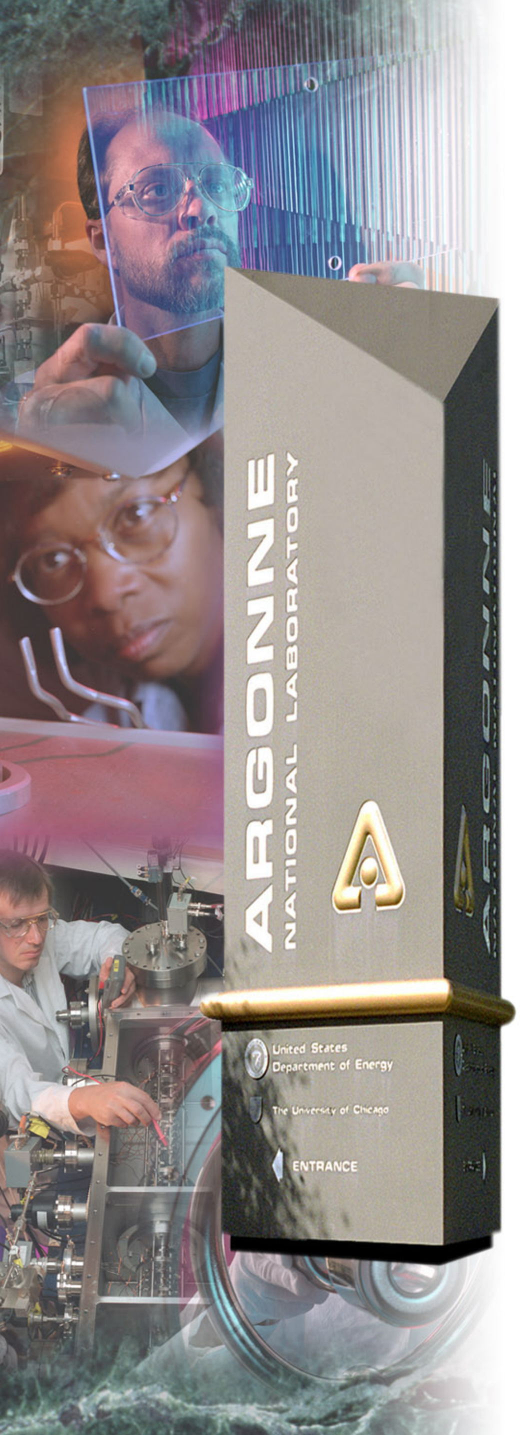

Efficiency Calculations for the Hybrid Copper-Chloride Thermochemical Cycle

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Objective

- **Provide an update of the development effort for the Cu-Cl cycle**
- **Illustrate the scoping flowsheet methodology at Level1, 2, and 2+ where we are starting to incorporate experimental results into a simulation program**
- **Invite participation and/or solicit comments on methodology for evaluating efficiency as a cycle is developed**

Results in GA-A24972

- **Summary of cycle evaluation for >200 cycles entitled High Efficiency Generation of Hydrogen Fuels using Solar Thermo-Chemical Splitting of Water by Barry McQuillan et al.**

- **Of 202 cycles, 67 were evaluated and 16 were selected as top rated**

- **Cu-Cl cycle was one of the 16 top cycles**

- **Report is a living document**
  - Mike Simpson’s cycle is not yet included
  - Other cycles are being found

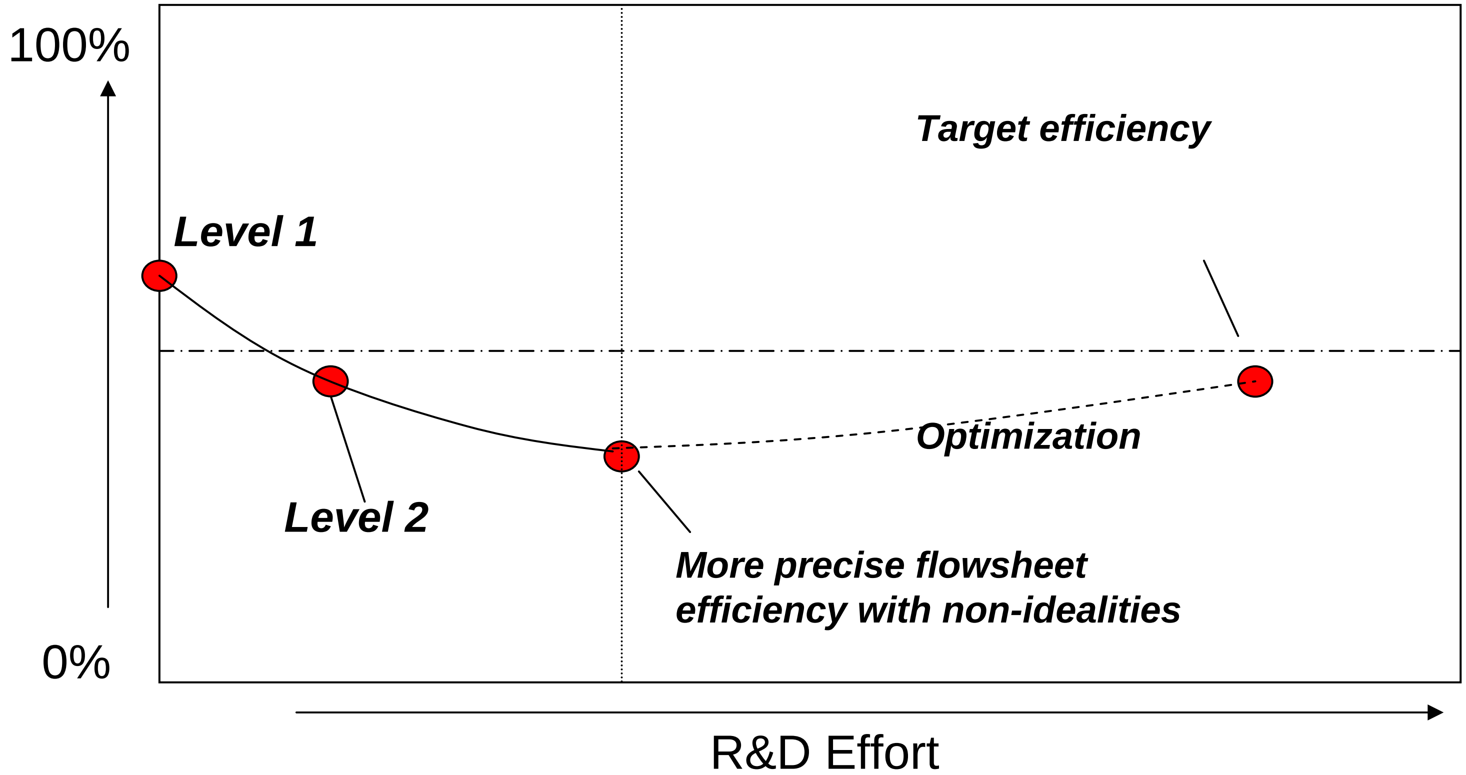
Outline

- **Introduction**
- **Illustration of the NHI methodology with results from the Cu-Cl cycle**
  - Results for Levels 1, 2, and 2+
  - Challenges when necessary data is lacking in HSC and other glitches
- **A more detailed look at the hydrolysis reaction**
  - Experimental results and the results of sensitivity studies with Aspen
- **Summary**

Cu-Cl Cycle's Status

- Identified as a promising low temperature cycle in a 1980 report (GRI-80/0023)
- Proof of principle work completed for all reactions in cycle
- Maximum temperature required in laboratory experiments is 530C
- Experimental work completed to date shows cycle is chemically viable and early assessment of efficiency showed thermodynamic viability
- What does NHI methodology say?

Efficiency changes with effort/knowledge



From Pascal Anzieu at CEA

Thermochemical cycle assessment levels

- **Level 1**
  - Stoichiometric reactions - 100% completion
    - *No competing reactions*
  - Heat and work inputs
    - *Heat: reaction, sensible, and latent*
    - *Work: electrochemical, chemical potential, and separation*
  - Reaction temperatures as proposed in the literature
  - Thermodynamic data from readily available databases
    - *HSC and/or others*

Assumptions in the methodology

- H_2O enters as a liquid at 25°C
- H_2 and O_2 are released at atmospheric pressure at 25 °C
  - One mole of water in Level 1
  - Number of moles varied in Level 2
- Work terms calculated through standard equations
- Solvation effects ignored for Level 1 and 2 efficiency calculations
- 10°C delta T needed as a driving force for heat exchange

Work terms

- **Electrochemical work: $\Delta G = nFE$ and ignore concentration terms**
- **Separation work: $W = - RT \Sigma n_i \ln(y_i)$,**

  where R is the gas constant, T is the absolute temperature, n_i is the amount of each species in the mixture and y_i is the concentration of each species
- **Chemical potential work: +ΔG of the reaction and ignore any work produced in - ΔG reaction because it is not useful work**

Efficiency defined

- **Efficiency (LHV) calculated with equation**

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

- **Efficiency of converting heat to work is assumed to be 50%.**

Reactions and temperatures in the Cu-Cl cycle

- **Hydrogen Production**
  - $2Cu + 2HCl(g) = H_2(g) + 2CuCl$ (450°C)
- **Intermediate Reactions**
  - $4CuCl = 2Cu + 2CuCl_2$ (Electrochemical)
  - $2CuCl_2 + H_2O(g) = Cu_2OCl_2 + 2HCl (g)$ (325°C)
- **Oxygen Production**
  - $Cu_2OCl_2 = 2CuCl + ½O_2 (g)$ (450-530°C)
- **Limitation #1.: No data for Cu_2OCl_2 in the HSC database**

Elimination of Cu_2OCl_2 rxns. → 3 rxn. cycle

- $2Cu + 2HCl(g) = H_2(g) + 2CuCl(l)$
- $4CuCl = 2Cu + 2CuCl_2$
- $2CuCl_2 + H_2O(g) = 2CuCl + \frac{1}{2}O_2(g) + 2HCl(g)$

- **No apparent need for thermodynamic data for Cu_2OCl_2**
- **Separation work is required for HCl and O_2**
  - In Level 1 and 2 separation methods are not defined

Level 1 analysis for stoichiometric reactions

Calculate all heat terms

Use Pinch analysis to optimize energy usage

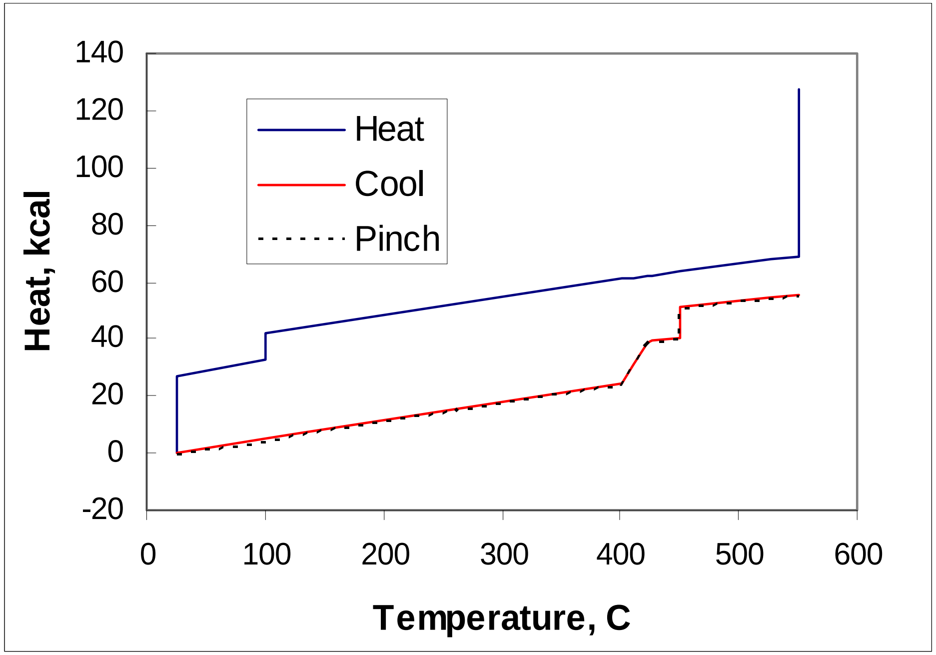
Calculate work terms

Summary of heats for Level 1 analysis

	Reaction #	Type	Moles	T_1 (°C)	T_2 (°C)	ΔH, kcal	ΔG, kcal
Cu	H_2 Gen.	Reaction	2	450	450	-11.16	-0.14
CuCl	EC	Reaction	4	25	25	26.82	31.7
$CuCl_2$	O_2 Gen.	Reaction	2	550	550	58.44	2.69
$CuCl_2$		Sensible	2	25	550	20.18	
Cu(s)		Sensible	2	25	450	5.26	
HCl(g)		Sensible	2	550	450	-1.45	
O_2 (g)		Sensible	0.5	550	25	-1.98	
H_2 (g)		Sensible	1	450	25	-2.94	
H_2O(l)		Sensible	1	25	100	1.35	
H_2O(l) = H_2O(g)		Latent	1	100	100	9.77	
H_2O(g)		Sensible	1	100	550	3.92	
CuCl(l)		Sensible	2	550	450	-2.89	
CuCl(l)		Sensible	4	450	423	-9.23	
CuCl(l) = CuCl(s)		Latent	4	423	423	-6.22	
CuCl		Sensible	[illegible]	423	25	-21.57	
					Total	**68.3**	

Pinch Analysis

- **Heat curve represents endothermic process**
- **Cool curve represents exothermic process**
- **Pinch is the amount of heat needed to drive the cool curve below the heat curve at every point, about 1 kcal**



Work terms

- **Electrochemical rxn.: $4CuCl \rightarrow 2Cu + 2CuCl_2$**
  - Only proof of principle work completed
  - Use experimentally determined value of 0.45 V to determine electrochemical work using Faraday's Law, $\Delta G = nFE$
  - Ignore concentration term in Faraday's Law

- **Separation work to separate HCl, oxygen in hydrolysis reaction**

- **Chemical potential work for reactions with + ΔG**

Level 1 efficiency calculation

	Energy, kcal/mol H_2	Heat Equivalent[a], kcal/mol H_2
Total heat-in	68.3	
Pinch heat	1.0	
Chemical potential work	2.69	5.4
Separation work	2.05	4.1
Electrochemical Work	20.76[b]	41.5
Sum of heat and work inputs		120.3
Enthalpy of formation, H_2 (LHV)	57.8	
Efficiency	48.0% (LHV)	

[a]Heat to electricity conversion factor of 50%

[b]Ignores any external heat need for the electrochemical reaction

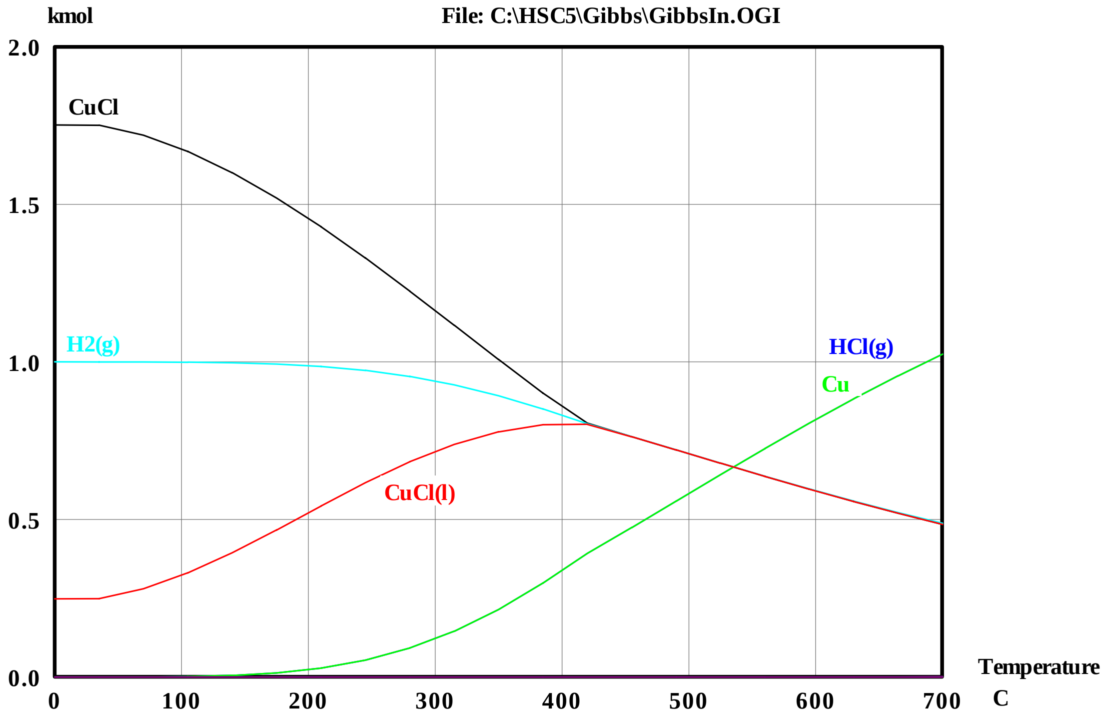
Level 2 analysis for equilibrium reactions

1. Use HSC to determine equilibrium compositions vs. temperature

2. Adjust reaction conditions

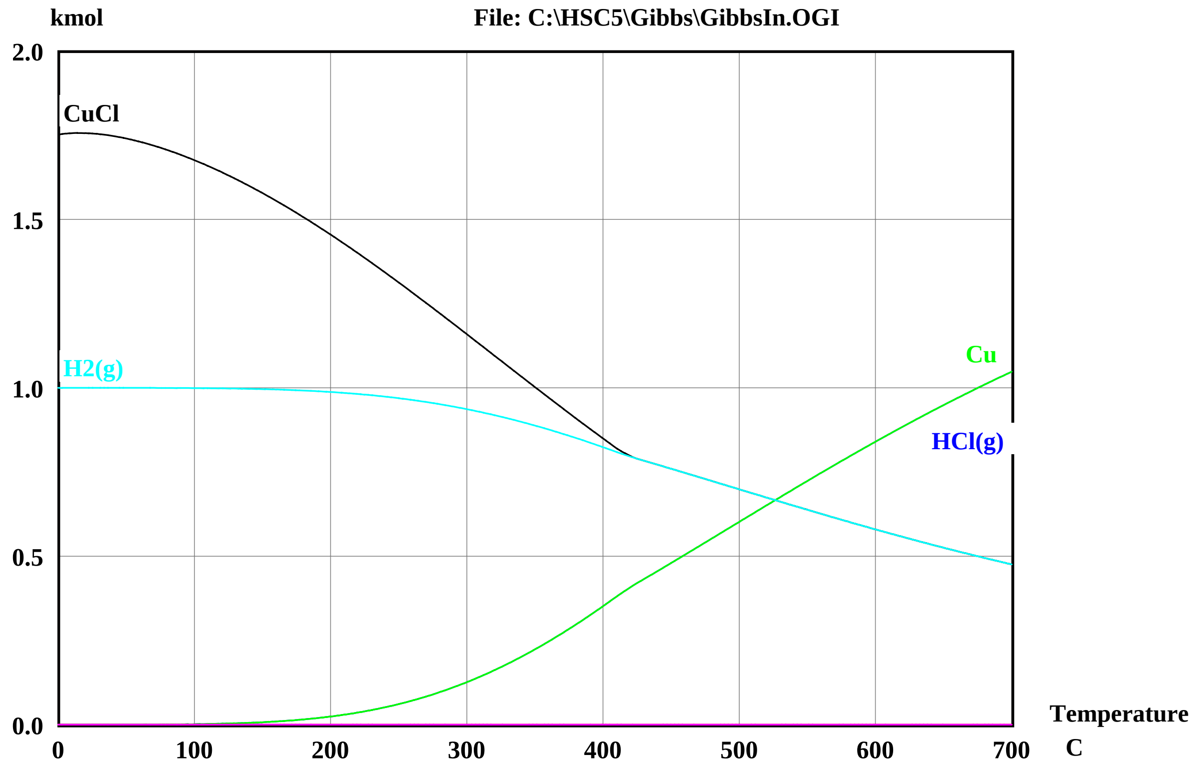
3. Calculate heat terms, pinch, and work terms

Equilibrium: 2Cu + 2HCl(g) → 2CuCl + H_2(g)



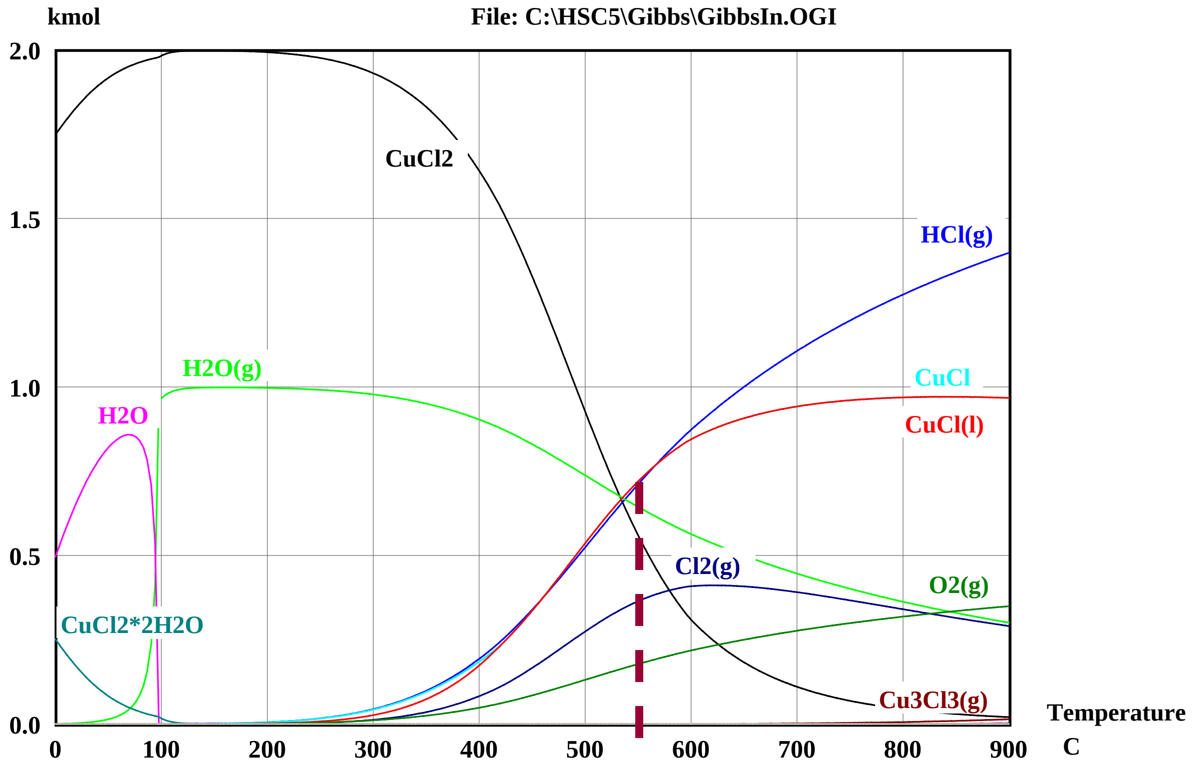
- **HSC limitation # 2: CuCl(s) and CuCl(l) present at 0 to 423°C but CuCl melts at 423°C**

Equilibrium: 2Cu + 2HCl(g) → 2CuCl + H_2(g)



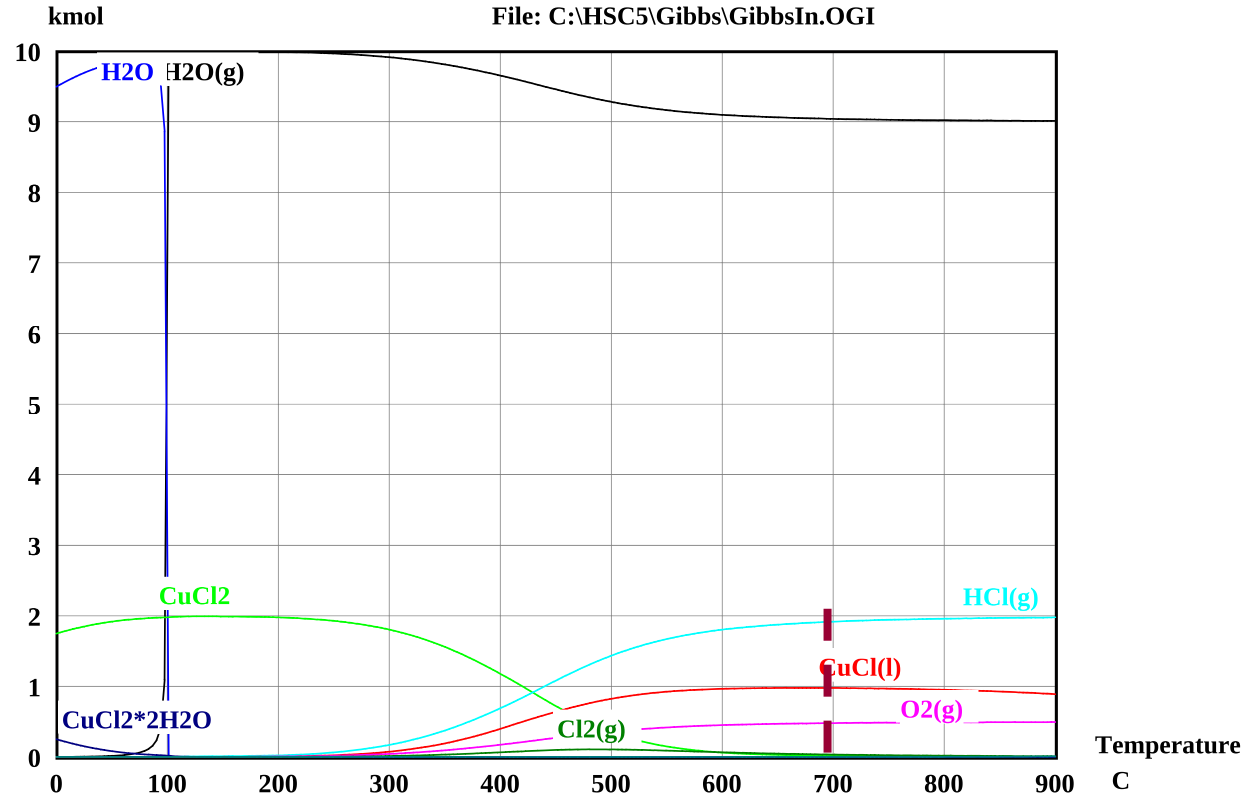
- **Mass balance is now incorrect**
- **HSC doesn't always handle liquid phases correctly**

$2CuCl_2 + H_2O(g) \rightarrow 2CuCl + 2HCl\ (g) + ½O_2(g)$



- **Equilibrium yields as a function of temperature**
- **Cl_2 formation is significant above 400C**

Additional water reduces Cl_2 formation



- **Cl_2(g) is 0.08 kmol at 510C, 0.03 kmol at 700C, and 0.003 kmol at 300C**

Summary of Level 2 Evaluations

	Temperature, °C			
	Level 1	Level 2		Level 2+
Conditions		Case 1	Case 2	Aspen
Water, mols	1	1	10	10
H_2 Formation Rxn.	450	100	450	450
Hydrolysis Rxn.	550	700	700	510
O_2 Formation Rxn.		700	700	550
Efficiency % (LHV)	48	41.5	39.6	42.4

Experimental results show that the hydrolysis rxn. can be run at 310-325°C

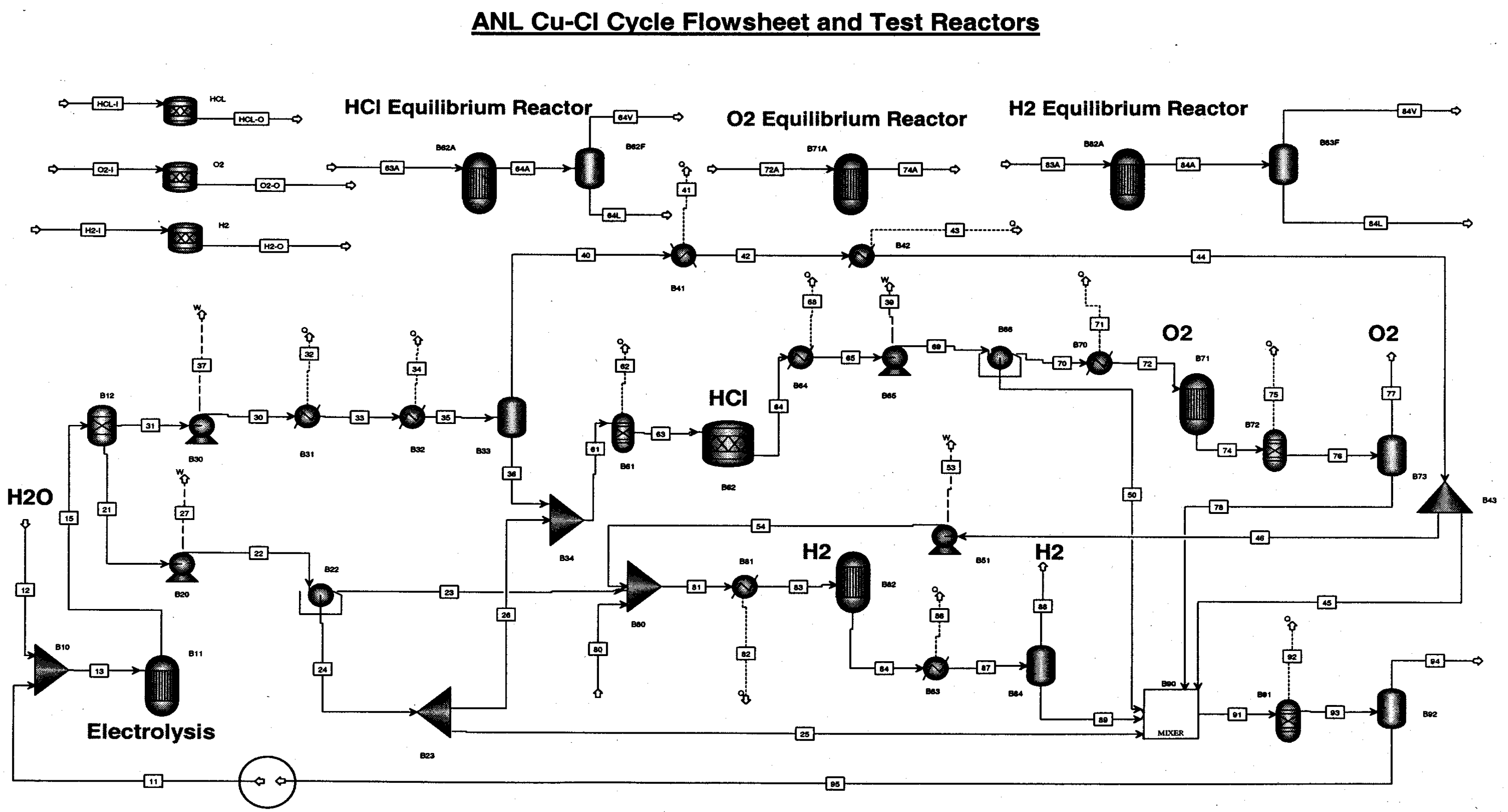
HSC not adequate so switch to simulation program

- **Level 2+ analysis conducted with Aspen Plus**
  - Estimated data can be added for Cu_2OCl_2
  - Hydrolysis reaction can be run at <700°C to minimize Cl_2 formation

- **Base enthalpy in Level 2+ same as in Levels 1 and 2 but no separation work, no chemical work**

- **Level 2+ includes the following:**
  - Heats of solution included for some but not all aqueous species
  - Separations accomplished with process steps
  - Hydrogen produced at 300 psi
  - T, P and compositions simultaneously varied
  - Some process design optimization included

Process Flow Diagram



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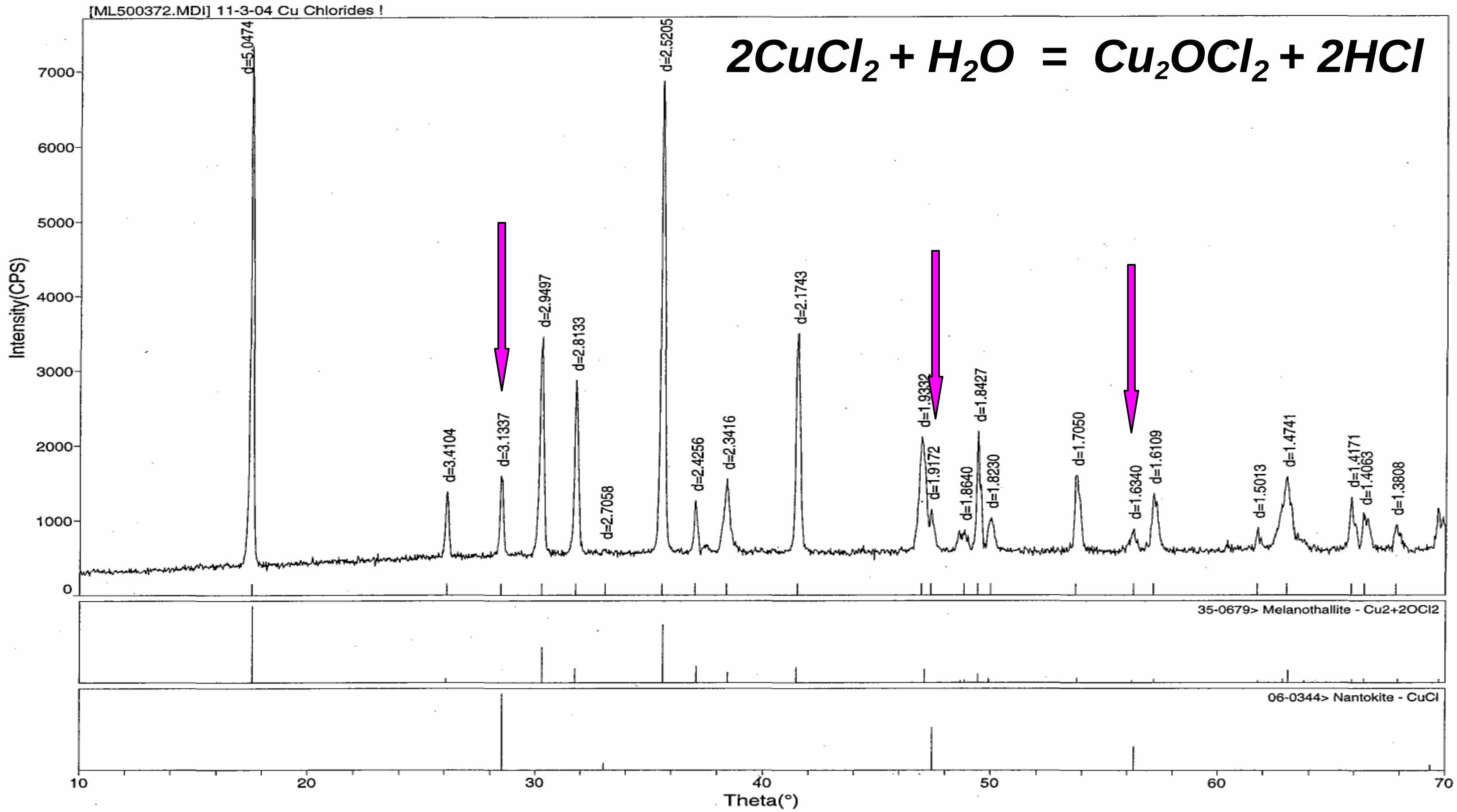
O_2 Formation Rxn.		700	700	550
Efficiency % (LHV)	48	41.5	39.6	42.4

Level 2+ includes some process design optimization

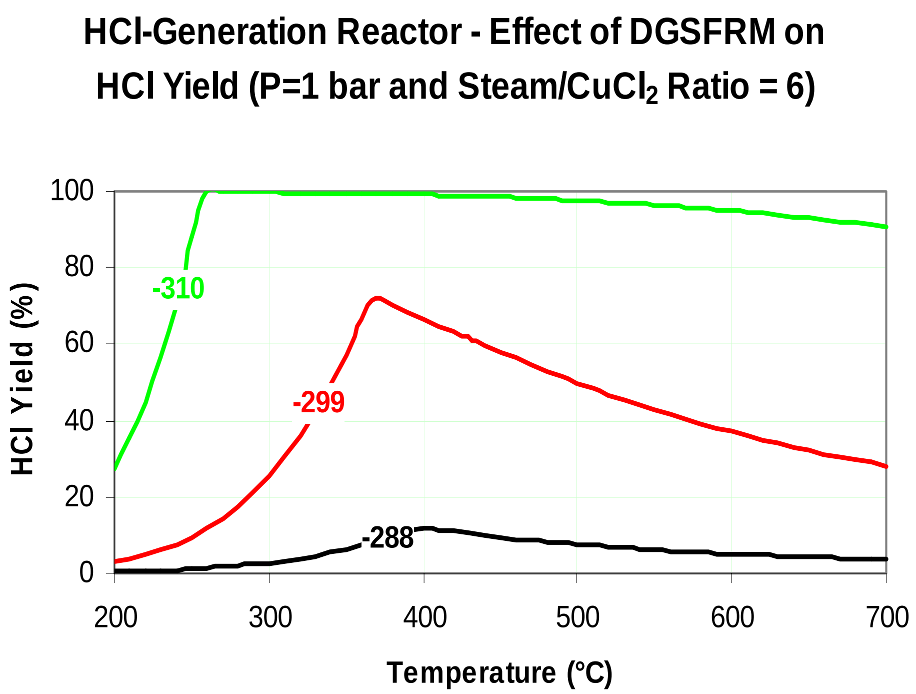
Experimental results show that the hydrolysis rxn. can be run at 310-325°C to further reduce chlorine formation

XRD data show Cu_2OCl_2 formed at 310-325C



Sensitivity studies show importance of correct thermodynamic data for Cu_2OCl_2

- **Est. thermodynamic data for Cu_2OCl_2**
  - Sensitivity studies indicate critical need for free energy of formation and heat capacity
- **Lower temperatures reduce amount of Cl_2 formed and reduce burden on materials**



Current simulation to be updated

- **Data to be added**
  - Measured values for the enthalpy and entropy of formation of Cu_2OCl_2
  - Measured values for the heat capacity for Cu_2OCl_2
  - Literature or measured values for the enthalpy of mixing of CuCl and $CuCl_2$ in aqueous HCl solutions
    - *Needed to model the electrochemical reaction*
- **Process flow diagram to be updated**
- **New sensitivity studies planned**

Summary

- **Scoping flowsheet methodology indicates promising Level 1 efficiency value**
- **Level 2 evaluations identify potential problem areas, such as Cl_2 formation, low oxygen yields at desired temperature**
- **HSC has some limitations as a database**
  - Incomplete HSC database prevents low temperature model
    - *No mechanism for adding necessary data (e.g. azeotropes)*
  - Equilibrium module does not handle liquid and solid phases well
  - P, T, and composition can not be varied simultaneously
- **Modeling (Level 2+) now done with a simulation program**
  - Preliminary results encouraging
  - Experimental and modeling efforts are iterative and consistent

Future work

- **Level 3 (accounts for real-world chemistry)**
  - Equilibrium reactors that include non-idealities such as the enthalpies of solvation, azeotrope formation, etc.
  - Sensitivity studies of process flowsheets
    - *P, T, and composition can be varied simultaneously*
  - Engineering feasibility studies
  - Measurement of unknown thermodynamic parameters
  - H_2 produced at 300 psi

- **Level 4 (accounts for engineering design)**
  - Kinetic reactors
  - Consideration of costs
  - Process design optimization completed
  - Materials

Level 2 efficiency calculations for the Cu-Cl cycle

	Level 2 (Case 1)[a] Reaction 1 at 110 °C, kcal	Level 2 (Case 2)[a] Reaction 1 at 450 °C and excess water, kcal
Total heat-in	68.3	68.3
Pinch heat	1.5	1.5
Chemical potential work	0	0
Separation work	28.1[b]	34.7[b]
Electrochemical work	41.5[c]	41.5[c]
Sum of heat and work inputs	139.4	146
Enthalpy of formation, H_2 (LHV)	57.8	57.8
Efficiency (LHV)	41.5%	39.6%

[a]Hydrolysis reaction run at 700 °C for both cases

[b]Converted to thermal equivalent using a 50% conversion factor for heat to electricity

[c]Based on experimental results [6, 7]