



**UNIVERSITY OF ROME “LA SAPIENZA”
NANOTECHNOLOGIES ENGINEERING**

**MEMBRANE APPLICATIONS IN
NANOTECHNOLOGY:
MEMBRANE MODULES**

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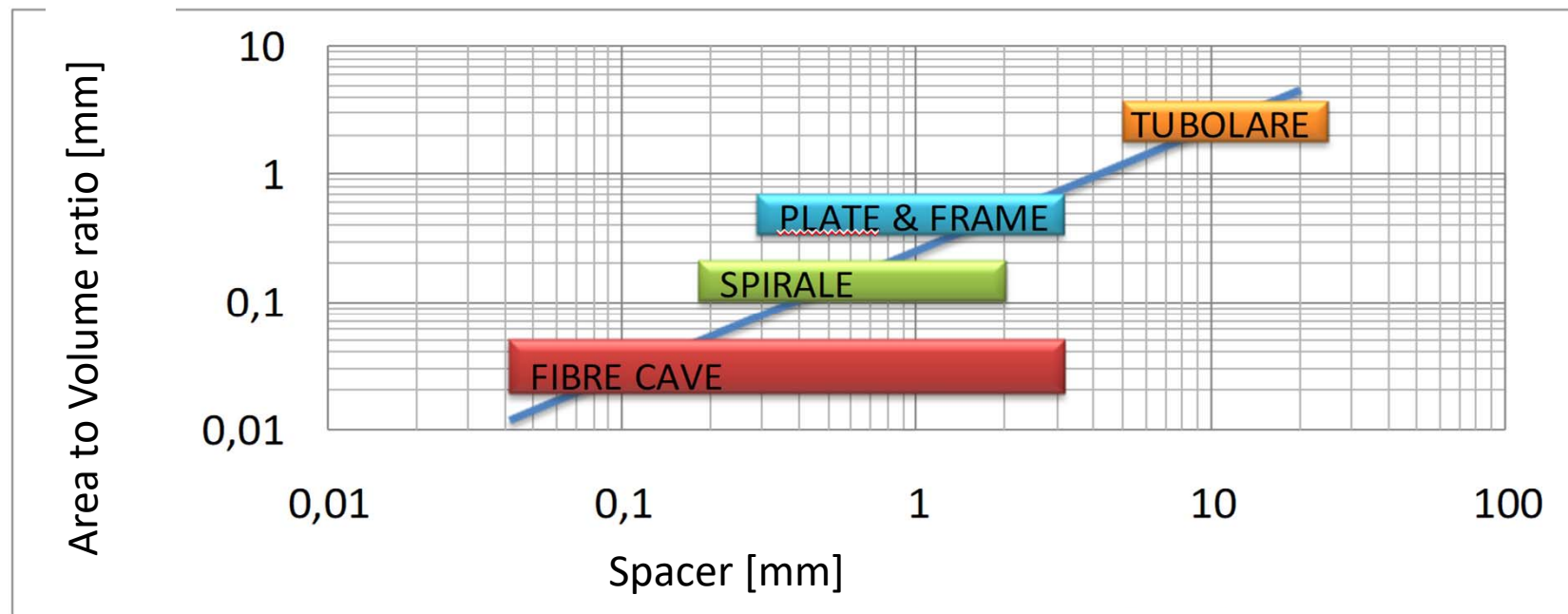
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Membrane modules

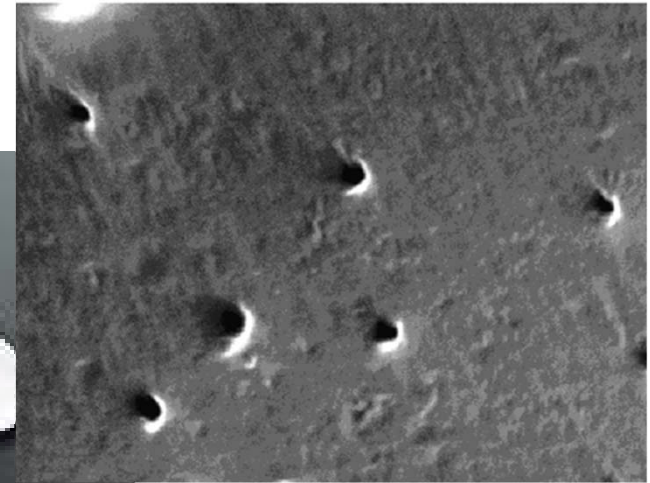
Five membrane module types:

- Flat sheet membranes
- Tubular membrane modules
- Plate&frame membrane modules
- Spiral wound membrane modules (SW)
- Hollow fiber membrane modules (HF)

Characterized by different spacers and area to volume ratio.



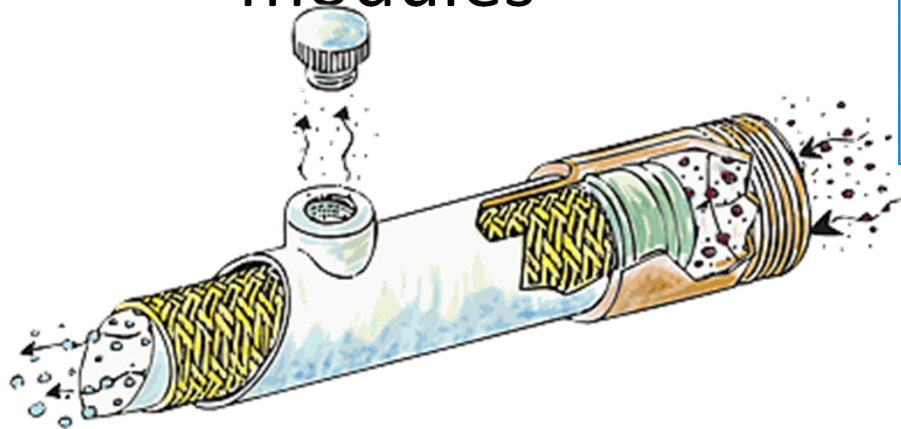
Flat sheet membranes



<u>Advantages</u>	<u>Disadvantages</u>	<u>Technologies</u>
Huge variety of membranes available	High costs	D, ED MF, UF, NF, RO HD
Can be washed easily	Membrane substitution may be time consuming	
Low energy consumption	Problems in seals	
	Very low area to volume ratio	

- Used in laboratories in batch cells
- Can give significant data on rejection values, less on productivity and longevity

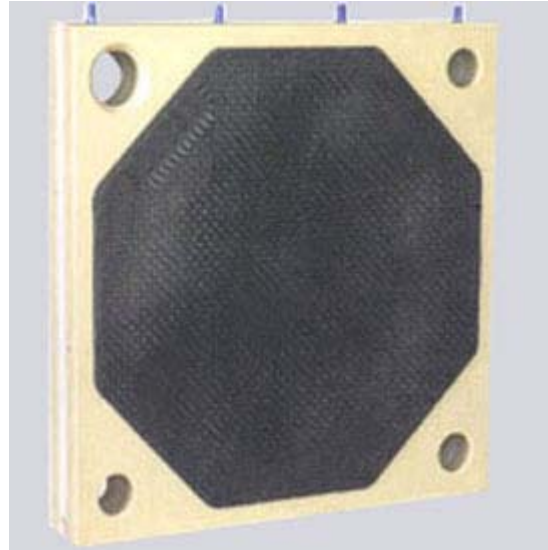
Tubular membrane modules



<u>Advantages</u>	<u>Disadvantages</u>	<u>Technologies</u>
Feed can contain suspended solids	High energy request	GS, HD UF, MF, NF, RO
Can work well also with fluids not following newton's law	High costs	
Can be mechanically washed	High hold-up	
	Low area to volume ratio	

- Used on untreated feedstocks

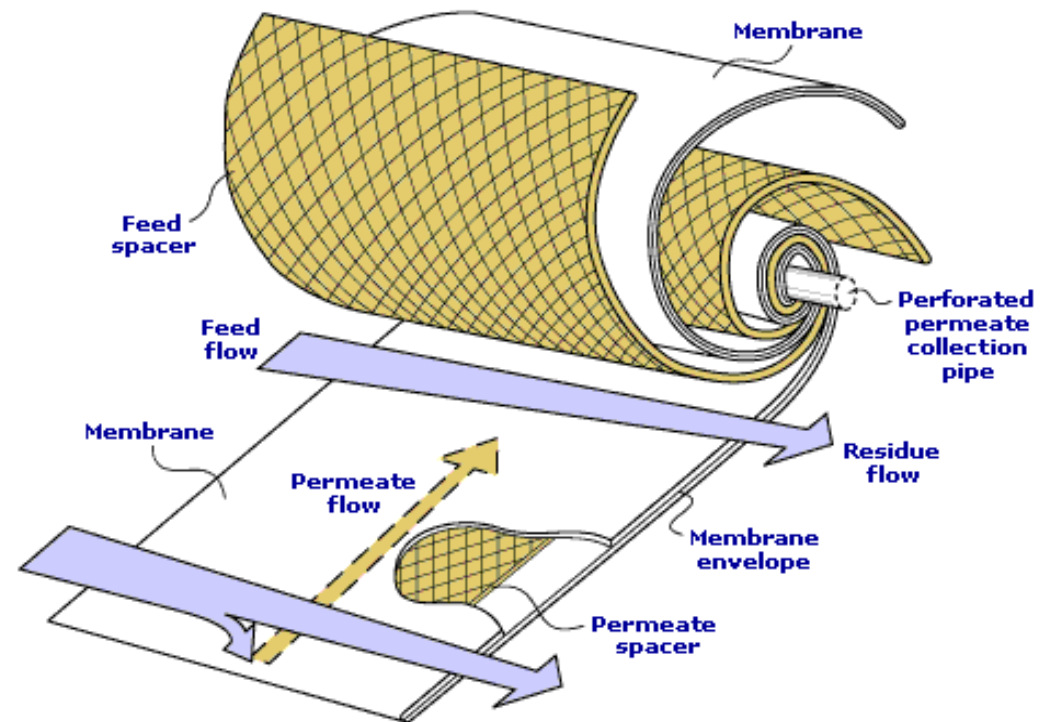
Plate&frame membrane modules



<u>Advantages</u>	<u>Disadvantages</u>	<u>Technologies</u>
Same as flatsheet membranes	Same as flatsheet membranes	D, ED MF, UF, NF, RO HD
Higher (average) area to volume ratio		

- Used in MBRs

SW

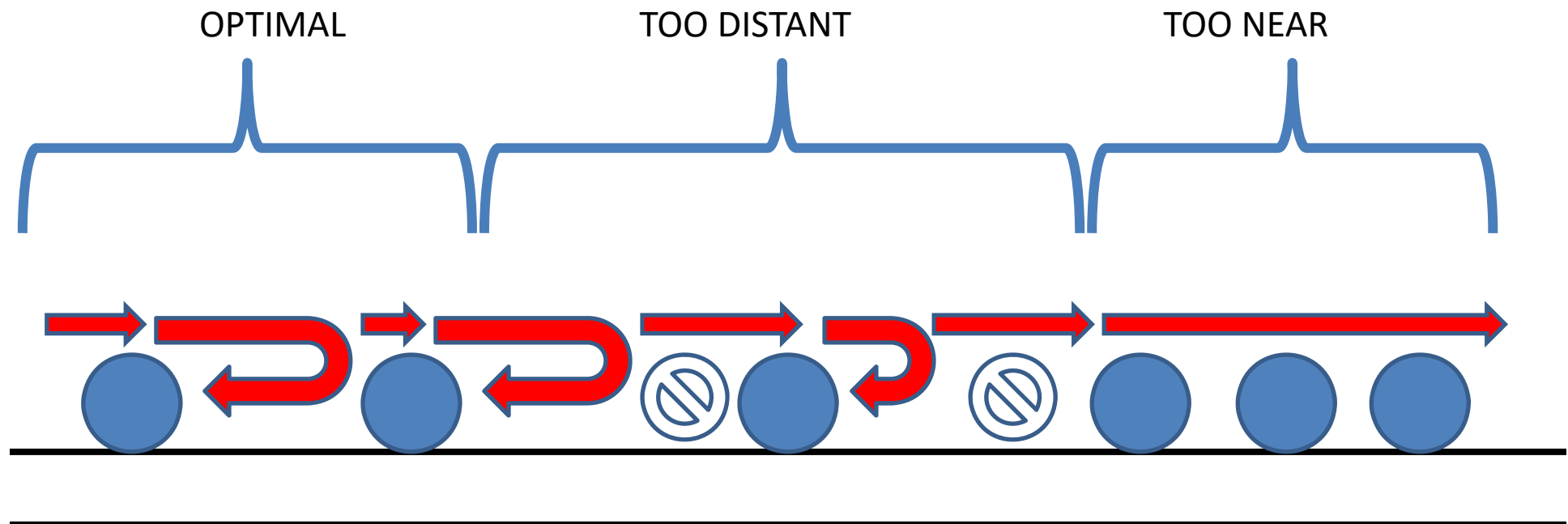


<u>Advantages</u>	<u>Disadvantages</u>	<u>Technologies</u>
Low hold-up	Cannot be backwashed	ED MF, UF, NF, RO
Compact	Presence of “dead spots”	
High variety of membranes available		
Low costs		

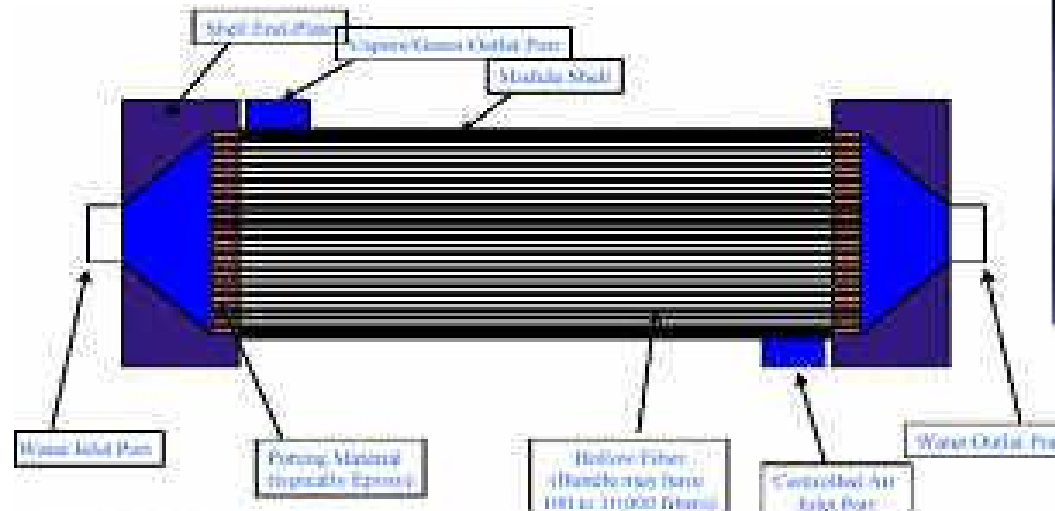
- Used in NF and RO

What are spacers?

MUST IMPROOVE TURBULENT HYDRODYNAMICS ON MEMBRANE SURFACE



HF



<u>Advantages</u>	<u>Disadvantages</u>	<u>Technologies</u>
Very compact	Prone to fouling	MF, UF
Very low hold-up	Cannot be used with viscous feedstocks	
Low costs	Limited variety of membranes available	
Back-washable		

- used for MF and UF



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**MEMBRANE APPLICATIONS IN
NANOTECHNOLOGY:
THE PROBLEM OF FOULING**

PROF. MARCO STOLLER

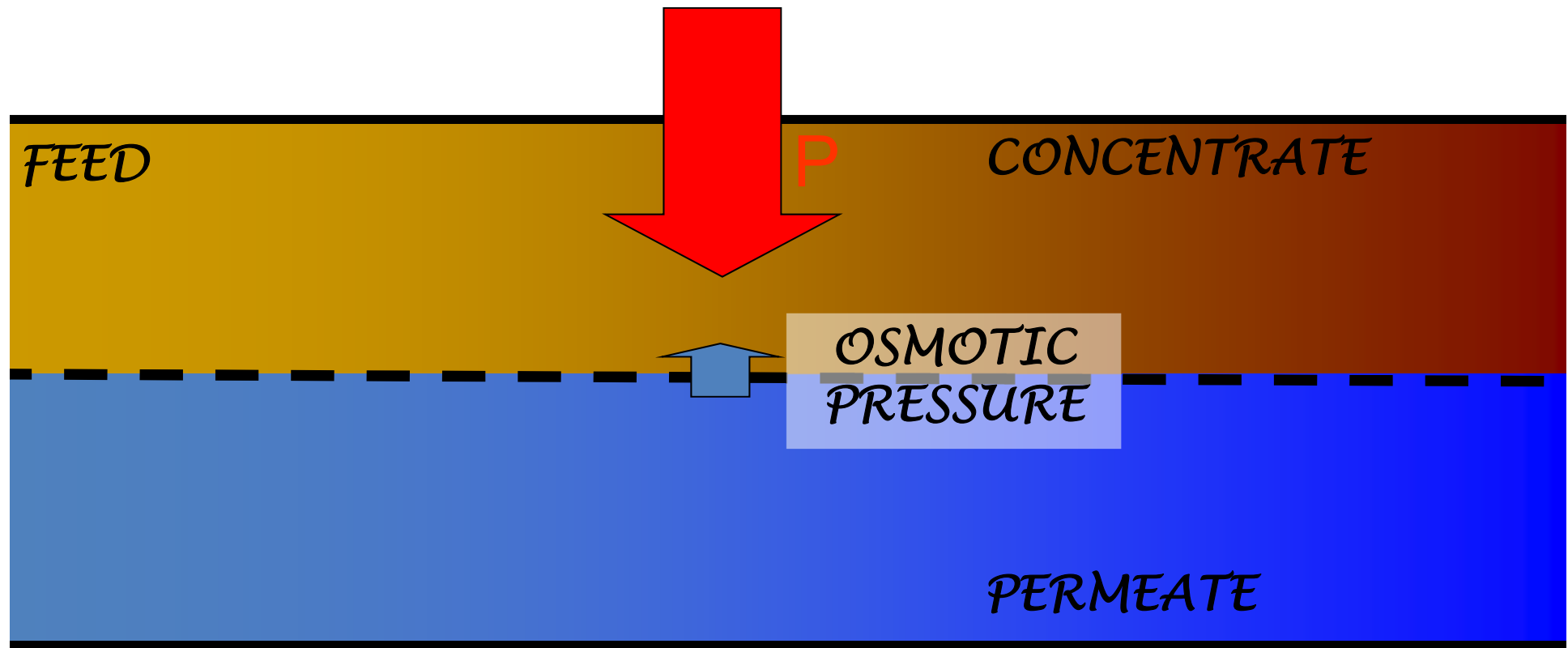
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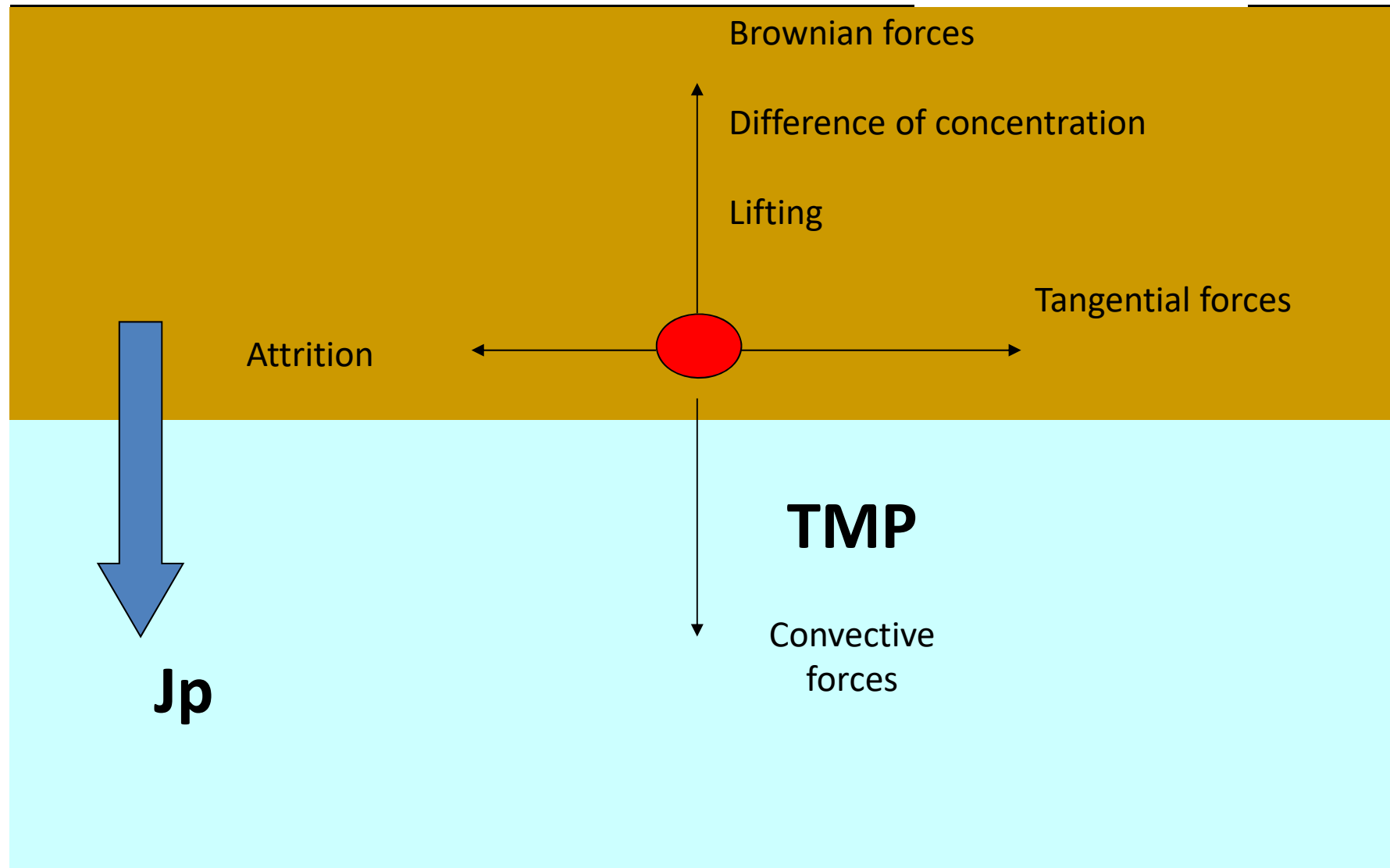
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Separation by membranes



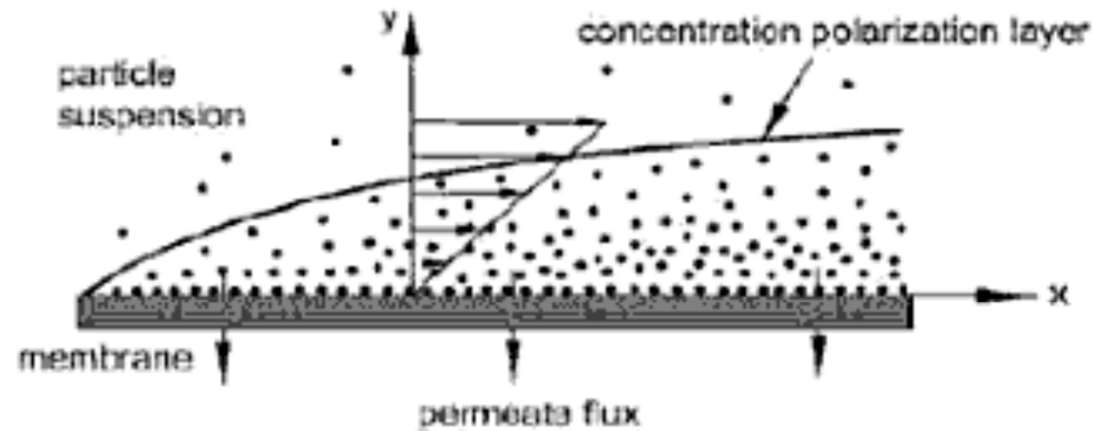
WUD Q VP HP EUD Q H#SUHV VXUH#WP S#@#S#0 π

Force balance on a particle

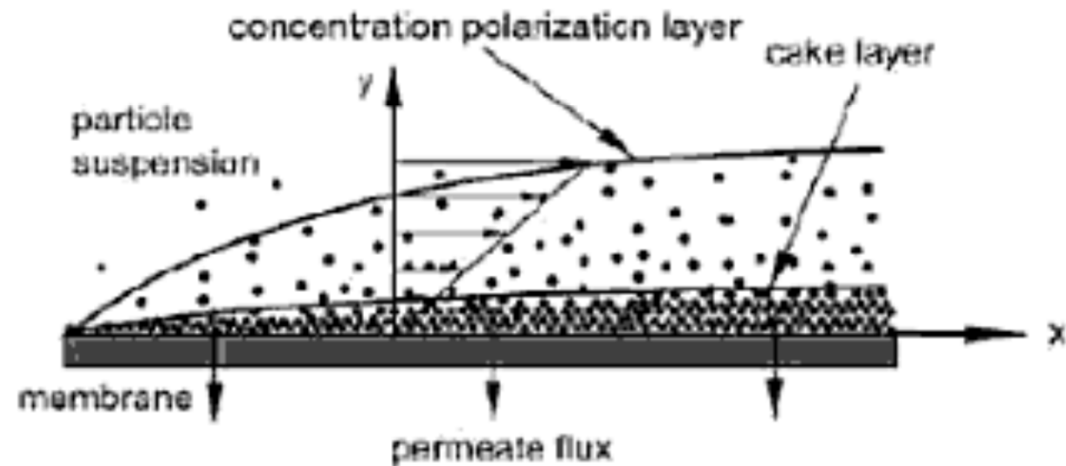


Polarization

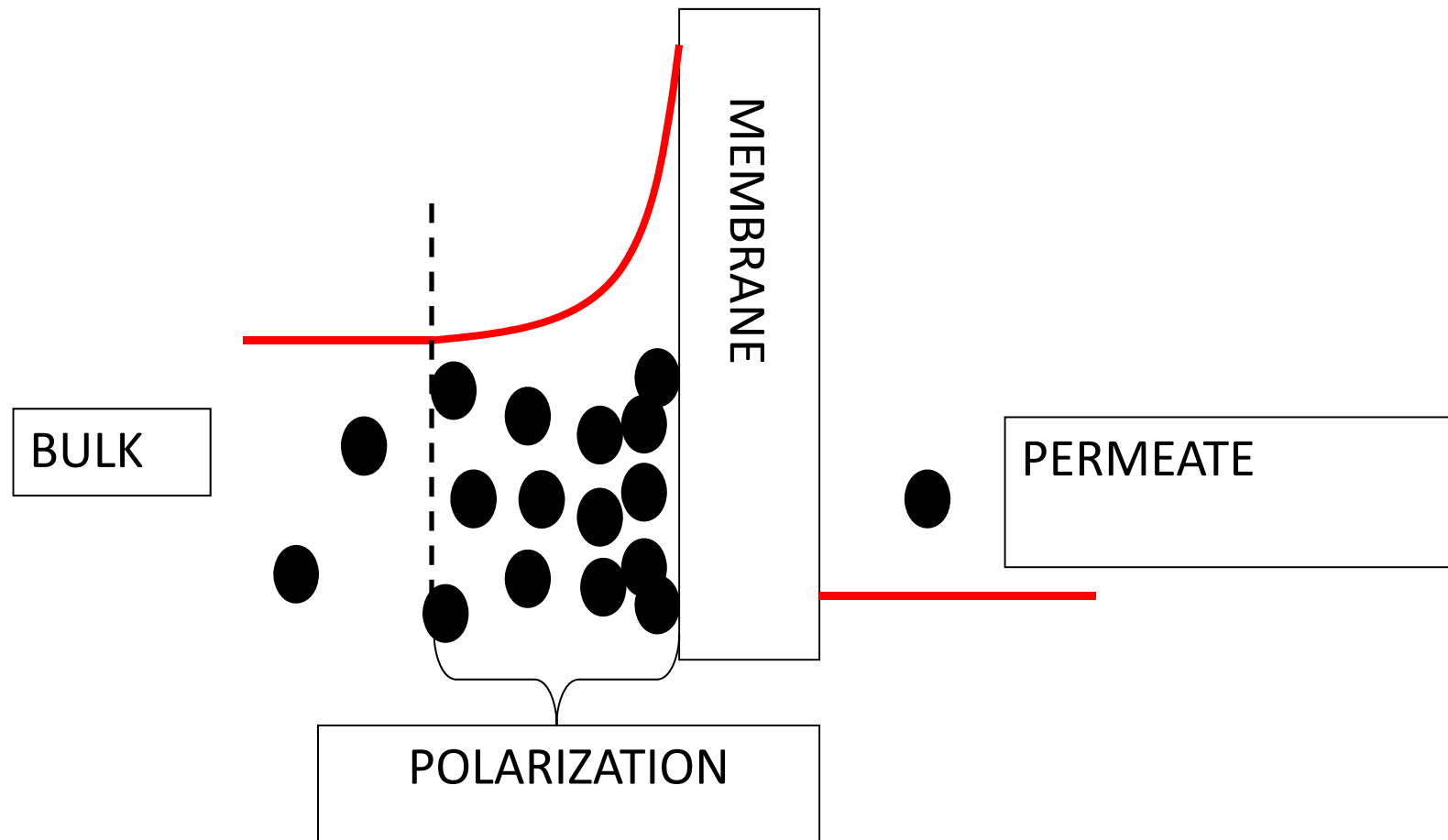
(a) Concentration Polarization



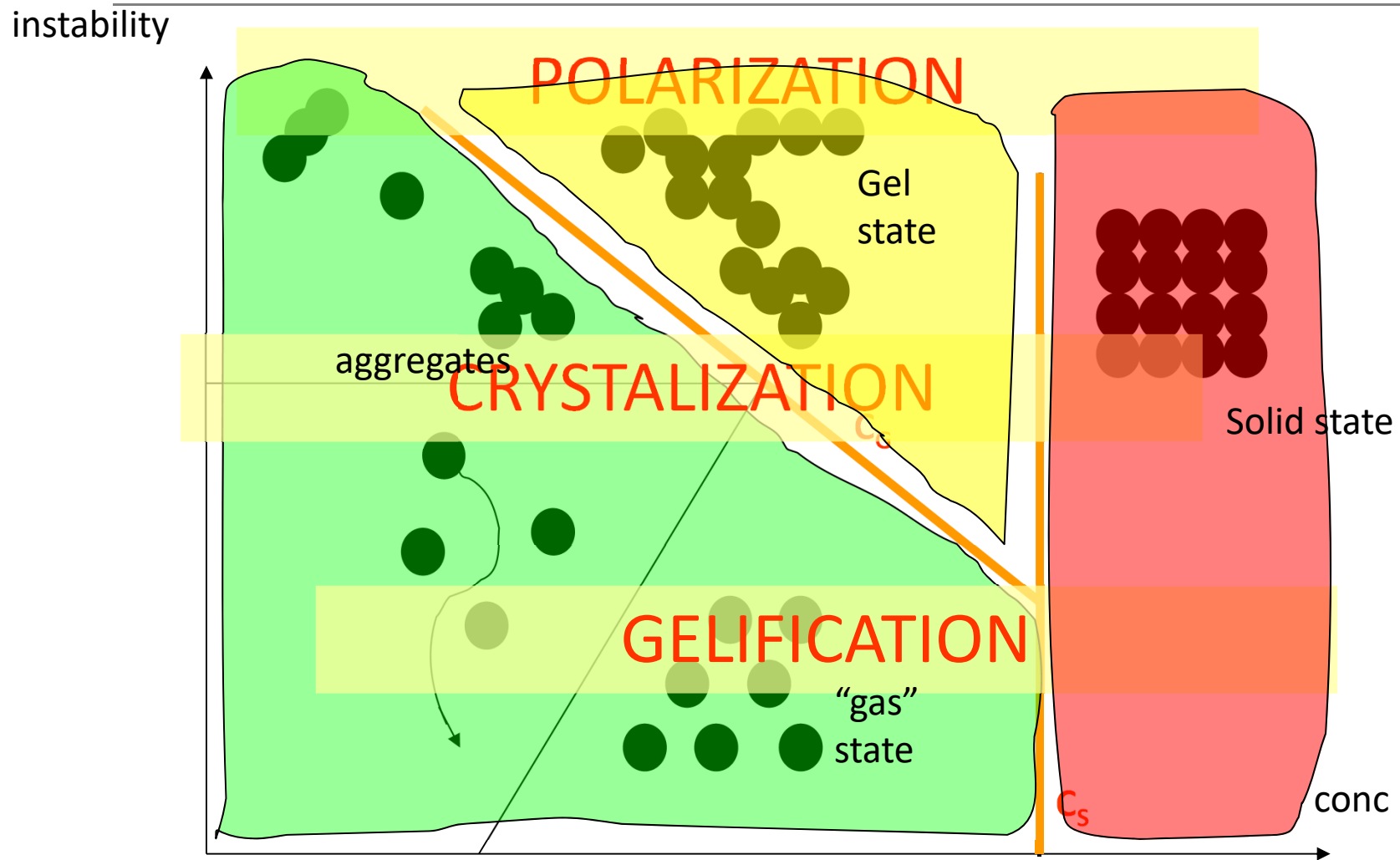
(b) Cake Formation



Polarization

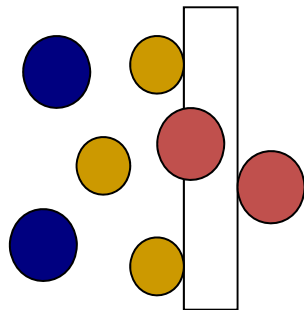


Fouling explained

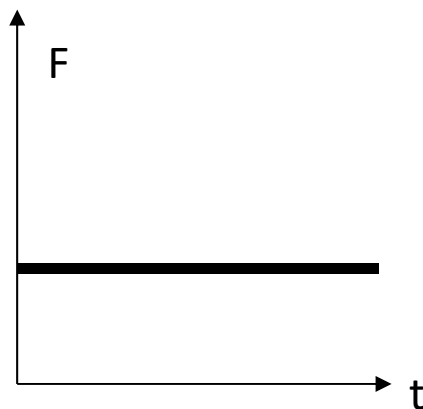


Fouling explained

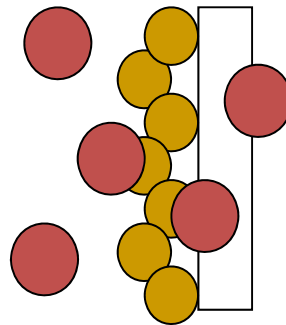
AT LOW TMP (P_1)



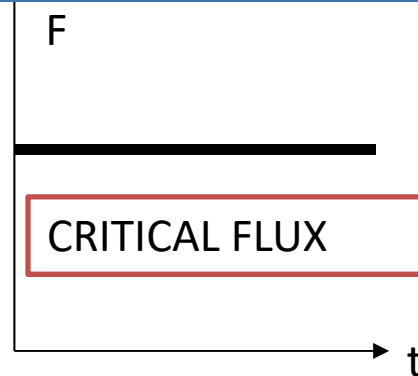
NO FOULING



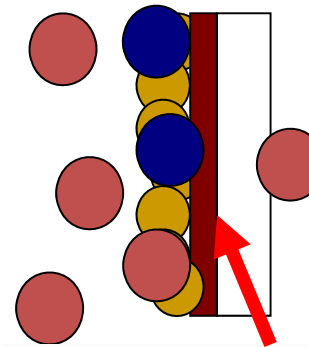
AT HIGHER TMP ($P_2 > P_1$)



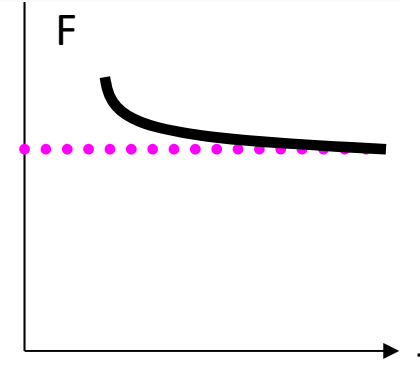
REVERSIBLE
FOULING



AT HIGH TMP ($P_3 > P_2$)

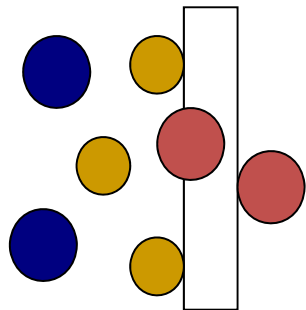


IRREVERSIBLE
FOULING

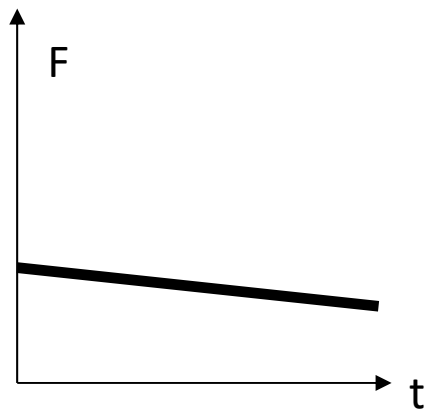


Fouling explained

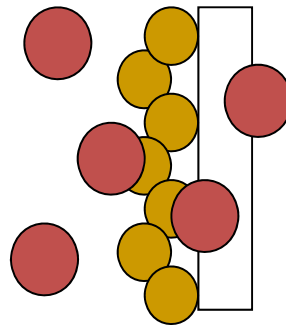
AT LOW TMP (P_1)



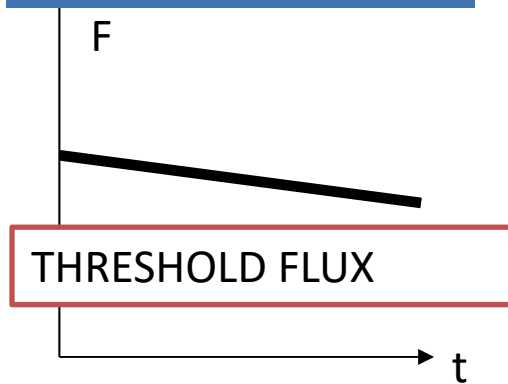
NO FOULING



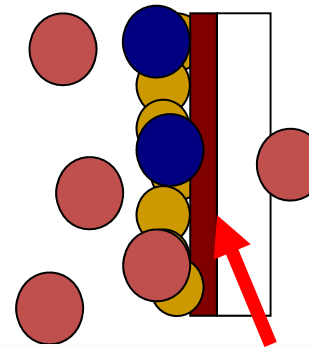
AT HIGHER TMP
($P_2 > P_1$)



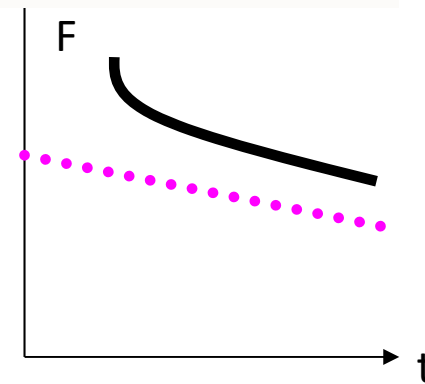
REVERSIBLE
FOULING



AT HIGH TMP ($P_3 > P_2$)

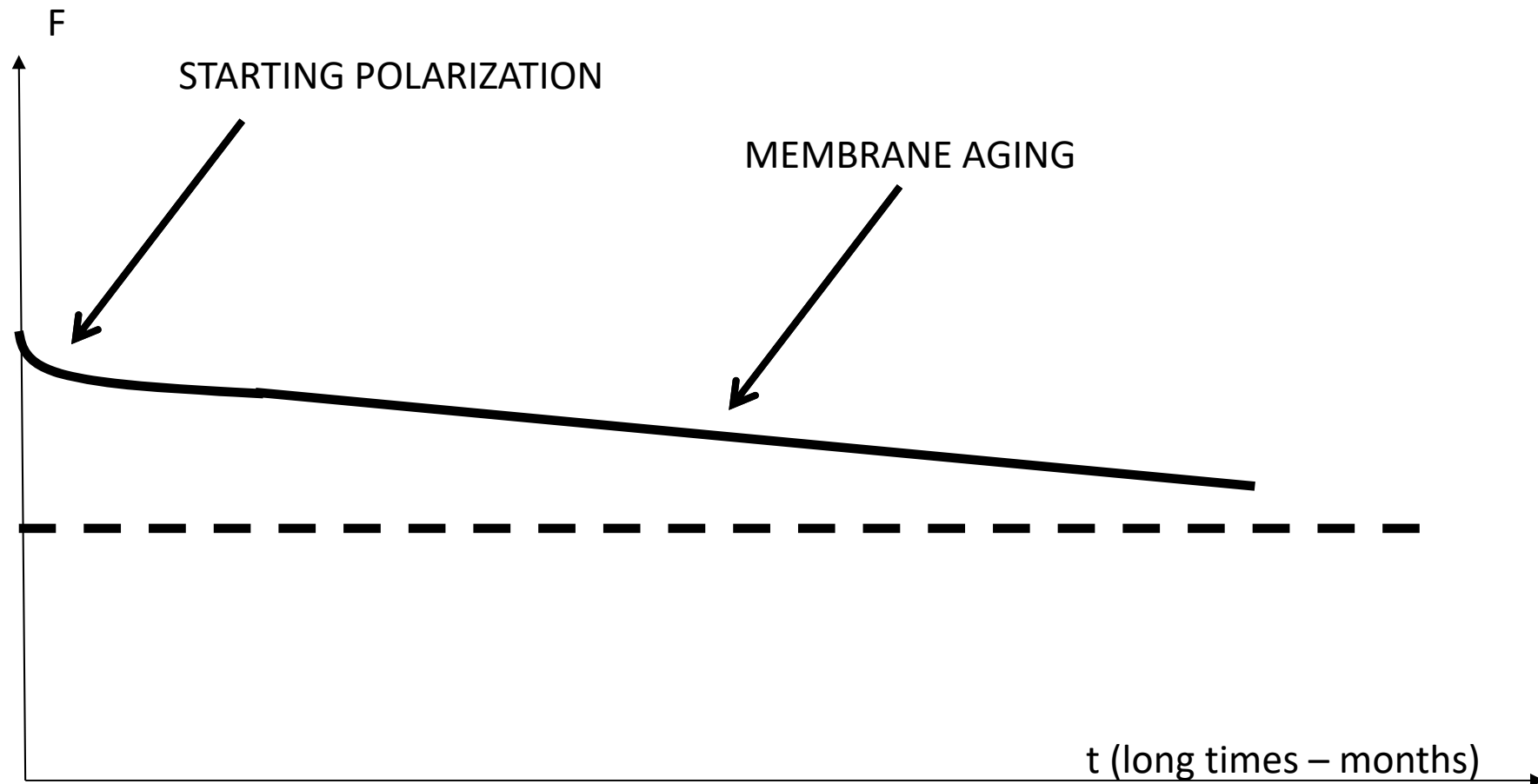


IRREVERSIBLE
FOULING



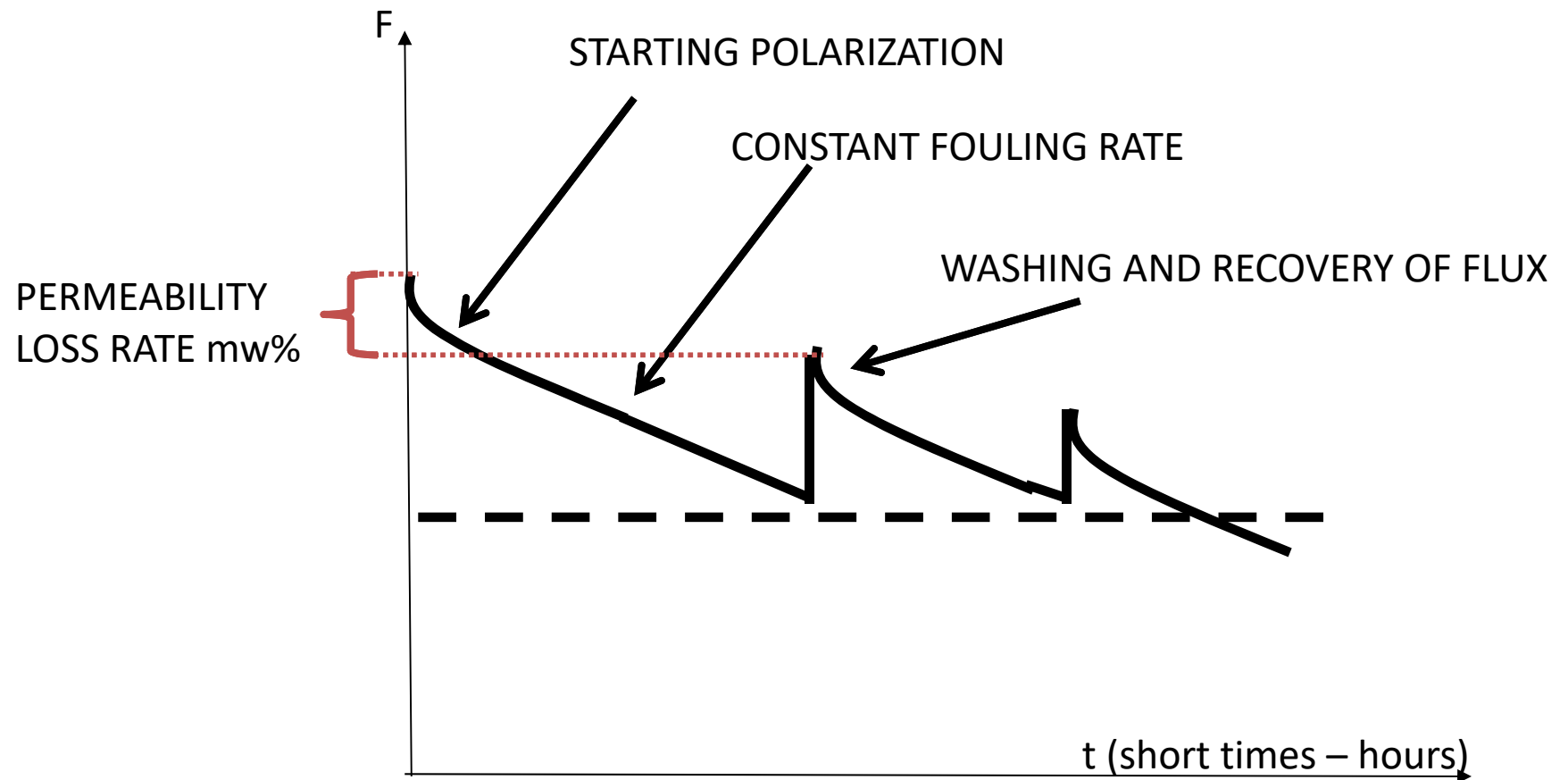
Fouling explained

FLUX PROFILE AT CRITICAL FLUX



Fouling explained

FLUX PROFILE AT THRESHOLD FLUX



This should be avoided...



The most important parameters

Are mainly influenced by the operating conditions (**TMP**, Feed flow rate, recovery):

- **PRODUCTIVITY**

PERMEATE FLUX

$$J_p = m (P - \pi) = m \text{ TMP}$$

- **SELECTIVITY**

REJECTION OF SOLUTES

$$R = \sigma [\text{TMP} / (\text{TMP} + \beta)]$$

- **LONGEVITY**

FOULING

$$J_p(t) = (m \text{ TMP} - J_c) \text{ EXP } (-B t) + J_c$$

The most important parameters

- **PRODUCTIVITY**

Has influence on membrane area $A \rightarrow$ investment costs

- **SELECTIVITY**

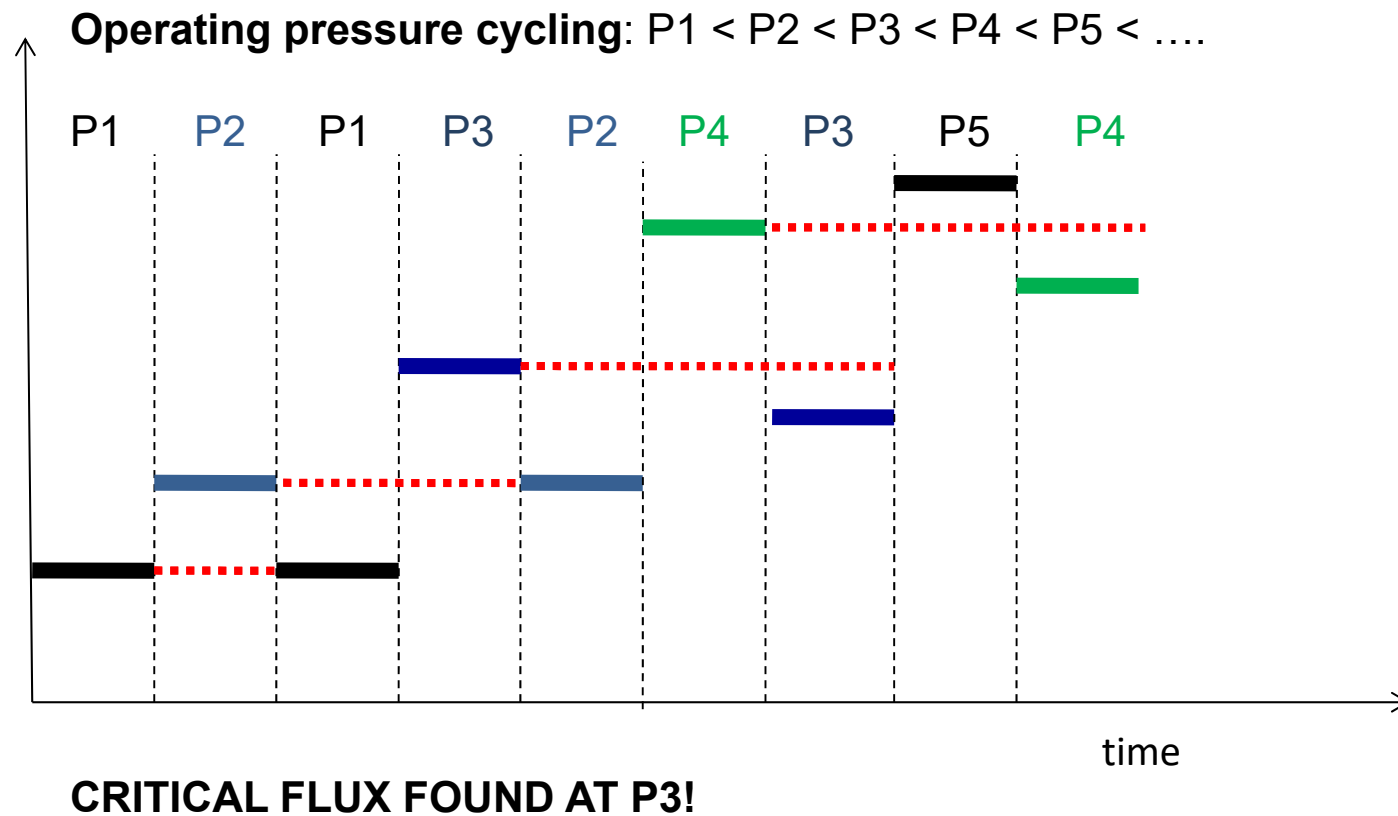
has influence on product quality \rightarrow product targets

- **LONGEVITY**

Has influence on membrane survival \rightarrow operational costs

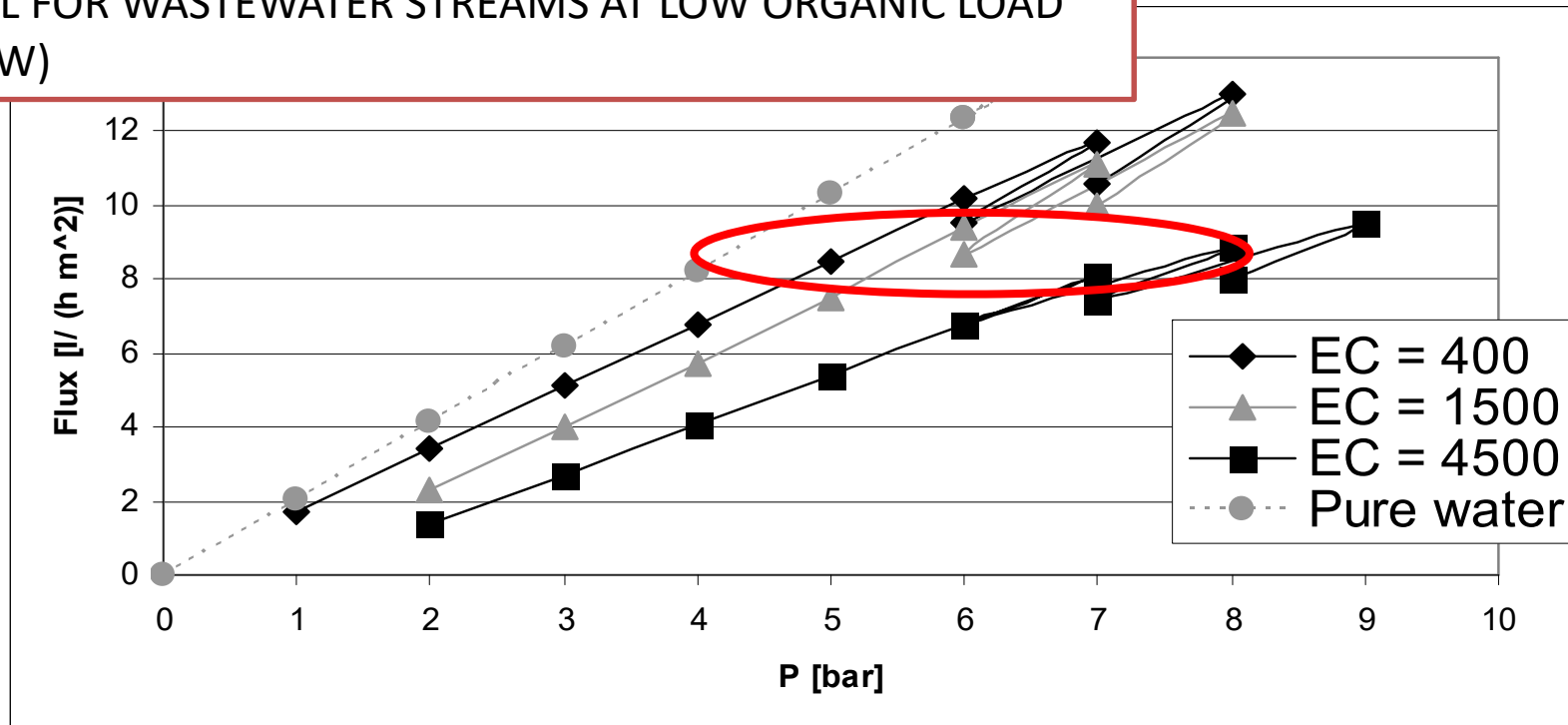
Critical flux determination

Permeate flow rate



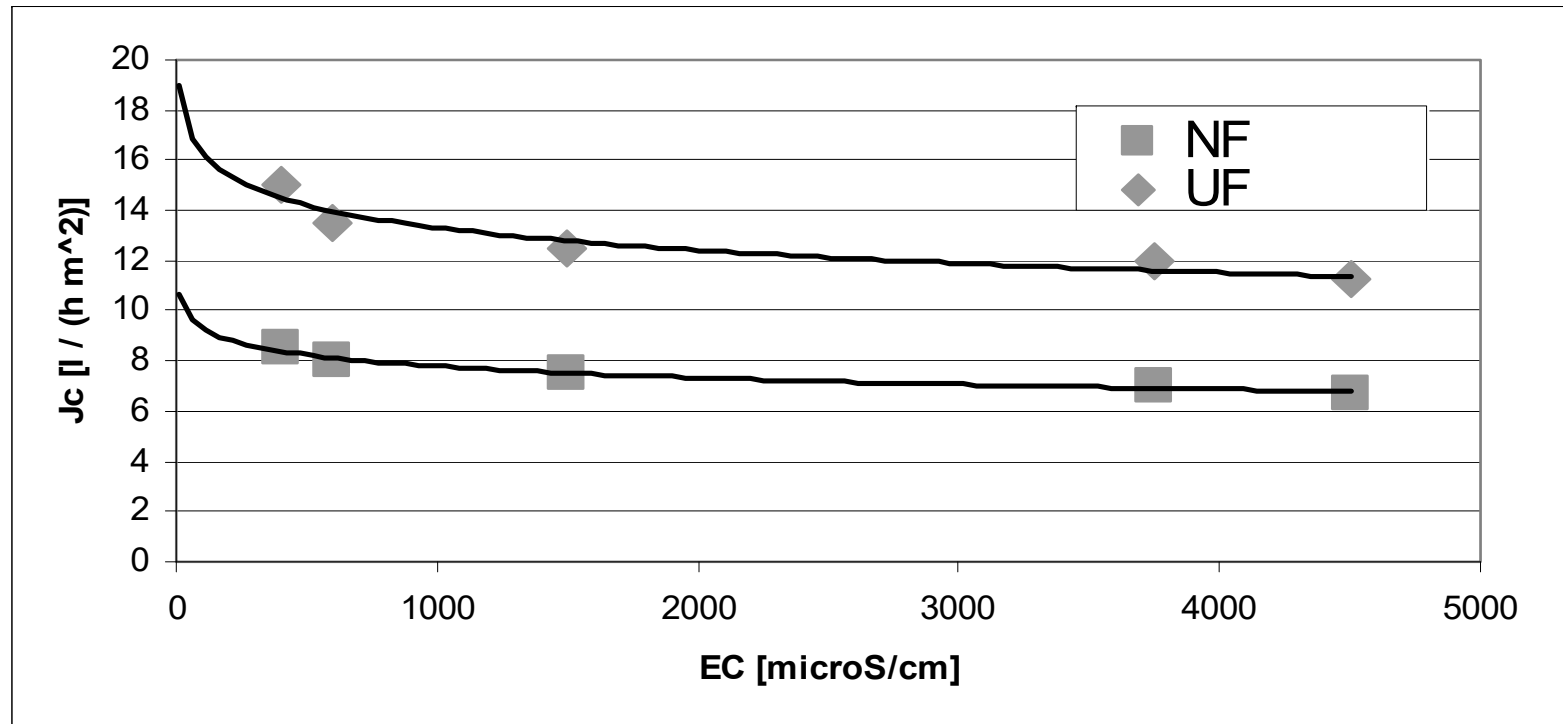
Critical flux determination

TYPICAL FOR WASTEWATER STREAMS AT LOW ORGANIC LOAD (OWWW)



The adopted method for critical flux value determinations is the one proposed by Benkhala, cycling the applied pressure up and down.

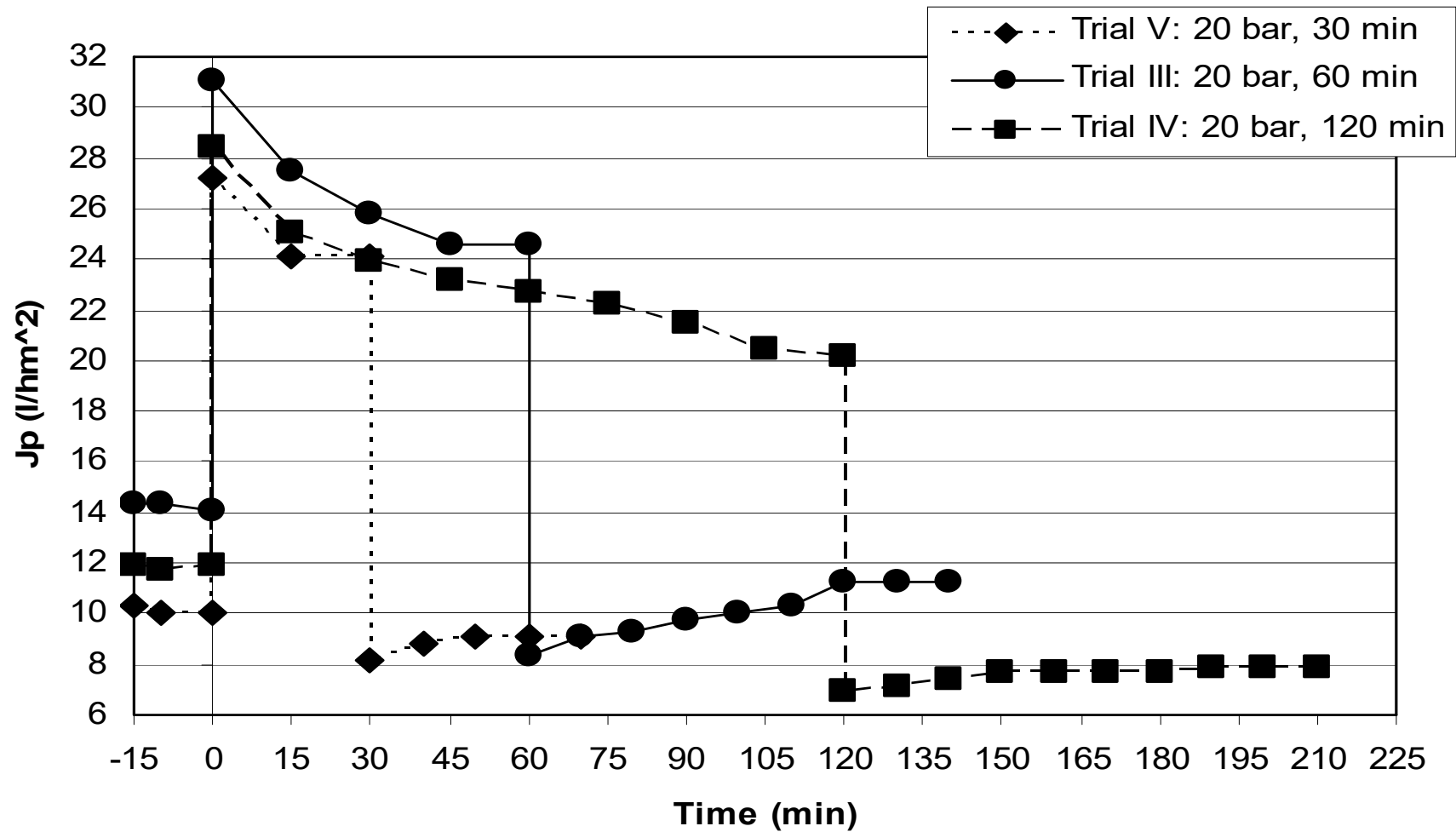
Critical flux fitting



$$J_{C, \text{UF}} = 22,24 - 1,292 \ln(\text{EC})$$

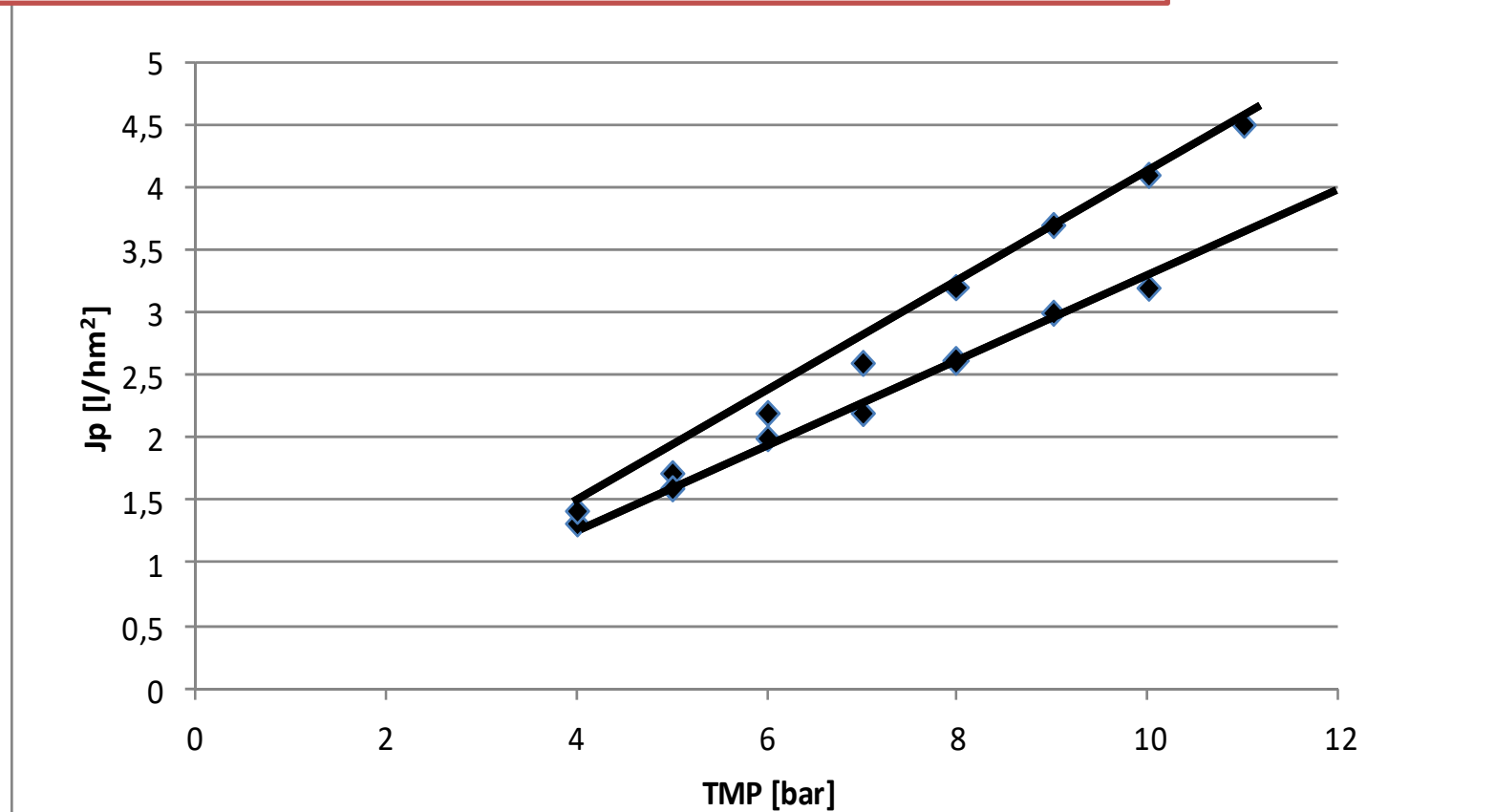
$$J_{C, \text{NF}} = 12,35 - 0,659 \ln(\text{EC})$$

Example of fouling curves

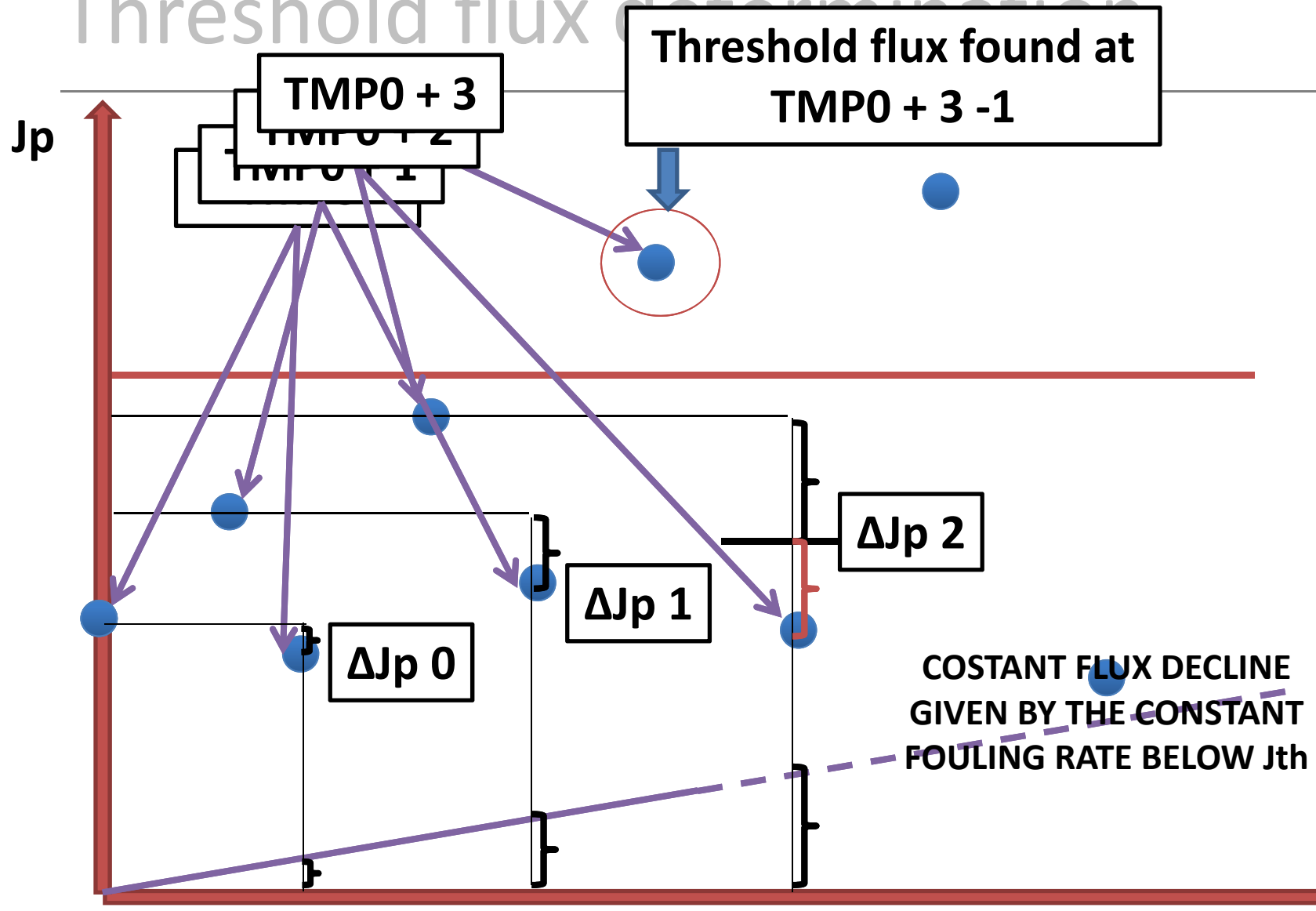


Threshold flux determination

TYPICAL FOR WASTEWATER STREAMS AT HIGH ORGANIC LOAD
(OMWW)



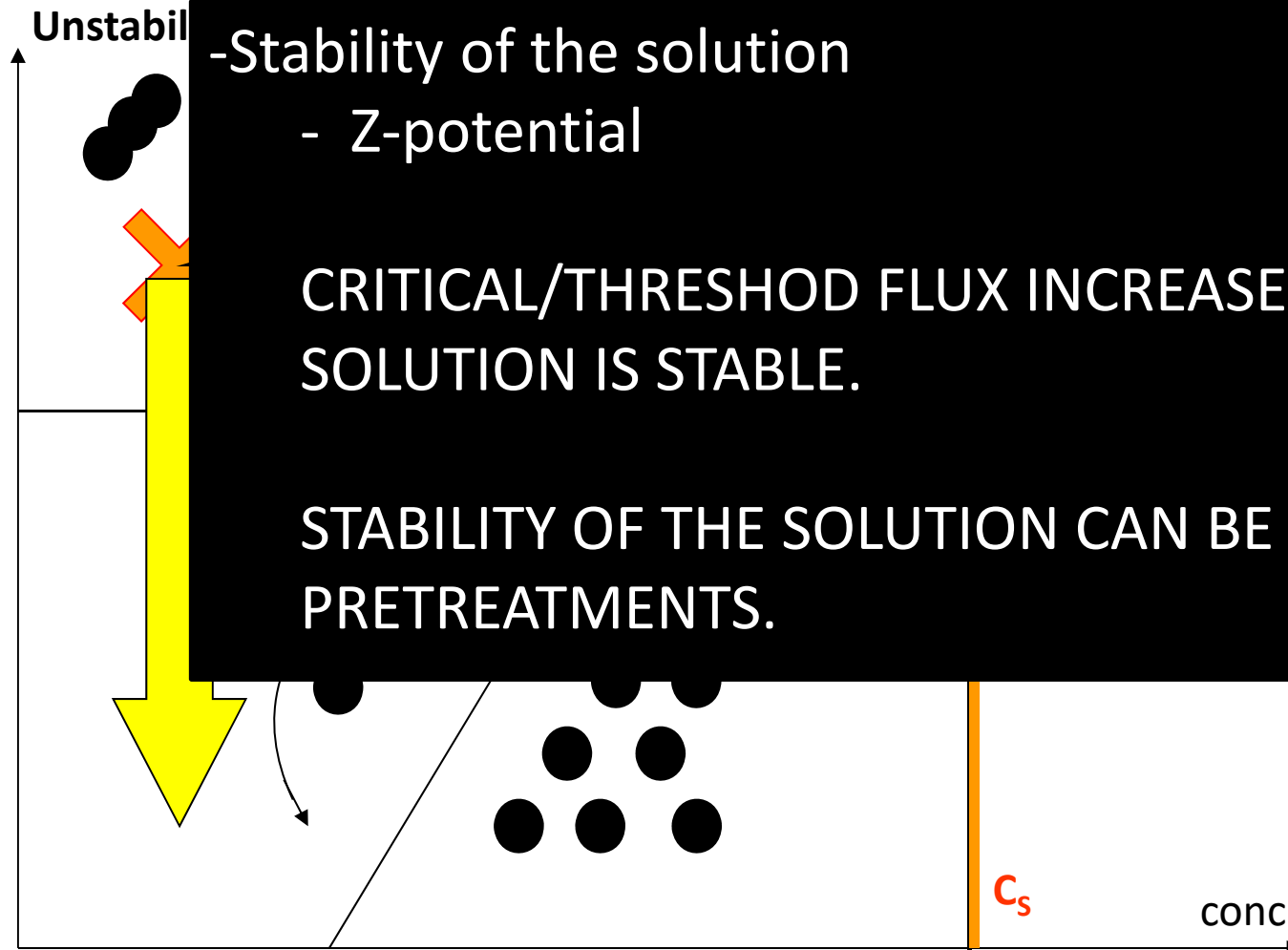
Threshold flux determination



Critical/threshold flux depends of

- Stability of the solution
 - Z-potential
 - Particle size distribution of suspended matter
- Concentration of solutes
 - C_s of solutes
- Hydrodynamics

Critical/threshold flux depends of





Critical/threshold flux depends of

CASE 1

-Stability of the solution

-Particle size distribution of suspended matter

CRITICAL/THRESHOLD FLUX VALUES INCREASES
WHEN MOST OF THE PSD IS OUTSIDE THE RANGE
1/10 TO 10 TIMES THE MEMBRANE PORE SIZE.

MEMBRANE PORE SIZE HAS TO BE CHOOSSEN WISELY.
PSD SHIFTS CAN BE PERFORMED BY PROPER
DESIGNED PRETREATMENTS.

MEM

Critical/threshold flux depends of

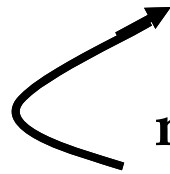
- Concentration of solutes
 - C_s of solutes
- Hydrodynamics

CRITICAL/THRESHOLD FLUX INCREASES WITH
ADDITION OF ANTIFOULANTS AND FEED FLOW RATE
VELOCITY.

Critical flux model

$$\frac{dm}{dt} = -b (J_p - J_c) \quad \text{if } J_p > J_c$$

$$\frac{dm}{dt} = 0 \quad \text{if } J_p \leq J_c$$



$$m = m_0 + m_1 c(EC)$$

$$\pi = \pi_0 + \pi_1 c(EC)$$

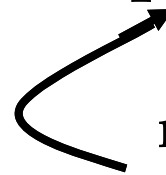
**PARAMETERS TO BE DETERMINED
EXPERIMENTALLY ARE**

m , π , Q_c and B

Critical flux model

$$J_p = [(m (P - \pi) - J_c] e^{(-Bt)} + J_c \quad \text{if } J_p > J_c$$

$$Q_p = m (P - \pi) \quad \text{if } J_p \leq J_c$$


$$m = m_0 + m_1 c(EC)$$
$$\pi = \pi_0 + \pi_1 c(EC)$$

**PARAMETERS TO BE DETERMINED
EXPERIMENTALLY ARE**

m, π, Q_c and B

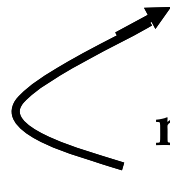
Threshold flux model

$$dm/dt = -a t - b (J_p - J_{th})$$

if $J_p > J_{th}$

$$dm/dt = -a t$$

if $J_p \leq J_{th}$



$$m = m_0 + m_1 c(EC)$$

$$\pi = \pi_0 + \pi_1 c(EC)$$

**PARAMETERS TO BE DETERMINED
EXPERIMENTALLY ARE**

m, π, Q_c and B

Boundary flux model

CRITICAL FLUX CONCEPT

$$a = 0$$

THRESHOLD FLUX CONCEPT

$$a \neq 0$$

BOUNDARY FLUX CONCEPT

$$\frac{dm}{dt} = -a t - b (J_p - J_b)$$

$$\text{if } J_p > J_b$$

$$\frac{dm}{dt} = -a t$$

$$\text{if } J_p \leq J_b$$

Rejection model

$$R = \sigma [(P - \pi) / (P - \pi + \beta)]$$

**PARAMETERS TO BE DETERMINED
EXPERIMENTALLY ARE**

σ and β

Feed & Bleed

CONTROL OF FOULING ISSUES: EASY!

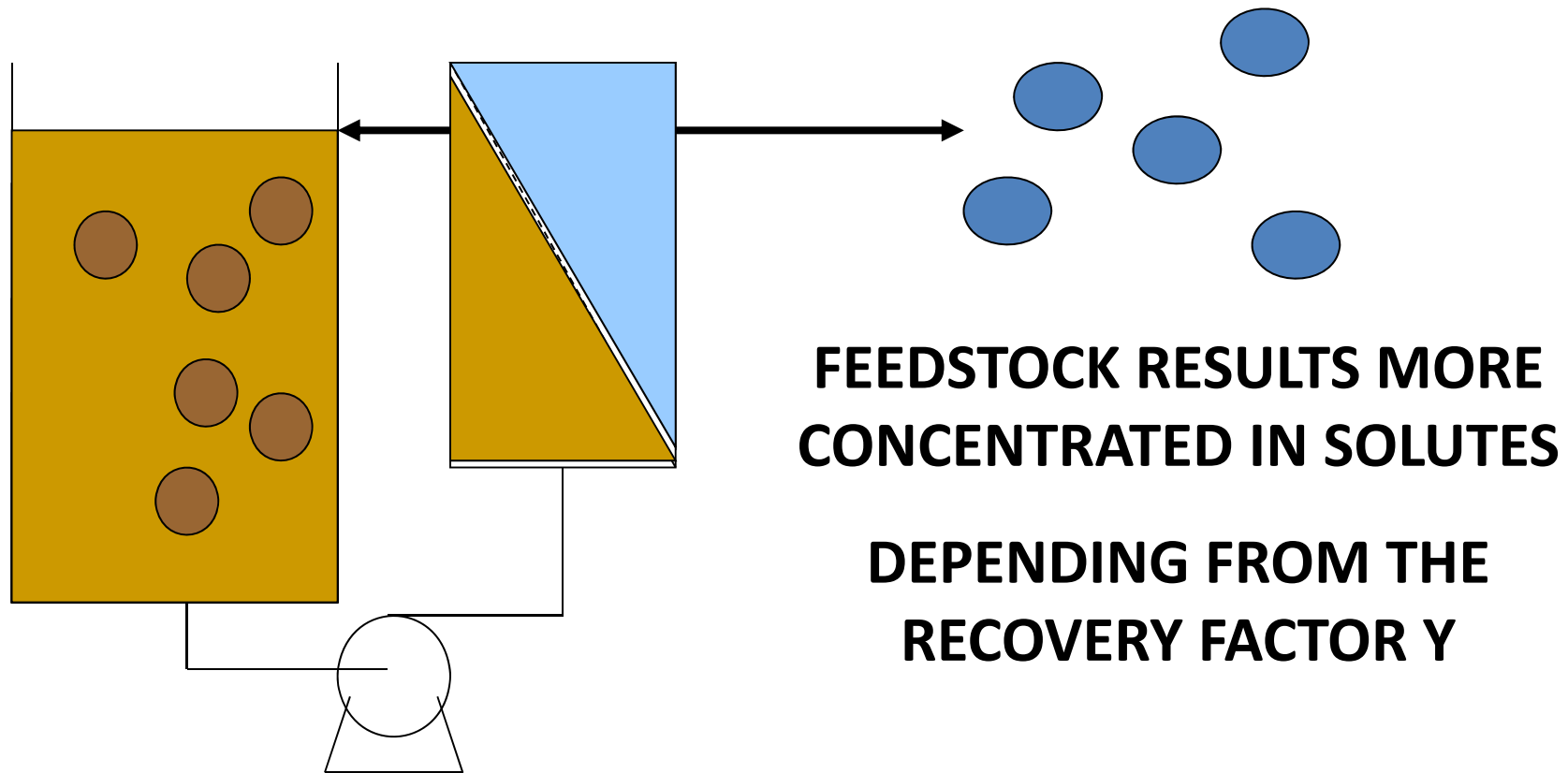
**JUST WORK BELOW CRITICAL OR THRESHOLD FLUX
(- 10%).**

**TRY TO INCREASE CRITICAL/THRESHOLD FLUX
VALUES, NOT THE TMP.**

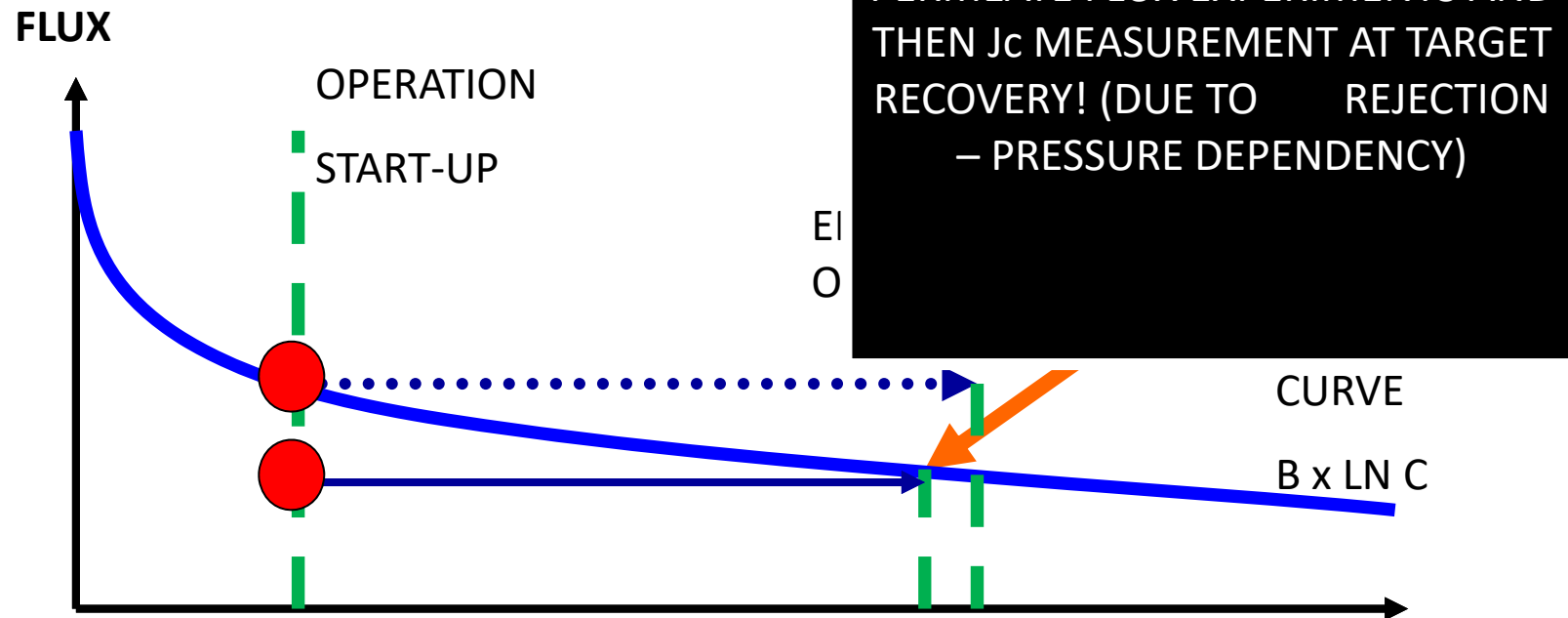
**MEASURE CRITICAL/THRESHOLD FLUX VALUES OF
THE SYSTEM PERIODICALLY.**

**COMPENSATE OSMOTIC PRESSURE VARIATIONS
ONLY.**

Batch concentration of the feed



Batch



Strategy 2: Operation start at primary flux value Heavy fouling estimated by critical operation. at end of operation. Fouling is avoided operating mostly in subcritical conditions.

Batch

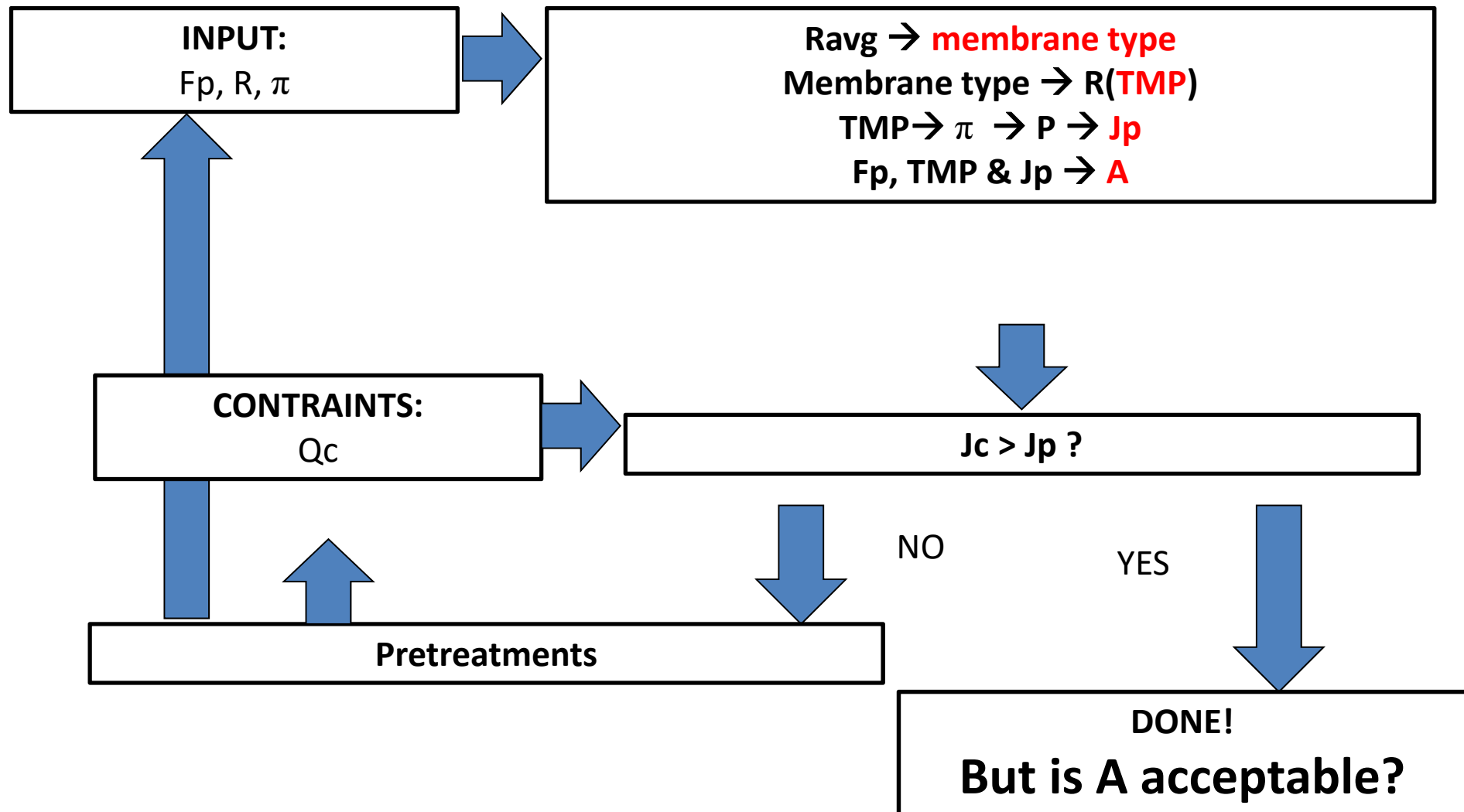
NOT SO EASY!

**DETERMINATION OF THE CRITICAL/THRESHOLD
FLUX CURVE.**

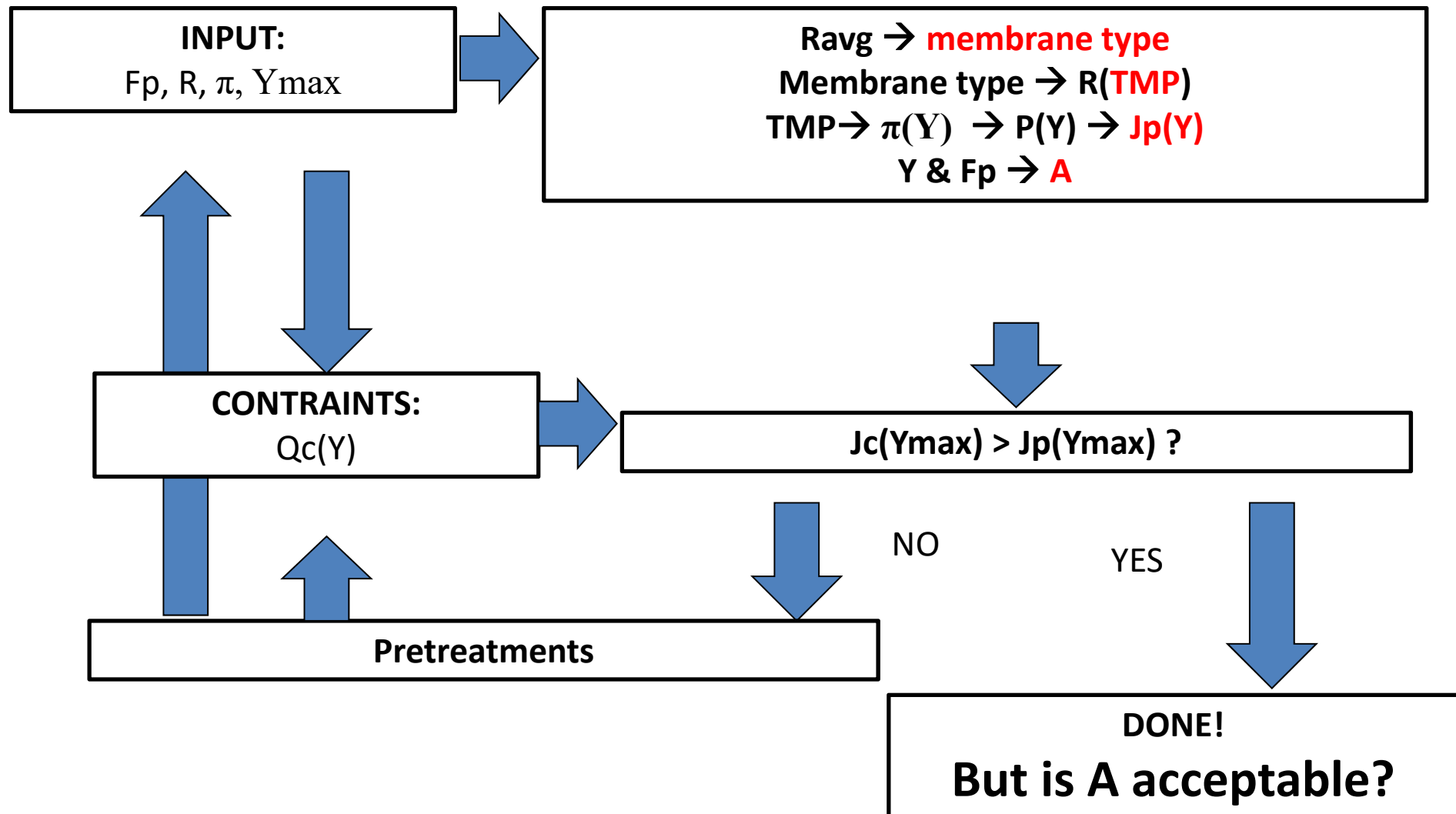
MAINTAIN THE FITTING CURVE UPDATED.

**→ USE OF SIMULATION MODEL FOR
DETERMINATION OF OPERATING PRESSURE.**

Feed & Bleed



Batch



Batch

**SAME APPLIES TO THRESHOLD FLUX SYSTEMS
BUT...**

**THE CONSTANT FOULING RATE DURING
OPERATION REQUIRES ADDITIONAL MEMBRANE
AREA TO OVERCOME WASHING PERIODS.**

Simulation model

	UF	NF
m_0 [l h ⁻¹ m ⁻²]	12,62	2,06
m_1 [l h ⁻¹ m ⁻² (μS/cm) ⁻¹]	-0,0016	-0,0003
π_0 [bar]	0	0
π_1 [bar (μS/cm) ⁻¹]	0,0001706	0,0003033
B [min ⁻¹]	0,01	0,086
σ_{EC} []	10	67,5
β_{EC} []	0	1
σ_{COD} []	55	95
β_{COD} []	1	2
a [l h ⁻² m ⁻² bar]	0,0009	0,0004

Results

BARE SYSTEM

CONTROLLED SYSTEM

VARIABLE	UF	NF	UF	NF
Operation time [min]	254	76	260	448
Membrane Area [m ²]	32	32	32	32
Feed stream flow rate [l/h]	426,1	250,0	415,8	222,0
Initial op. pressure [bar]	1,38	4,71	1,35	4,22
Final op. pressure [bar]	1,81	32,0	1,44	7,80
Initial critical flow rate [l/h]	426,1	250,0	426,1	249,8
Final critical flow rate [l/h]	416,4	247,6	416,0	222,1
Recovery [%]	90	17,6	90	90
Product EC [μS/cm]	972	448	972	710
Product COD [mg/l]	793	239	800	472

Validation

