Process Integration for Clean Technology

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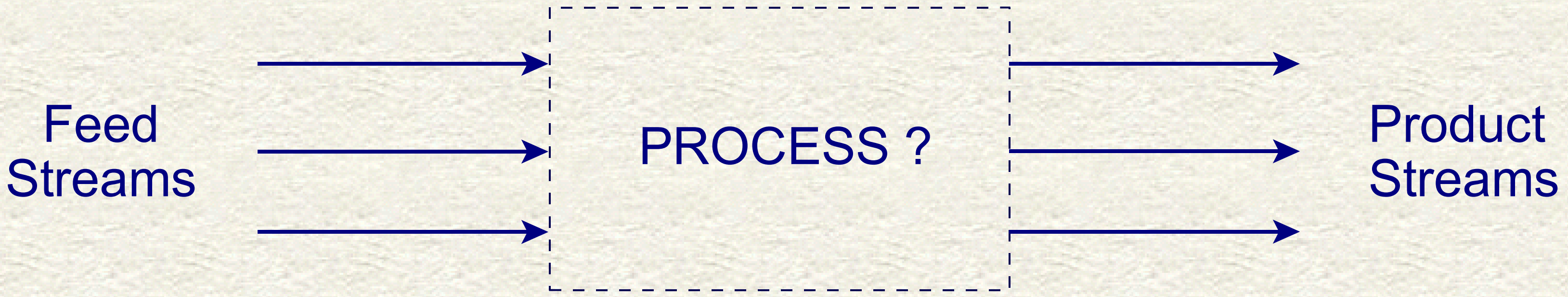
Outline

1. Sources of Process Waste
2. Reactor Design for Clean Technology
3. Water System Design to Minimise Aqueous Effluents
4. Minimising Combustion Emissions
5. Concluding Remarks

1. Sources of Process Waste

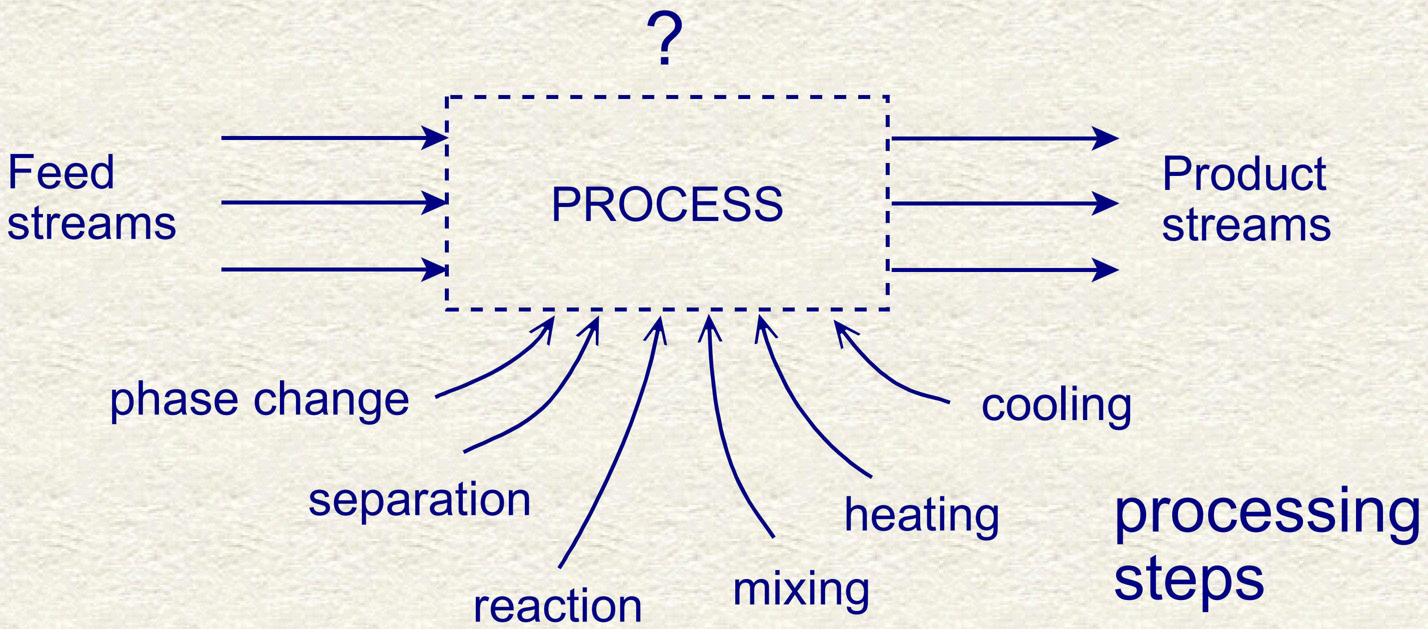
How do we go about the design of a chemical process?

FIRST: Process Integration



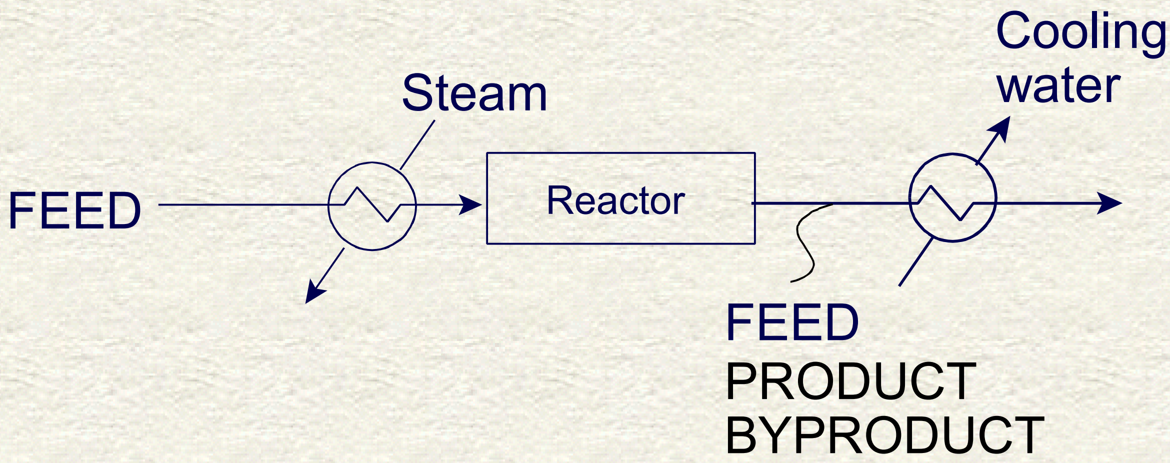
THEN: Simulation

What is process integration?

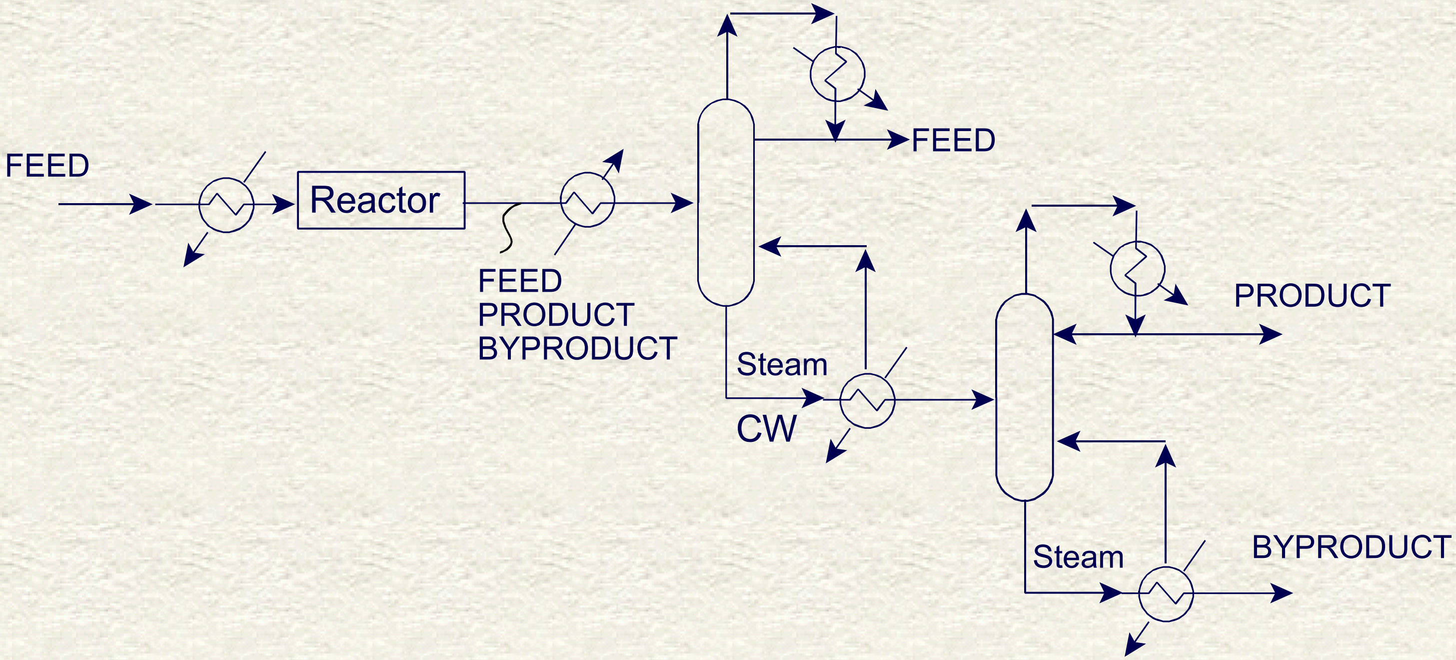


selection of processing steps and connections between steps

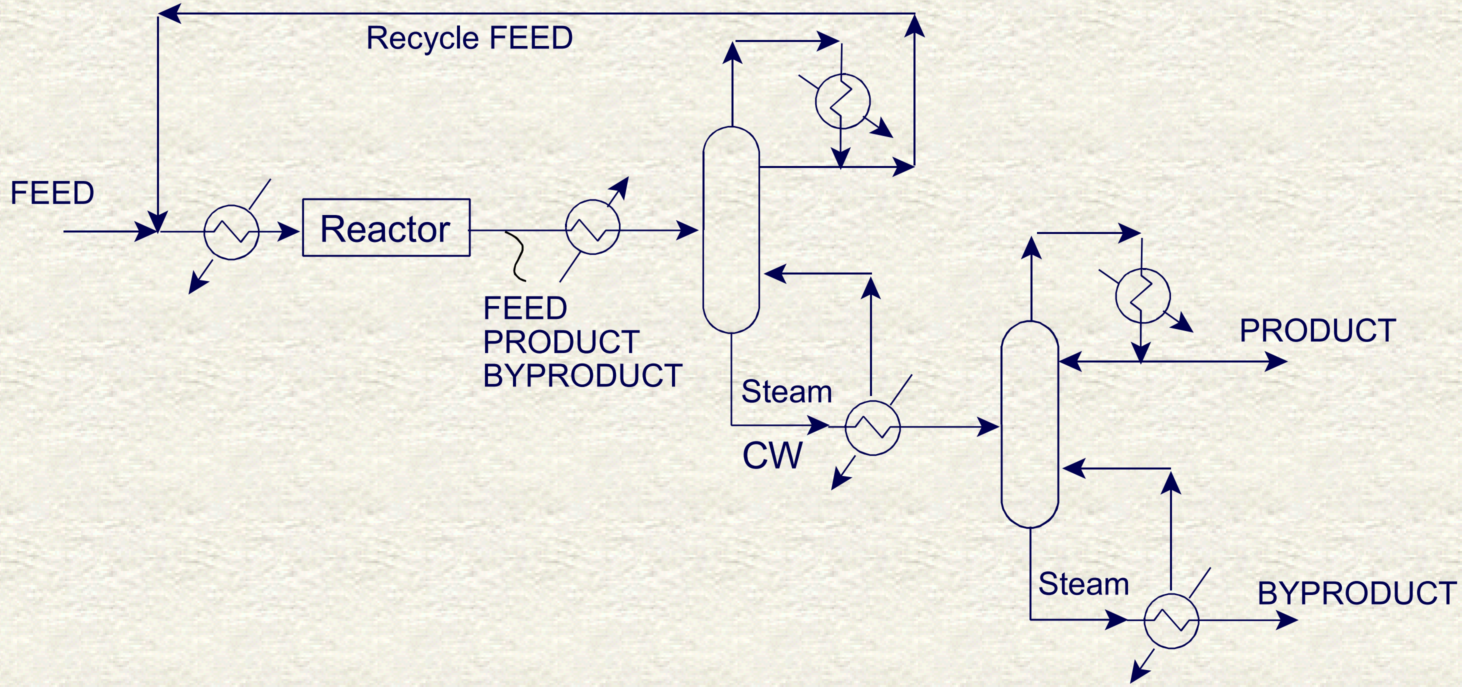
Process design starts with the reactor



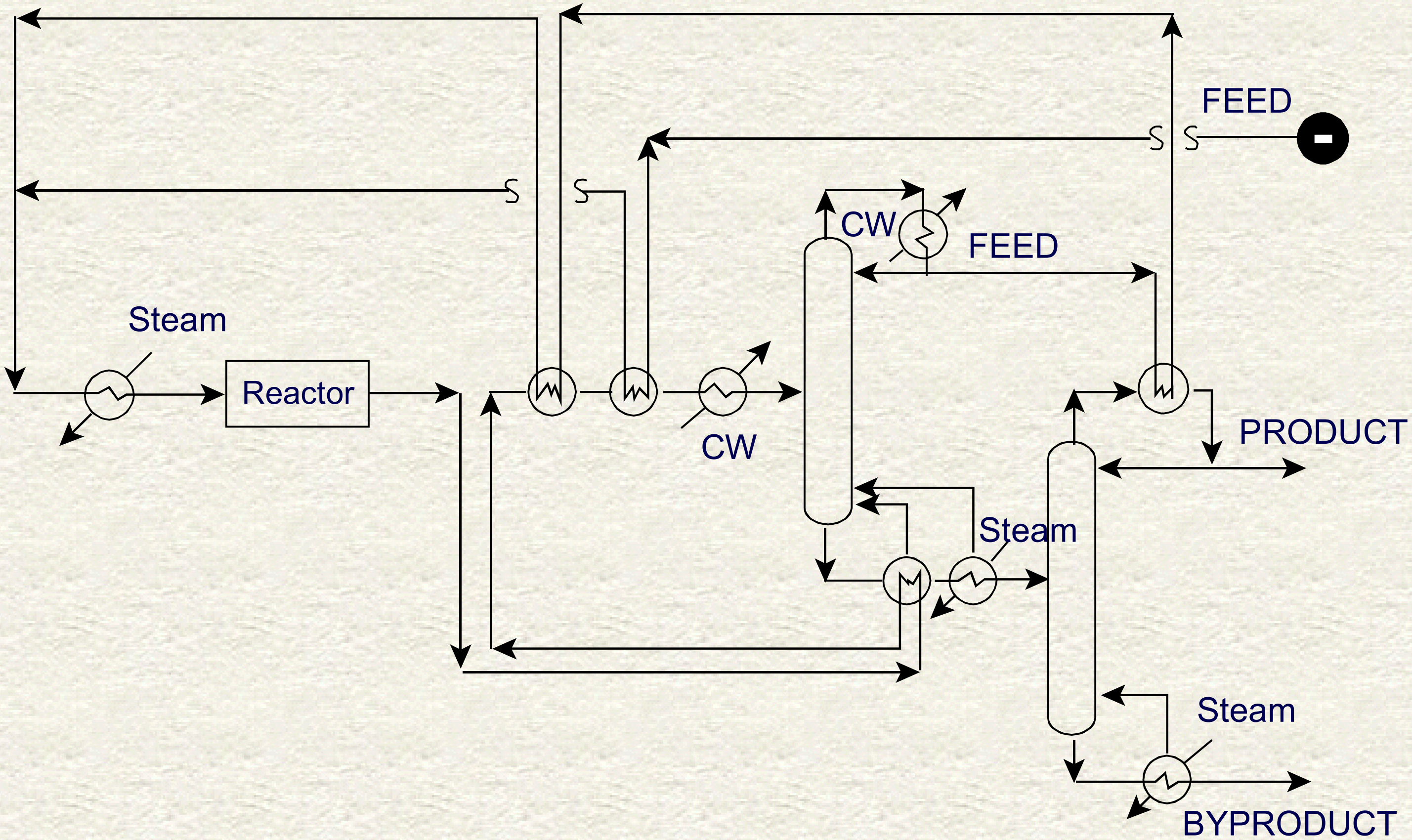
Now add the separation system



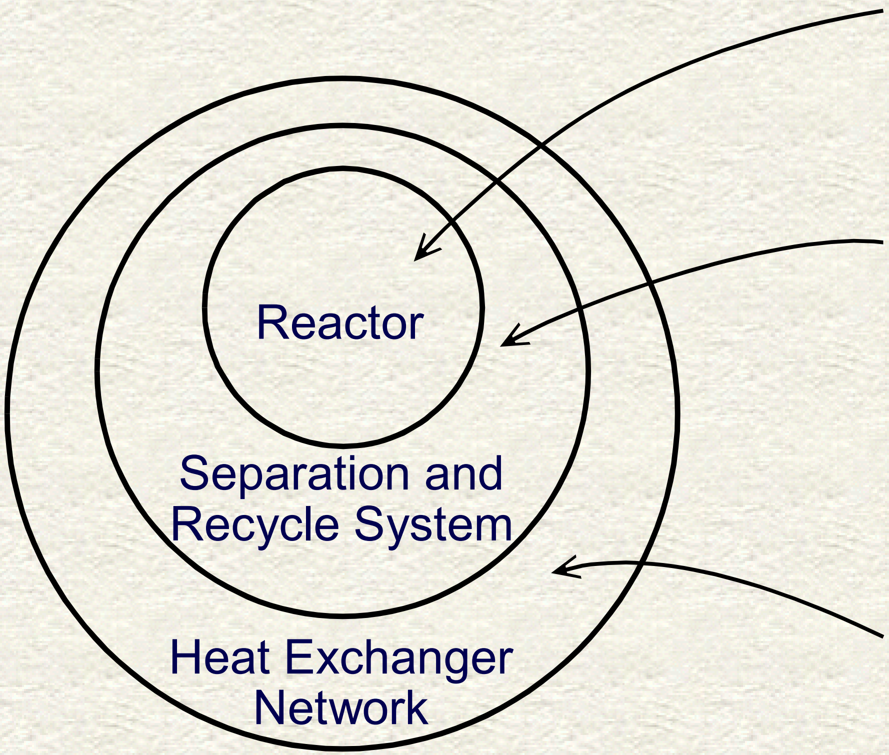
Now connect up the recycles



Now recover heat where possible



The ‘onion model’ for the hierarchy of process design

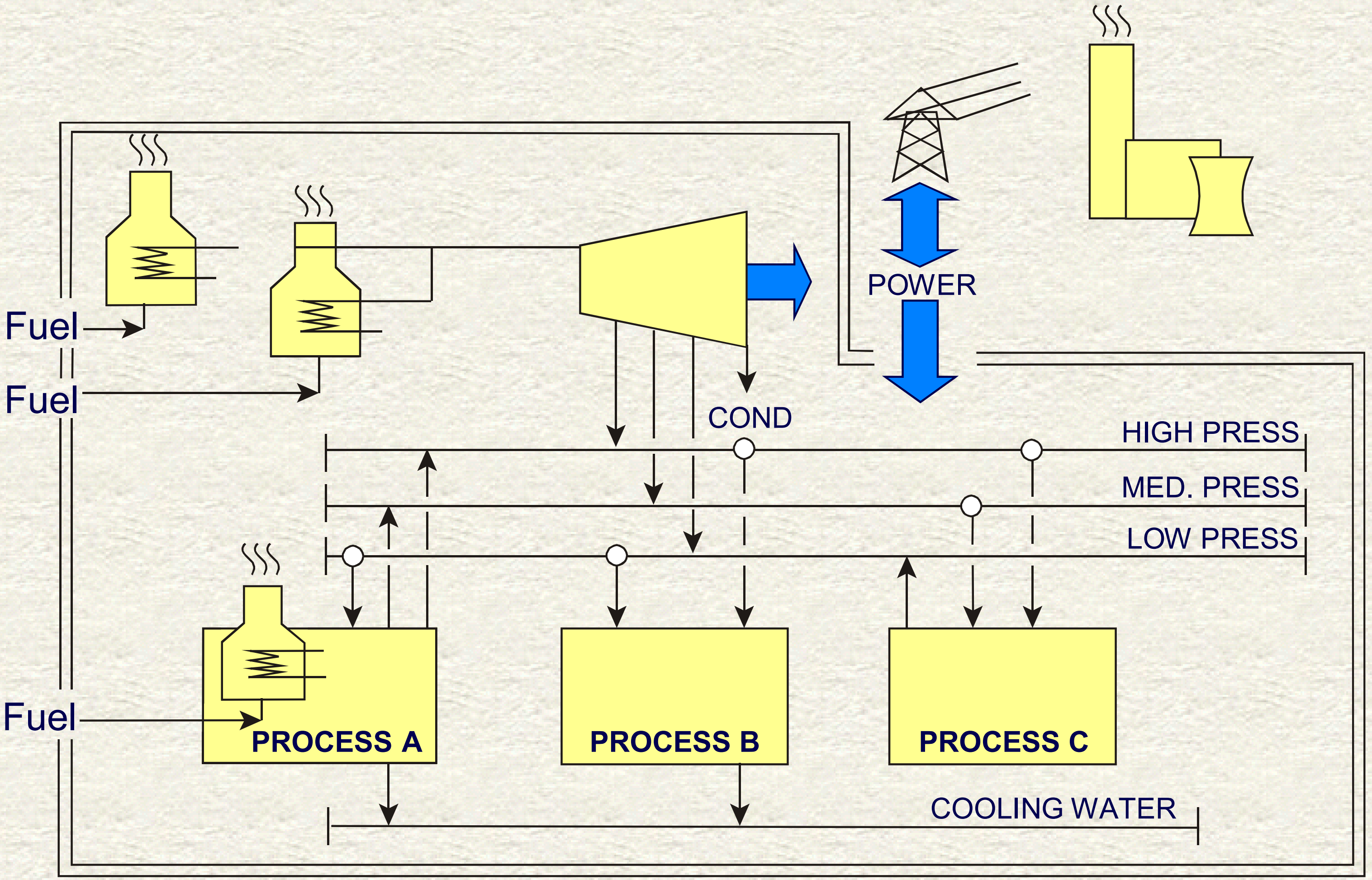


Reactor:
central to process synthesis problem

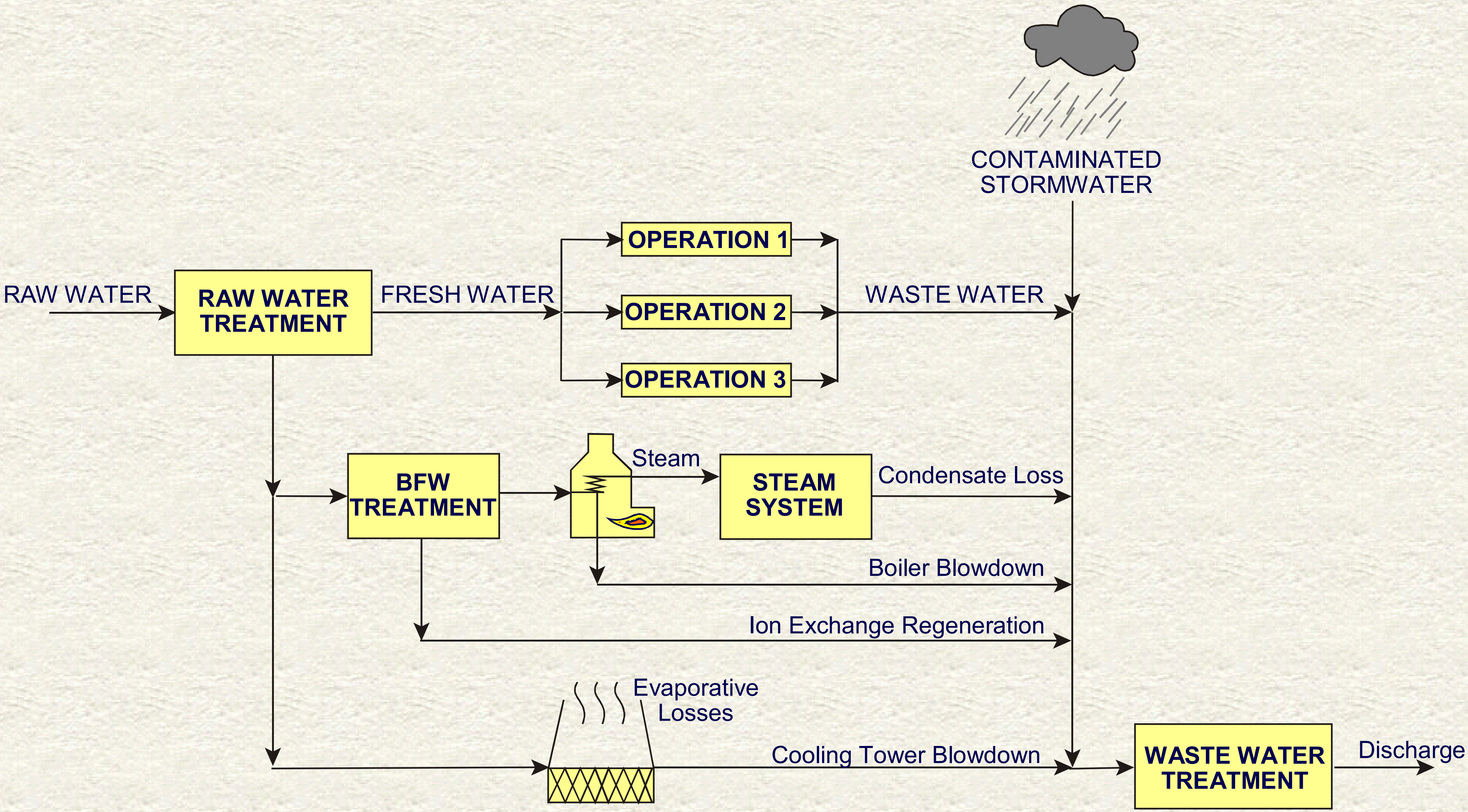
Reactor + Separation System:
together define process heating and cooling requirements

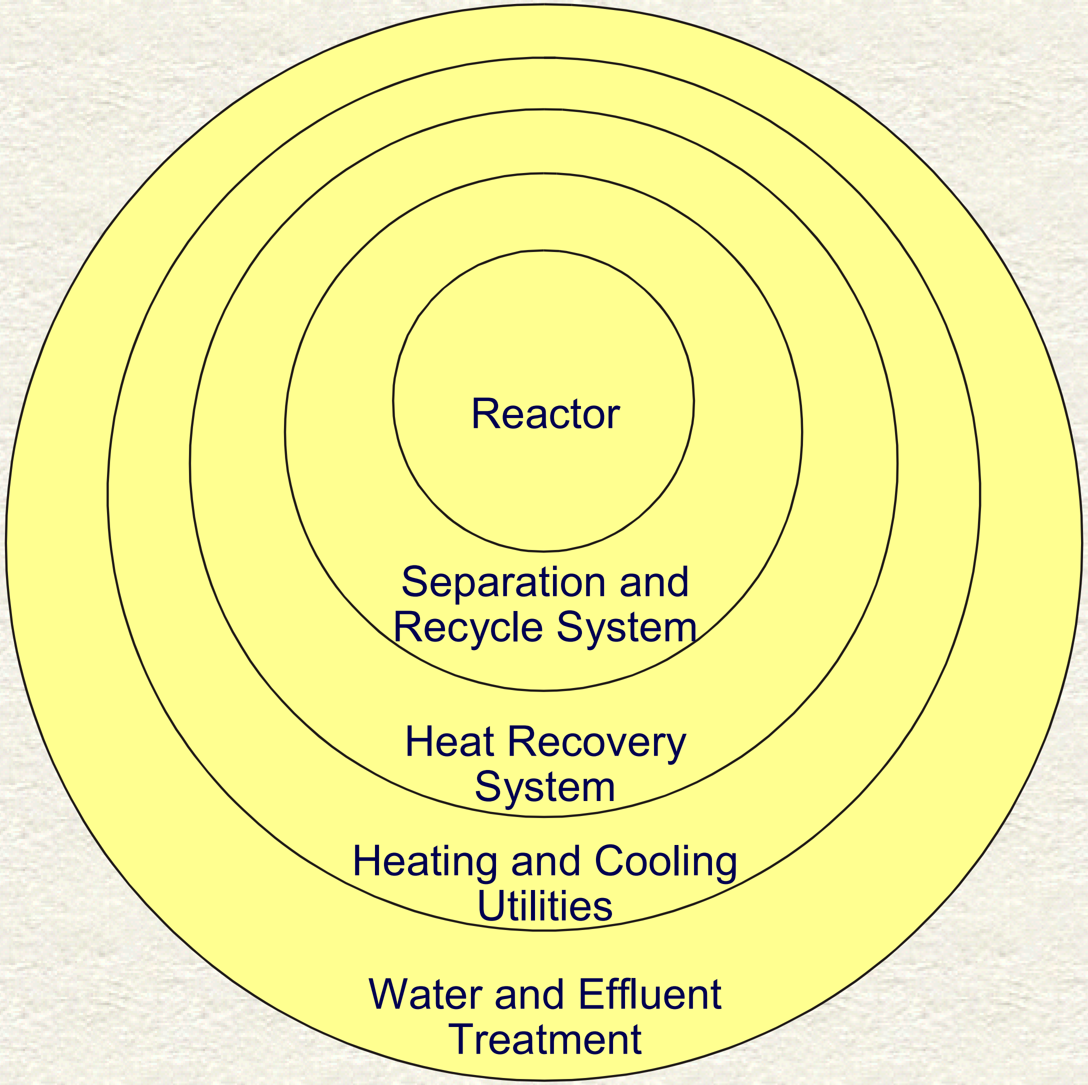
Heat Exchanger Networks
recovers heat and dictates the need for external utilities

The process requires external heating and cooling utilities

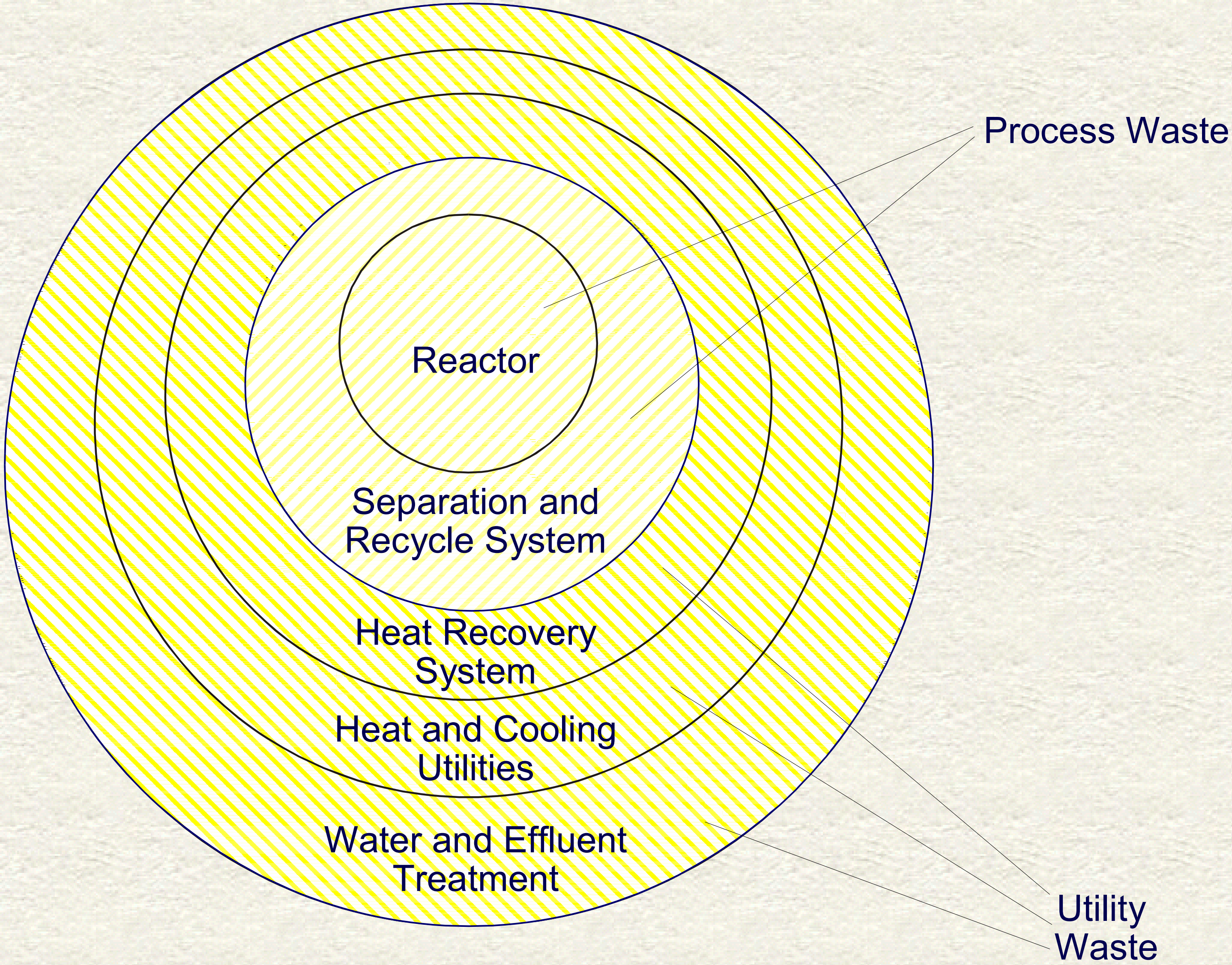


Water and effluent treatment system





The hierachy of process design



The hierachy of waste generation

Three sources of process waste:

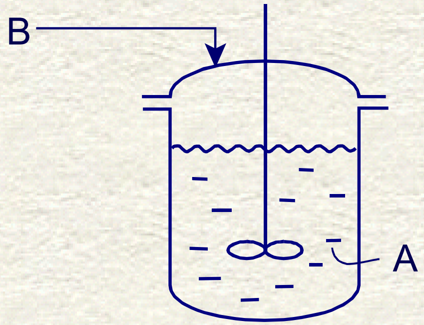
- Reactor
- Separation and recycle systems
- Process operations

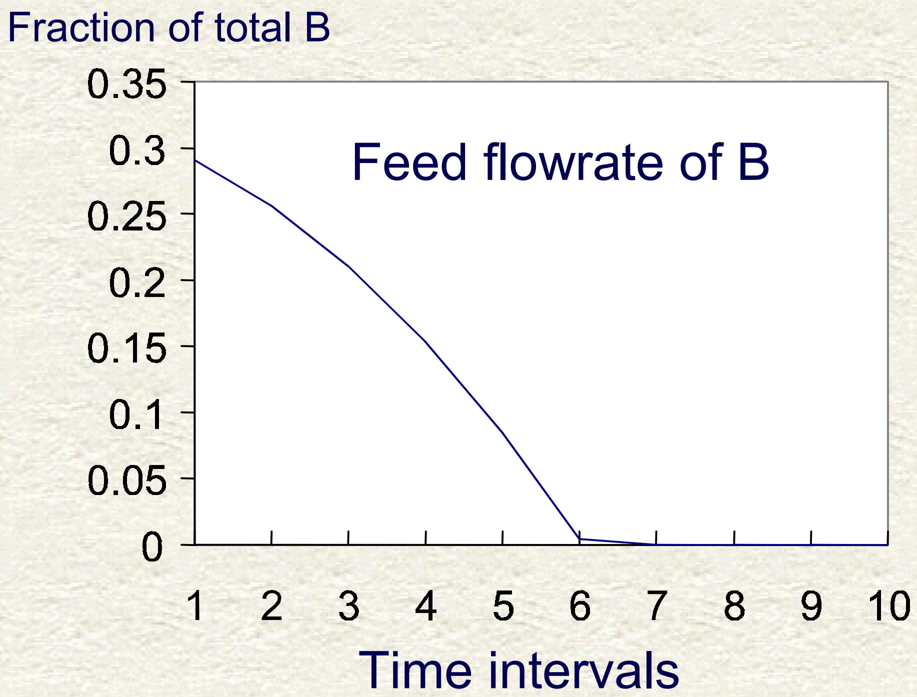
1. Waste Minimisation in Reactors

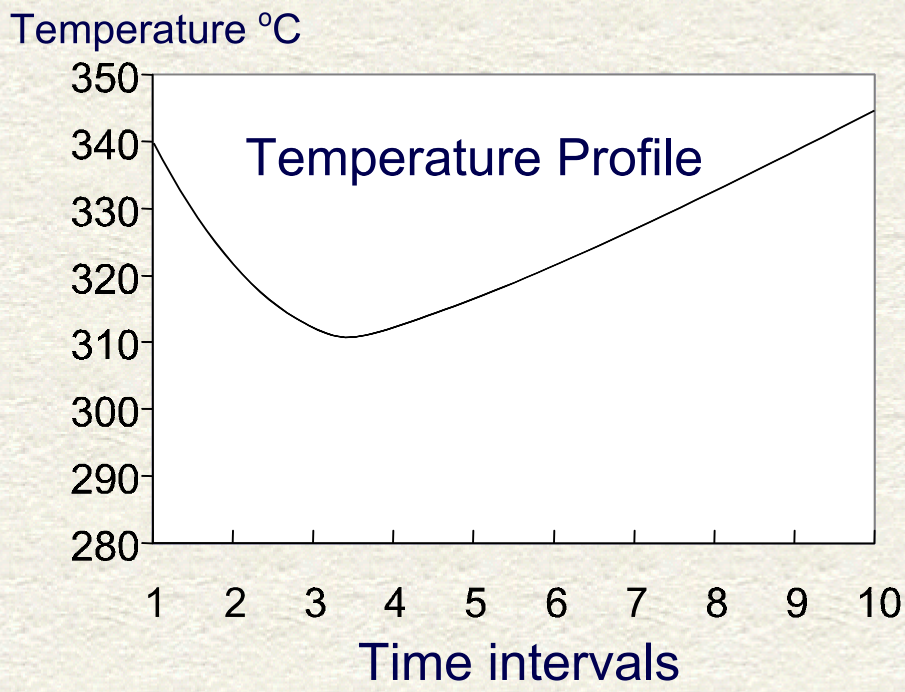
- Changing the reaction path to reduce or eliminate the formation of unwanted byproducts.
- Increasing reactor conversion when separation and recycle of unreacted feed is difficult.
- Increasing process yields of raw materials through improved selectivity in the reactor.
- Reducing catalyst waste by changing from homogeneous to heterogeneous catalysts and protecting catalysts from contaminants and extreme conditions that will shorten their life.

(Smith, “Chemical Process Design”, McGraw - Hill)

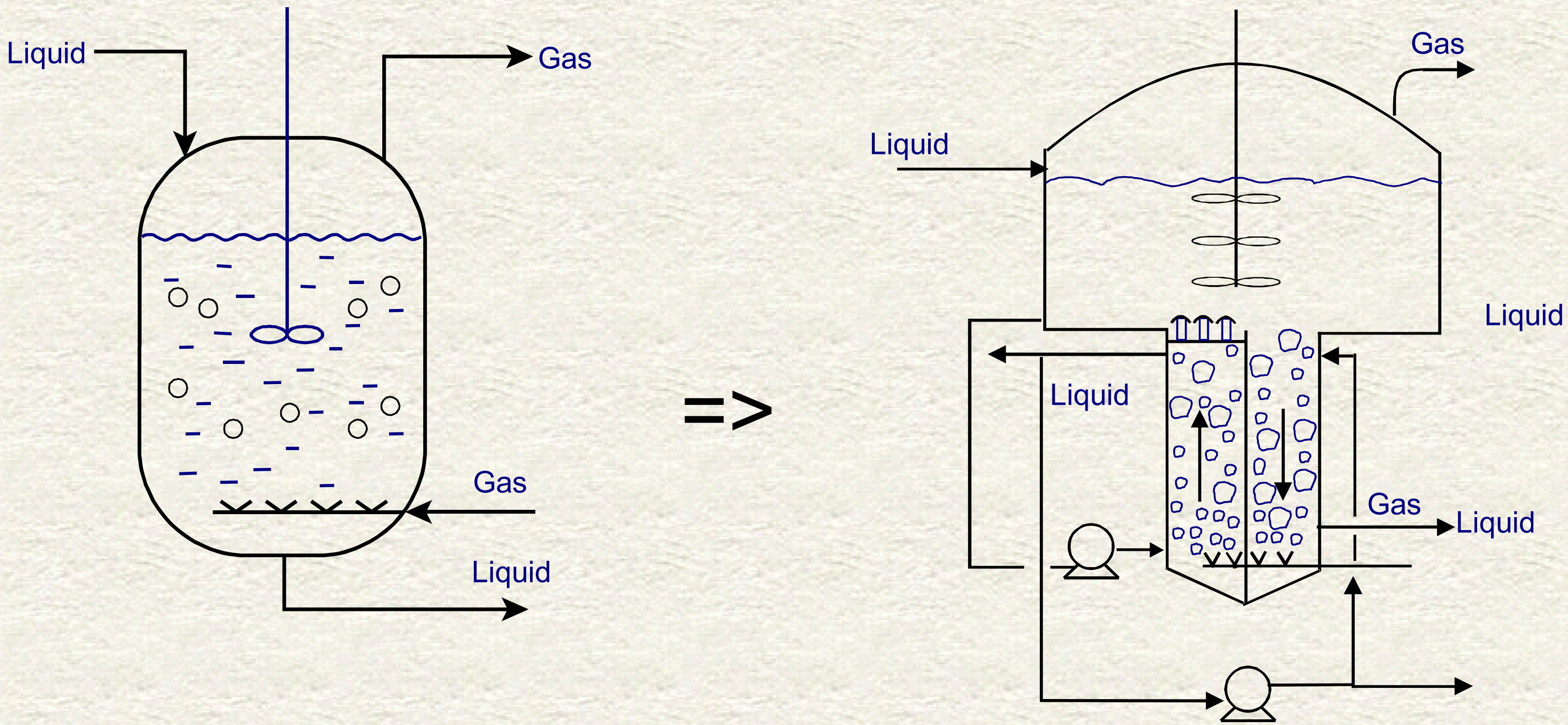
For example, advanced control of reaction conditions in batch reactors





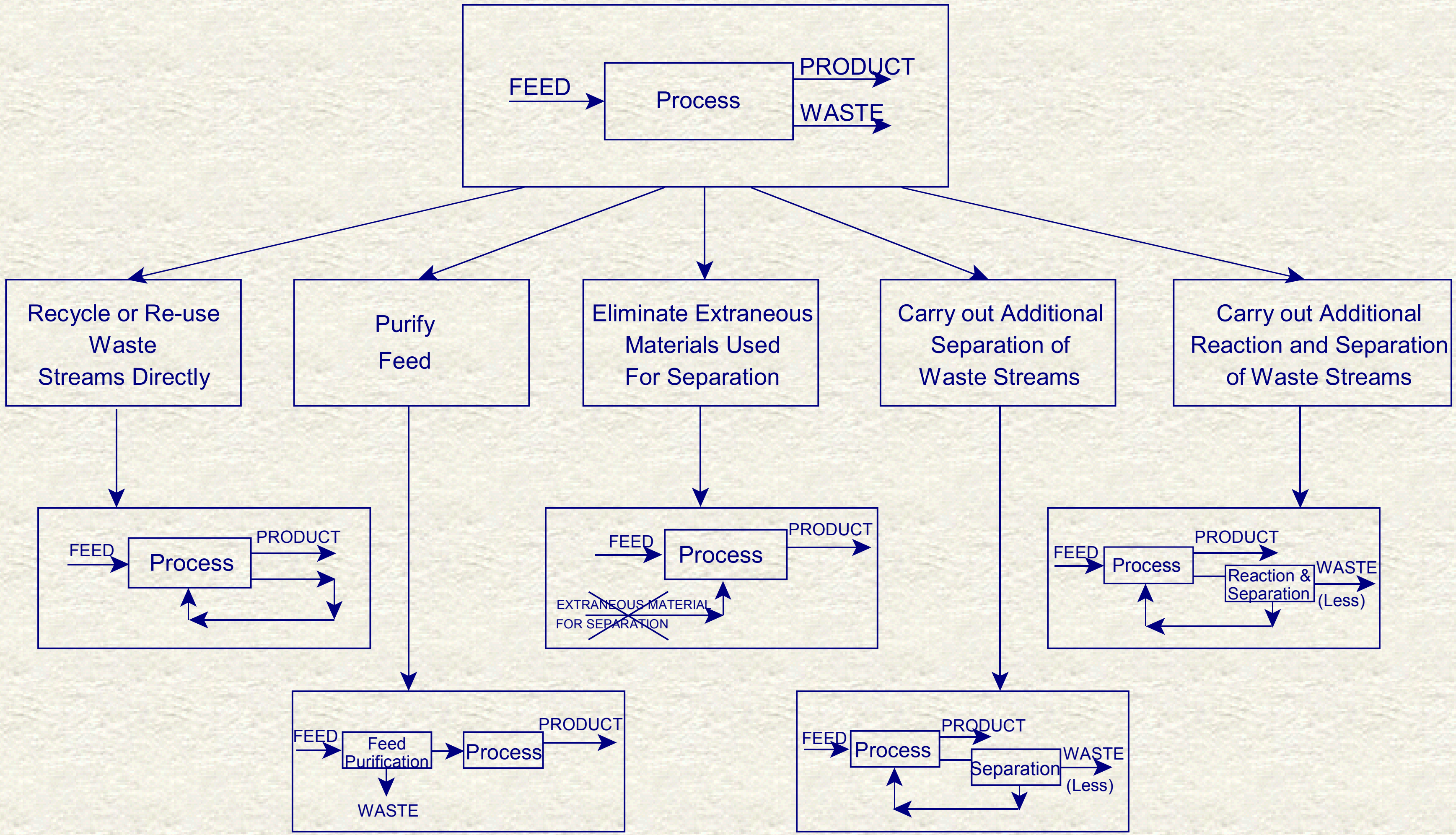


For example, changing the reactor configuration to exploit novel designs

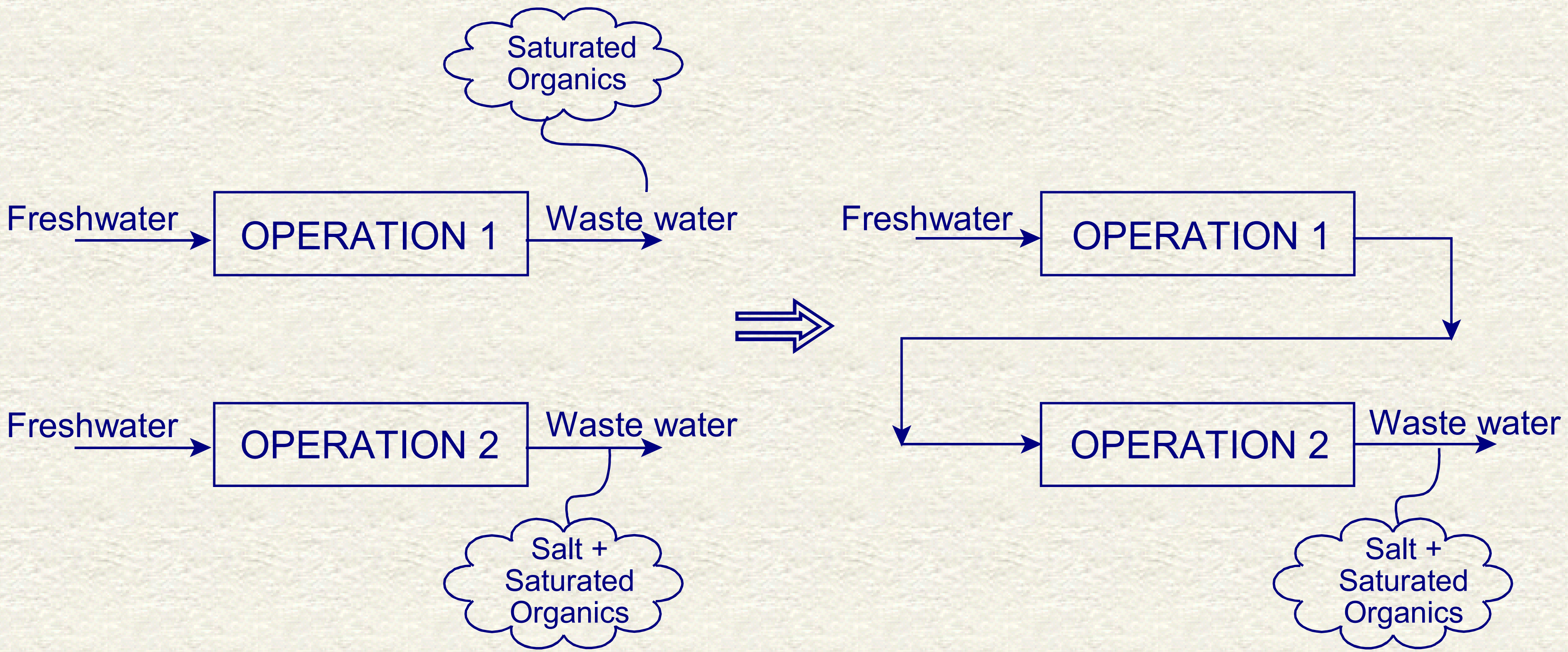


.....and so on

2. Waste Minimisation in Separation and Recycle Systems



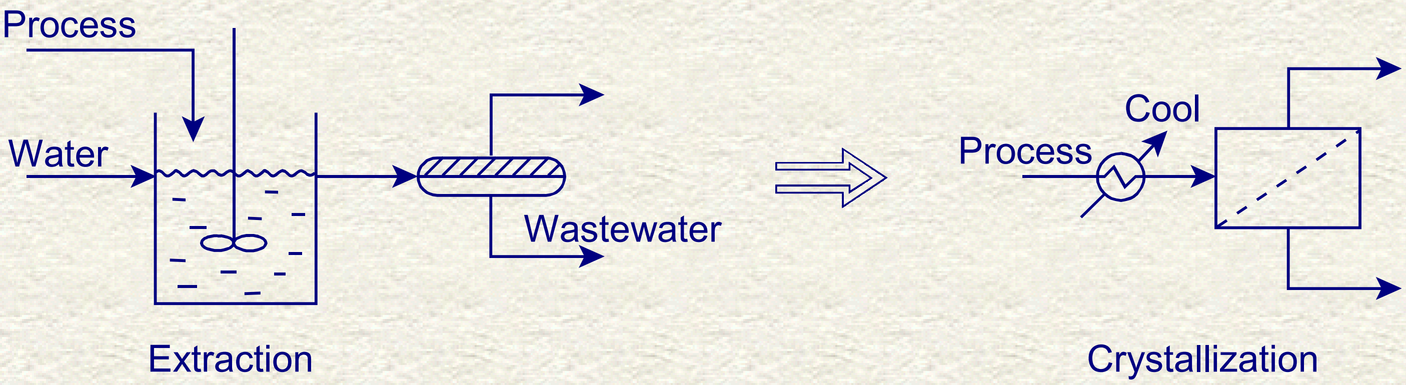
For example, recycle or re-use waste streams

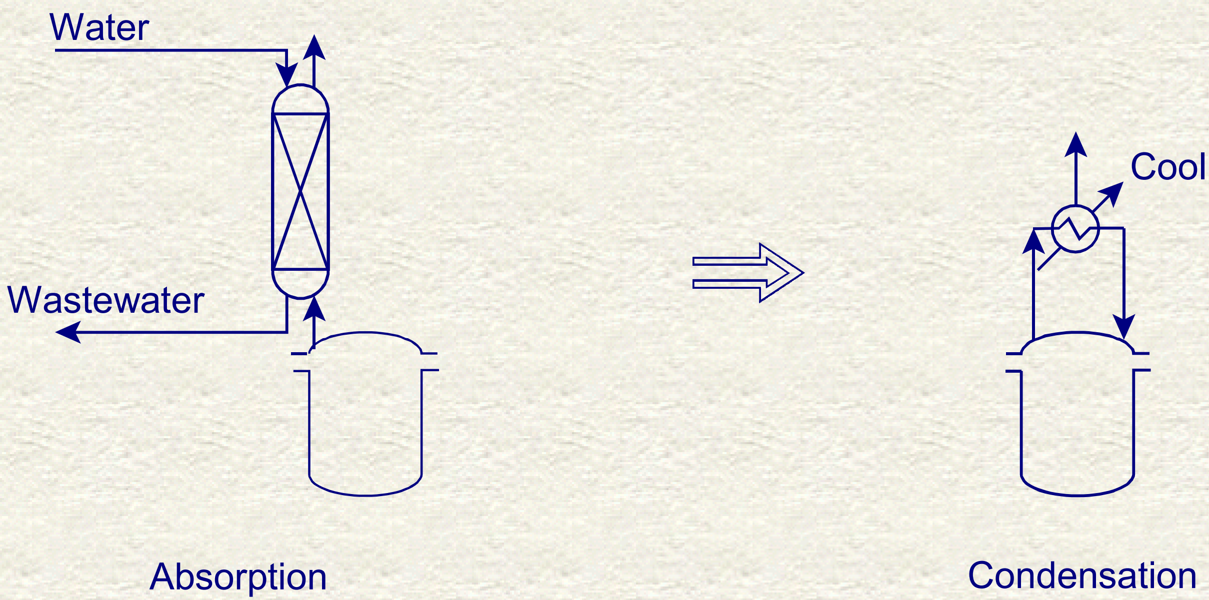


Load Before Re-use = $LOAD_1 + LOAD_2$

Load After Re-use = $LOAD_2$

For example, eliminate extraneous materials



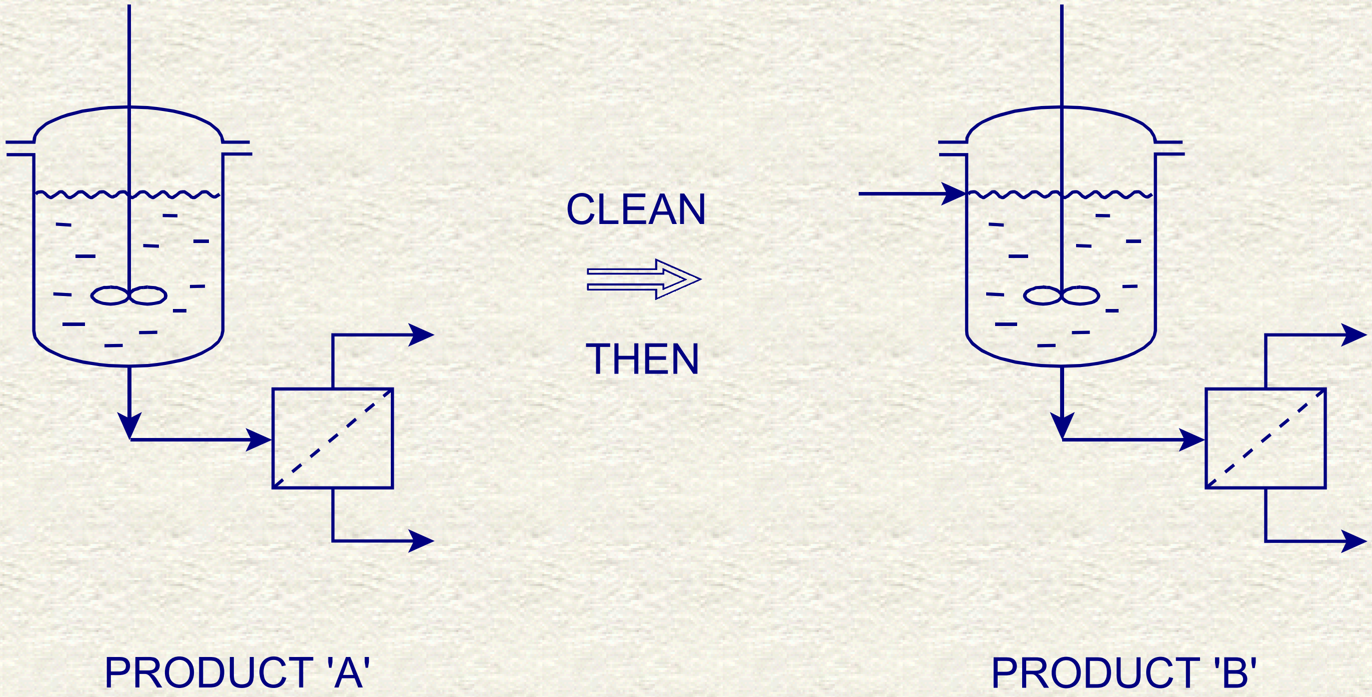


.....and so on

3. Waste Minimisation from Process Operations

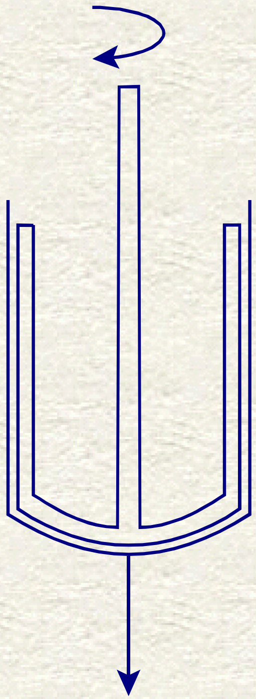
- Batch operations
- Product changeovers
- Equipment washing
- Upset conditions

For example, in multi-product plants:

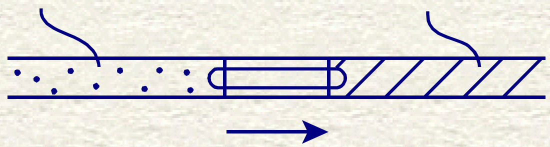


Schedule operations to minimise product changeovers

For example, equipment cleaning for viscous materials



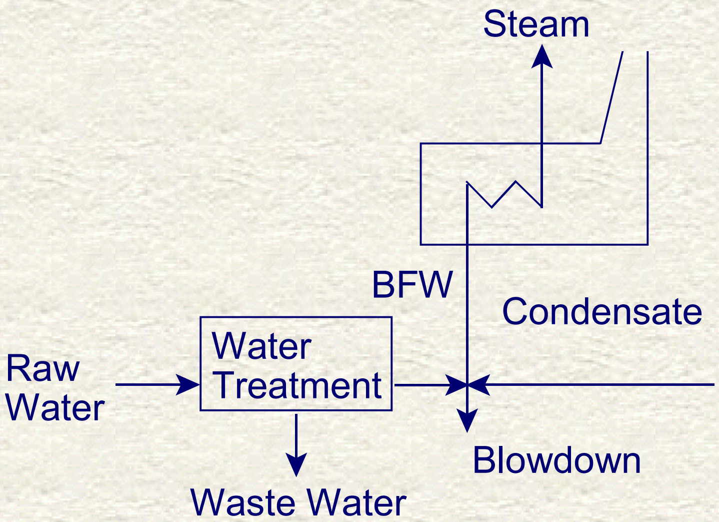
Vessel wall wipers



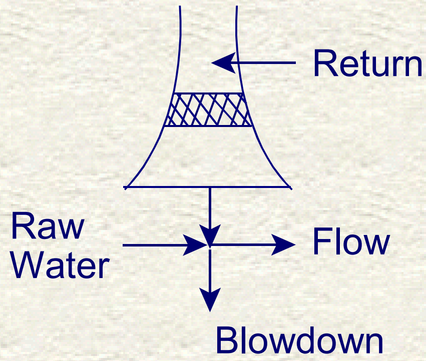
Pipeline Pigging

...and so on

Utility waste



Steam Boiler



Cooling Tower

Most utility waste from heating and cooling utilities

Combustion emissions can be reduced by :

- changing fuel
- changes to the utility system (e.g. better cogeneration)
- process changes
- improved heat recovery
- chemical treatment (for NO_x and $S0_x$)

Aqueous emissions can be reduced by :

- re-use of water (perhaps with partial treatment)
- more efficient hot and cold utility system design

But

How can process integration help in producing clean technology ?

Let's look at some examples

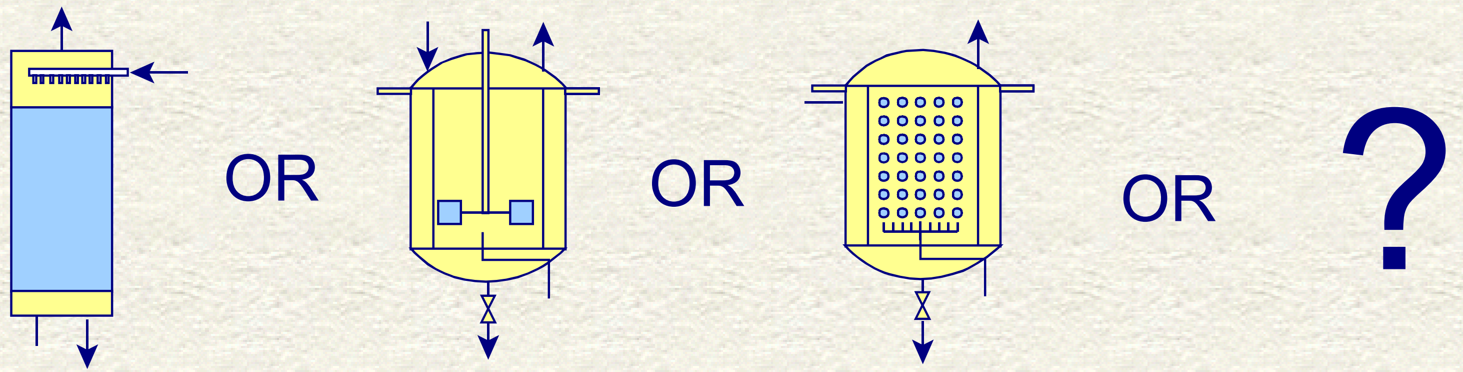
2. Reactor Design for Clean Technology

Chemical Reactor Design: The Problem

Physical properties
• Physical parameters
• Phase equilibria

Reaction kinetics
• Mechanism
• Kinetics parameters
Mass transfer models

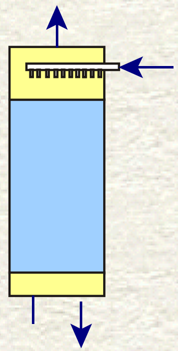
Specifications
• Operational constraints
• Product specifications
• Process requirements



• Reactor type and interconnections
• Mixing pattern, recycle/bypass structures

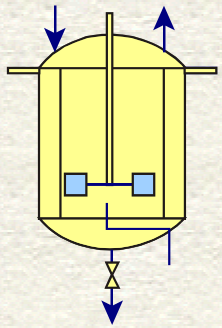
Common Industrial Practice

Choose a reactor
because...



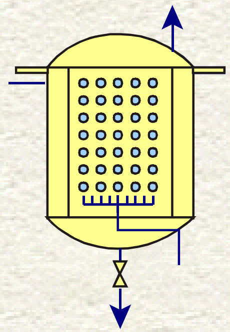
Reminds us of a
similar system

or



It has been
used before

or



There is no time to
search properly and
this works !

- Investigate various conventional or proven designs
- Scaleup by experimentation and rigorous modelling

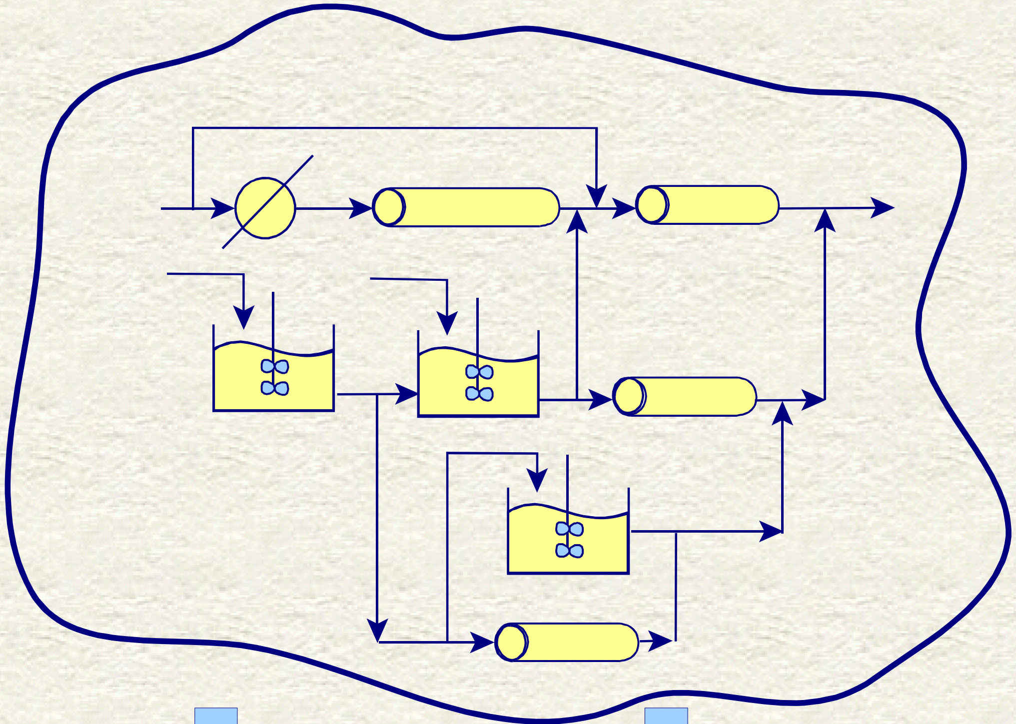
- Heuristics and expert systems can help.

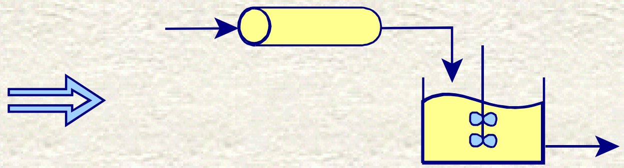
BUT

- These will direct us back to conventional designs.

INSTEAD LET US TAKE A
FUNDAMENTAL APPROACH

Reactor Network

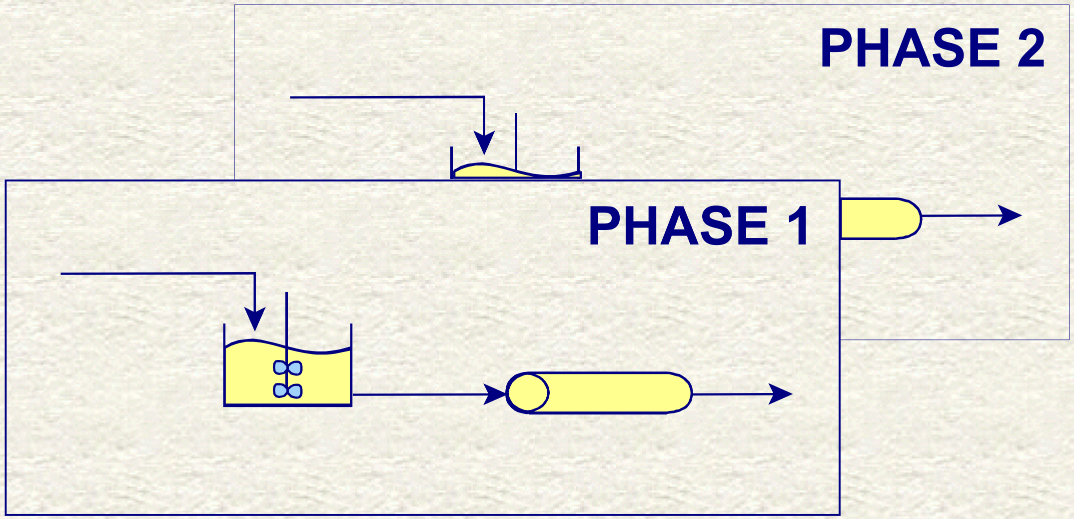




Optimal
Solution

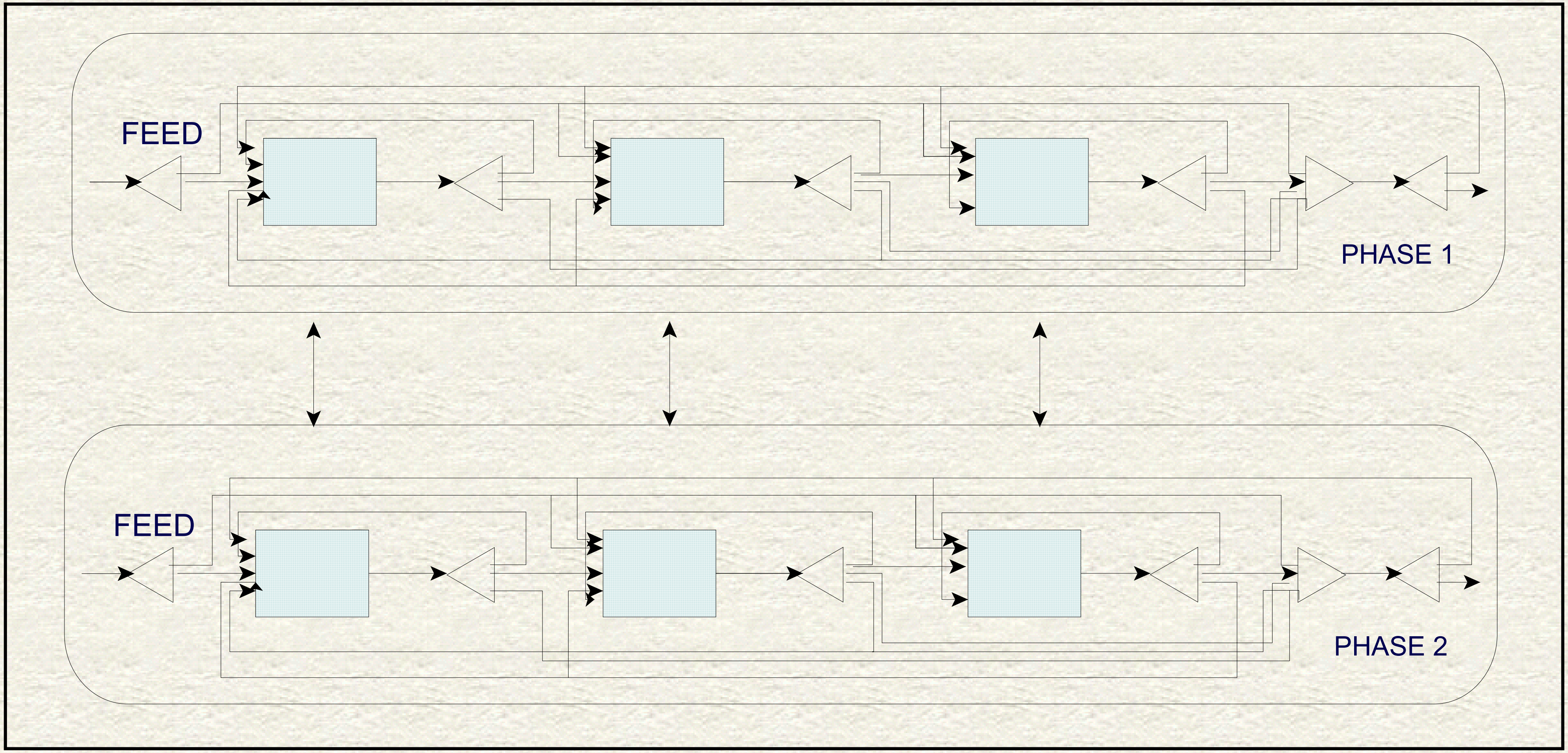
Types   Combinations   Targeting Tools

From Homogeneous to Multiphase . .



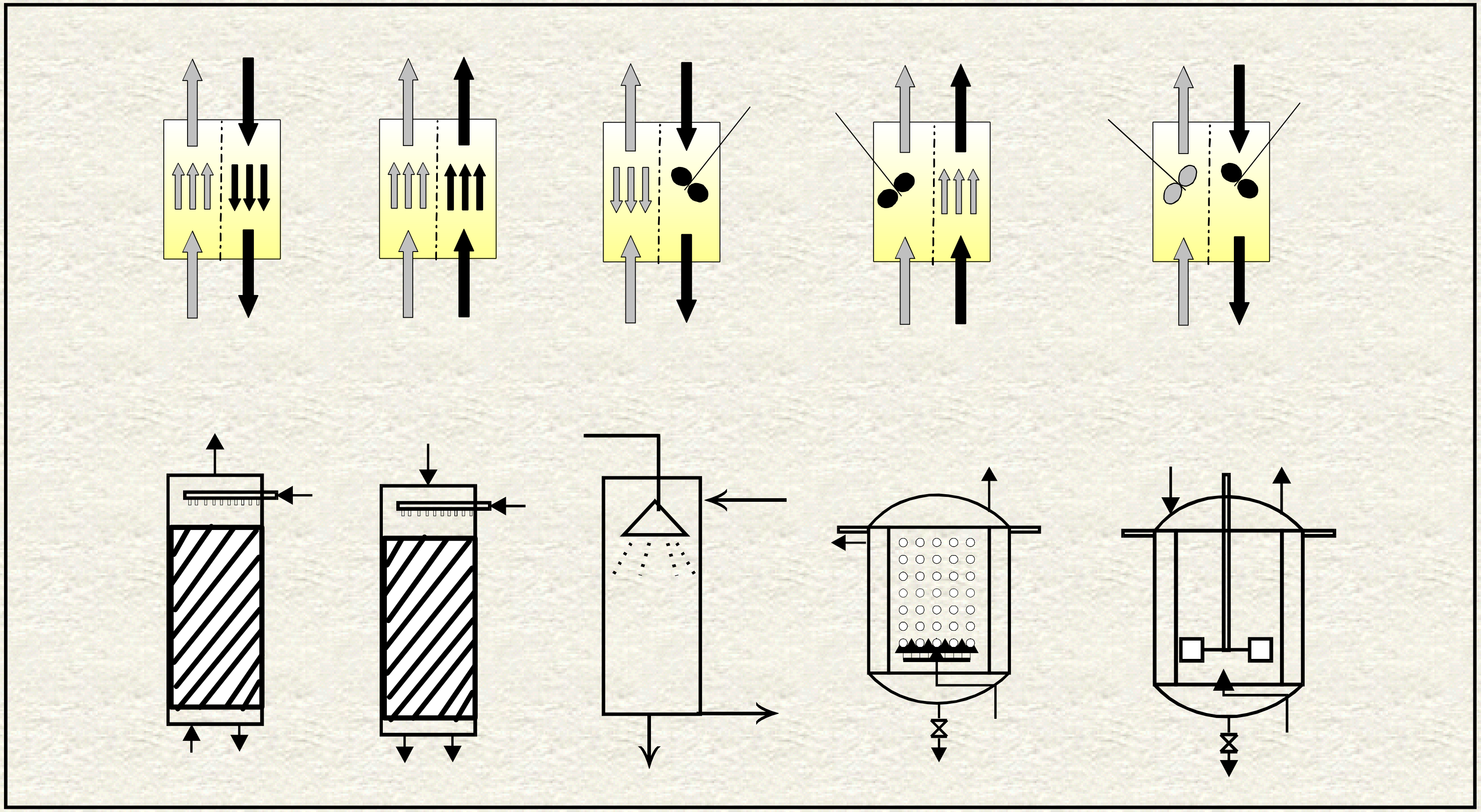
Reactor network for each phase
Phase interaction through mass transfer

Multiphase Reactor Network Superstructure using Generic Reactor Compartments



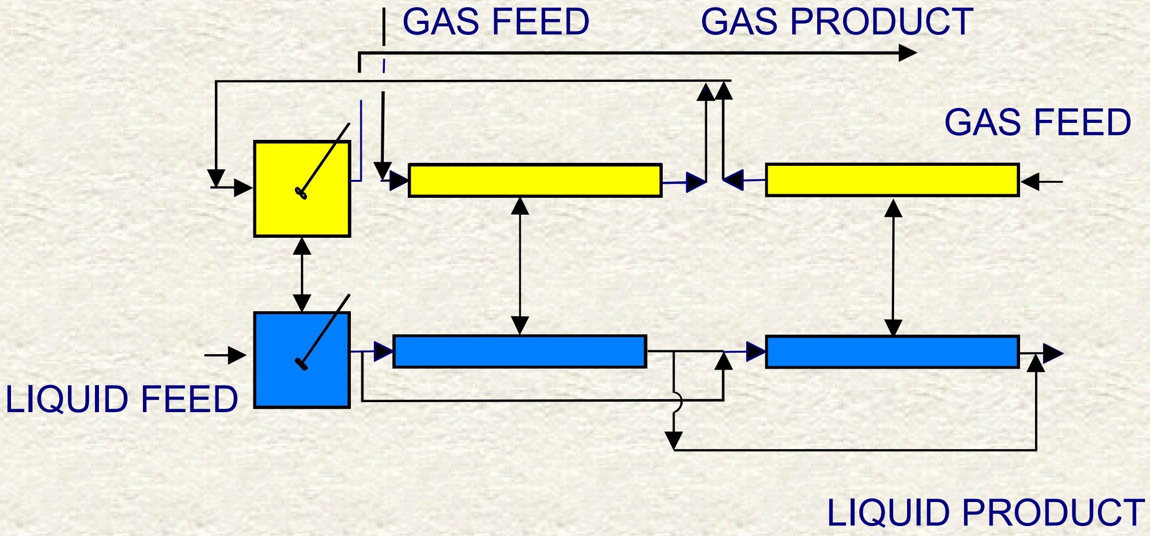
- Two phase representation using reactors in pairs
- Can be extended to any number of phases

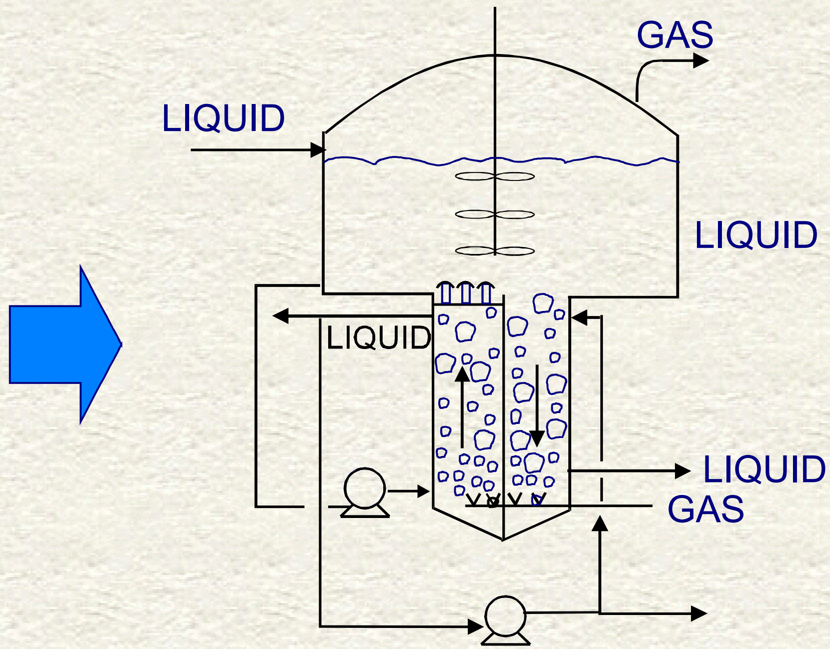
Different possible combinations of mixing patterns considered between every contacting pair of phases



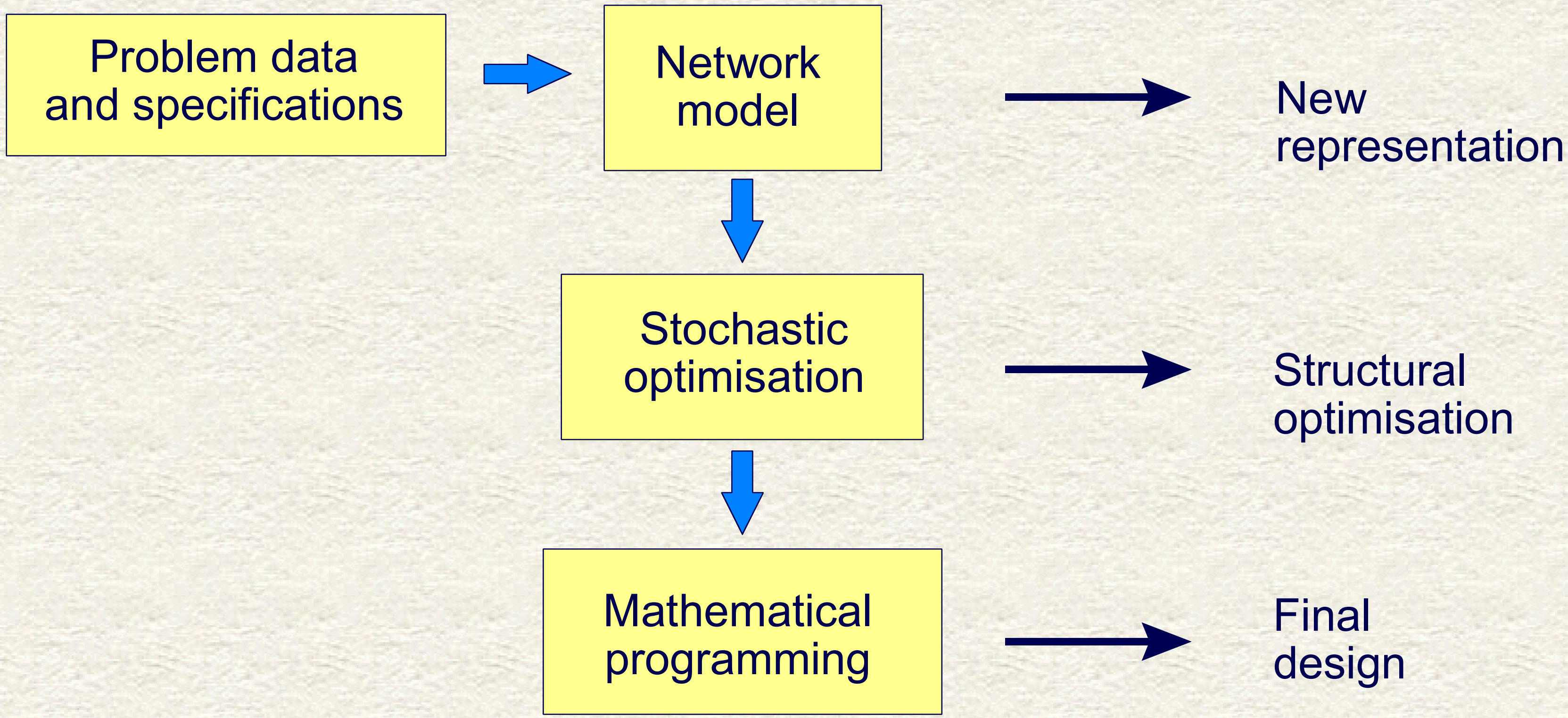
Conventional Designs

... and Novel Designs



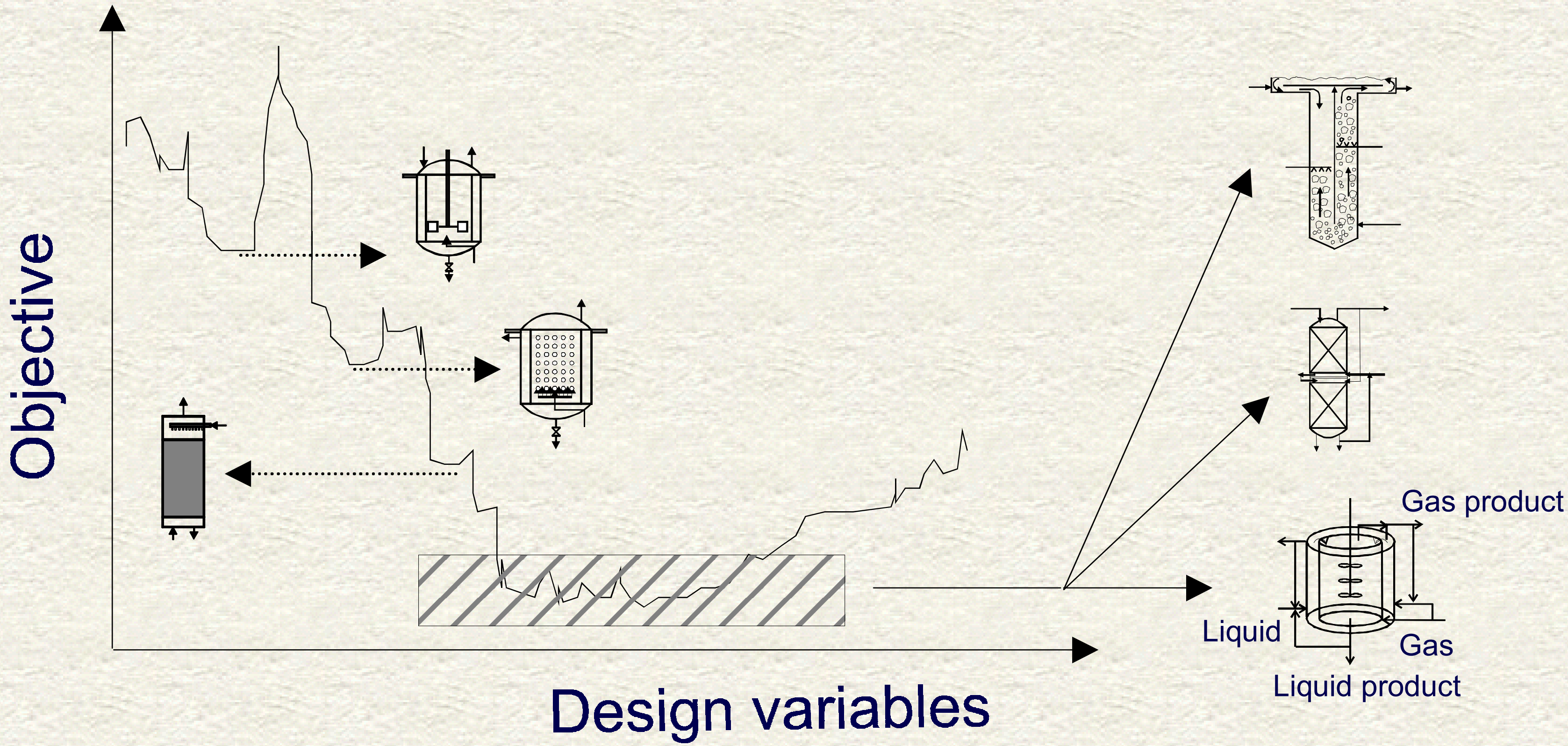


Simultaneous Optimisation Approach



Design Problem: Targeting vs Optimality

"Optimal Solution" replaced with ...



... TARGETS and DESIGN OPTIONS

Case Study: Synthesis of "-Chlorocarboxylic Acids

$Cl_2 + C_4A$ ė $MC_4A + HCl$

$2Cl_2 + C_4A$ ė $DC_4A + 2HCl$

C_4A - "-monochlorobutanoic acid, DC_4A - ","-dichlorobutanoic acid

$$r_1 = y\left[(k_1 + k_2)C_{L_{MC_4A}}^{1/2} + \sqrt{k_1 k_2}\, C_{L_{DC_4A}}^{1/2} + k_2 C_{L_{C_4A}}^{1/2}\right] \Big/ \left(1 + k_3 C_{L_{Cl_2}}\right)$$

$$r_2 = k_3 r_1 C_{L_{Cl_2}}$$

$$k_1 = e^{\left(5.22 - 3120/T\right)} \qquad k_2 = e^{\left(0.00176 - 1880/T\right)} \qquad k_3 = 0.00136$$

$y = 0.037$ Catalyst molar fraction

Salmi T, Paatero E, Fagerstolt K, Chem. Eng. Sci., 48(1993), pp.735-751.

Problem Data

Feed and Reaction Conditions

- P = 10 bar
- Liquid feed: 13.3 kmoles of C_4A
- Gas feed: 100 kmoles of Cl_2
- Temperature bounds: 100 ^{O}C # T # 500 ^{O}C

Phase equilibria and mass transfer

- $H_{Cl2} = H_{HCl}$ = 211.76 bar
- a = 254.6 m^2/m^3 , g_g = 0.5, $*_L = 10^{-4}$ m
- $D_{Cl2} = 6.66*10^{-9}$ m^2/sec, $D_{Cl2} = 8.45*10^{-9}$ m^2/sec

Film model for mass transfer

Salmi T, Paatero E, and Fagerstolt K, Chem. Eng. Sci., 48(1993), pp.735-751

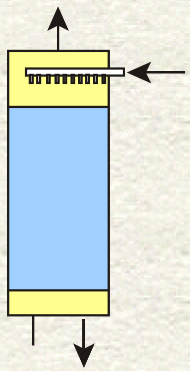
Romanainen and Salmi T, Chem. Eng. Sci., 47(1992), pp.2493-2498

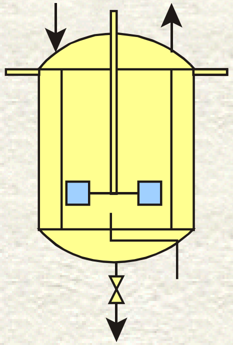
Conventional Designs

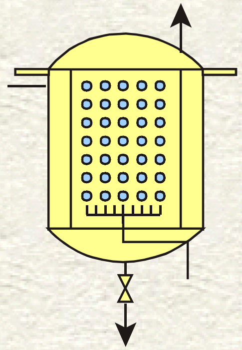
Counter current packed bed

Mechanically agitated vessel

Bubble column







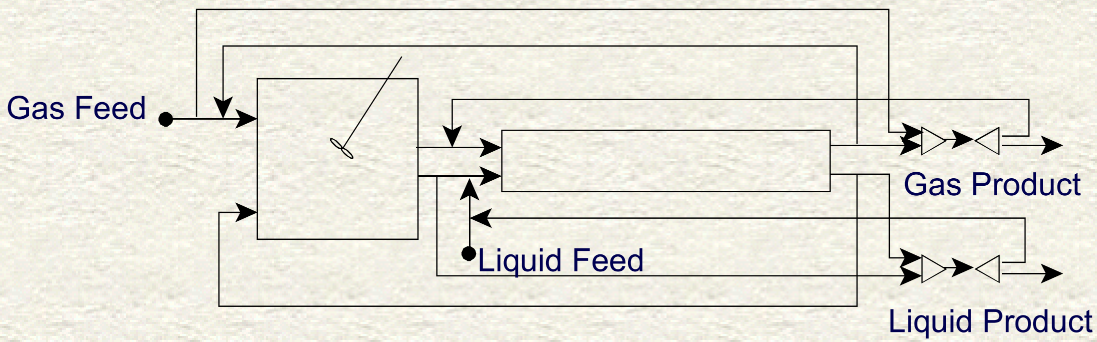
Yield = 69.5%

Yield = 74.4%

Yield = 72.8%

Results

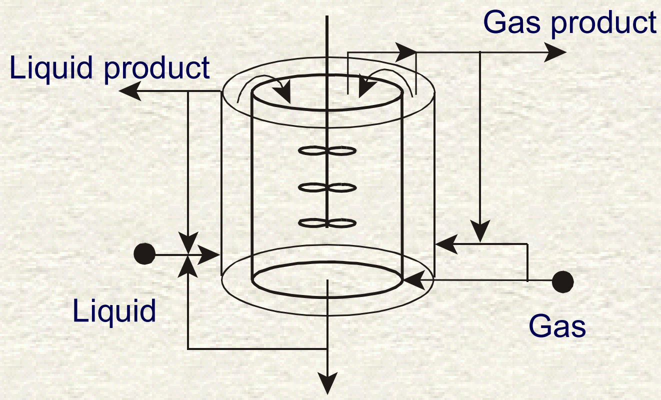
Network model

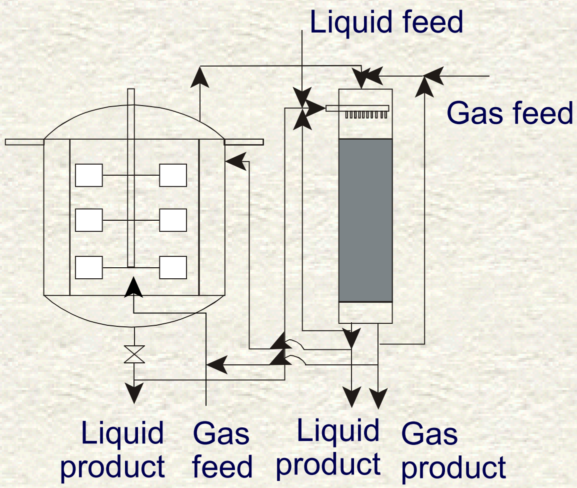


Yield = 96.9%

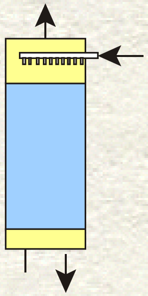
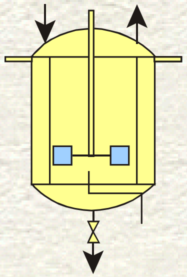
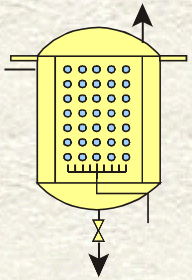
Vol = 9.93m^3

Reactor designs





Results and Comparison

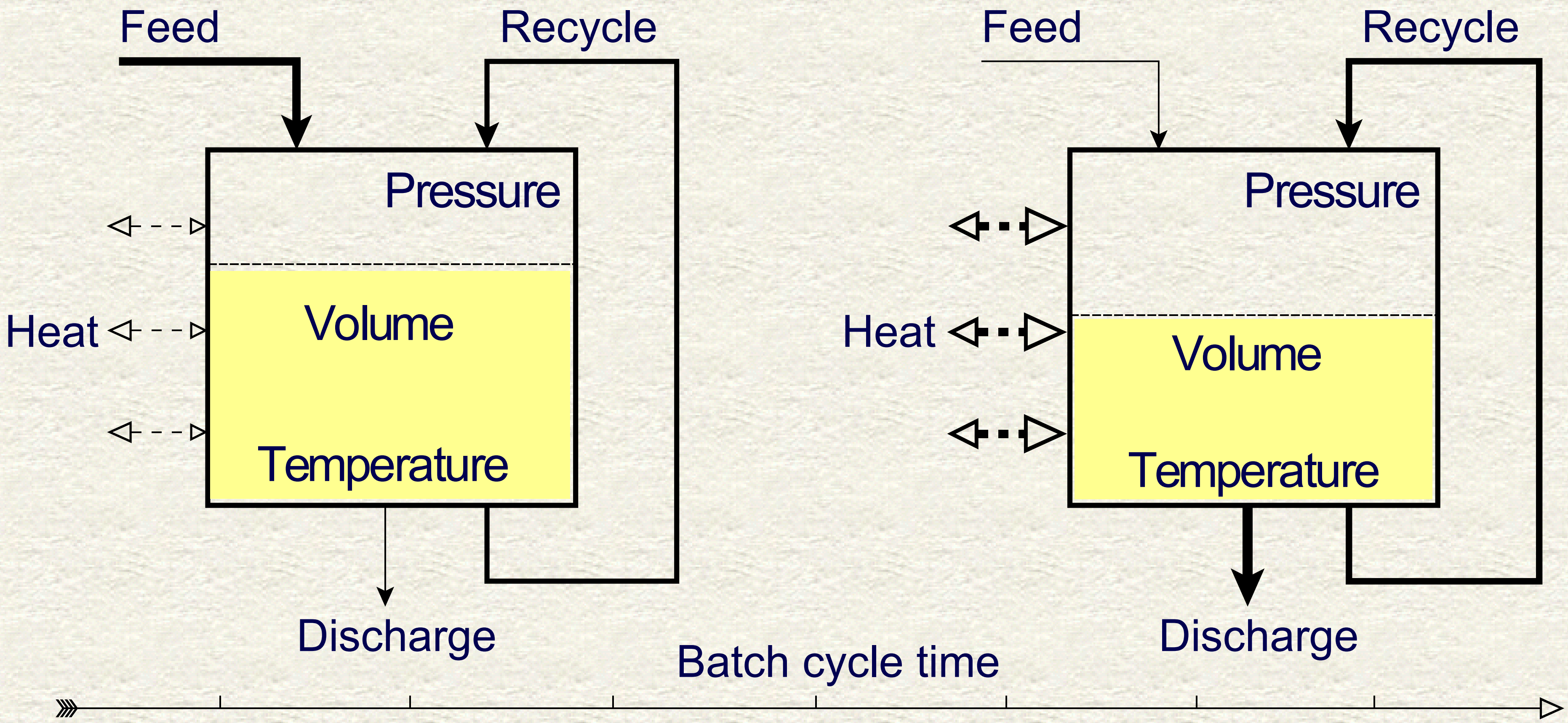
	Yield	Volume (m^3)
	69.5 %	16.1
	74.4 %	12.0
	72.8 %	12.2
New design	96.9 %	9.9

But

This used continuous reactor technology.

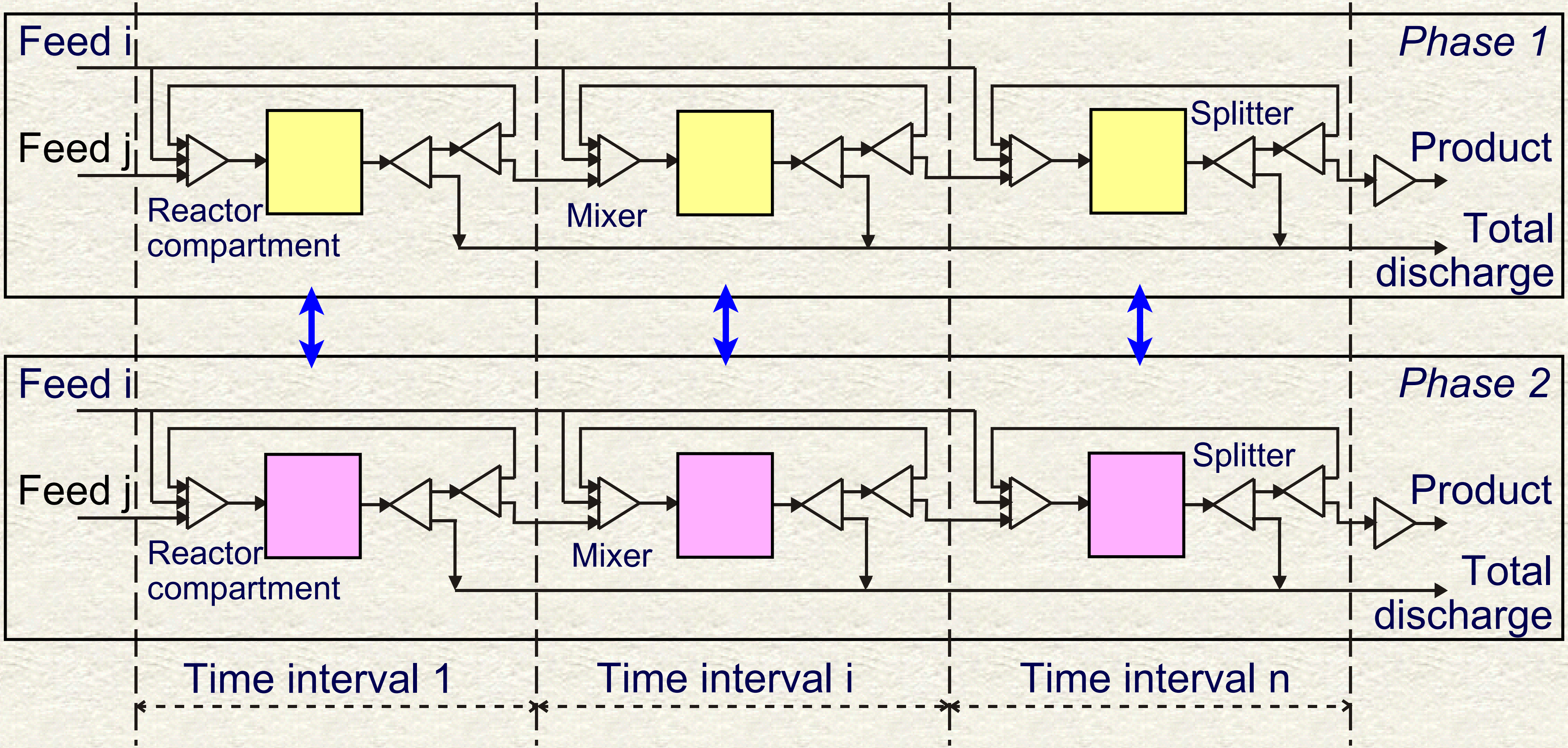
Can we adapt the approach to batch processes ?

Schematic Diagram of Batch Reactor



All the variables shown vary with reaction time

Virtual Superstructure of Mutiphase Batch Reactor



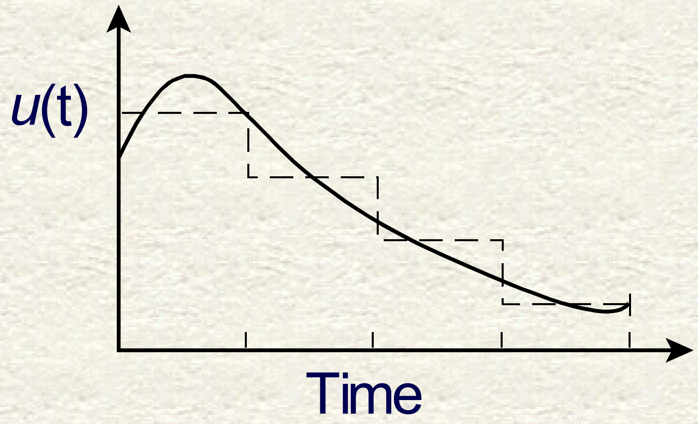
This superstructure model of batch reactors converts the dynamic optimisation problem into structural optimisation problem which decides

- The existence of streams and units
- The parameter values corresponding to each stream or unit

The task now becomes how to optimise them SIMULTANEOUSLY

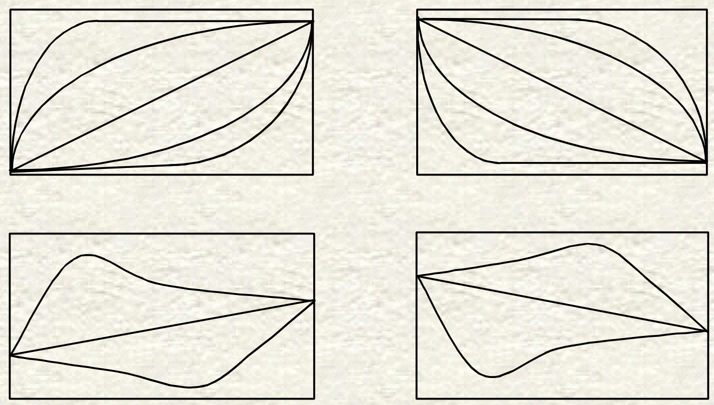
Profile Implementation

Rather than generate profiles by integrating differential equations



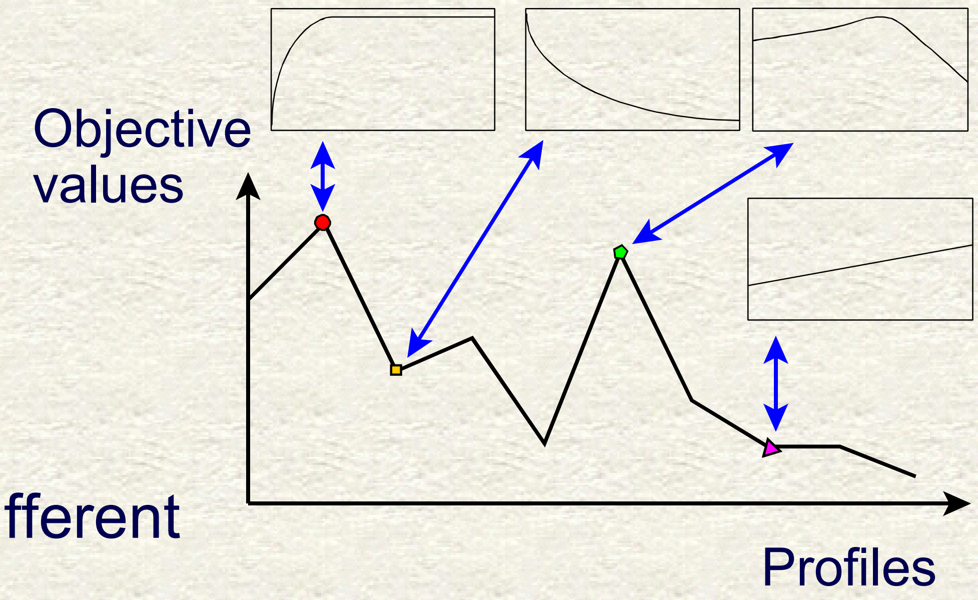
We propose

Impose a shape of profile directly for each variable



Profile Search for Optimisation

Then, evaluate the objective values for each set of imposed profiles



Search profiles with different

- Shapes
- Start and end conditions

The optimal profiles can then be found

Objective:

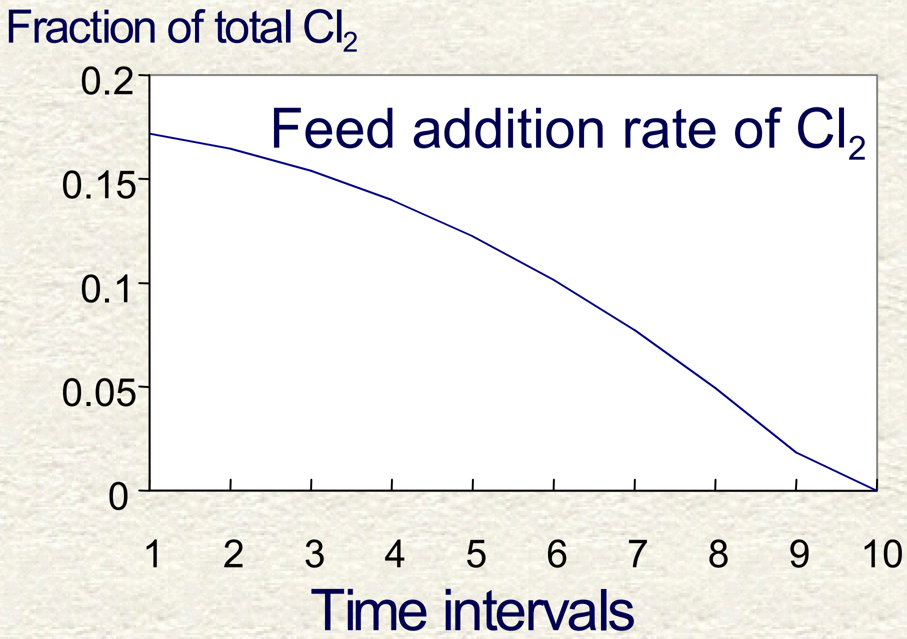
Fractional yield of MC_4A to C_4A

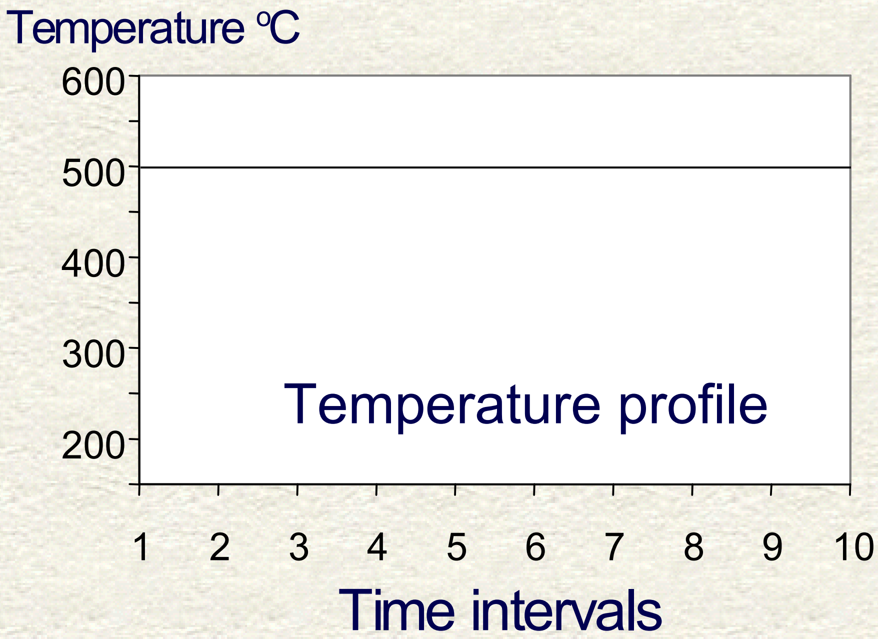
Optimise

- Batch cycle time
- Feed addition rate (semi-batch)
- Temperature

simultaneously

Results Illustration





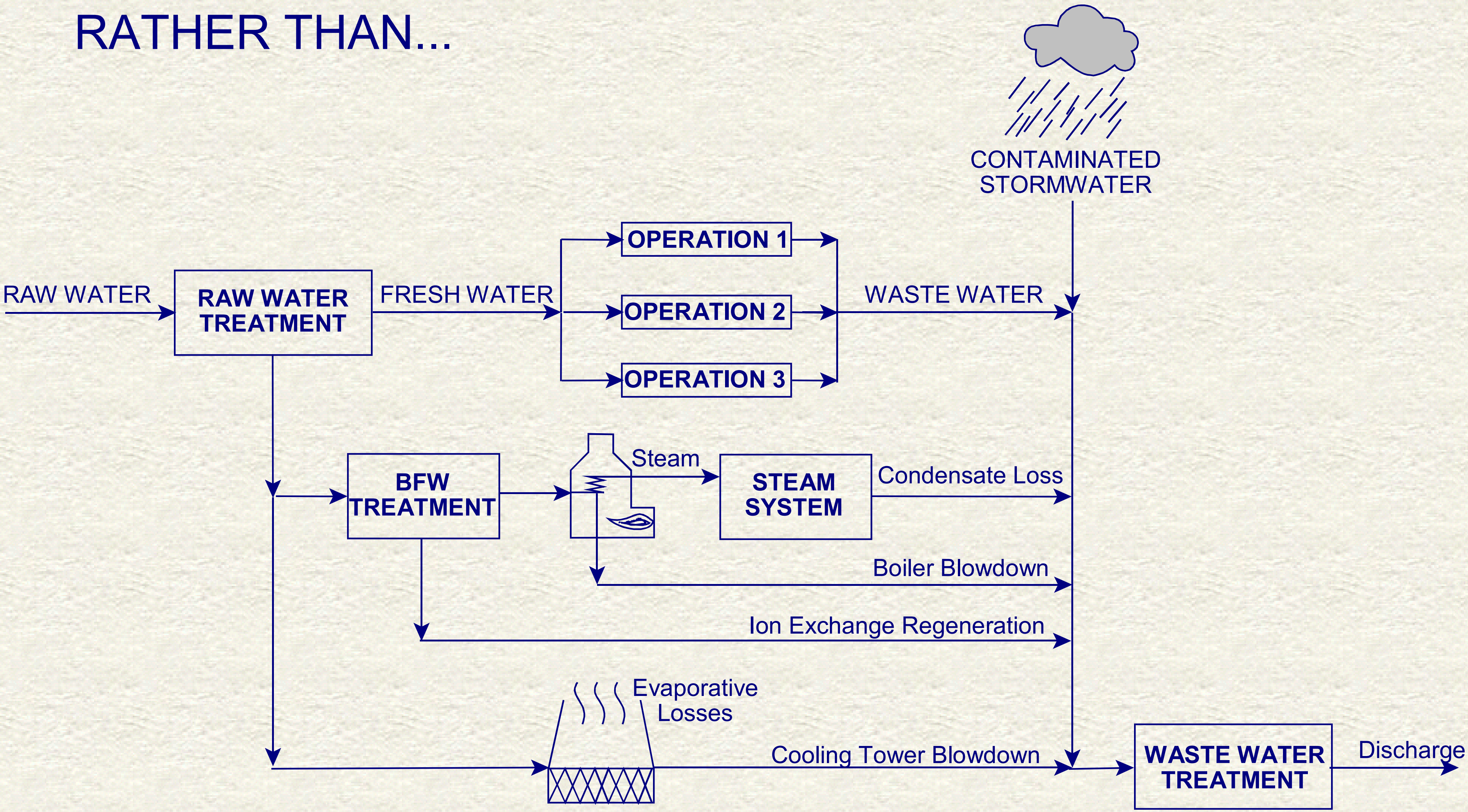
- No recycle, all unreacted and produced gas is discharged, final batch time at 1.03hr
- Following the above operating conditions, the fractional yield of MC_4A to C_4A can reach 99.7%

Results and Improvements

Reactor & operating mode	Fractional yield of MC_4A to C_4A
Counter current packed bed (continuous)	66.7%
Mechanically agitated vessel (continuous)	71.7%
Bubble column (continuous)	69.9%
Semi-batch with constant addition rate of Cl_2 (optimised) and constant temperature (optimised)	72.3%
Semi-batch with constant addition rate of Cl_2 (optimised) under optimised temperature profile	72.3%
Semi-batch with optimal addition rate of Cl_2 under optimised temperature profile	99.7%

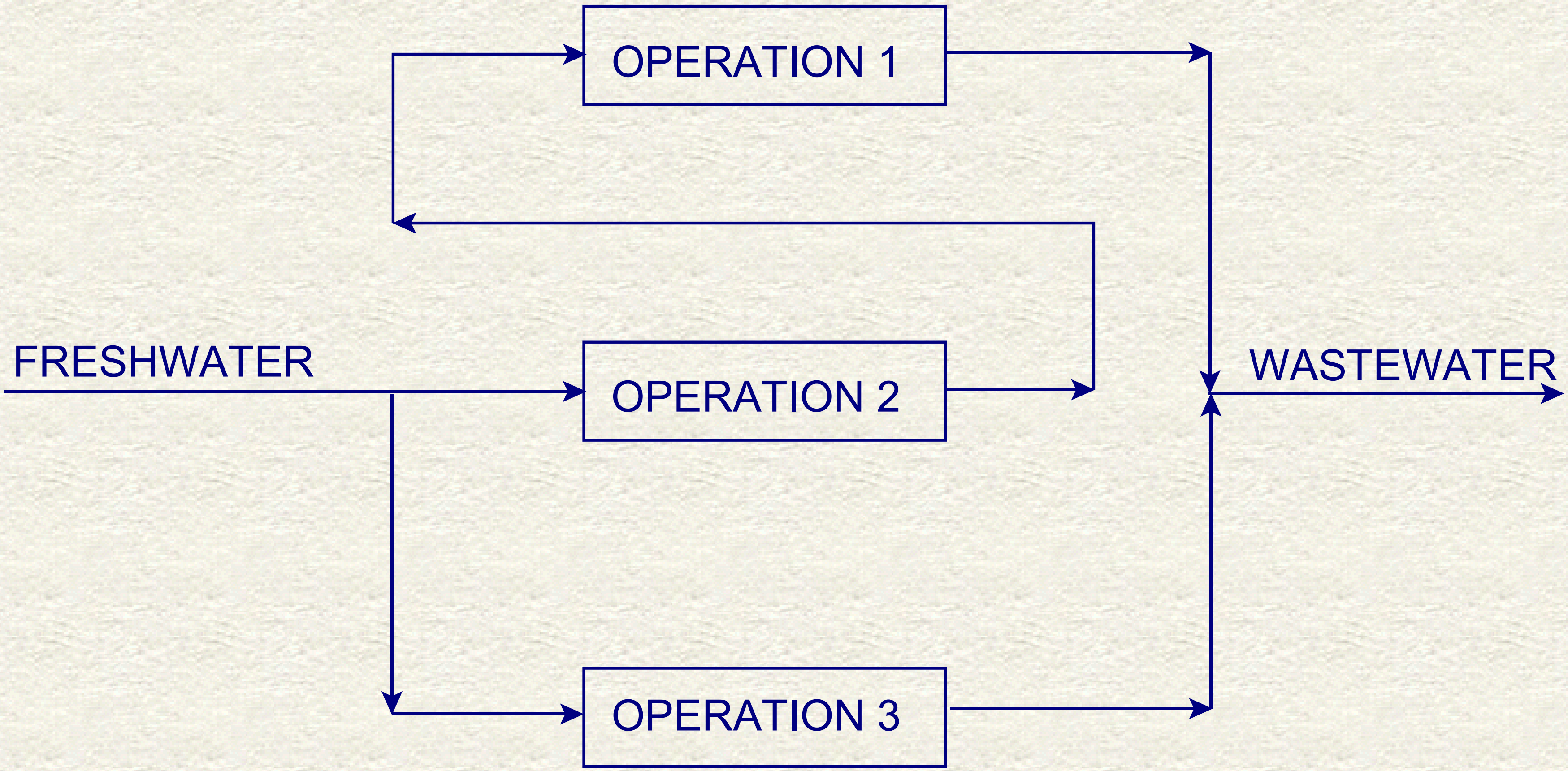
3. Water System Design to Minimise Aqueous Effluents

RATHER THAN...



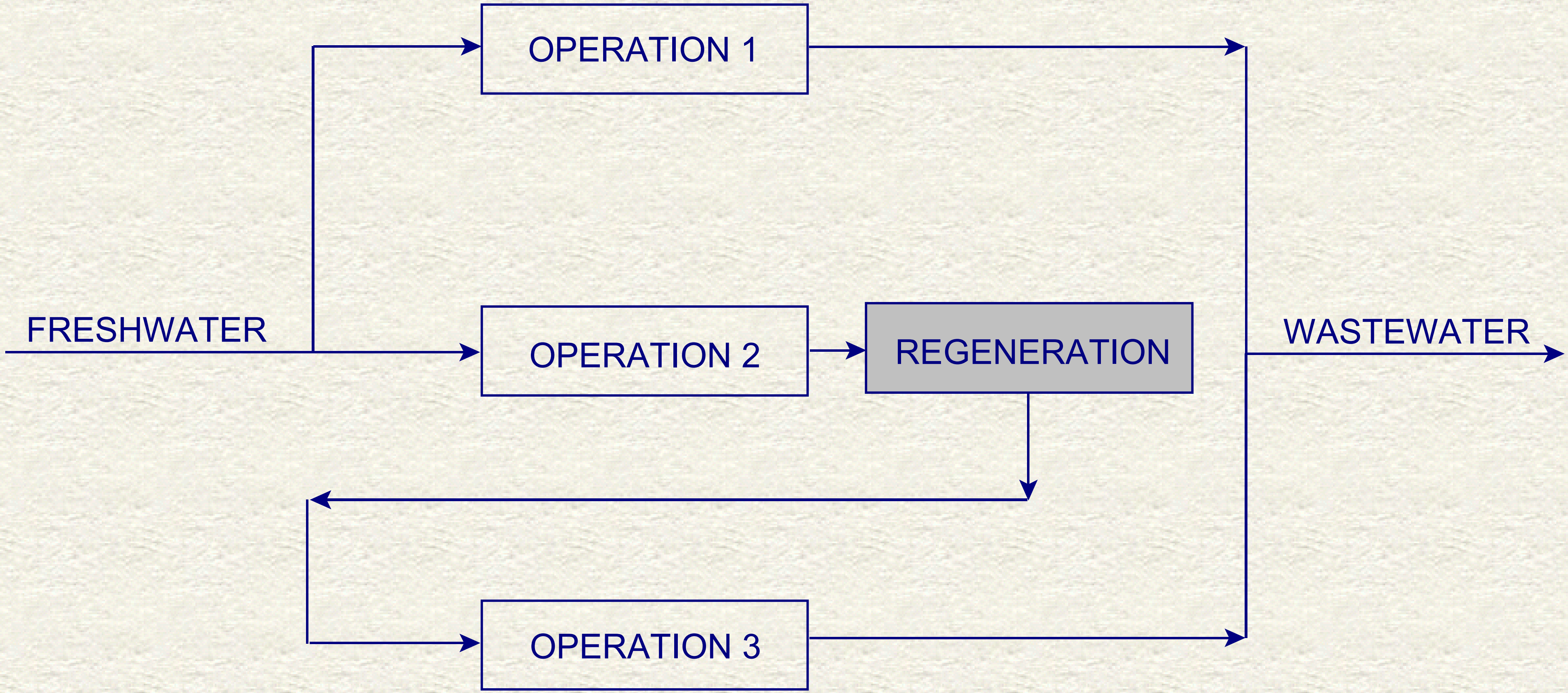
CONTAMINATED STORMWATER
RAW WATER
RAW WATER TREATMENT
FRESH WATER
OPERATION 1
OPERATION 2
OPERATION 3
WASTE WATER
BFW TREATMENT
Steam
STEAM SYSTEM
Condensate Loss
Boiler Blowdown
Ion Exchange Regeneration
Evaporative Losses
Cooling Tower Blowdown
WASTE WATER TREATMENT
Discharge

1. RE-USE



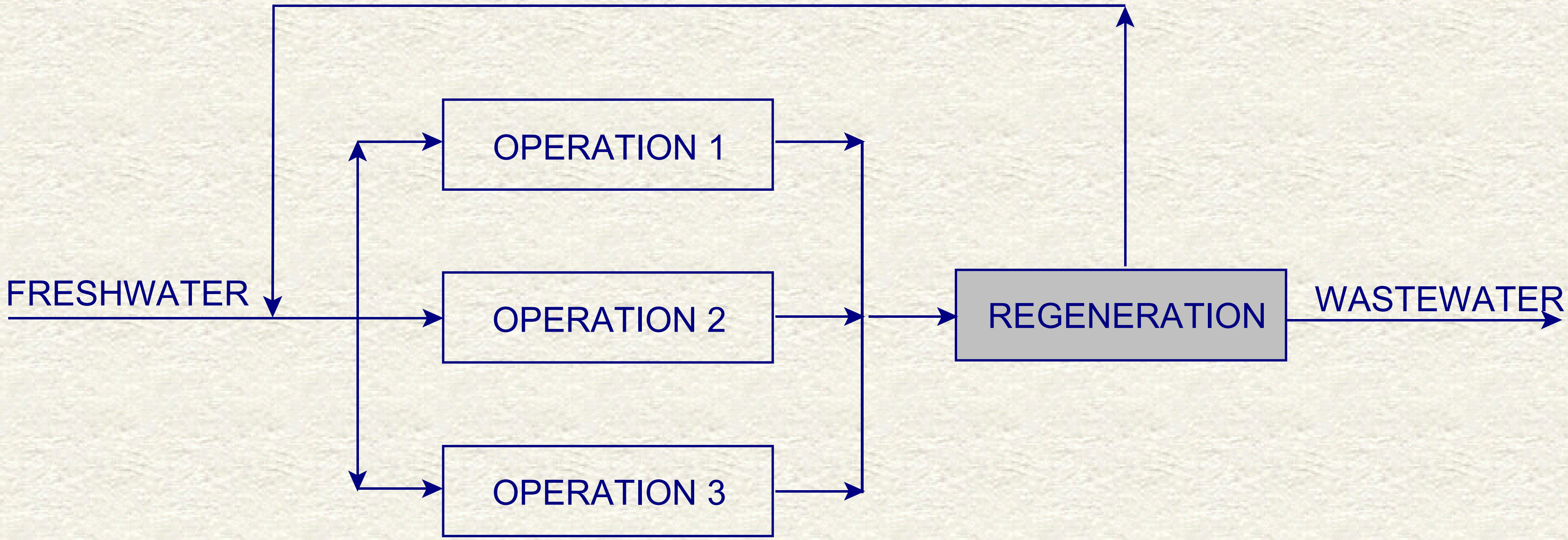
Water re-used in different operations

2. REGENERATION RE-USE



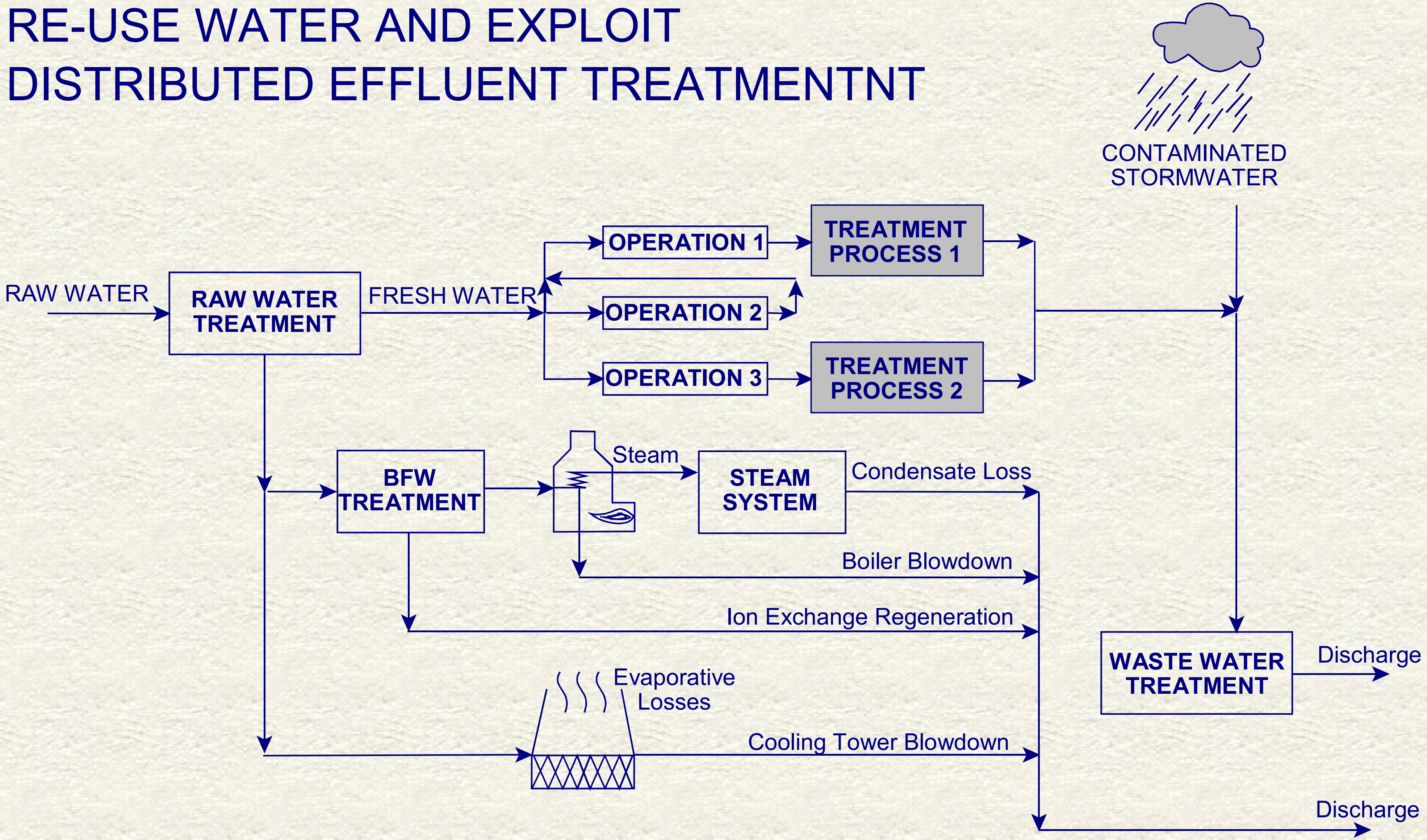
Water regenerated to be re-used in different operations
(Note: Water never sees the same operation twice)

3. REGENERATION RECYCLING

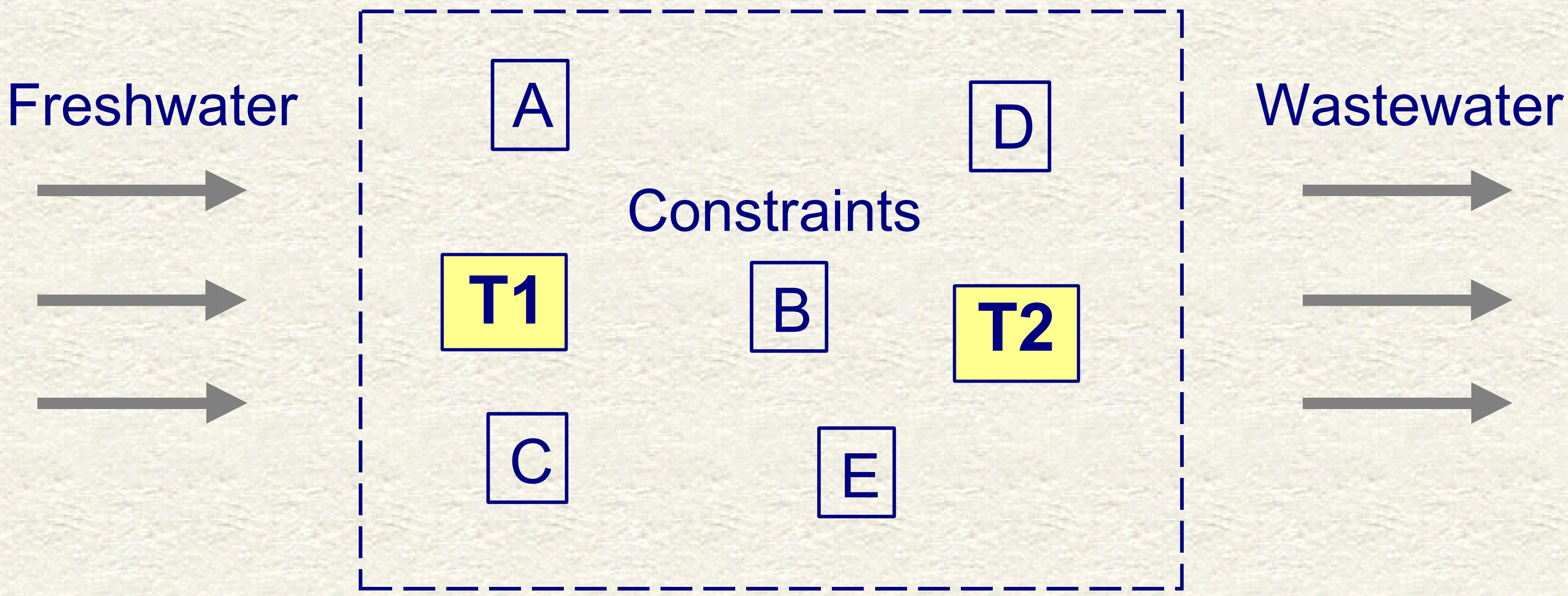


(Note: water can be recycled to processes in which it has been used previously - compare regeneration re-use)

RE-USE WATER AND EXPLOIT DISTRIBUTED EFFLUENT TREATMENTNT

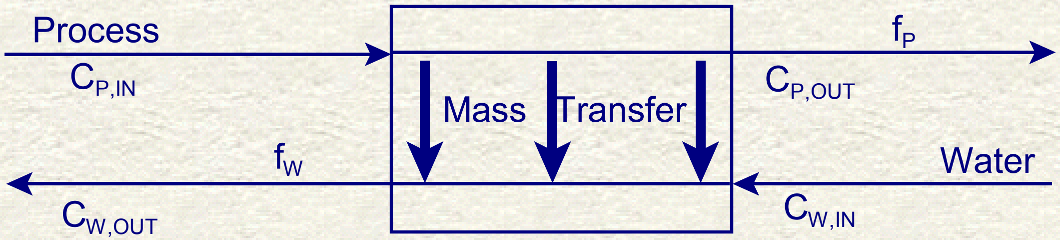


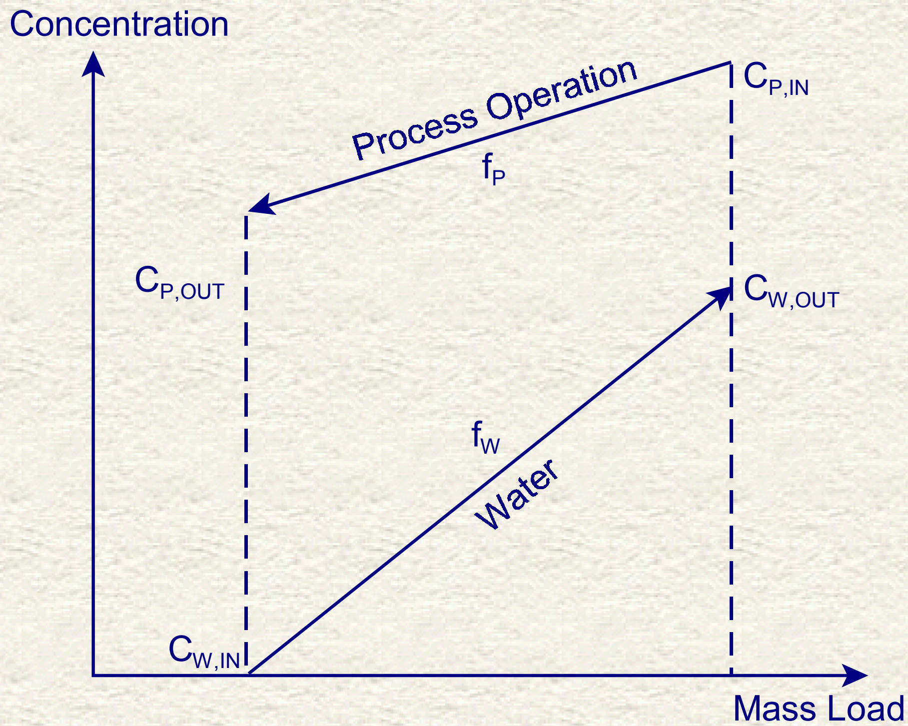
Design Problem



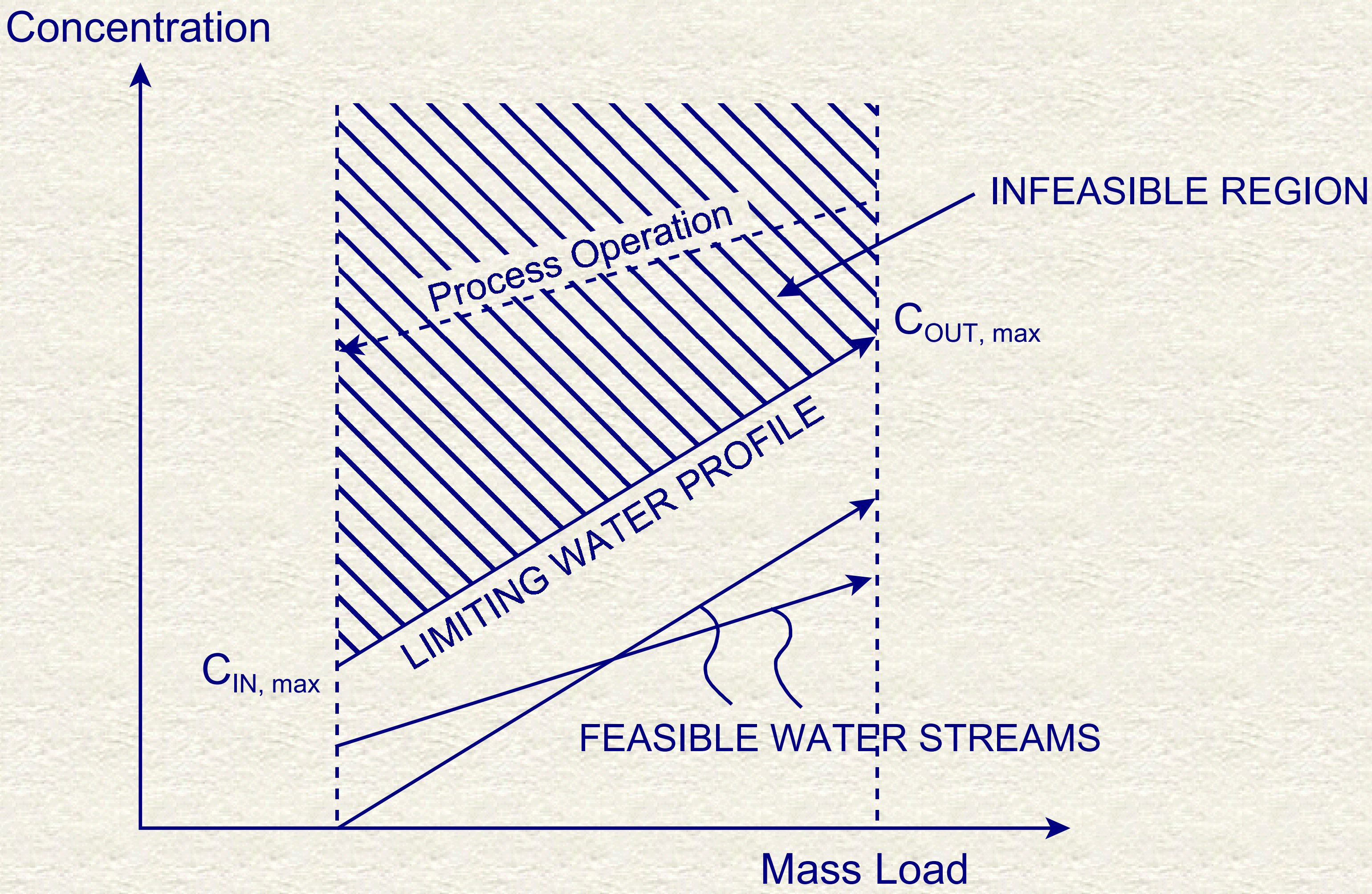
Network design ?

Water Use Analysis

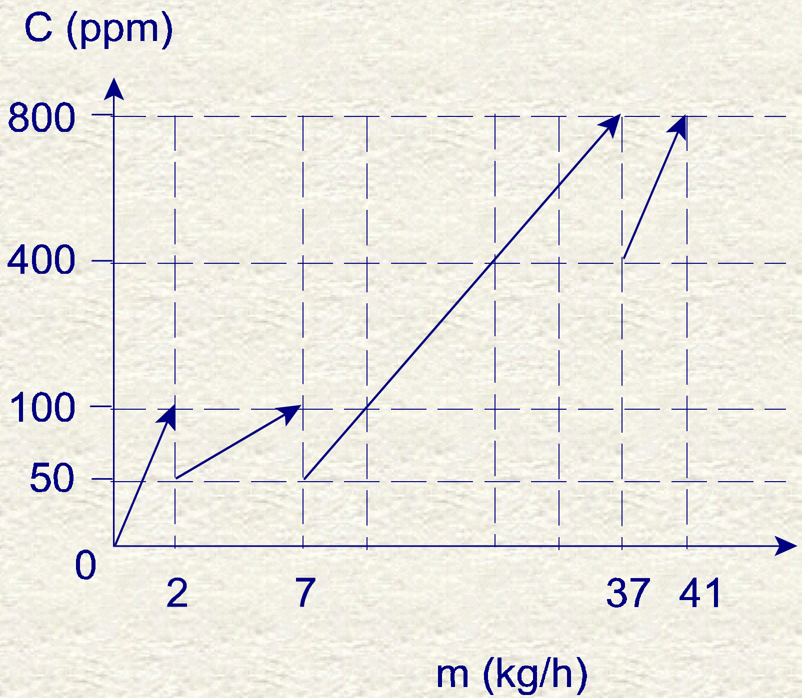




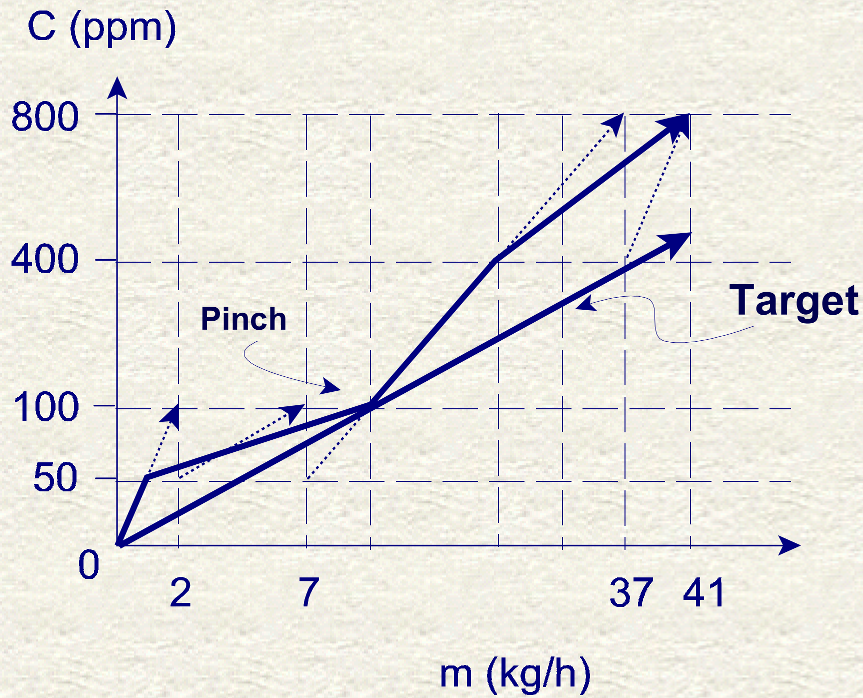
Limiting Water Profile



Water re-use

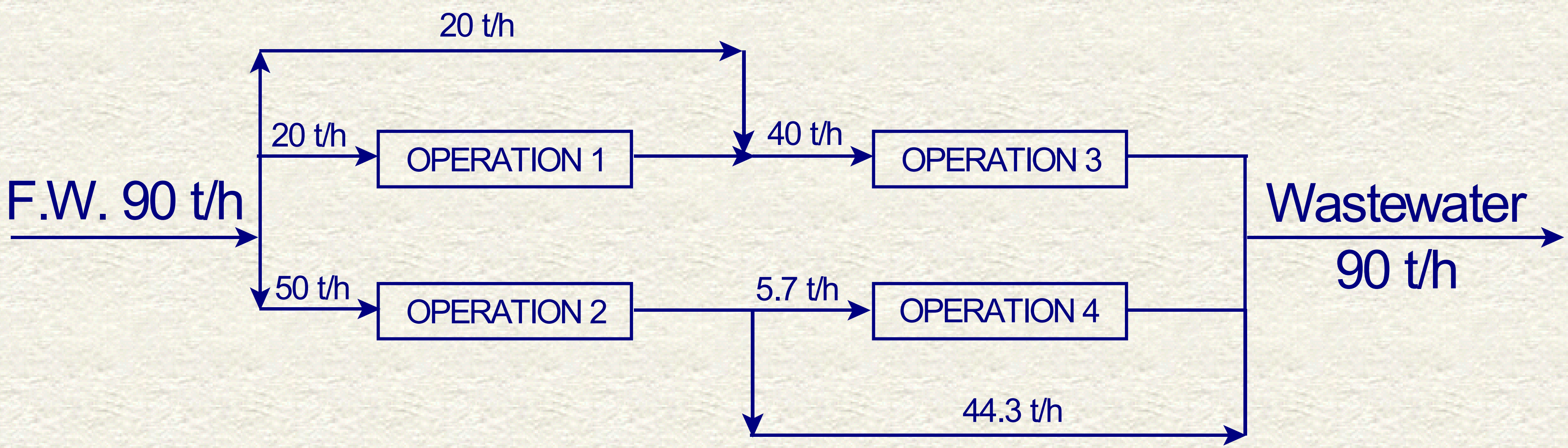


C (ppm)
800
400
100
50
0
2
7
37
41
m (kg/h)



C (ppm)
800
400
100
50
0
2
7
37
41
m (kg/h)
Pinch
Target

Design for re-use

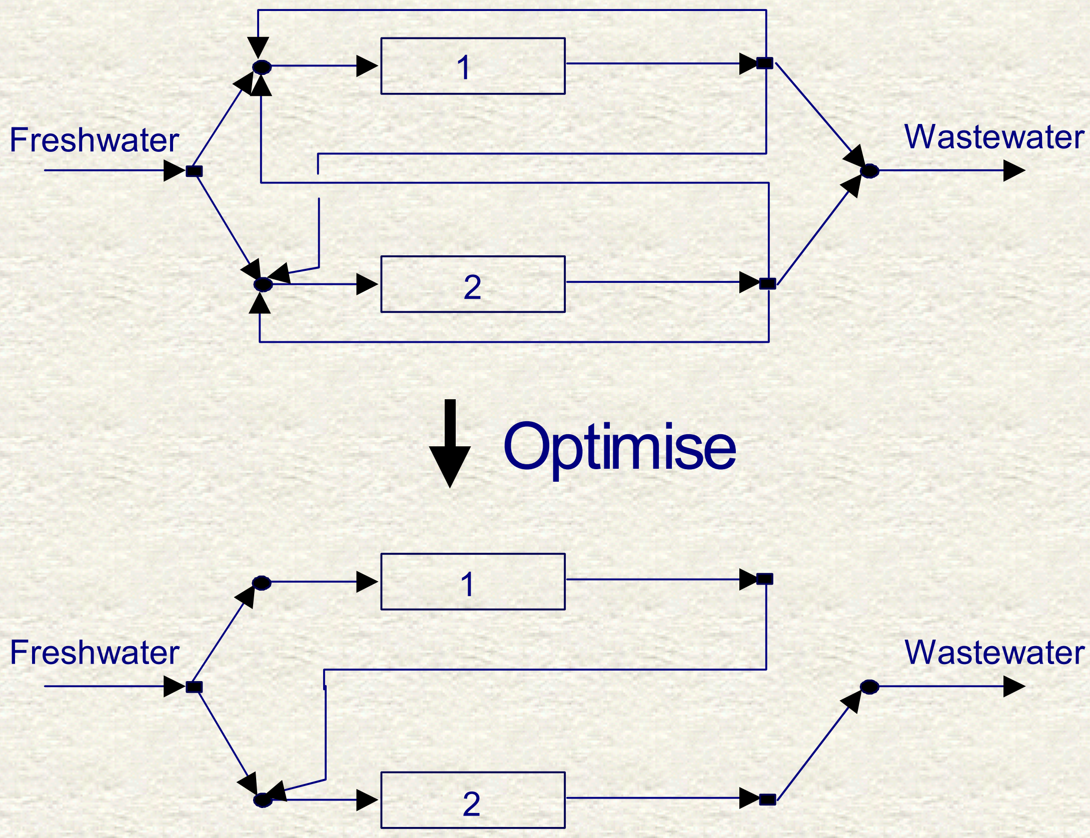


Only one of the possibilities

Remarks

- Target and design for single contaminants straightforward
- Tedious for large problems
- Extension to multiple contaminants difficult
- Cannot deal with different mass transfer models
- Does not allow constraints to be included
- Does not consider capital cost

Superstructure Approach



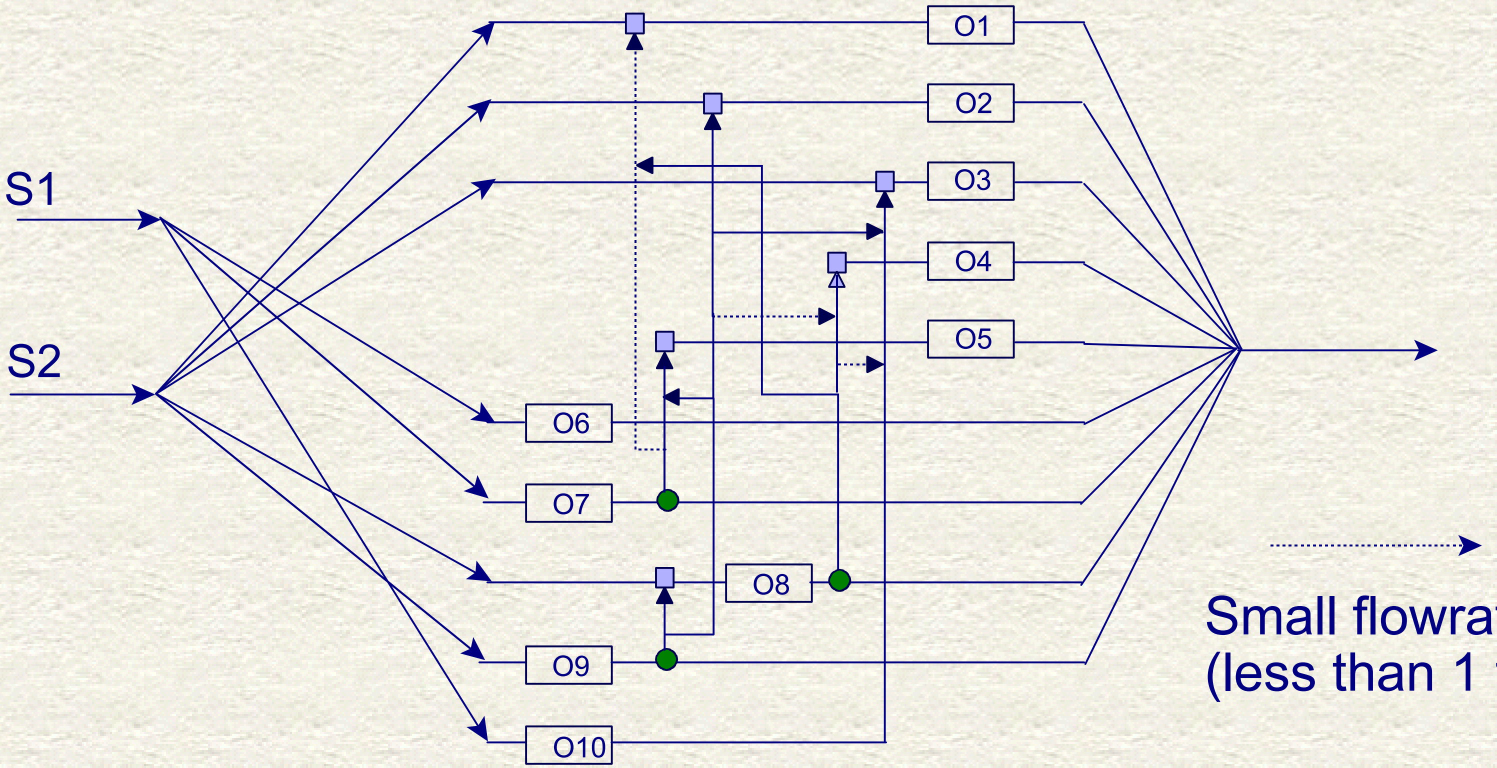
(Doyle and Smith, Trans IChemE, 75B, 181-189, 1997)

Example

Process	Flowrate	Contam	Cmaxin	Cmaxout
O1	24.87	A	200	25000
		B	500	20000
		C	100	28500
		D	1500	230000
O2	40.98	A	350	8000
		B	3000	9000
		C	500	24080
		D	400	3000
O3	39.20	A	350	3500
		B	450	2500
		C	150	1500
		D	500	1500
O4	4.00	A	800	15000
		B	650	5000
		C	450	700
		D	300	1500
O5	3.92	A	1300	2000
		B	2000	7000
		C	2000	9000
		D	4000	10000

Process	Flowrate	Contam	Cmaxin	Cmaxout
O6	137.5	A	3000	12000
		B	2000	10000
		C	100	8000
		D	0	200
O7	290.96	A	450	2000
		B	0	3000
		C	250	1000
		D	650	12000
O8	23.81	A	100	3450
		B	250	4000
		C	200	700
		D	550	7000
O9	65.44	A	150	1000
		B	450	1000
		C	3000	4000
		D	100	100
O10	4.00	A	0	100
		B	0	100
		C	0	100
		D	0	100

Solution Without Piping Costs or Complexity Considerations

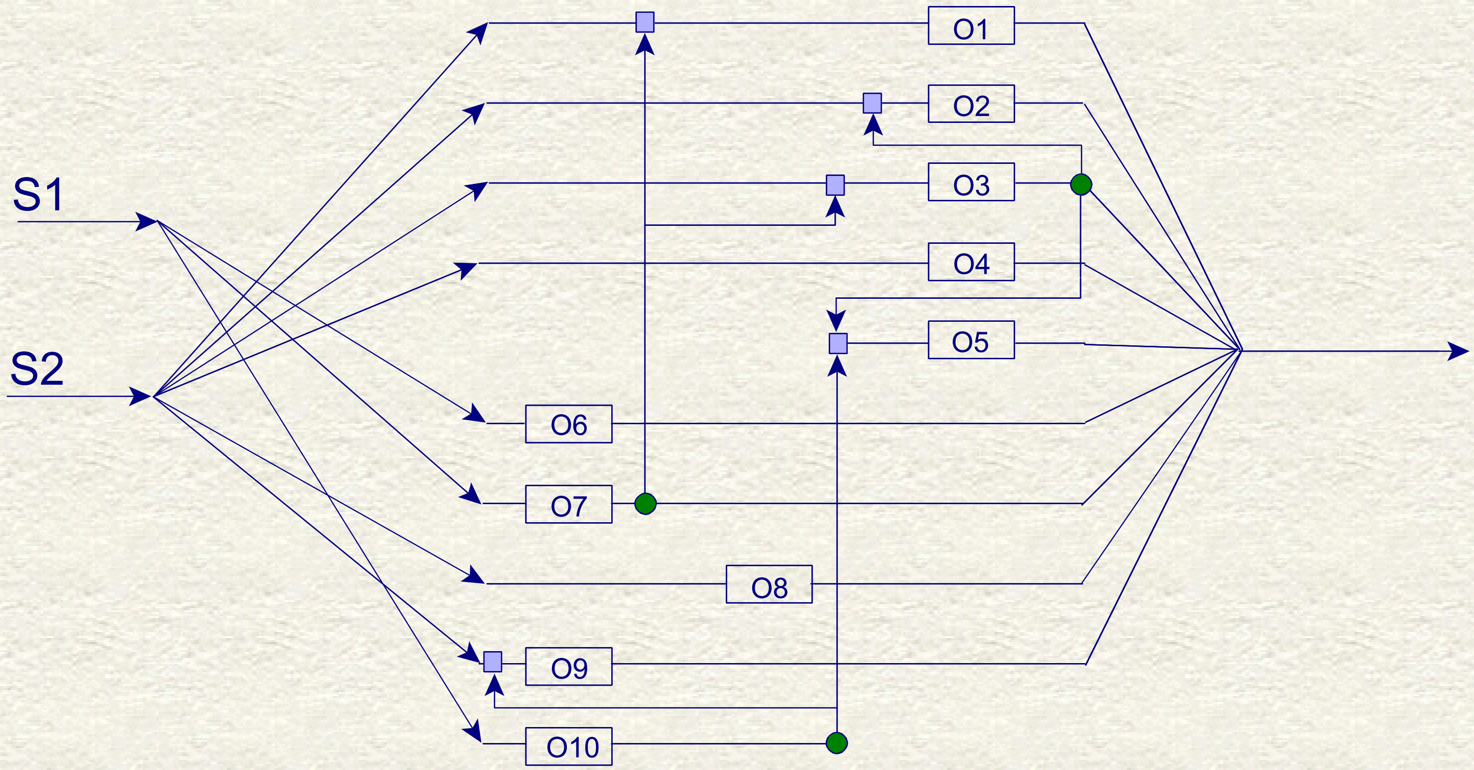


Flowrate s1= 432.4 t/h s2=158.3 t/h

Now include:

- minimum flowrate of 1 t/h
- number of streams to any mixing junction to be maximum of 2
- include piping costs (pipe run lengths, materials of construction, diameters calculated from flowrates)

Minimise Total Cost



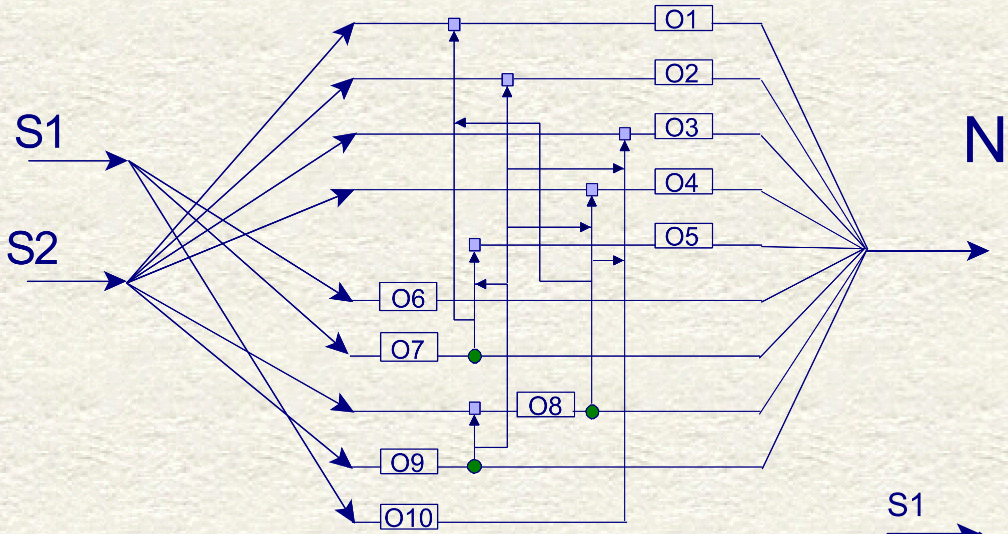
Flowrate s1= 432.4 t/h s2= 175.2 t/h
(freshwater flowrate penalty 2.8%)

Comparison of results

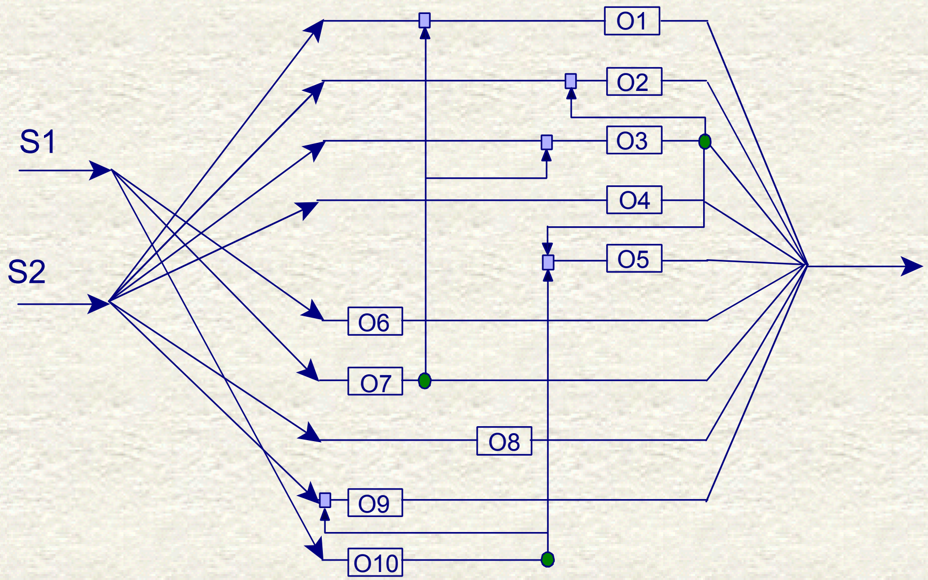
Method	Water Cost (k£)	Capital Cost (k£)	Total Annualised Cost (k£)
Conventional	1,857	1,180	3,037
Constraints on complexity	1,858	1,049	2,907
Constraints on complexity + piping cost	1,870	812	2,682

Annualisation period: 3 years
Interest rate: 10%

Different structures for water networks



No Constraints



Minimum total cost

4. Minimising Combustion Emissions

Minimising Combustion Emissions at Source

- Increased energy efficiency at point of use
- Increased energy efficiency of the utility system
- Improvements to combustion processes
- Changing fuel

4.1 Increased Energy Efficiency at Point of Use

Two broad approaches to improve energy efficiency:

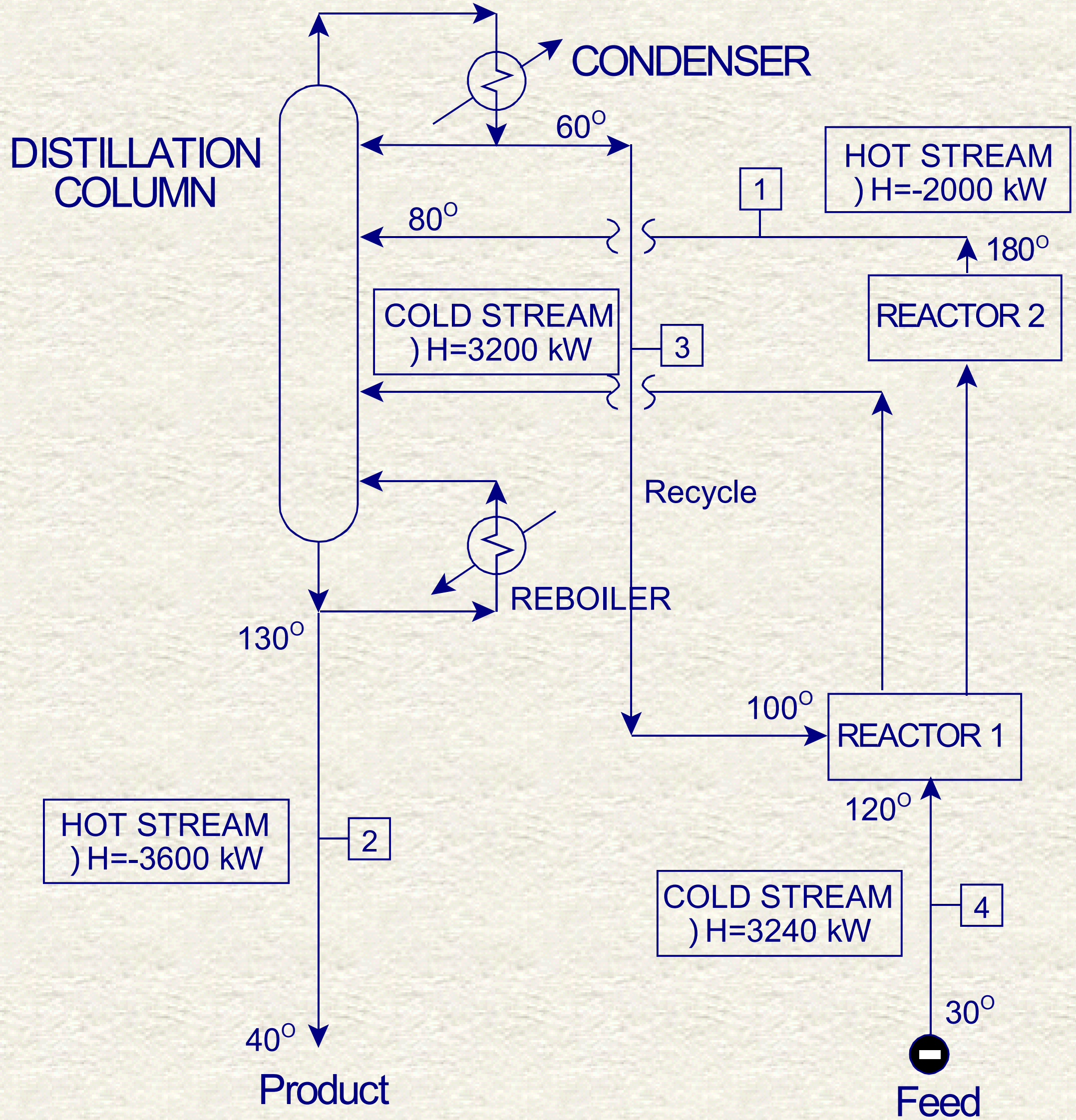
(i) Conventional

- Better lagging
- Better control systems
- etc

(ii) Process Integration

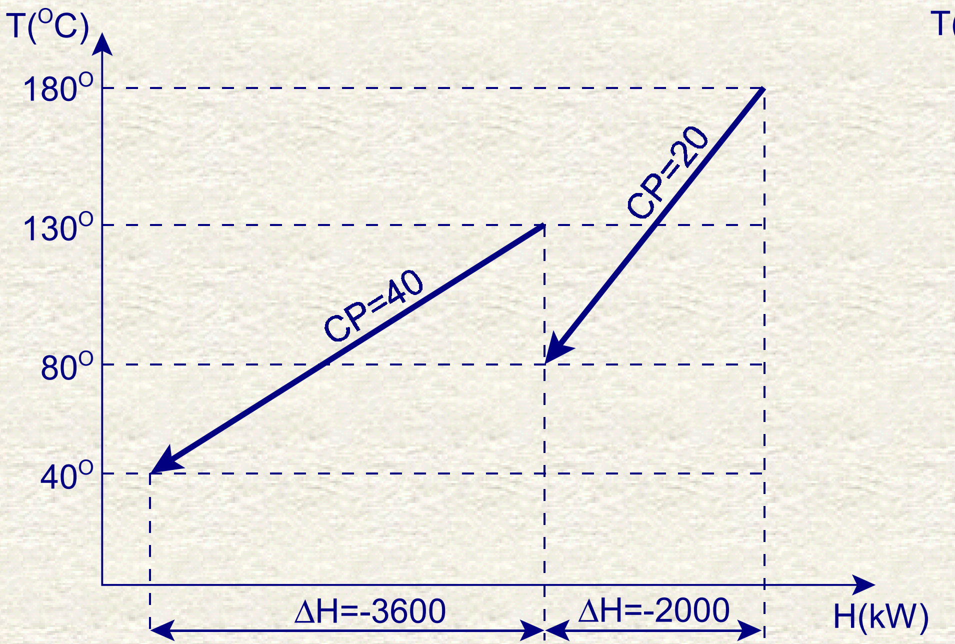
- Better heat recovery

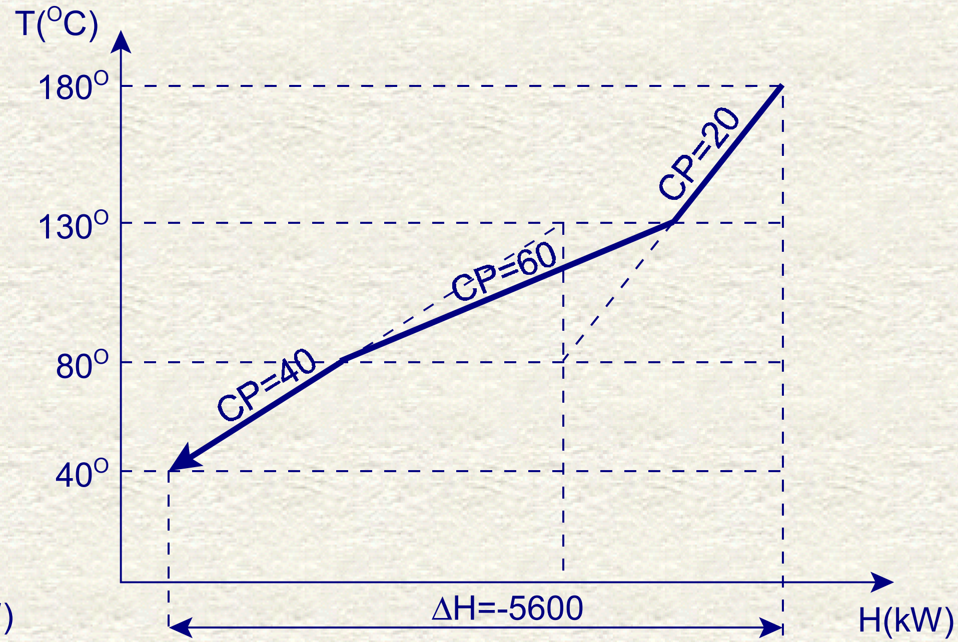
HERE WE SHALL CONCENTRATE ON
PROCESS INTEGRATION



The heating and cooling duties for our simple flowsheet

The composite hot curve

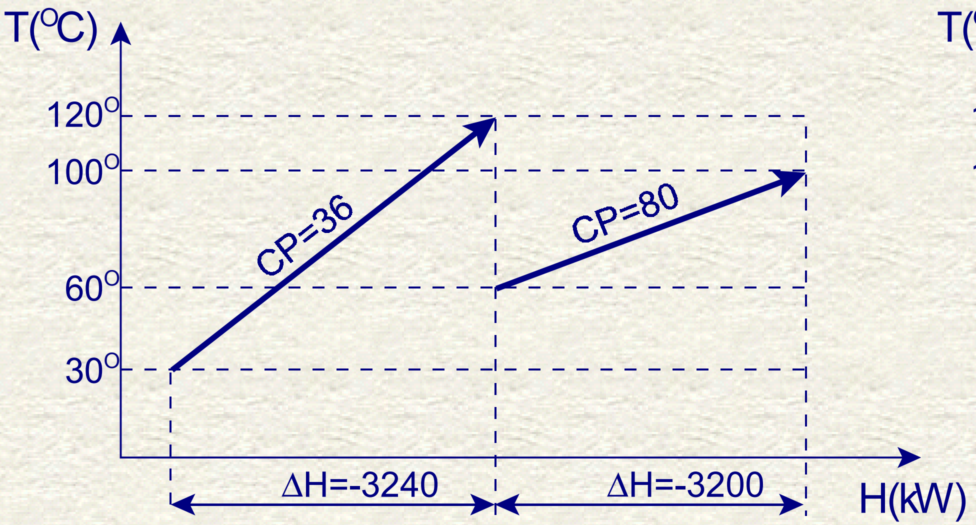


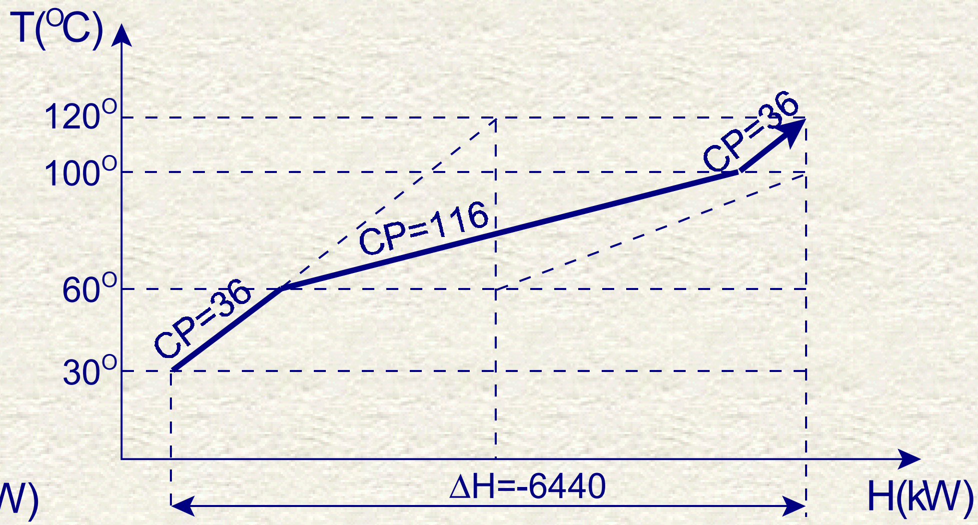


$\Delta H = m\ Cp\ \Delta T = CP \cdot \Delta T$

The composite hot curve represents the total cooling requirement in each temperature interval

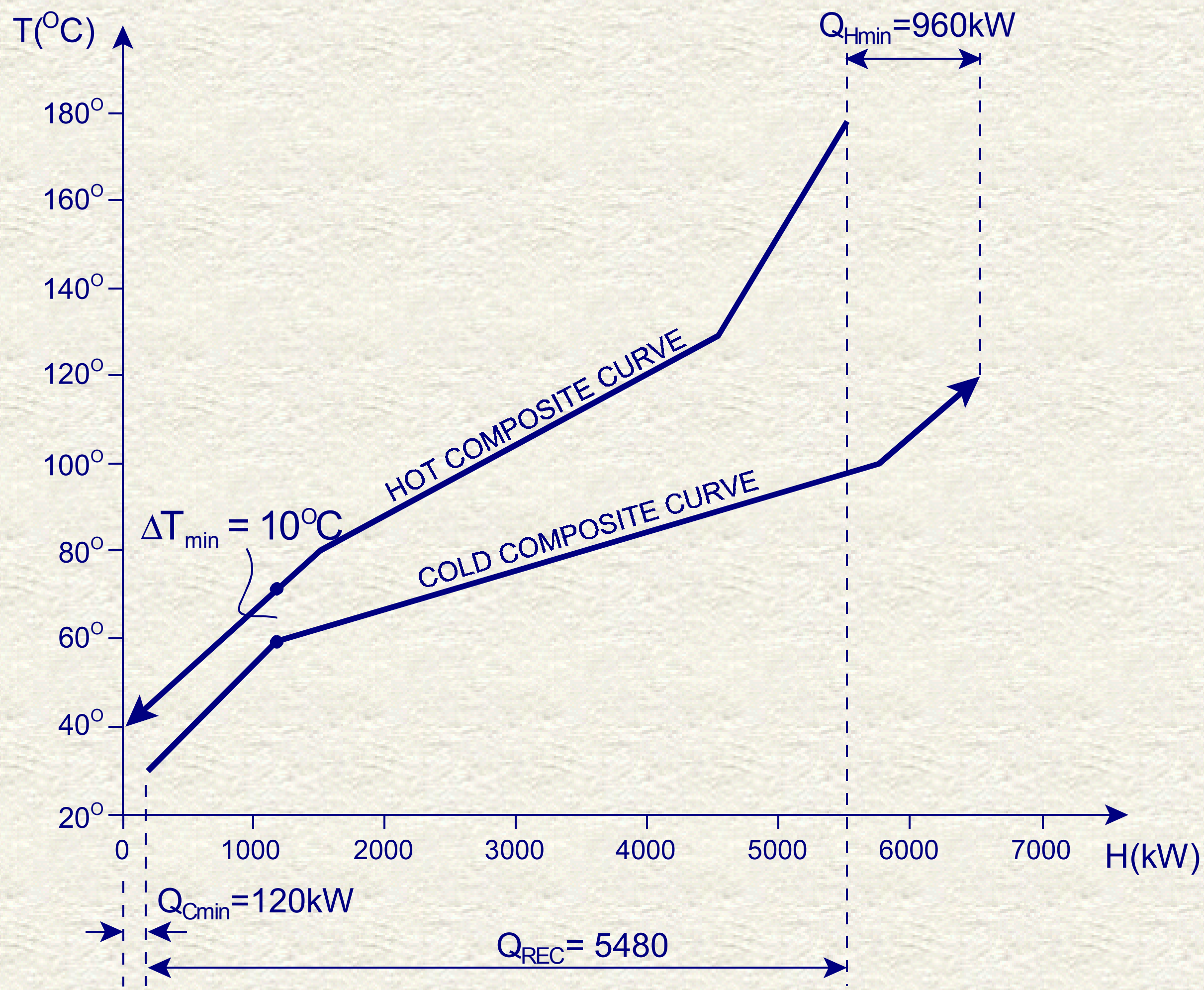
The composite cold curve



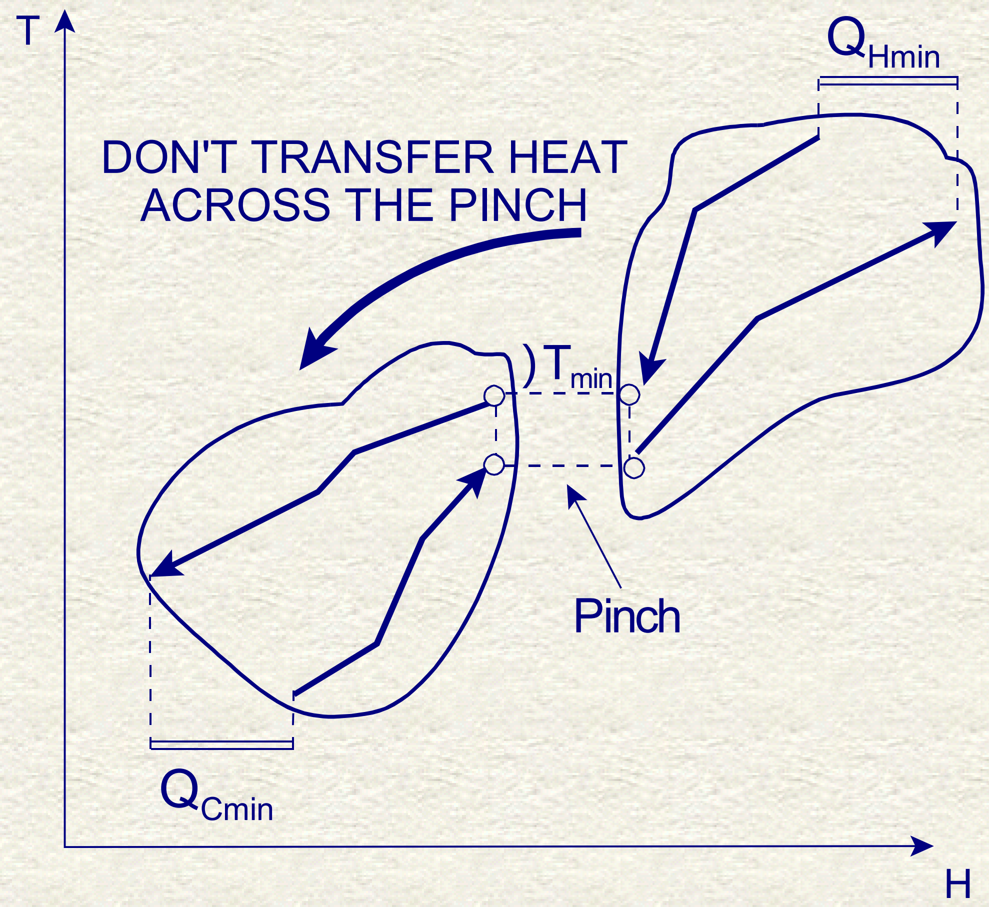


The composite cold curve represents the total heating requirement in each temperature interval.

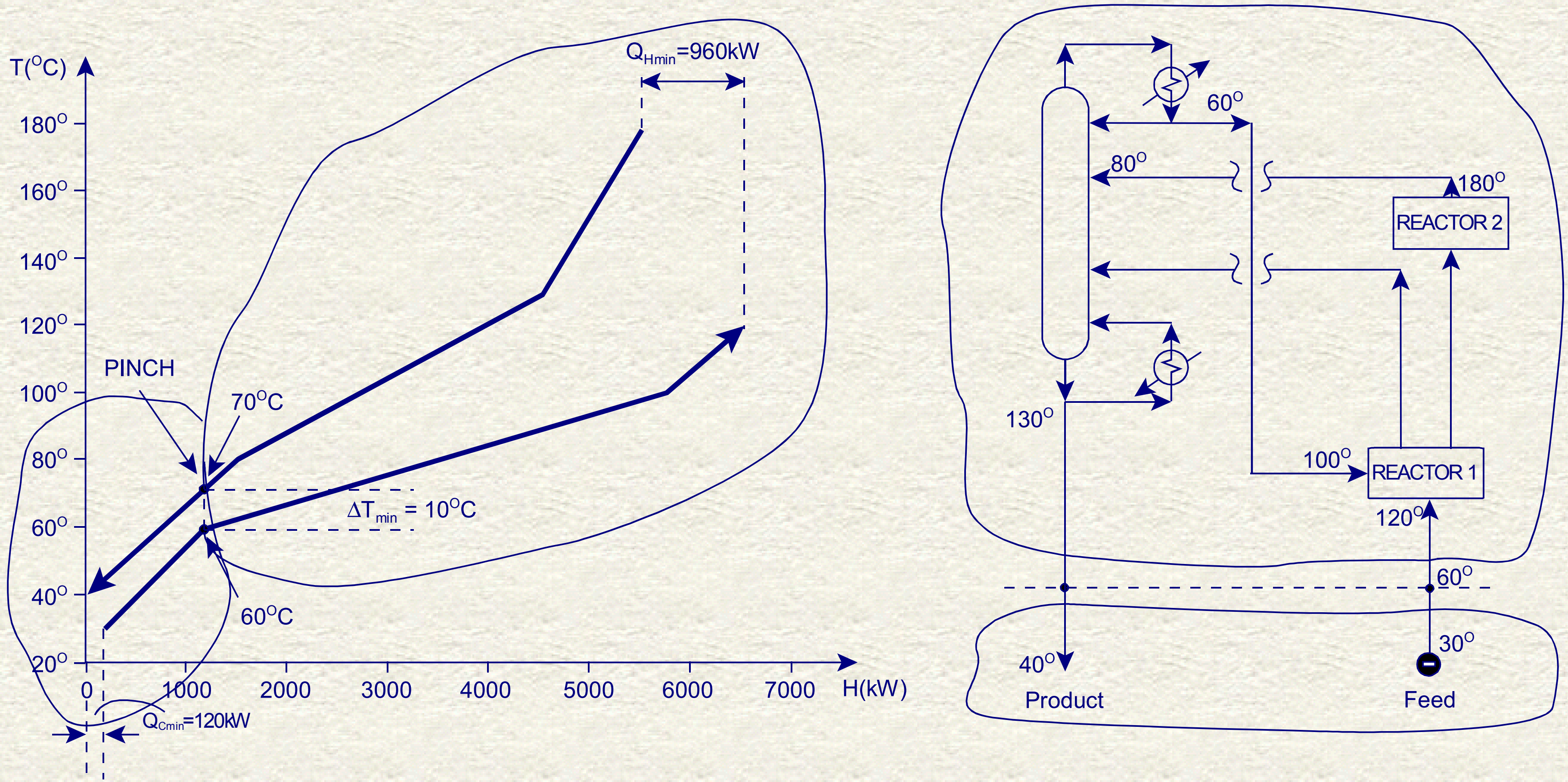
For new designs



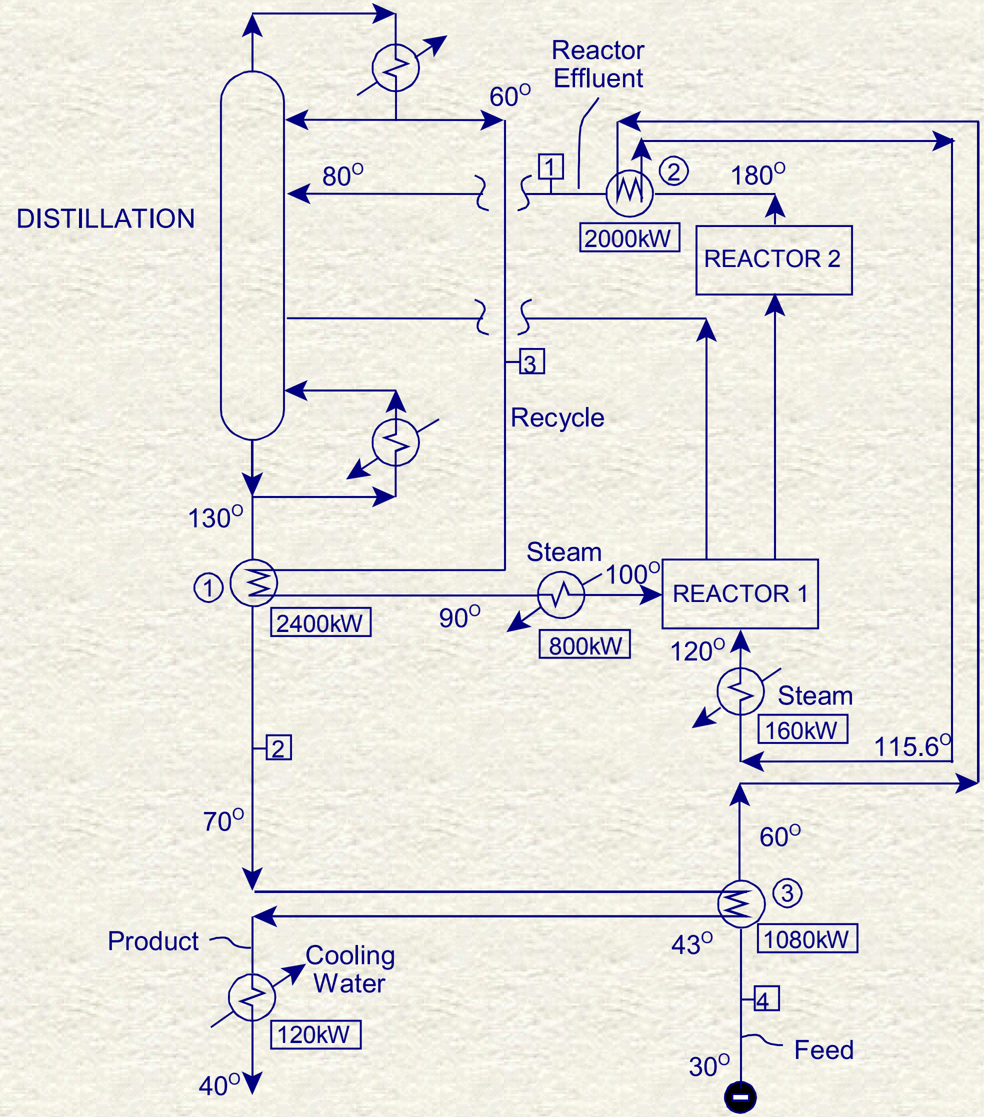
The composite curves set energy targets before design



Pinch design method allows targets to be achieved in design

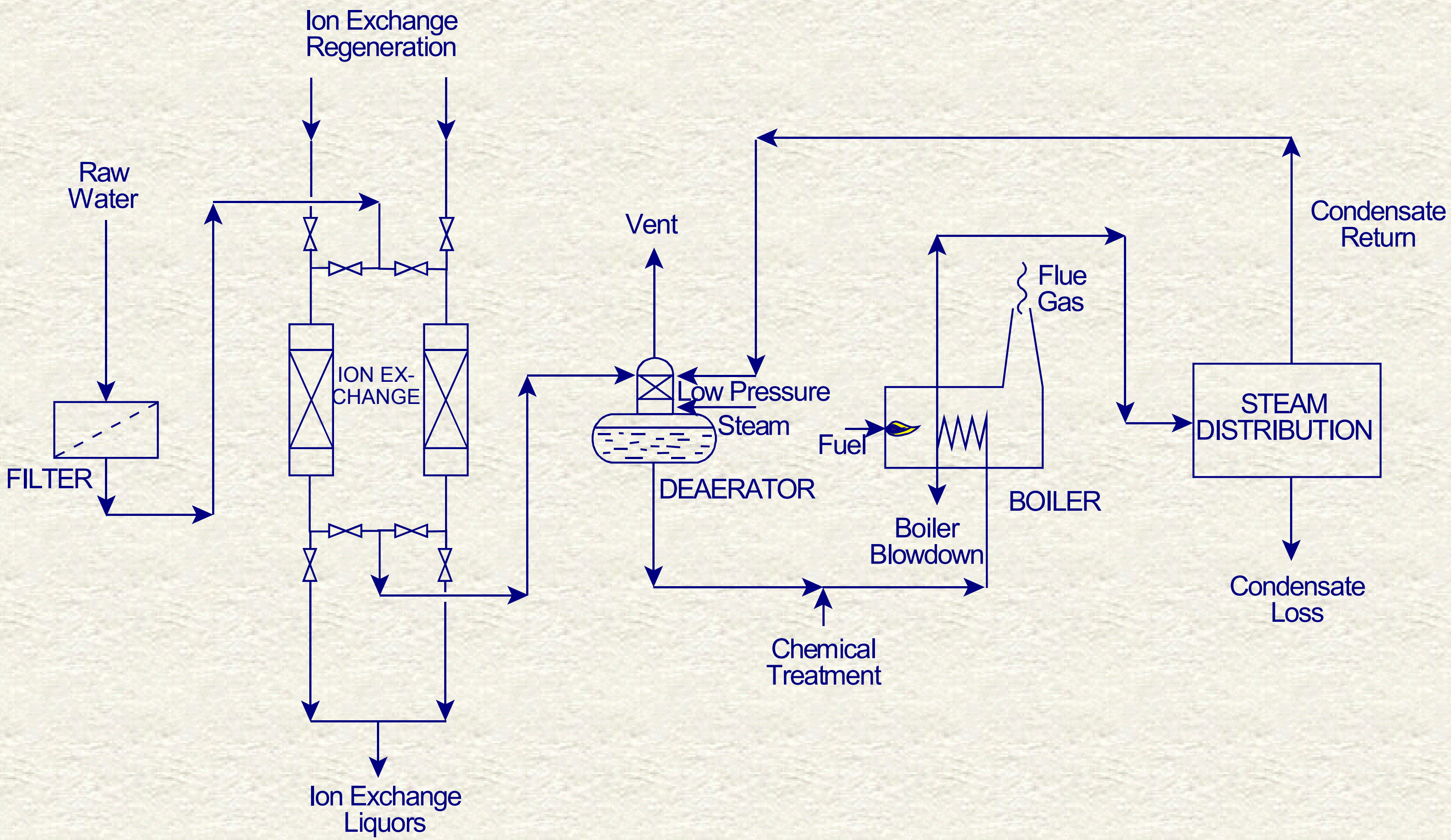


Divide the process at the pinch



Design now achieves the target of 960 kW steam

4.2 Increased Energy Efficiency of the Utility System

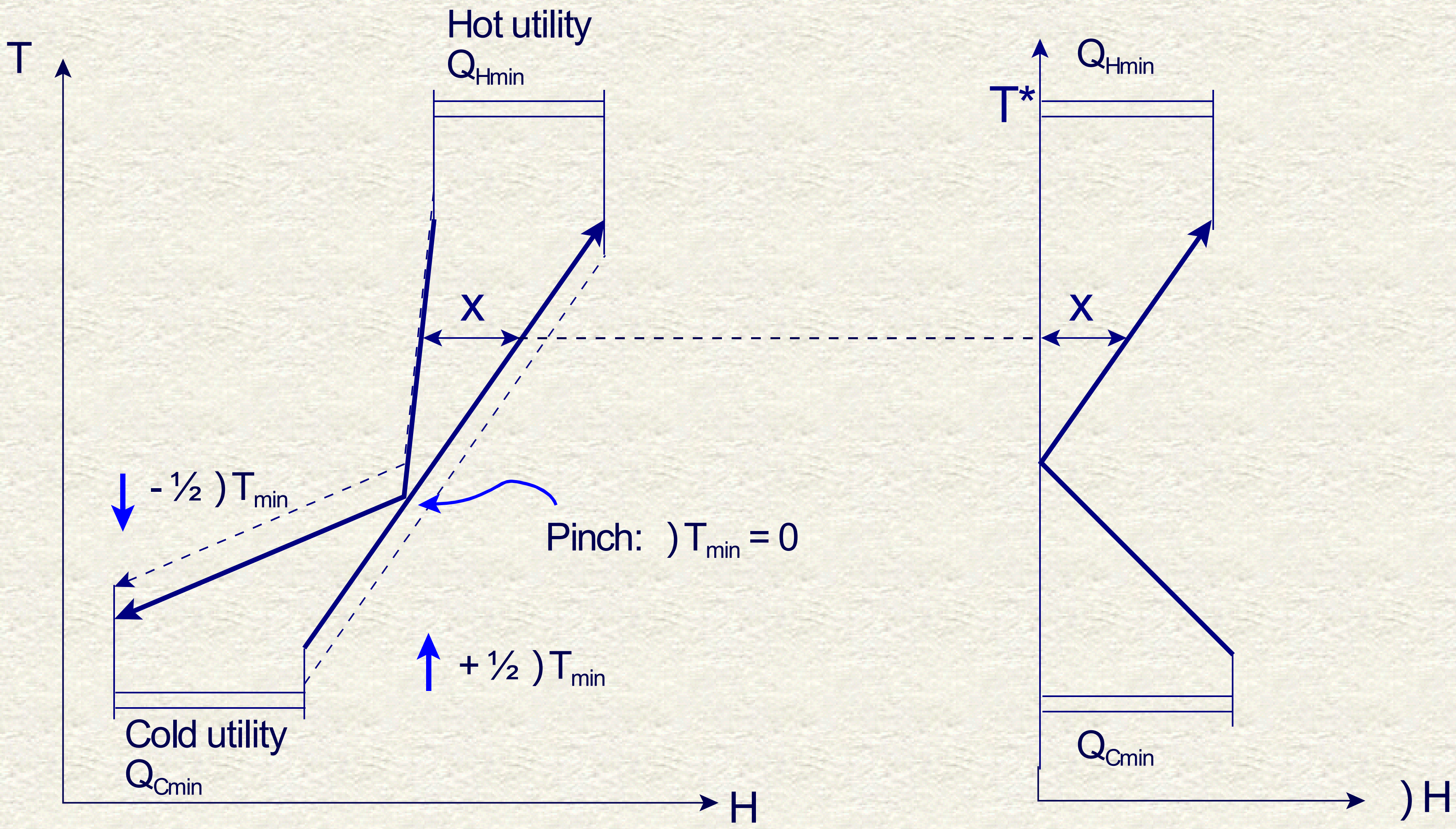


Conventional energy saving

- Increase condensate return
- Better maintenance of steam traps
- etc.

HERE WE SHALL CONCENTRATE ON PROCESS INTEGRATION

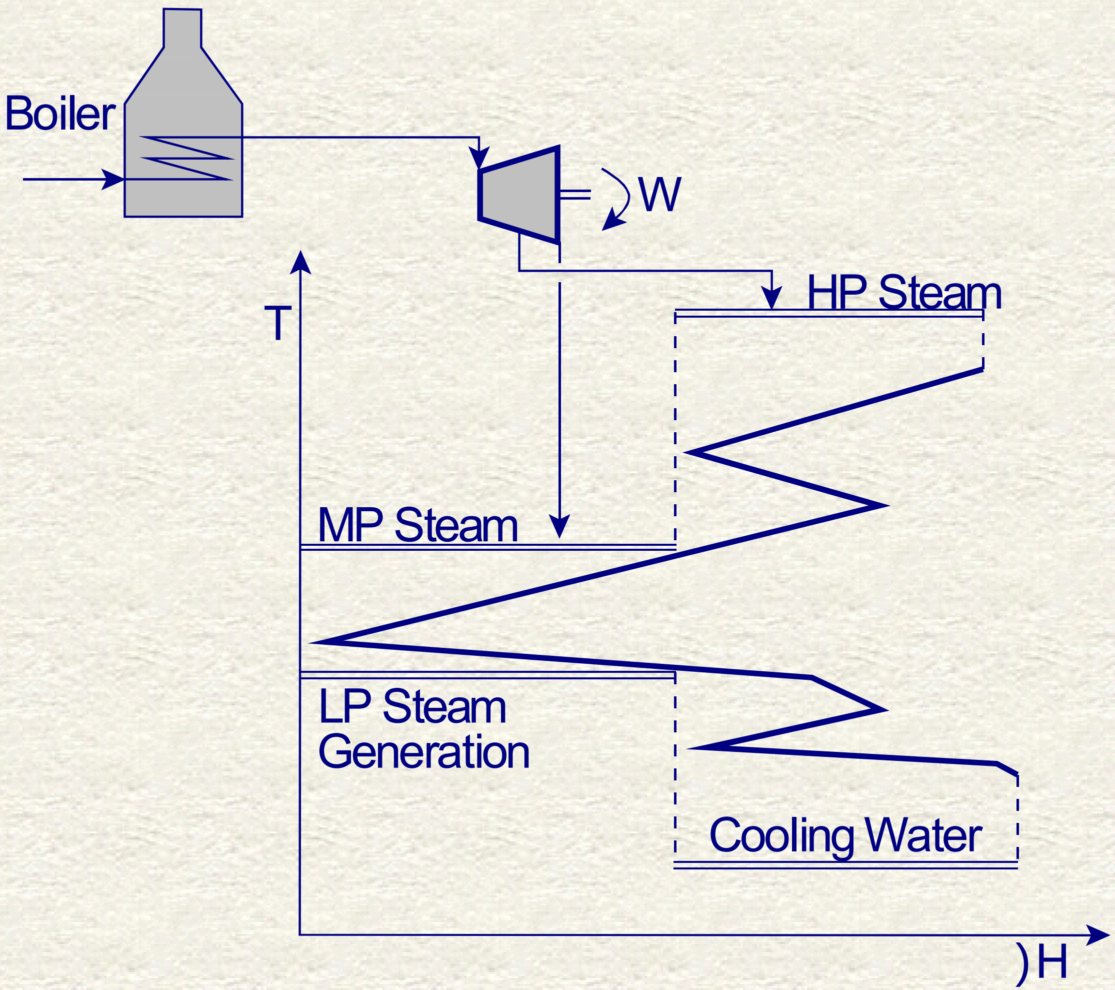
To understand the process/utility interface



"Shifted" Composites

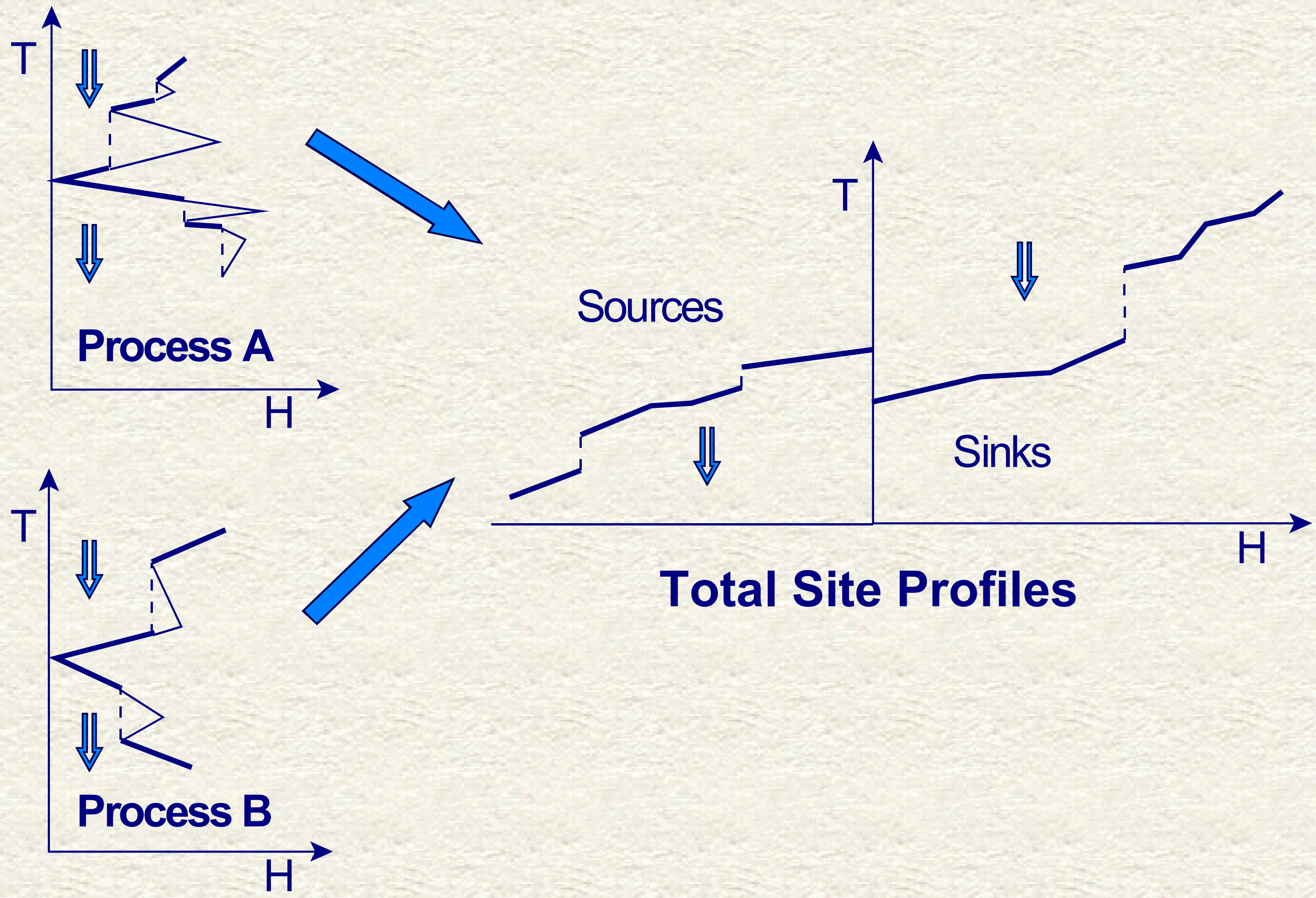
Grand Composite

Grand Composite Curve

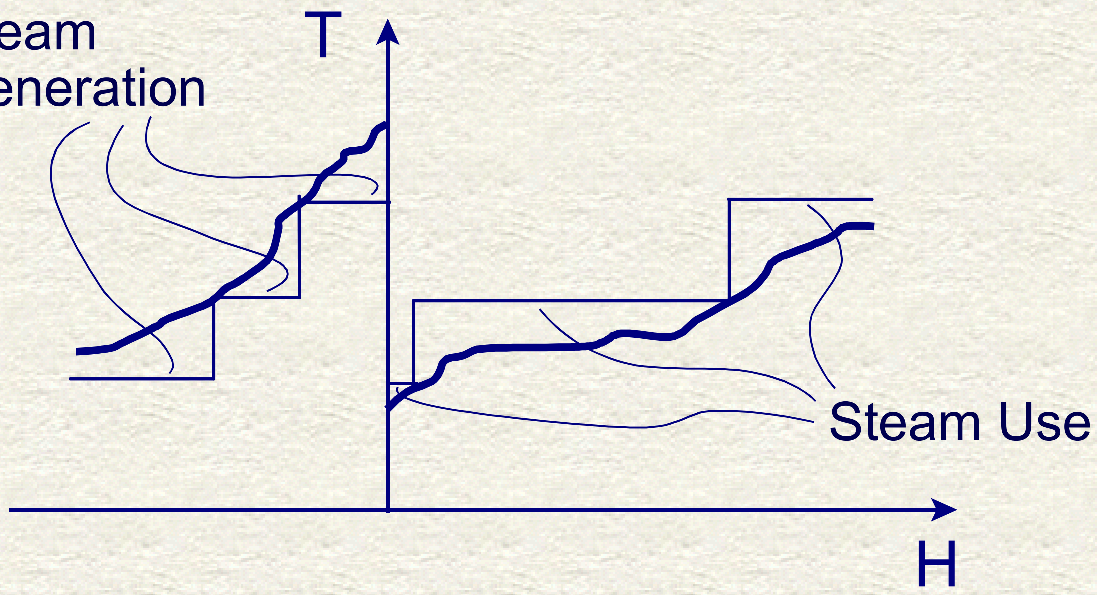


Allows best utility mix to be selected

Total Site Profiles

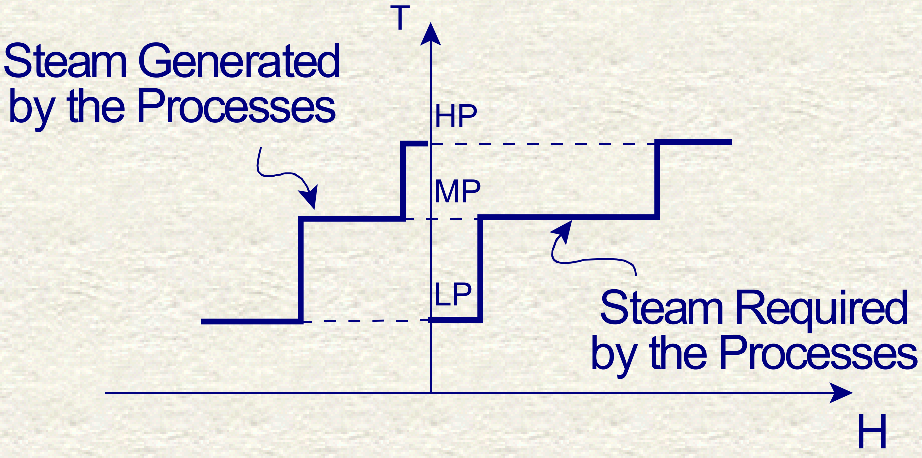


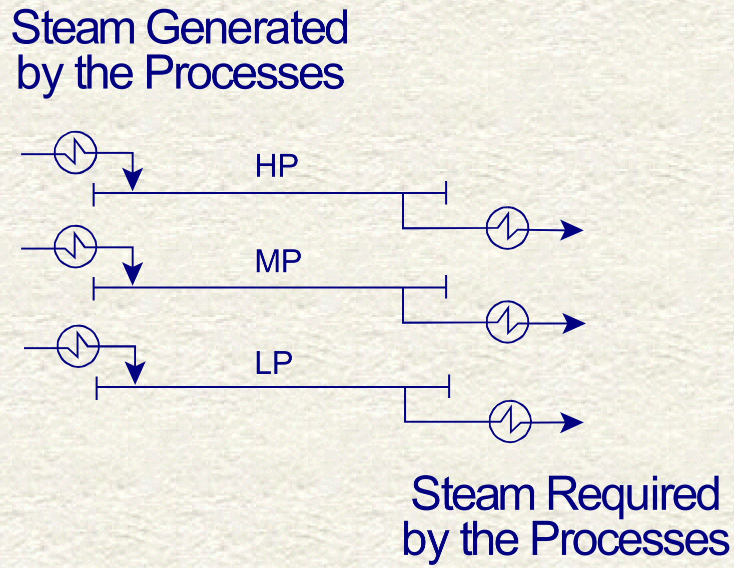
Total site profiles



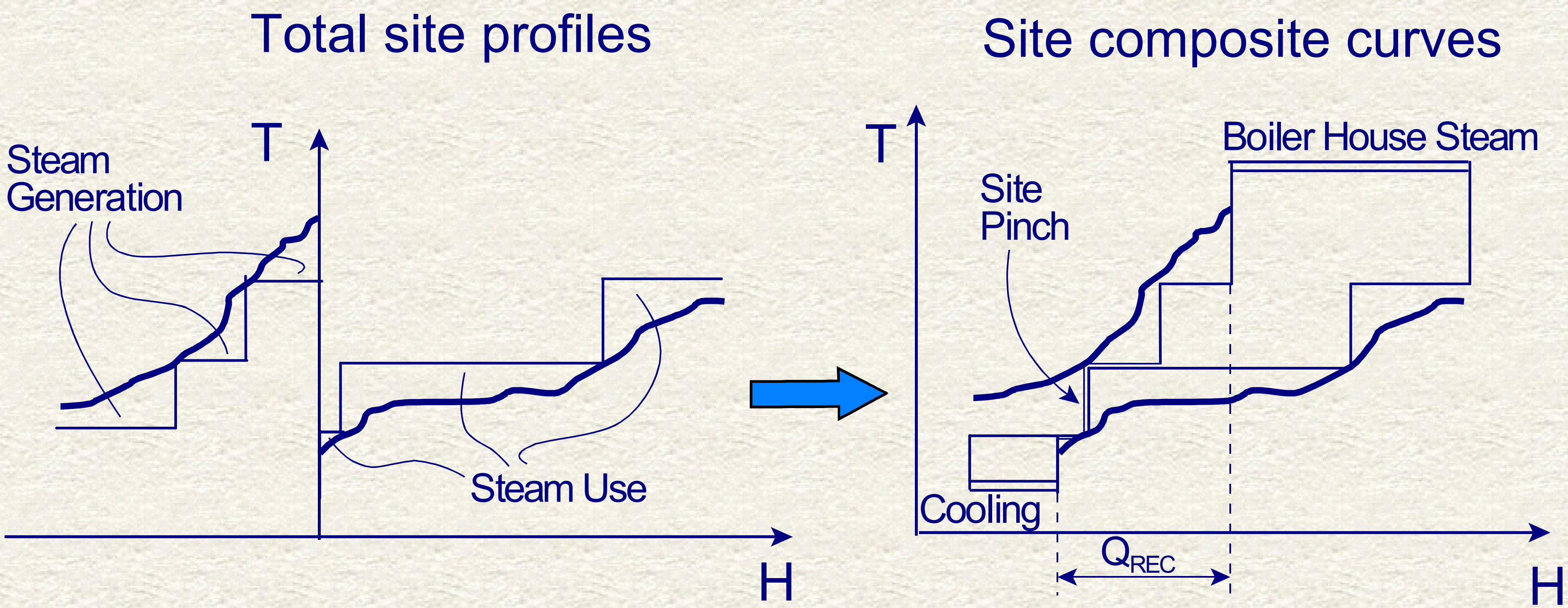
- Allow steam generation and useage to be targeted for the whole site

BUT, heat recovery through the steam system is possible



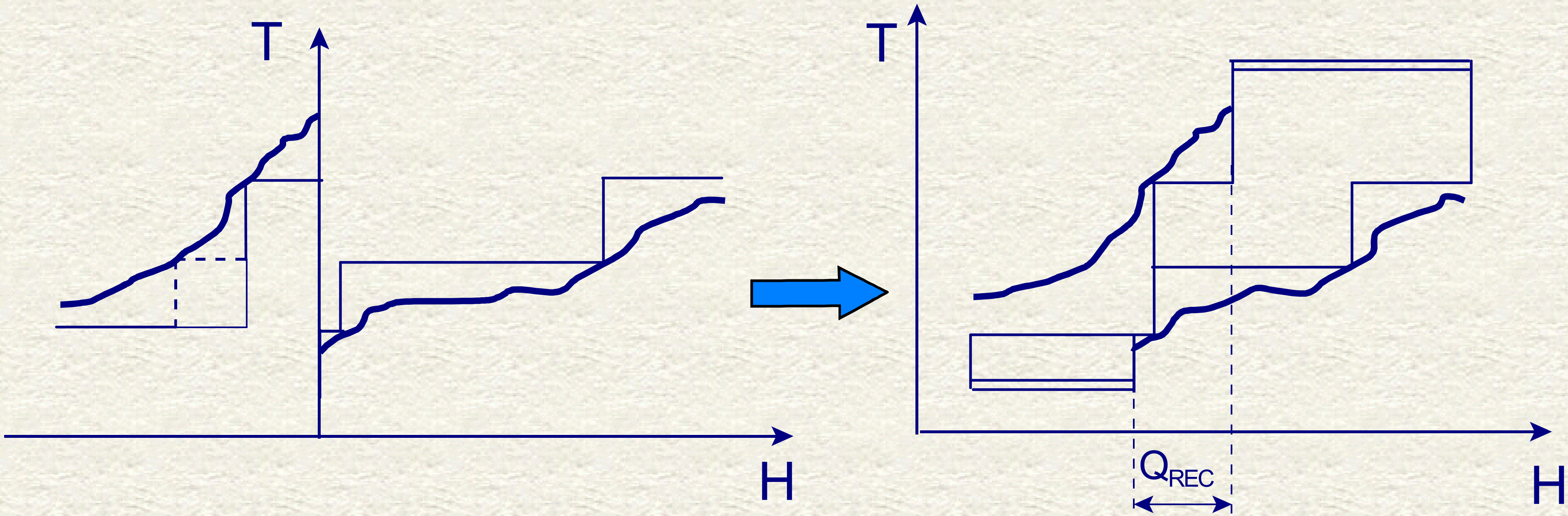


Steam System Profiles



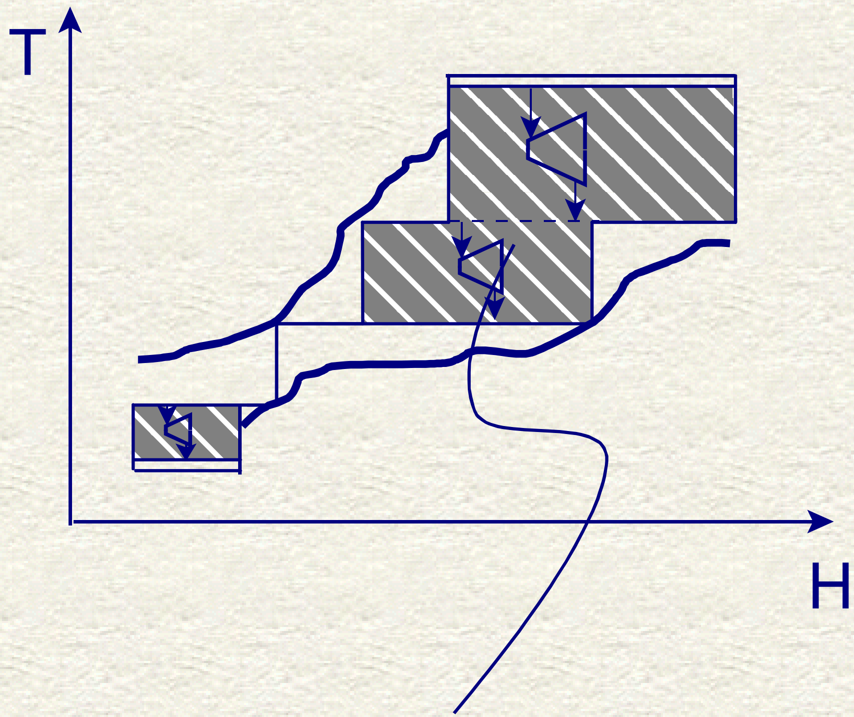
- Site composite curves allow heat recovery opportunities via the steam system to be identified

Poor matching of steam system against the site profiles



Leads to missing heat recovery opportunities (through the steam system) and hence excessive fuel consumption in the boiler house

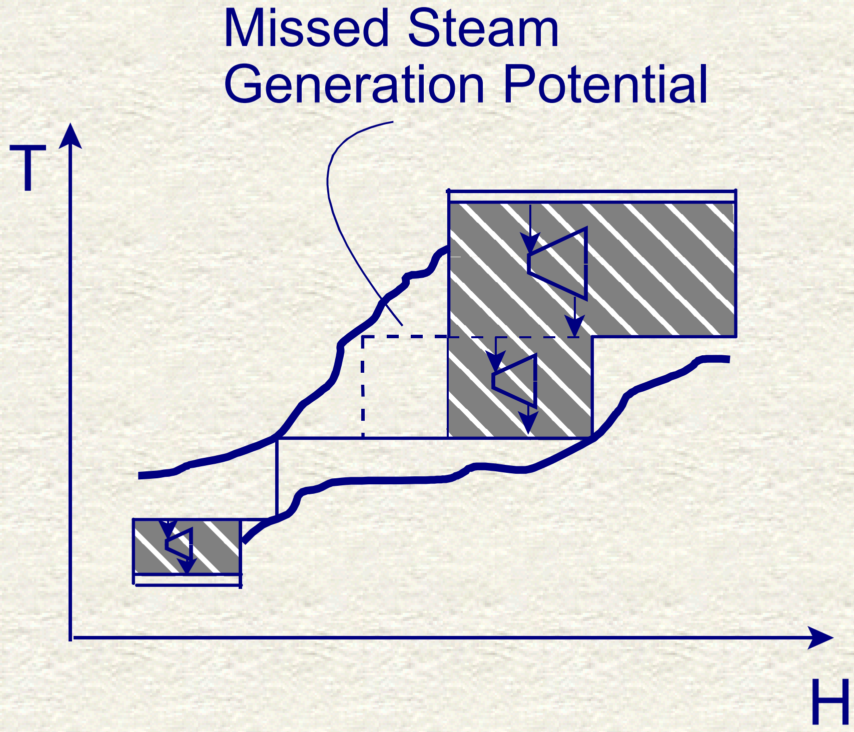
In terms of cogeneration potential



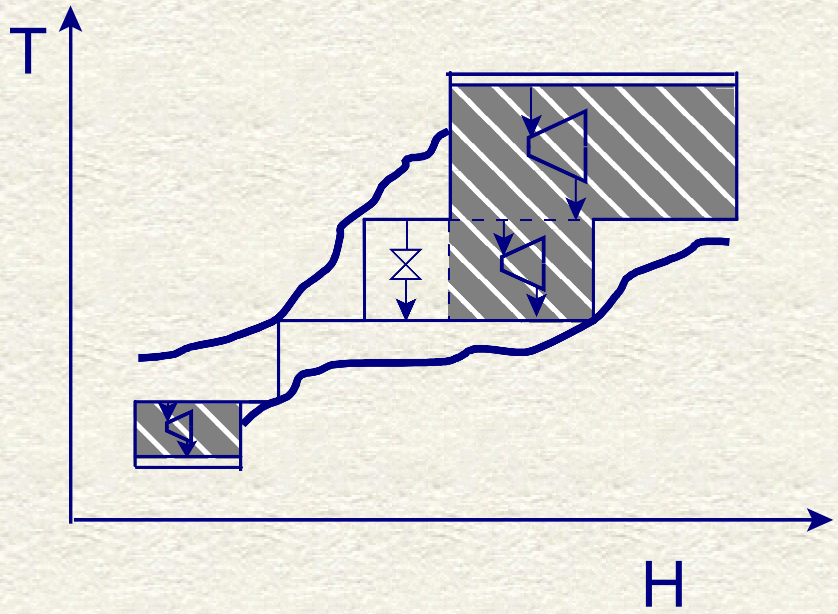
Area % Shaftwork

(Raissi, PhD Thesis, UMIST, 1994)

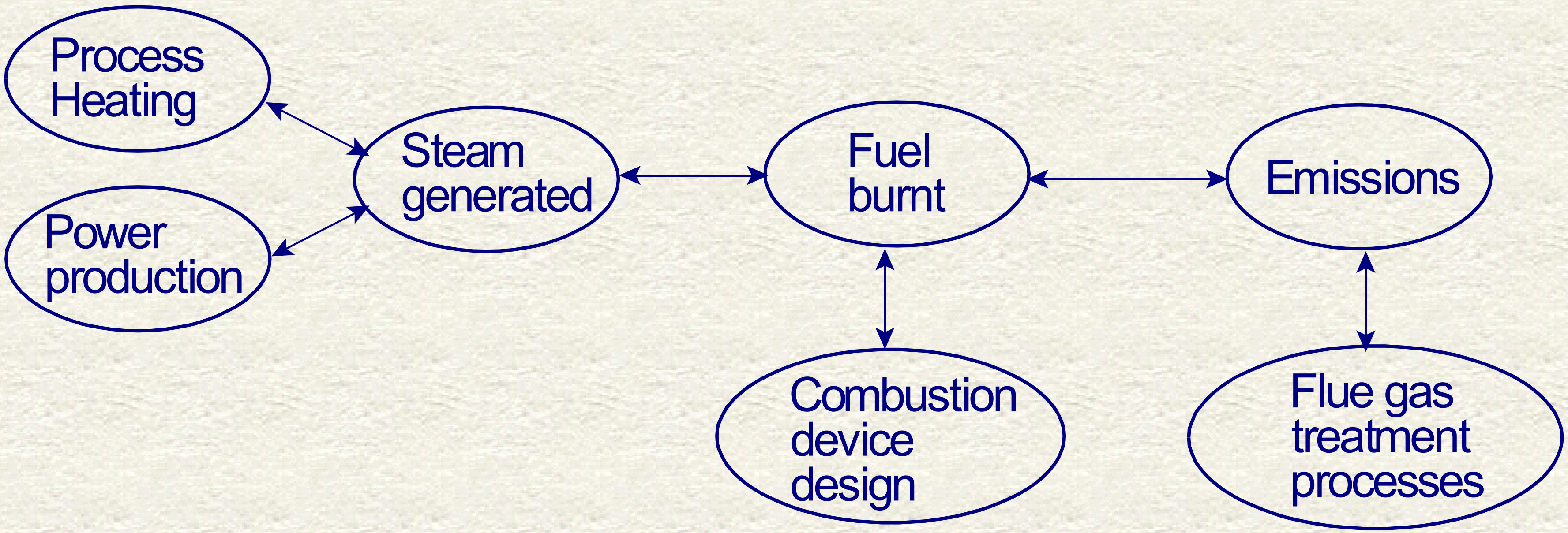
Cogeneration opportunities can be lost



Poor match between profiles and steam system reduces power generation potential.



Too much let-down leads to missed power generation opportunities.



- Compex interactions exist
- Need to consider impact of all aspects of utility system, combustion process design and treatment processes on flue gas emissions.
- Require process integration techniques to understand these interactions.

5. Concluding Remarks

AND FINALLY

Many environmental problems from the process industries.

Waste from:

- Reaction systems
- Separation and recycle systems
- Process operations
- Utility systems

Process integration has a major role to play in solving these problems through the development of clean technology.