

# ***A Scoping Flowsheet Methodology for Evaluating Alternative Thermochemical Cycles***

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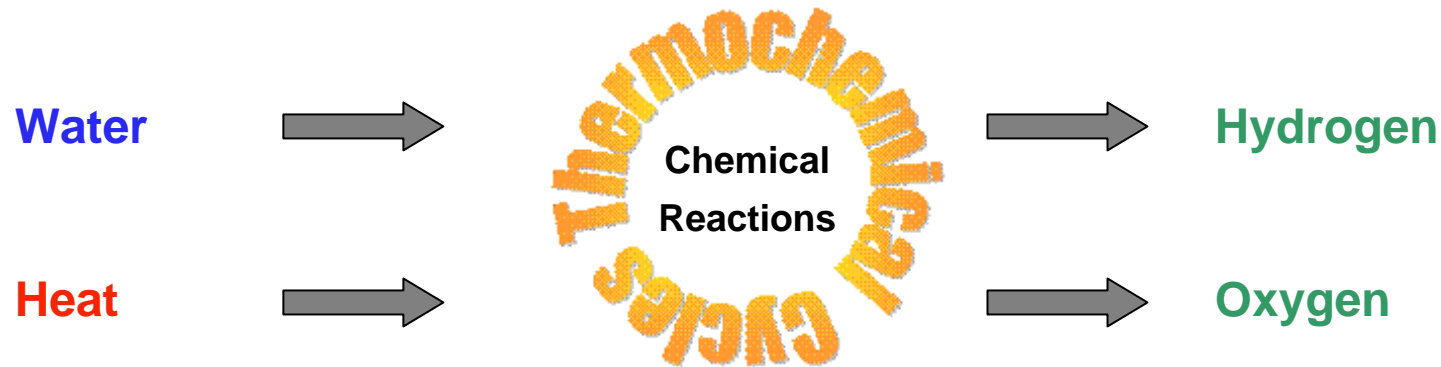
# Outline

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- **Introduction**
  - Background
  - Problem: No 'simple' but consistent method for evaluating cycle efficiency
- **Overview of Nuclear Hydrogen Initiative's (NHI) scoping flowsheet methodology for calculating efficiency**
  - Description of levels
- **Illustration of methodology with the Mg-Cl cycle**
- **Summary**

# Definitions

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- **Alternative cycles:** Cycles other than the U.S. DOE baseline cycles
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- **Possible alternative cycles:**
  - Cycles suggested in the literature that were either not developed or contained a barrier that current technology may overcome
  - New cycles

# *How to measure a cycle's potential*

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- **Efficiency is an important metric**
- **But a simple, consistent method is needed**

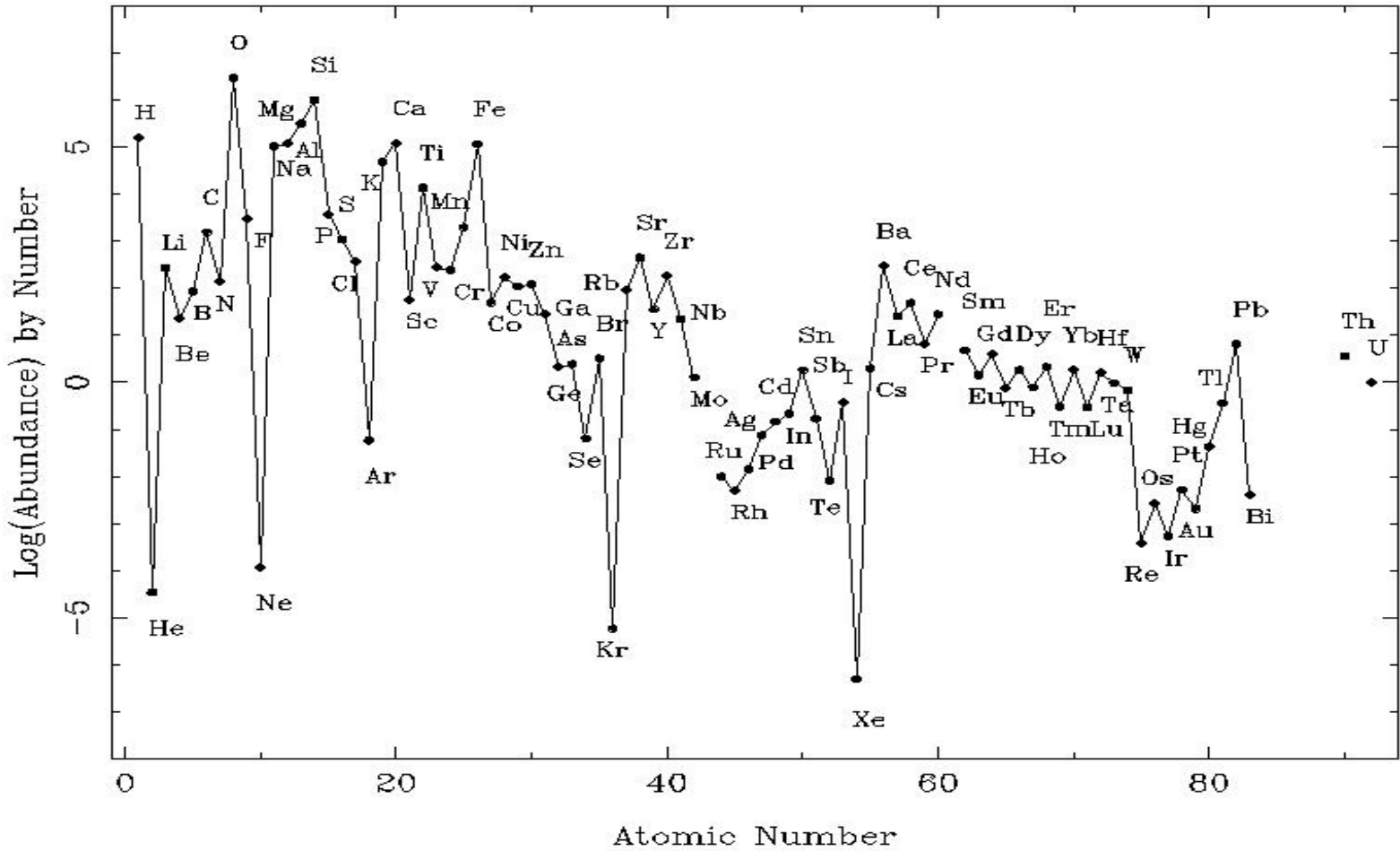
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# Phase I Evaluation

## General screening criteria for evaluating alternative cycles

# High natural abundance

Logarithmic Crustal Abundances:  $\text{Log}(\text{Si}) = 6.0$



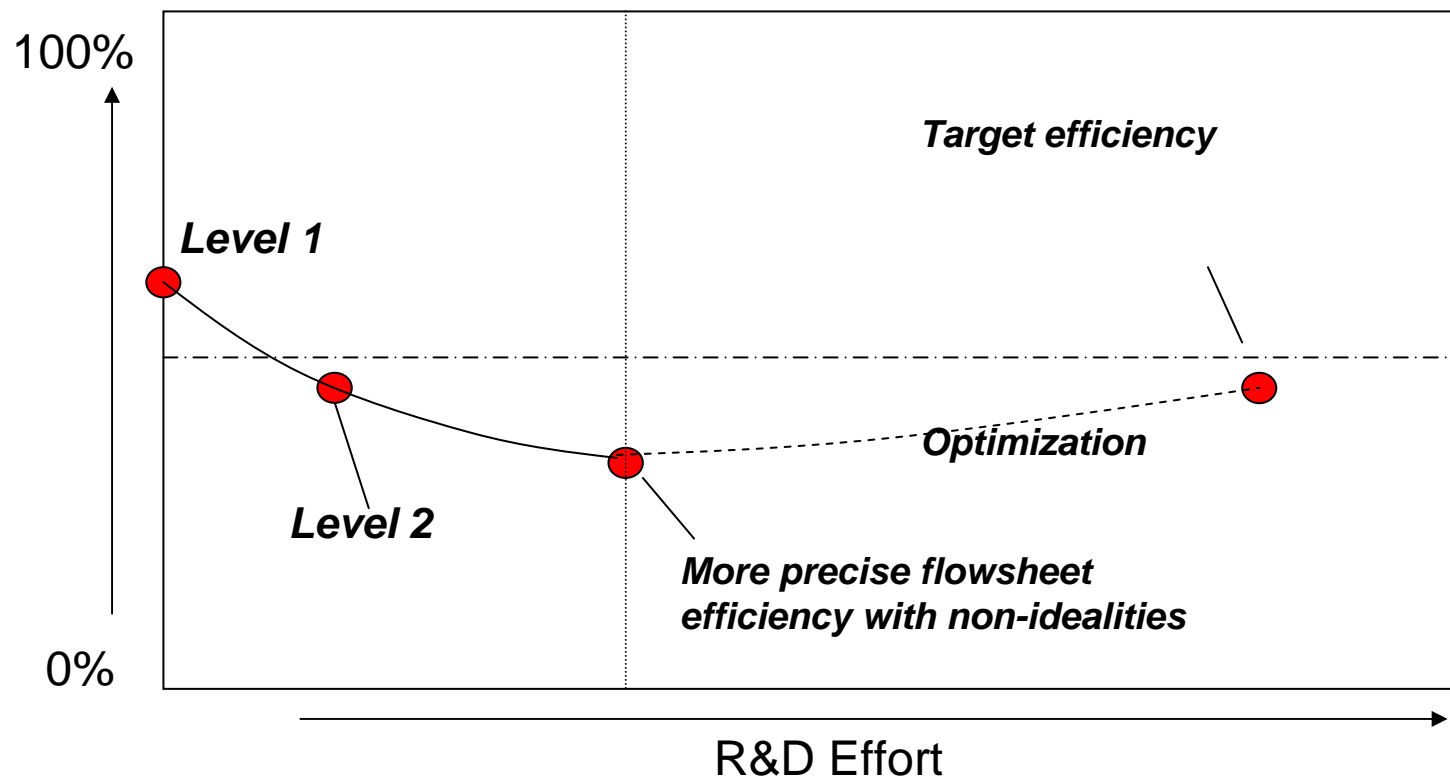


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# Phase II Evaluation

## Scoping flowsheet methodology to calculate efficiency consistently

# Efficiency changes with effort



From Pascal Anzieu at CEA

# Thermochemical cycle assessment levels

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- **Level 1**

- Stoichiometric reactions go to 100% completion
  - *No competing product formation*
- Heat and work inputs
  - *Heat: reaction, sensible, and latent*
  - *Work: electrochemical, chemical potential, and separation*
- Reaction temperatures as proposed in the literature
- Sources of thermodynamic data specified
  - *We are using HSC*

# ***Assumptions in the methodology***

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- **H<sub>2</sub>O enters as a liquid at 25°C**
- **H<sub>2</sub> and O<sub>2</sub> are released at atmospheric pressure at 25 °C**
  - One mole of water is used in Level 1
  - Number of moles to be determined in Level 2
- **Work terms calculated through standard equations, not measured**
- **Solvation effects ignored for Level 1 and 2 evaluations**
- **10°C  $\Delta T$  used as the driving force for heat exchange**
- **Energy usage optimized with pinch analysis**

# Work terms

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- **Electrochemical work:  $\Delta G = nFE$** 
  - Ignore concentration terms-no information typically available
- **Separation work:  $W = - RT \sum n_i \ln(y_i)$ , where R is the gas constant, T is the absolute temperature,  $n_i$  is the number of moles of each species in the mixture and  $y_i$  is the concentration of each species**
- **Chemical potential work:  $+\Delta G$  of the reaction and ignore any work produced from  $-\Delta G$**

# ***Definitions in the methodology, Cont.***

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

$$E = \frac{-\Delta H_{25^{\circ}C}^{\circ} (H_2O(g))}{Q_{hot} + \frac{W}{0.5}}$$

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

# Reactions and temperatures in the Mg-Cl cycle

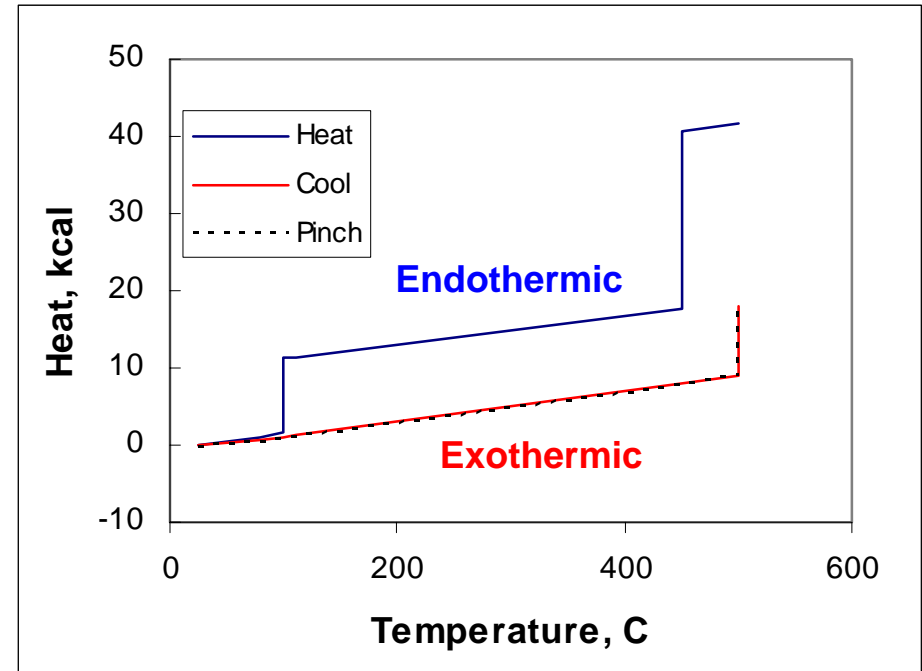
- $\text{MgCl}_2 + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{MgO}$  450 °C
- $\text{MgO} + \text{Cl}_2 (\text{g}) \rightarrow \text{MgCl}_2 + \frac{1}{2}\text{O}_2 (\text{g})$  500 °C
- $2\text{HCl} \rightarrow \text{H}_2 (\text{g}) + \text{Cl}_2 (\text{g})$  75 °C
  - HCl dissociated electrochemically

# Summary of heats from HSC database

Reaction #	Type	Moles	T <sub>in</sub> <sup>a</sup> (°C)	T <sub>out</sub> <sup>b</sup> (°C)	ΔH, kcal	ΔG, kcal
MgCl <sub>2</sub> 1	Reaction		450	450	22.92	-0.84
MgO 2	Reaction		500	500	-8.79	-0.32
HCl 3	Reaction		75	75	<b>44.19</b>	<b>45.79</b>
MgCl <sub>2</sub>	Sensible	1	500	450	-0.98	
MgO	Sensible	1	450	500	0.59	
HCl(g)	Sensible	2	450	75	-5.28	
Cl <sub>2</sub> (g)	Sensible	1	75	500	3.68	
O <sub>2</sub> (g)	Sensible	0.5	500	25	-1.49	
H <sub>2</sub> (g)	Sensible	1	75	25	-0.35	
H <sub>2</sub> O(l)	Sensible	1	25	100	1.35	
H <sub>2</sub> O(g)	Sensible	1	100	450	3.00	
H <sub>2</sub> O(l) = H <sub>2</sub> O(g)	Latent	1	100	100	9.77	
Total					68.61	

# 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
- For Mg-Cl level-1 analysis:  
0.2 kcal are needed for pinch



# Work terms

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- **Electrochemical rxn.  $2\text{HCl} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$**
- **Theoretical voltage from Faraday's Law = 0.99V**
  - $\Delta G = + 45$  kcal for reaction as written but
  - Cell design has been optimized and operating voltage is 1.5 V
  - Electrochemical work =  $2 \cdot 96,473 \cdot 1.5$  or 289kJ or 69 kcal
- **No chemical potential work for thermal reactions**
- **Small work term for separations**

# Summary of heat and work; Level 1 efficiency

	Energy, kcal	Heat Equivalent <sup>a</sup> , kcal
Total high temperature heat <sup>b</sup>	24.2 <sup>b</sup>	
Pinch	0.2	
Separation work	0.82	1.64
Chemical potential work	0	0
Electrochemical work	69.2	138.4
Enthalpy of formation, H <sub>2</sub> (LHV)	57.8	
Efficiency	35.1% (LHV)	

<sup>a</sup>Heat to electricity conversion factor of 50%

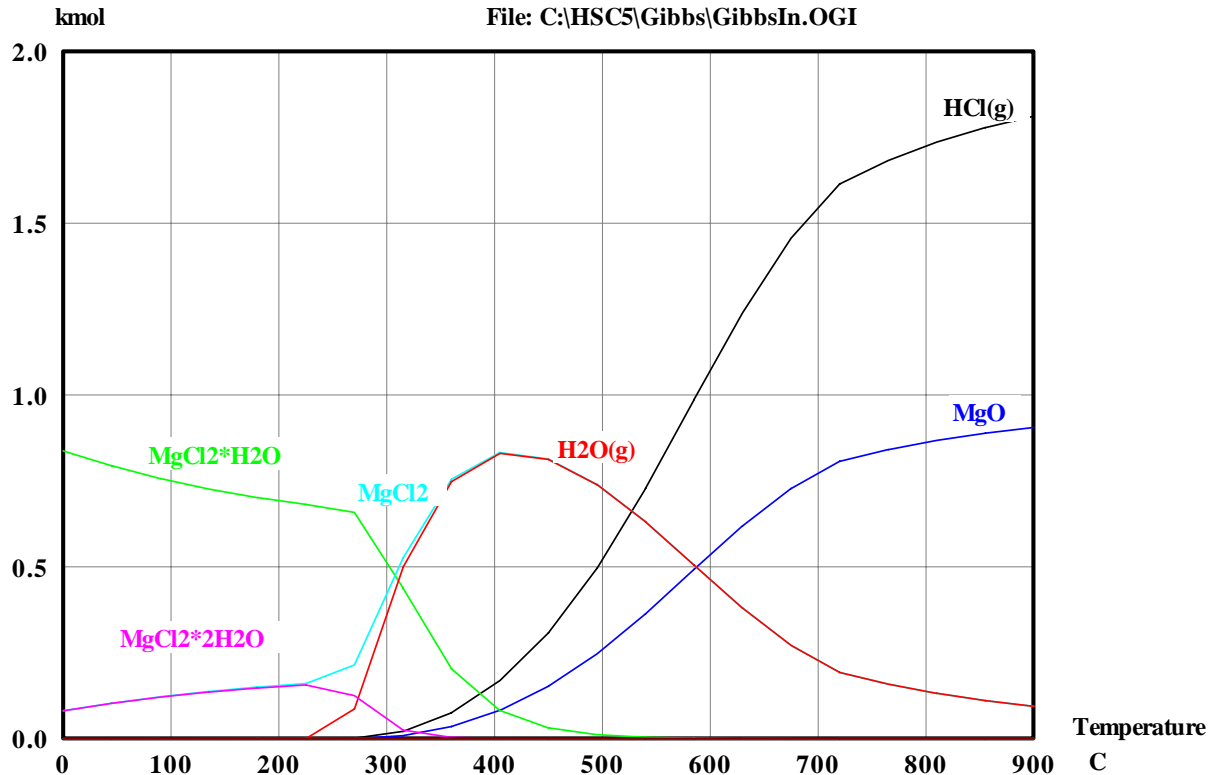
<sup>b</sup>Ignores any external heat need for the electrochemical reaction

# Thermochemical cycle assessment levels

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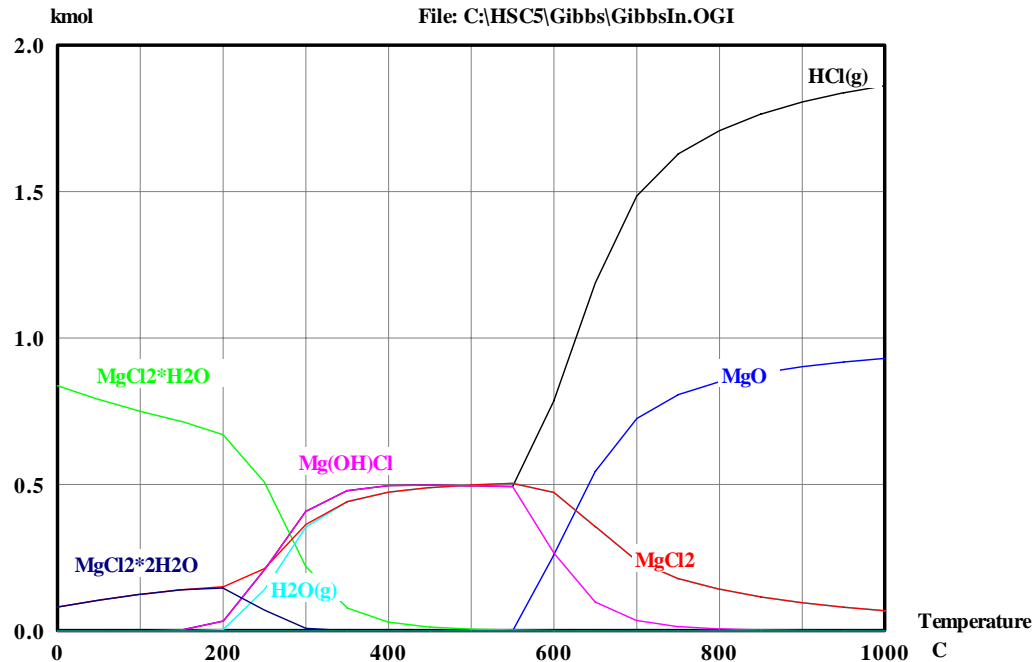
- **Level 2**
  - Equilibrium compositions
    - *Less than 100% yields*
    - *Competing products allowed*
  - Heat and work inputs defined as before
    - *Chemical potential work is usually 0*
    - Reaction conditions adjusted to increase desired yields

# Equilibrium for $MgCl_2 + H_2O \rightarrow 2HCl(g) + MgO$



- Only magnesium chloride and its hydrates are allowed to form in HSC
- MgO yields are relatively low at 450 °C

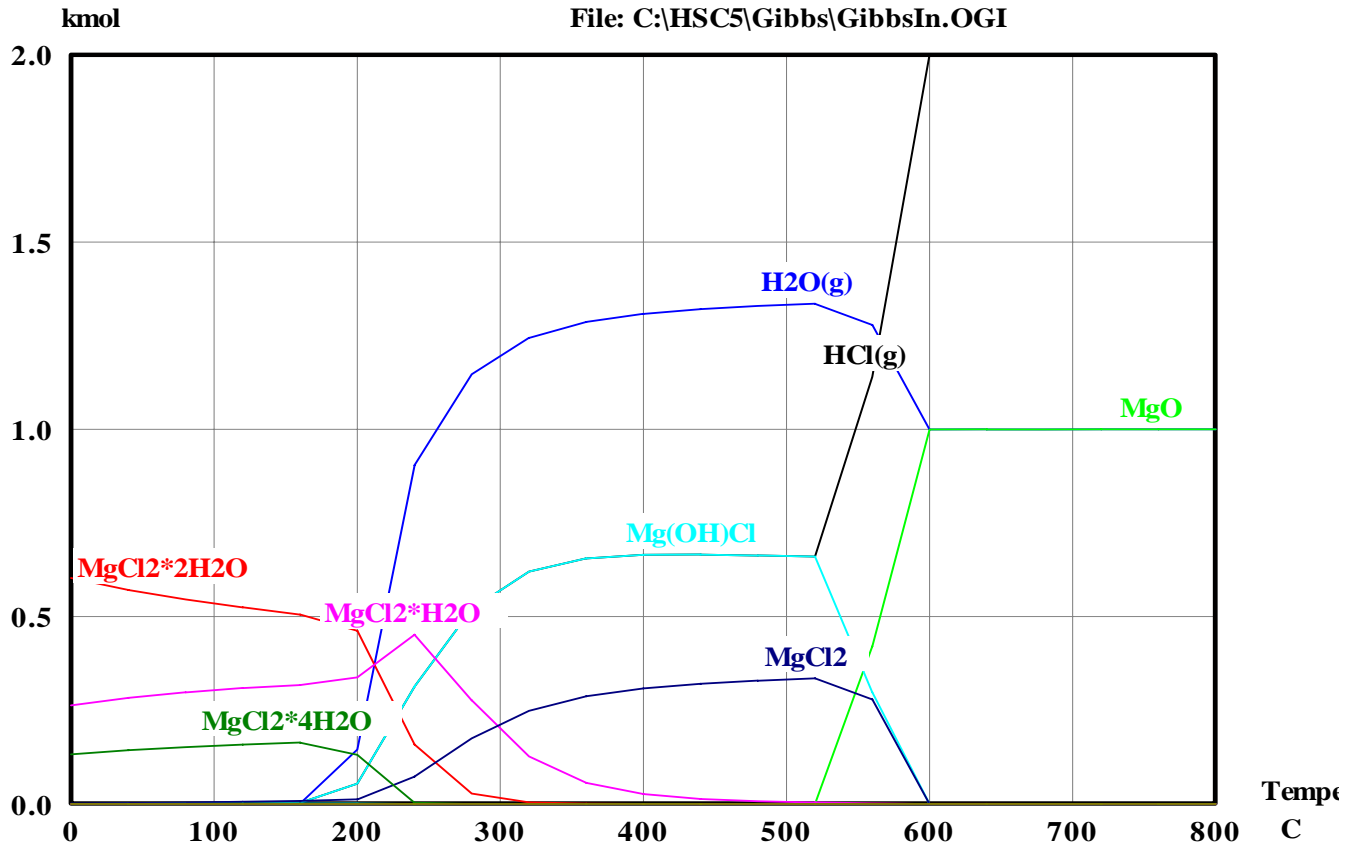
# When $Mg(OH)Cl$ is allowed as a product



- $Mg(OH)Cl$  is primary product at the  $450^\circ C$  rxn. temperature

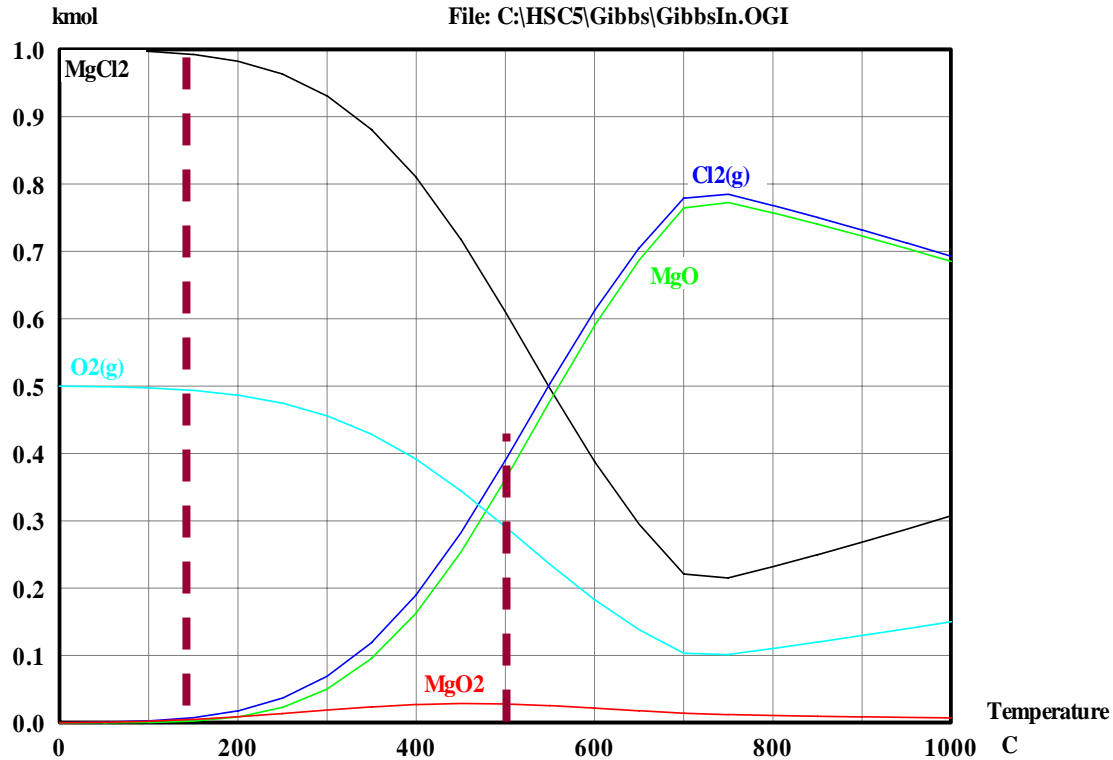
# Additional water lowers reaction temperature

## $MgCl_2 + 2H_2O \rightarrow MgO + 2HCl + H_2O$



- With 2 mols of water in feed, temperature can be lowered to 600 °C

# Chlorination rxn.: $MgO + Cl_2(g) \rightarrow MgCl_2 + \frac{1}{2}O_2$



- 2 cases: chlorination at 110 °C and at the literature value of 500 °C

# ***Consider kinetics of chlorination rxn.***

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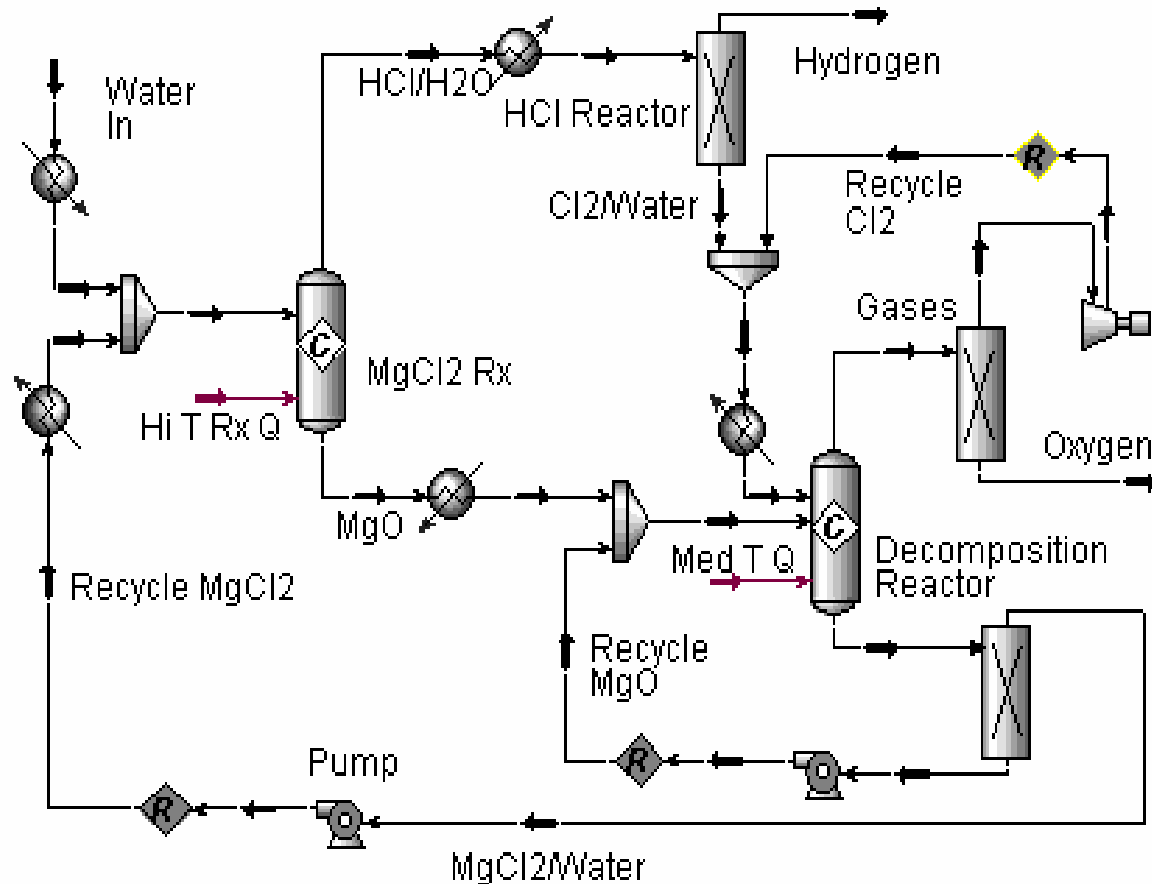
- **The times required for substantial equilibrium to be attained for the chlorination of MgO are 5 h at 477°C, 3h at 527°C, and 1.5 h at 627°C**
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- **At 500°C, the yield of MgO is about 40%**
  - Significant recycling required
- **Separations**
  - HCl and unreacted water in the hydrolysis reaction
  - Oxygen and chlorine in the chlorination reaction

# ***Summary of efficiencies for different cases***

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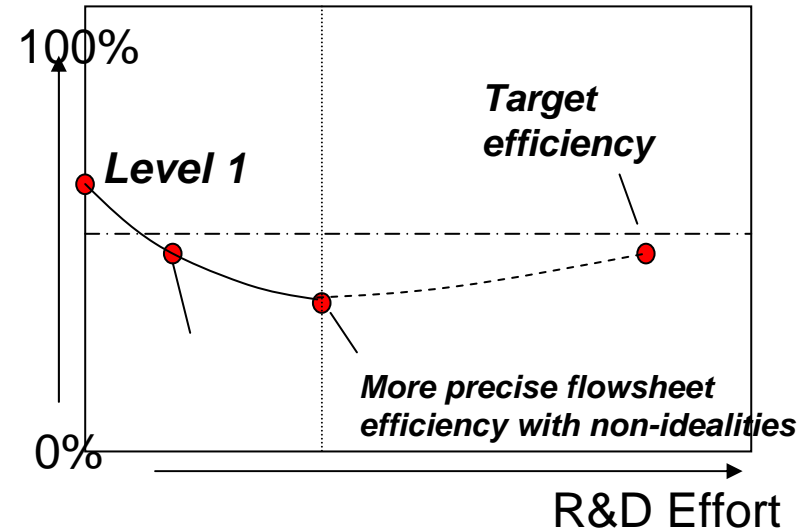
	Temperature, C			
	Level 1	Level 2		
Conditions		Case 1	Case 2	Case 3
Water, mols	1	1	2	2
Chlorination Rxn.	500		110	500
Hydrolysis Rxn.	450	>700	600	600
Efficiency % (LHV)	35	NA	33	30

# Process Flow Diagram for Level 2, Case 3: Starting point for process optimization



# Summary

- The methodology shows the ability to rapidly screen processes with reasonable realism at Level 1
- More accurate Level 2 simulations can find problem areas and indicate critical R&D
- If promising Level 2, start input of real chemistry and process design
  - Cut off in SHGR report was about 35% (LHV)



# ***Future work: evaluate at higher levels***

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- **Level 3 (accounts for real-world chemistry)**
  - Include non-idealities such as the energies of solvation, azeotrope formation, etc, into equilibrium reactors and eventually kinetic reactors
  - Determine engineering feasibility
  - Measure any unknown thermodynamic parameters
  - Use sensitivity studies for process design optimization
  
- **Level 4 (accounts for engineering design)**
  - Consideration of costs
  - Process design optimization completed
  - Materials

# ***Possible areas for collaboration***

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- **Materials for very aggressive conditions: corrosive materials, high temperatures, moderate pressures**
- **Real time measurement of concentrations of HX, HX-H<sub>2</sub>O, X<sub>2</sub>, X<sub>2</sub>-H<sub>2</sub>O**
- **Membranes for separating gas mixtures**
- **Counter flow apparatus for laboratory-scale work**
- **Modeling**
- **Measurement of thermodynamic data**
- **Independent assessment of engineering feasibility**



# ***Tomorrow-results for the Cu-Cl cycle***

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- **Cu-SO<sub>4</sub>**
  - **Zn-SO<sub>4</sub>**
  - **Cu-Cl**
- These cycles had high reported efficiencies in the literature**
- **Other cycles may be identified in the future**

