed without unnecessarily causing material of construction problems. Process conditions, such as pressures, temperatures, and feed concentrations, were systematically varied for the equilibrium reactors with Aspen Plus in order to find conditions where the yields were close to 100%, as desired. For instance, Figure 2 shows that the yield of oxygen was 95% of the desired value of 25 kmol/h at 550°C with the feed concentrations used in the simulation, and that no by-product salts were produced. Temperature increase improves the conversion for reaction #4. Figure 3 shows that temperature increases for the hydrogenation reaction #1 decrease conversion, so the reaction was run at 400°C. The effect of pressure was also studied. Figure 4 shows that pressure increase for reaction #1 increases conversion, so that reactor was run at 24 bar instead of atmospheric pressure. In the final design, the reactor was run at the higher pressure of 24 bar and 425 °C to get complete conversion. Pressure increases were done using pumps and at lower temperatures, rather than using gas compressors at higher temperatures. This minimizes metallurgy issues, as well as providing higher efficiencies. When conversions from any of the reactions were below 100%, recycle was increased as necessary to fully convert 50 kmol/hr of water feed into 50 kmol/hr of hydrogen product in the flow sheet.

Sensitivity studies were also done to show the effect of the concentration of reactants and by-products on equilibrium conversions. Figure 5 shows the effect of varying the HCl input rate into reaction #1. As expected, increasing the flow of one of the reactants increases the conversion, up to the point of complete conversion of the other reactants. Although, not shown, increasing the HCl in the feed to reaction #3 (where it is a product) decreases the equilibrium

conversion level. Because of azeotrope formation, it was difficult to get either pure water or pure HCl streams from separations in the simulation, so streams of mixed HCl in water were used to save excessive separation energy losses. Since several water reject streams were available in the simulation varying in their content of HCl, the appropriate water-rich stream or HCl-rich stream was routed to each reaction in order to achieve high yields. The chosen streams for each reactor are shown in Figure 1. The optimal temperatures for the reactors in the Aspen simulation were sometimes different from those used in the proof-of-concept experiments, but the maximum process temperature used was 550 °C. Since only estimated thermodynamic data were available for Cu_2OCl_2 , the simulation forced the formation of this compound for a yield of 100%. Other assumptions in this model were the following:

1. H_2 and O_2 generation reactions are near 100% completion by choice of reaction conditions; H_2 is discharged at the separator at 23 bar (338 psi).
2. The molar ratio of water to CuCl_2 is 10 to 1 in the hydrolysis reaction run at 510°C;
3. The electrochemical cell's potential is 0.4V;
4. Efficiency of converting heat to electricity is 50%;
5. The driving force in the pinch analysis for optimizing energy usage is 10°C;
6. The maximum temperature was 550°C.

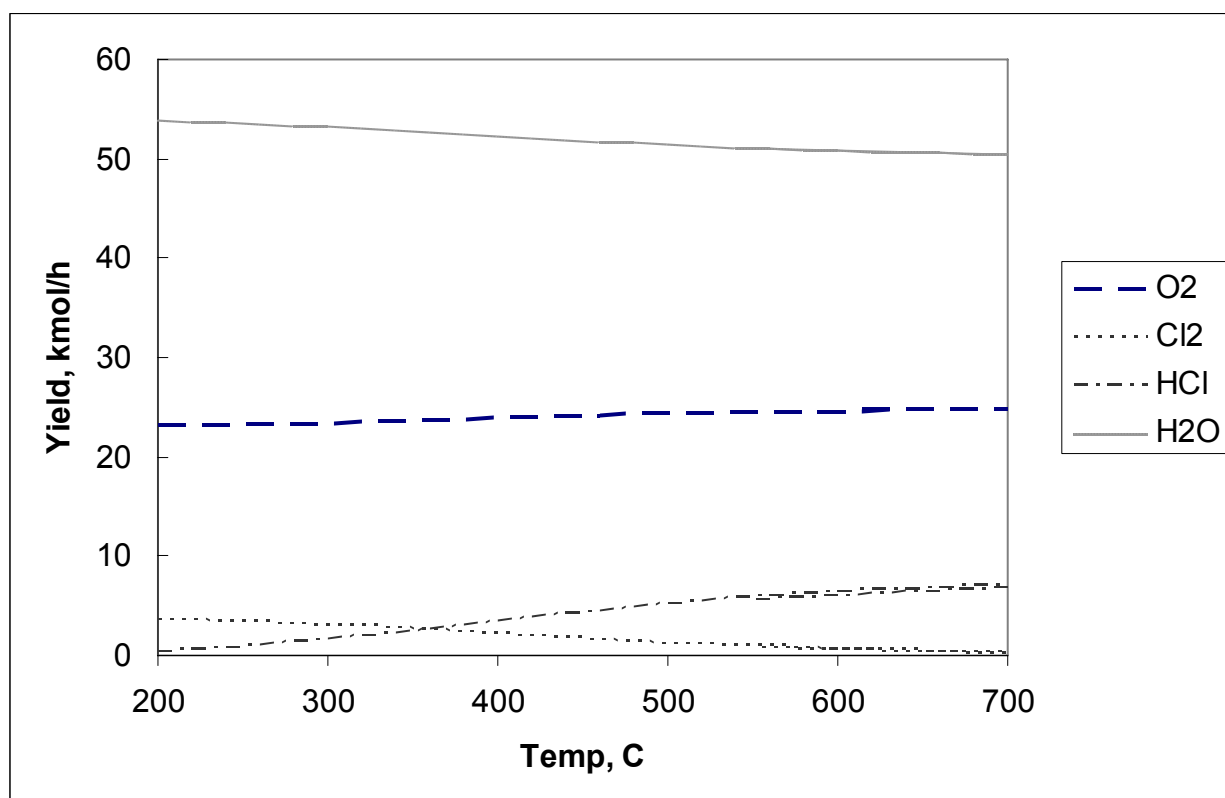


Figure 2. Effect of Temperature on Equilibrium Yield of Products from Reaction #4 Using Aspen Plus Simulation

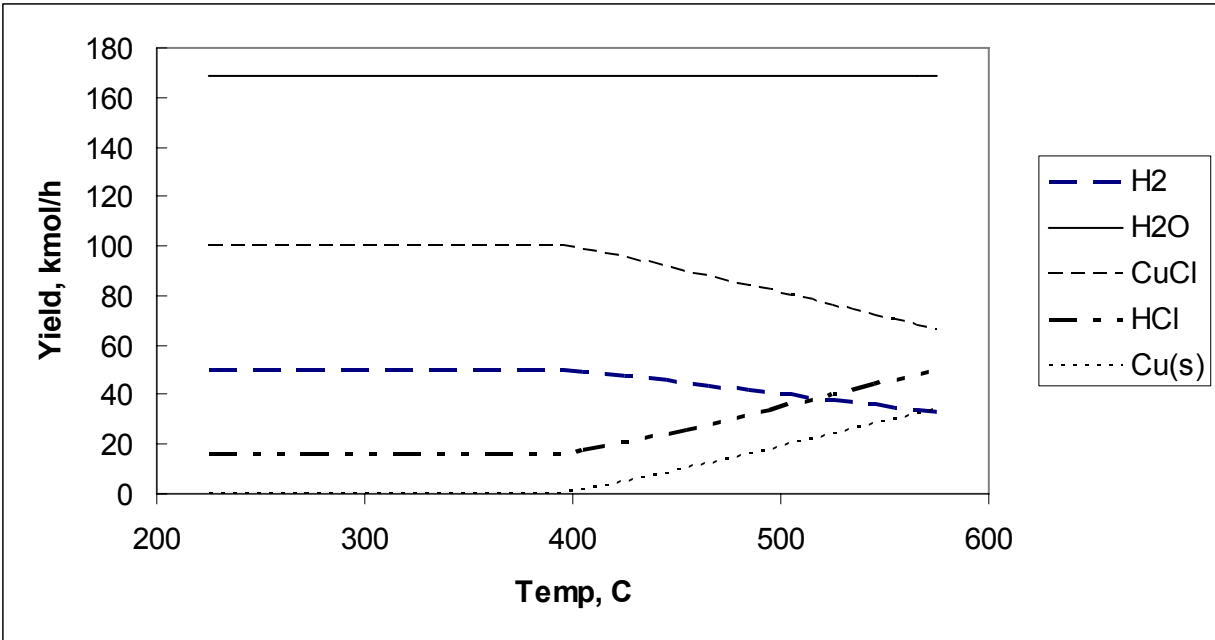


Figure 3. Effect of Temperature on Equilibrium Yield of Products from Reaction #1 Using Aspen Plus Simulation

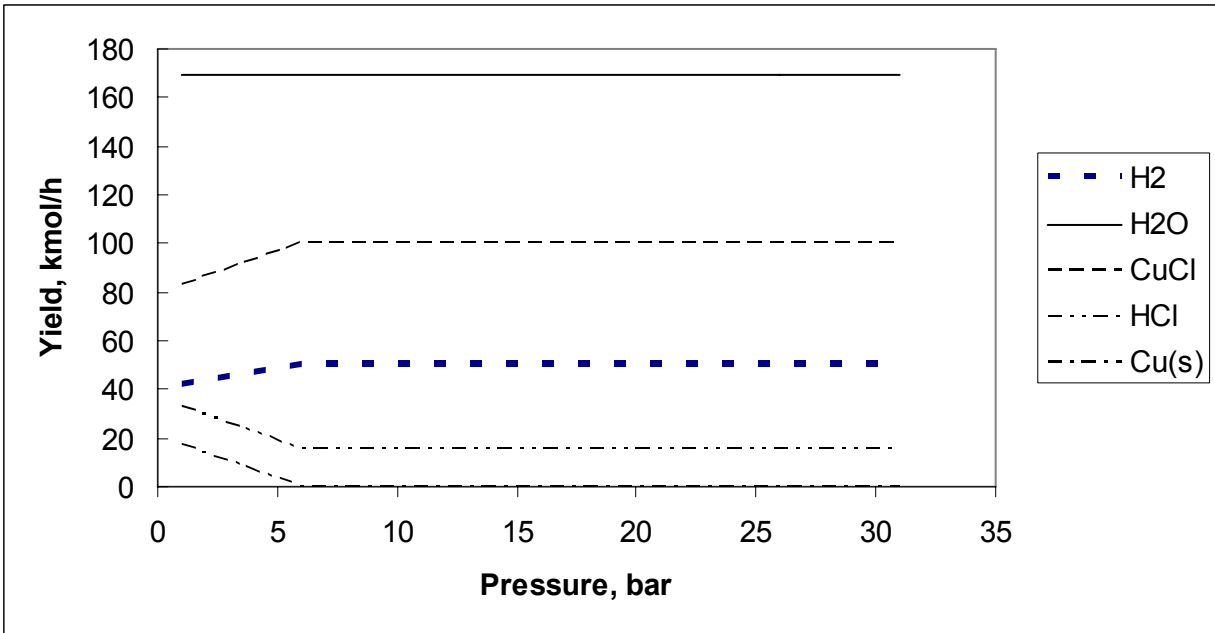


Figure 4. Effect of Pressure on Equilibrium Yield of Products from Reaction #1 Using Aspen Plus Simulation

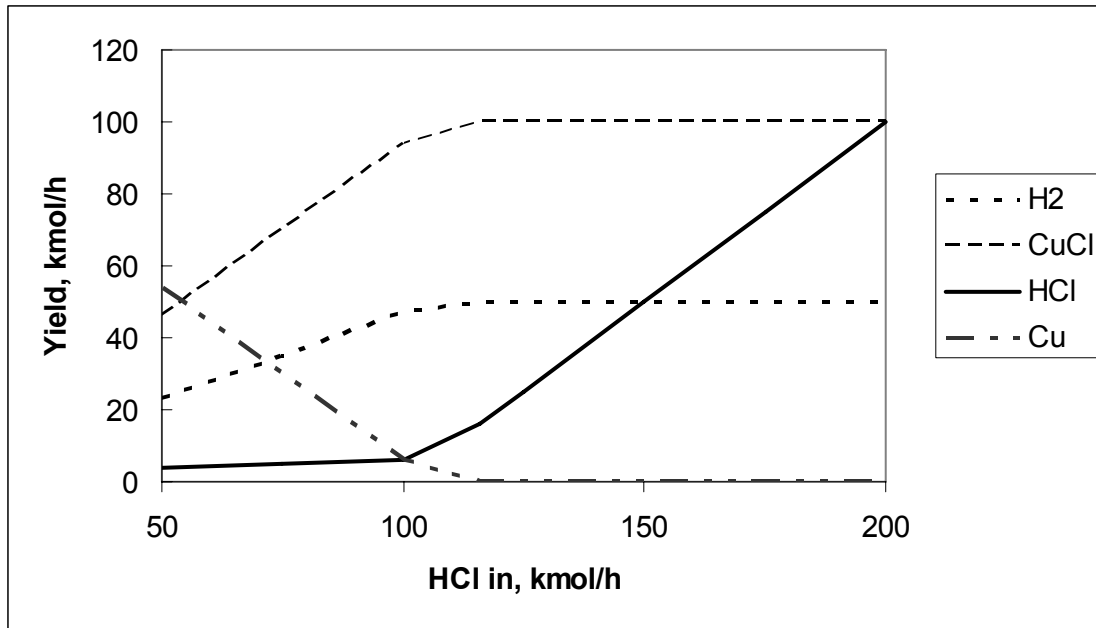


Figure 5. Effect of HCl Input on Equilibrium Yields from Reaction #1

Thermal Efficiency

A thermal efficiency was calculated for the process. In order to ensure that there was an adequate temperature driving force for matching all the heat duties in the flow diagram, a pinch analysis was done assuming a minimum 10°C approach temperature. Figure 6 shows the composite cooling and heating curves derived from the simulation. An additional 0.4×10^6 cal/hr is needed to have the minimum approach temperature met, above the 0.95×10^6 cal/hr from the sum of all heat sources and sinks.

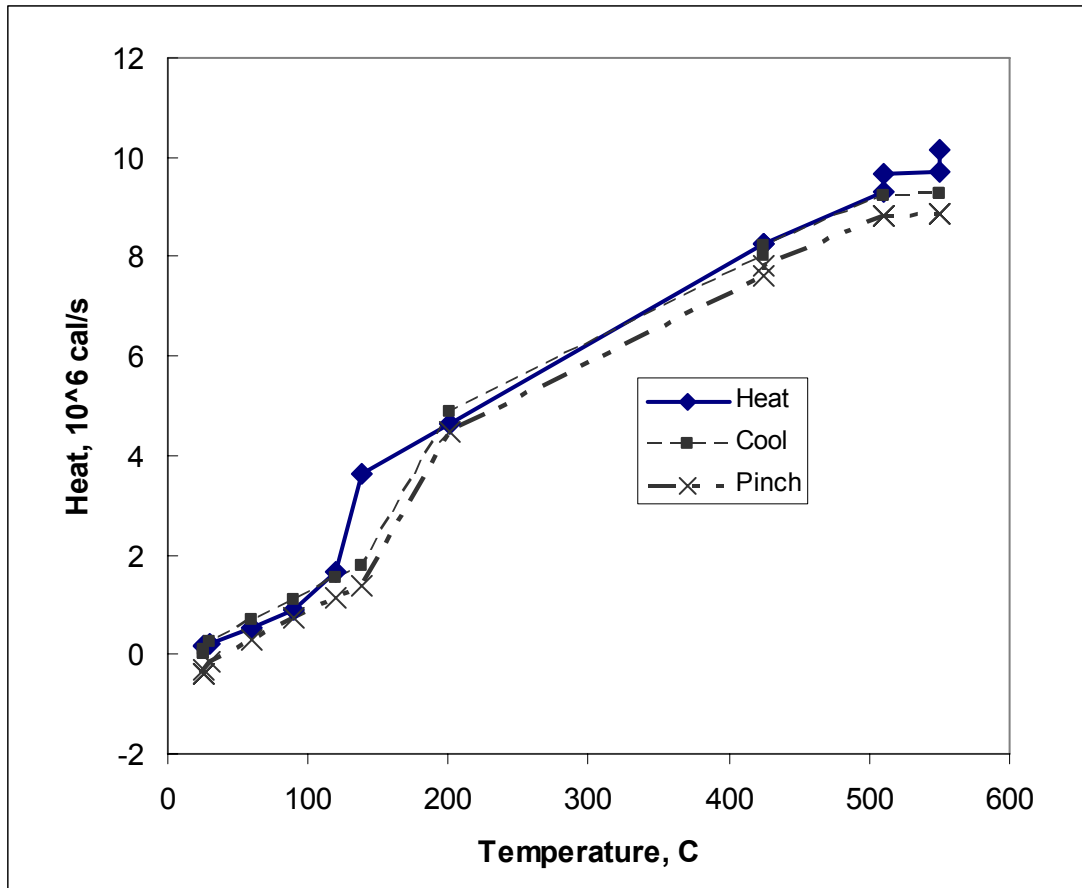


Figure 6. Composite Heating and Cooling Curves for Pinch Analysis

Table 2 shows that the thermal efficiency calculated from this model was 41% (LHV) if an estimate for the shaft work input was made, which justified continued R&D effort. The Aspen Plus simulation assumed a 10 psi pressure drop in each piece of processing equipment. This allowed the work input to be calculated for all the pumps in the process. The electrical work for the pumps was converted to equivalent thermal energy using a 50% conversion factor. Without the shaft work, the calculated efficiency was 43%. Sensitivity studies using the Aspen model showed that the yield for HCl (and indirectly that for $\text{CuO}\cdot\text{CuCl}_2$) was especially sensitive to the value assumed for the free energy of formation of $\text{CuO}\cdot\text{CuCl}_2$, as well as the reaction temperature. For example, an uncertainty of ± 11 kJ/mol was sufficient to change the yield of HCl by a factor of 7 at 300 °C.

Table 2. Thermal Efficiency Calculation for the Cu-Cl Cycle

<u>Component</u>		<u>Rate</u>		<u>Bases</u>	<u>MW</u>
Hydrogen	100.6	kg/hr	241.8	kJ/mol LHV	3.38
Heat In					3.97
Pinch					1.68
Electrolysis	2	electrons/H ₂	0.4	V	2.16
Pumps	222	kW			0.44
Work/heat	50%				
Efficiency	41%				
	43%	w/o pumps			

Future & Ongoing Experimental Work

The results of the simulation and the experimental work indicated that of the three thermal reactions, the hydrolysis reaction was the least understood. Further investigation of this reaction is probably the most important for determining whether this cycle can produce hydrogen cost effectively. Low yields of CuO•CuCl₂ would significantly increase expensive recycle and lead to a difficult separation of HCl and Cl₂. Our new work was therefore concerned with optimizing the hydrolysis reaction using both modeling work and experimental work.

In order to prepare a more robust simulation, we needed measured values of the enthalpy of formation and the free energy of formation for CuO•CuCl₂. Since CuO•CuCl₂ is not commercially available, a new method for synthesizing it was developed. This material was characterized by analysis of its chloride content (titration with AgNO₃), by X-ray diffraction, and by Raman spectroscopy. These characterizations indicated a purity of 99+%. The enthalpy of formation at 25 °C was measured using two different methods and compared with the literature data. A value of 381 ± 3 kJ/mol was determined to be the most reliable. The heat capacity was measured over three temperature regions: (1) from about 4 °K (liquid He) to 64 °K (liquid N₂), (2) from 64 °K to 360 °K, and (3) from 298 to 700 °K. The low temperature heat capacities were used to calculate the entropy. Figure 7 shows how the new data compares with published heat capacity information. The free energy of formation was then derived from the experimental values for the enthalpy of formation and entropy values. All other thermodynamic data for the various chemical species were checked against literature values and the most reliable selected for inclusion in the physical property database. These data were checked for consistency. Heat capacity varied from 0.48 J/K-g at 311 °K to 0.52 J/K-g at 698 °K. The new thermodynamic data are being added to the physical properties database used in the Aspen Plus simulations, and then sensitivity studies will be reexamined and process conditions will be re-optimized.

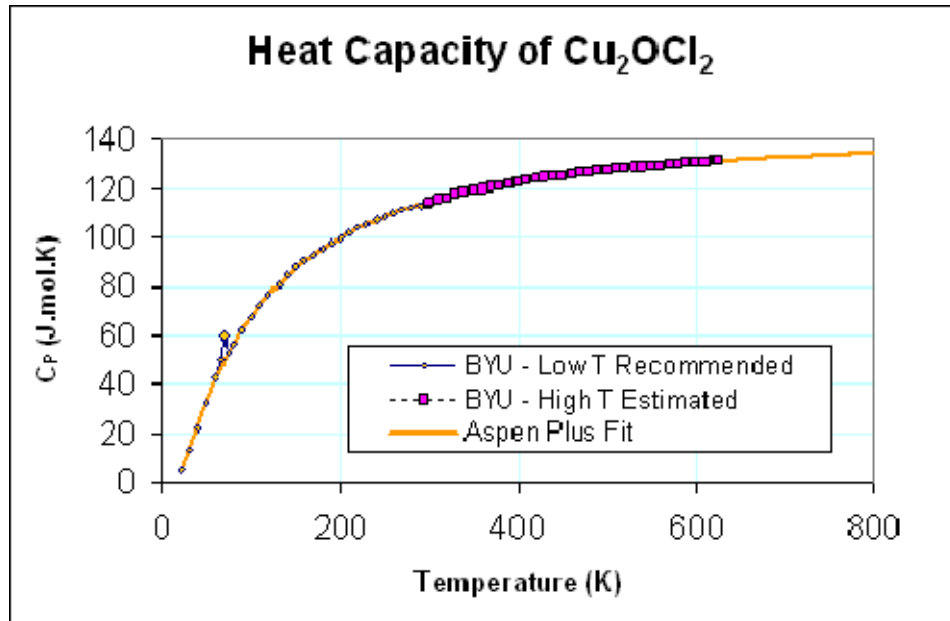


Figure 7. Heat Capacity Data for Copper Oxychloride

Because concentrations of salts and acid were varied in order to optimize yields, experimental values were also derived for the heats of solution for key chemicals in the process as a function of concentration. These are reported in Table 3. These values will be used to update the Aspen Plus properties so that an accurate heat balance can be made for the ANL CuCl process in the simulation. Figure 8 shows how the heat of solution for CuCl₂ varies with concentration.

Table 3. Heats of Solution for key chemicals in the CuCl process

Chemical	In 120 ml water +	ΔH_s , kJ/mol
CuCl ₂	-	-48.9 ± 0.3
CuCl ₂	0.1 M HCl	-47.3 ± 0.3
CuO	4.0 M HCl	-50.9 ± 0.1
CuO•CuCl ₂	0.1 M HCl	-96.9 ± 0.5
CuO•CuCl ₂	4.0 M HCl	-68.2 ± 1.2

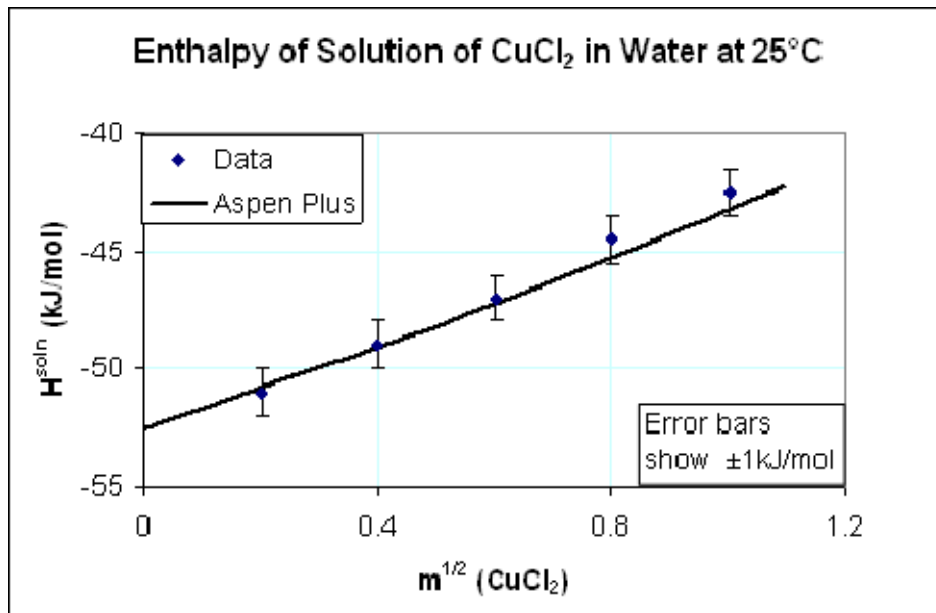


Figure 8. Heat of Solution for CuCl₂ in Water

New experimental work is concerned with the hydrolysis of CuCl₂ to form HCl and the CuO•CuCl₂. A new reactor system was fabricated. Experimental variables, e.g., temperature, flow rate, humidity, particle size of the CuCl₂, reactor design, were varied to maximize the production of HCl and to minimize the competing CuCl₂ decomposition reaction. This work is ongoing.

This cycle is well matched to several of the reactor concepts described in the Global Nuclear Energy Partnership, such as the Na-cooled reactor, the supercritical water reactor, and the gas reactor. Since the heat source is fossil-fuel free, the overall process does not lead to greenhouse gas emissions.

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