Nanofiltration Membrane Fouling Upon Treatment of Industrial and Municipal Wastewaters

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water reuse and desalination: experience and opportunity

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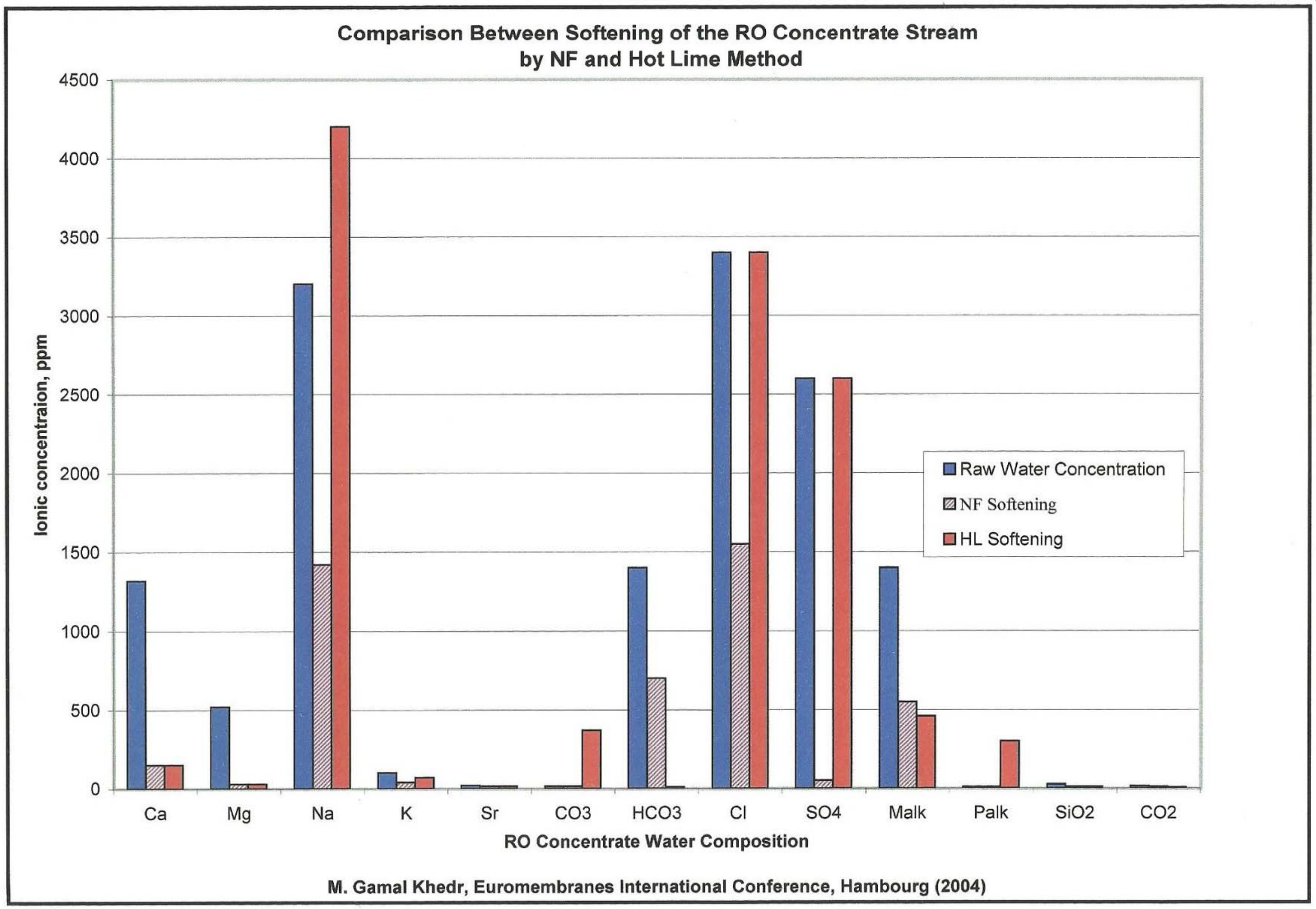
Nanofiltration Membrane Fouling:

- The main application problem of NF in treatment of wastewater streams is membrane fouling.
- Fouling Leads to:
  - Decrease of Process Efficiency.
  - Decrease of Process Cost Effectiveness.
  - Threat To Environmental Safety.

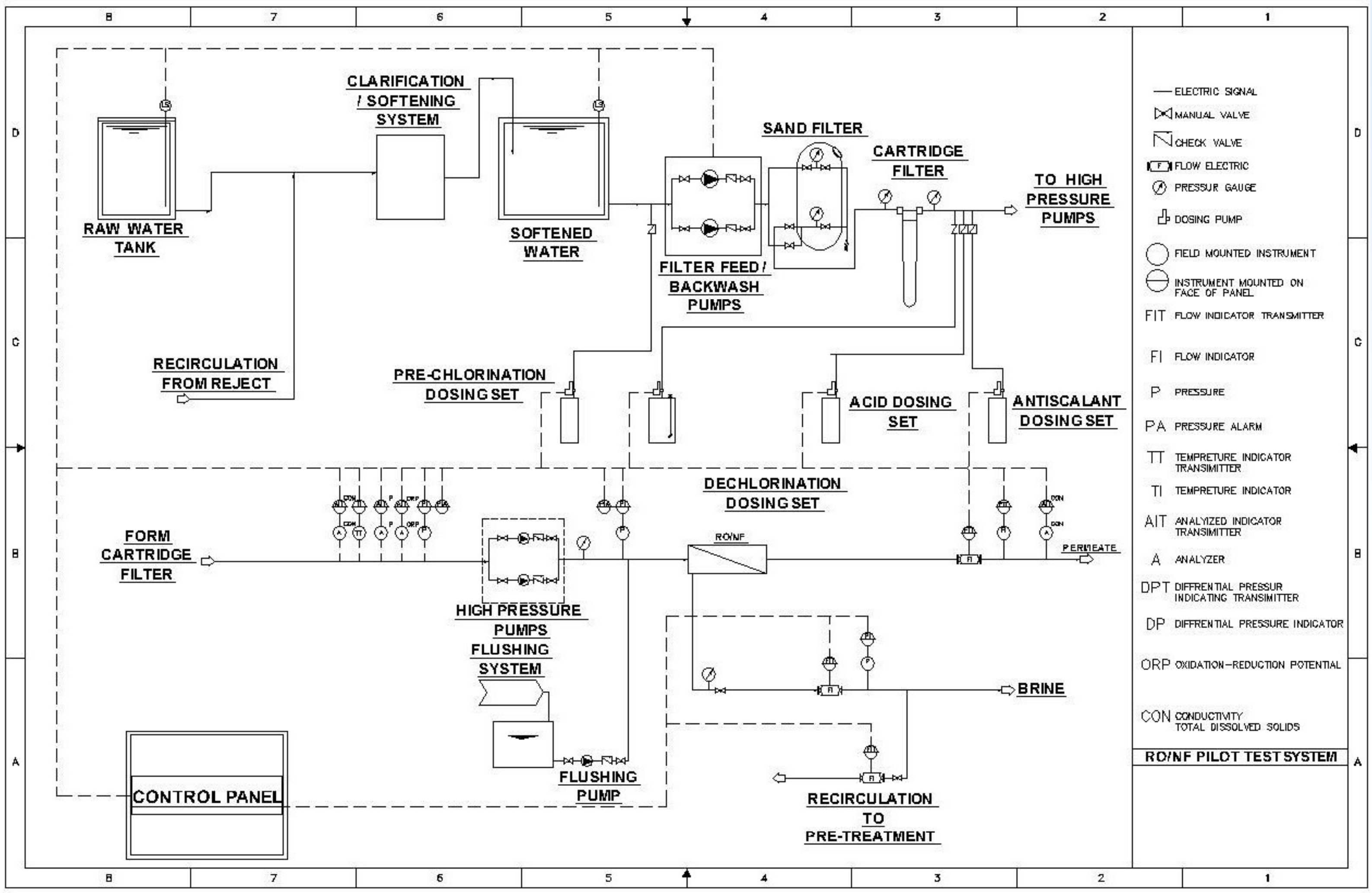
Reported Fouling Aspects are:

- Lowering of permeation rate.
- Modification of rejection selectivity and lowering of product quality.
- Repeated system shutdown for membrane cleaning.
- Shortening of effective membrane lifetime.


Comparison Between Softening of the RO Concentrate Stream
by NF and Hot Lime Method
Ionic concentraion, ppm
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Raw Water Concentration
NF Softening
HL Softening
Ca
Mg
Na
K
Sr
CO3
HCO3
Cl
SO4
Malk
Palk
SiO2
CO2
RO Concentrate Water Composition
M. Gamal Khedr, Euromembranes International Conference, Hambourg (2004)

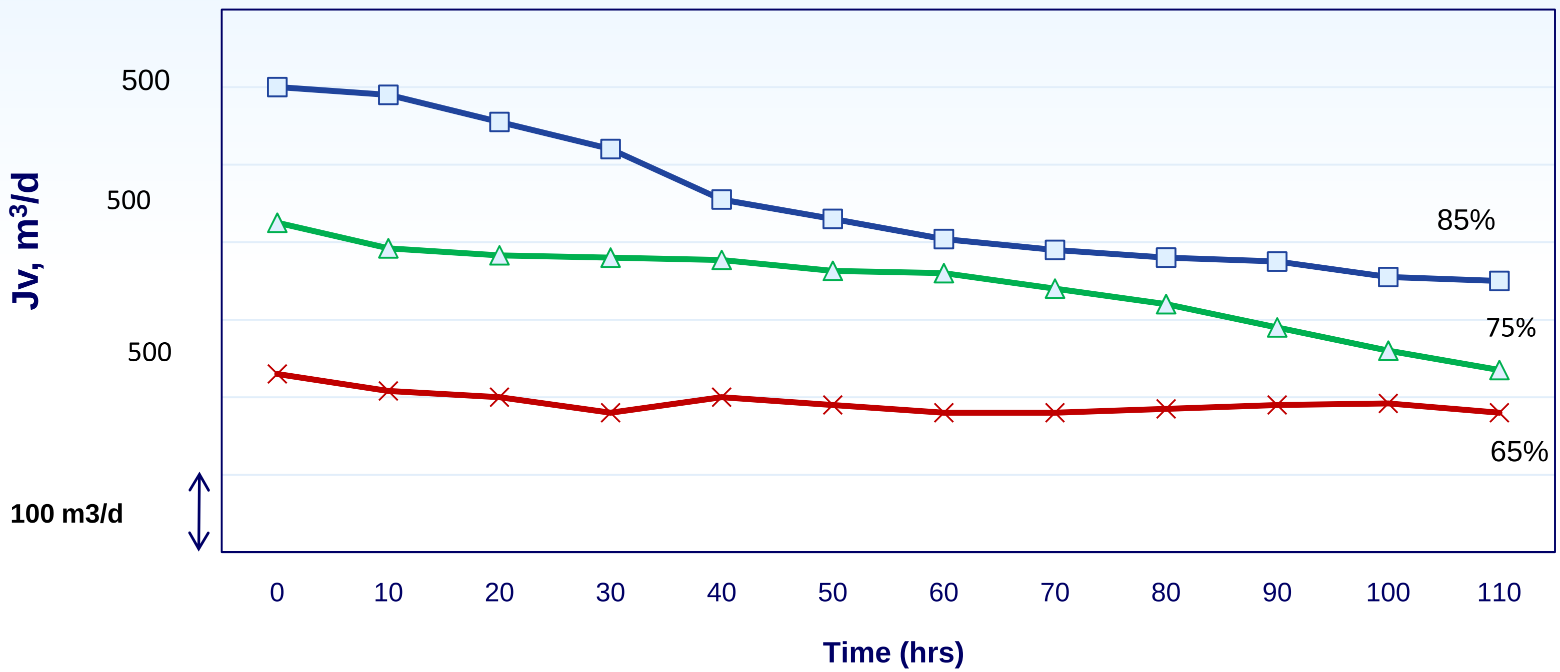
Typical Raw Wastewater Analysis

Component	Concentration ppm	Parameter	Value
Ca^{2+}	122.8	TDS	1543.7 ppm
Mg^{2+}	12.5	pH	7.6
Na^{+}	424.8	TOC	64 ppm
K^{+}	17.0	Bacterial count	Too numerous to count
NH_4^{+}	12.8		
NO_3^{-}	46.0		
Cl^{-}	630.0		
SO_4^{2-}	160.4		
SiO_2	22.5		

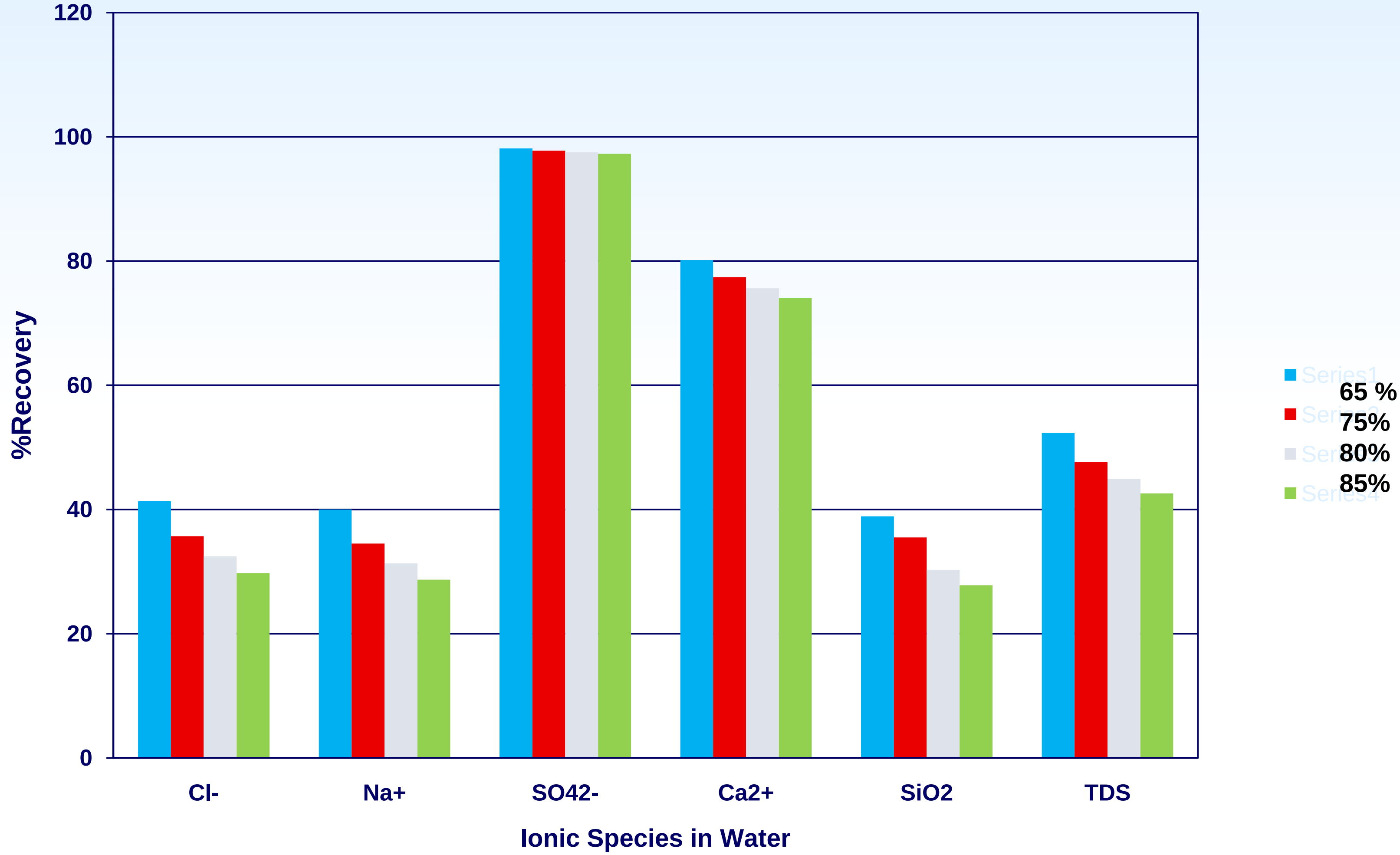


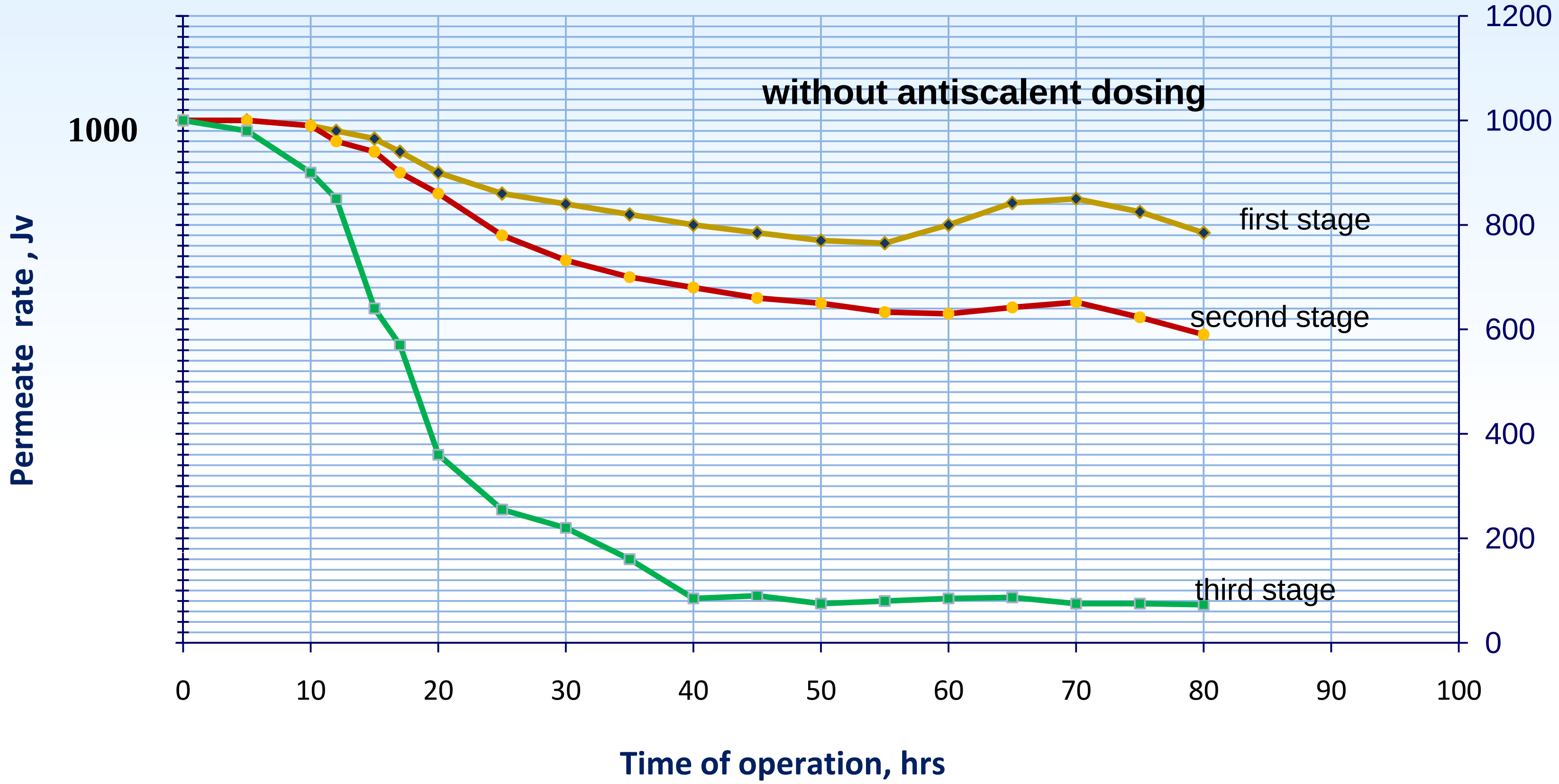
Schematic representation of the pilot plant

Variation of rate of permeation, Jv, with time at various recoveries

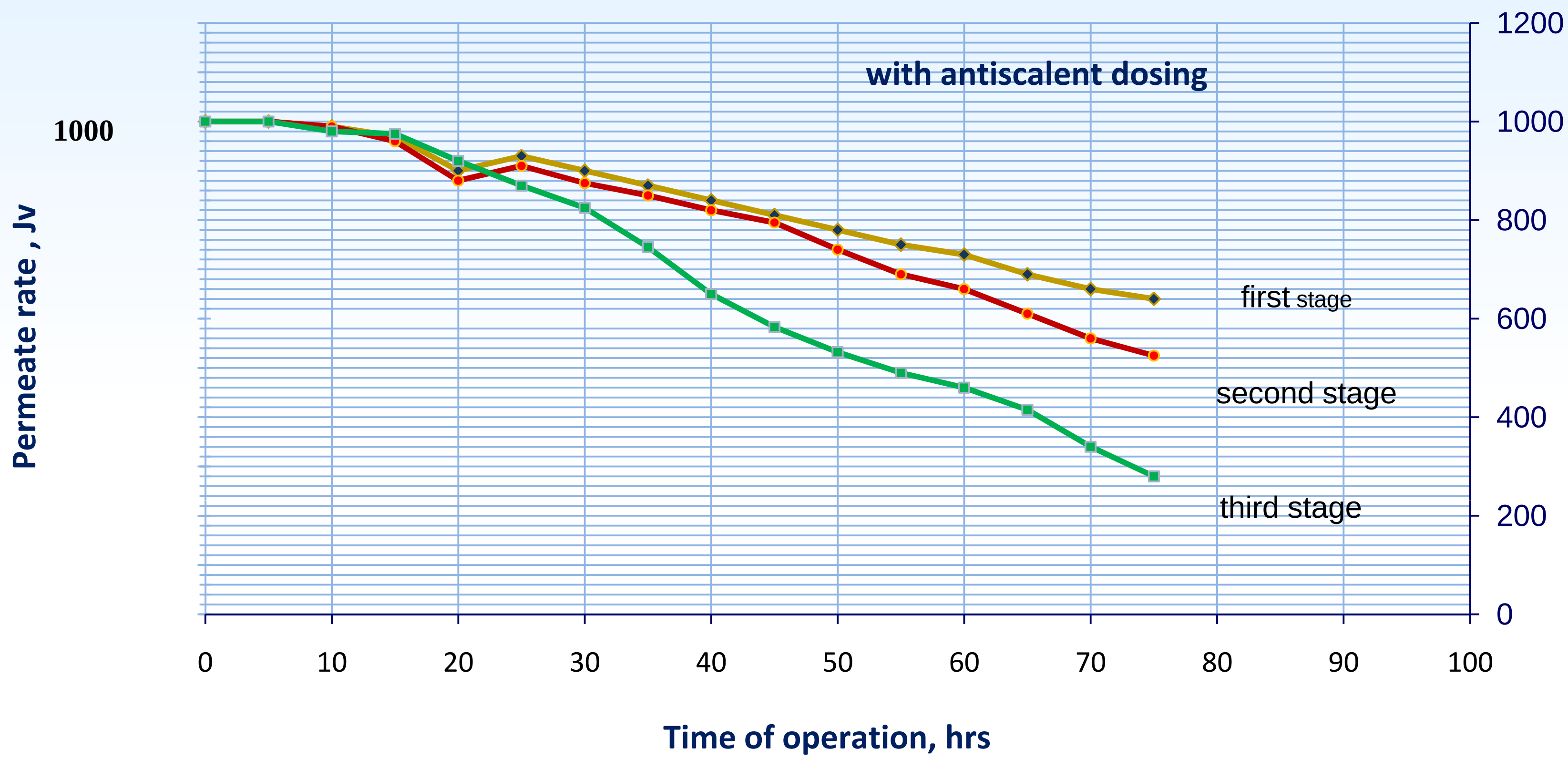


Variation Of Percent Rejection of Wastewater Components With Percent Recovery





Variation of permeate rate with time for the three stages of the NF system



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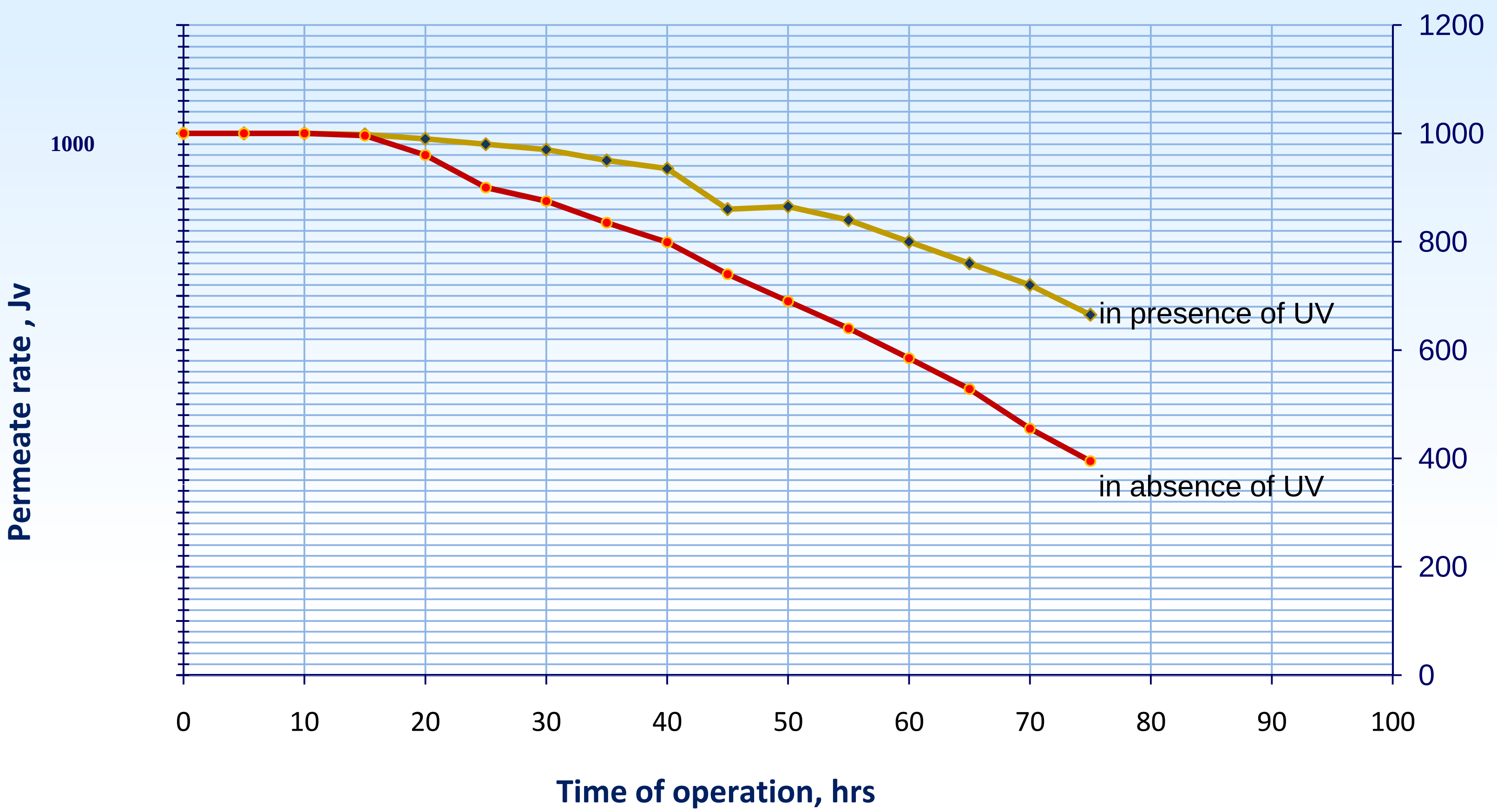

Variation of permeation rate with time in presence of organic or organic/biofouling

Analysis of fouling Deposit (energy dispersive X-ray results)

Sample	Major Elements	Minor Elements	< Minor < 1%
Fresh membrane surface	–	S	
Deposit on membrane, case 1 (deposit on membrane surface)	Ca, P	Si, Fe	Ti, Al, Mg
Deposit removed from membrane, case 2 (deposit removed from membrane surface)	Ca, P	Si	Fe, Ti, Al, Mn

Common Forms of Membrane Fouling

Nature of fouling deposit	Source
Inorganic scale	Deposition of sparingly soluble salts of Ca, Mg, Sr, Ba or of SiO_2
Organic Fouling	Adsorption on membrane surface of dissolved organic compounds.
Particulate Fouling	Accumulation of suspended particles which escaped filtration.
Colloidal Fouling	Adsorption of colloidal organic or inorganic compounds
Biofouling	Adsorption of microorganisms and their metabolic products

Development of The Fouling Film

1. Colloidal Fouling

- Through **convective entrainment** of organic, silt, and colloidal particles and adsorption on membrane surface.
- Through **electrostatic interaction** between the surfaces charges of the colloid particles.
- Through interaction between the polyvalent cations like iron or aluminum accumulated by membrane rejection in the diffusion layer with the stabilizing charge of colloidal particles.

2. Primary Scale Deposition

Parallel to 1 particularly in the last stages:

Deposition of supersaturating of sparingly soluble salts/compounds in view of:

- Inadequate acid or antiscalent dosage.
- Exceeded system design parameters:
  - Too high recovery
  - Too slow brine flow

3. Biofouling

a) Primary bacterial adhesion

- Minimum initial bacteria adsorption takes place due to electrostatic repulsion.
- Fixation on membrane surfaces by ECPS connections.
- Surface free energy of interaction.

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b) Film Growth and propagation

is controlled by : Type of bacteria

Ambient Temperature

Availability and nature of nutrition:

C-rich compounds Important growth + weak adhesion

N-rich compounds Limited growth + Strong adhesion

c) Film Denaturation

Fouling film progressively becomes more dens, sticky, adherent and of lower permeability due to physical, chemical, and/or biological alterations.

Biofilm further interferes with other wastewater components.

4. Secondary Scale Deposition

Both forms 1 to 3 lead to formation of a film which acts as a Secondary Membrane on the membrane surface:

↓

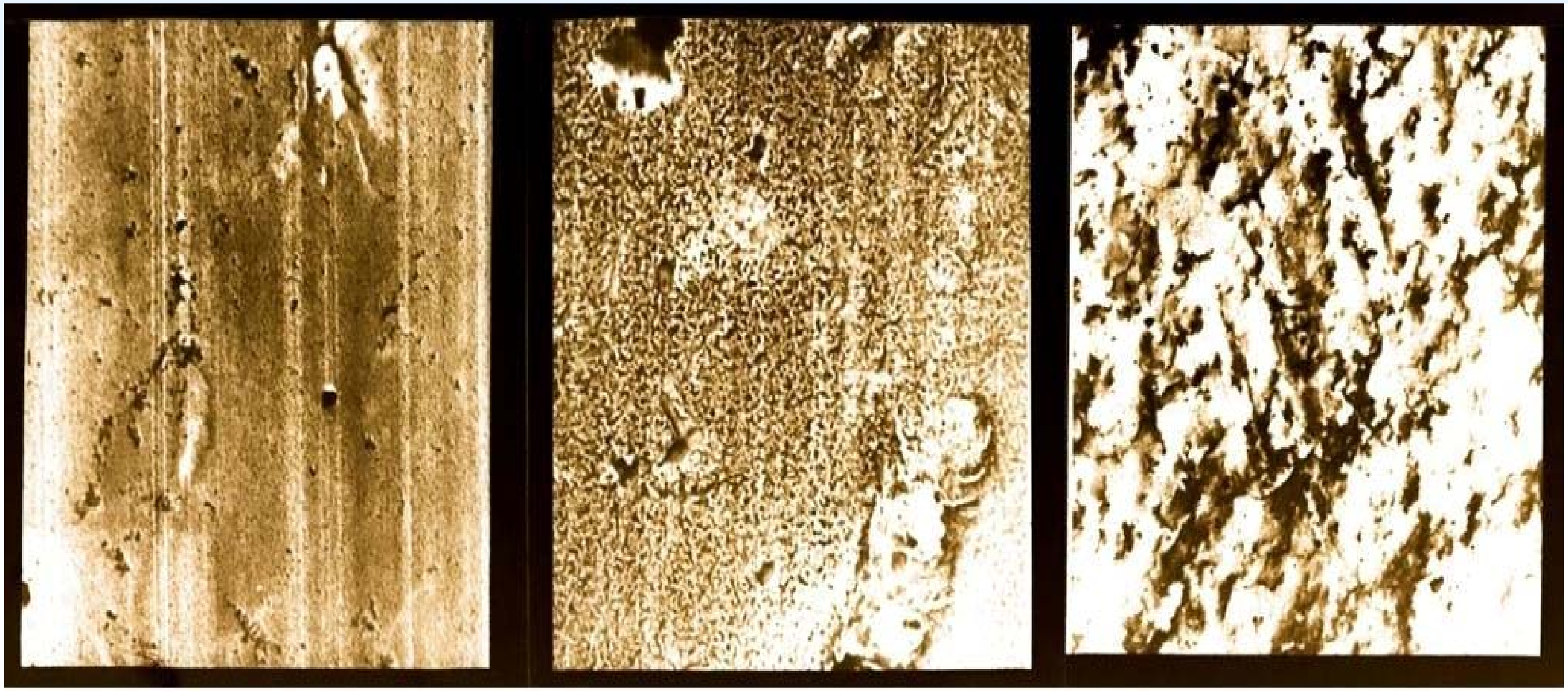
higher ΔP (feed-permeate)

higher ΔP (feed-brine)

↓

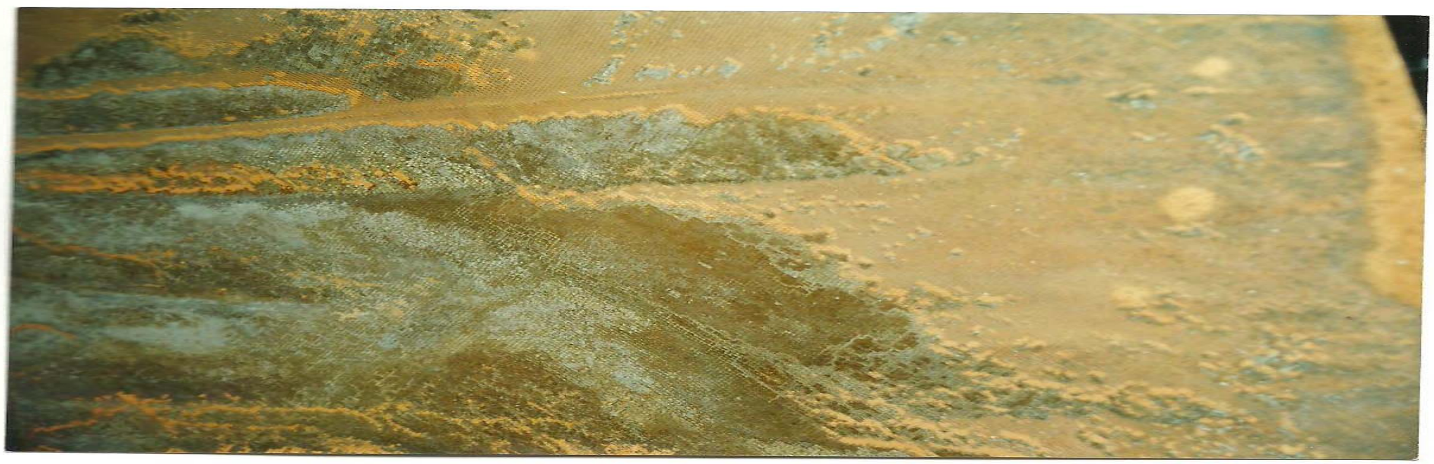
- Impaired hydrodynamic conditions ⟶ severe concentration polarization ⟶ localized scale deposition, **(secondary scale deposition).**

Interaction of different forms of membrane fouling.



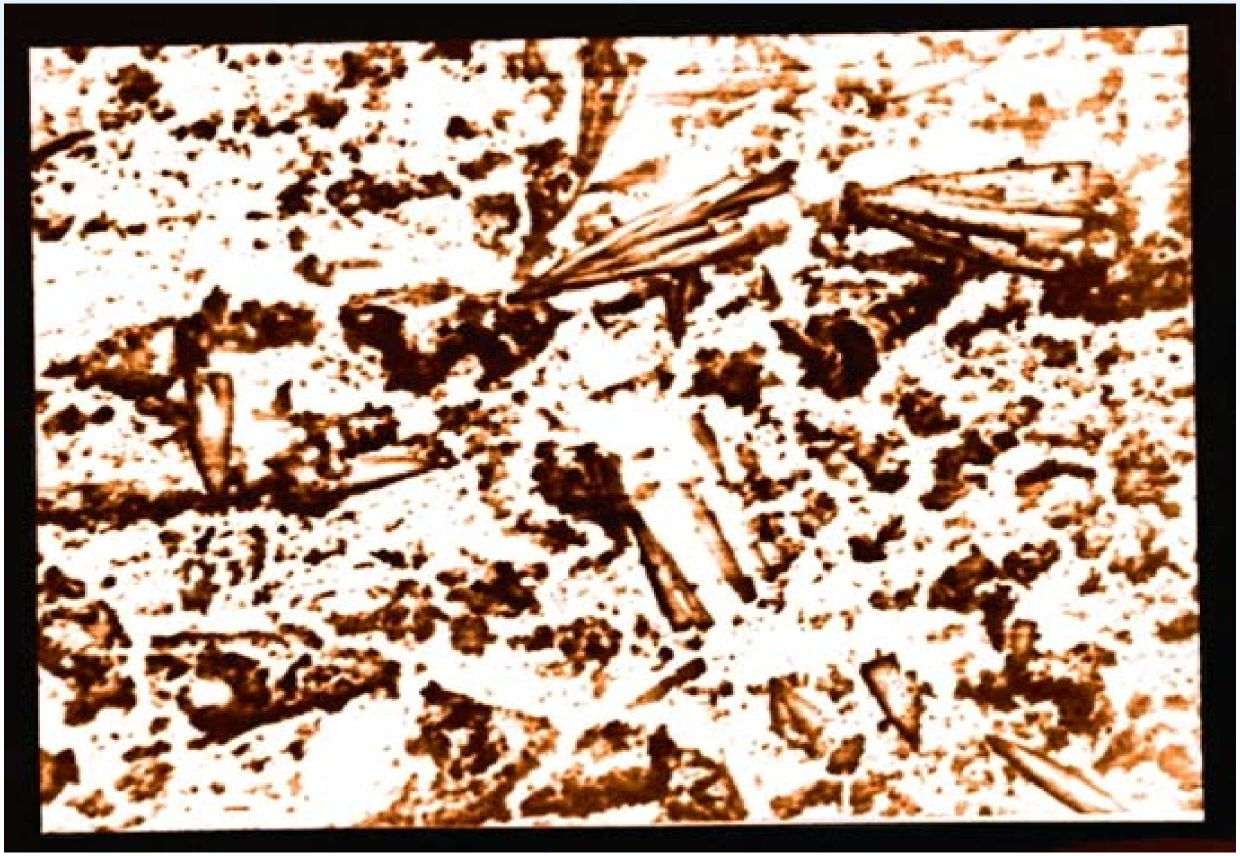
SE micrograph for membrane samples showing advance of fouling as function of time

Thick fouling deposit on the membrane surface

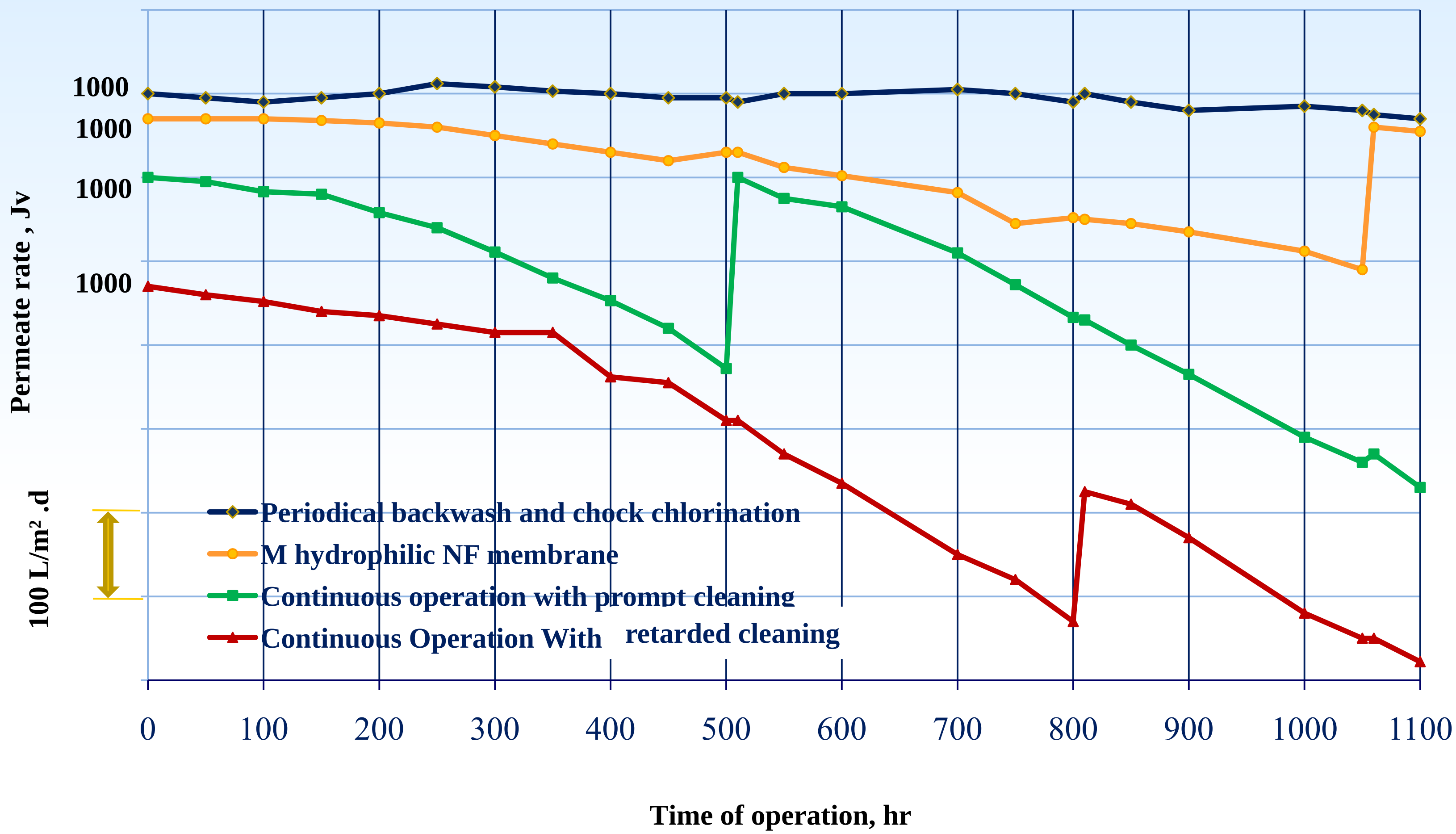


Blocking of the feed spacer and secondary scale deposition

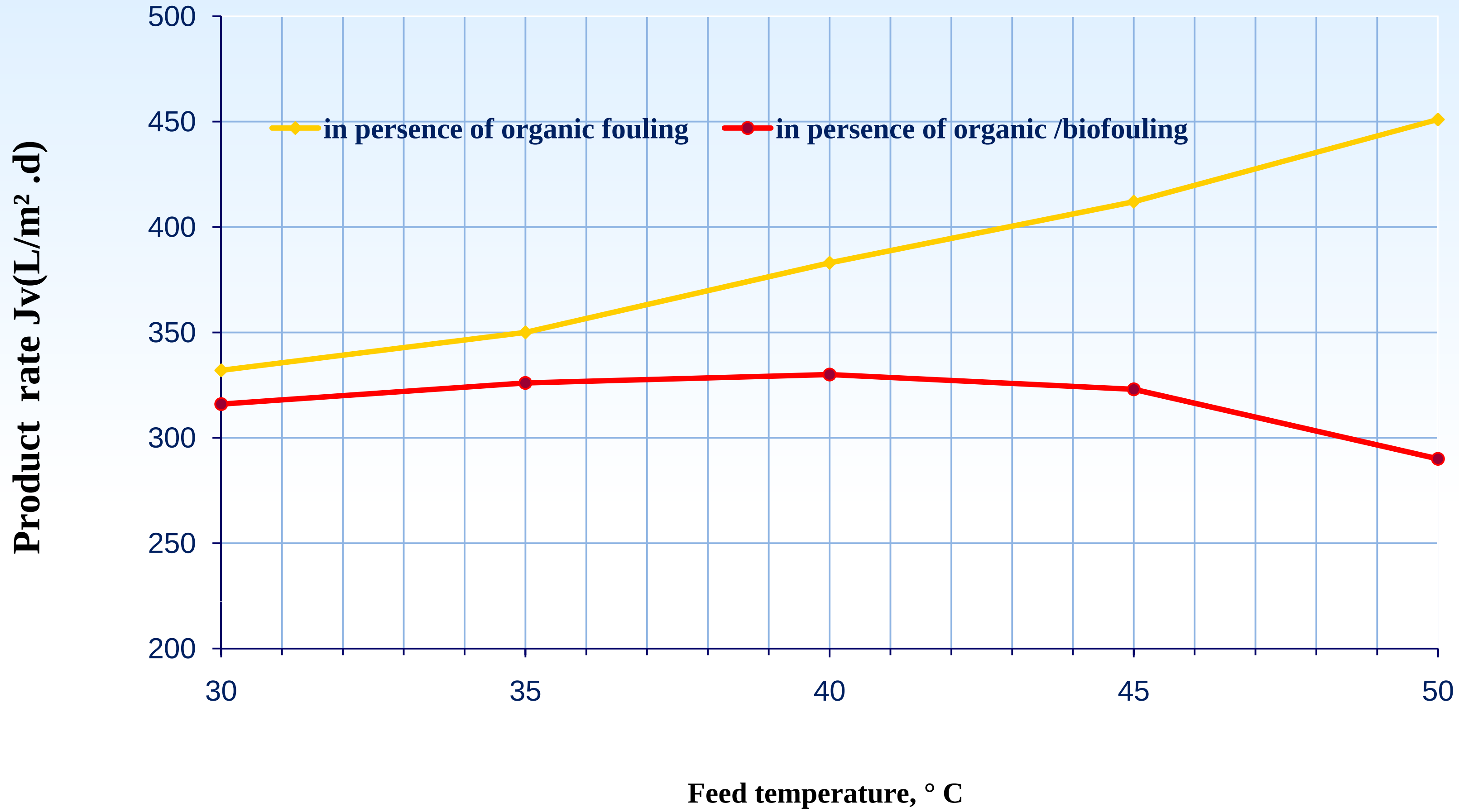

Membrane
Autopsy



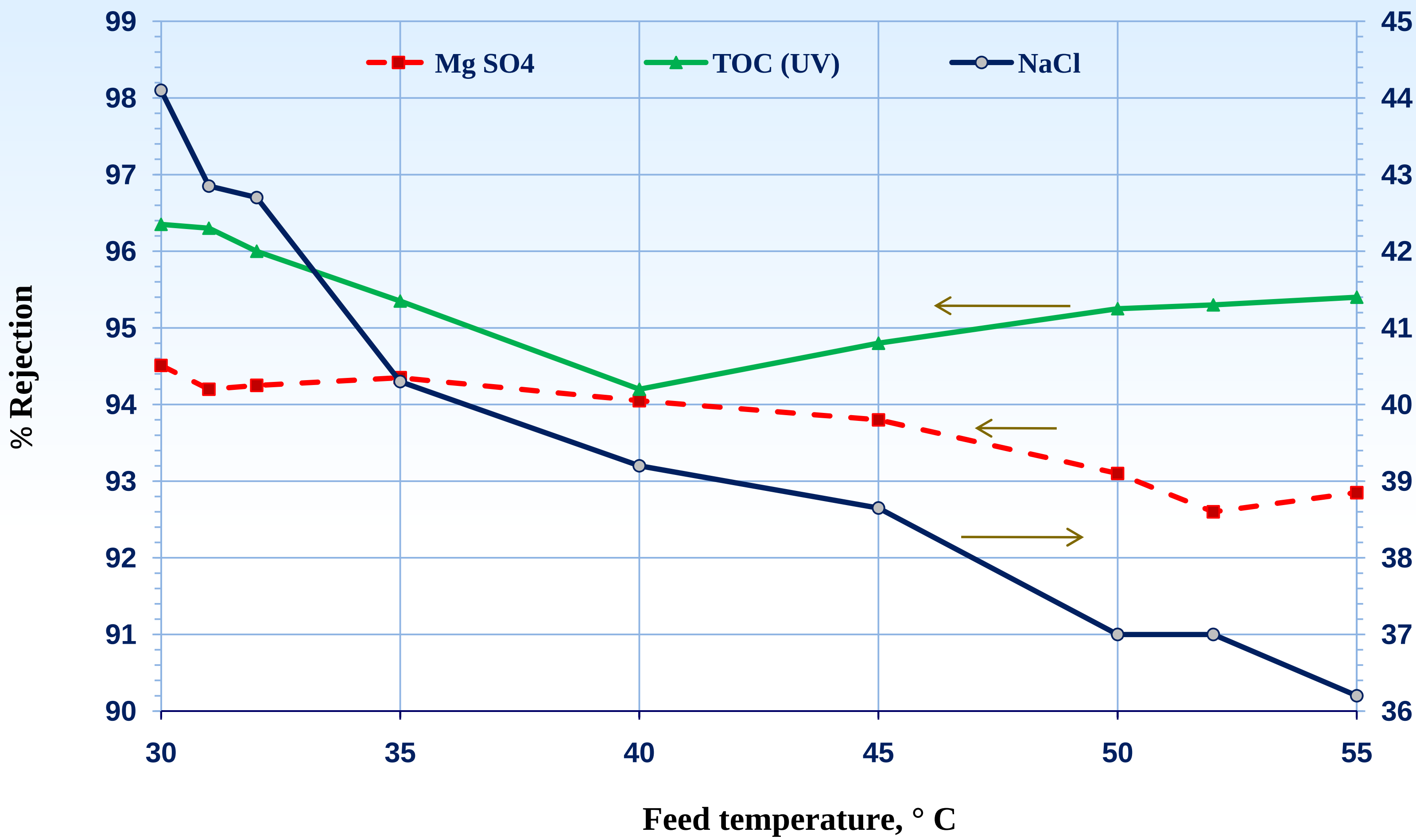
Inorganic scale crystal bundles embedded in the organic/biofilm matrix



Decline of product rate for various types of NF membranes upon fouling and remedy



Variation of NF product rate with feed temperature



Variation of NF rejection of various components with temperature

Conclusions

1. Results of NF treatment of highly contaminated industrial and municipal wastewaters showed that for the higher the percent recovery , i.e. process efficiency and permeate flux, the higher will be the increase of membrane fouling. The present investigation aims to minimize the development of fouling while realizing the highest possible process efficiency.

2. **Results of inspection of fouled membrane surface by SE microscopy and of periodical analysis of the accumulated fouling deposit were correlated to the observed decline in NF performance.**

   Mechanism of development of fouling film is established.

   Importance of interaction between the different forms of fouling on the decline of NF performance is demonstrated.

3. The main factors that enabled to control the fouling of NF membranes are:

a) Hindrance of the adsorption of organics and microorganisms on membrane surface through promoting its hydrophilicity.

b) Selection of membranes of lower surface charge and surface roughness.

c) Periodical backwash of membranes coupled with intermittent choc chlorination.

d) High temperature NF (HTNF),

4. HTNF, e.g. in case of hot wastewater streams, showed accelerated product rates with control of organic fouling and increased rejection of high molecular weight organics.

   Knowledge of the wastewater composition would enable the selection of the adequate temperature range of HTNF for the optimum product rate and rejection performance.