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Development of the ANL Low Temperature Copper Chloride Process

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Features of Thermochemical Cycles

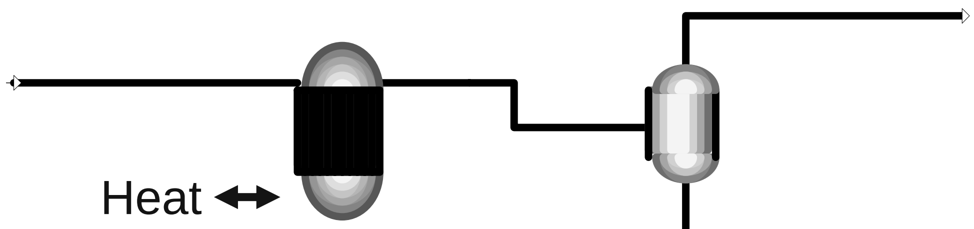
- Overall $H_2O(l) = H_2(g) + ½ O_2(g)$
- Over 300 Cycles Proposed in the Literature
- Most require high temperature steps (> 850 °C)
  - Solar collector (intermittent plant operation)
  - High temperature nuclear cycle (materials issues)
- ANL CuCl process is one of several processes that show promise and require peak temperatures below 550 °C

ANL Copper Chloride Process

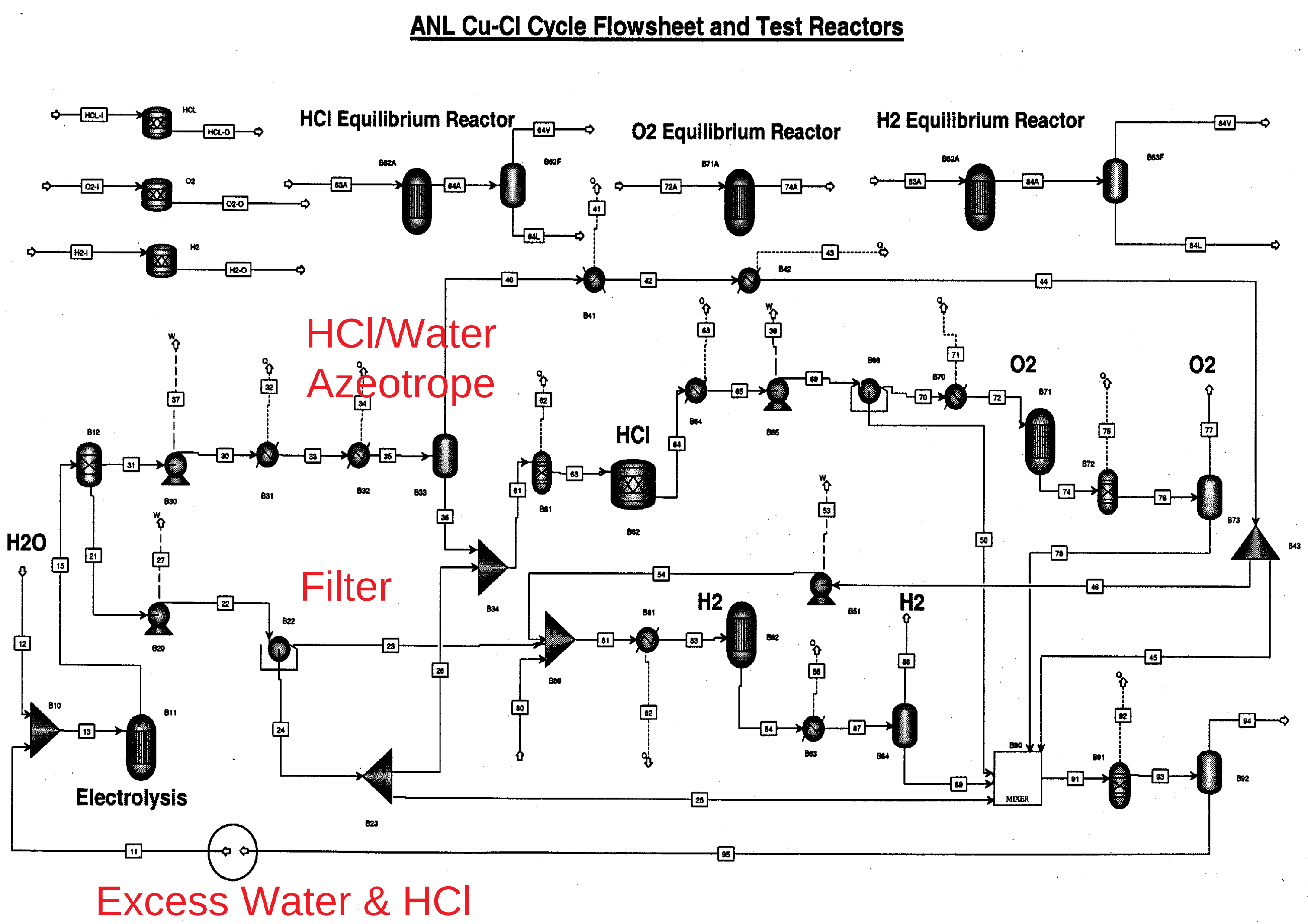
#	Reaction Stoichiometry	Temperature (°C)
1	$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$	425-450
2	$4CuCl(s) \rightarrow 2CuCl_2(a) + 2Cu$ (Electrochemical)	<100
3	$2CuCl_2(s) + H_2O(g) \rightarrow CuO \bullet CuCl_2\ (s) + 2HCl(g)$	300-375
4	$CuO \bullet CuCl_2\ (s) \rightarrow 2CuCl(l) + \frac{1}{2}O_2(g)$	450-530

Overall $H_2O = H_2 + \frac{1}{2}\ O_2$

Aspen Plus Simulation of Individual Reactions

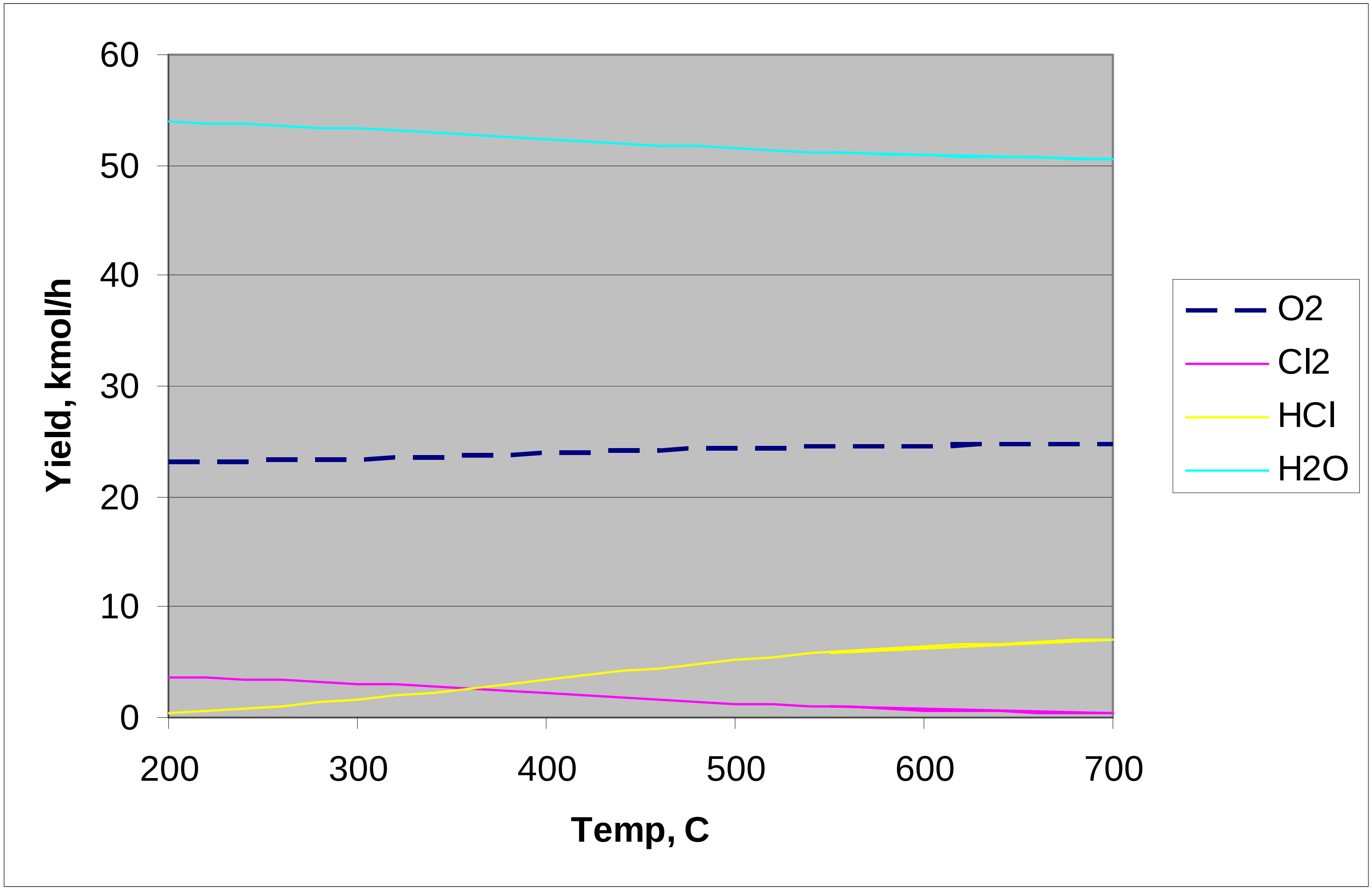


Process Flow Diagram



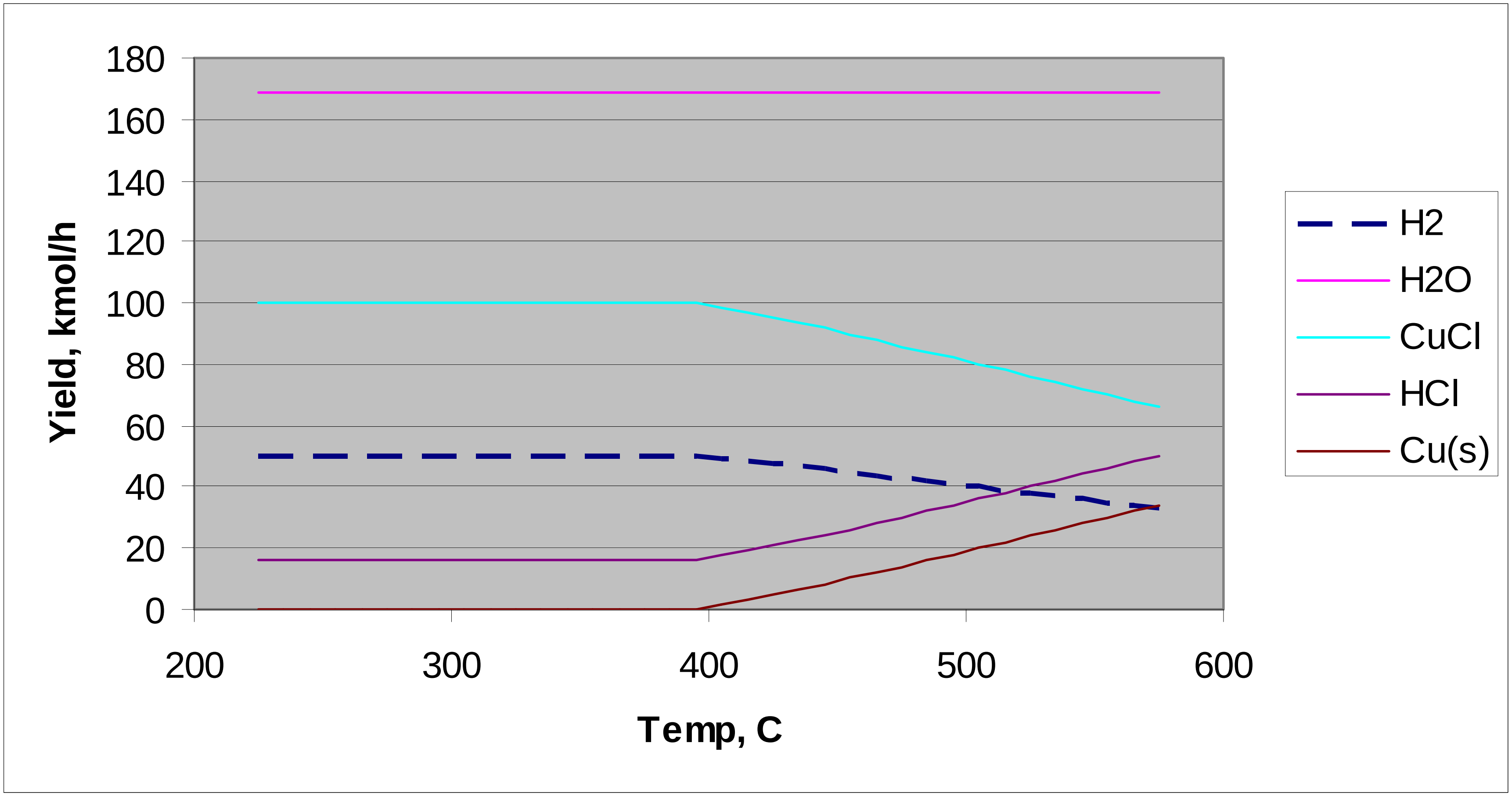
Effect of temperature on oxygen formation reaction (#4)

$$CuO \bullet CuCl_2\,(s) \rightarrow 2CuCl(l) + \tfrac{1}{2}O_2(g), \quad \text{Pressure} = 2\ \text{bar}$$



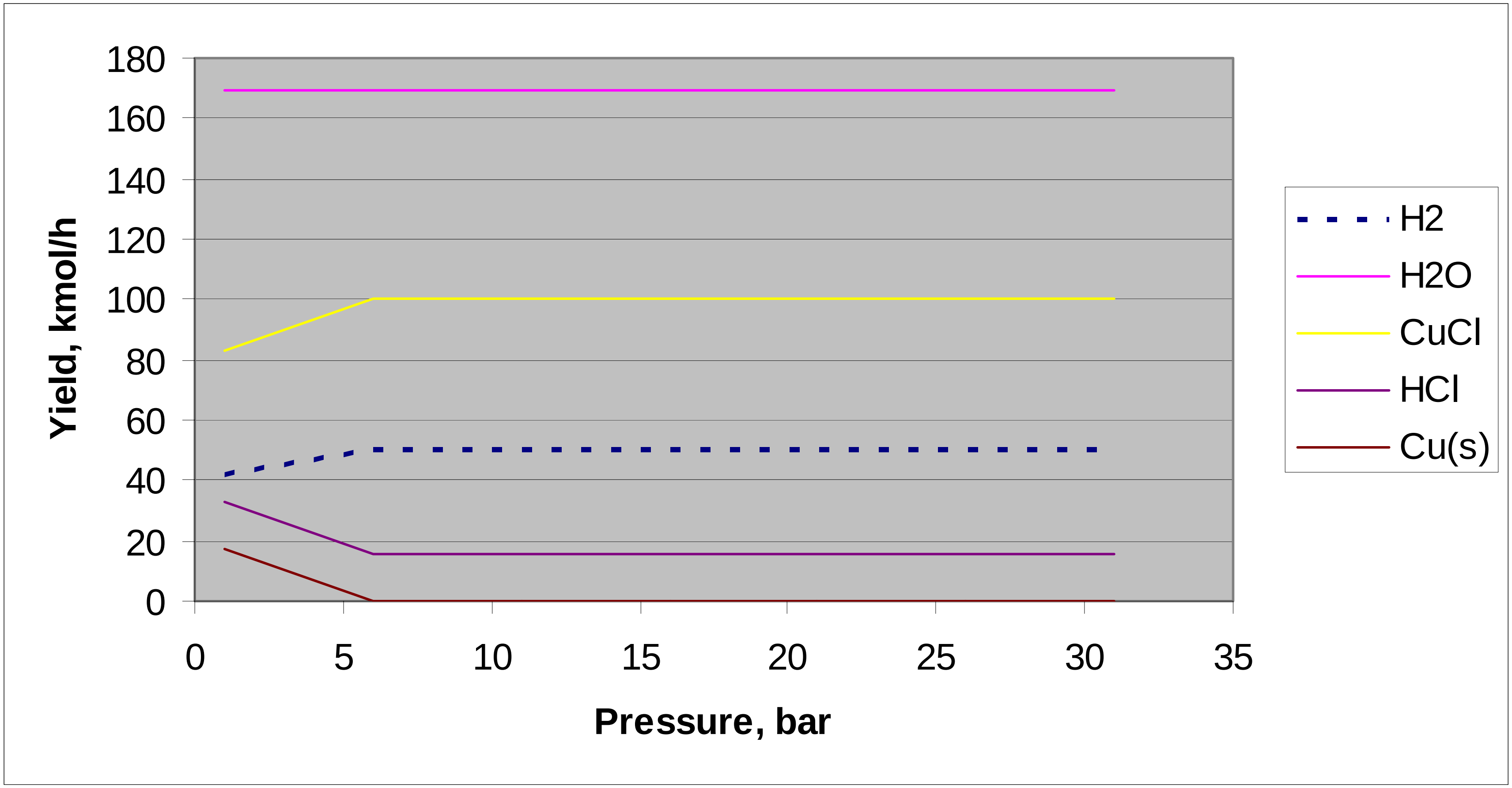
Effect of temperature on hydrogen formation reaction (#1)

$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$, Pressure = 28 bar



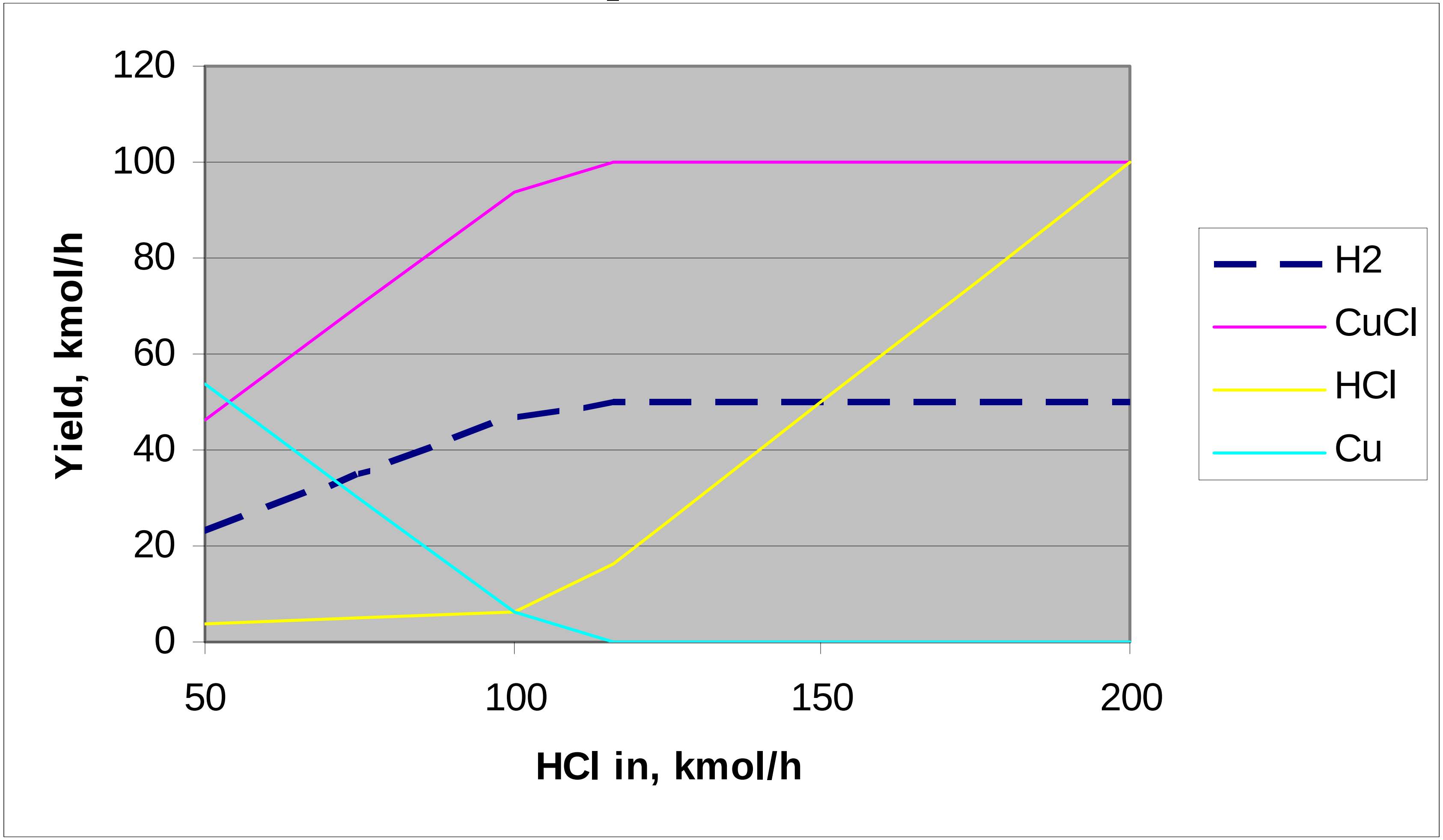
Effect of pressure on hydrogen formation reaction (#1)

$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$, Temperature = 320 °C



Effect of excess HCl on hydrogen formation reaction (#1)

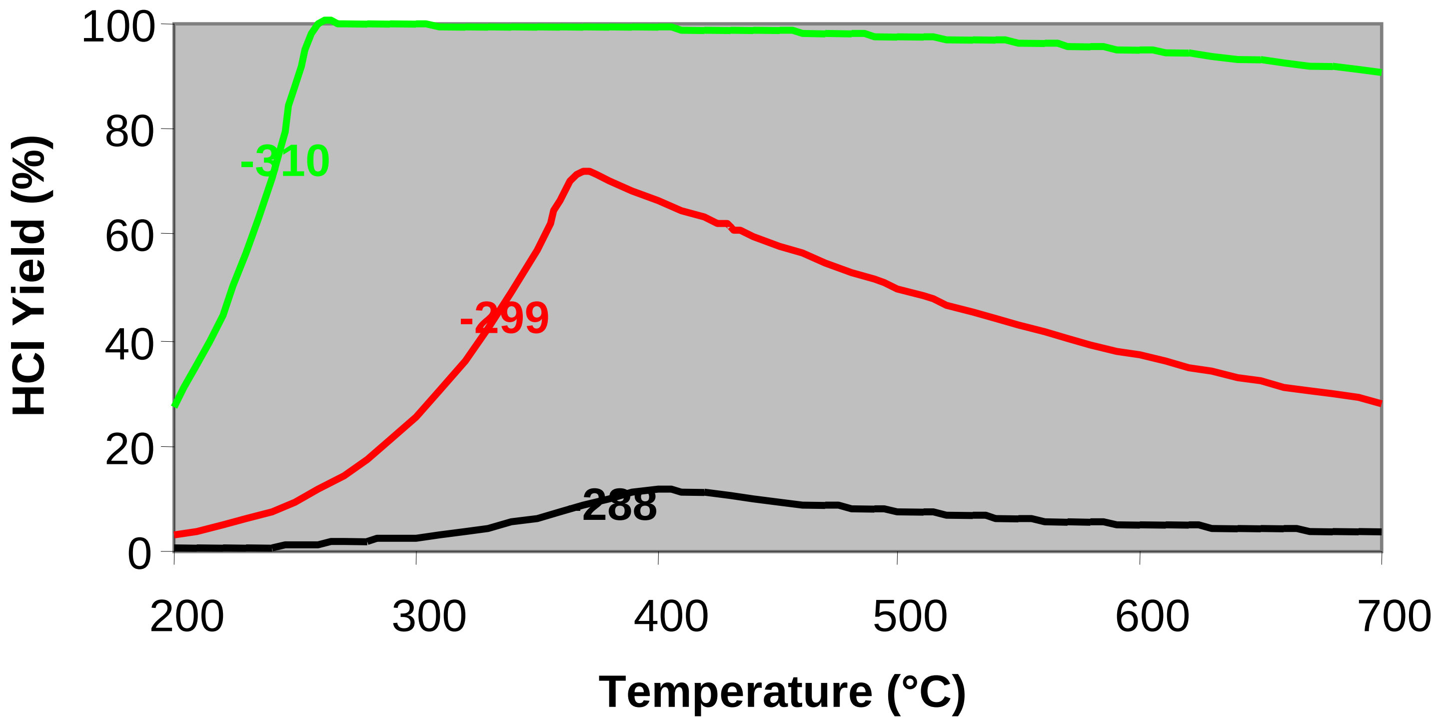
$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$, Temperature 320 °C, Pressure 28 bar



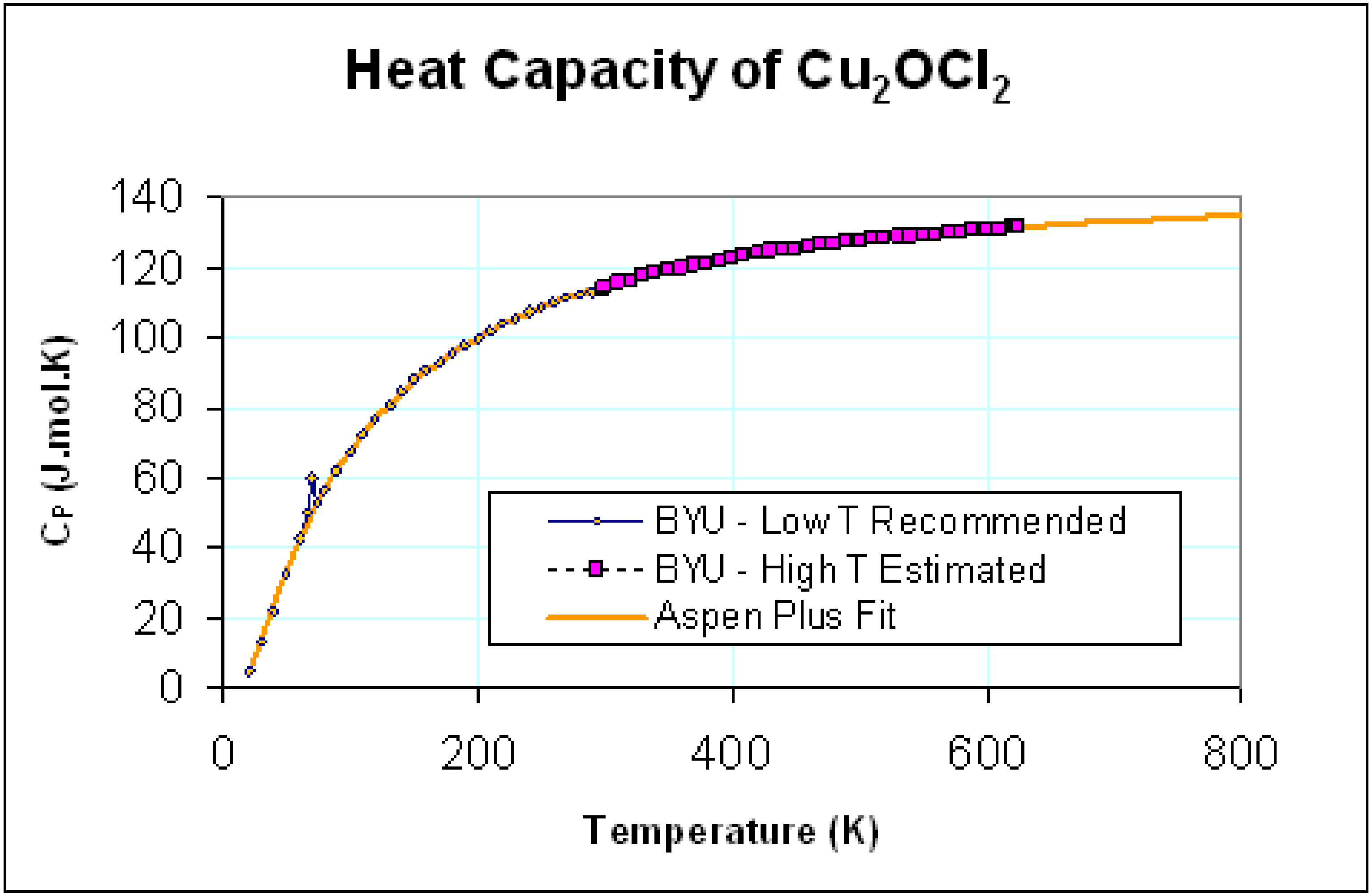
Effect of heat of formation of copper oxychloride on equilibrium yields from reaction #3

$$2CuCl_2(s) + H_2O(g) \rightarrow CuO \bullet CuCl_2\,(s) + 2HCl(g)$$

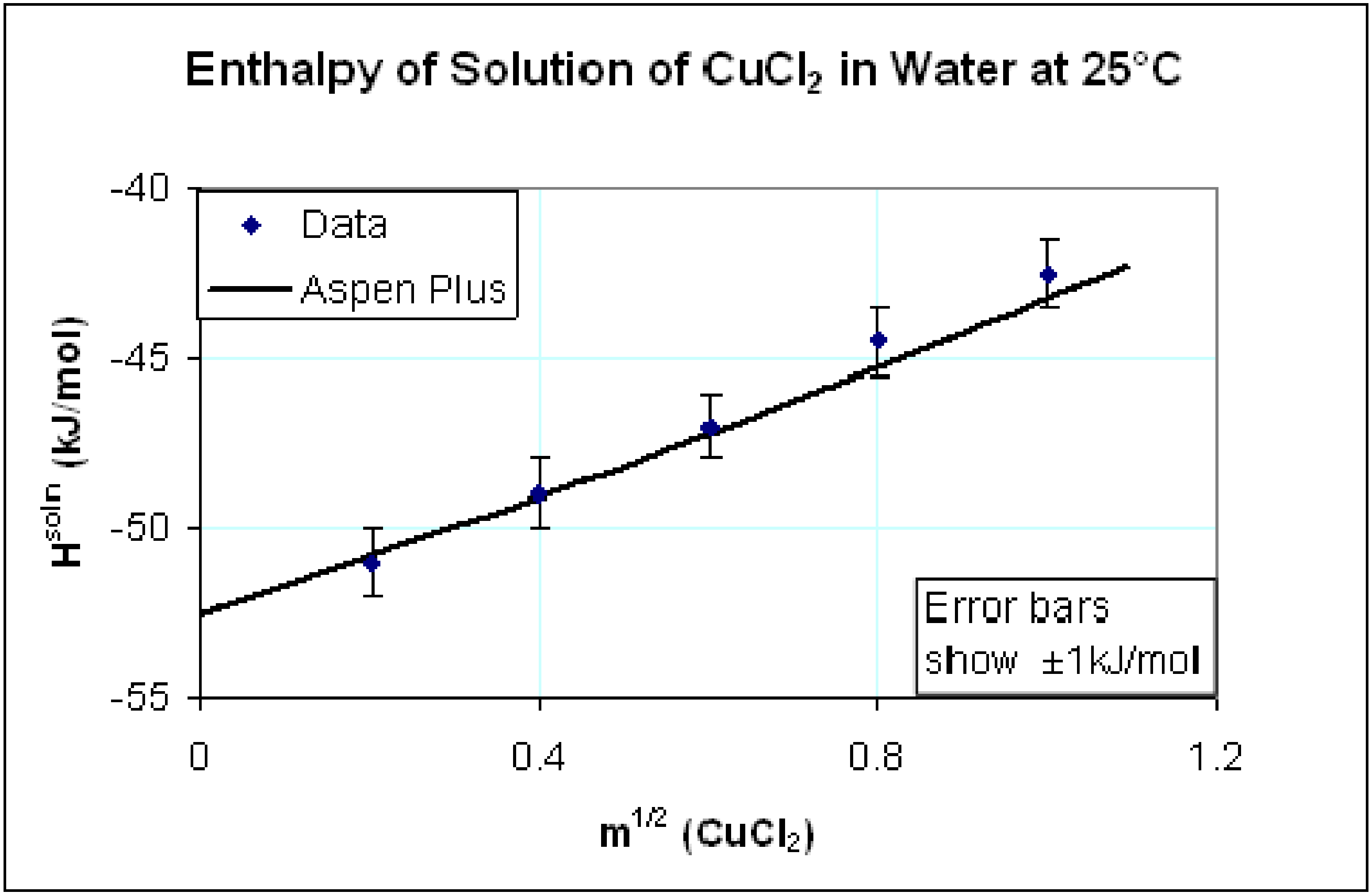
Pressure = 1 bar, Steam/copper = 6



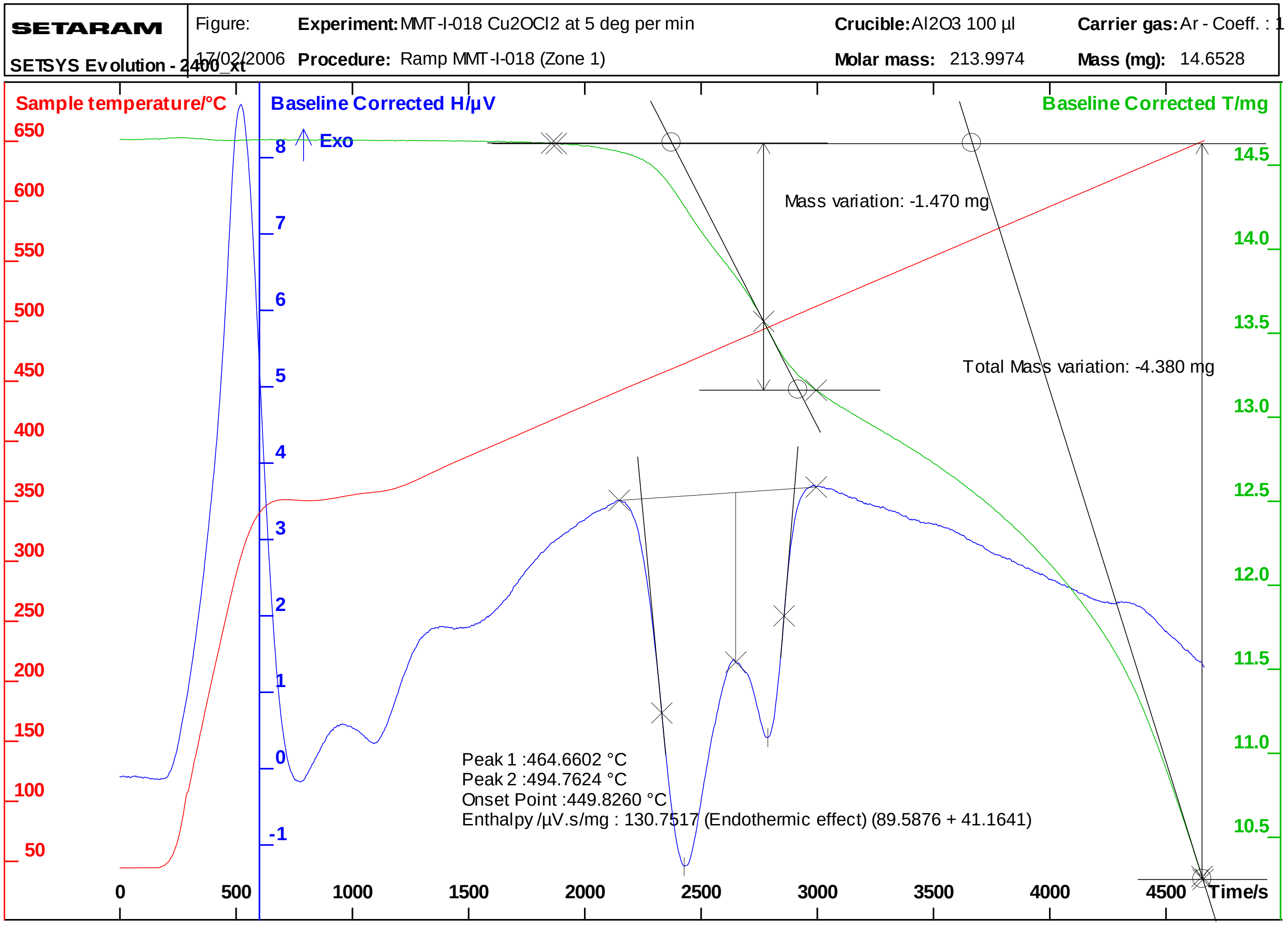
Data collection for heat capacity of copper oxychloride



Data collection for enthalpy of solution of copper salts



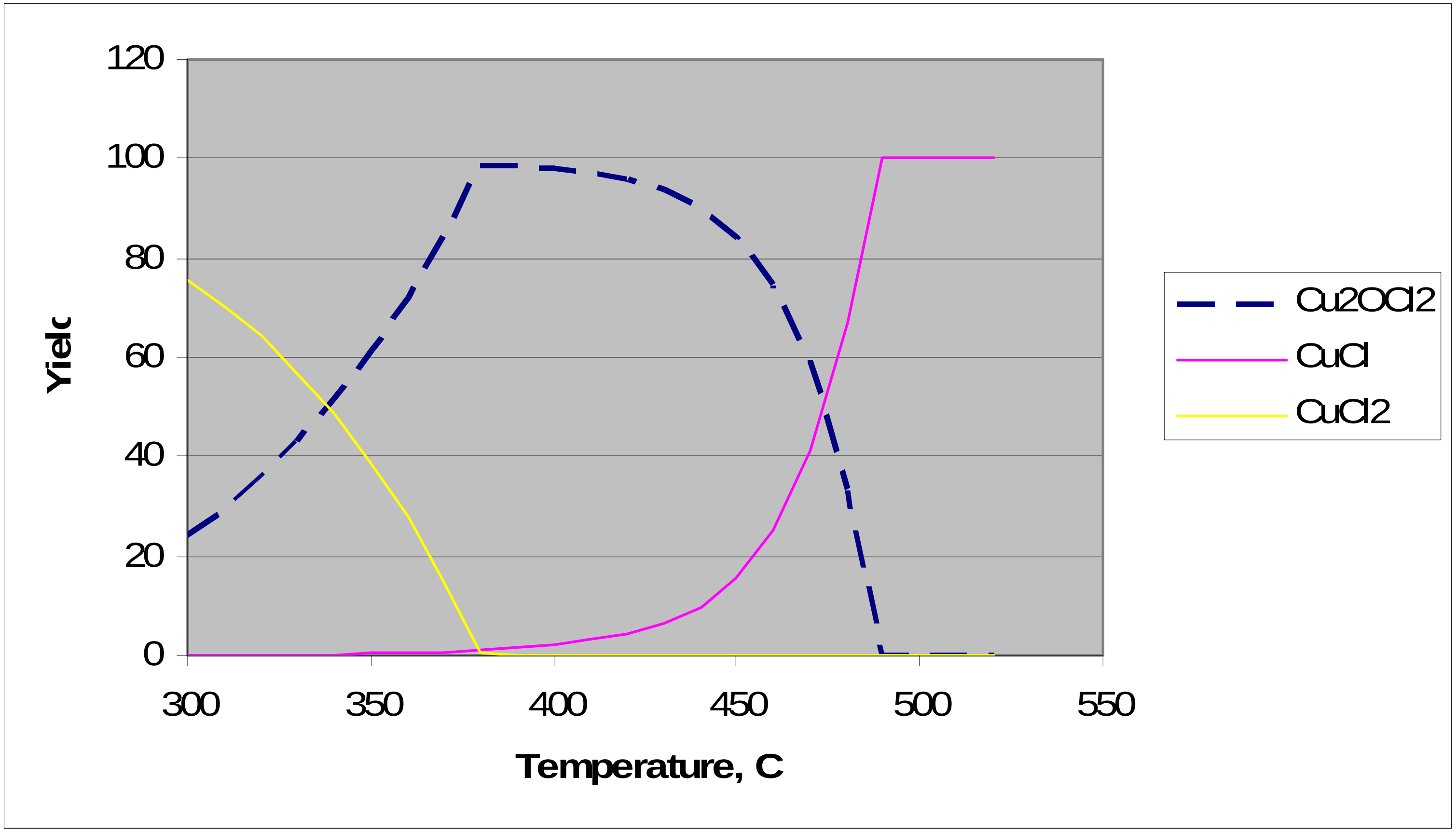
Thermogravimetric data for oxychloride decomposition



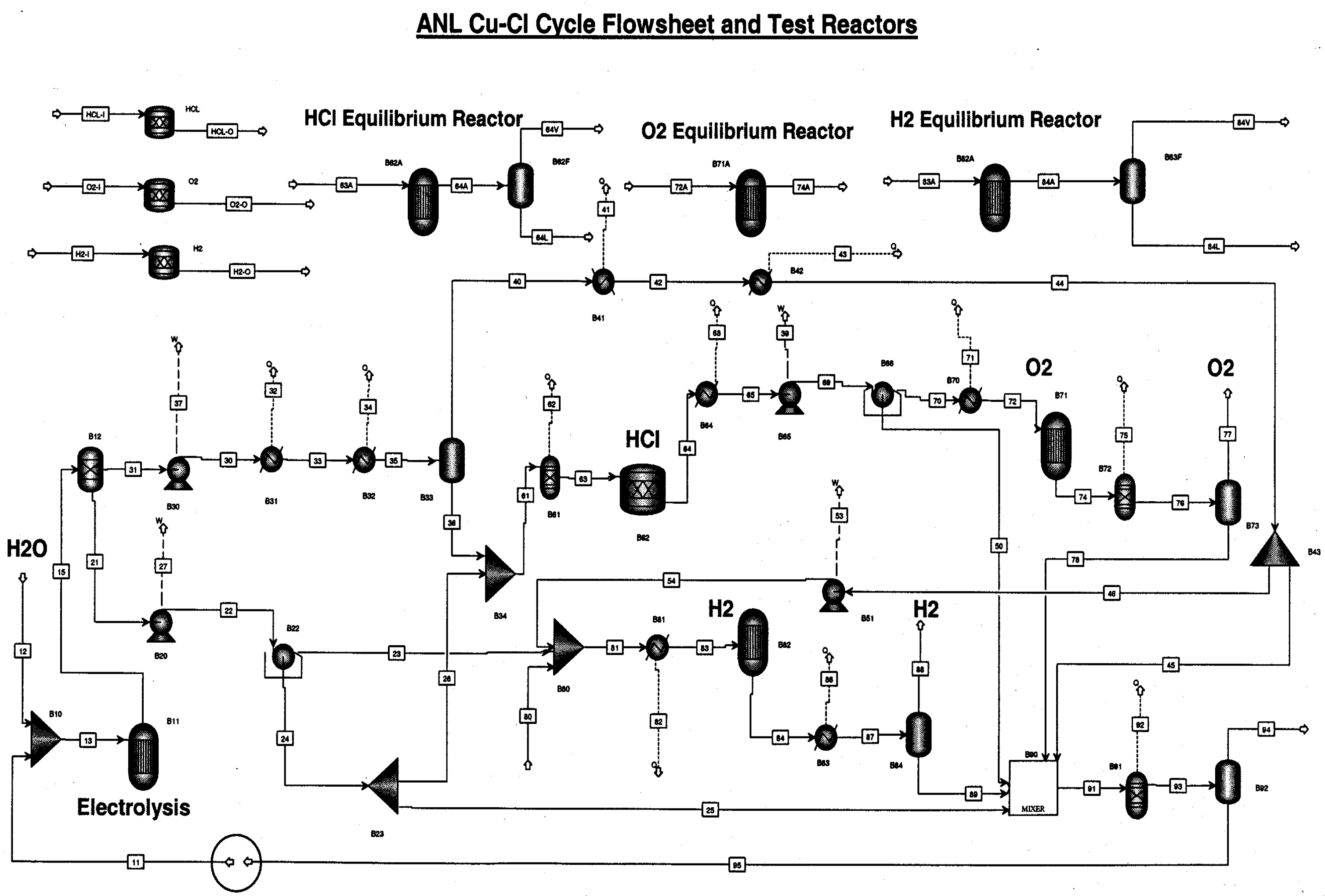
Effect of temperature on oxychloride reaction (#3)

$$2CuCl_2(s) + H_2O(g) \rightarrow CuO \bullet CuCl_2\ (s) + 2HCl(g)$$

Steam/Cu = 17, Pressure 2 bar



Process Flow Diagram



Thermal Efficiency of ANL CuCl Process

$$E = \frac{-\Delta H^{\circ}_{25^{\circ}C}\left(H_2O\right)}{Q_{hot} + \frac{W}{0.5}}$$

The thermal efficiency of the process was obtained by dividing the heating value (LHV) of the hydrogen product out by the sum of thermal heat in plus electrical energy in (converted to thermal equivalent with a 50% factor)

E = 44% with thermal + electrolysis energy
= 41% including " + shaft work

Future Work for Argonne CuCl Process

- Match Physical Property Parameters in Aspen to Data
  - Enthalpy of Formation
  - Heat Capacity vs. Temperature
  - Free Energy of Formation
- Optimize Process Conditions
  - Temperature and Pressure
  - Stream Compositions (Separation Sequence)
- Equipment Selection
  - Single Stage vs. Multi Stage Separations
  - Reactor Types and Residence Times (Kinetics)
  - Other (Filters, Pumps, etc.)
- Cost Analysis

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