Evaluation and Design of Water-Splitting Cycles

Scott Mullin, Jacob Tarver, Uchenna Odi

University of Oklahoma

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Overview

- Need for hydrogen
- Water-splitting cycles as solution
- Current evaluation methods
- Efficiency defined
- Our methodology as improvement
- Results of our analysis
- Economics
- Conclusions

Accomplishments

- Novel methodology
  - Rapidly screen cycles without detailed process flowsheets
  - Optimize T, P and excess reactants for non-spontaneous reactions
- Scoping algorithm
  - Calculations refined for best cycles
- Found better cycles than currently favored Sulfur-Iodine and UT-3

Hydrogen Economy

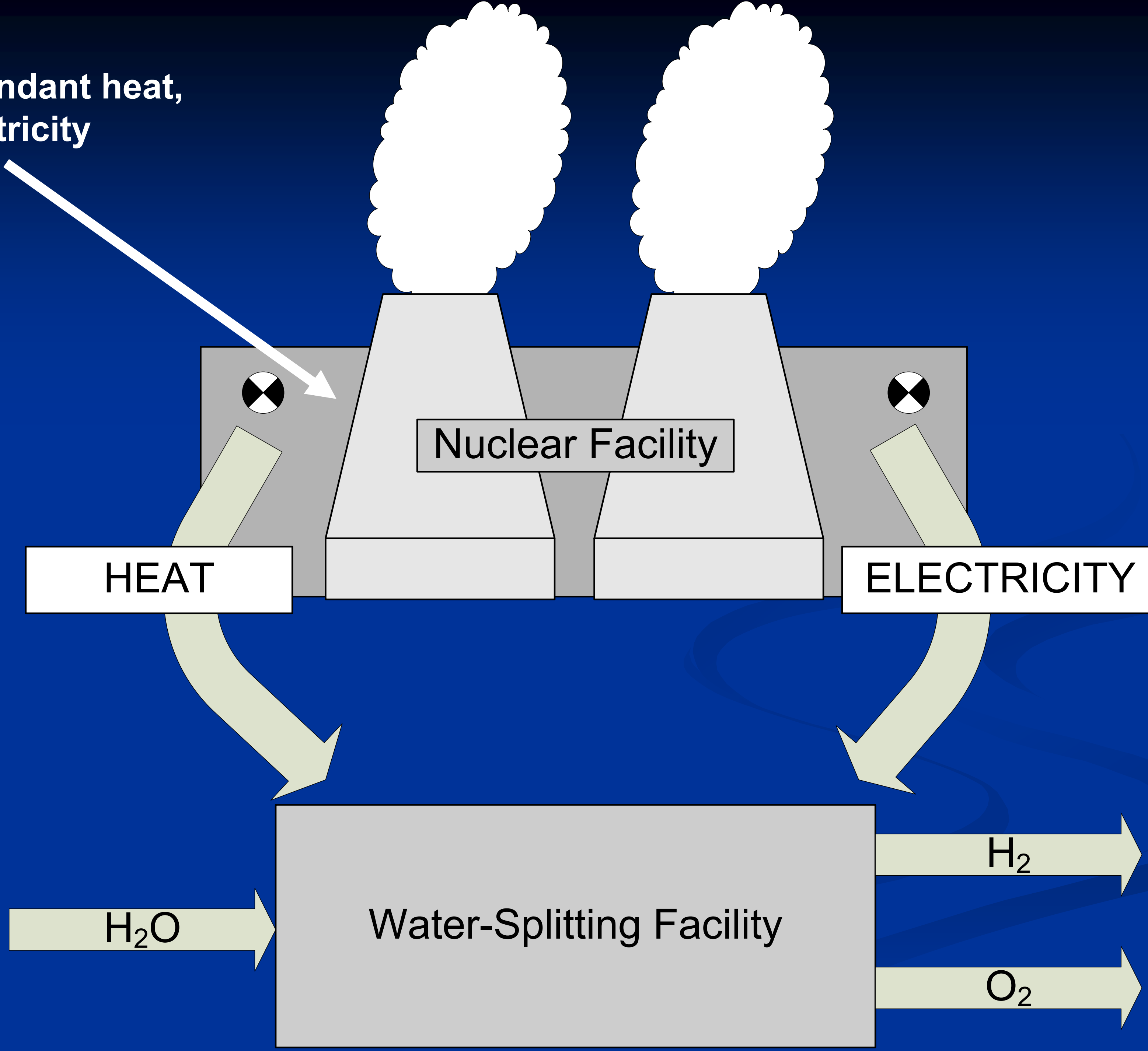
- Currently 11 million tons/year
- In H_2 economy[†]:
  - 200 million tons/year for transportation
  - 450 million tons/year for all non-electric
- H_2 is not a natural resource
  - Must be produced
- Steam reformation of methane
  - CO_2 output
  - Rising fuel prices

[†] K. R. Schultz 2003, General Atomics, DOE grant

Alternative H_2 Production

- ✗ **Petroleum**
  - CO_2, expensive
- ✗ **Electrolysis, high T electrolysis**
  - Premature, inefficient
- ✗ **Photocatalytic reactors**
  - Premature
- ☑ **Thermochemical cycles**
  - Efficient, established processing techniques

Abundant heat, electricity



Nuclear Facility

HEAT

ELECTRICITY

H_2O

Water-Splitting Facility

H_2

O_2

Water-Splitting Cycles

- "New" technology, chosen by DOE through Nuclear Hydrogen Initiative
- Efficient hydrogen production
  - 50-60% currently, 80-90%+ possible
- Use 950ºC or cooler process heat
- 202 cycles known, but few researched
  - Others can be found, as described by Holiastos and Manousiouthakis 1998

Economics

- $1 billion for water-splitting facility
  - $100 million range annual energy costs
- Which cycle is best?
- Few cycles researched in detail
  - Process design too complex
- Efficient cycles desirable
  - **Justify increased equipment costs**

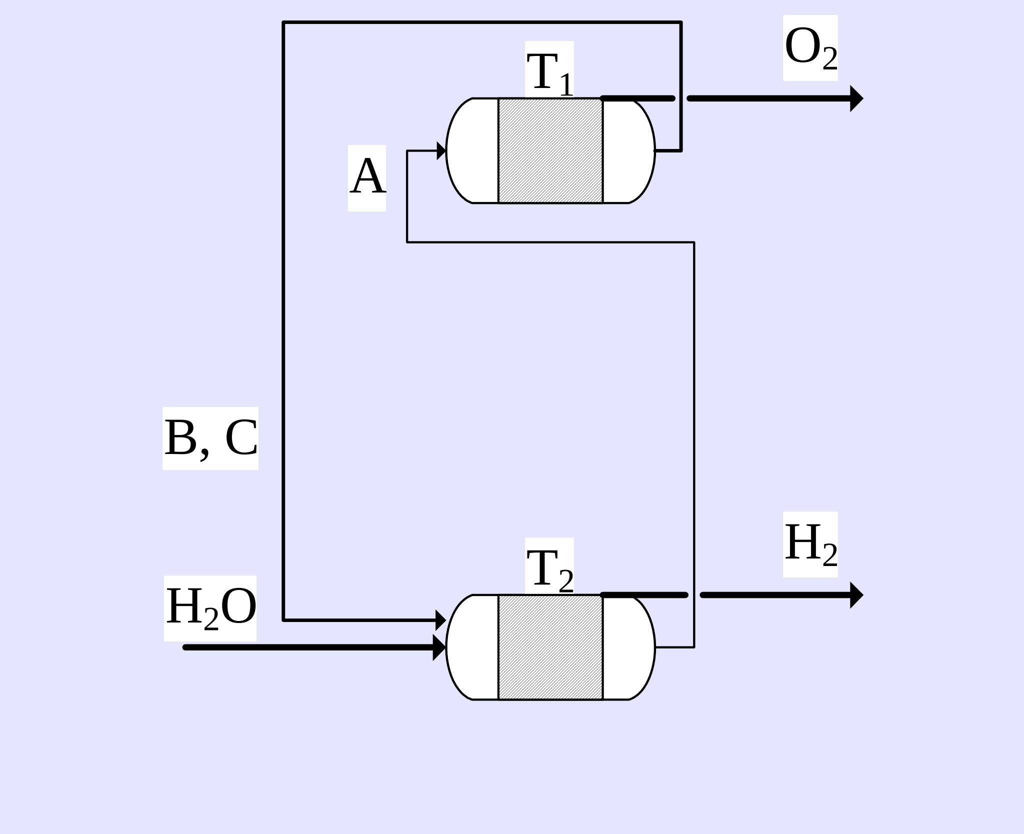
Bottom line: saving few % efficiency has huge savings over plant lifetime

Cycles

- Most are thermochemical, some hybrid electric
- Any number of reactions, species
- Named after institutions or chemicals
- Steady-state operation

Sample 2-step cycle

T_1	$A \longrightarrow B + C + O_2$
T_2	$B + C + H_2O \longrightarrow A + H_2$



Efficiency

- Theoretical, 1 mol basis for cycle comparison
- Minimum reversible energy (heating and work) requirement
  - Performance limit
- Thermodynamics: JANAF tables for state functions, pure component averages

$$\eta = \frac{\Delta H_f^{\circ}(H_2O)}{Q + W}$$

Q is total heat requirement

W is separation, electric and shaft work†

†Shaft work (pumping, compression) small compared to other terms

Previous Surveys

- Brown et al 2000 scored cycles based on known characteristics
  - Good starting point, but not reproducible
  - Arbitrary criteria, no emphasis on efficiency
    - Elemental abundance, “corrosivity”, # elements
    - Rejects cycles with “too positive” free energies
    - Favors well-researched cycles

	Score[†]			
	0	1	2	3
# reactions	6	-	-	5
# separations	10	9	8	7
# elements	7	-	6	-
Least abundant element	Ir	Rh, Tc, Os, Ru, Re, Au	Pt, Bi, Pd, Hg, Se	Ag, In, Cd, Sb, Tm, Tl, Lu

Brown’s method is good at identifying cycles based on estimated process complexities, but is not quantitative or reproducible. What happens if you change the weights, or add further scoring criteria?

[†] Adapted from Brown et al 2000

Previous Surveys cont'd

- Cycles are complex, so Lewis et al 2005 developed systematic approach
  - Scoping method based on efficiency
    - Quantitative, standard basis
  - Oversimplifications
    - Requires detailed flowsheets
      - Not truly scoping
    - Assumes 50% loss of all work energy
    - Does not estimate real separation energy

Our method is truly scoping, based on theoretical requirements

General Methodology

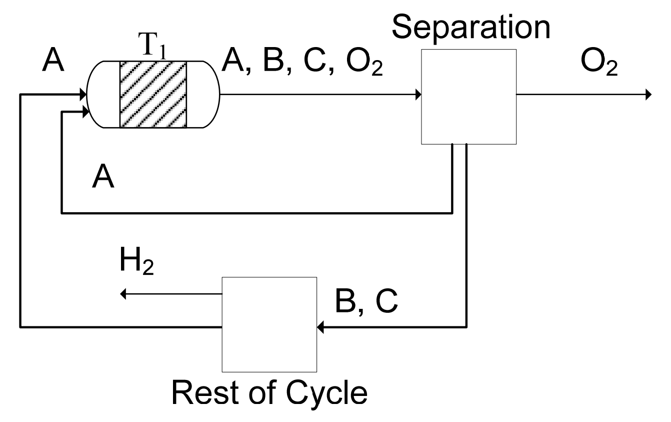
- Cyclic nature couples all calculations
- Decouple the problem
  - Find realistic estimates for Q, W
  - Refine calculations for best cycles
    - Account for additional energy requirements
  - Economic analysis of best cycles
- Apply methodology to all cycles
  - Evaluate the 202 from literature
  - Find unknown cycles

Equilibrium

- Excess reactants added to shift reactions to the right
- How do we handle excess after the reaction?
    - Requires optimization, coupled equations

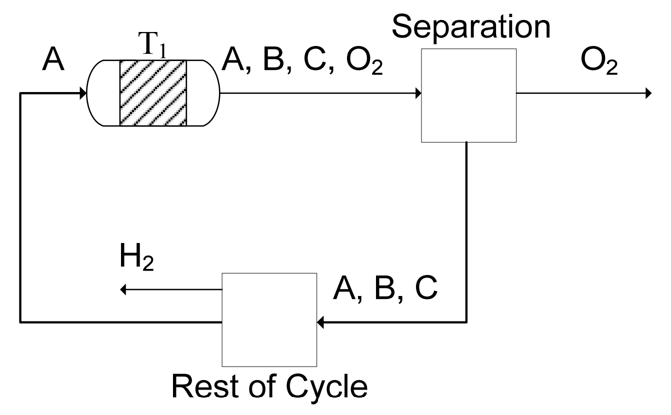
$$K_{eq} = K_x P^{\sum \nu} = \frac{\prod\limits_{\text{products}} \left(\frac{n_i}{\sum n_i} \right)^{\nu_i}}{\prod\limits_{\text{reactants}} \left(\frac{n_i}{\sum n_i} \right)^{\nu_i}} P^{\sum \nu}$$

Excess Reactant Handling



Immediate recycle: full separation energy costs

T_1	$A \longrightarrow B + C + O_2$
T_2	$B + C + H_2O \longrightarrow A + H_2$



No recycle: saves separation energy, but negatively shifts equilibrium in most cases and increases heat cascade requirement

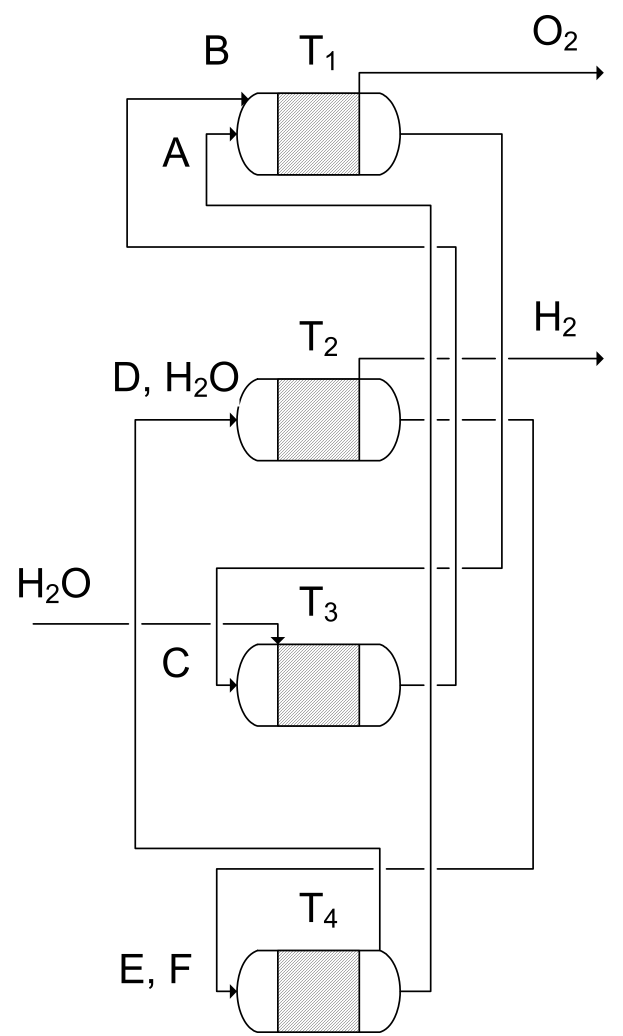
We optimize T, P, # excess mols and their handling

Cycles cont’d

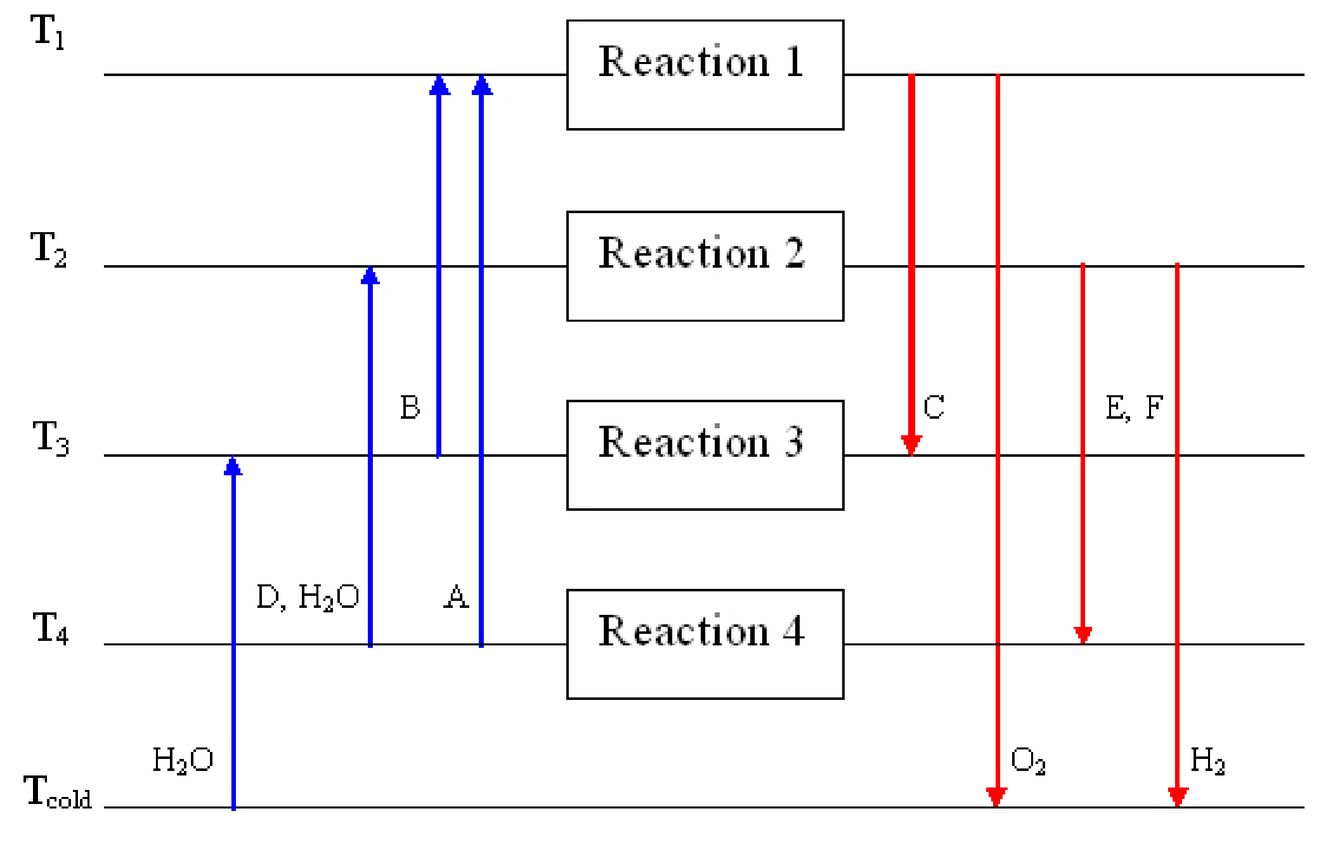
- Methodology accounts for arbitrarily complex cycles

T_1	$A + B \longrightarrow C + O_2$
T_2	$D + H_2O \longrightarrow E + F + H_2$
T_3	$C + H_2O \longrightarrow B + F$
T_4	$E + F \longrightarrow A + D + H_2O$

Conditions optimized for each reactor

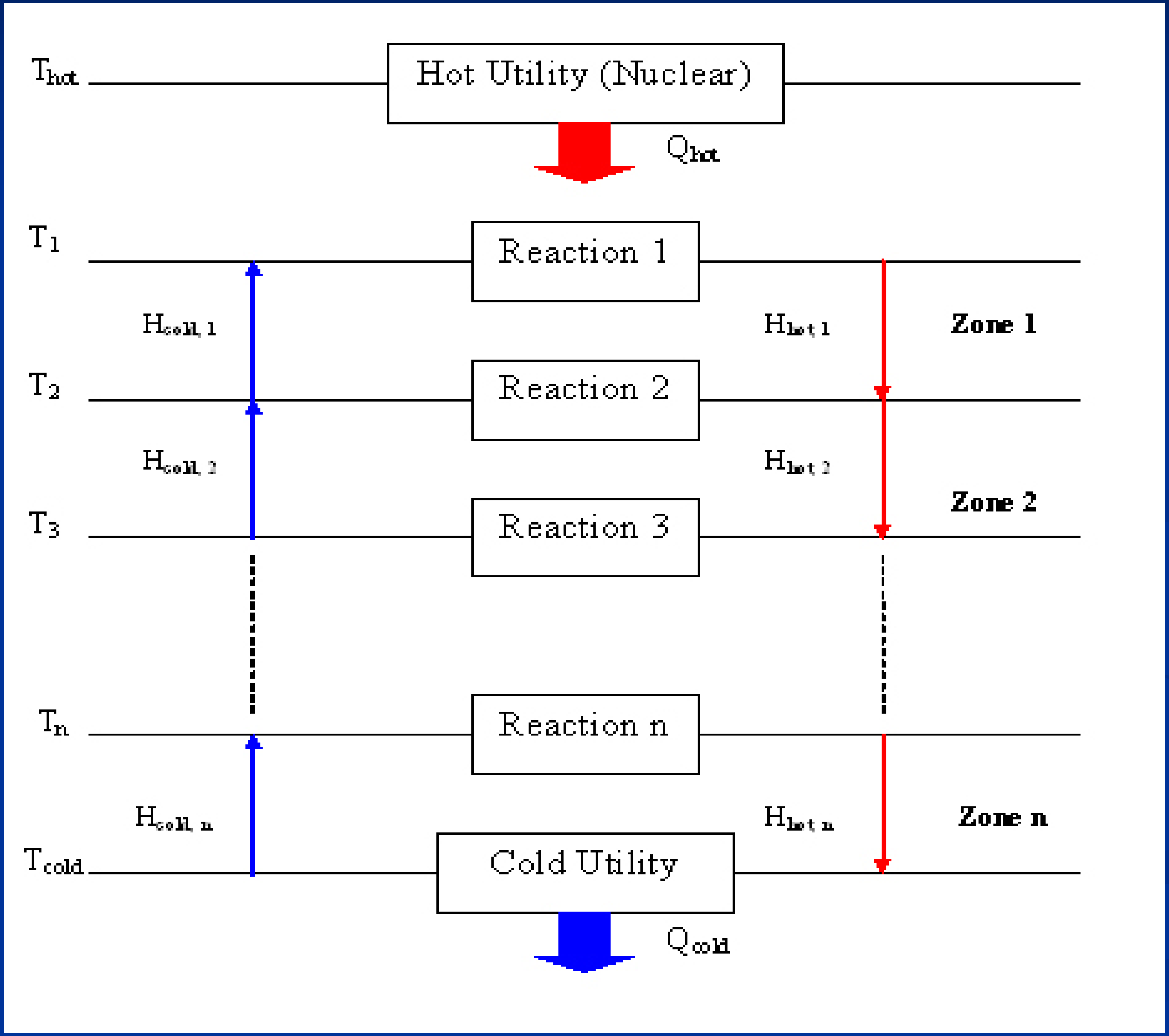


Heat Requirements



- Maximize heat recovery from exothermic reactions and cooling streams
- Pinch occurs when there is not enough heat to power reactions or heat streams, requiring input from the hot utility

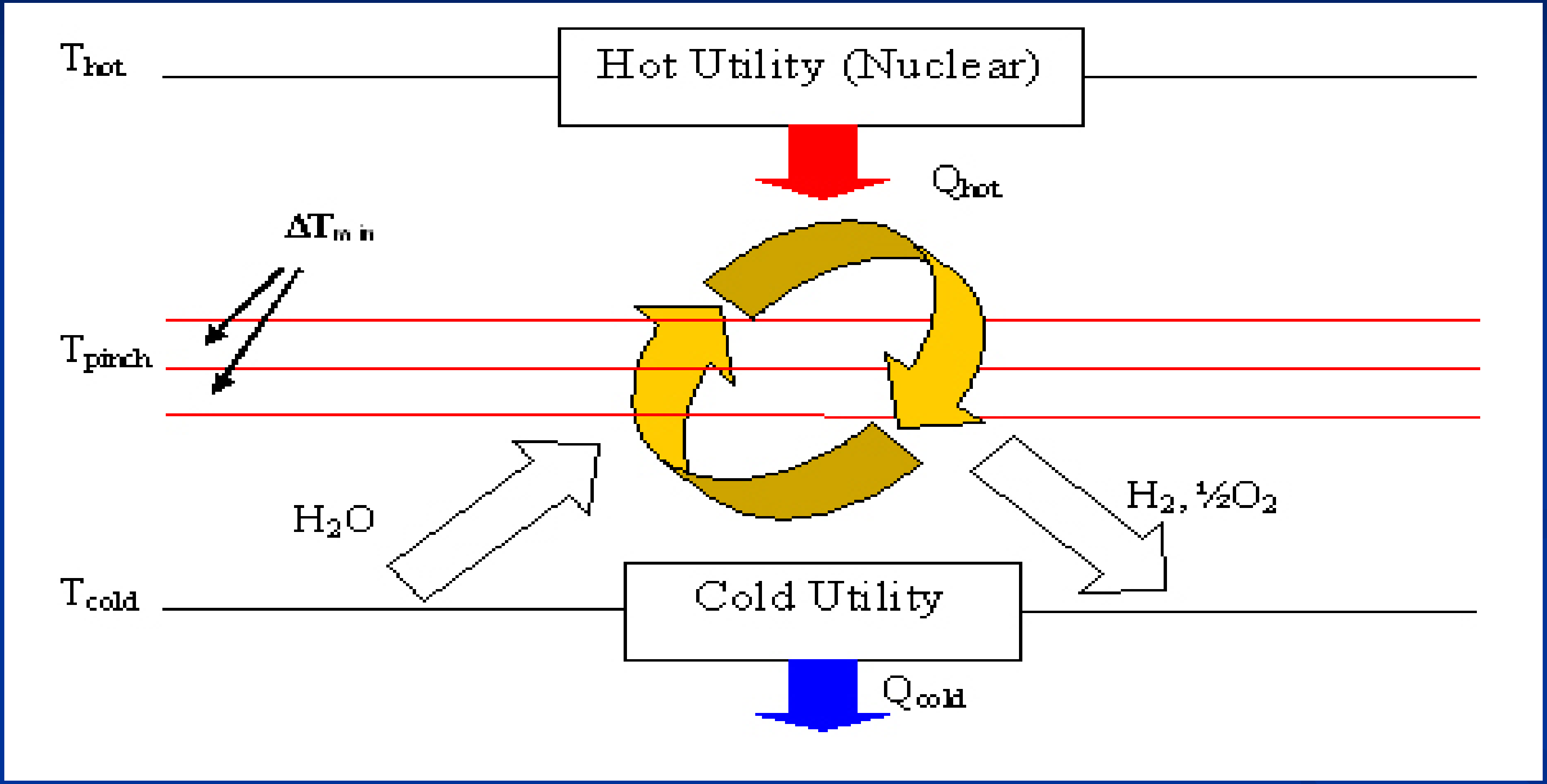
Generic Heat Integration



H_{hot} is total enthalpy of cooling streams

H_{cold} is total enthalpy of heating streams

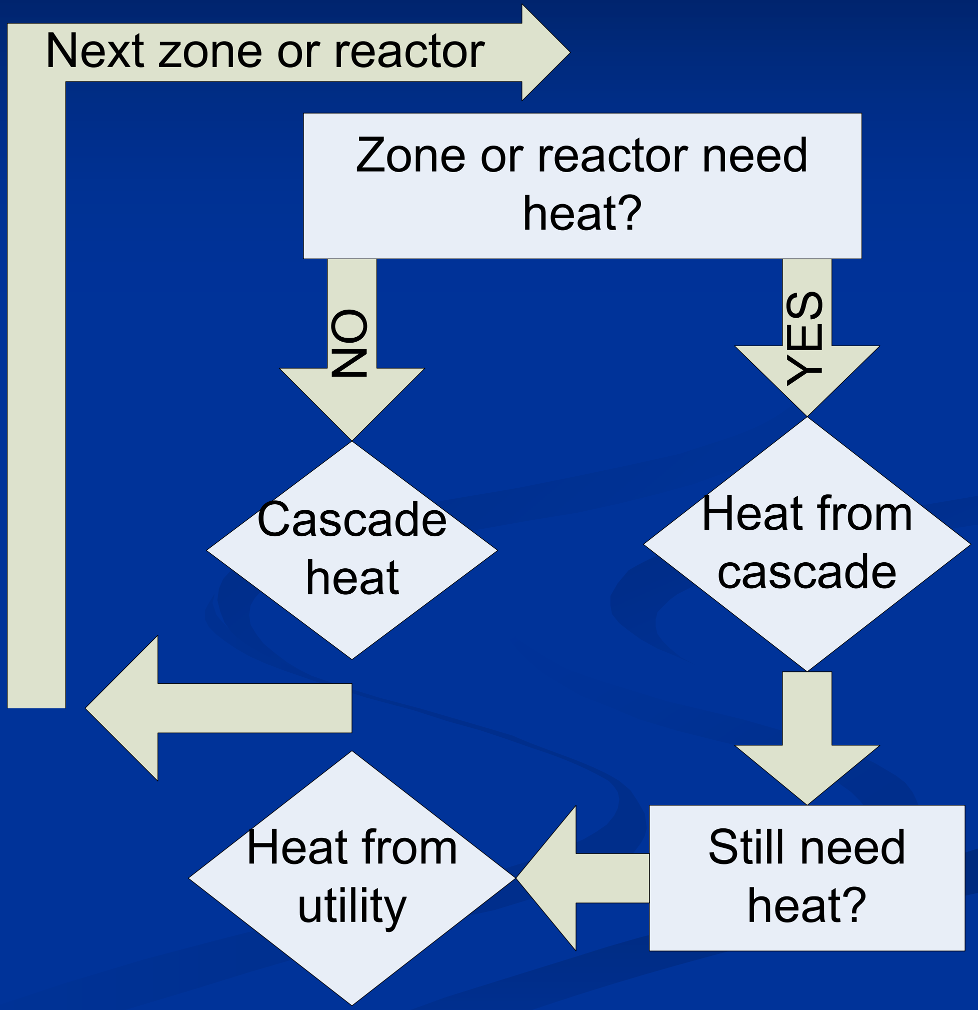
Pinch Point and Approach Temp.



Heat is added above the pinch. Heat transfer over the pinch (greater than the minimum heat requirement) goes to cold utility and is wasted. ΔT_{min} is closest feasible temperature, since complete heat transfer requires infinite exchanger area.

Heat Integration Method[†]

- Zonal analysis
  - Approach temperature
- Simplifying algorithm
  - Keep track of total heat usage, advancing to successive zones and reactors
  - Cold utility ignored
    - Leftover heat sometimes useful for electricity generation



Next zone or reactor

Zone or reactor need heat?

NO

YES

Cascade heat

Heat from cascade

Still need heat?

Heat from utility

[†] PT&W Plant Design and Economics for Chemical Engineers

Electrical Work

- Nernst equation for electrolytic cells
- Assume steady-state operation of electrolytic cells
  - New electrolysis methods efficient compared to batch process[†]
- Hybrid cycles treated same in heat integration

$$W_{elec} = -nFE^{\circ}$$

$$E^{\circ} = E^{\circ}_{(298)} + \int_{298}^{T} \frac{d(E^{\circ}(T))}{dT}$$

[†] Motupally et al 1998

Separation Work

- Minimum separation estimate

$$W_{sep} = -\Delta G = -\Delta \sum_{i=0} n_i \mu_i = -RT\Delta \sum_{i=0} n_i \ln x_i$$

Assuming isothermal separation

$$W_{sep} = RT\left[\left(\sum_{i=0} n_i \ln x_i\right)_{out} - \left(\sum_{i=0} n_i \ln x_i\right)_{in}\right]$$

- Phases self-separate
  - We don’t pay for it
- Estimate separation efficiencies

$$W = \frac{W_{sep,ideal}}{\eta_{separation}}$$

This provides us with a minimum requirement. Chemical mixing and individual processes will increase W. Assign efficiencies to each process: e.g. assume distillation columns 50% efficient

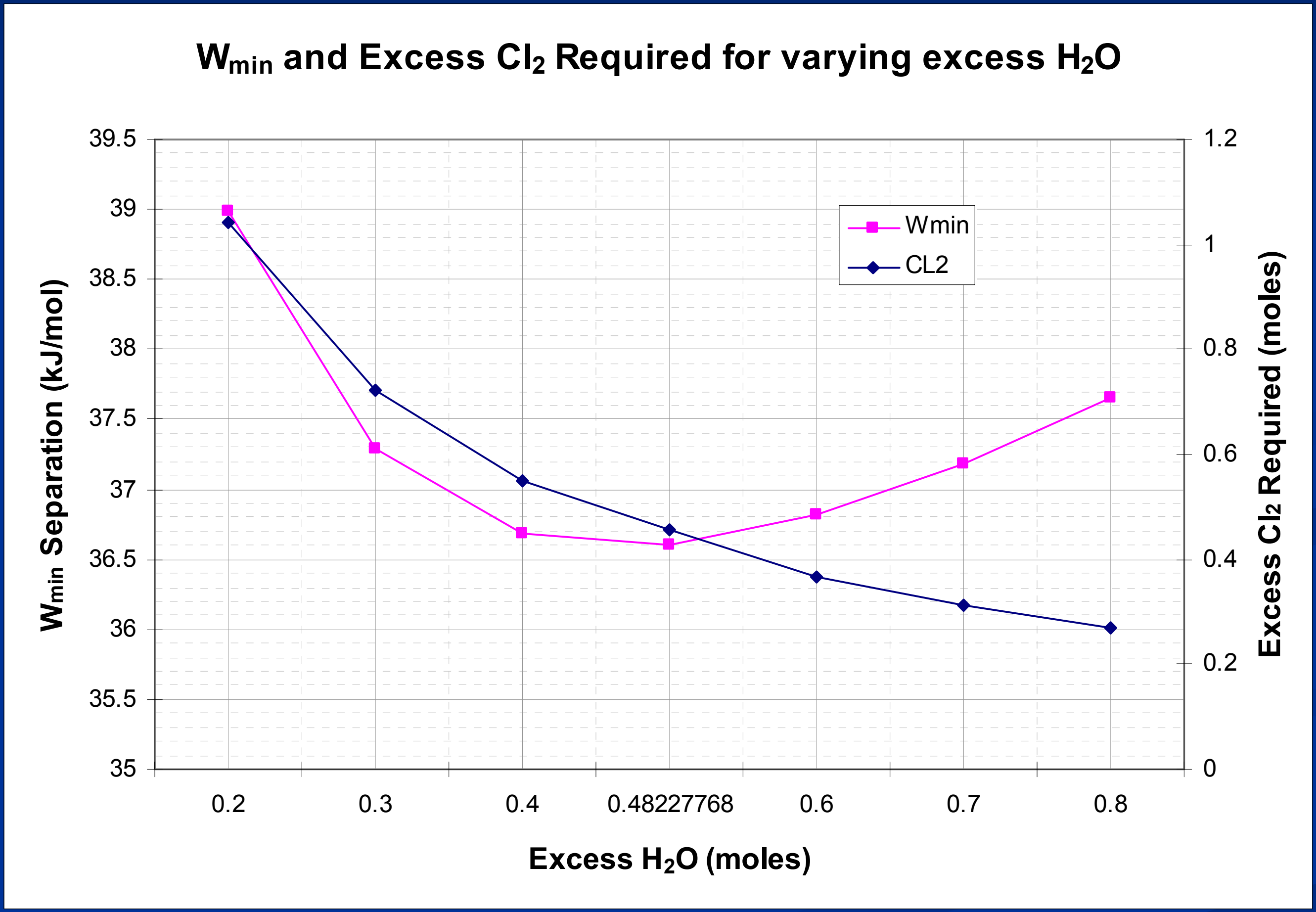
Solution Procedure

- Most reactions go to completion
  - No excess reactants to handle
  - Optimize reactors individually
- For other reactions
  - Find equilibrium concentrations
    - Newton method to solve for conversion
  - Know how much product we need from connectivity

Solution Procedure cont'd

- Computer algorithm finds optimum efficiency for each T
    - P easy to find
    - Finds Q and W for each # mols excess
        - Optimize these for each recycle scheme
- Computer crawls through solutions, and maximizes efficiency

Example Optimization



$Cl_{2\ (g)} + H_2O_{\ (g)} \text{ -> } 2HCl_{\ (g)} + ½O_{2\ (g)},\ \Delta G_{rxn} = -17$ kJ / cycle mol

Sample Thermochemical Cycles

- Julich

$$Fe_3O_{4(s)} + 3FeSO_{4(s)} \xrightarrow{T = 1073\ K} 3Fe_2O_{3(s)} + 3SO_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

$$3FeO_{(s)} + H_2O_{(g)} \xrightarrow{T = 973\ K} Fe_3O_{4(s)} + H_{2(g)}$$

$$3Fe_2O_{3(s)} + 3SO_{2(g)} \xrightarrow{T = 473\ K} 3FeO_{(s)} + 3FeSO_{4(s)}$$

- Ispra Mark 9

$$3FeCl_{2(s)} + 4H_2O_{(g)} \xrightarrow{T = 923\ K} Fe_3O_{4(s)} + 6HCl_{(g)} + H_{2(g)}$$

$$\tfrac{3}{2}Cl_{2(g)} + Fe_3O_{4(s)} + 6HCl_{(g)} \xrightarrow{T = 693\ K} 3FeCl_{3(l)} + 3H_2O_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$3FeCl_{3(s)} \xrightarrow{T = 423\ K} \tfrac{3}{2}Cl_{2(g)} + 3FeCl_{2(s)}$$

Sample Thermochemical Cycles

- Sulfur Iodine

$$H_2SO_{4(g)} \xrightarrow{T = 1123\ K} SO_{2(g)} + H_2O_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$2HI_{(g)} \xrightarrow{T = 573\ K} I_{2(g)} + H_{2(g)}$$

$$I_{2(g)} + SO_{2(g)} + 2H_2O_{(l)} \xrightarrow{T = 473\ K} 2HI_{(g)} + 1H_2SO_{4(g)}$$

- US-Chlorine

$$Cl_{2(g)} + H_2O_{(g)} \xrightarrow{T = 1123\ K} HCl_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$2CuCl_{2(s)} \xrightarrow{T = 773\ K} 2CuCl_{(l)} + Cl_{2(g)}$$

$$2CuCl_{(s)} + 2HCl_{(g)} \xrightarrow{T = 473\ K} 2CuCl_{2(s)} + H_{2(g)}$$

Sample Thermochemical Cycles

- Gaz de France

$$2K_2O_{(s)} \xrightarrow{T = 1098\ K} K_{(g)} + K_2O_{2(s)}$$

$$2K_{(l)} + 2KOH_{(l)} \xrightarrow{T = 998\ K} 2K_2O_{(s)} + H_{2(g)}$$

$$K_2O_{2(s)} + H_2O_{(l)} \xrightarrow{T = 398\ K} KOH_{(s)} + \tfrac{1}{2}O_{2(g)}$$

- UT-3 Tokyo

$$CaBr_{2(l)} + H_2O_{(g)} \xrightarrow{T = 1023\ K} CaO_{(s)} + HBr_{(g)}$$

$$4H_2O_{(g)} + 3FeBr_{2(s)} + Br_{2(g)} + CaO_{(s)} \xrightarrow{T = 873\ K}$$
$$CaBr_{2(s)} + \tfrac{1}{2}O_{2(g)} + Fe_3O_{4(s)} + HBr_{(g)} + H_{2(g)}$$

$$Fe_3O_{4(s)} + 8HBr_{(g)} \xrightarrow{T = 573\ K} Br_{2(g)} + 3FeBr_{2(s)} + 4H_2O_{(g)}$$

Sample Thermochemical Cycles

- Ispra Mark 4

$$Cl_{2(g)} + H_2O_{(g)} \xrightarrow{T = 1123\ K} 2HCl_{(g)} + \tfrac{1}{2}O_{2(s)}$$

$$H_2S_{(g)} \xrightarrow{T = 1073\ K} S_{(g)} + H_{2(g)}$$

$$2FeCl_{3(l)} \xrightarrow{T = 693\ K} Cl_{2(g)} + 2FeCl_{2(s)}$$

$$2FeCl_{2(s)} + 2HCl_{(g)} + S_{(l)} \xrightarrow{T = 473\ K} 2FeCl_{3(s)} + H_2S_{(g)}$$

- Ispra Mark 7A

$$\tfrac{3}{2}Cl_{2(g)} + \tfrac{1}{2}Fe_2O_{3(s)} \xrightarrow{T = 1273\ K} FeCl_{3(l)} + \tfrac{3}{4}O_{2(g)}$$

$$3FeCl_{2(s)} + 4H_2O_{(g)} \xrightarrow{T = 923\ K} Fe_3O_{4(s)} + 6HCl_{(g)} + H_{2(g)}$$

$$3FeCl_{3(l)} \xrightarrow{T = 693\ K} \tfrac{3}{2}Cl_{2(g)} + 3FeCl_{2(s)}$$

$$Fe_3O_{4(s)} + \tfrac{1}{4}O_{2(g)} \xrightarrow{T = 623\ K} \tfrac{3}{2}Fe_2O_{3(s)}$$

$$Fe_2O_{3(s)} + HCl_{(g)} \xrightarrow{T = 393\ K} 2FeCl_{3(l)} + 3H_2O_{(l)}$$

Sample Thermochemical Cycles

- Ispra Mark 7B

$$\tfrac{9}{2}Cl_{2(g)} + \tfrac{3}{2}Fe_2O_{3(s)} \xrightarrow{T = 1273\ K} 3FeCl_{3(l)} + \tfrac{9}{4}O_{2(g)}$$

$$3FeCl_{2(s)} + 4H_2O_{(g)} \xrightarrow{T = 923\ K} Fe_3O_{4(s)} + 6HCl_{(g)} + H_{2(g)}$$

$$3FeCl_{3(l)} \xrightarrow{T = 693\ K} \tfrac{3}{2}Cl_{2(g)} + 3FeCl_{2(s)}$$

$$6HCl_{(g)} + \tfrac{3}{2}O_{2(g)} \xrightarrow{T = 673\ K} 3Cl_{2(g)} + 3H_2O_{(g)}$$

$$Fe_3O_{4(s)} + \tfrac{1}{4}O_{2(g)} \xrightarrow{T = 623\ K} \tfrac{3}{2}Fe_2O_{3(s)}$$

Sample Hybrid Cycles

- Westinghouse

$$H_2SO_{4(g)} \xrightarrow{T = 1123\ K} SO_{2(g)} + H_2O_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$SO_{2(g)} + 2H_2O_{(l)} \xrightarrow{T = 350\ K} H_2SO_{4(g)} + H_{2(g)}$$

- Ispra Mark 13

$$H_2SO_{4(g)} \xrightarrow{T = 1123\ K} SO_{2(g)} + H_2O_{(g)} + \tfrac{1}{2}O_{2(g)}$$

$$2HBr_{(aq)} \xrightarrow{T = 350\ K} Br_{2(aq)} + H_{2(g)}$$

$$Br_{2(l)} + SO_{2(g)} + 2H_2O_{(l)} \xrightarrow{T = 350\ K} HBr_{(g)} + H_2SO_{4(g)}$$

- Hallett Air Products

$$Cl_{2(g)} + H_2O_{(g)} \xrightarrow{T = 1073\ K} 2HCl_{(g)} + \tfrac{1}{2}O_{2(g)}$$

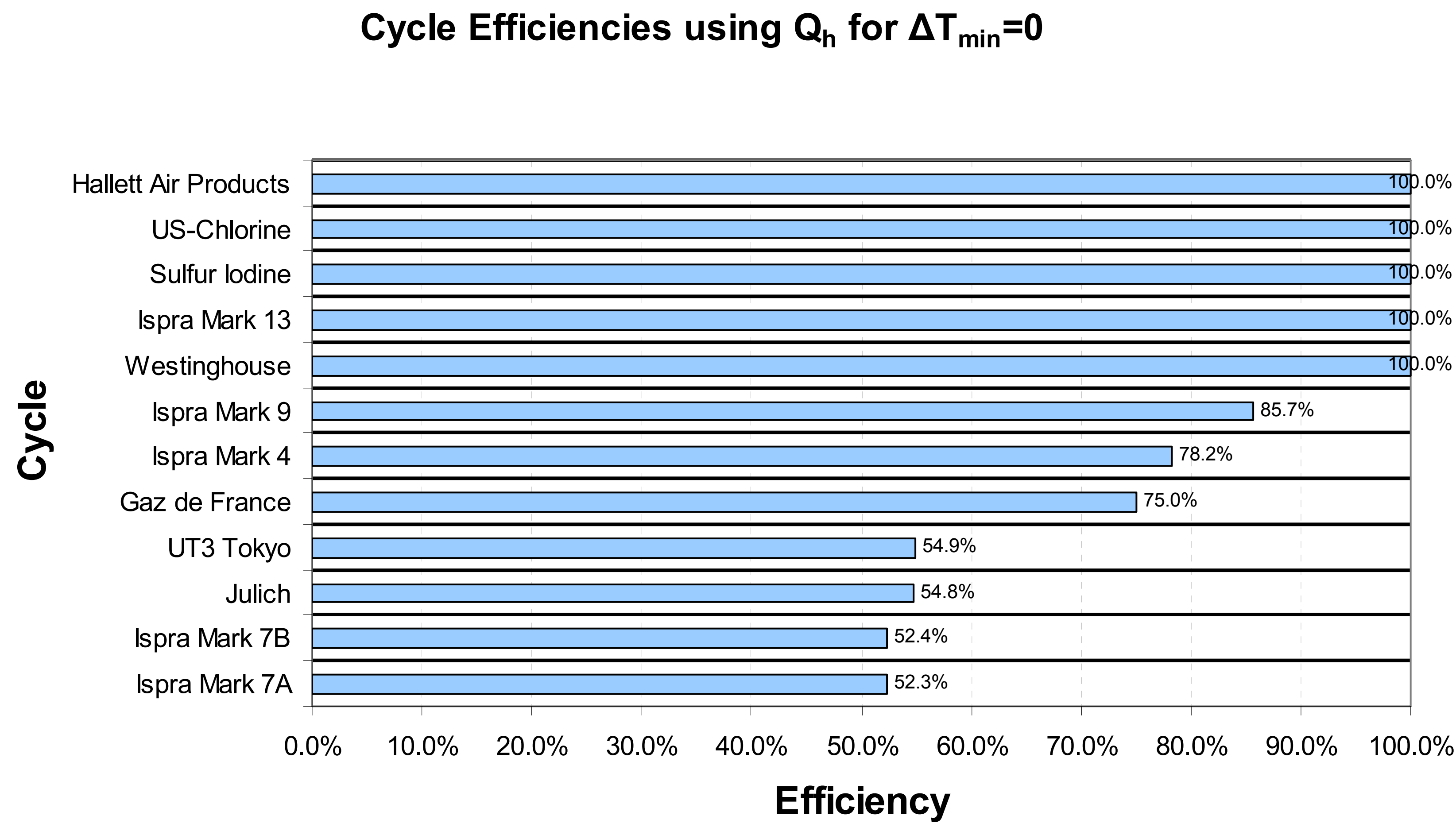
$$2HCl_{(g)} \xrightarrow{T = 298\ K} Cl_{2(g)} + H_{2(g)}$$

Results

- Cycle rankings based on Q_H analysis with $\Delta T_{min}=0$

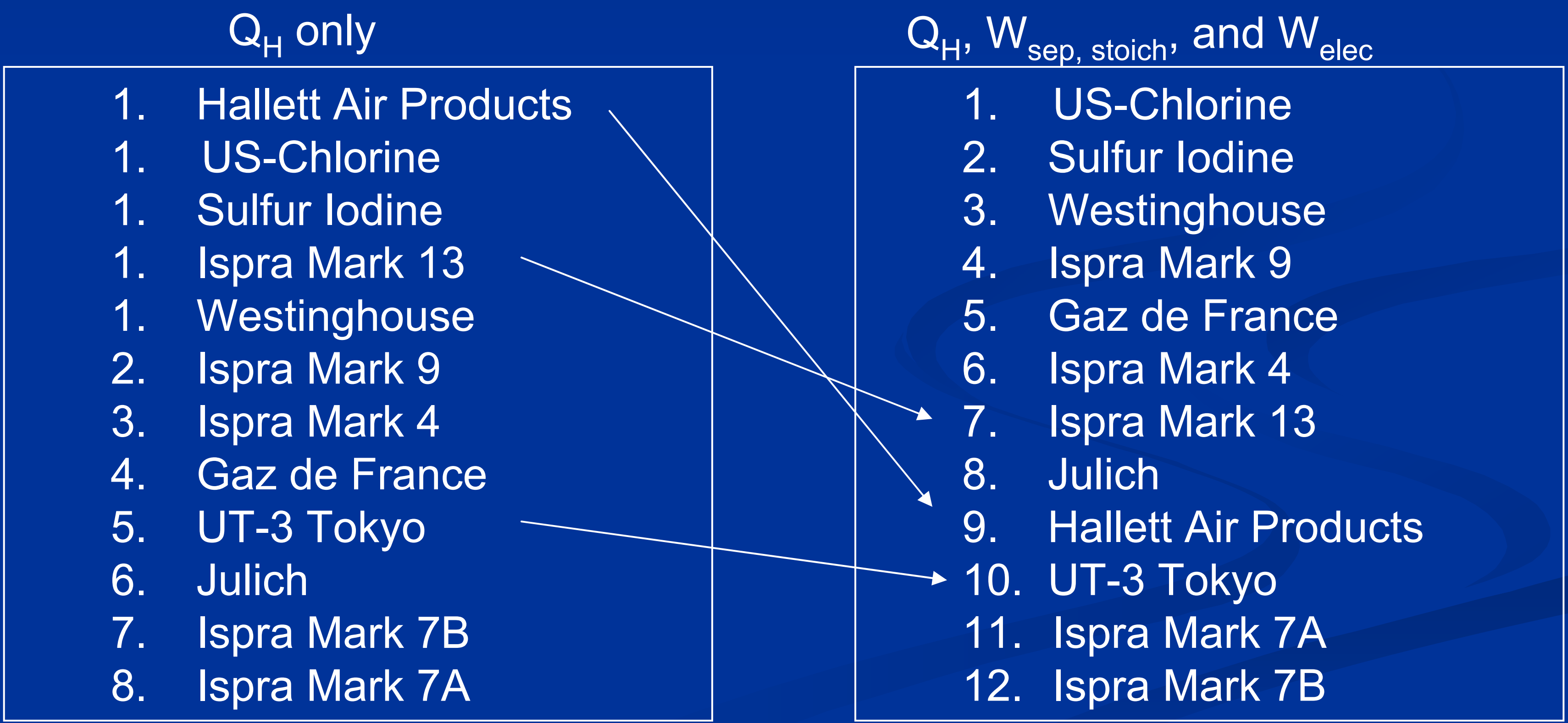
1.	Hallett Air Products
1.	US-Chlorine
1.	Sulfur Iodine
1.	Ispra Mark 13
1.	Westinghouse
2.	Ispra Mark 9
3.	Ispra Mark 4
4.	Gaz de France
5.	UT-3 Tokyo
6.	Julich
7.	Ispra Mark 7B
8.	Ispra Mark 7A

Q_H analysis with ΔT_{min}=0



Results cont.

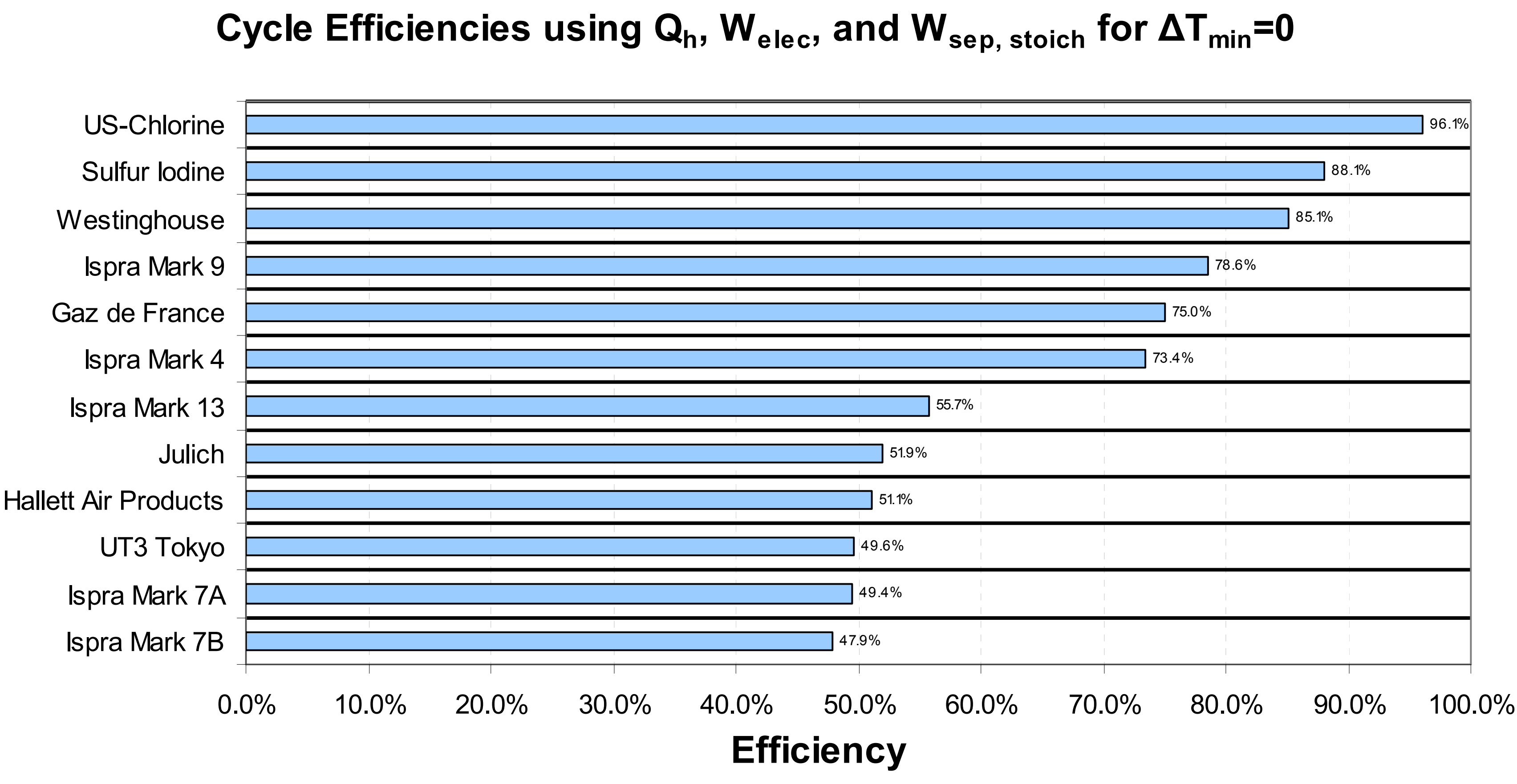
- Now we consider $W_{sep, stoich}$ and W_{elec} as well



Q_H only	Q_H, $W_{sep, stoich}$, and W_{elec}
1. Hallett Air Products	1. US-Chlorine
1. US-Chlorine	2. Sulfur Iodine
1. Sulfur Iodine	3. Westinghouse
1. Ispra Mark 13	4. Ispra Mark 9
1. Westinghouse	5. Gaz de France
2. Ispra Mark 9	6. Ispra Mark 4
3. Ispra Mark 4	7. Ispra Mark 13
4. Gaz de France	8. Julich
5. UT-3 Tokyo	9. Hallett Air Products
6. Julich	10. UT-3 Tokyo
7. Ispra Mark 7B	11. Ispra Mark 7A
8. Ispra Mark 7A	12. Ispra Mark 7B

Note: arrows indicate only cycles that change 3+ positions

Q_H, W_{elec}, and stoichiometric separation analysis with ΔT_{min}=0

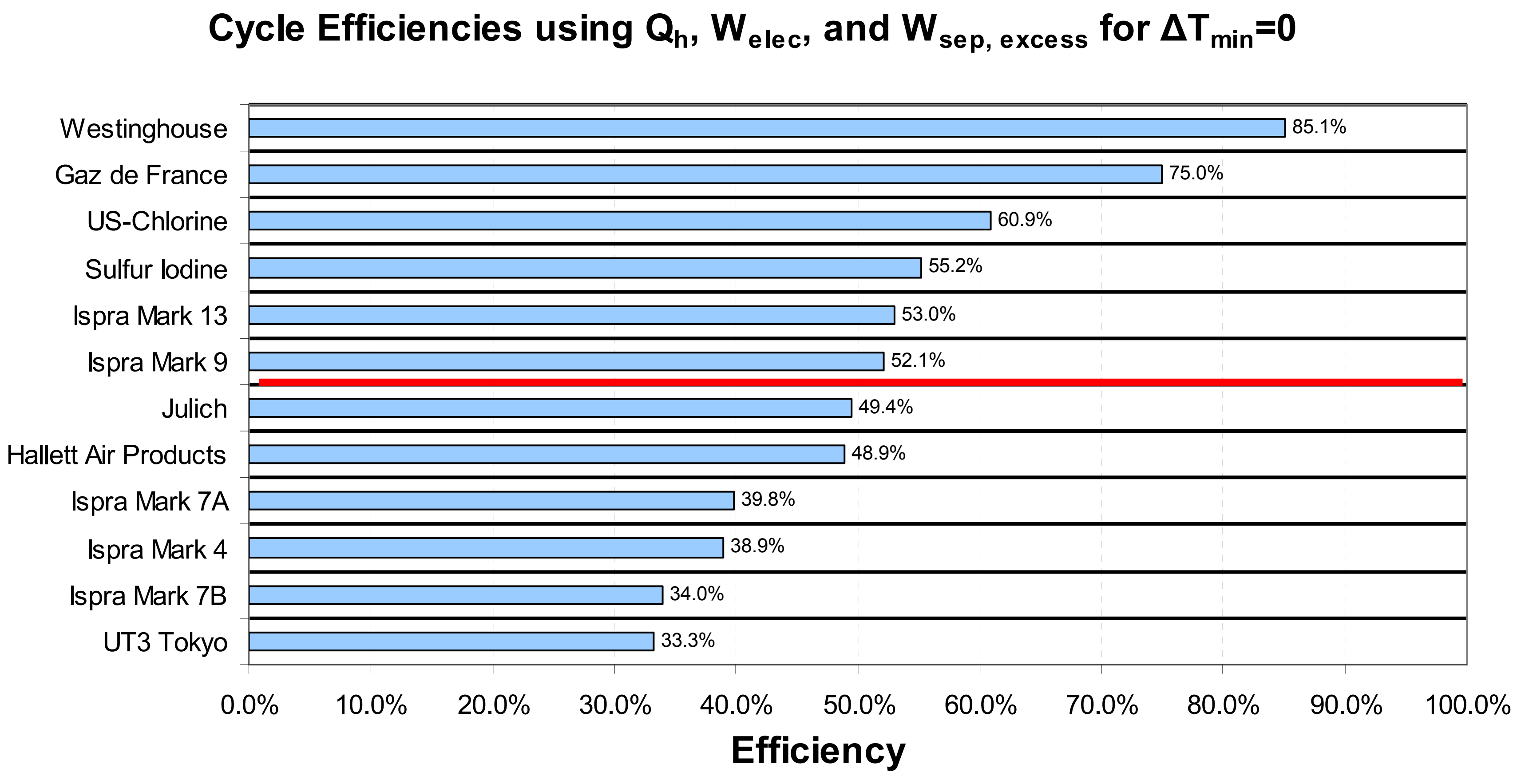


Results cont'd

- Now we substitute $W_{sep,\ stoich}$ with $W_{sep,\ excess}$

	Q_H, $W_{sep,\ stoich}$, and W_{elec}		Q_H, $W_{sep,\ excess}$, and W_{elec}
1.	US-Chlorine	1.	Westinghouse
2.	Sulfur Iodine	2.	Gaz de France
3.	Westinghouse	3.	US-Chlorine
4.	Ispra Mark 9	4.	Sulfur Iodine
5.	Gaz de France	5.	Ispra Mark 13
6.	Ispra Mark 4	6.	Ispra Mark 9
7.	Ispra Mark 13	7.	Julich
8.	Julich	8.	Hallett Air Products
9.	Hallett Air Products	9.	Ispra Mark 7A
10.	UT-3 Tokyo	10.	Ispra Mark 4
11.	Ispra Mark 7A	11.	Ispra Mark 7B
12.	Ispra Mark 7B	12.	UT-3 Tokyo

Q_H, W_{elec}, and excess separation analysis with ΔT_{min}=0



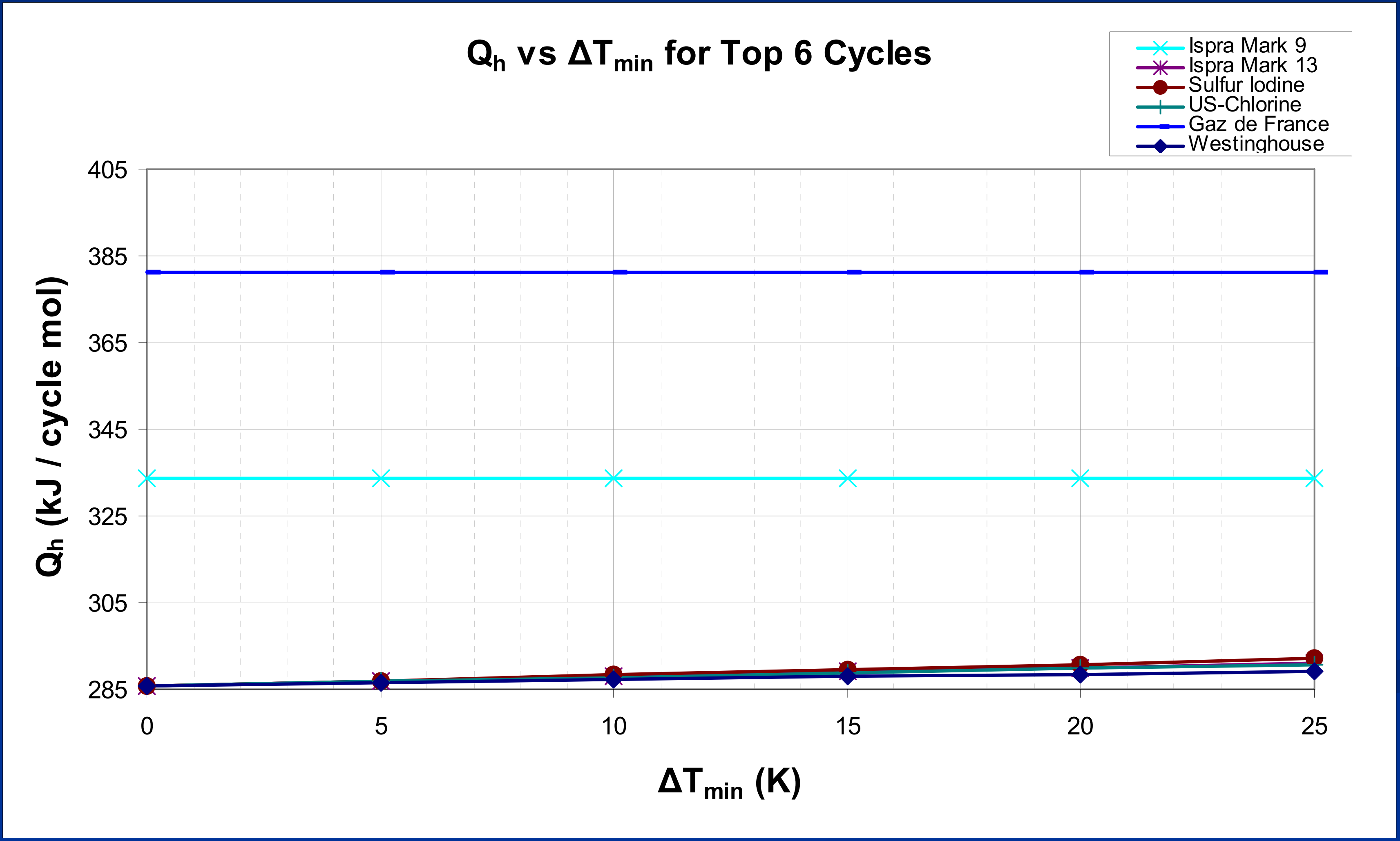
Top 6 Thermochemical Cycles

- Based upon full analysis at $\Delta T_{min}=0$

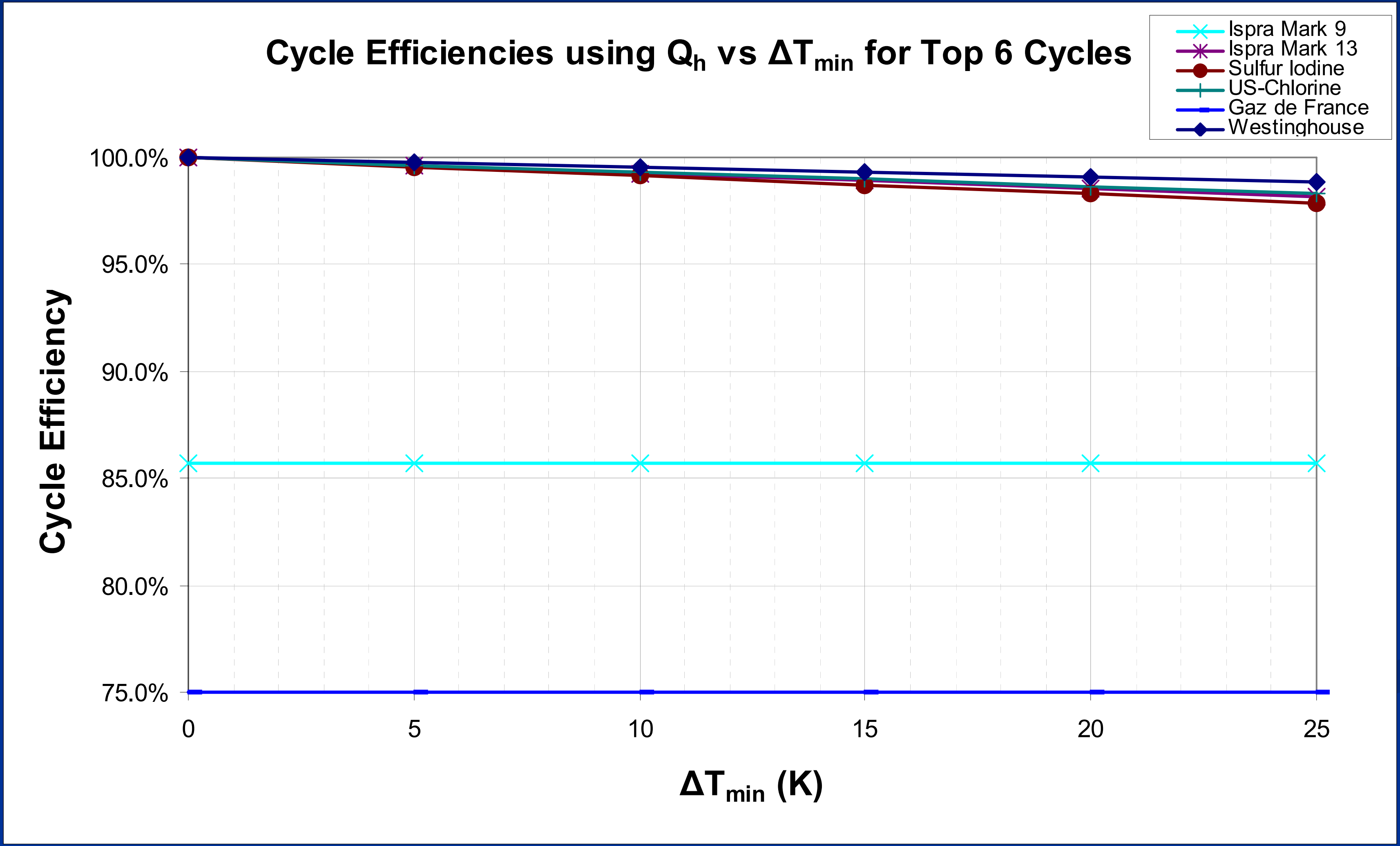
1. Westinghouse
2. Gaz de France
3. US-Chlorine
4. Sulfur Iodine
5. Ispra Mark 13
6. Ispra Mark 9

- What about $\Delta T_{min} > 0$?
  - Some cycles more sensitive

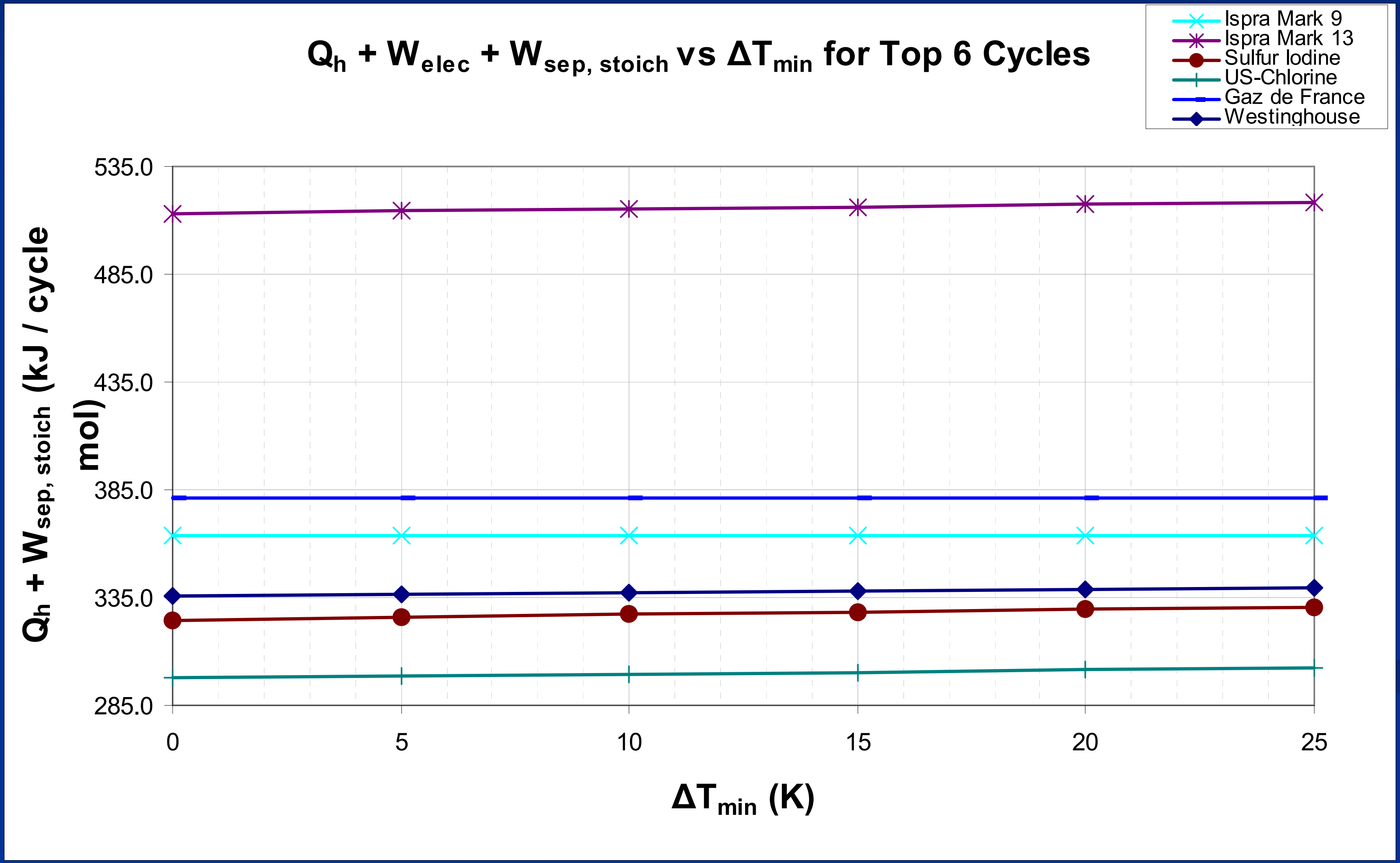
Effect of ΔT_{min} on Q_H



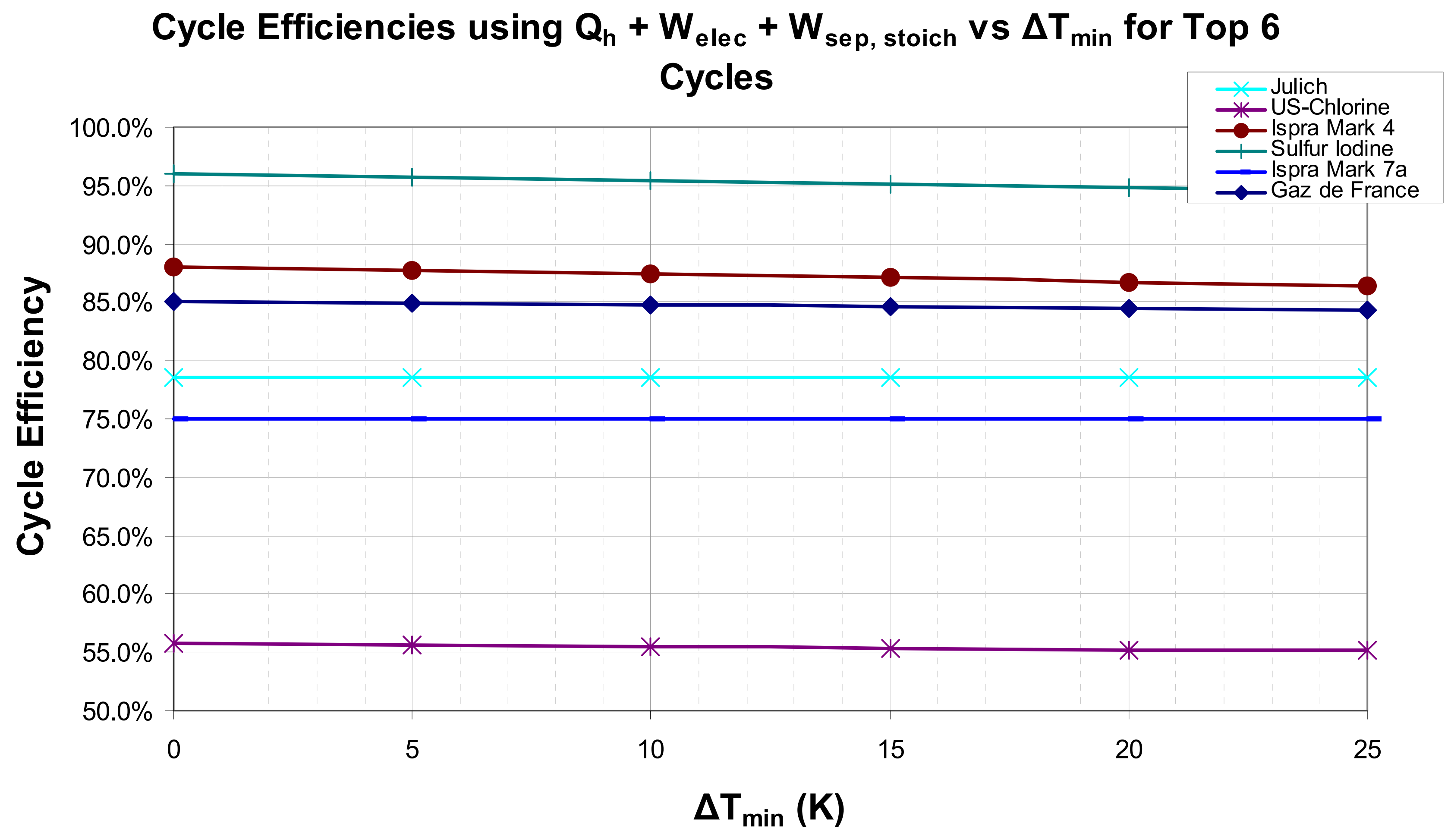
Corresponding Efficiency


Cycle Efficiencies using Q_h vs ΔT_{min} for Top 6 Cycles

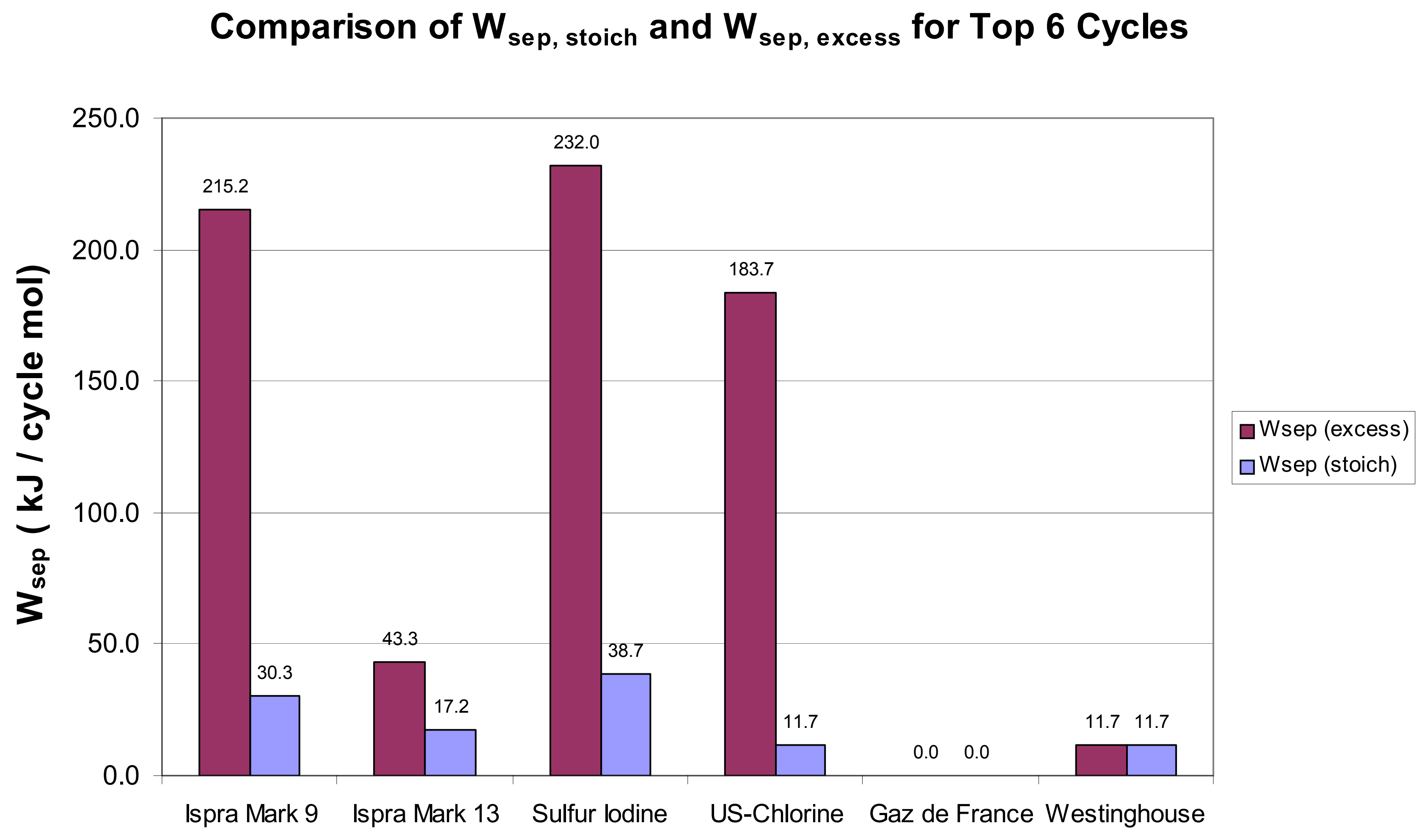
Effect of ΔT_{min} on $Q_H + W_{elec} + W_{sep,\ stoich}$



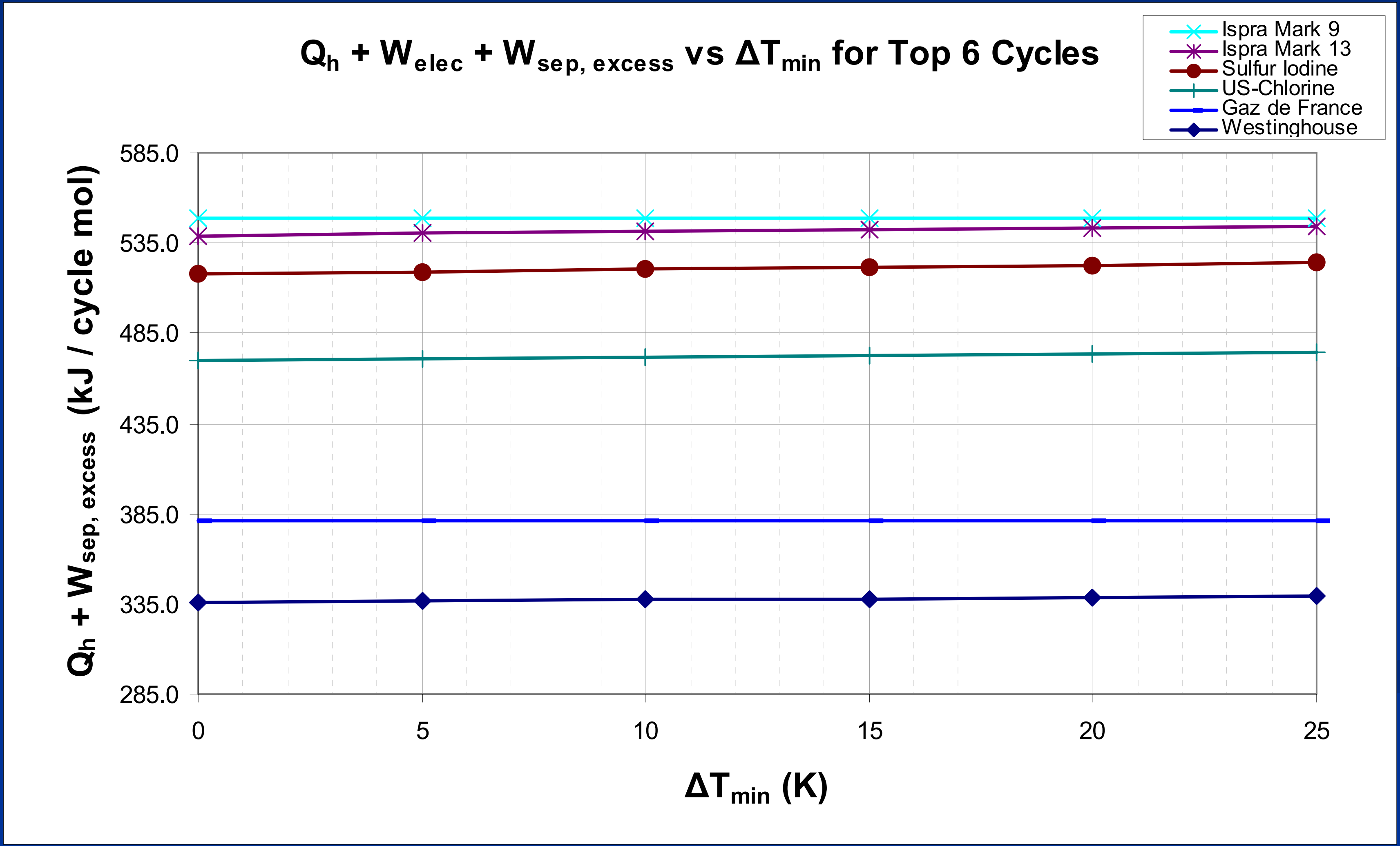
Corresponding Efficiency



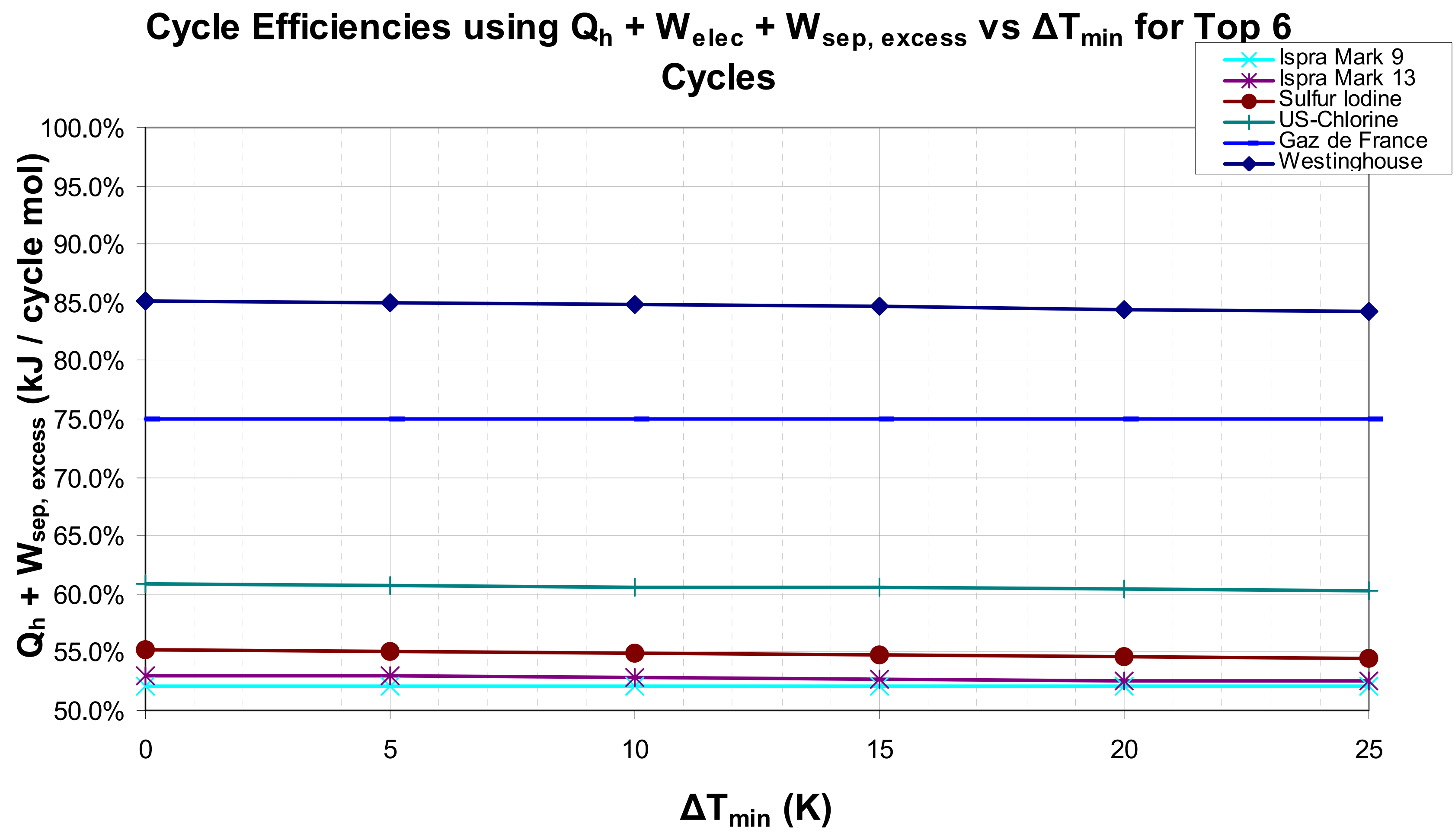
$W_{sep,\ stoich}$ vs. $W_{sep,\ excess}$



Effect of ΔT_{min} on $Q_H + W_{elec} + W_{sep,\ excess}$



Corresponding Efficiency



Efficiency: Literature Comparison[†]

	Reported (thermal)	Theoretical (thermal)	Theoretical (heat/work)
Sulfur-Iodine	52%[‡]	100%	55%
Tokyo UT-3	49%[‡]	55%	33%
Westinghouse	50%	100%	85%

[†] Brown et al 2000

[‡] 10% additional efficiency projected with electricity co-generation

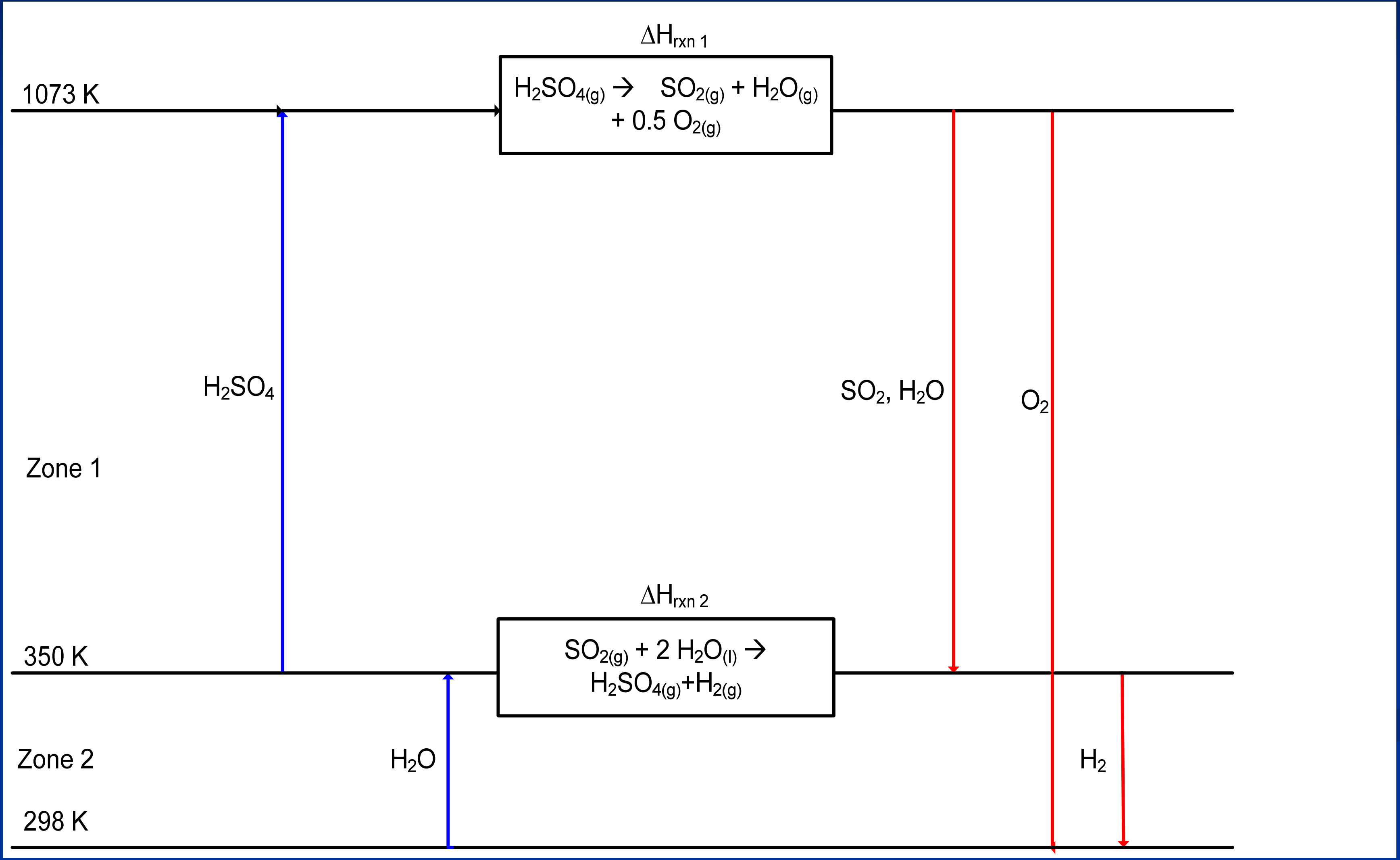
Good Cycle Characteristics

- Hottest reaction exothermic, cascades heat to power rest of the cycle
  - Minimizes Q
- Products phase separate from each other, and from reactants
  - Minimizes W
- No high T, P, corrosivity, etc. as described by Brown et al 2000

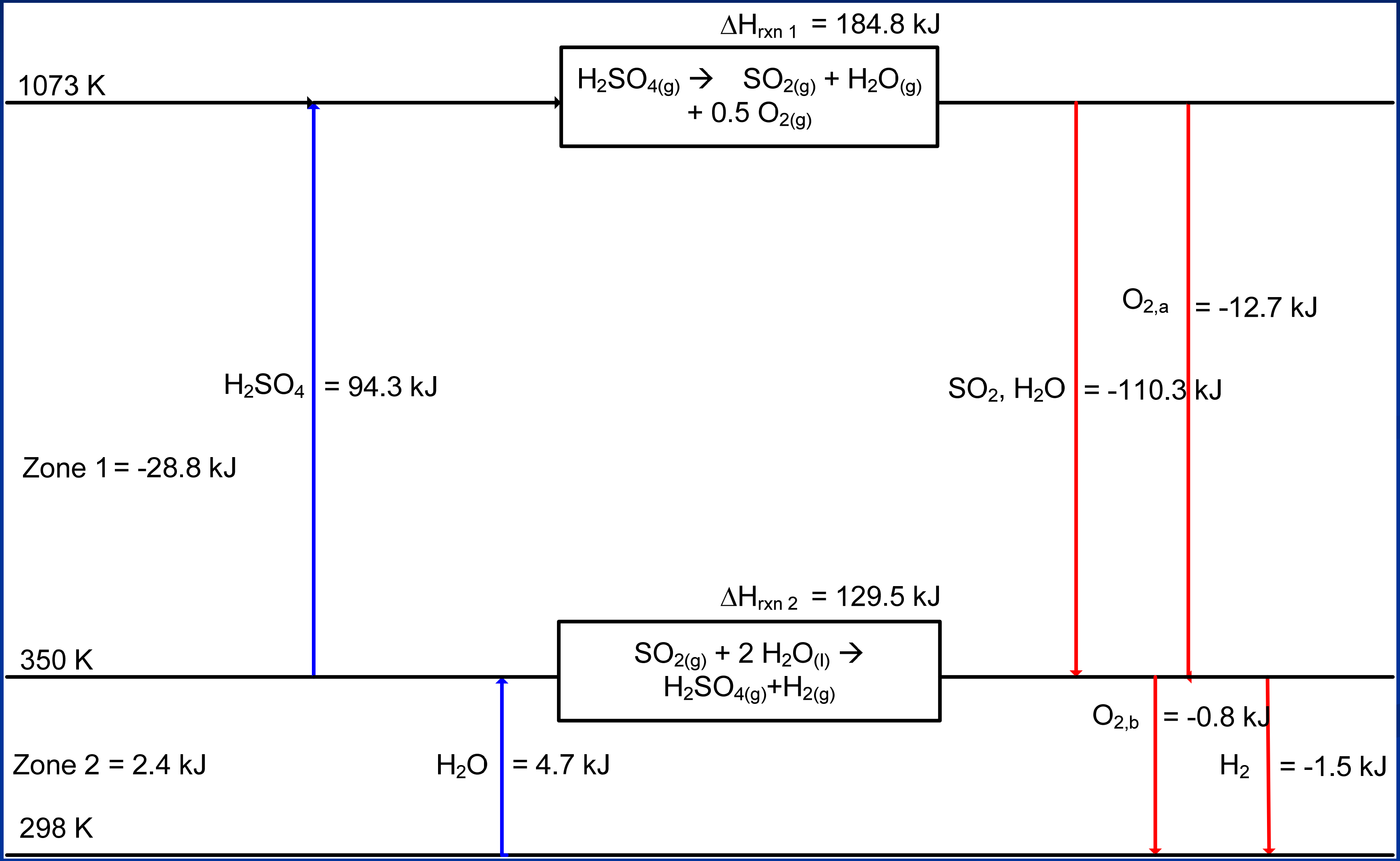
Economic Methodology

- 500 ton/day production target
  - Enough for 0.95 million cars, according to Schultz
- Heat Integration
  - Temperature intervals
  - Cascades
  - Heat exchanger network
- Process Flow Diagrams
  - Assumptions
  - Solids handling
  - Capital cost

Westinghouse Cycle - Heat Profile



Westinghouse Cycle - Heat Profile



$\Delta H_{rxn\ 1}$ = 184.8 kJ

1073 K

$H_2SO_{4(g)} \rightarrow SO_{2(g)} + H_2O_{(g)} + 0.5\ O_{2(g)}$

$O_{2,a}$ = -12.7 kJ

H_2SO_4 = 94.3 kJ

SO_2, H_2O = -110.3 kJ

Zone 1 = -28.8 kJ

$\Delta H_{rxn\ 2}$ = 129.5 kJ

350 K

$SO_{2(g)} + 2\ H_2O_{(l)} \rightarrow H_2SO_{4(g)} + H_{2(g)}$

$O_{2,b}$ = -0.8 kJ

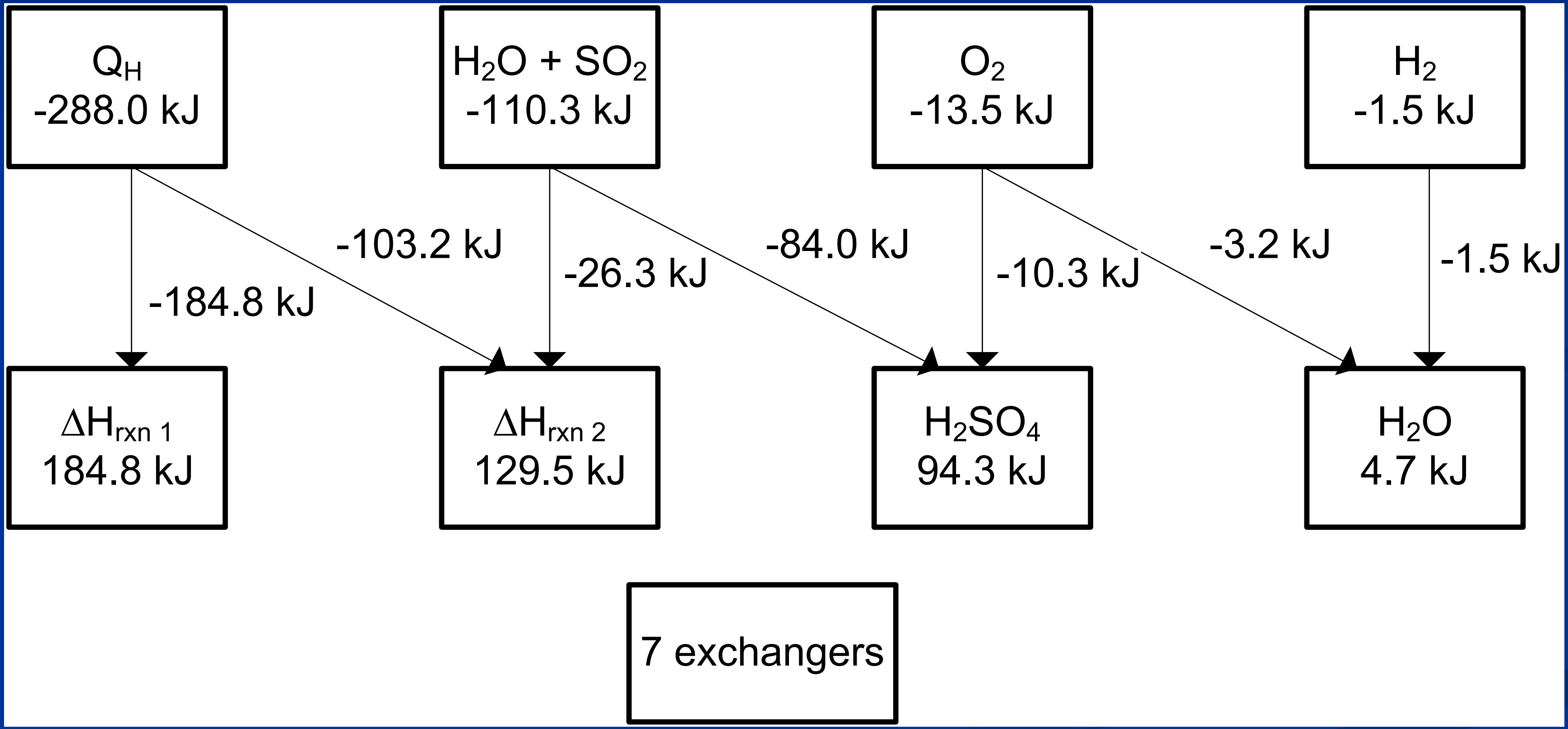
Zone 2 = 2.4 kJ

H_2O = 4.7 kJ

H_2 = -1.5 kJ

298 K

Westinghouse - Heat Cascade



Q_H
-288.0 kJ

$H_2O + SO_2$
-110.3 kJ

O_2
-13.5 kJ

H_2
-1.5 kJ

-184.8 kJ

-103.2 kJ

-26.3 kJ

-84.0 kJ

-10.3 kJ

-3.2 kJ

-1.5 kJ

$\Delta H_{rxn\ 1}$
184.8 kJ

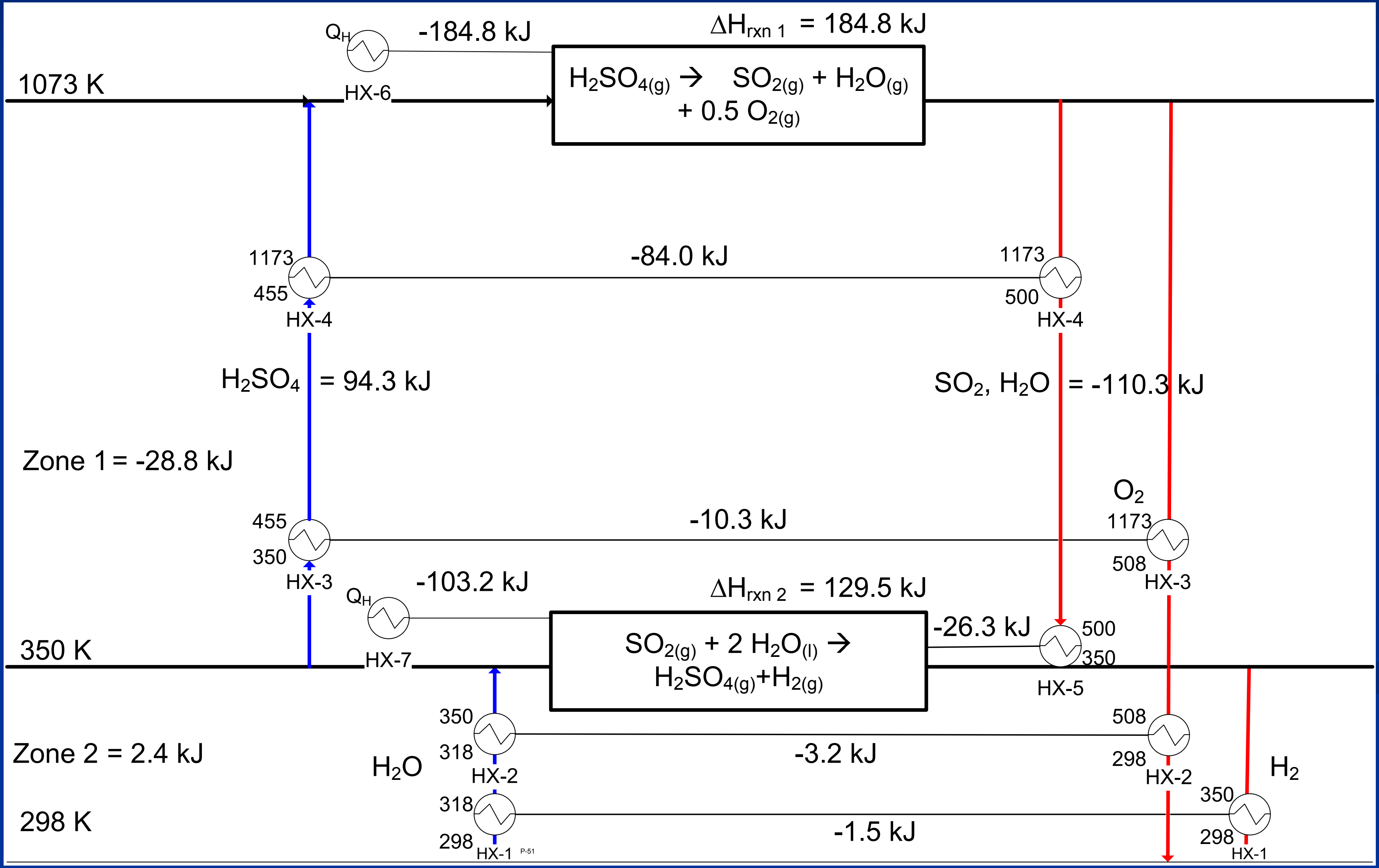
$\Delta H_{rxn\ 2}$
129.5 kJ

H_2SO_4
94.3 kJ

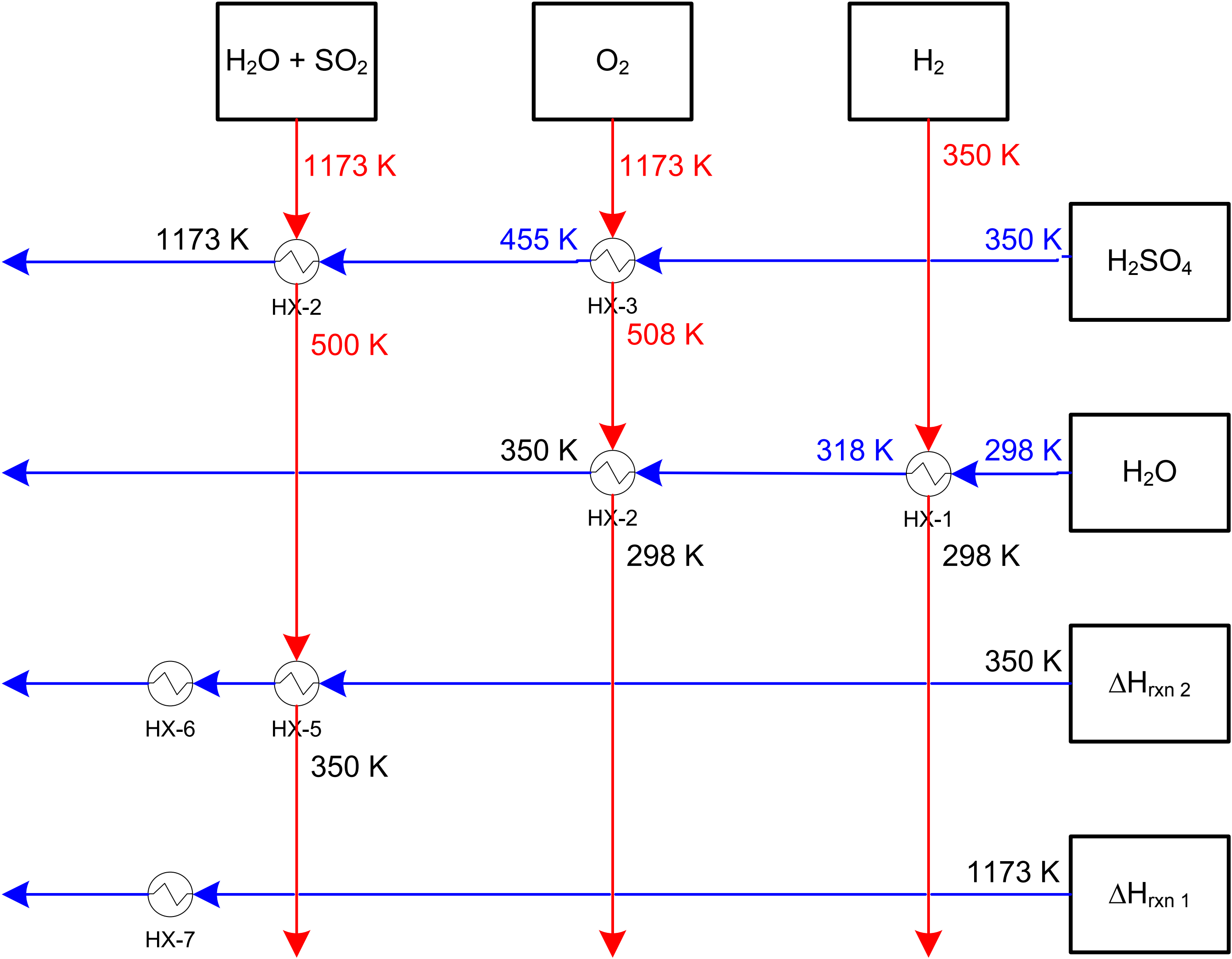
H_2O
4.7 kJ

7 exchangers

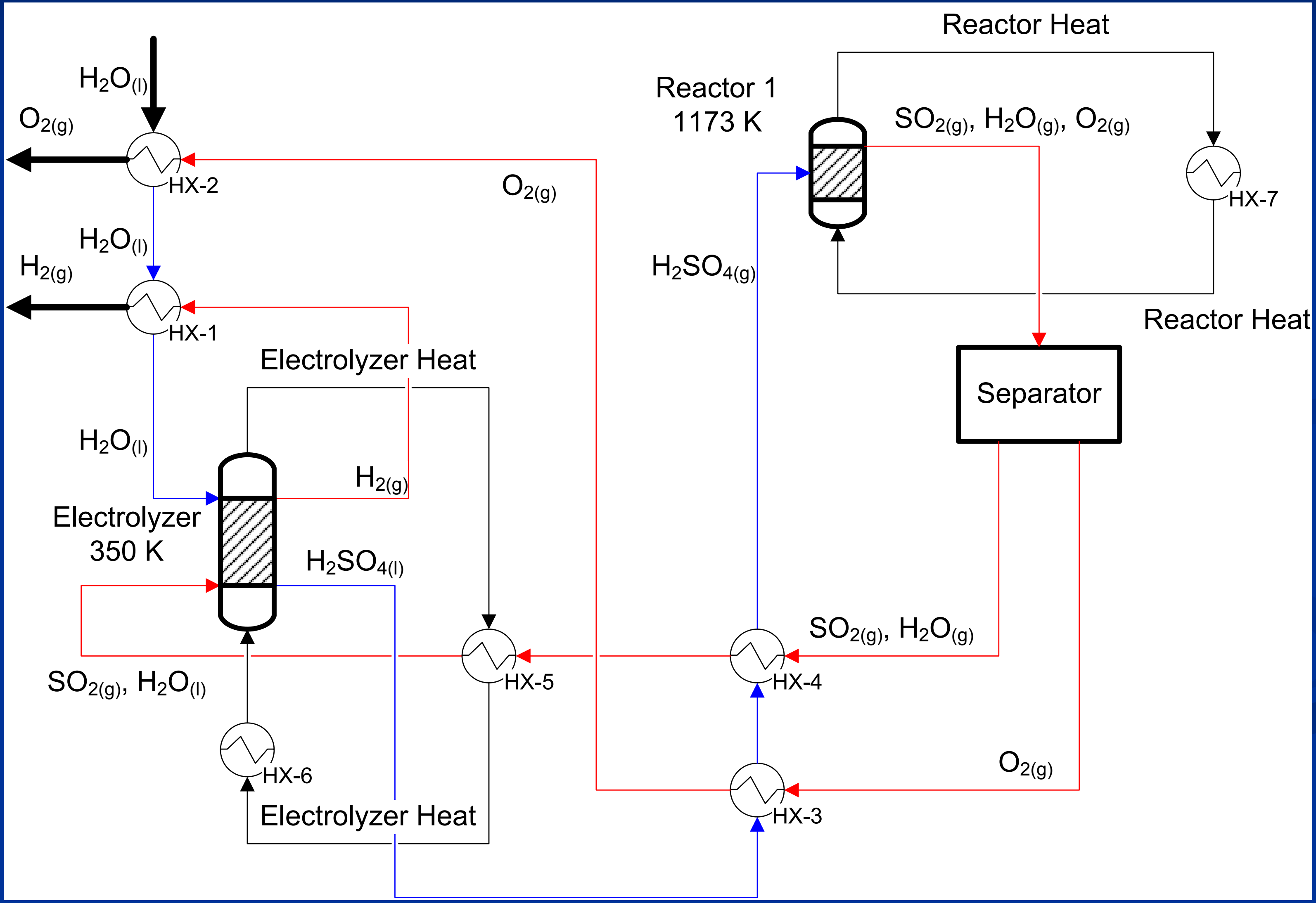
Westinghouse - Heat Exchanger Network



Westinghouse - Heat Exchanger Network

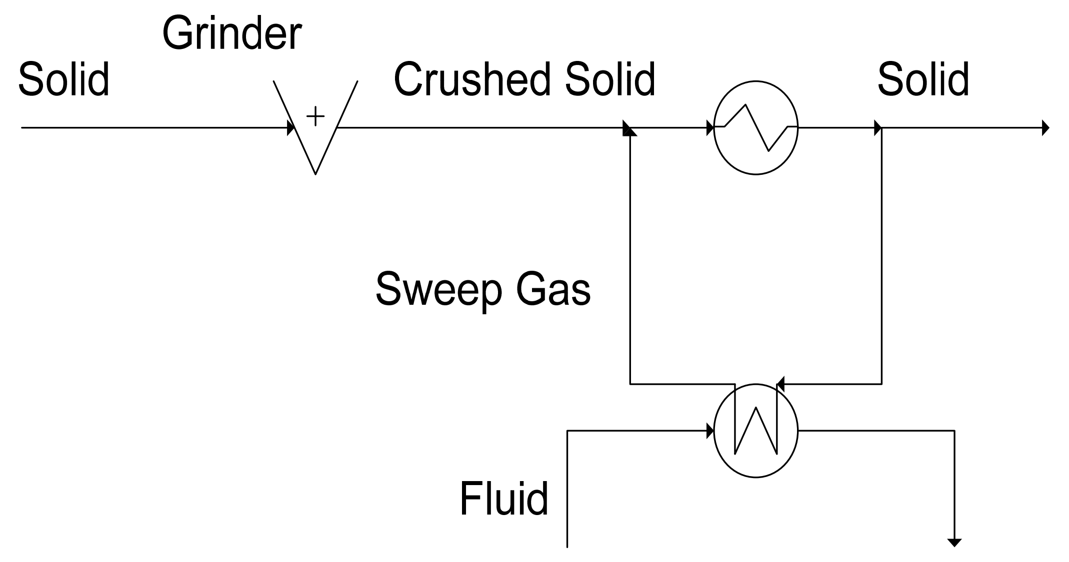


Westinghouse - Process Flow Diagram

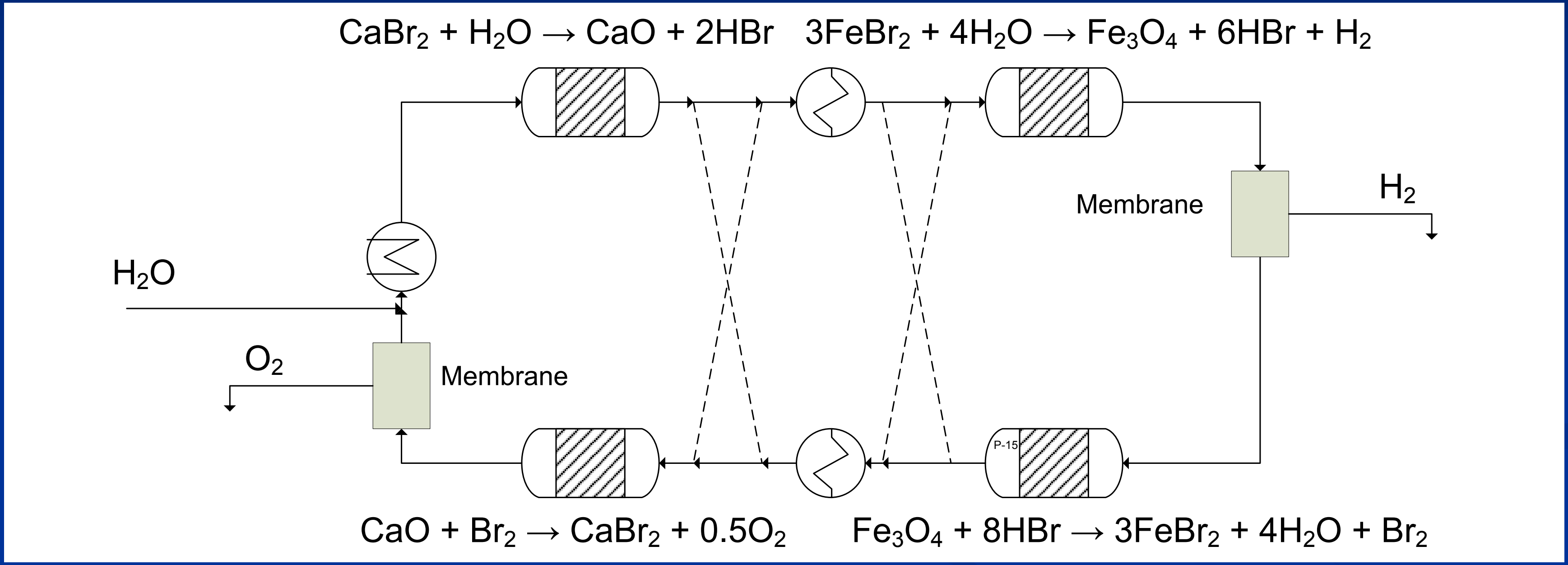


Handling Solids

- Physical transport of solids difficult
  - Grinders necessary
- Slow heat transfer between solids
  - Use sweep gas as intermediate heat carrier
- Solid separations
  - Usually oxides and halide salts – solvent separation



UT-3 University of Tokyo[†]



$CaBr_2 + H_2O \rightarrow CaO + 2HBr$

$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2$

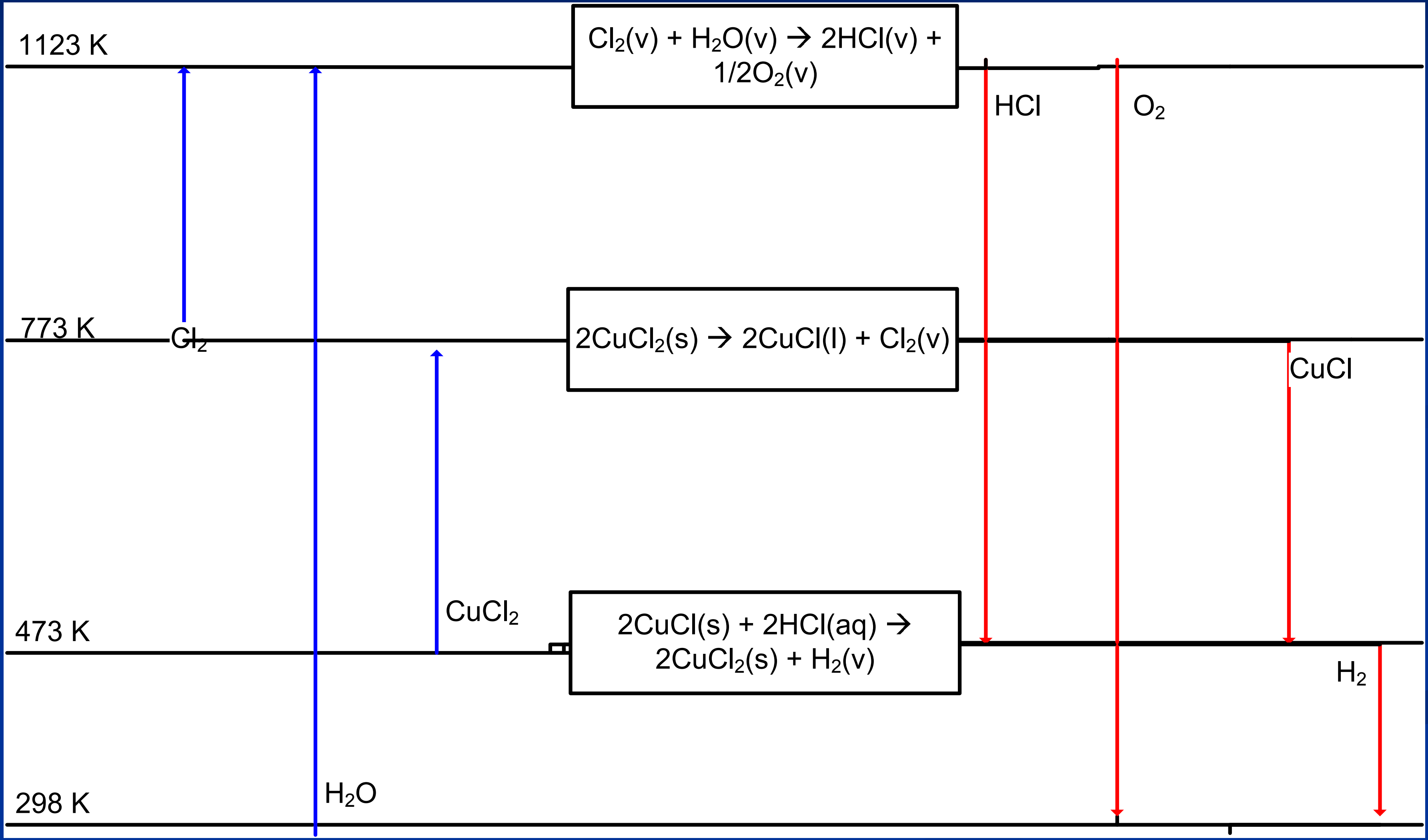
$CaO + Br_2 \rightarrow CaBr_2 + 0.5O_2$

$Fe_3O_4 + 8HBr \rightarrow 3FeBr_2 + 4H_2O + Br_2$

- Solids do not move – reactors run in parallel batch
  - Preserves efficiency, but increases capital costs and instability
- Reported thermal efficiency 49%, compared to 55% theoretical

[†] Adapted from Brown et al 2000

US Chlorine – Heat Cascade

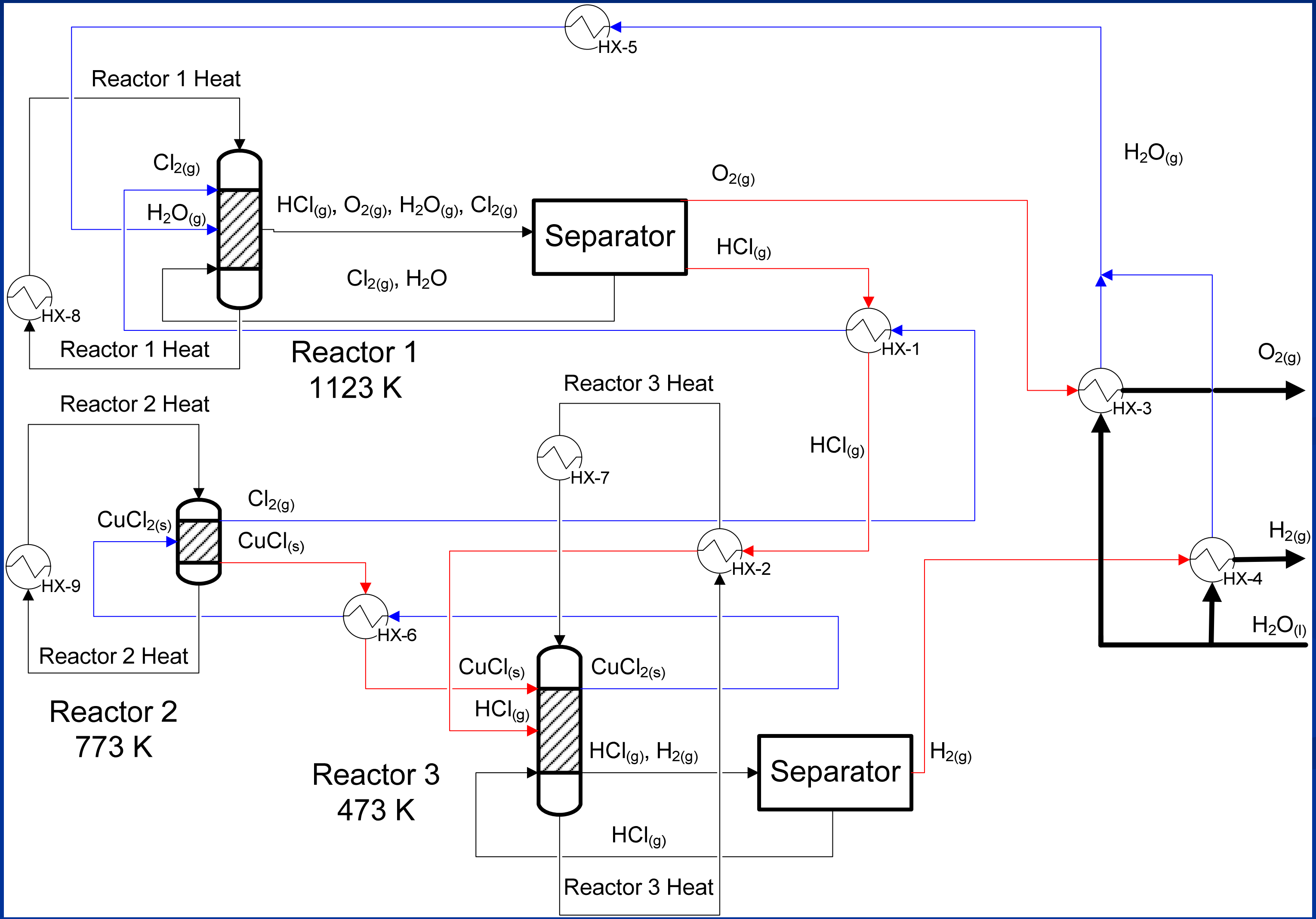


$Cl_2(v) + H_2O(v) \rightarrow 2HCl(v) + 1/2O_2(v)$

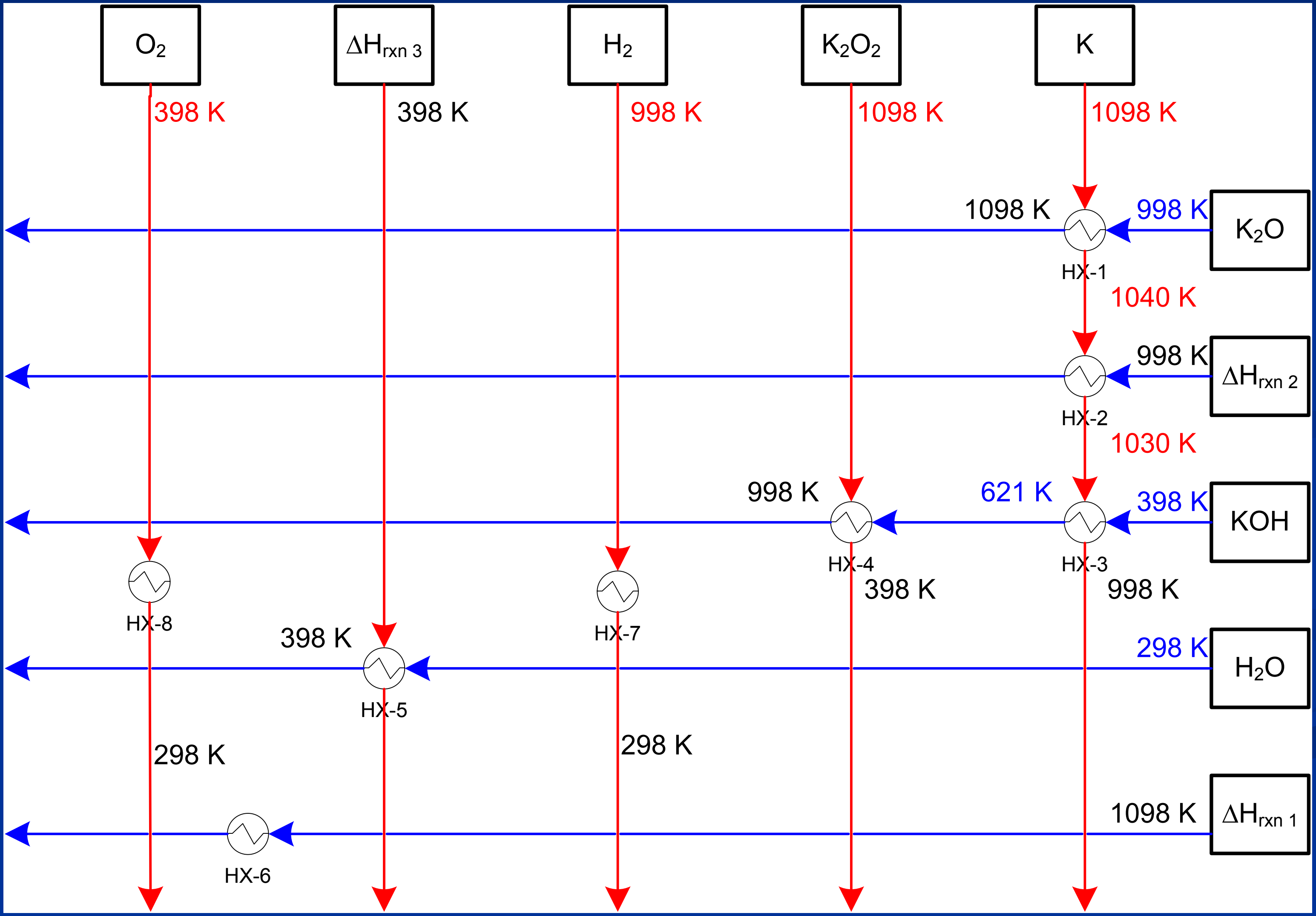
$2CuCl_2(s) \rightarrow 2CuCl(l) + Cl_2(v)$

$2CuCl(s) + 2HCl(aq) \rightarrow 2CuCl_2(s) + H_2(v)$

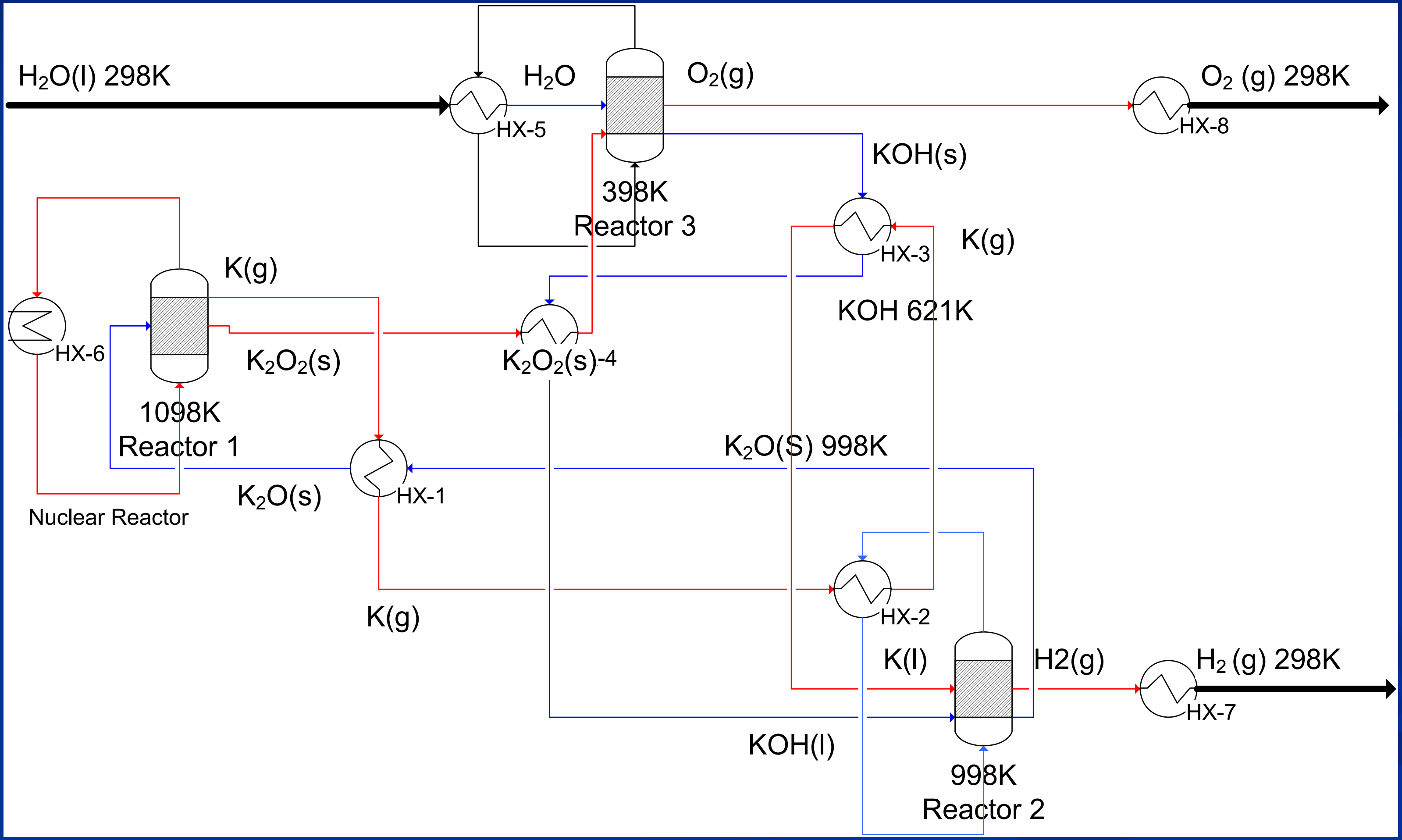
US Chlorine – Process Flow Diagram



Gaz de France - Heat Exchange Network



Gaz de France



Capital Cost

- New technology
- Processes involve highly corrosive materials and high temperatures[†]
  - Resistance to degradation involved within the cycles
  - High temperature quality material required
  - Research involved for design
- Some kinetics are currently unknown
- Contract work involved

[†] Perret et al 2004

Capital Cost cont'd

- 500 tons/day hydrogen production
- Equilibrium (complete reaction)
- Maximum heat exchange area possible
- Highly corrosive materials
- Scale up has never been done

Capital Cost Results

	Westinghouse	Gaz de France	US-Chlorine
Efficiency	85%	75%	60%
FCI	\$3,100,000,000	\$6,200,000,000	\$3,100,000,000
Energy Cost	\$27,000,000	\$39,000,000	\$38,000,000
Process Cost, \$/lb H_2 produced	\$0.07	\$0.11	\$0.11

Conclusions

- Scoping methodology can screen large number of cycles with reasonable accuracy
- Sulfur-Iodine and other popular cycles are not necessarily best
- Find cycles with phase separations and good heat cascade

Questions?

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