

**Pan American Advanced Studies Institute Program on Process Systems Engineering
August 16-25, 2005, Iguazu Falls, Argentina.**

Synthesis of Wastewater Treatment Networks

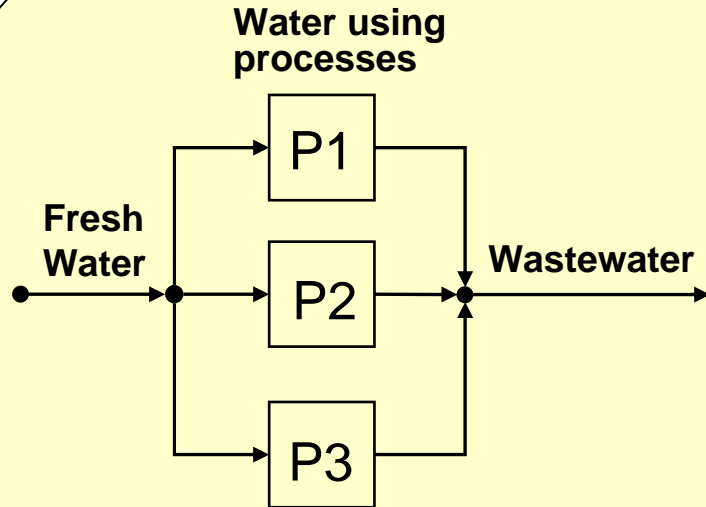
Juan M. Zamora



Casa abierta al tiempo

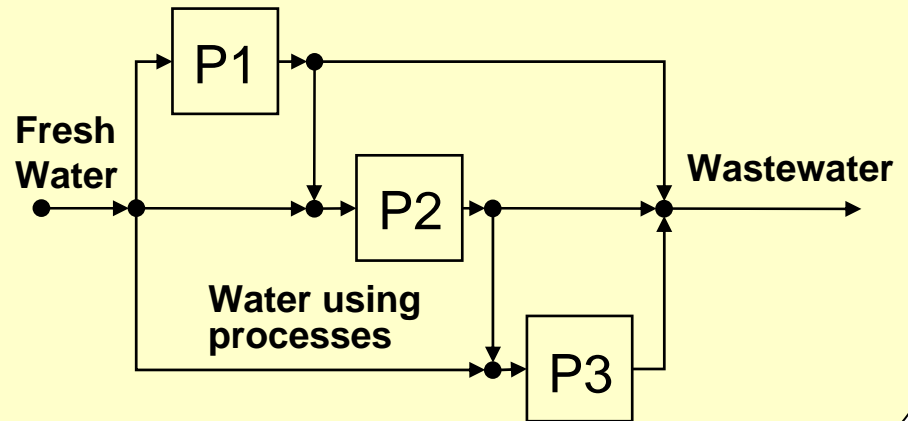
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Water is an Intensively Used Resource in Industry



- FCC
- Visbreaking
- Sweetening
- Hydrotreating

- Crude oil desalting
- Crude oil distillation
- Coking operations
- Hydrocracking



- 
- Steam generation
 - Cooling water
 - Liquid-liquid extraction
 - Washing operations
 - Cooling of blast furnaces
 - Ether Synthesis
 - Steam stripping
 - Alkylation
 - Many other

Great Volumes of Contaminated Wastewaters are Generated

CONVENTIONAL

- Biochemical oxygen demand (BOD)
- Total suspended solids (TSS)
- pH
- Oil and Grease (O&G)

NON CONVENTIONAL

- Ammonia
- Chemical oxygen demand (COD)
- Chlorine
- Fluorides

TOXIC

- Acrylonitrile
- Benzene
- Carbon tetrachloride
- Chloroform
- Phenol
- Lead
- Toluene
- H₂S
- Mercaptans
- Sulfides
- Cyanides
- Chromates

Effluents Discharge is Regulated by Environmental Standards

Limits are imposed on

- Biochemical Oxygen Demand (BOD)
- Total Suspended Solids (TSS)
- pH
- Oil and Grease (O&G)
- Total Organic Carbon (TOC)
- Chemical Oxygen Demand (COD)
- Total Petroleum Hydrocarbons (TPH)
- Temperature
- Color
- Odor

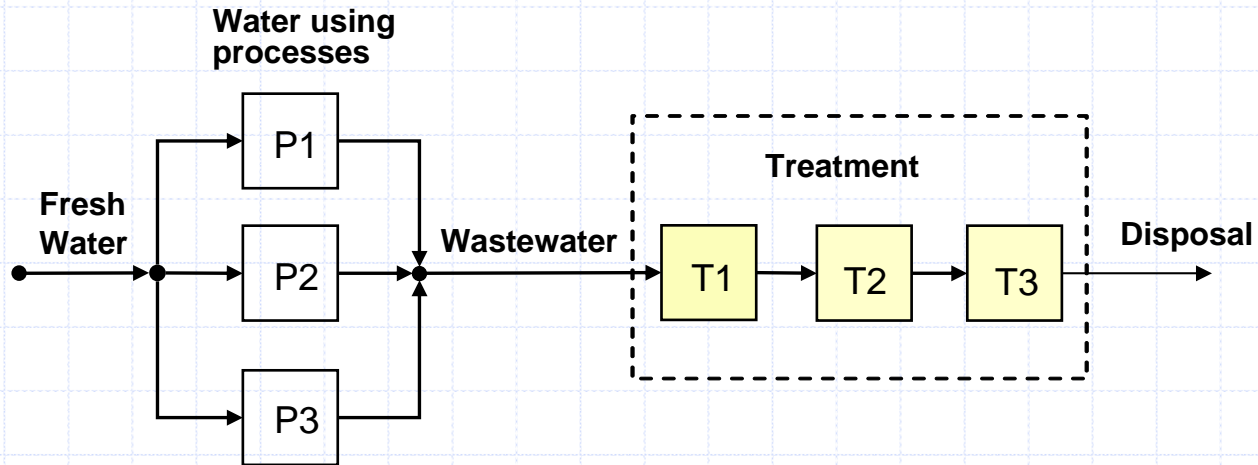
Wastewater Treatment Costs

- Type and concentration of contaminants present in effluent streams.
- Amount of wastewater that is treated and discharged.
- Discharge standards on the water quality of the receiving disposal site.



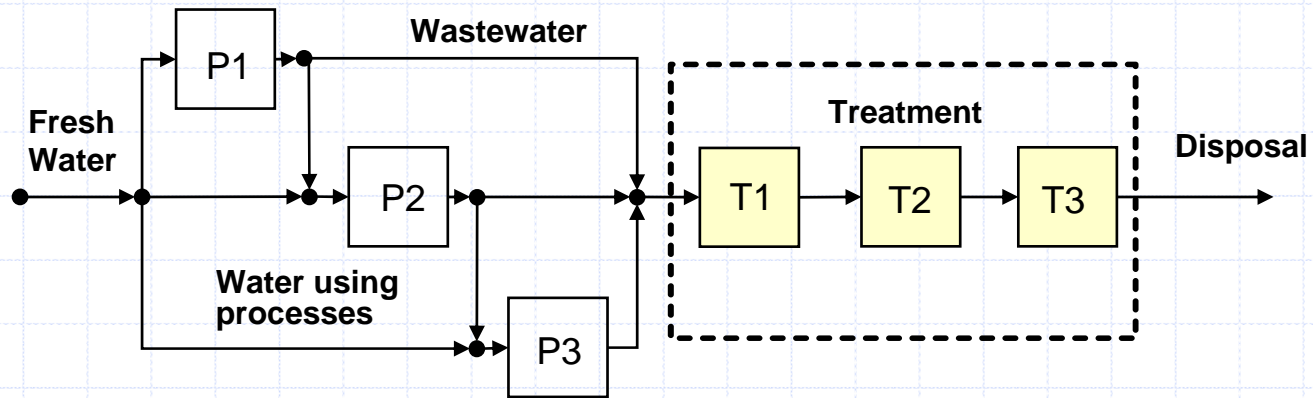
The Performance of a Processing Industry Depends Heavily on an Effective Effluent Treatment System

A Typical Centralized, Sequential Effluent Treatment System



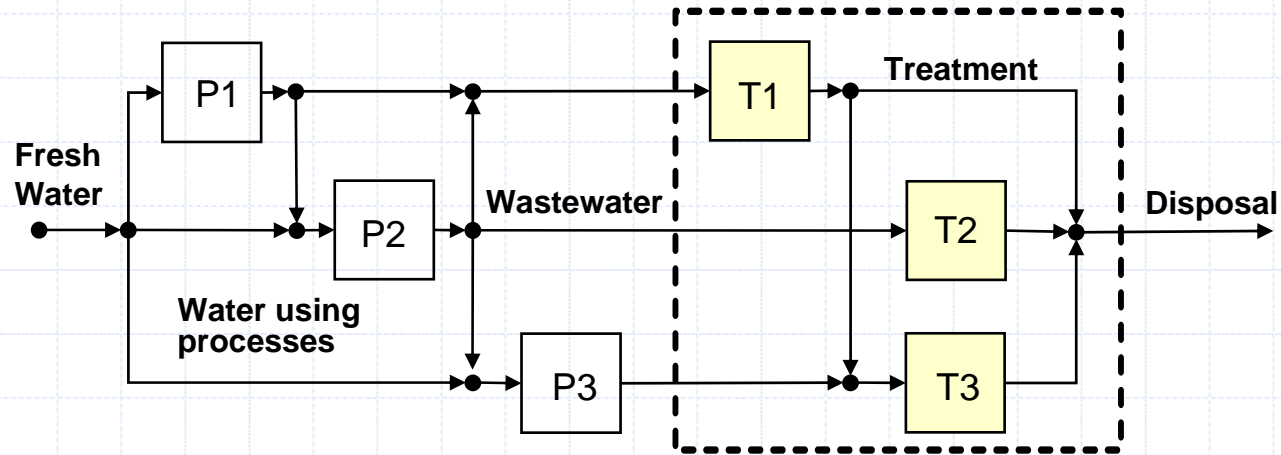
- Primary treatment
Physical treatment processes
- Secondary treatment
Removal of soluble matter
- Tertiary treatment
Effluent polishing to final discharge standards

Main Features of a Sequential Effluent Treatment System



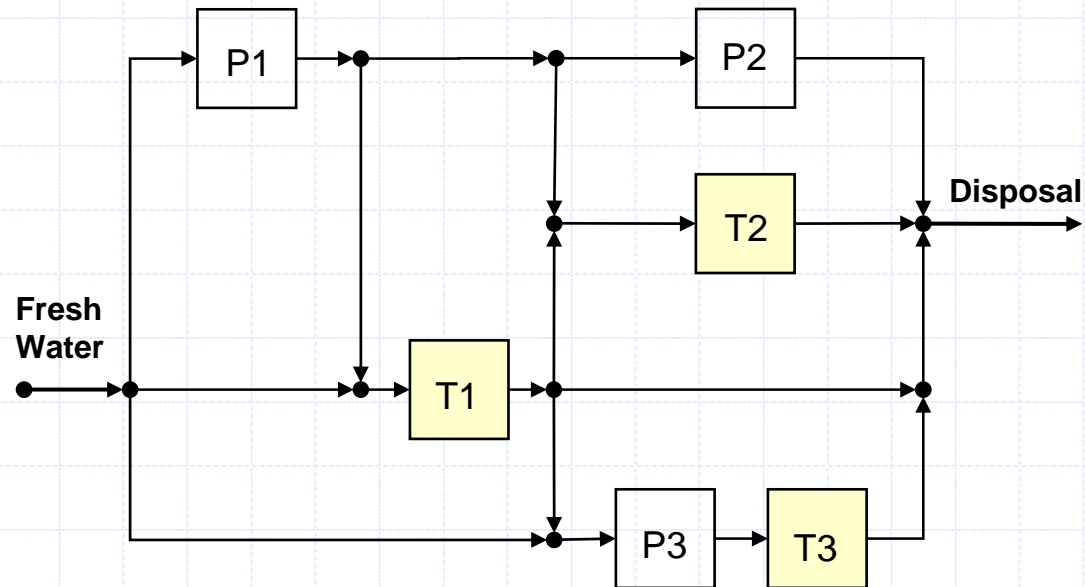
- All effluent streams are mixed before treatment.
- Large volumes of wastewater have to be processed.
- Low concentration of contaminants in treatment units.

A Distributed Effluent Treatment System



- Subsets of effluent streams receive specialized treatment.
- Reduced volumes of effluents are processed in treatment units.
- Accounts for differences in concentrations of contaminants in the various effluent streams.

A Decentralized, Distributed Effluent Treatment System

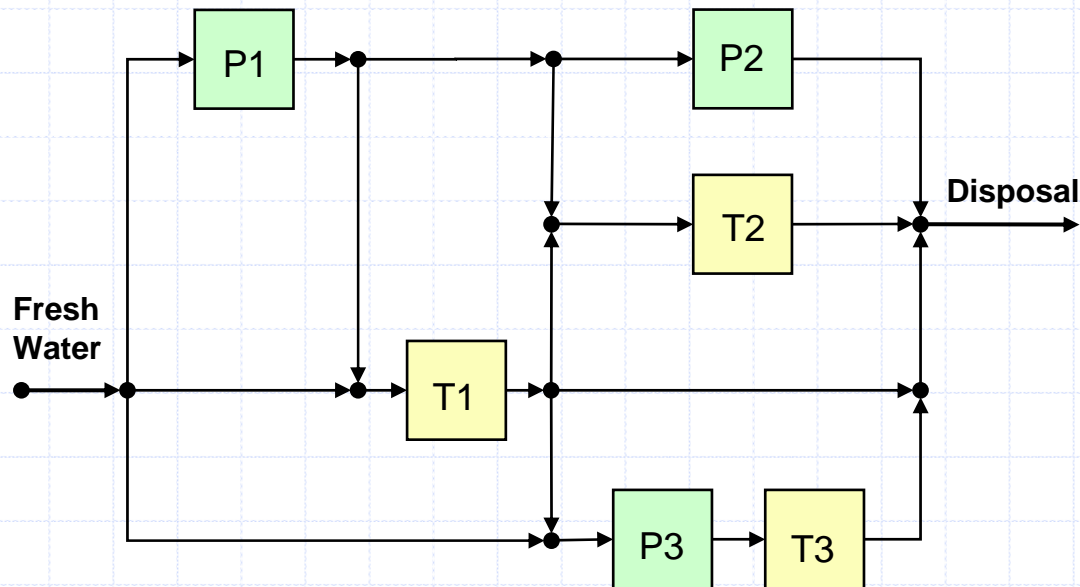


- Targets specific types of contaminants at the source.
- Accounts for different costs between particular treatments.
- Costs of expensive treatment processes are reduced.

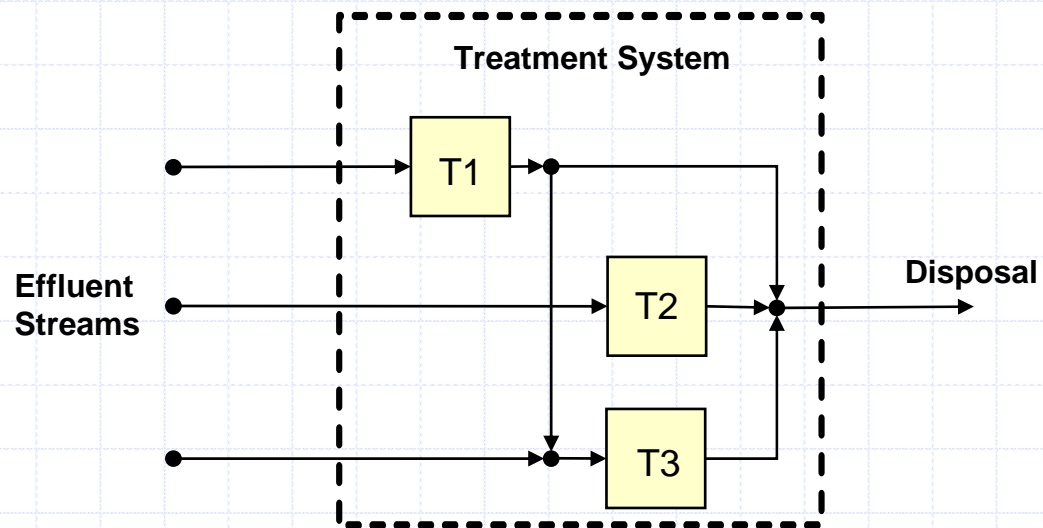
Synthesis of Integrated Water Systems

Simultaneous synthesis of the water allocation, and the effluent treatment networks

- All the water using processes and water treatment operations are integrated into a single system.
- The total cost of freshwater consumption and wastewater treatment is minimized.



Synthesis of Distributed Effluent Treatment Systems



Problem Statement

Given

- A set of effluent streams,

$$i \in I \longrightarrow S_i \quad i \in I$$

- A set of contaminants present in the effluent streams,

$$j \in J \longrightarrow C_{i,j} \quad i \in I, j \in J$$

- A set of treatment plants,

$$k \in K \longrightarrow R_{j,k} \quad j \in J, k \in K$$

- Treatment cost information,

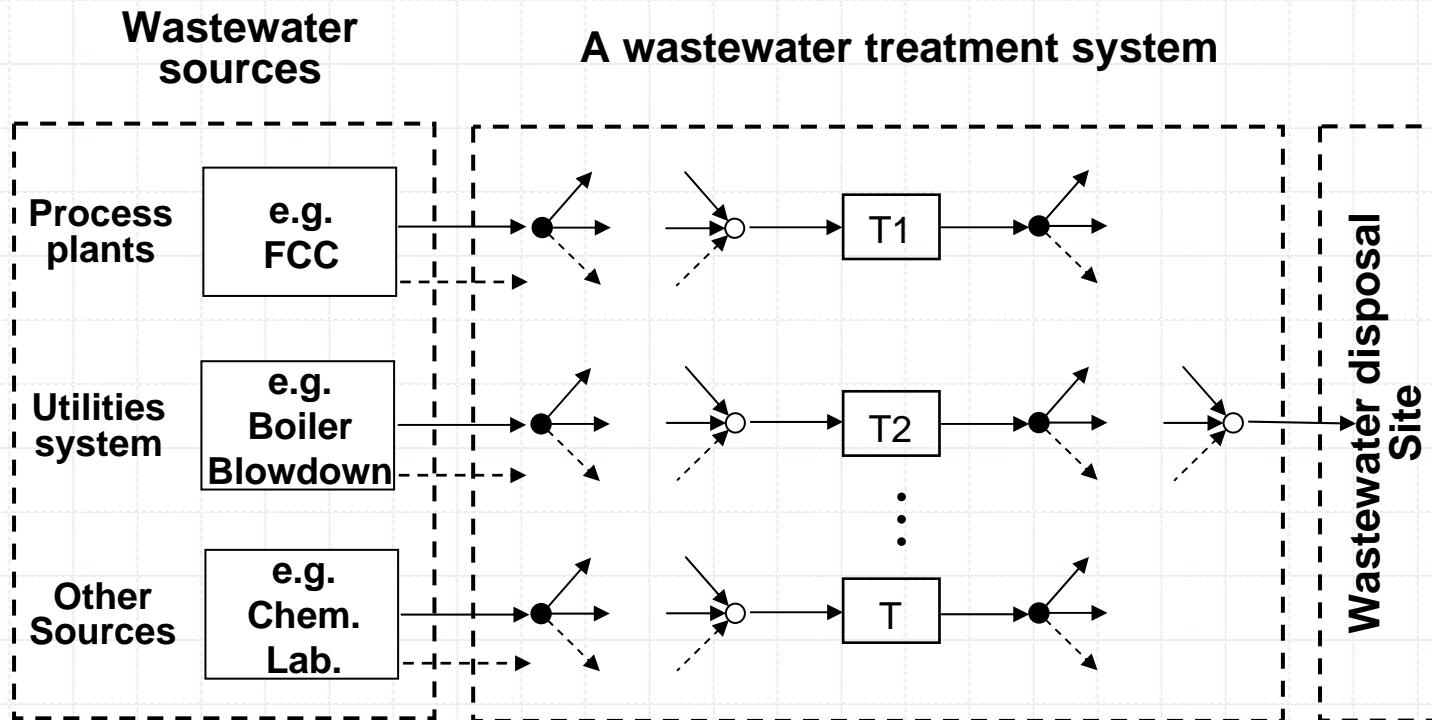
$$(CC_k + CO_k) t_k^\beta \quad k \in K$$

- The task of reducing the concentrations of all the contaminants in order to meet environmental limits before the final discharge.

$$c_{j,e} \leq c_{j,e}^U \quad j \in J$$

Determine

The topology and operating flowrates of the wastewater treatment network that will achieve the required removal of contaminants at minimum total cost.



Additional design constraints

- The enforcement of total, partial or no treatment at all for a subset of the wastewater streams.
- The specification of minimum and maximum flowrates through treatment units.

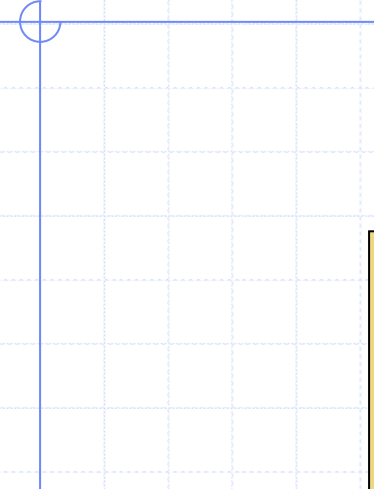
$$t_k^L \leq t_k \leq t_k^U ;$$

- The specification of maximum concentrations of contaminants at the inlet of treatment units.

$$cin_{j,k} \leq cin_{j,k}^U ; \quad cout_{j,k} \leq cout_{j,k}^U ;$$

- The specification of target concentrations of contaminants at the outlet of the treatment units.

$$cout_{j,k} = cout_{j,k}^T ;$$



State of the Art

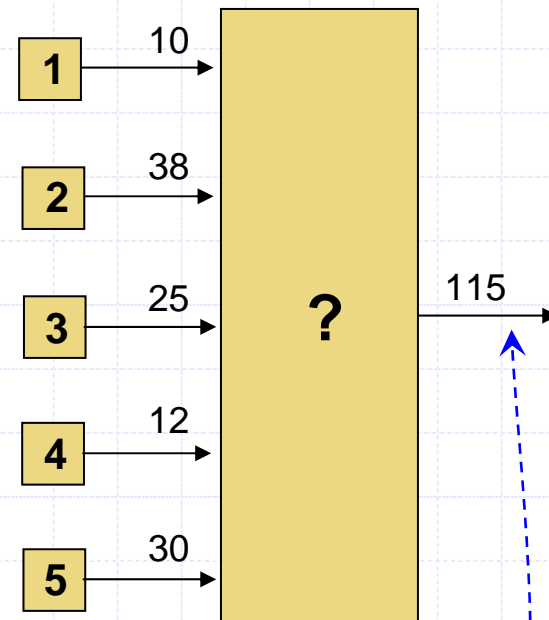
Example 1

A Design Problem Involving a Single Treatment Unit

(Zamora, Hernández and Castellanos 2004)

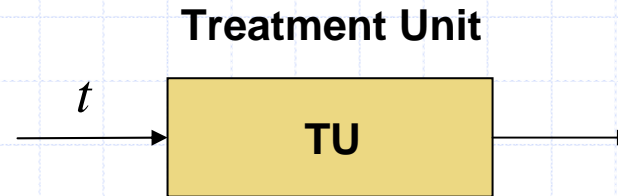
Wastewater stream data for Example 1.

Stream number	flowrate (t/h)	contaminant concentration (ppm)		
		A	B	C
1	10	930	300	400
2	38	350	0	150
3	25	200	700	350
4	12	0	350	300
5	30	700	150	900



Environmental concentration limits (ppm)

A	60
B	50
C	70



Removal ratios (%) for treatment unit

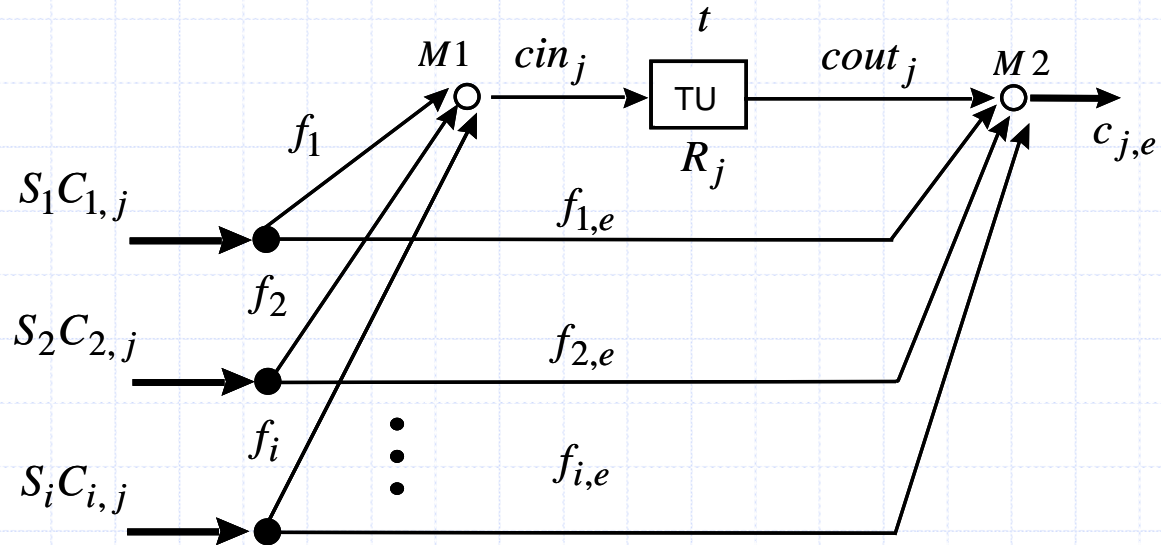
Treatment Unit	contaminant		
	A	B	C
TU	95	85	80

Design constraints

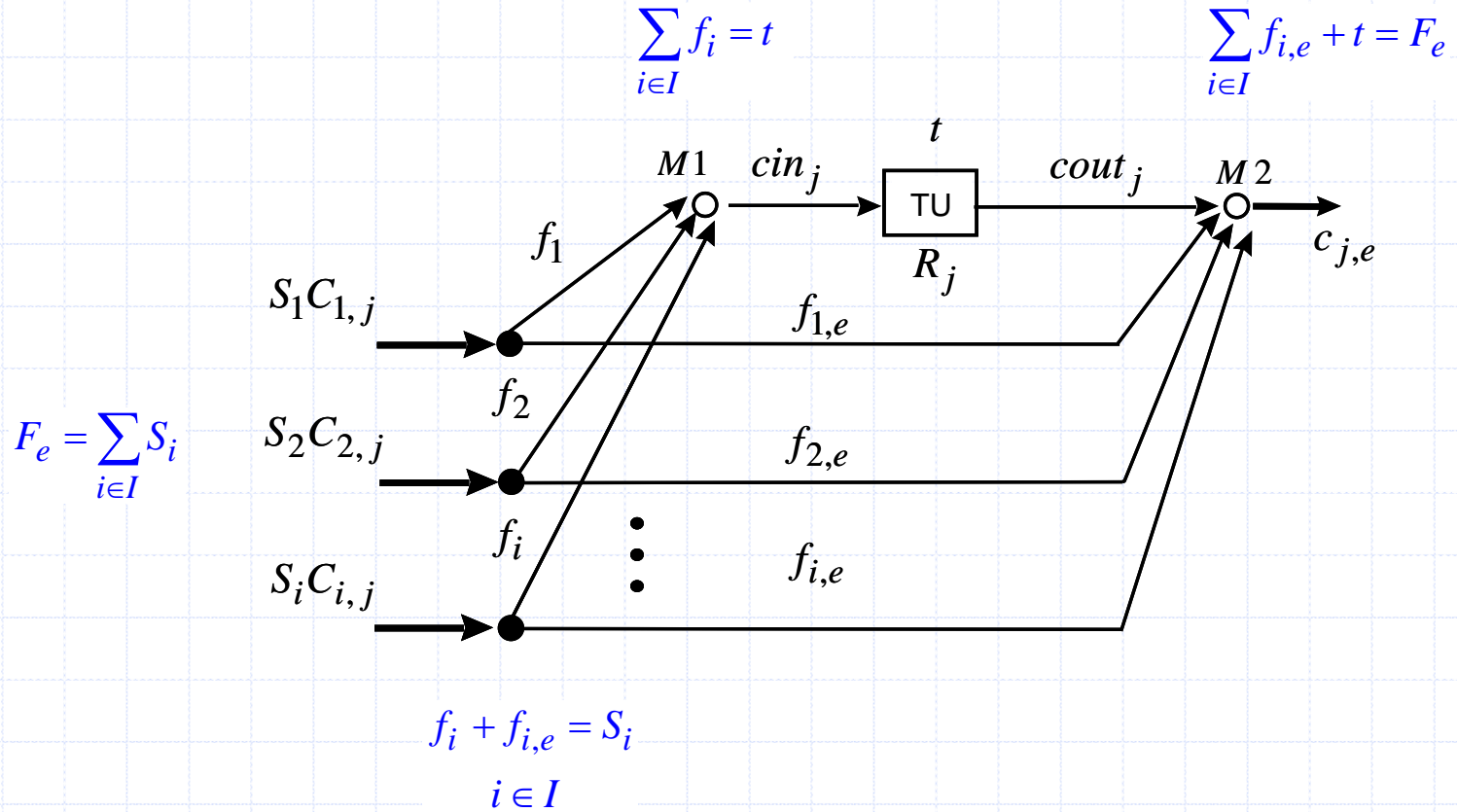
- **Treatment costs are proportional to total treatment flowrate.**
- **Concentration of A at the inlet of the treatment unit should be at most 430 ppm.**
- **Concentration of C at the outlet of treatment unit should be 45 ppm.**
- **At the inlet of treatment unit flowrate of stream 4 should be at least one third of flowrate of stream 3.**

Single-Unit Basic Superstructure for Effluent Treatment

(Zamora, Castellanos and Hernández, 1999; Zamora, Hernández and Castellanos 2004)



No Loss of Wastewater Assumption

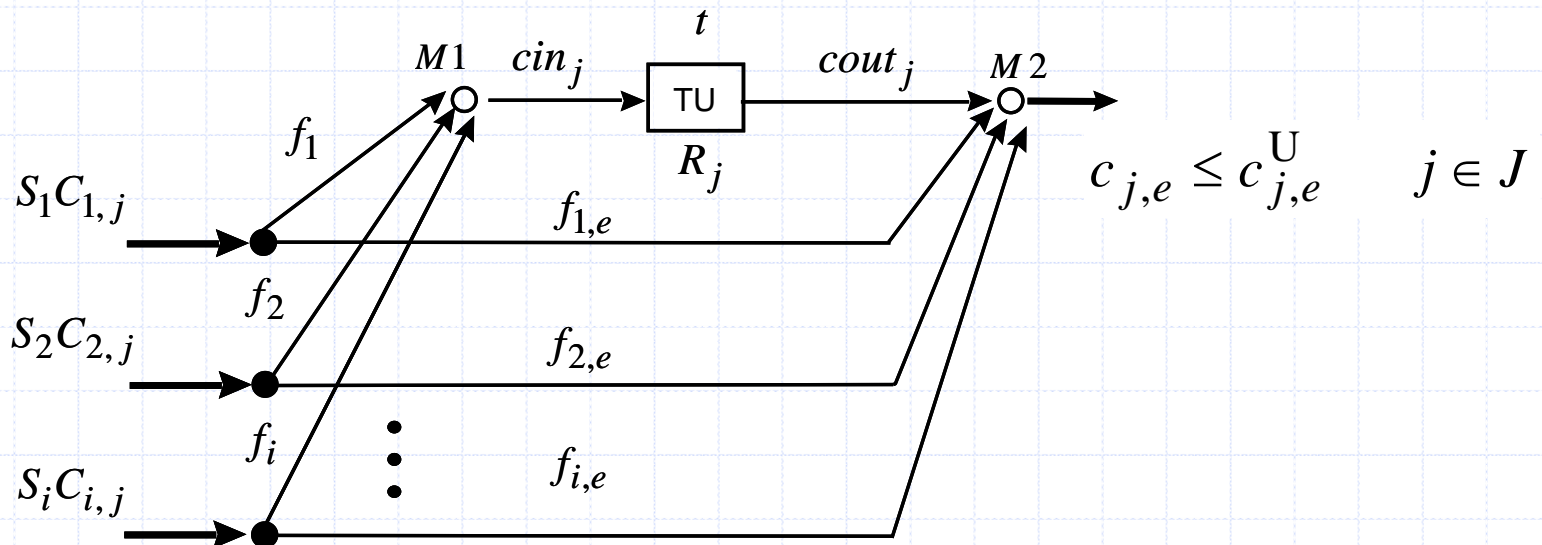


Material Balances for Contaminants

$$\sum_{i \in I} f_i C_{i,j} = t \text{ cin}_j \quad j \in J$$

$$t \text{ cout}_j = t \text{ cin}_j (1 - R_j) \quad j \in J$$

$$\sum_{i \in I} f_{i,e} C_{i,j} + t \text{ cout}_j = F_e c_{j,e} \quad j \in J$$



$$\sum_{i \in I} f_{i,e} C_{i,j} + (1 - R_j) \sum_{i \in I} f_i C_{i,j} = F_e c_{j,e} \quad j \in J$$

LP Model for the Solution of Example 1

Minimize $(CC + CO) t$

$$f_i + f_{i,e} = S_i \quad i \in I$$

$$\sum_{i \in I} f_{i,e} C_{i,j} + (1 - R_j) \sum_{i \in I} f_i C_{i,j} = F_e c_{j,e} \quad j \in J$$

$$\sum_{i \in I} f_i = t$$

$$\sum_{i \in I} f_i C_{i,j} - t \text{cin}_j^U \leq 0$$

$$\sum_{i \in I} f_{i,e} + t = F_e$$

$$10^3 \Delta m_j^L - R_j \sum_{i \in I} f_i C_{i,j} \leq 0 \quad j \in J$$

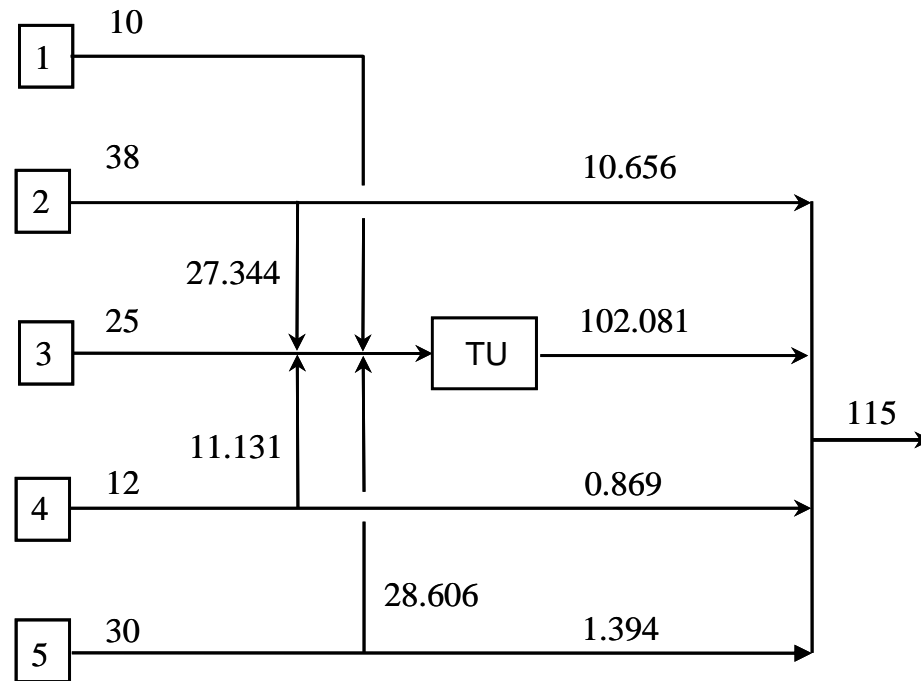
$$0 \leq f_i, f_{i,e} \leq S_i \quad i \in I$$

$$(1 - R_j) \sum_{i \in I} f_i C_{i,j} - t \text{cout}_j^U \leq 0 \quad j \in J$$

$$0 \leq t \leq F_e$$

$$F_e = \sum_{i \in I} S_i$$

Optimal Solution of Example 1



Design of Distributed Wastewater Treatment Networks Involving Two or More Treatment Units

- **Water pinch approach**

Wang and Smith, 1994.

Kuo and Smith, 1997.

- **Approaches based on the optimization of a network superstructure.**

Takama, Kuriyama, Shiroko and Umeda, 1980, 1981.

Zamora and Grossmann, 1998.

Galan and Grossmann, 1998.

Alva-Argáez, Kokossis and Smith, 1998.

Huang, Chang, Ling and Chang, 1999.

Benko, Rév and Fonyó, 2000.

Tsai and Chang, 2001.

Lee and Grossmann, 2003.

Hernández-Suárez, Castellanos-Fernández and Zamora, 2004.

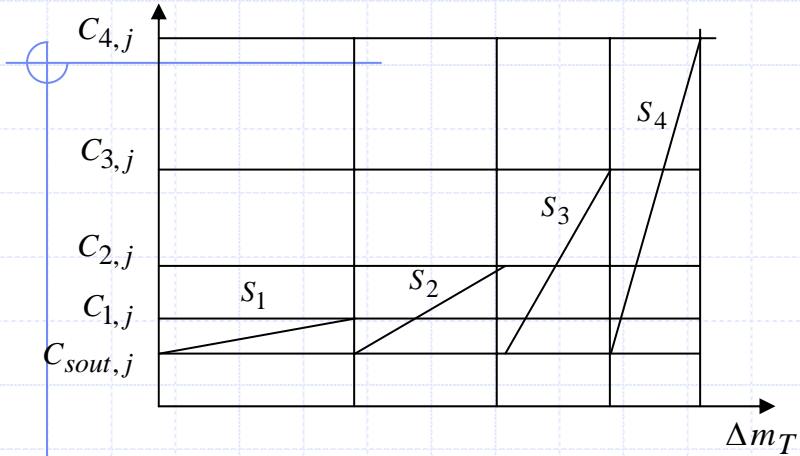
Gunaratnam, Alva-Argáez, Kokossis, Kim and Smith, 2005.

Water Pinch Approach

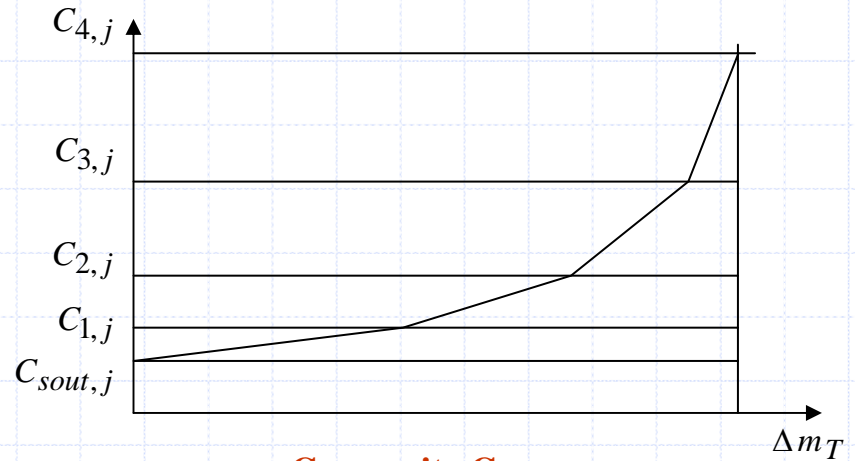
(Wang and Smith 1994; Kuo and Smith, 1997)

- **TARGETING.**
Minimum effluent treatment flowrates through treatment plants are computed.
- **SUBNETWORKS DESIGN.**
Alternative minimum treatment flowrate subnetworks are developed to accomplish the removal of particular contaminants.
- **SUBNETWORK SELECTION.**
The subnetwork exhibiting the least exergy loss due to mixing is included in the overall network design.
- **RETARGETING.**
The set of streams that emerge from the selected subnetwork is considered in a re-targeting step for the removal of the remaining contaminants.

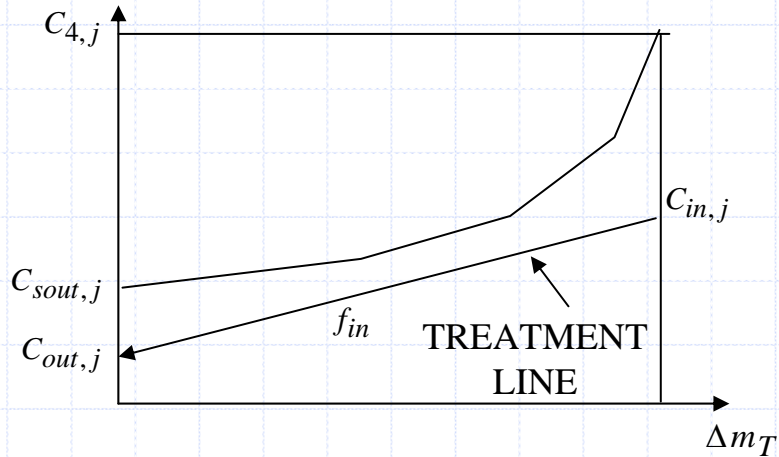
Targeting Stage



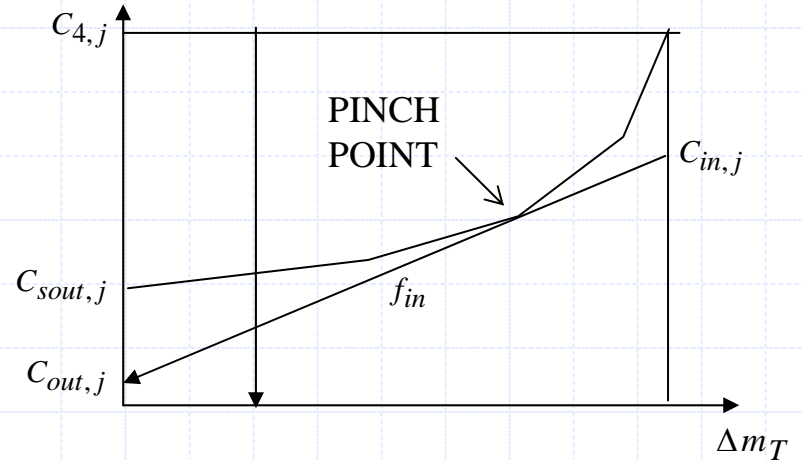
Mass of contaminant j to be removed



Composite Curve

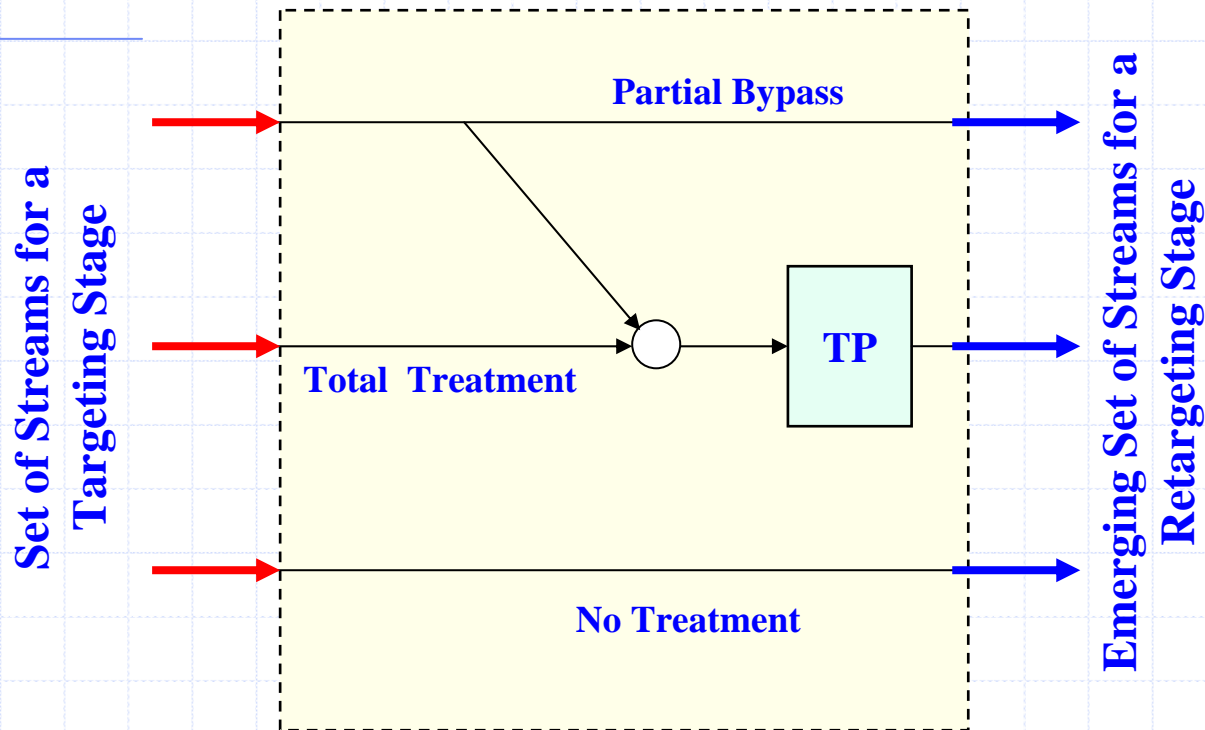


Composite curve and a treatment line



Treatment line for minimum treatment flowrate

Development of Treatment Subnetworks



Design Rules

(Wang and Smith 1994; Kuo and Smith, 1997)

- Streams above pinch are totally treated.
- Streams at pinch are partially treated.
- Streams below pinch are not treated at all.

Example 2

Design of a Distributed Effluent Treatment System

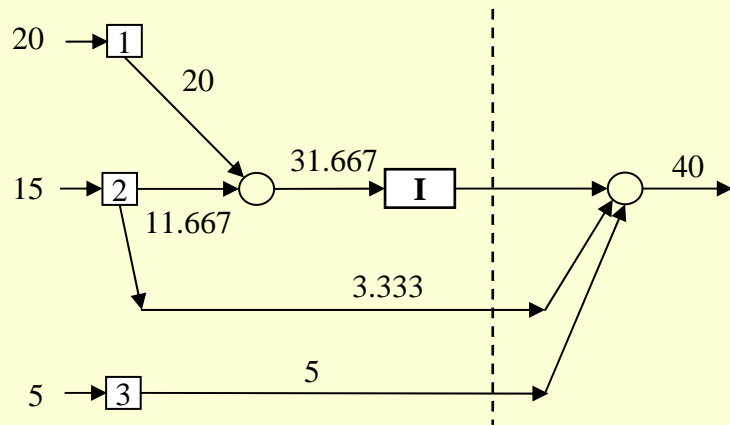
(Kuo and Smith, 1997)

Stream Number	Flowrate (t/h)	Contaminant		
		A (ppm)	B (ppm)	C (ppm)
1	20	600	500	500
2	15	400	200	100
3	5	200	1000	200

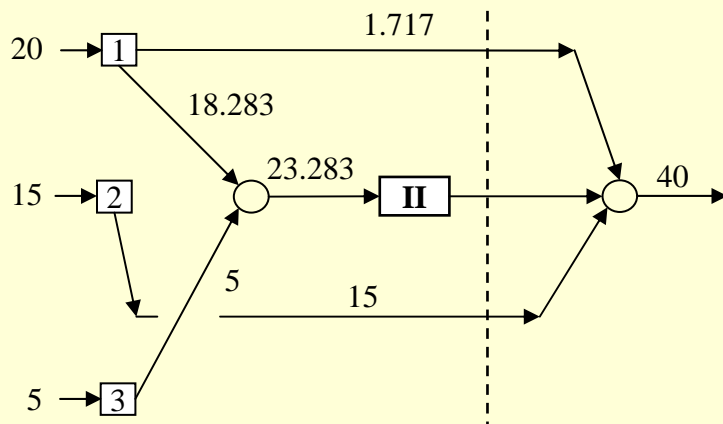
Process Number	Contaminant Removal Ratio (%)		
	A	B	C
I	90	0	0
II	0	99	0
III	0	0	80

- Treatment costs are proportional to total treatment flowrate.

Subnetwork for Contaminant A

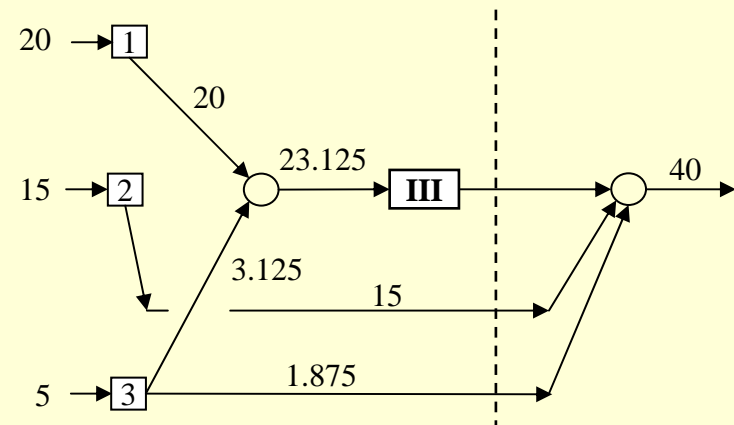


Subnetwork for Contaminant B

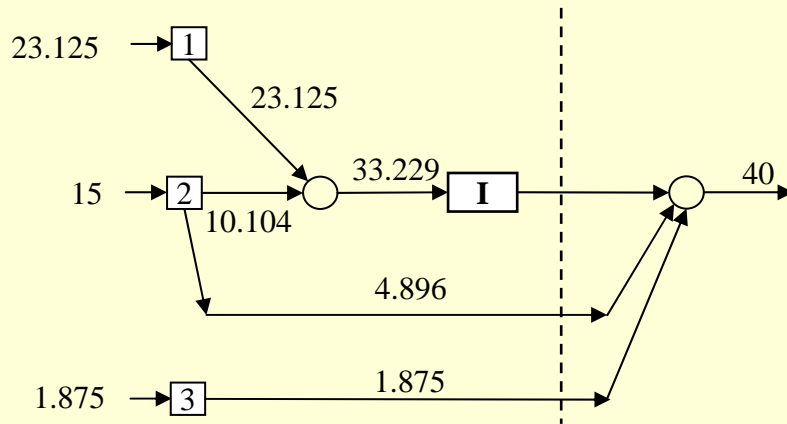


Minimum Treatment Flowrate Subnetworks (t/h)

Subnetwork for Contaminant C

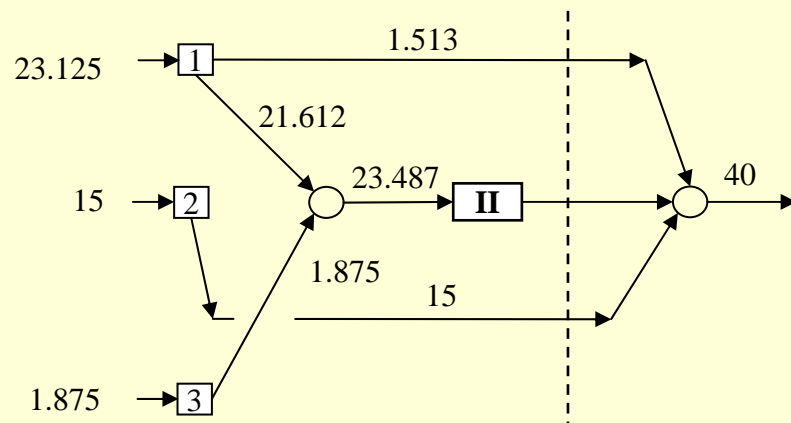


Subnetwork for Contaminant A

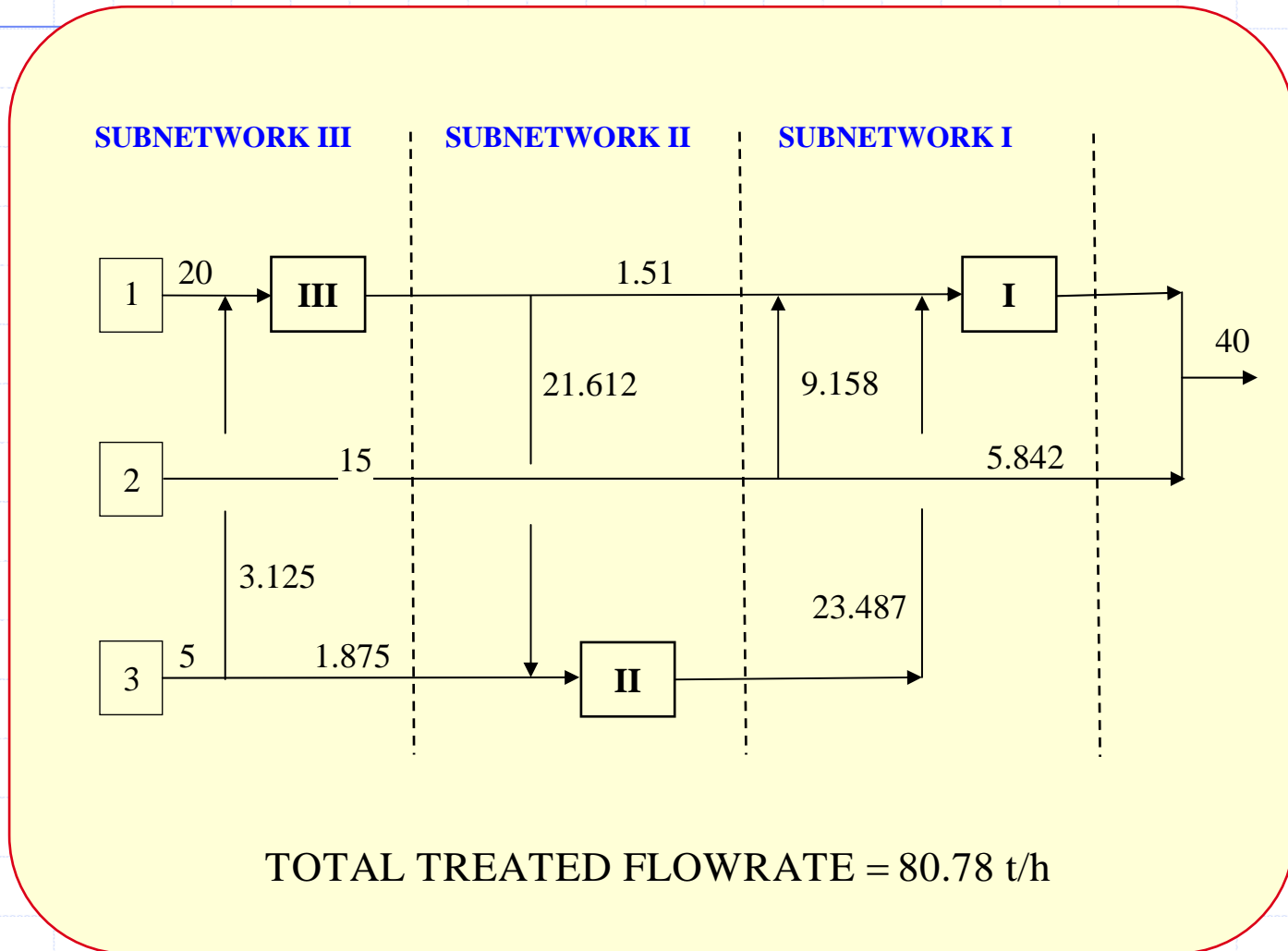


Retargeting

Subnetwork for Contaminant B



Optimal Design for the Distributed Effluent Treatment System

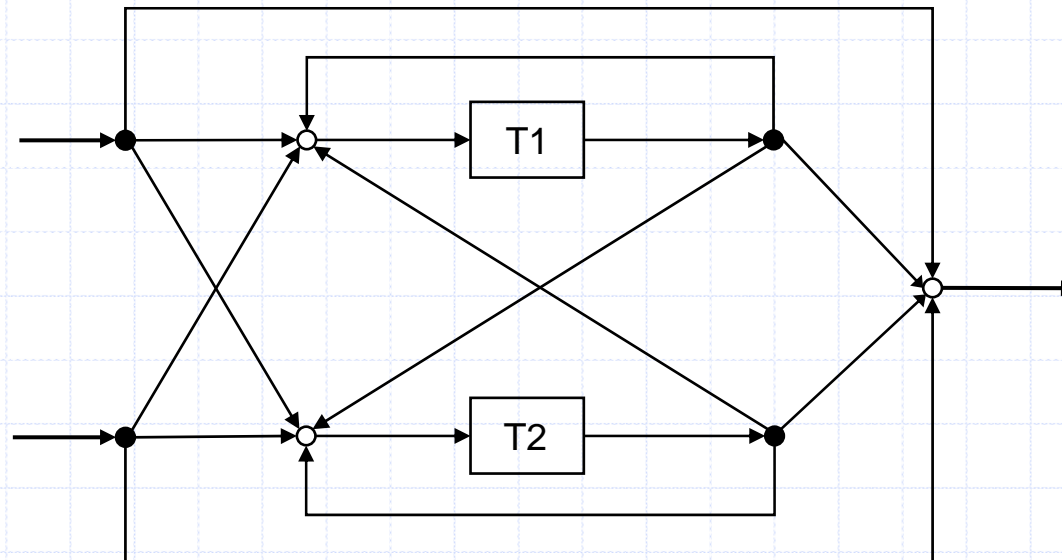


Some Limitations of the Water Pinch Approach

- Due to graphical nature, It is not easy to manage design constraints.
- For multiple-unit, multicontaminant problems the minimum total treatment flowrate target is not rigorous.
- When two or more treatment units are capable of removing a given contaminant, extra simplifying assumptions have to be made in order to resolve the issues of treatment unit arrangement, and mass load distribution.
- Suboptimal network designs might be obtained.

Superstructure Based Approaches for the Synthesis of Distributed Effluent Treatment Systems

- A network superstructure is utilized.
- The optimization of the superstructure removes the redundant features of the design.



Takama, Kuriyama, Shiroko and Umeda (1980)

First NLP approach reported for the simultaneous synthesis of the water allocation, and the effluent treatment networks.

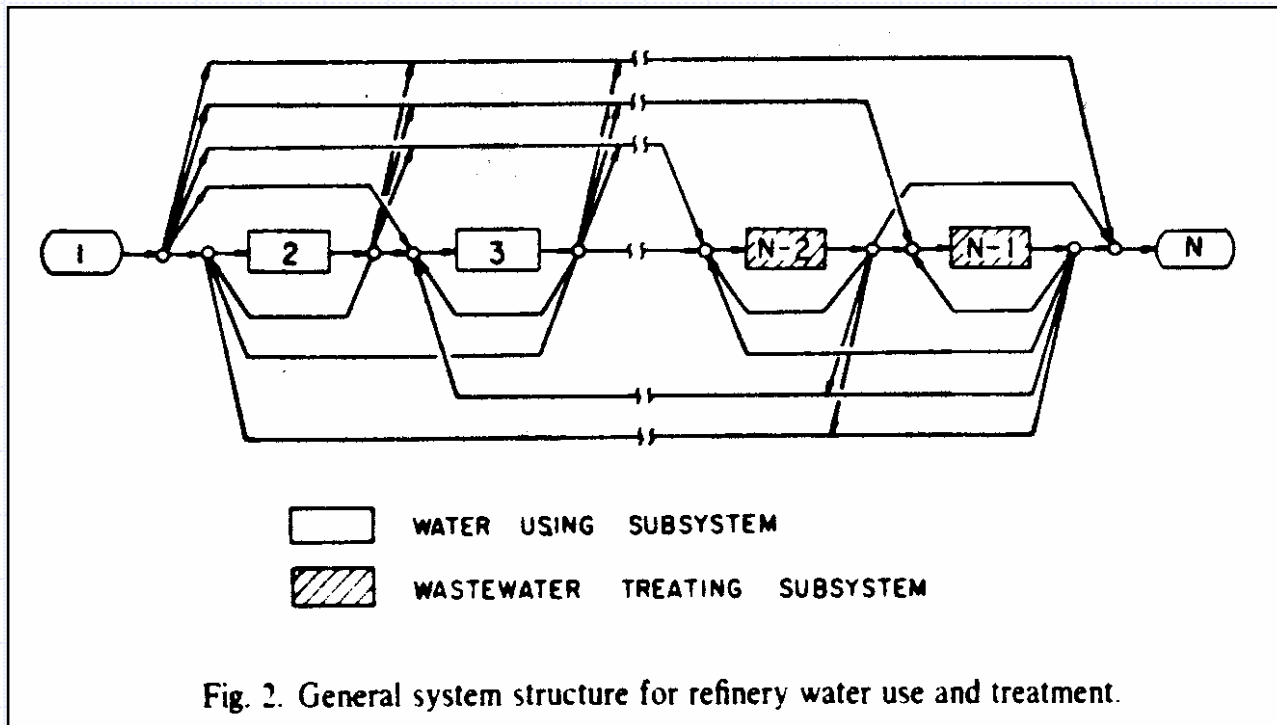
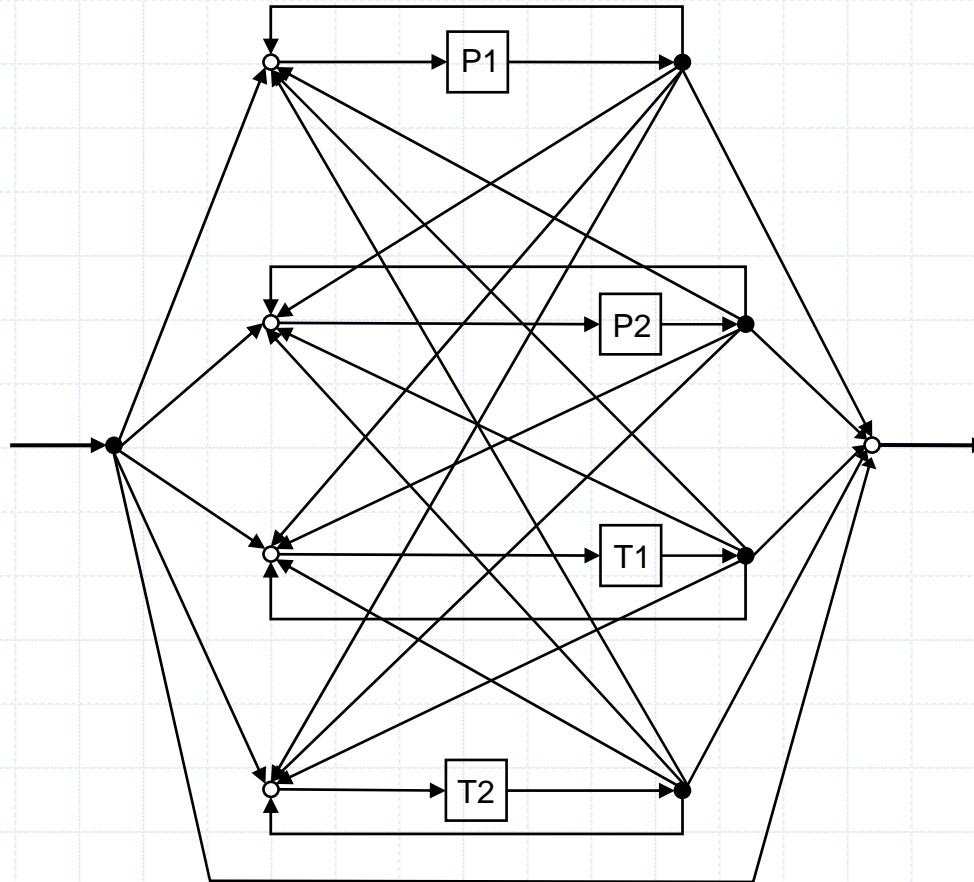


Fig. 2. General system structure for refinery water use and treatment.

The network superstructure by Takama et al. includes possibilities for water reuse, regeneration-reuse, recycling and treating.



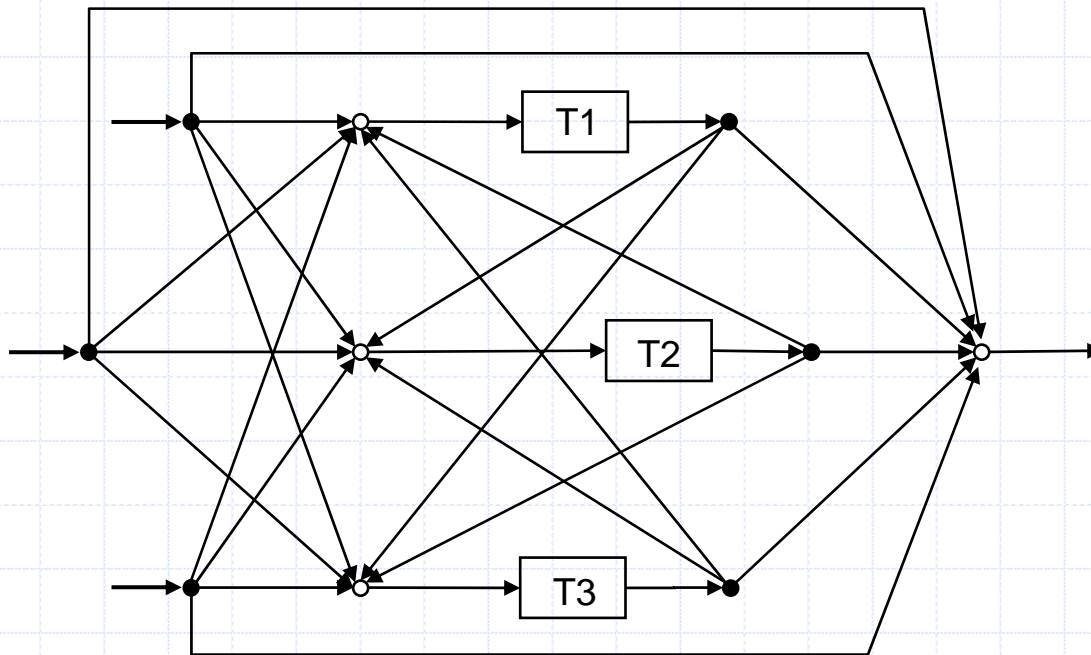
An Obstacle for Superstructure Based Approaches

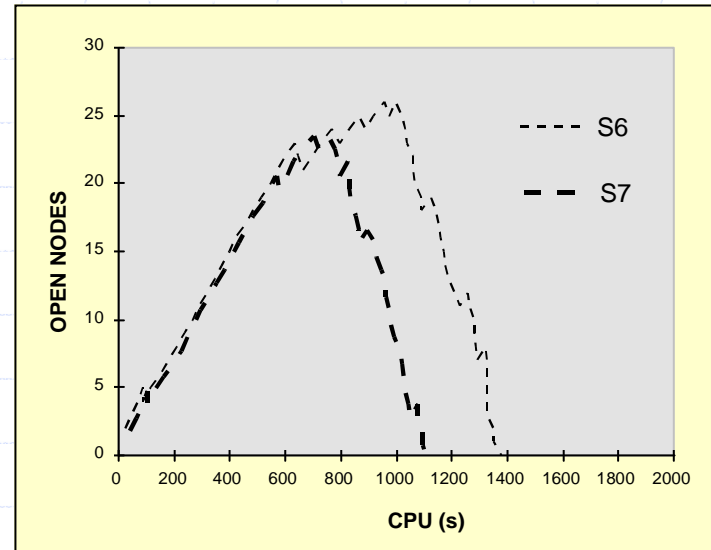
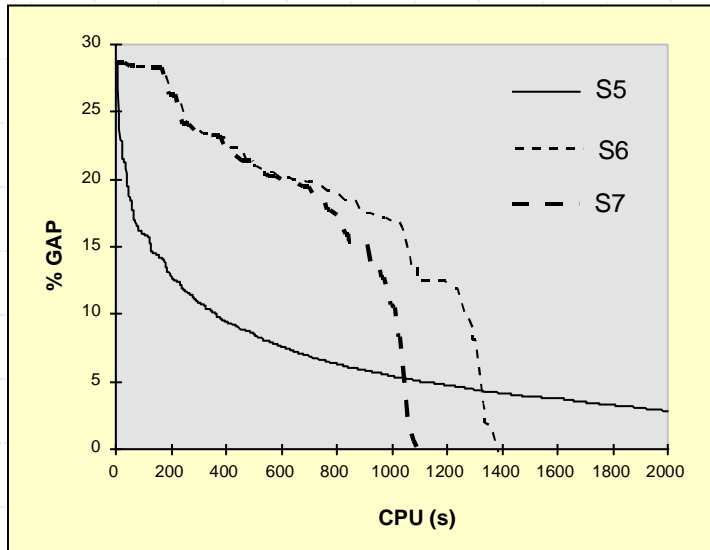
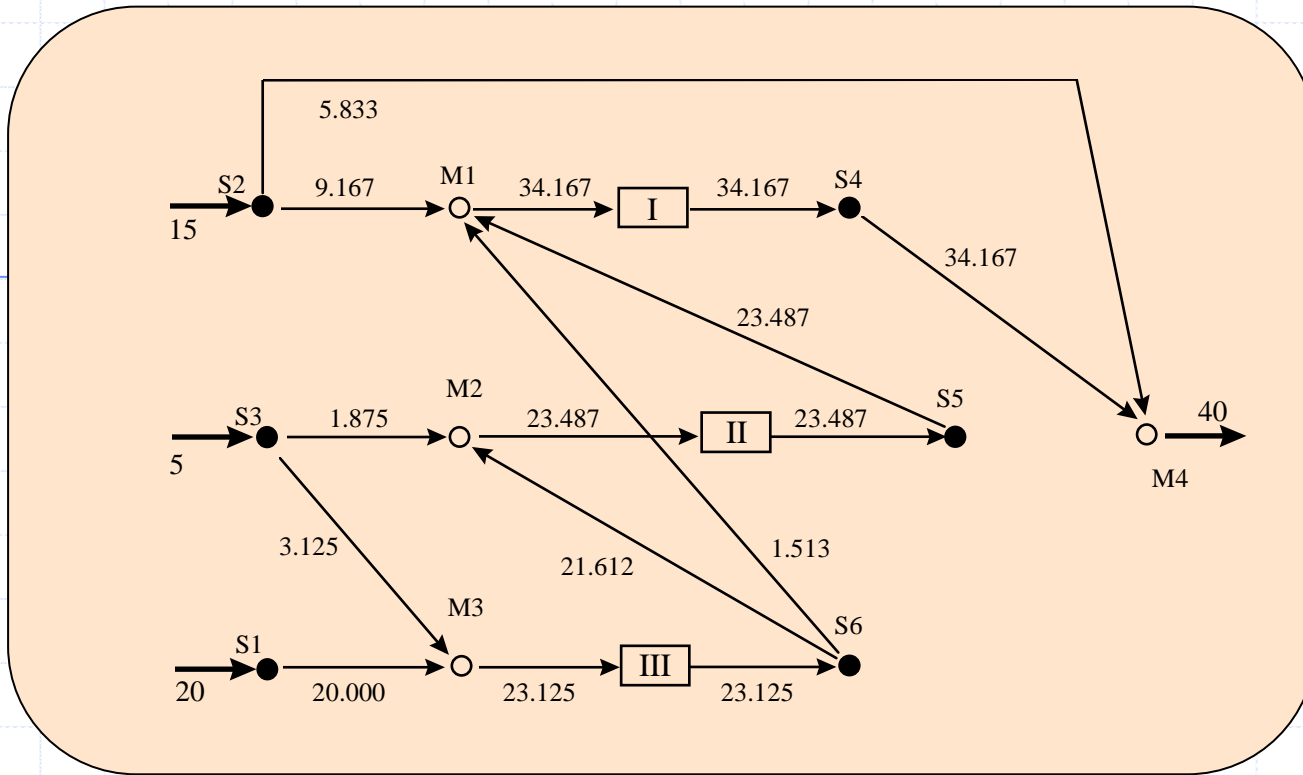
Simultaneous design techniques for the synthesis of distributed wastewater treatment systems (and integrated water management networks too!) rely on the solution of nonconvex mathematical models.

The development of globally optimal solutions for nonconvex mathematical models constitutes a challenging problem.

Zamora and Grossmann (1998)

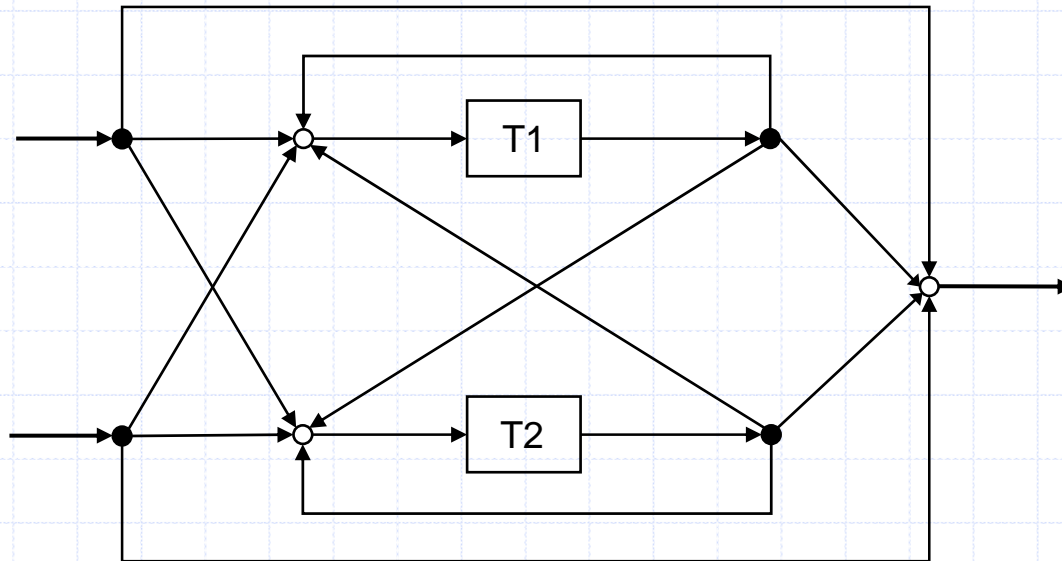
The branch and contract algorithm is utilized for the global optimization of Problem Example 2.



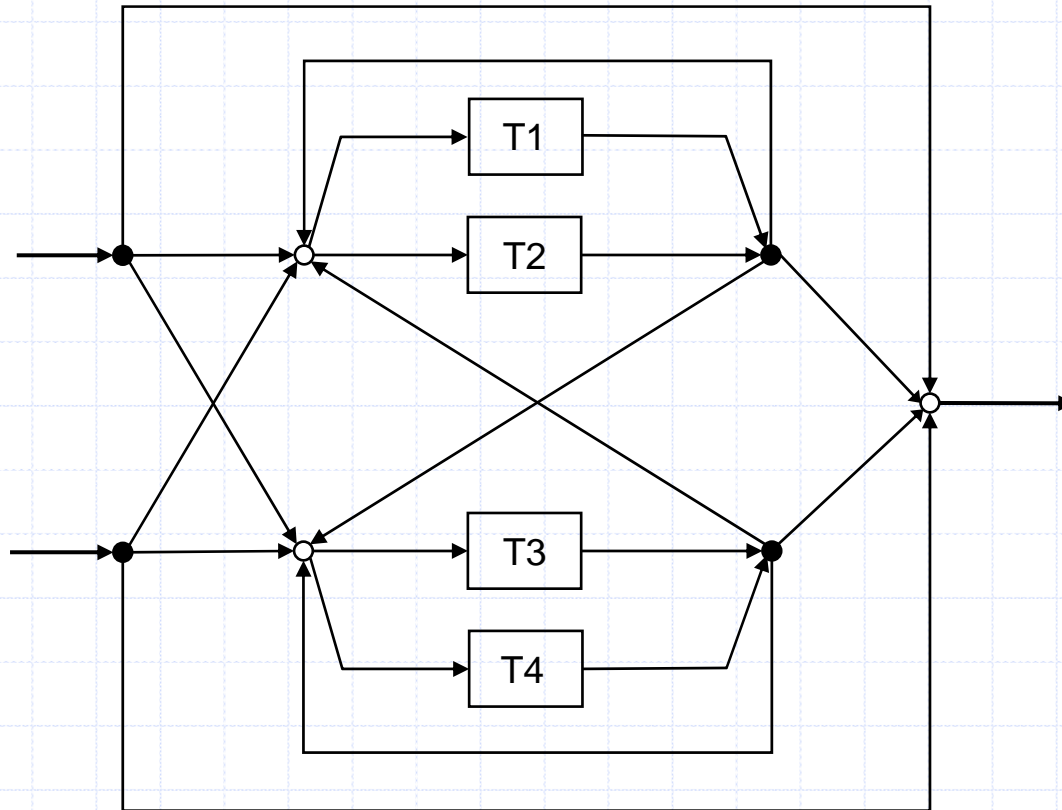


Galan and Grossmann (1998)

A multi-start solution procedure based on LP relaxations to generate starting points for the NLP solver is utilized.



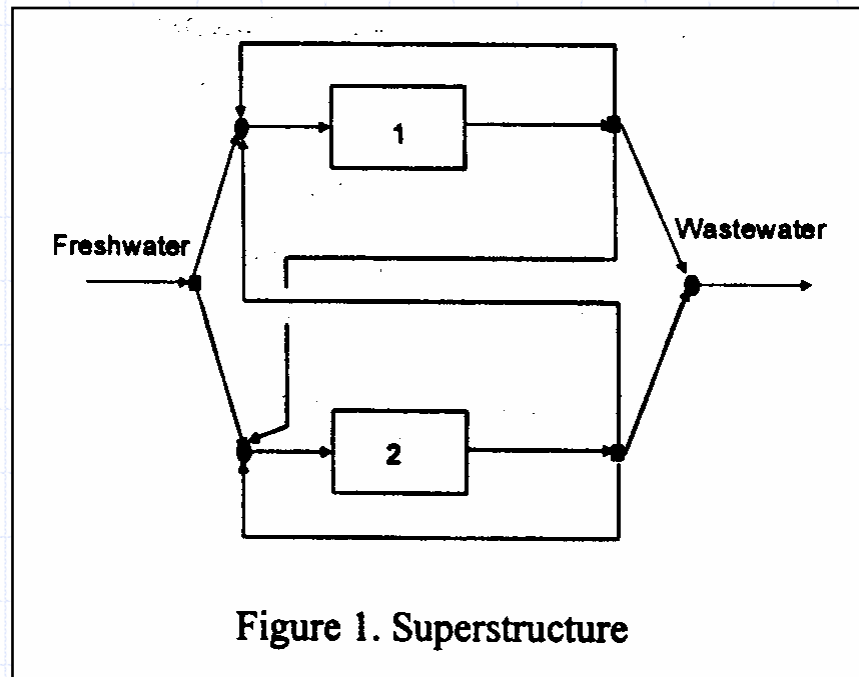
An MINLP model is also developed to account for alternative treatment technologies in the synthesis of distributed wastewater treatment networks.



Alva-Argáez, Kokossis, and Smith (1998)

Alva-Argáez (1999)

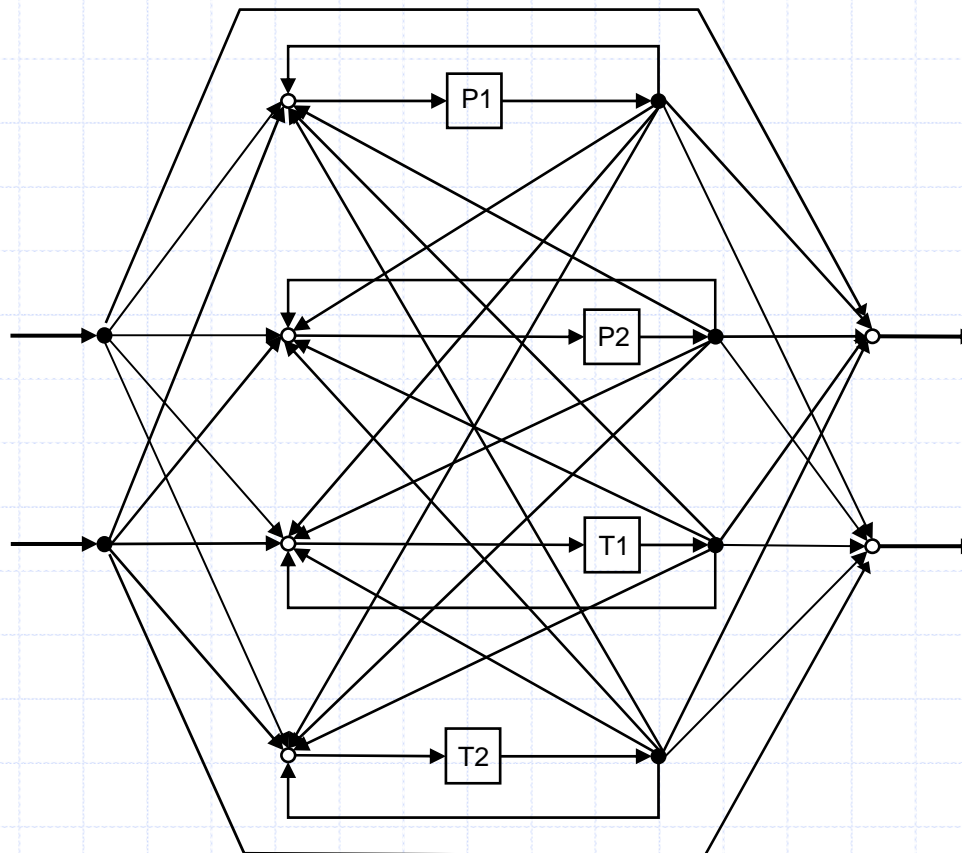
MINLP approach for the simultaneous synthesis of the water allocation, and the effluent treatment networks.

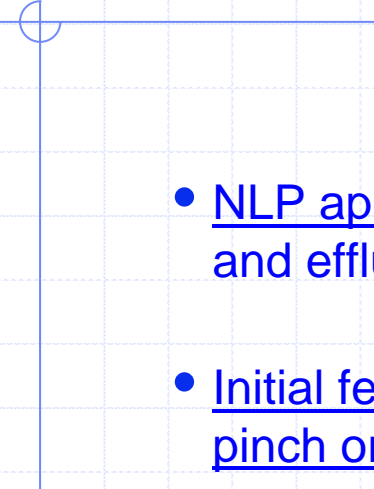


The solution procedure is based on the decomposition of the original MINLP problem into a sequence of MILP problems.

Huang, Chang, Ling and Chang (1999)

The superstructure by Takama et al. is extended by including multiple water sources and sinks, water losses and repeated water treatment units.



- 
- NLP approach for the simultaneous synthesis of the water allocation, and effluent treatment networks.
 - Initial feasible solutions for the NLP model are provided by water pinch or by fixing several key variables at “reasonable” levels.
 - The idea of fixed outlet concentrations of contaminants at outlet of treatment units is introduced.

Benko, Rév and Fonyó (2000)

- Cover-and-eliminate NLP approach for the synthesis of integrated water management networks.
- All candidate system alternatives are covered by including them in a network superstructure.
- The recursive optimization of the network superstructure eliminates units and streams associated with inferior network designs.

Tsai and Chang (2001)

- The work by Huang, Chang, Ling and Chang (1999) is extended.
- The network superstructure is furnished with a set of fictitious mixer units that perform no stream transformation but expand the design search space by providing additional stream mixing and splitting nodes.
- The associated NLP model is solved by utilizing a genetic algorithm.
- Interesting results are presented for the retrofit of a water usage and treatment network in a refinery.

Lee and Grossmann (2003)

Rigorous global optimization algorithm for the solution of bilinear nonconvex generalized disjunctive programming problems.

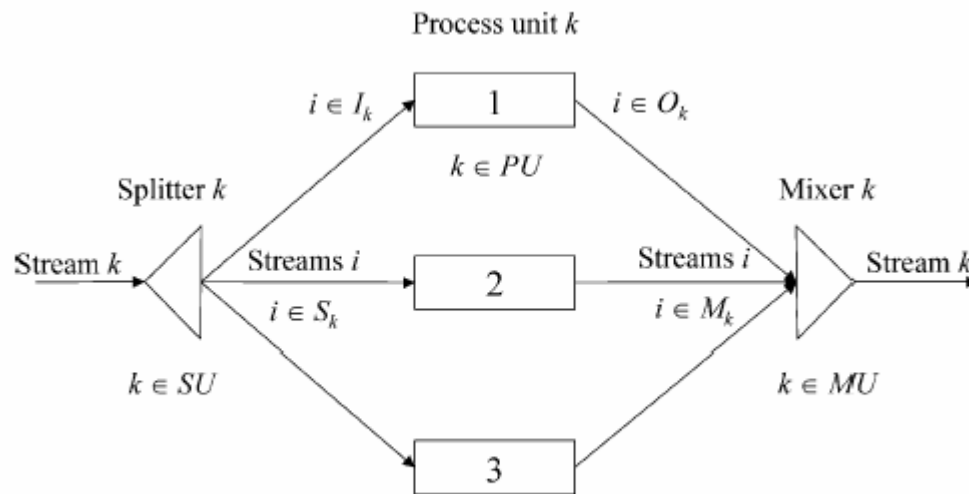
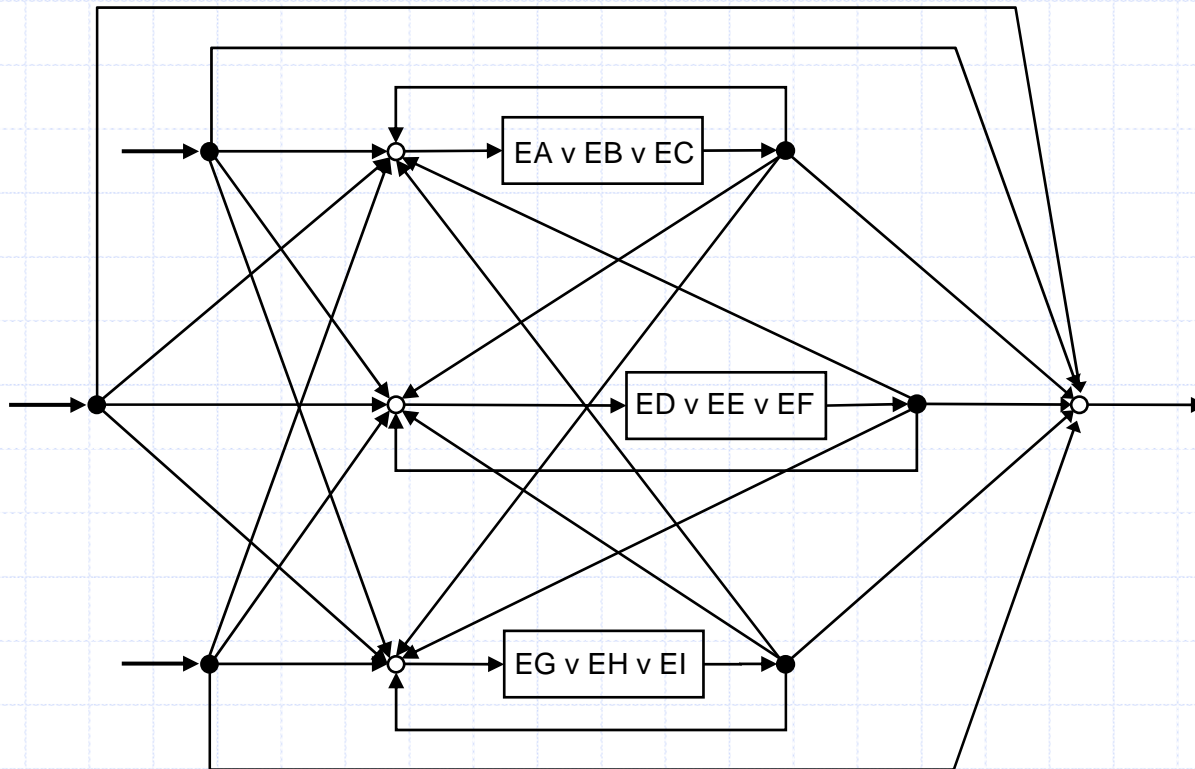


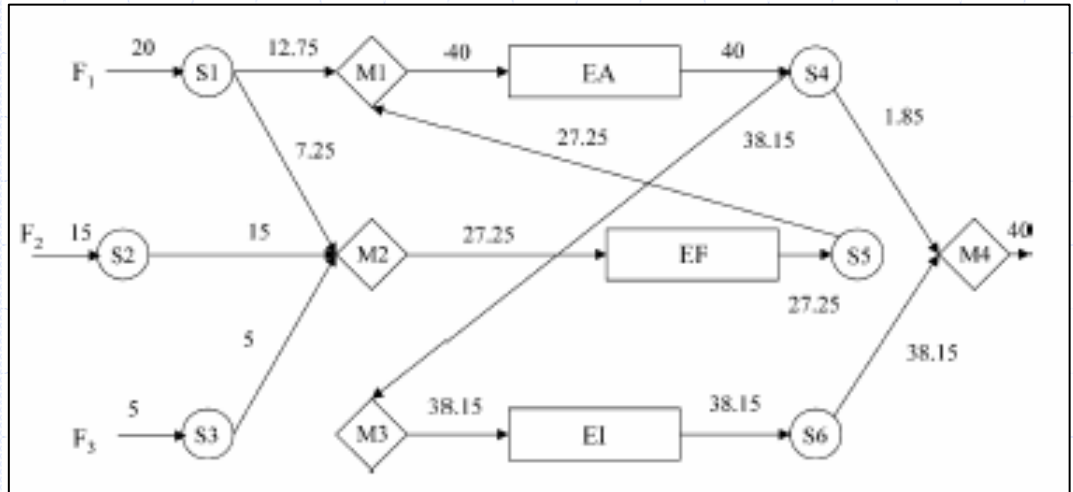
Fig. 1. Superstructure of process networks.

Discrete choices for process networks are expressed as disjunctions, which are relaxed by a convex hull formulation.



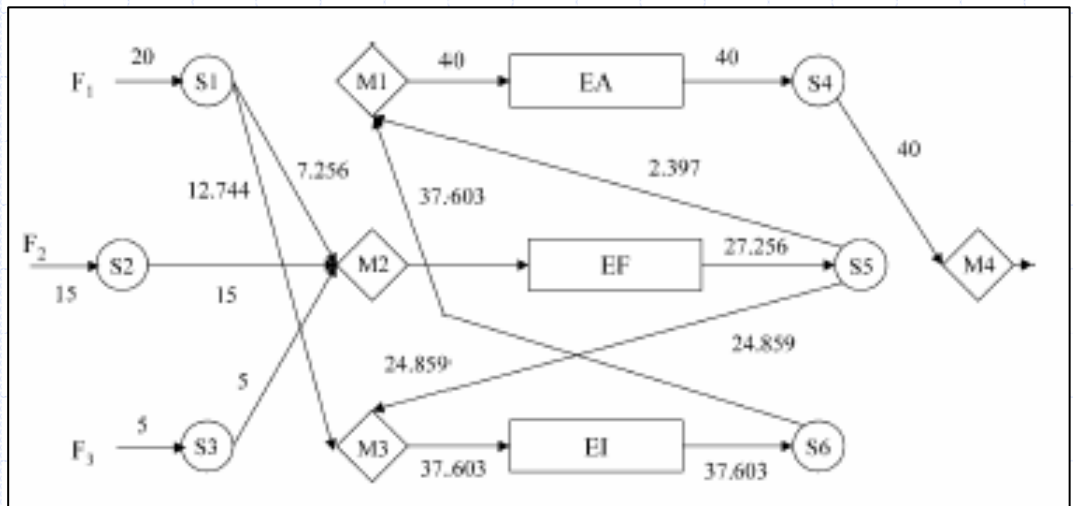
Heuristic solution
Galan and Grossmann (1998)

\$1 697 253



Optimal solution
Lee and Grossmann (2003)

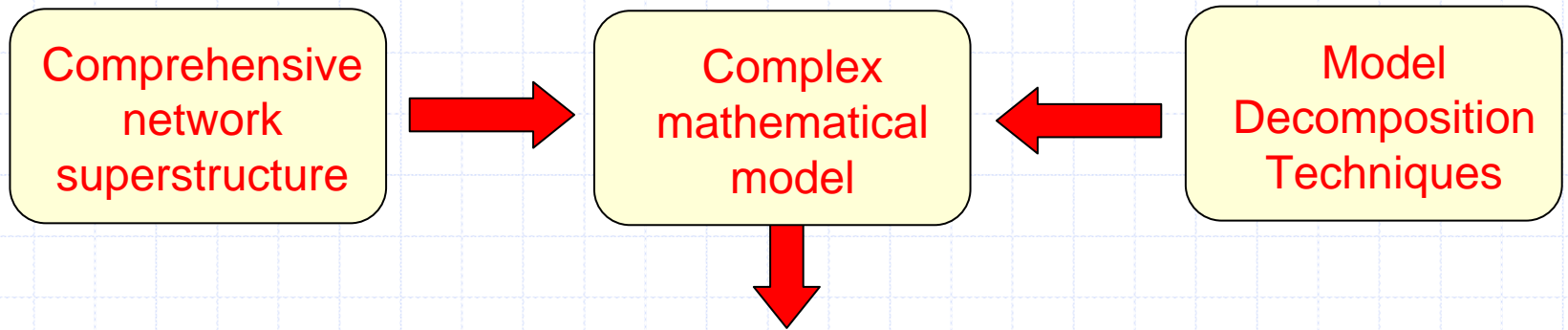
\$1 692 583
(-0.27%)



Gunaratnam, Alva-Argáez, Kokossis, Kim and Smith (2005)

- MINLP model by Alva-Argáez (1999) for the synthesis of integrated water management networks is reformulated.
- Same network superstructure as in Alva-Argáez (1999), and Huang, Chang, Ling and Chang (1999). Multiple water sources and sinks, water losses and gains. Piping and sewer costs are included.
- Network complexity is controlled through constraints on flowrates, maximum number of streams at mixers and costs of piping.
- Solution approach based on the decomposition of MINLP model, and engineering insight to project bilinear terms in a recursive manner.

A Design Paradigm

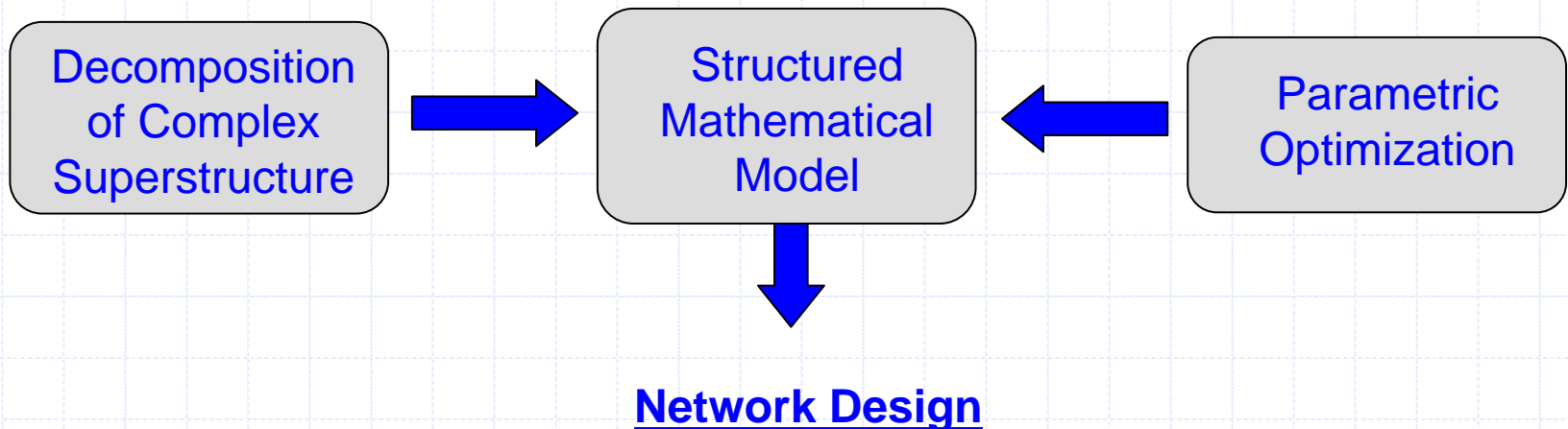


Network Design

Optimal or suboptimal
solution?

Hernández-Suárez, Castellanos-Fernández and Zamora (2004)

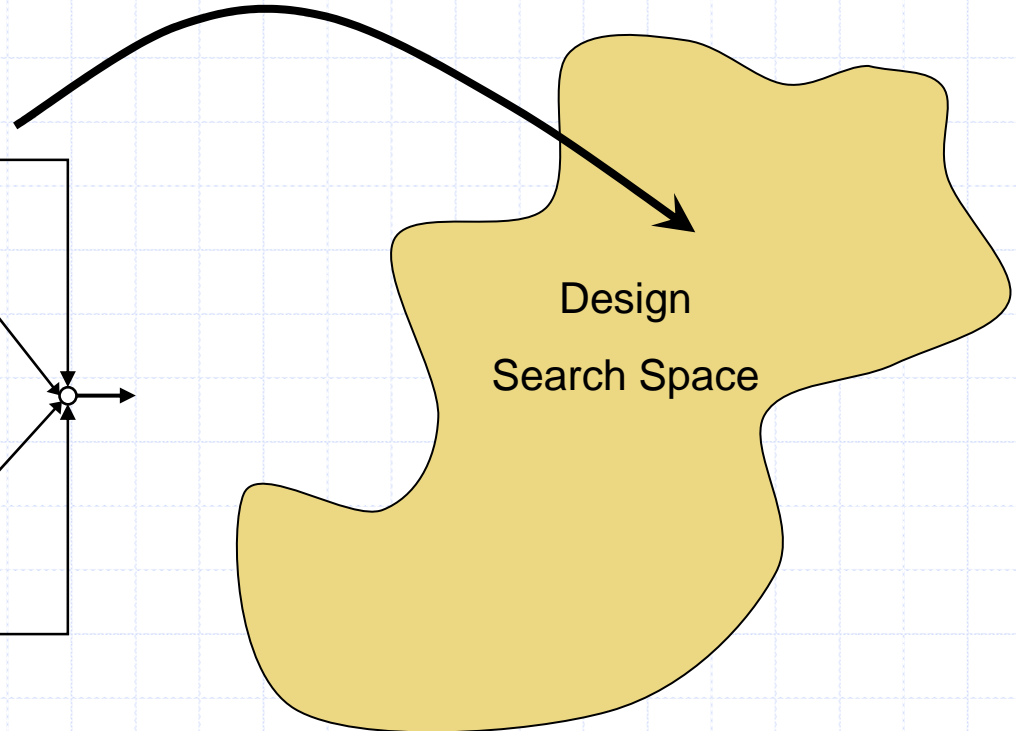
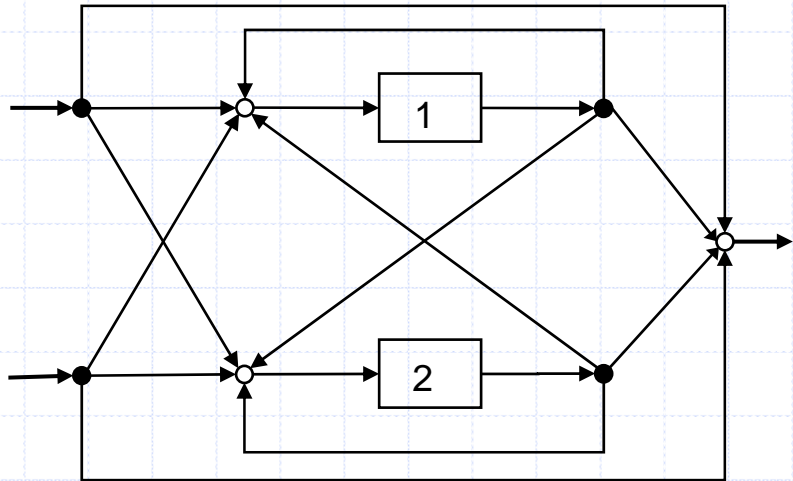
Superstructure Decomposition and Parametric Optimization Approach



How far can go with this approach?

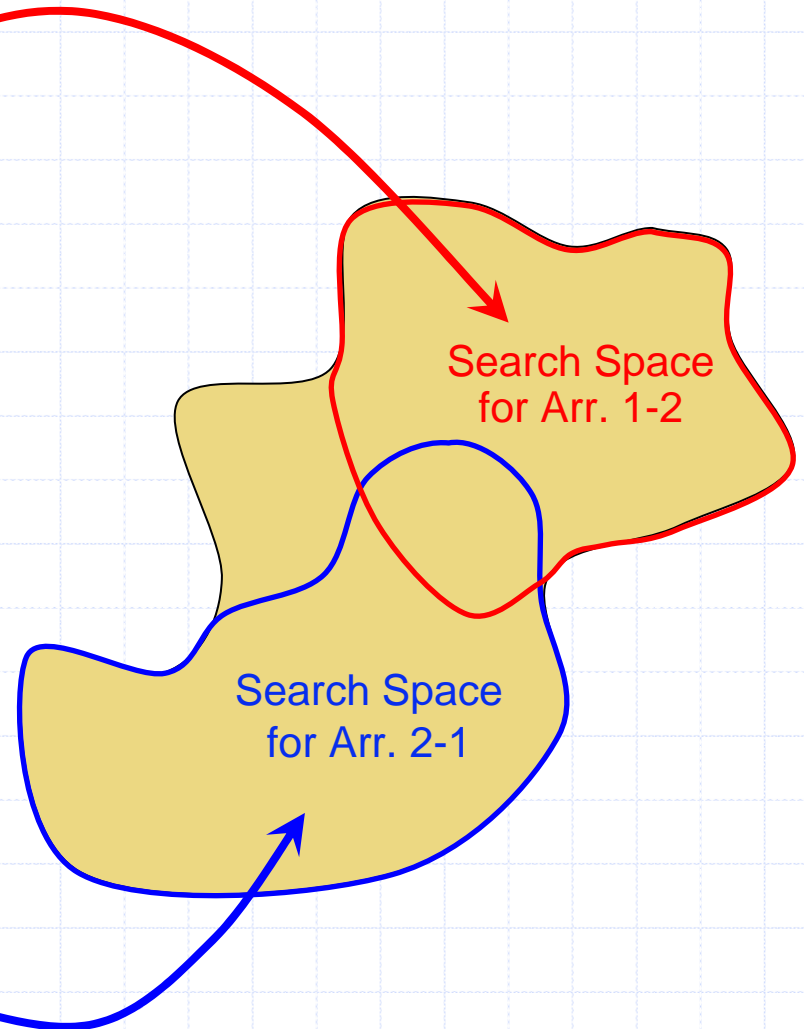
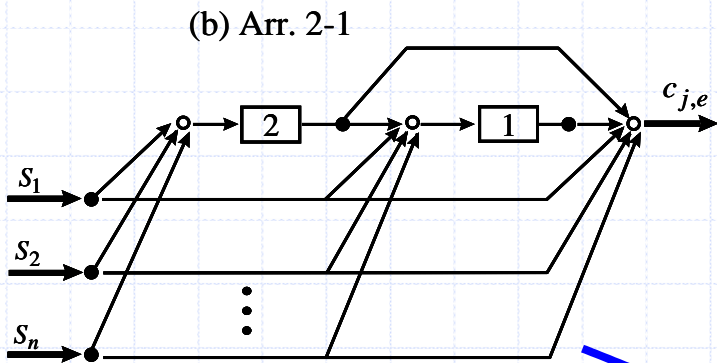
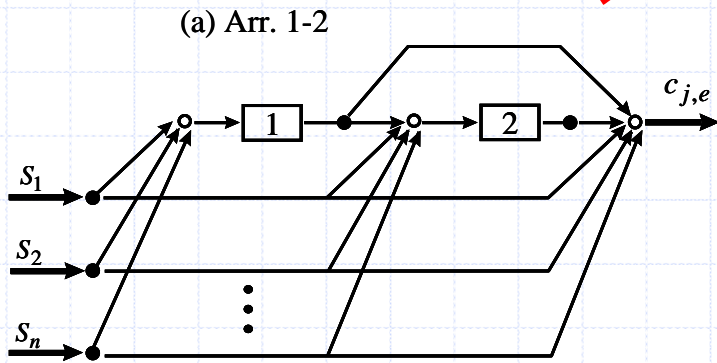
Superstructure Decomposition

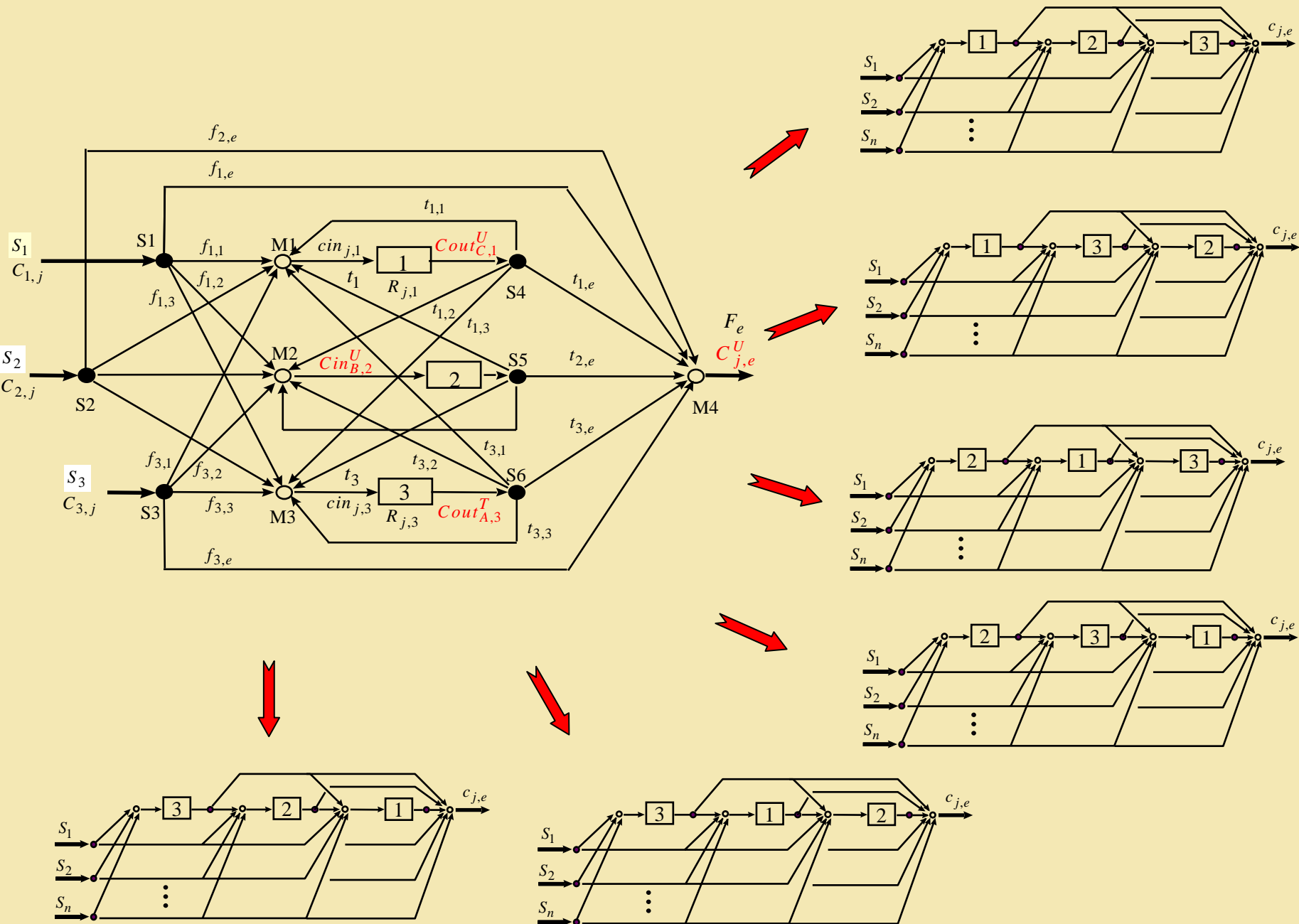
Network Superstructure



Basic Network Superstructures

Partitioning the Design Search Space





NLP Model BNS-n

$$\text{Minimize } t = \sum_{k \in K} (CC_k + CO_k) t_k$$

$$\sum_{k \in K} f_{i,k} + f_{i,e} = S_i \quad i \in I$$

$$\sum_{\substack{l \in K \\ l > k}} \alpha_{k,l} + \alpha_{k,e} = 1 \quad k \in K$$

$$\sum_{i \in I} f_{i,k} + \sum_{\substack{l \in K \\ l < k}} \alpha_{l,k} t_l = t_k \quad k \in K$$

$$\sum_{i \in I} f_{i,e} + \sum_{k \in K} \alpha_{k,e} t_k = F_e$$

$$\sum_{i \in I} f_{i,k} C_{i,j} + \sum_{\substack{l \in K \\ l < k}} \alpha_{l,k} (1 - R_{j,l}) \frac{10^3 \Delta m_{j,l}}{R_{j,l}} = \frac{10^3 \Delta m_{j,k}}{R_{j,k}} \quad j \in J, k \in K$$

$$\sum_{k \in K} \Delta m_{j,k} \geq \Delta m_j^L \quad j \in J$$

$$\sum_{i \in I} S_i C_{i,j} - \sum_{k \in K} \sum_{i \in I} f_{i,k} C_{i,j} + \sum_{k \in K} (1 - R_{j,k}) \alpha_{k,e} \frac{10^3 \Delta m_{j,k}}{R_{j,k}} = F_e c_{j,e} \quad j \in J$$

LP Model BNS-nL

Problem Parameters and Additional Constraints

$$\Delta m_j^U = \frac{1}{10^3} \left[1 - \prod_{k \in K} (1 - R_{j,k}) \right] \sum_{i \in I} S_i C_{i,j} \quad j \in J$$

$$c_{j,e}^L = \left[\prod_{k \in K} (1 - R_{j,k}) \right] \frac{\sum_{i \in I} S_i C_{i,j}}{\sum_{i \in I} S_i} \quad j \in J$$

$$10^3 \Delta m_j^L = \sum_{i \in I} S_i C_{i,j} - \sum_{i \in I} S_i c_{j,e}^U \quad j \in J$$

$$10^3 \Delta m_{j,k} - C_{in_{j,k}}^U R_{j,k} t_k \leq 0 \quad j \in J, k \in K$$

$$10^3 (1 - R_{j,k}) \Delta m_{j,k} - R_{j,k} C_{out_{j,k}}^T t_k \leq 0 \quad j \in J, k \in K$$

$$10^3 m_j^U = \sum_{i \in I} S_i C_{i,j} \quad j \in J$$

Bounds

$$0 \leq c_{j,e}^L \leq c_{j,e} \leq c_{j,e}^U \quad j \in J$$

$$0 \leq f_{i,k}, f_{i,e} \leq S_i \quad i \in I, k \in K$$

$$0 \leq t_k^L \leq t_k \leq t_k^U \leq F_e \quad k \in K$$

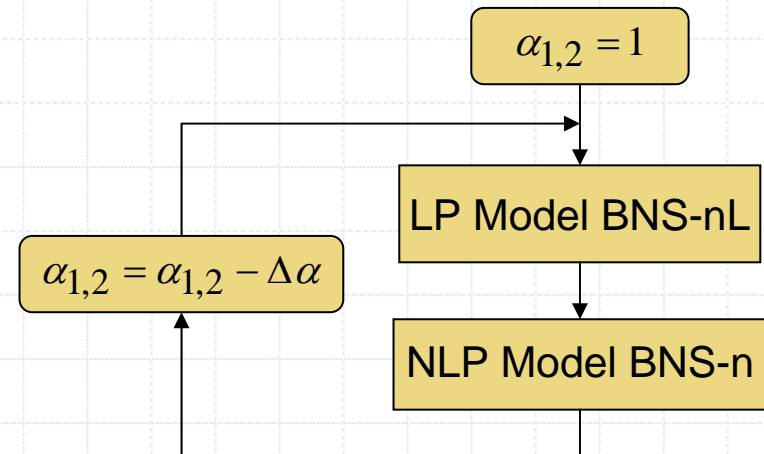
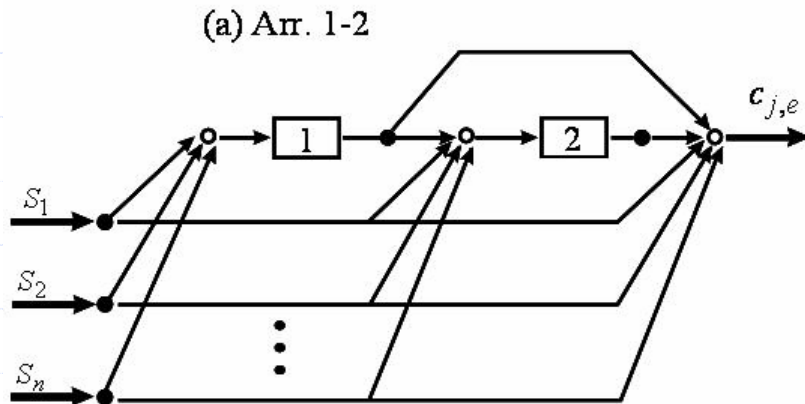
$$0 \leq \Delta m_{j,k}^L \leq \Delta m_{j,k} \leq \Delta m_{j,k}^U \leq m_j^U \quad j \in J, k \in K$$

$$0 \leq \alpha_{1,k}, \alpha_{k,e} \leq 1 \quad 1, k \in K, 1 < k$$

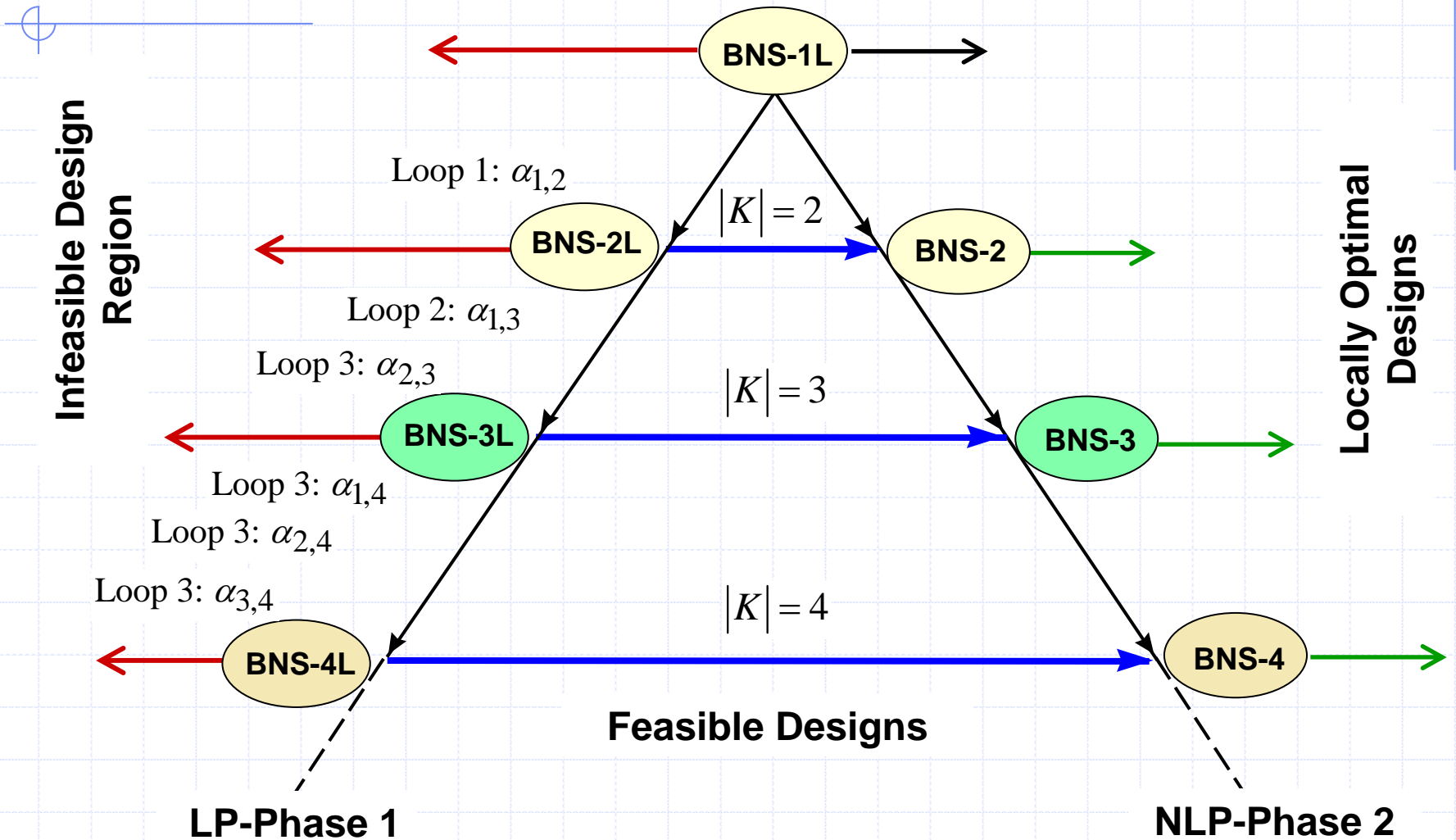
No. of Treatment Units in Problem

Split Fraction Variables Present in Mathematical Model

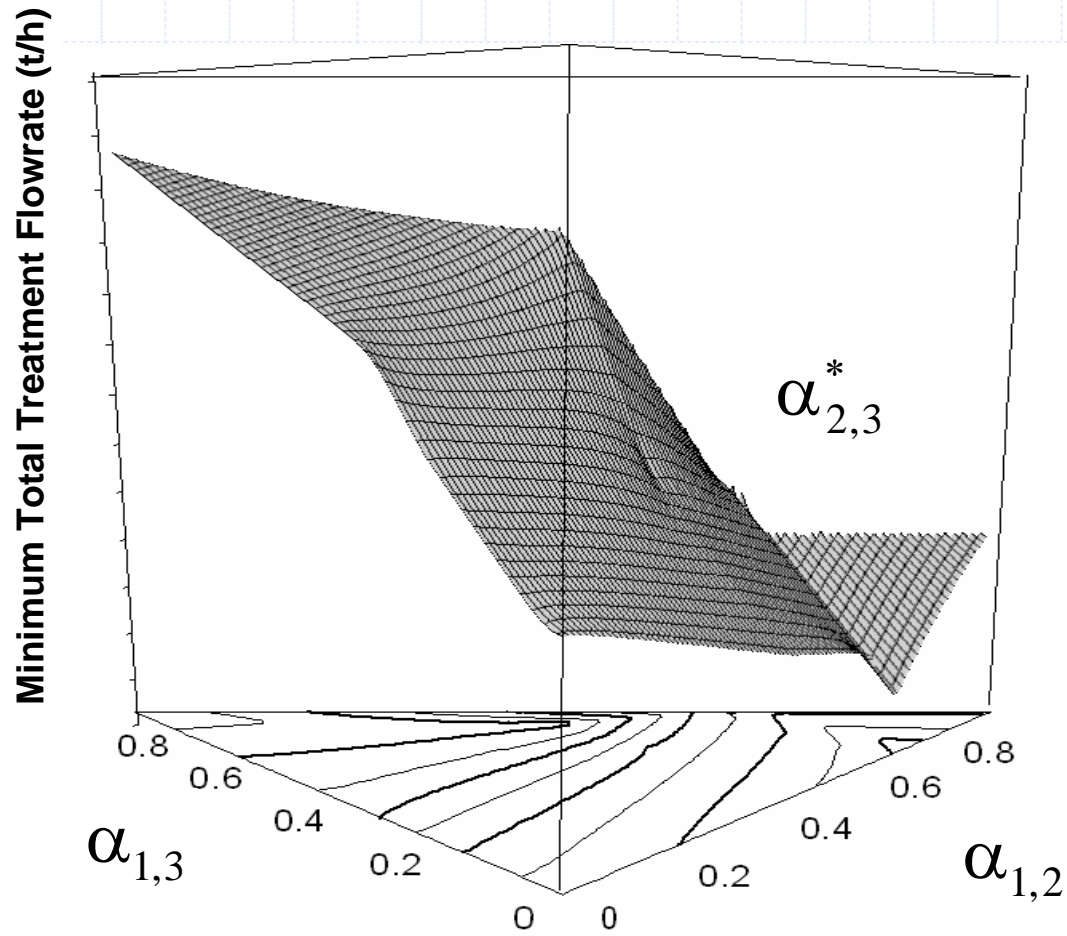
1	0
2	$\alpha_{1,2}$
3	$\alpha_{1,2}, \alpha_{1,3}, \alpha_{2,3}$
4	$\alpha_{1,2}, \alpha_{1,3}, \alpha_{1,4}, \alpha_{2,3}, \alpha_{2,4}, \alpha_{3,4}$
5	$\alpha_{1,2}, \alpha_{1,3}, \alpha_{1,4}, \alpha_{1,5}, \alpha_{2,3}, \alpha_{2,4}, \alpha_{2,5}, \alpha_{3,4}, \alpha_{3,5}, \alpha_{4,5}$
6	$\alpha_{1,2}, \alpha_{1,3}, \alpha_{1,4}, \alpha_{1,5}, \alpha_{1,6}, \alpha_{2,3}, \alpha_{2,4}, \alpha_{2,5}, \alpha_{2,6}, \alpha_{3,4}, \alpha_{3,5}, \alpha_{3,6}, \alpha_{4,5}, \alpha_{4,6}, \alpha_{5,6}$



Systematic Exploration of the Partitioned Design Region



Minimum Total Treatment Flowrate Surface



Maximum Costs for Systematic Exploration of the Design Region Associated with a Basic Network Superstructure

No. of treatment units	No. of split fraction variables	Maximum no. of LP and NLP problems in exploration						
		$\Delta\alpha=0.05$	$\Delta\alpha=0.1$	$\Delta\alpha=0.2$	$\Delta\alpha=0.25$	$\Delta\alpha=0.3\bar{3}$	$\Delta\alpha=0.5$	$\Delta\alpha=1$
1	0	1	1	1	1	1	1	1
2	1	21	11	6	5	4	3	2
3	3	4,851	726	126	75	40	18	6
4	6	8.59×10^6	208×10^3	7,056	2,625	800	180	24
5	10	91.3×10^9	209×10^6	889×10^3	184×10^3	28,000	2700	120
6	15	4.9×10^{15}	627×10^9	224×10^6	23.2×10^6	1.57×10^6	680×10^3	720

Example 3

Design of a Distributed Effluent Treatment System

(Takama et al. 1980; Kuo and Smith, 1997)

Wastewater stream data

stream number	flowrate (t/h)	contaminants		
		H2S (ppm)	OIL (ppm)	SS (ppm)
1	13.1	390	10	250
2	32.7	16,780	110	400
3	56.5	25	100	350

Removal ratios (%) for treatment processes

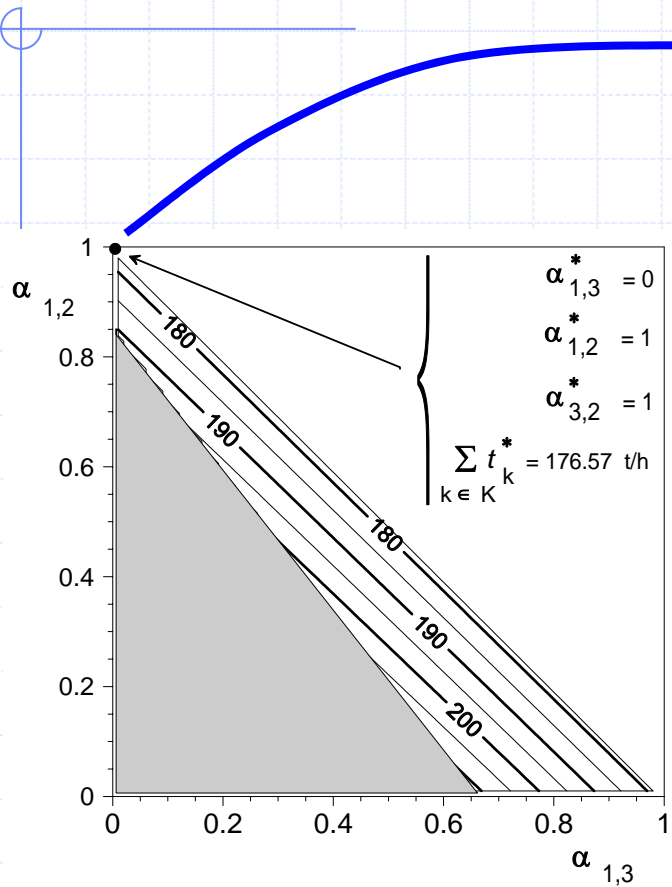
treatment processes	H2S	OIL	SS
1	99.9	0	0
2	90	70	98
3	0	70	50

Environmental concentration limits (ppm)

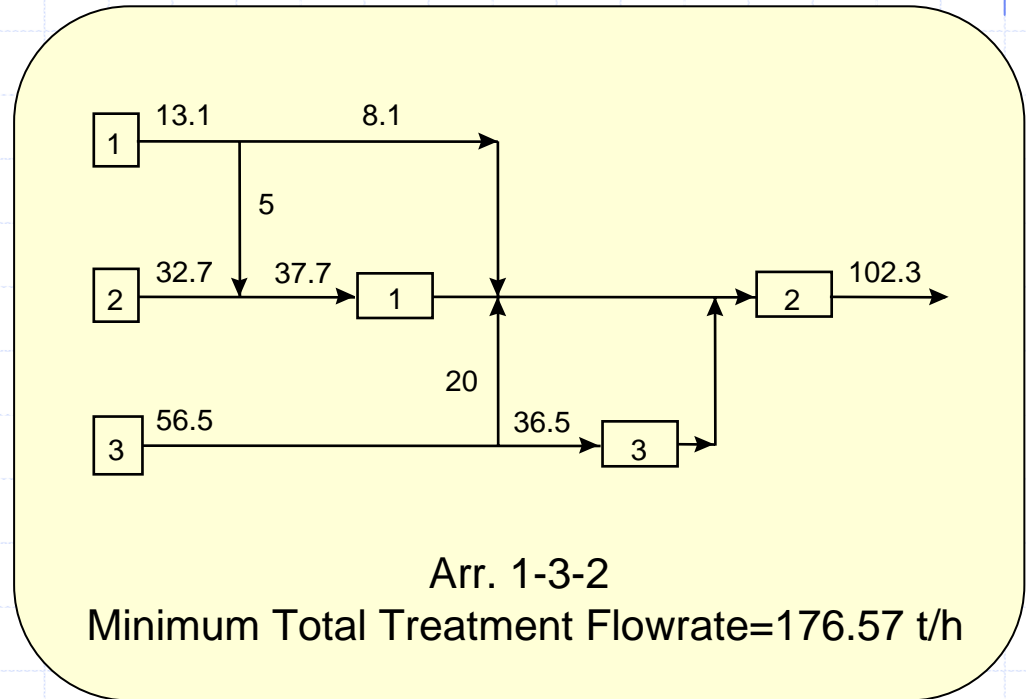
H2S	5
OIL	20
SS	100

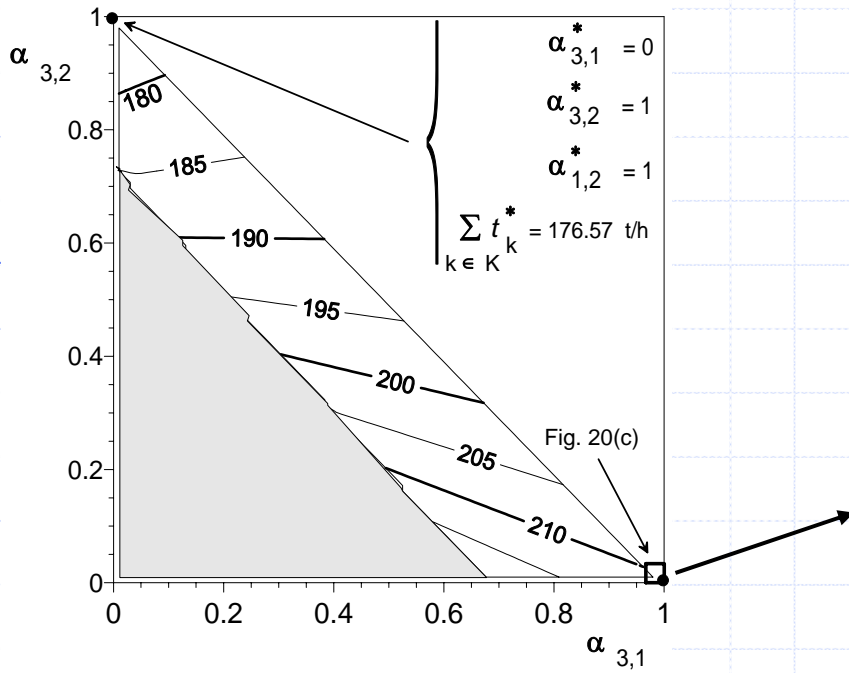
- Treatment costs are proportional to total treatment flowrate.
- Treatment unit 2 cannot precede treatment unit 3.

Minimum Total Treatment Flowrate Maps and Network Designs

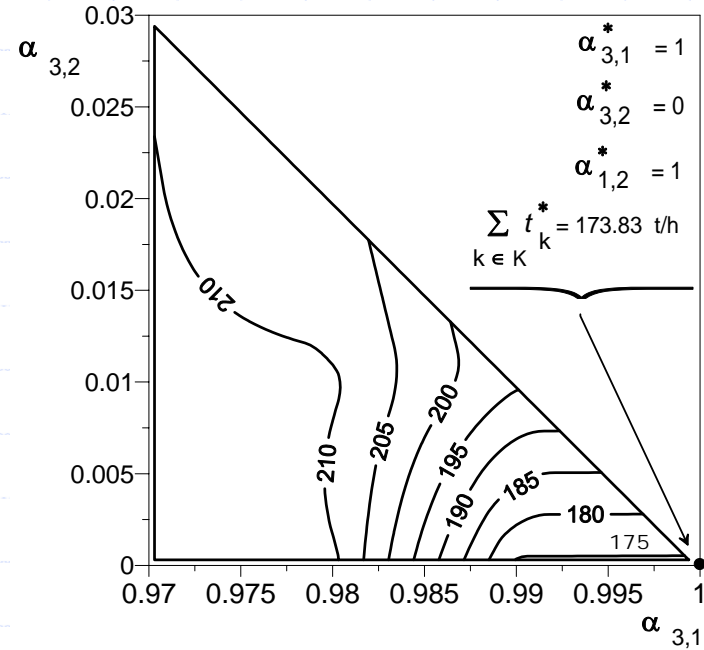


(a) Arr. 1-3-2

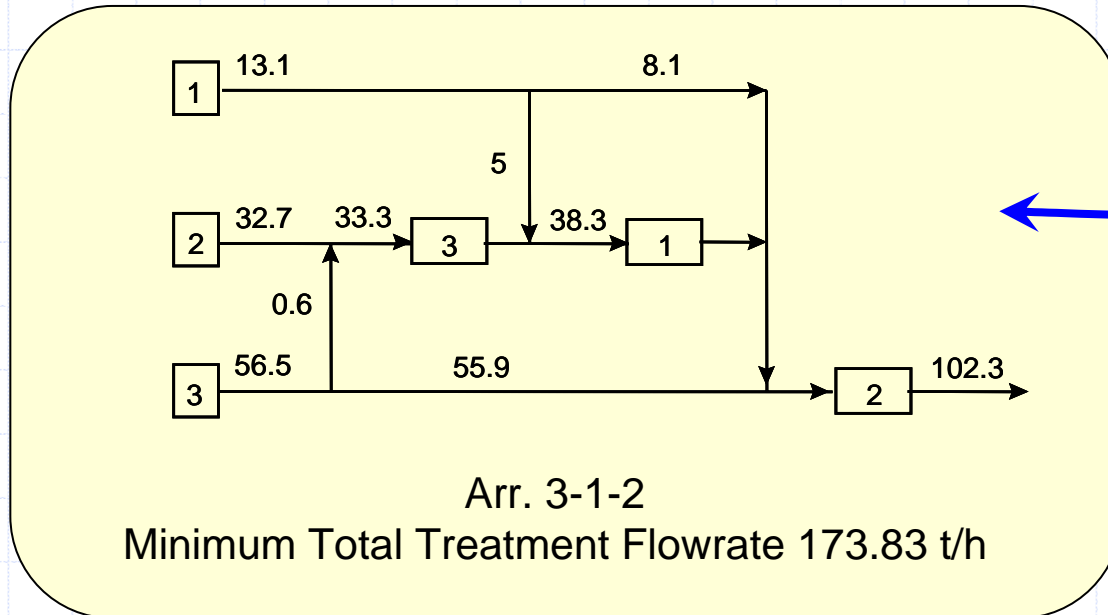


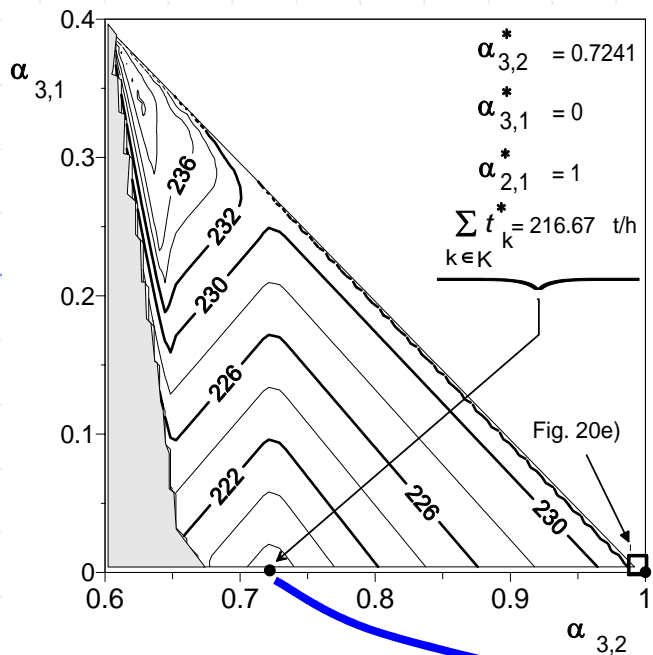


(b) Arr. 3-1-2

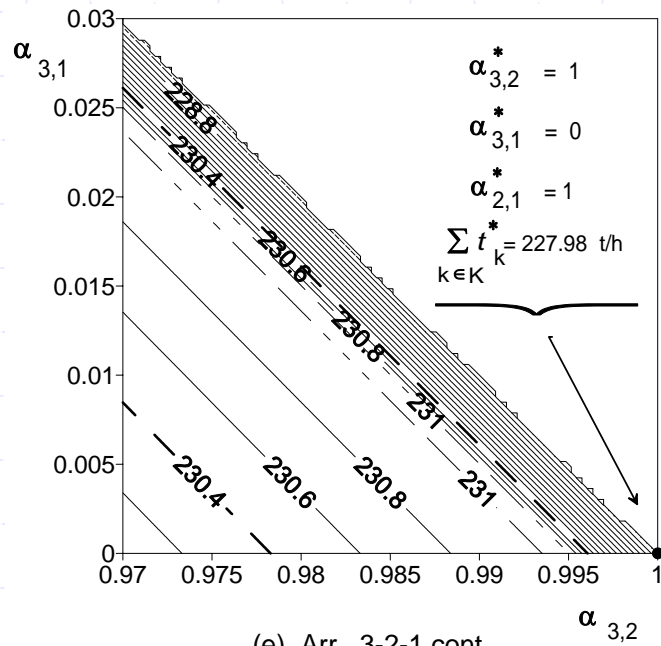


(c) Arr. 3-1-2 cont.

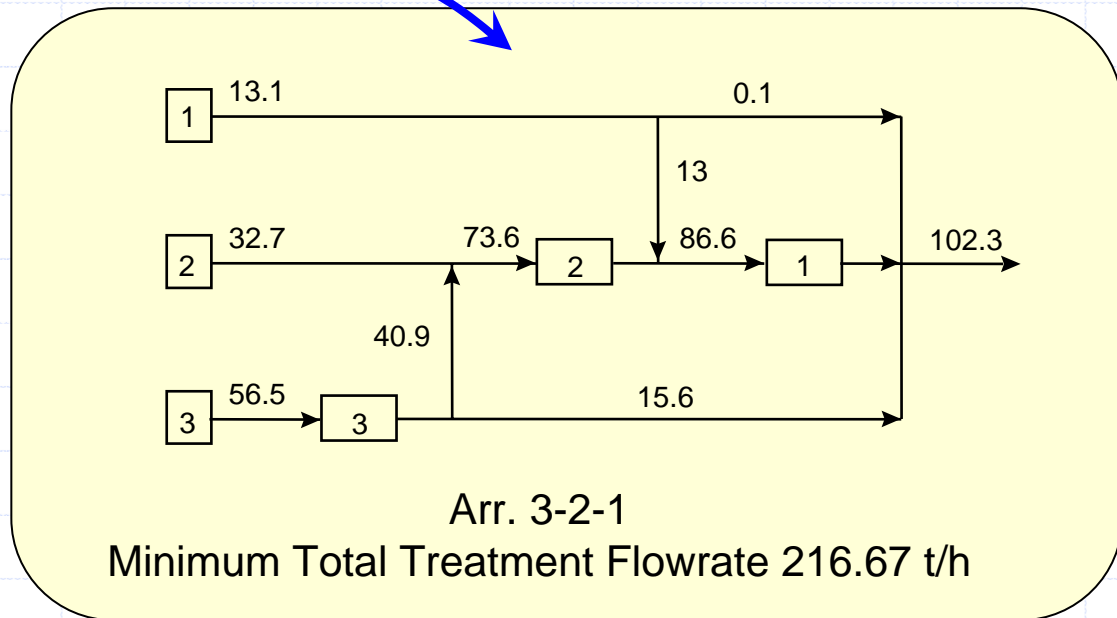




(d) Arr. 3-2-1



(e) Arr. 3-2-1 cont.



Effectiveness and Computational Costs

Arr.	Minimum total treatment flowrate (t/h)						
	$\Delta\alpha = 0.05$	$\Delta\alpha = 0.1$	$\Delta\alpha = 0.2$	$\Delta\alpha = 0.25$	$\Delta\alpha = 0.3\bar{3}$	$\Delta\alpha = 0.5$	$\Delta\alpha = 1$
1-3-2	176.56	176.56	176.56	176.56	176.56	176.56	176.56
3-1-2	173.83	173.83	173.83	173.83	173.83	173.83	173.83
3-2-1	216.66	216.66	216.66	216.66	216.66	216.66	227.98

Arr.	Actual number of LP and NLP problems solved in Example 3						
	$\Delta\alpha = 0.05$	$\Delta\alpha = 0.1$	$\Delta\alpha = 0.2$	$\Delta\alpha = 0.25$	$\Delta\alpha = 0.3\bar{3}$	$\Delta\alpha = 0.5$	$\Delta\alpha = 1$
1-3-2	952	178	52	38	24	12	5
3-1-2	661	152	45	34	20	12	5
3-2-1	445	133	41	29	18	11	5

Example 4

Analysis of the Treatment Section of an Integrated Water Network

(Tsai and Chang, 2001))

Water sources

Source No.	Contaminants (ppm)		Max Flowrate. (t/h)
	A	B	
W1	10	20	∞
W2	600	300	50

Process Data for Water Using Units

Unit No.	Solute	Mass Load (Kg/h)	Max Inlet Concentration (ppm)	Max Outlet Concentration (ppm)
U1	A	10	200	600
	B	5	100	300
U2	A	2	40	120
	B	8	120	360

Process Data for Treatment Units

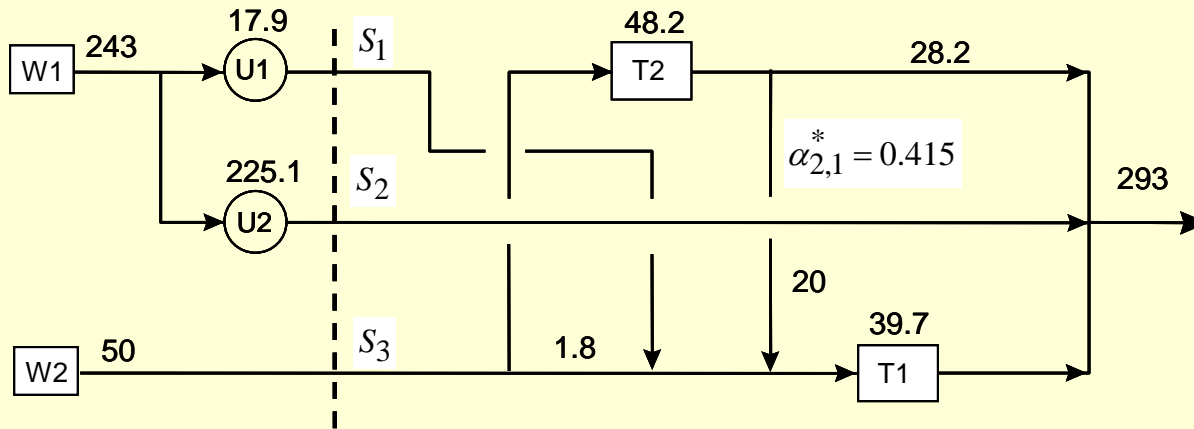
Treatment Unit	Removal Ratio (%)		Max. Flowrate (t/h)
	A	B	
T1	80	10	50
T2	20	70	50

Environmental concentration limits (ppm)

A	75
B	75

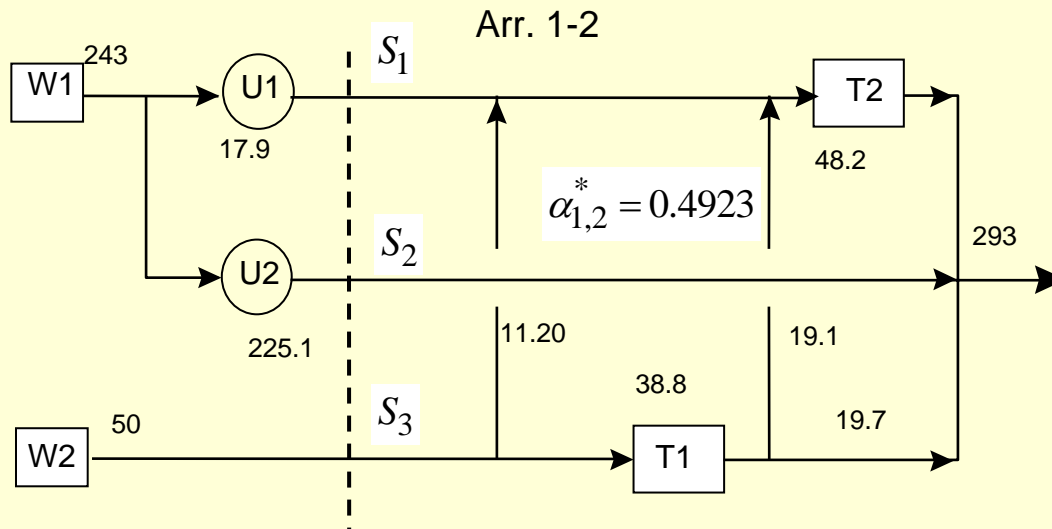
- Treatment costs are proportional to total treatment flowrate.

Total Treatment Flowrate = 87.90 t/h



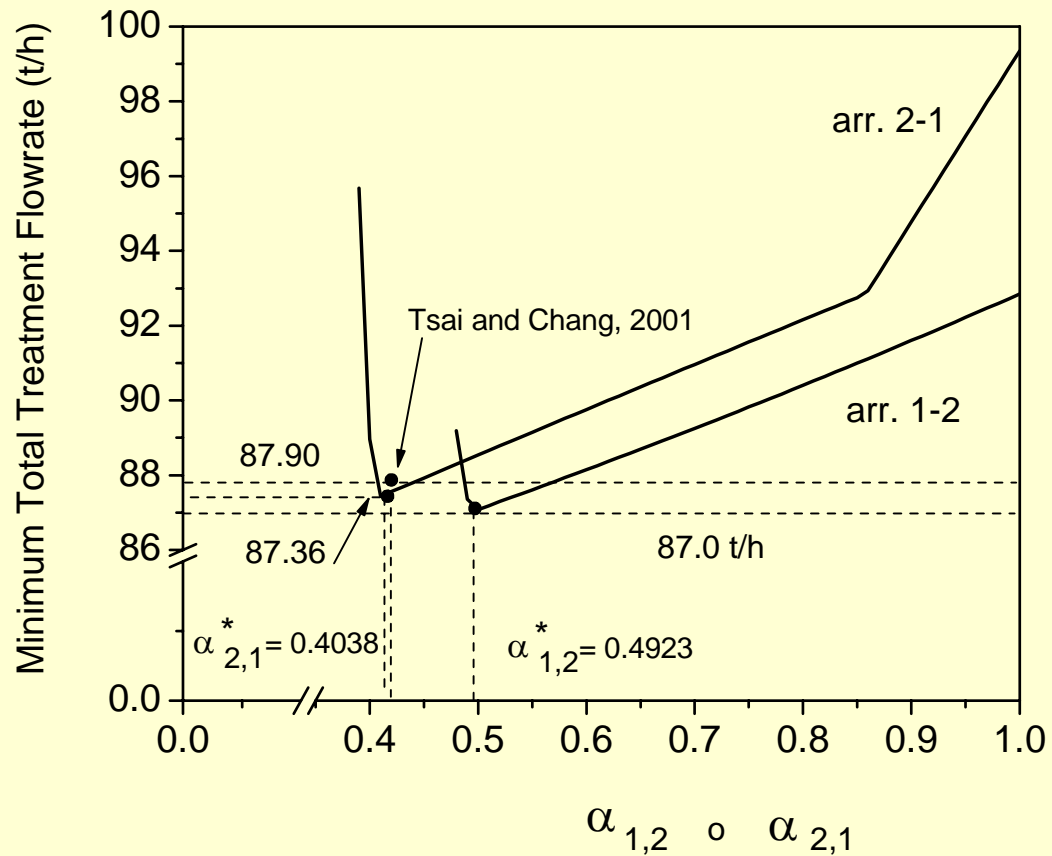
Genetic Algorithm
Tsai and Chang (2001)

Total Treatment Flowrate = 87.00 t/h



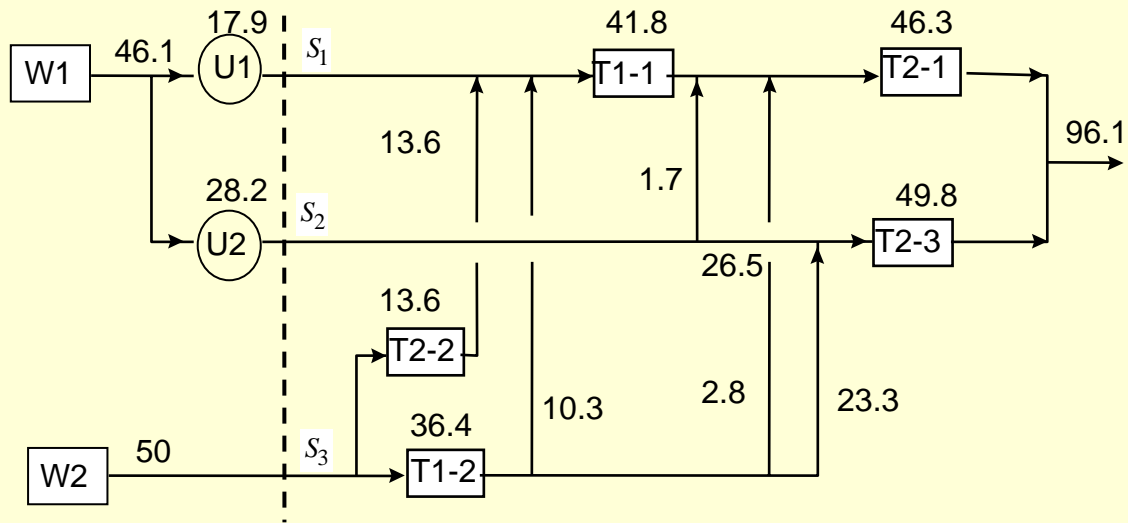
Parametric Optimization
Hernández-Suárez (2004)

Minimum Total Treatment Flowrate Curves



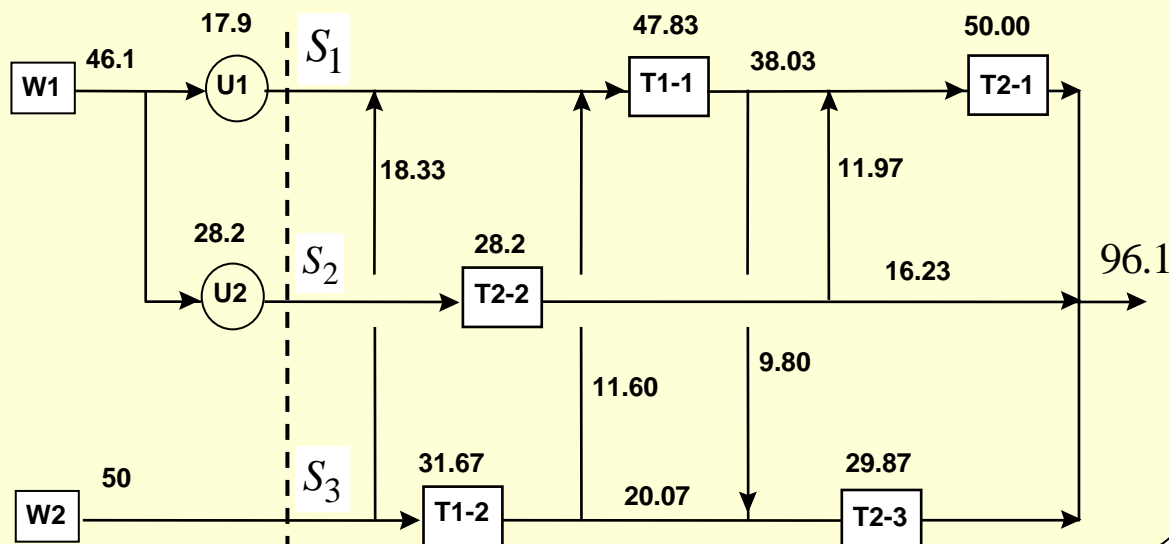
Allowing Repeated Treatment Units

Total Treatment Flowrate = 187.90 t/h



Genetic Algorithm
Tsai and Chang (2001)

Total Treatment Flowrate = 187.57 t/h



Parametric Optimization
Hernández-Suárez (2004)