Recent Innovations to keep membranes clean

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Managing Director
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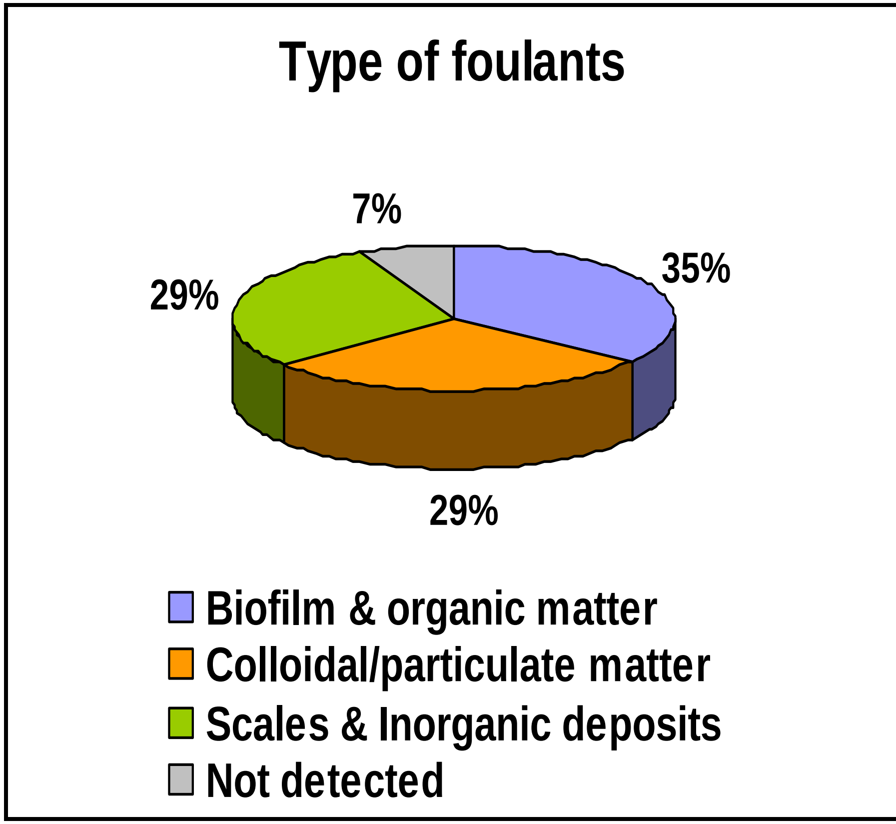
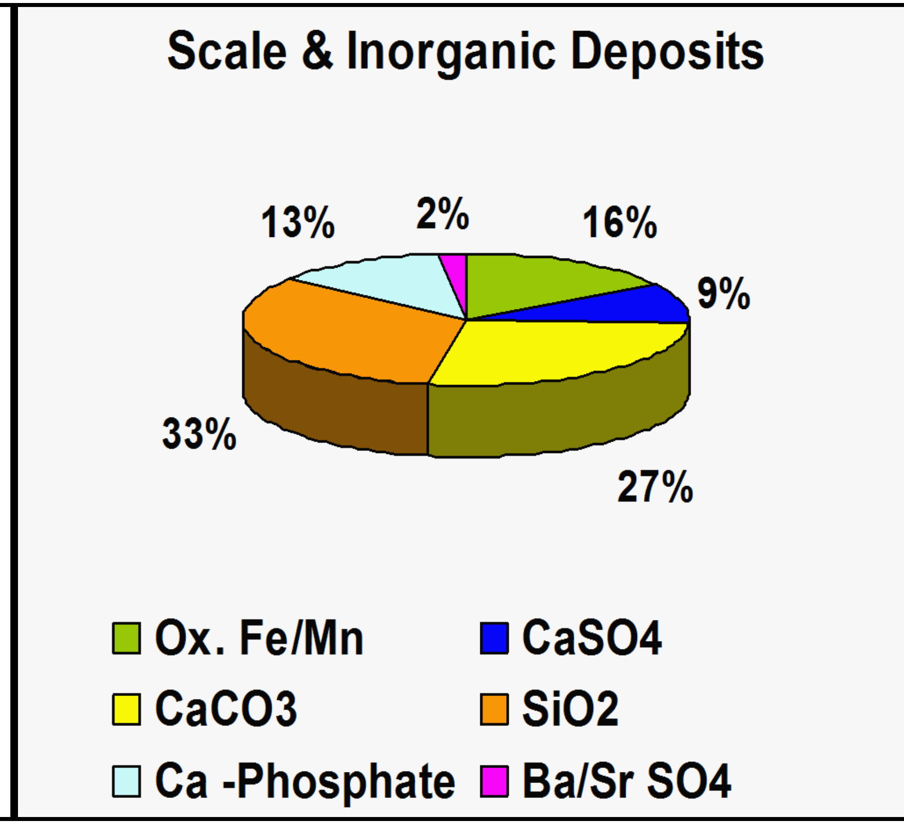
Why keep membranes clean

- Poor permeate quality and flow, increased operation pressures
- Higher energy requirements
- Water wastage – lower recoveries
- Operational Expenditure – membrane cleaning, membrane replacement

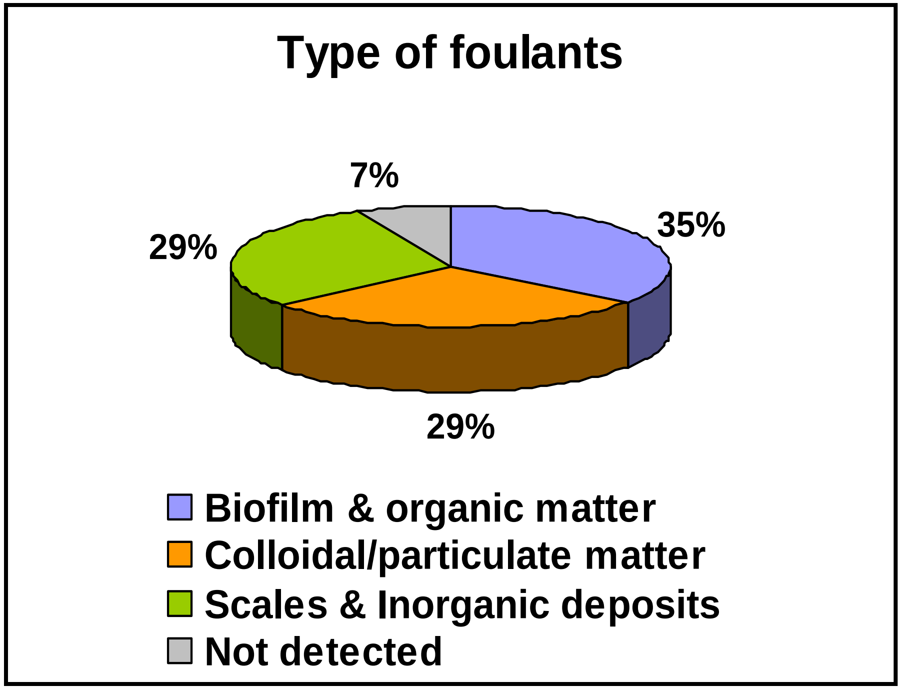
- Membrane Autopsies 2002-2009

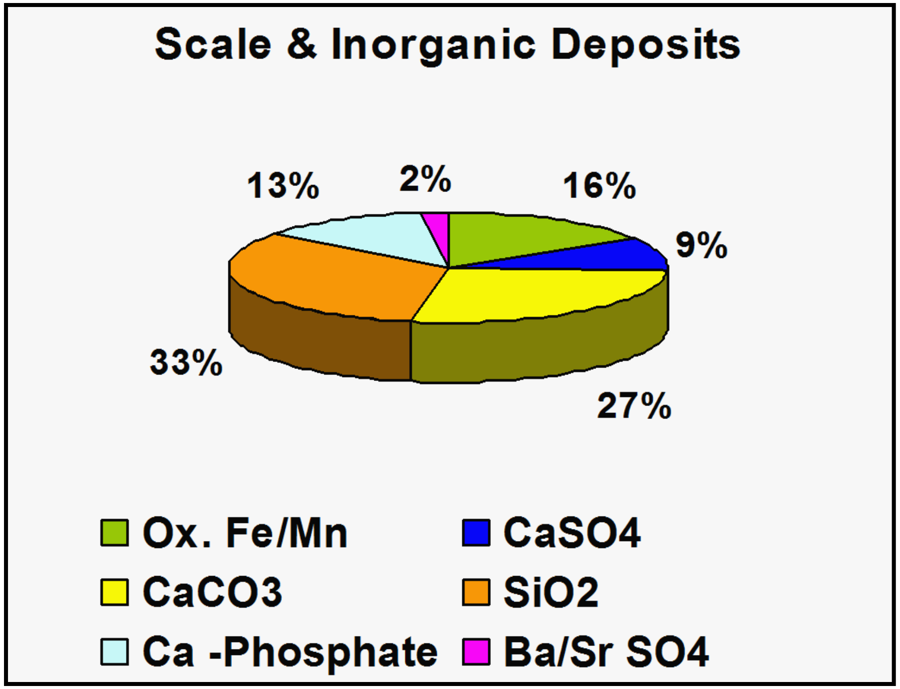




Membrane pressure damage

Autopsy results 2001 - 2009





Recent Innovations

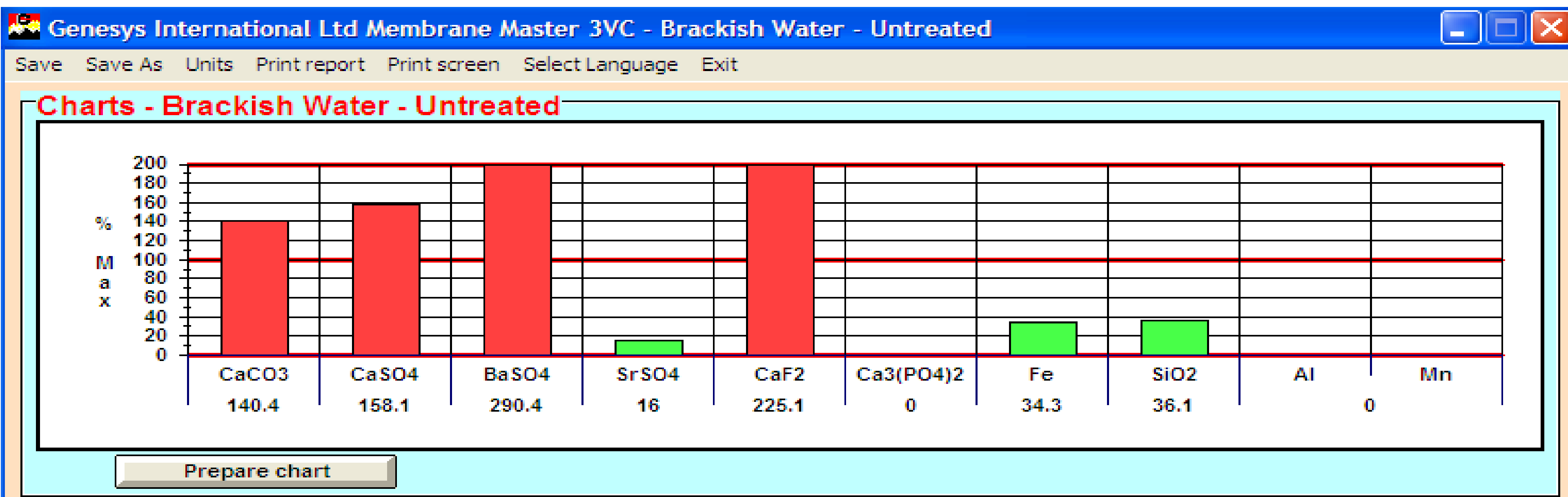
• **Scaling**	**Advanced antiscalants for calcium phosphate, calcium sulphate & silica**
• **Cleaners**	**Remove clay & biofouling**
• **Flocculant**	**Reduce use of iron & aluminium coagulant**
• **Lab techniques**	**Autopsy and particle counting**

Acid v's Antiscalant

- Acid dosing traditionally used to control scale in membrane plants - LSI
- High dose rate v's antiscalant
- Health & Safety – transport, storage and handling issues
- Poor activity against some scales

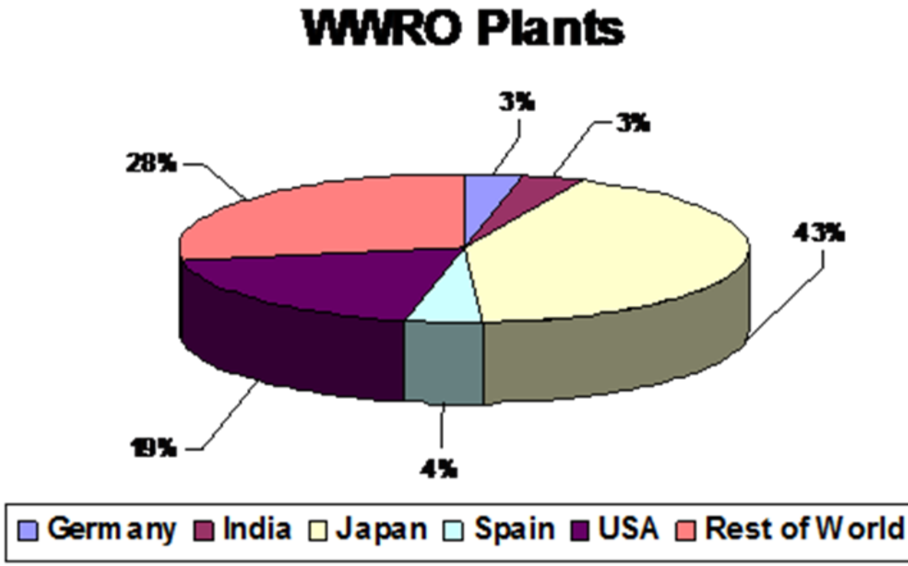
Feed Water Challenges

- Capacity of BWRO has increased by 7 million m³/day since 2002
- Scarcity of water requires use of “difficult” feed waters
- High in silica, sulphates, phosphates
- Drive to reduce operation costs
- Demand to increase recovery rates



WWRO Plant

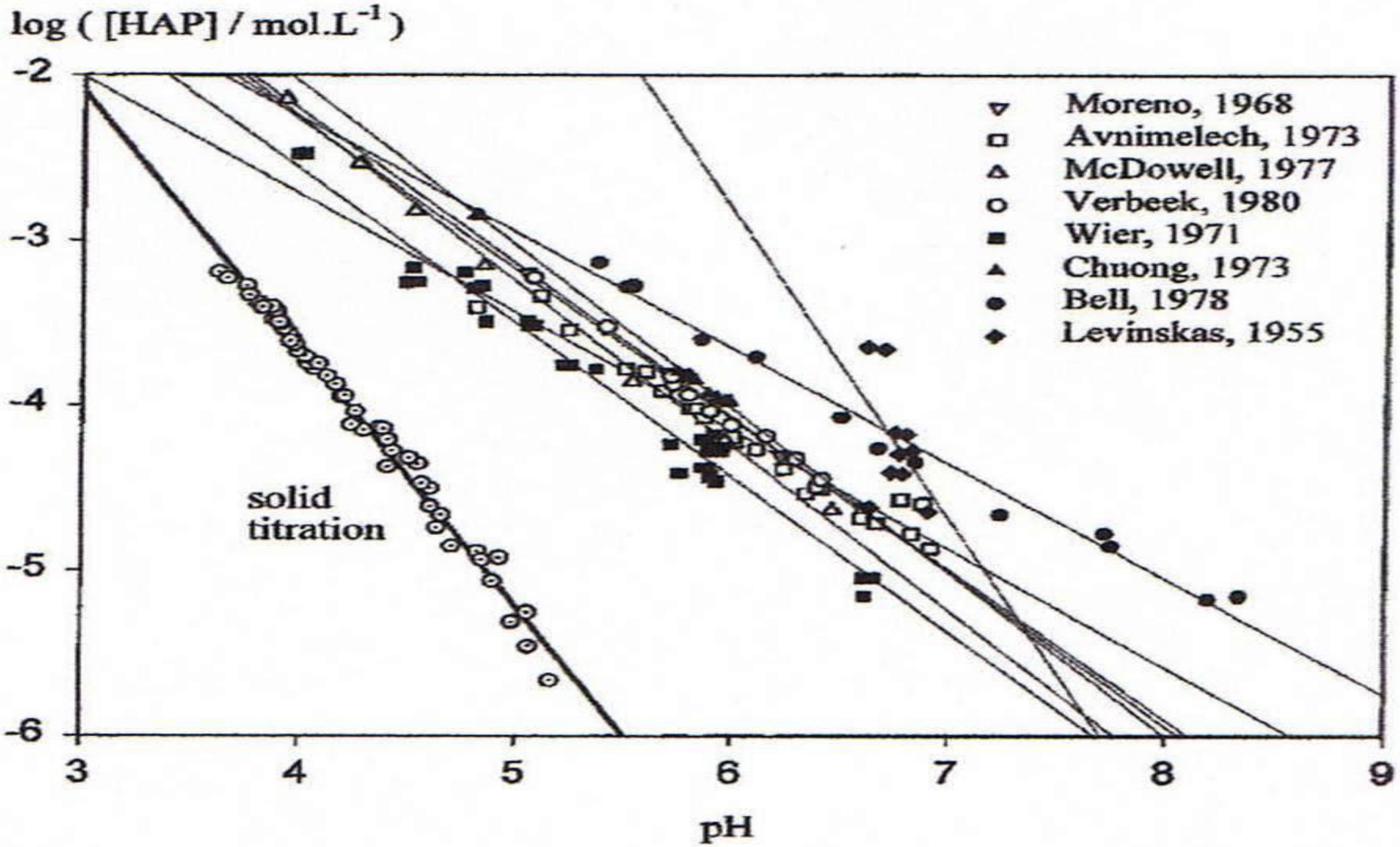
- Current Total Capacity 2,342,079 m^3/day (IDA)
- Total 713 plants & increasing!
- Largest in Middle East (Sulaibiya 375,000 m^3/day)
- New projects in Australia, Singapore & Europe
- WWRO approx 50% of cost of SWRO.
- Calcium phosphate Issues

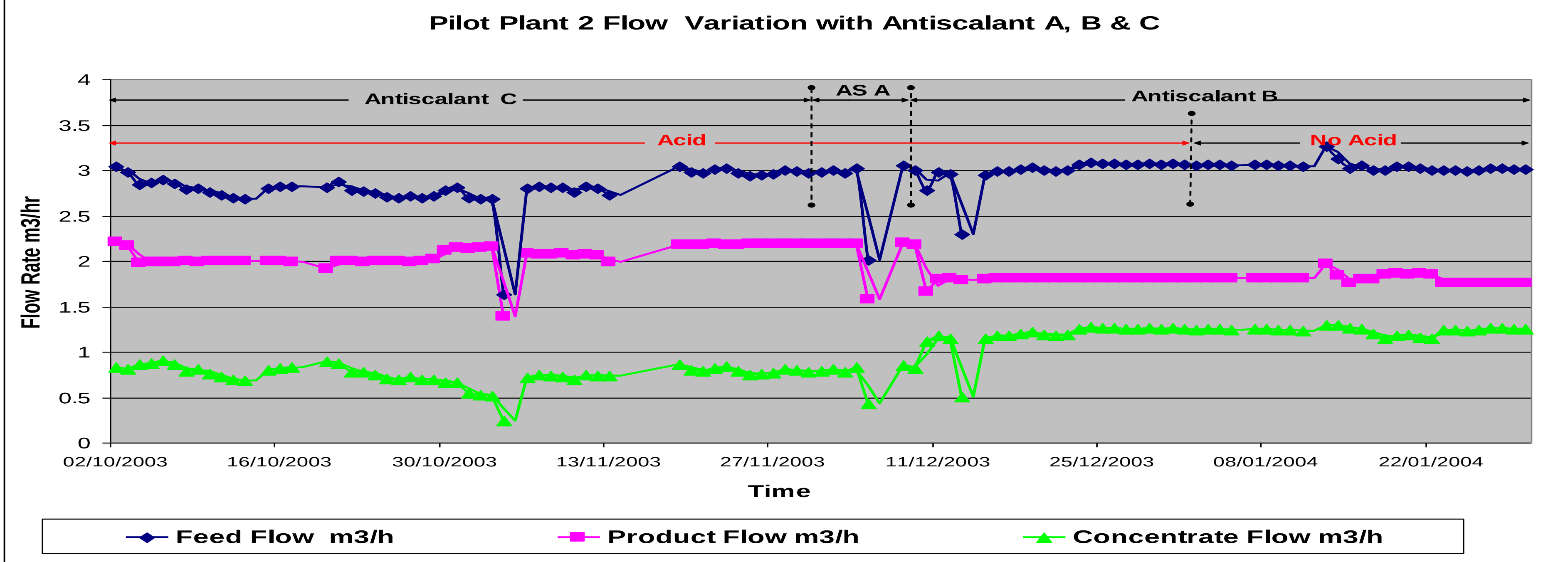


Calcium Phosphate Chemistry

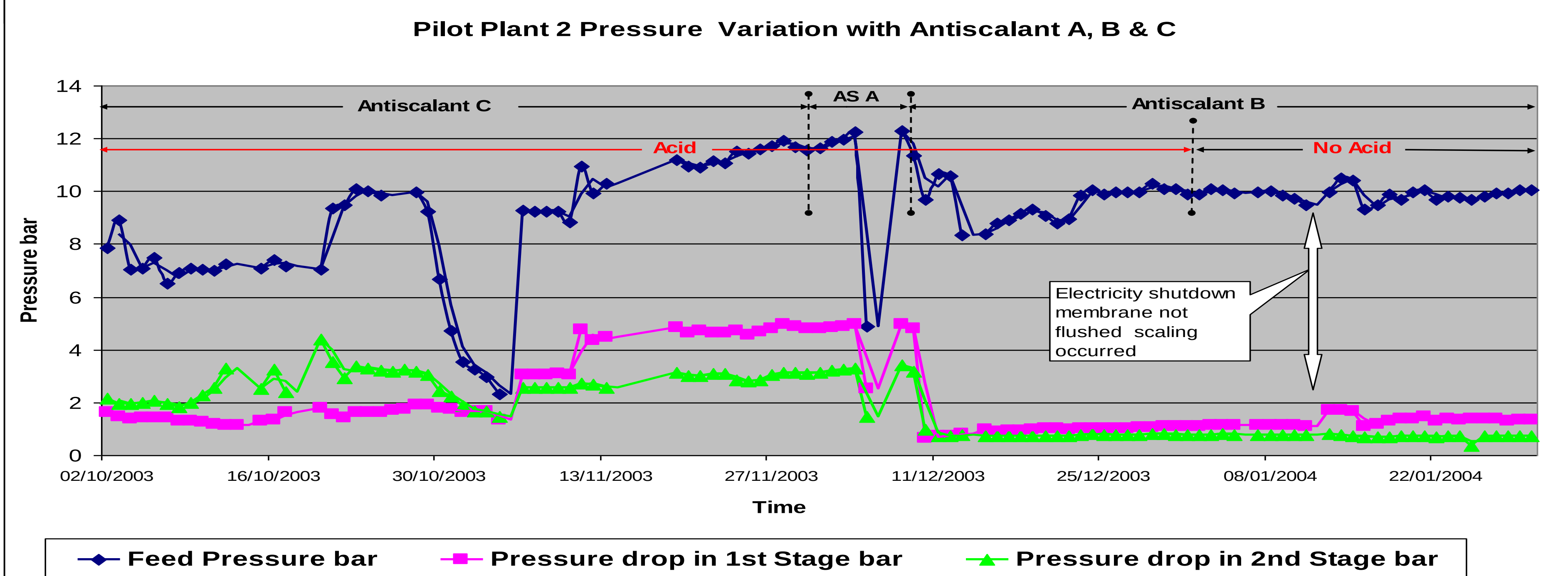
Chemical Name	Formula	Abb. Name	Mineral Name	Structure	Solubility Product mol/litre
Amorphous calcium phosphate rock	$Ca_9(PO_4)_6$	ACP		Amorphous	
Monocalcium phosphate	$Ca(H_2PO_4)_2$	MCP			
Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	DCPD	Brushite	Amorphous	2.32×10^{-7}
Dicalcium phosphate	$CaHPO_4$	DCP	Monetite	Amorphous	1×10^{-7}
Tricalcium phosphate	$Ca_3(PO_4)_2$	TCP	Whitlockite	Amorphous	2.07×10^{-33}
Tetracalcium phosphate	$Ca_4O(PO_4)_2$	TTCP	Hilgenstockite	Amorphous	
Pentacalcium hydroxylapatite	$Ca_5(PO_4)_3(OH)$	HAP	Hydroxyapatite	Hexagonal	2.34×10^{-59}
Pentacalcium fluoroapatite	$Ca_5(PO_4)_3(F)$	FAP	Fluoroapatite	Hexagonal	3.16×10^{-60}
Octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4$	OCP			2×10^{-49}
Calcium pyrophosphate	$Ca_2P_2O_7$	CPP			

Hydroxyapatite Solubility





Pilot Plant 2 Flow Variation with Antiscalant A, B & C
Flow Rate m3/hr
4
3.5
3
2.5
2
1.5
1
0.5
0
Antiscalant C
AS A
Antiscalant B
Acid
No Acid
02/10/2003
16/10/2003
30/10/2003
13/11/2003
27/11/2003
11/12/2003
25/12/2003
08/01/2004
22/01/2004
Time
Feed Flow m3/h
Product Flow m3/h
Concentrate Flow m3/h

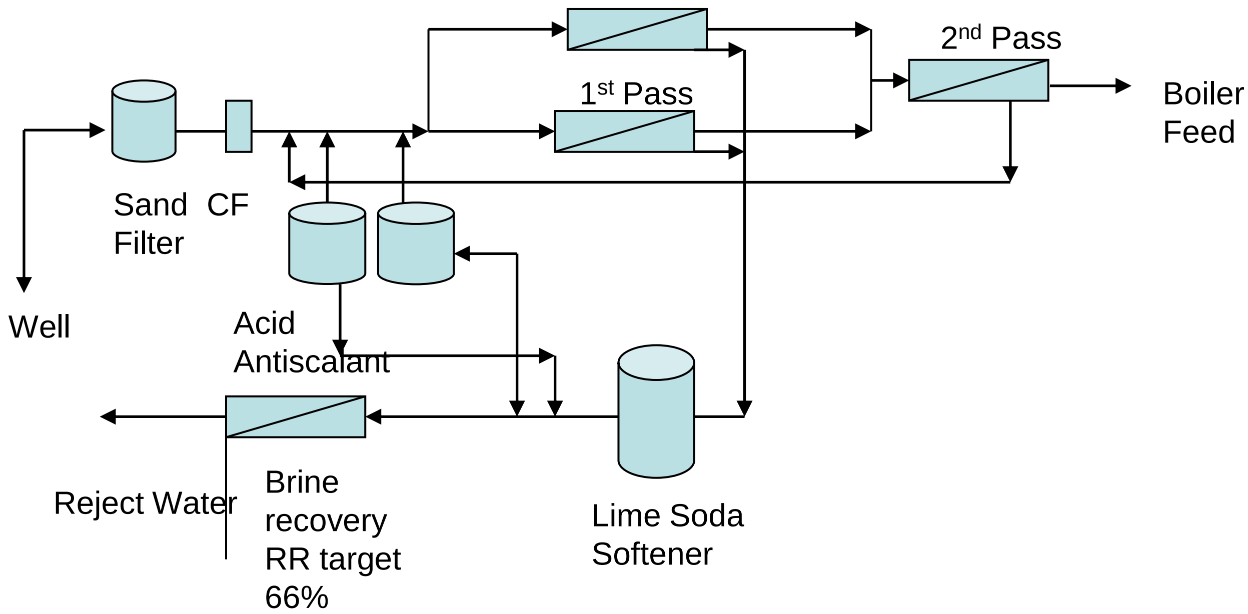


Pilot Plant 2 Pressure Variation with Antiscalant A, B & C
Pressure bar
14
12
10
8
6
4
2
0
Antiscalant C
AS A
Antiscalant B
Acid
No Acid
Electricity shutdown membrane not flushed scaling occurred
02/10/2003
16/10/2003
30/10/2003
13/11/2003
27/11/2003
11/12/2003
25/12/2003
08/01/2004
22/01/2004
Time
Feed Pressure bar
Pressure drop in 1st Stage bar
Pressure drop in 2nd Stage bar

Genesys PHO

- Initial trial work shows excellent results
- Confirmed under operational conditions
- Reduces or stops need for acid dosing
- Performance exceeds conventional anti-scalants
- 3-5 mg/l Genesys PHO increases saturation by 150 times
- Highly effective against all scaling species
- Enhanced threshold inhibition is key to effectiveness

Efficient operation at high sulphate levels



2 pass BWRO - Hydranautics CPA3 & 4

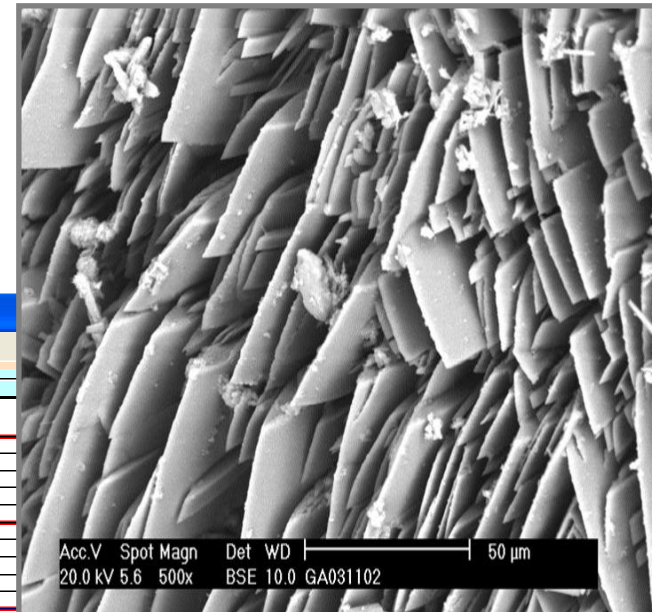
•1st pass	3,400m³/day 64% Recovery	Actual 48%
•2nd pass	1,400m³/day 85% Recovery	Actual 85%
•Brine recovery	66% recovery	Actual - inoperable

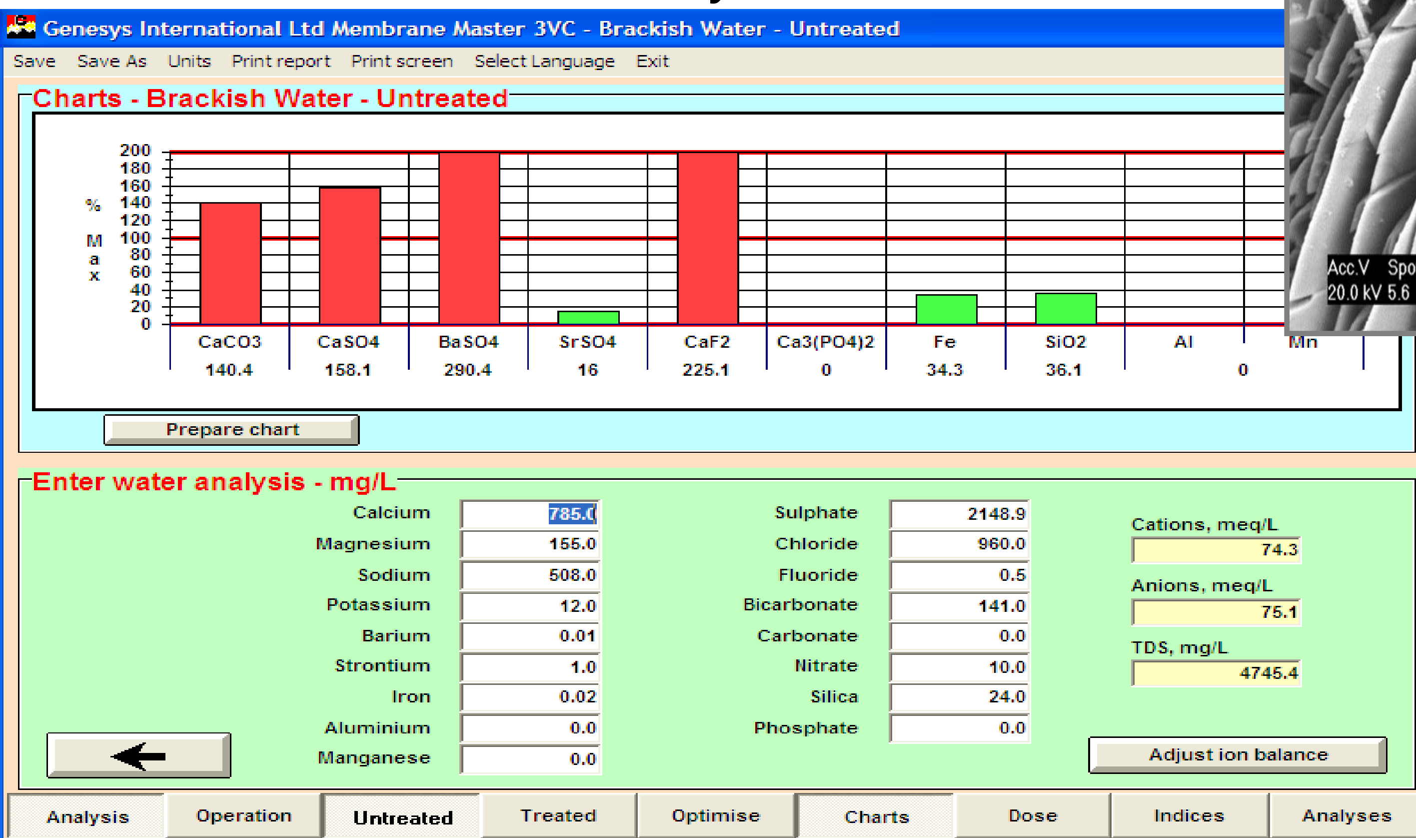
Operational Issues

- High calcium and sulphate levels
- Acid dosing 132kg/day HCl
- 1st. Pass Recovery only 48%
- Feed Pressure 2 Bar above Target.
- High ΔP
- Membranes cleaned every 4 weeks
- Membranes replaced annually

Genesys Solution

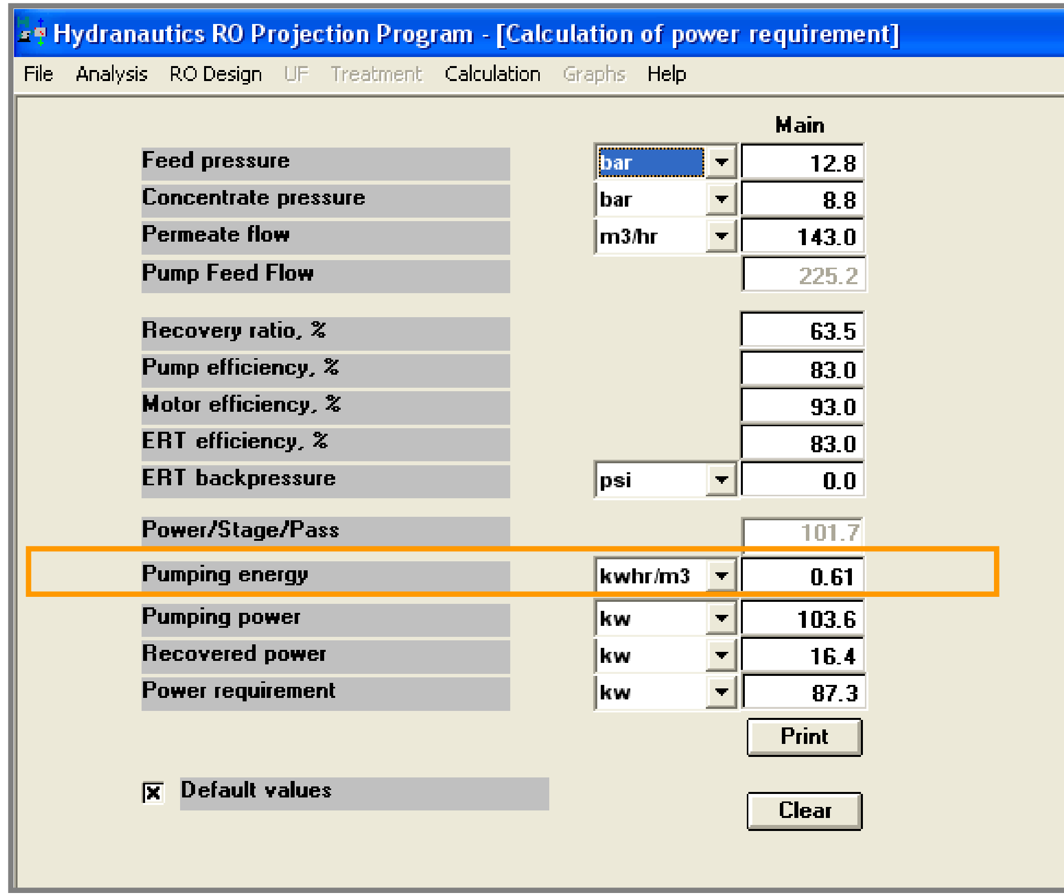
- Membrane Autopsy
- Detailed Site Survey & feed water analysis
- Feed Water software projection
- On site trial with Genesys CAS





Genesys Recommendations

- Genesys CAS replaced conventional antiscalant
- Chlorine, acid and bisulphite dosage stopped
- Recovery increased 48 to 61%
- Membrane manufacturer software used to calculate water and energy savings



Operational Impact – Genesys CAS

Total Cost Saving	Skid 1a
Water Saving, m^3/annum	1,121,280
Energy Saving kWhr	857,000
Energy Costs Saving, US$/annum	$60,000
Membrane Replacement US$ pa	$39,000
Chemical Saving, US$ pa	$37,000
Total Saving, US$ pa	$136,000

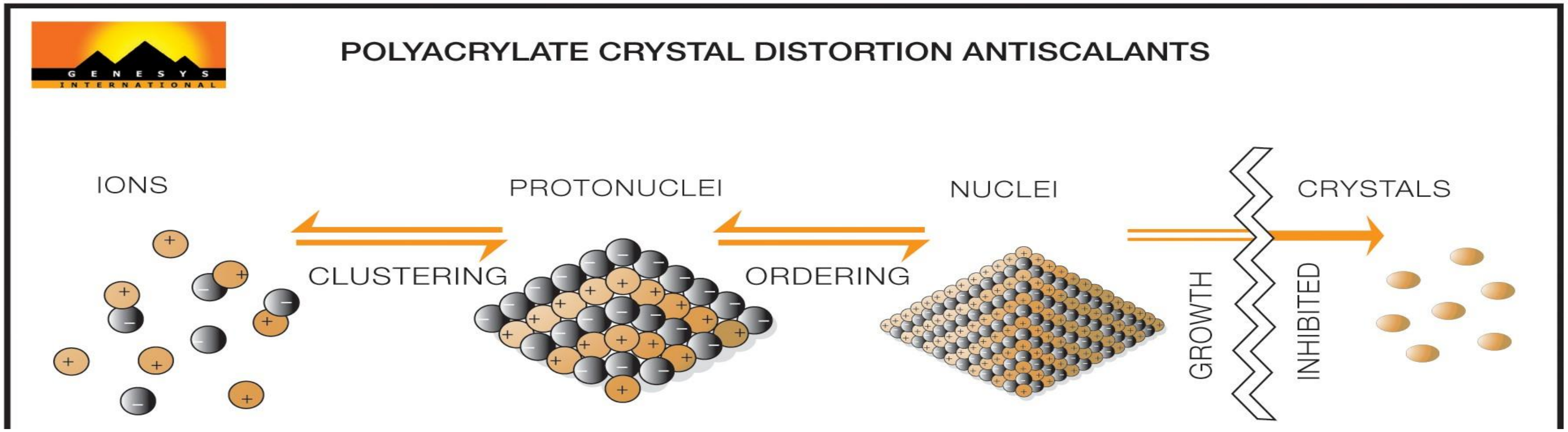
Efficient operation at high silica levels

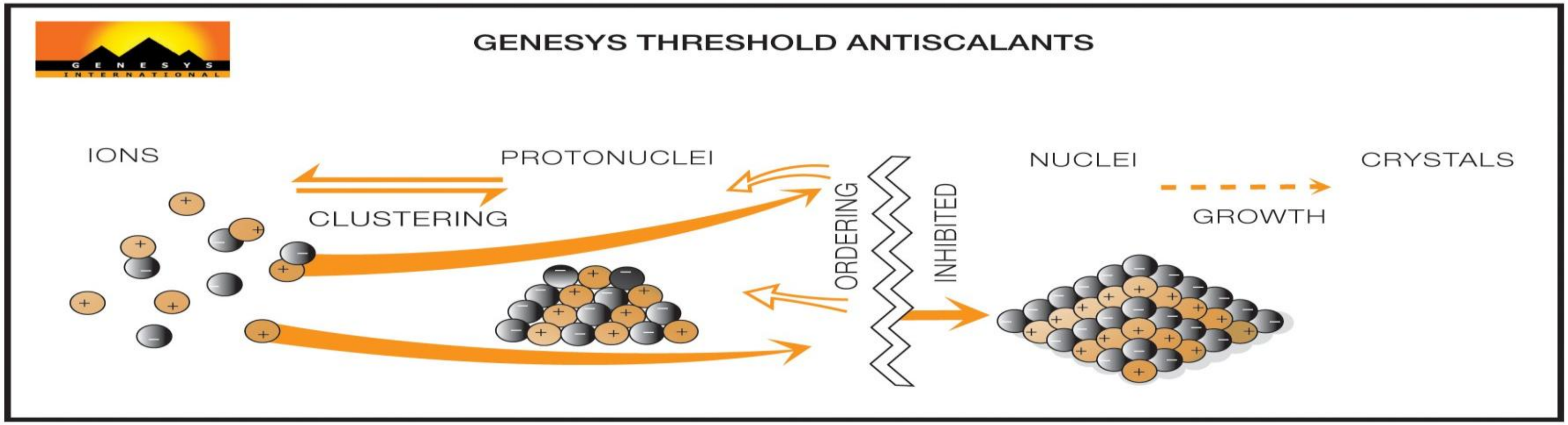
- Silicon Dioxide, SiO_2. Silicon and oxygen are the two most common elements in the Earth's crust.
- Silica solubility: increases with pH & temperature

Silica Chemistry

1. Colloidal Silica – Non-reactive
2. Dissolved Silica – Reactive

- Colloidal Silica doesn't permeate and so will foul membranes – Alumino-silicates clay
- Silica deposition increases in presence of iron. Manganese and aluminium





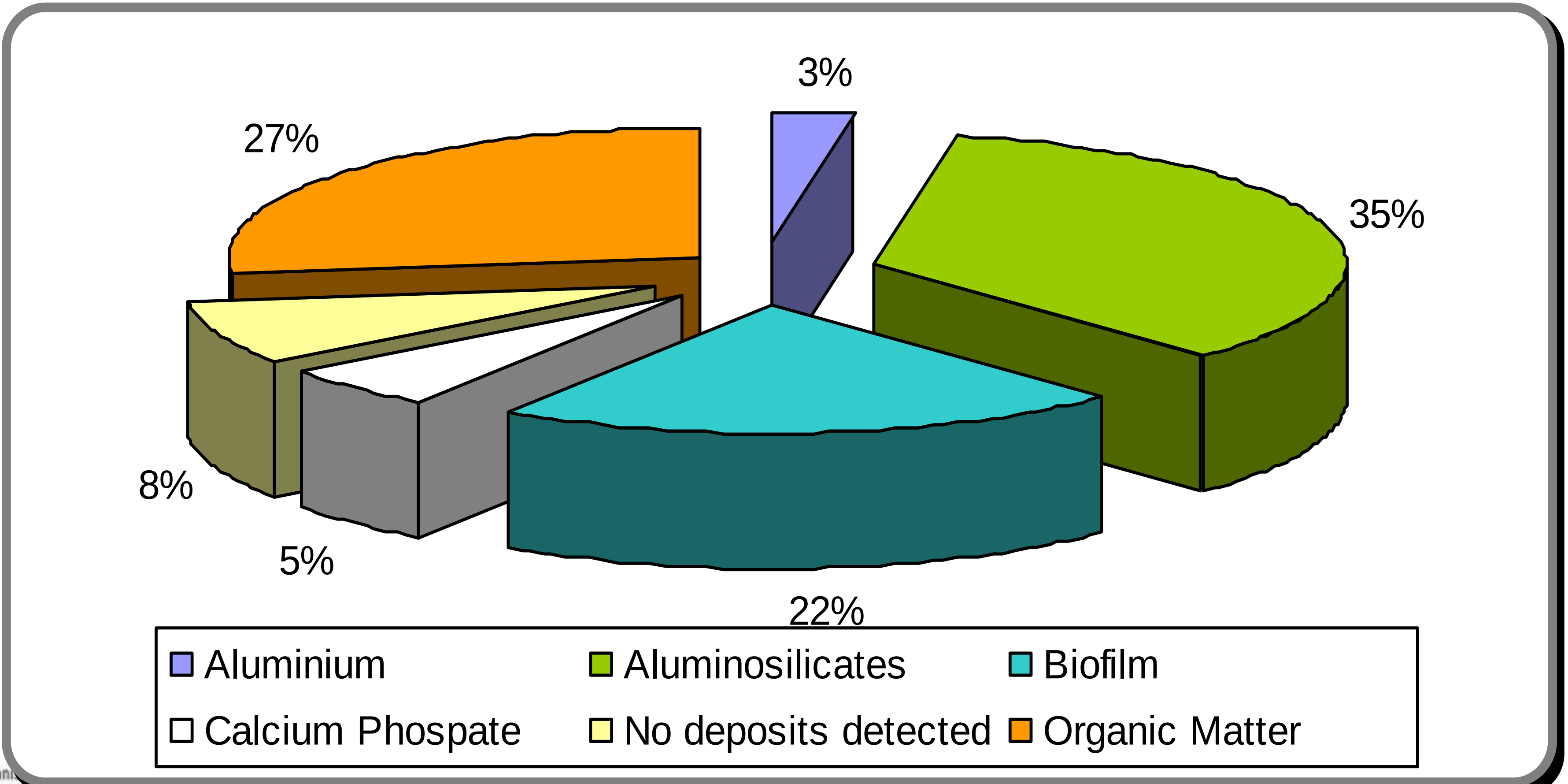
Genesys Si – combines phosphonate and polymeric compounds

Silica Case Study – Genesys SI

Case Study	BWRO Arica Chile
Parameters	**Improvements**
Feed Silica 60mg/l	Reject 256mg/l
pH 7.2 (reduced to 6.5 H_2SO_4)	Recovery rate Improved to 75%
4 skids – 2 stage 864 elements	3.8mg/l Genesys SI
Permeate 18,000 m^3/day	Water saving 2,566,680 m^3/year
Operating Recovery 60%	Energy Saving 3,836,160 kWhr/year
Silica fouling – 2 monthly cleaning	Energy Costs US$268,531

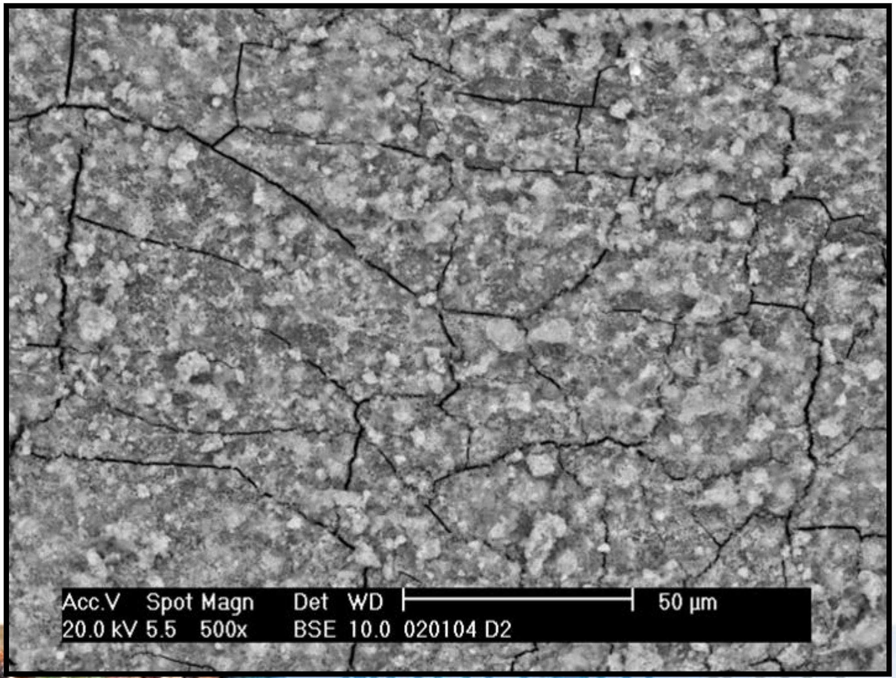
Cleaning Clay from Fouled membranes

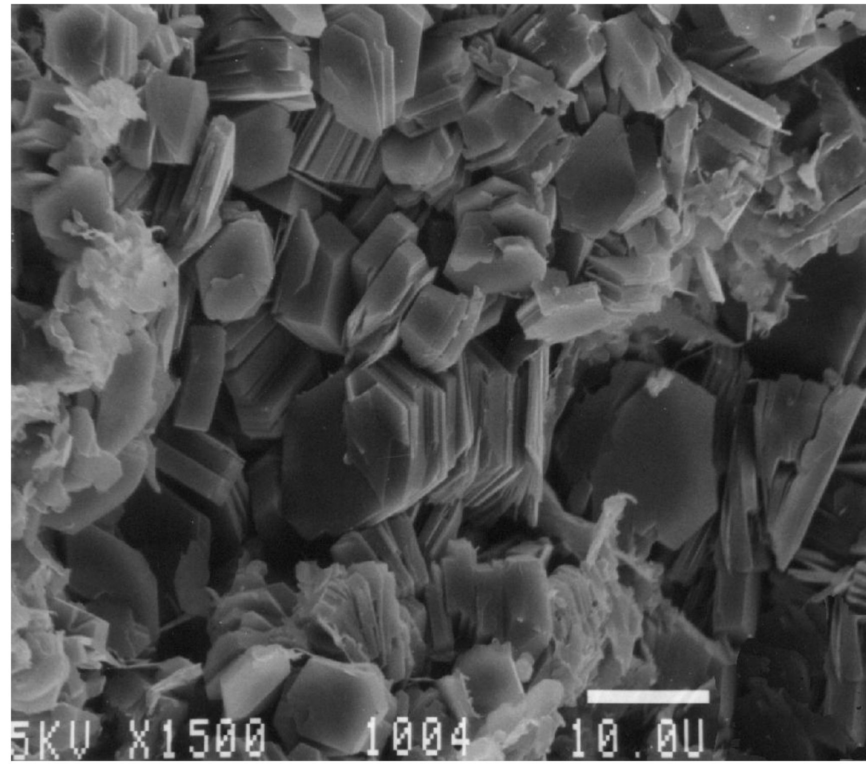
Lead Elements 2001-2009 Source: GMP Laboratory Madrid



Surface Waters – Clay Fouling

- Most common foulant in lead membrane elements
- Clay is colloidal alumino-silicates
- Source is erosion products in surface waters
- Reduction in flux and increases ΔP

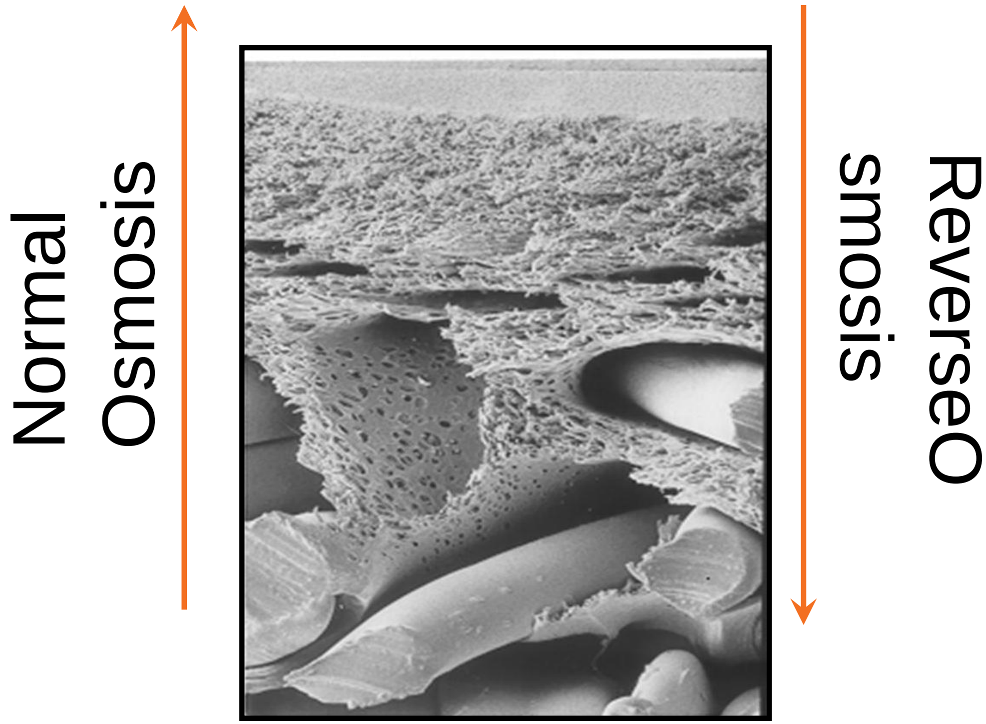




Sheet structure – Tetrahedron rings
Water in mineral crystal structure
Plasticity – irreversible deformation under pressure

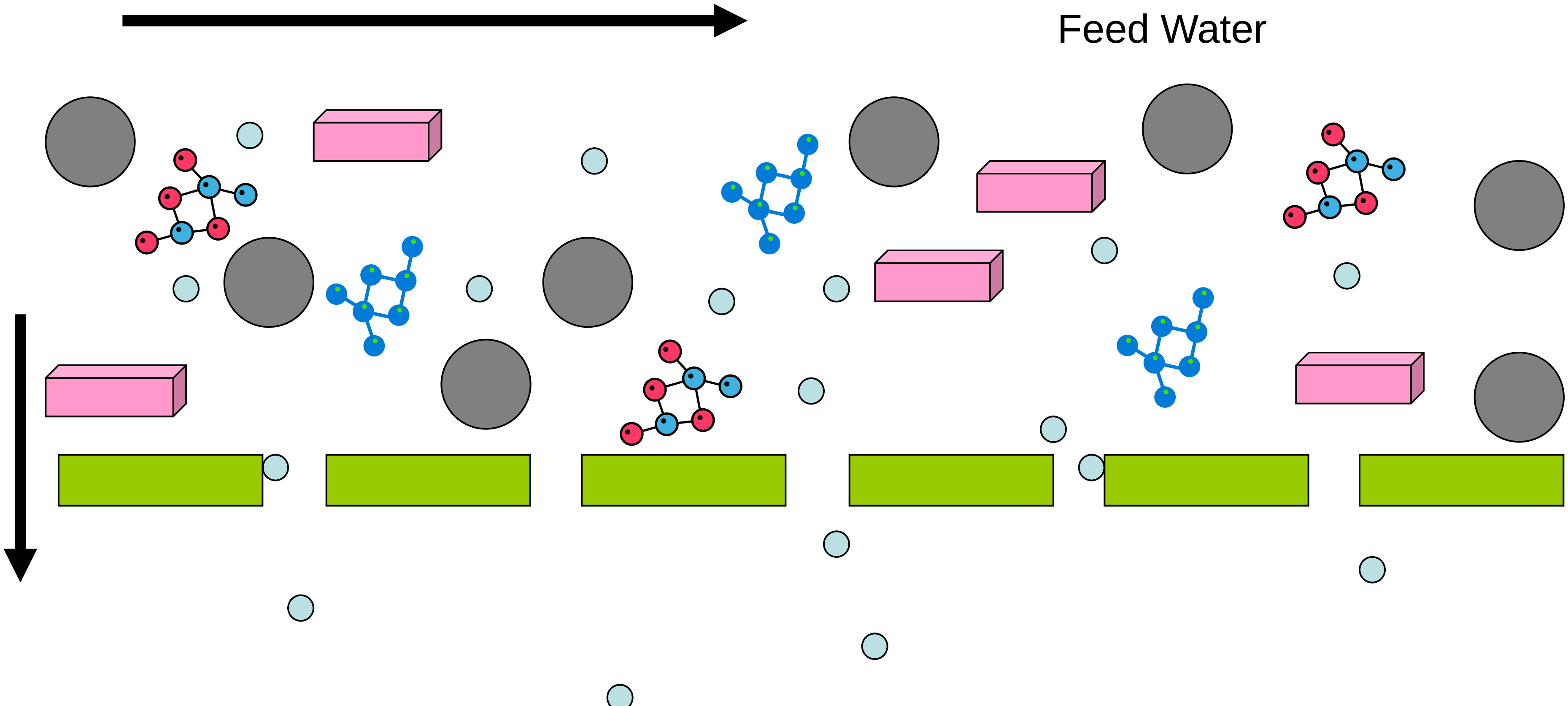
Powdered product - 100% active

- Phosphate cleaner, detergent,
- Surfactant
- Ionic strength builder to generate normal osmosis, helps “clear” the pores.



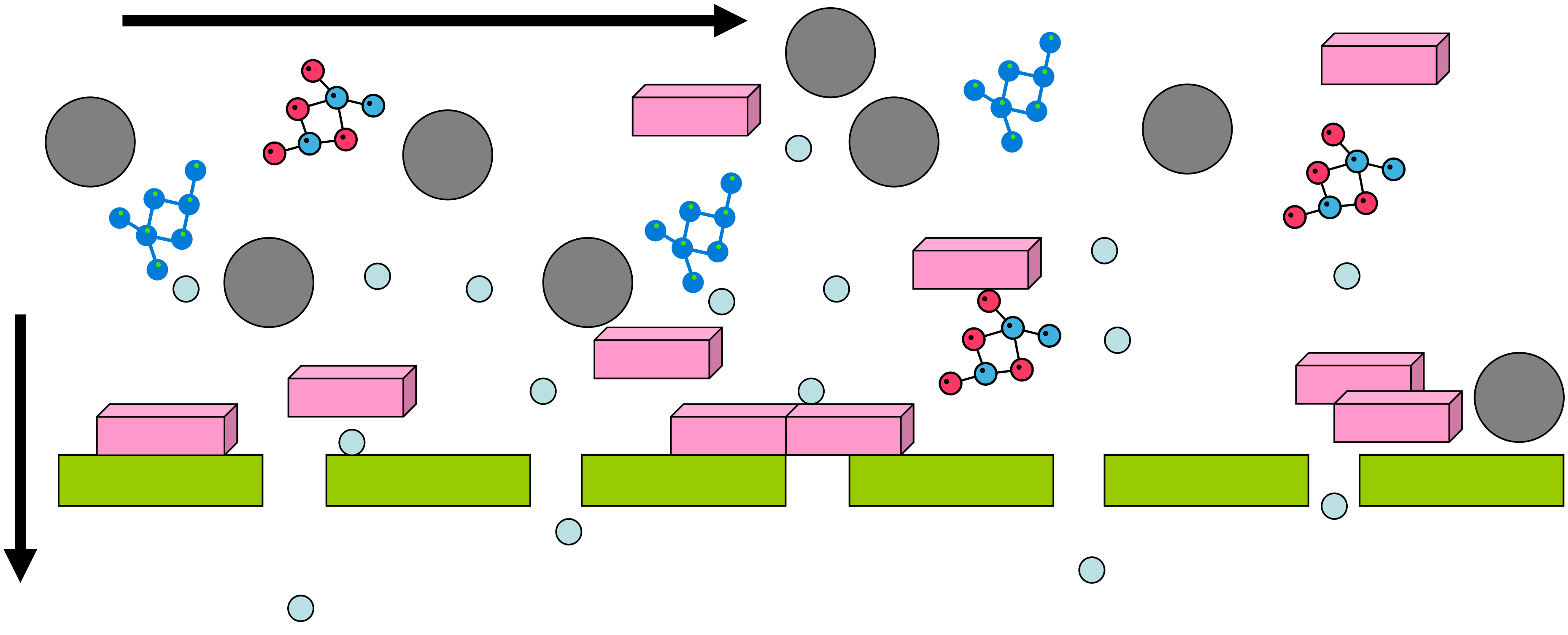

BW30-400-FR

Clay Fouling Mechanism



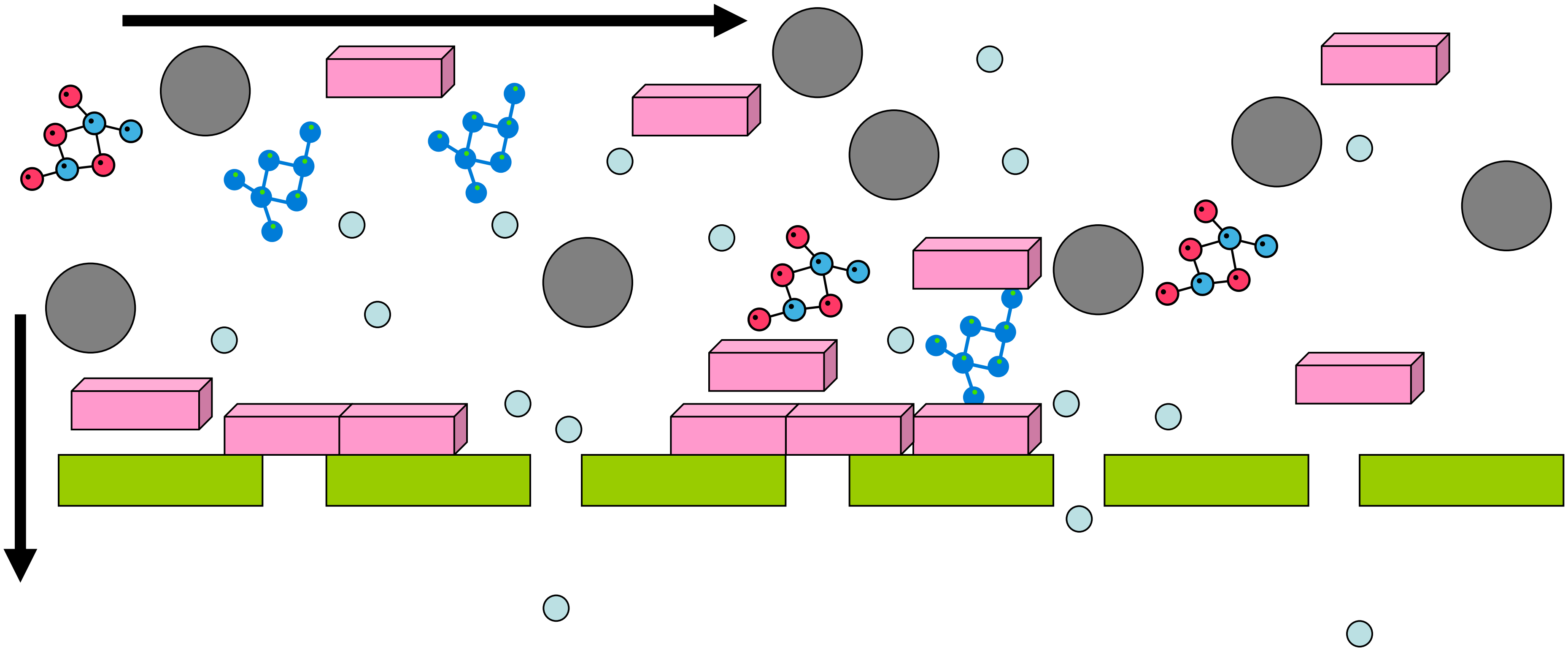
•Particles <2µm pass through pre-treatment system

Clay Fouling Mechanism



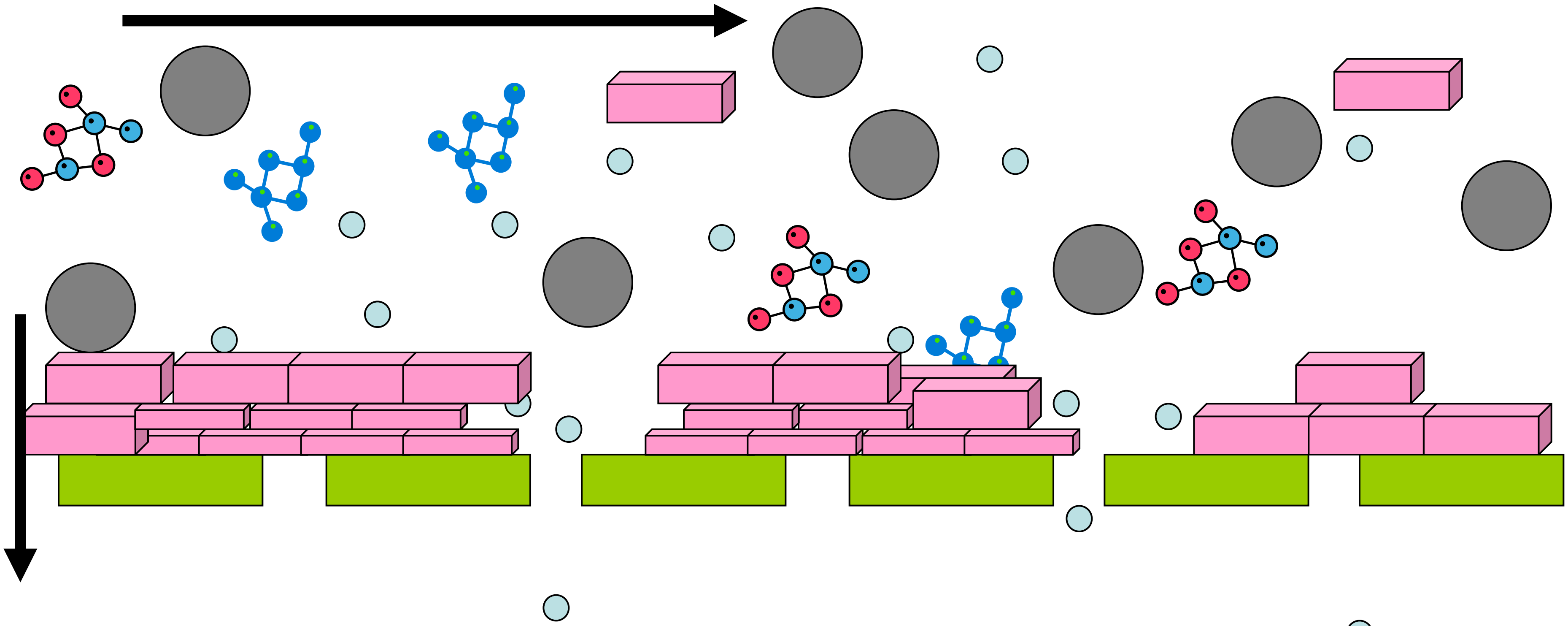
- Clay particles begin to foul membrane surface forming cake layer

Clay Fouling Mechanism



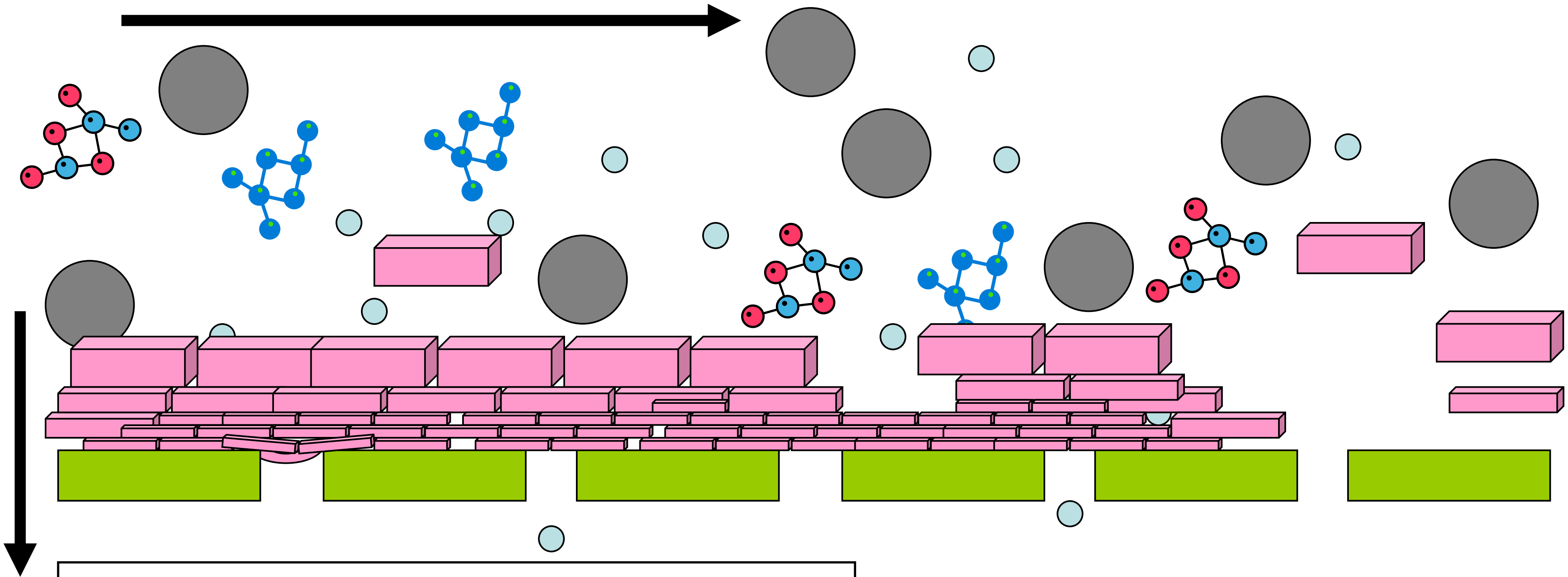
- Fouling begins to reduce flow
- Feed pressure increased to compensate

Clay Fouling Mechanism



- Plasticity – increased feed pressure deforms & compresses particles
- Pores become blocked & foulant less permeable to water.

Clay Fouling Mechanism

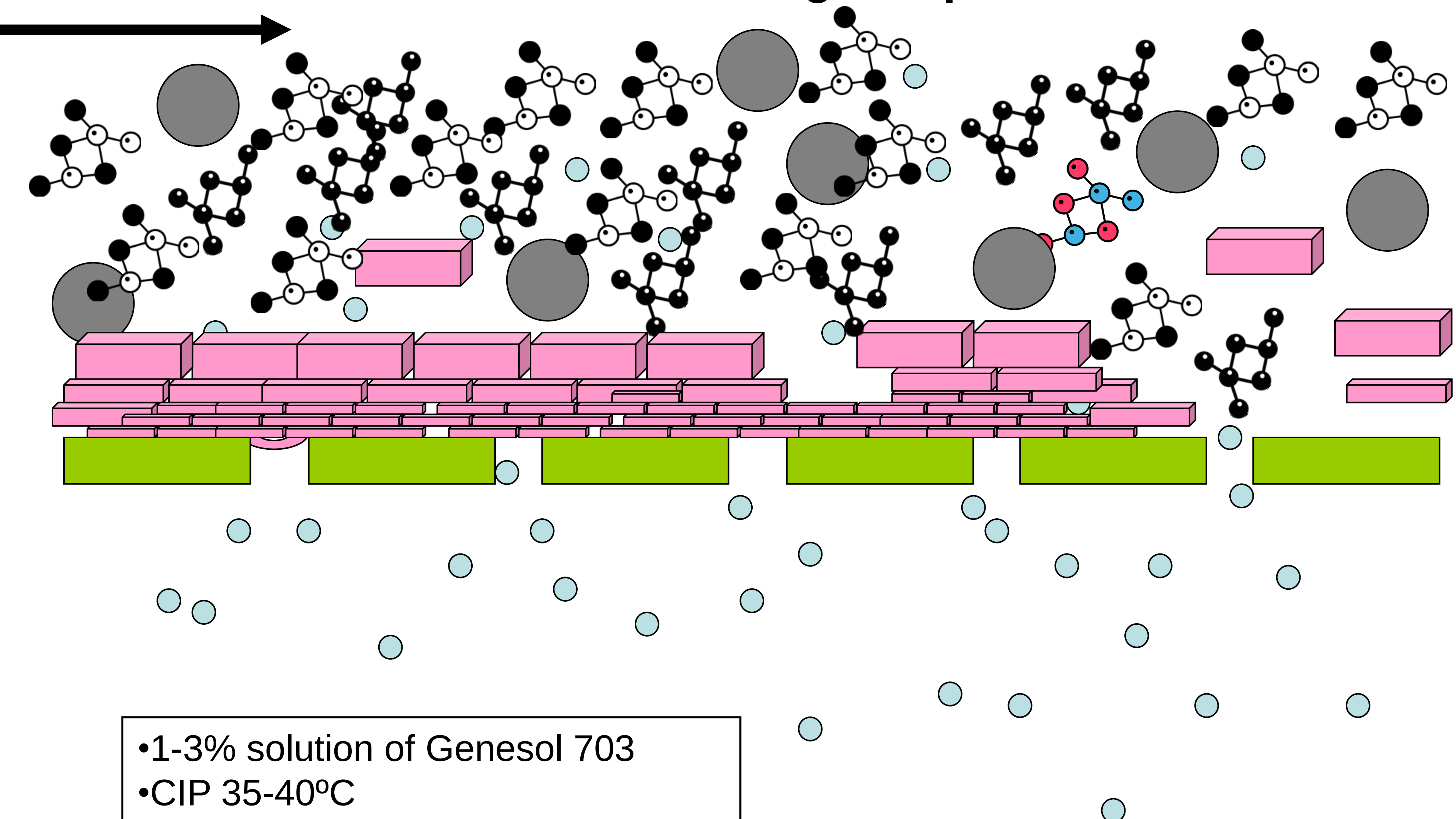


•Cake layer continues to compress & becomes impermeable to water

•Permeate flow reduced

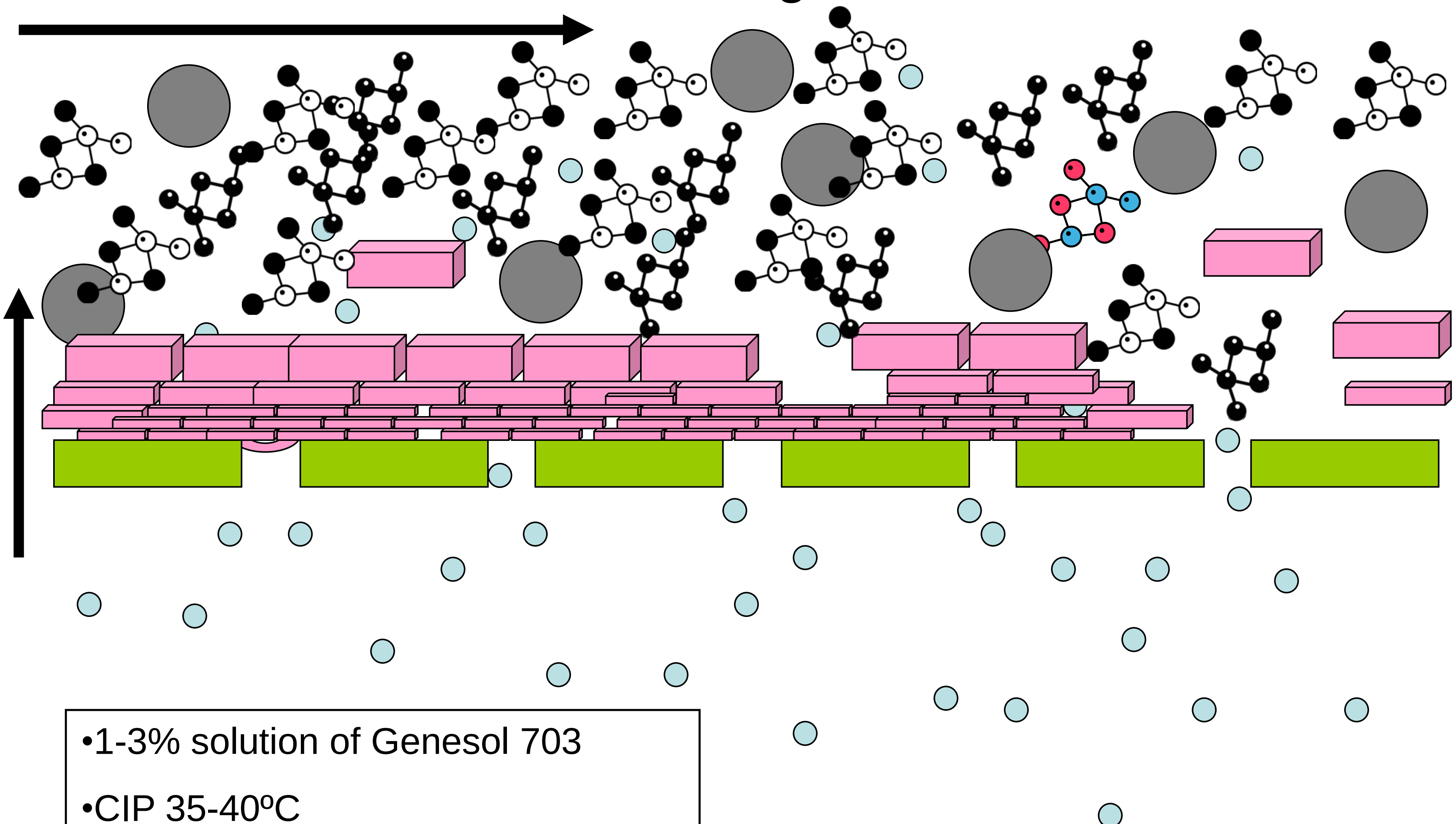
•Normal Cleaning solution can't penetrate layer

Genesol 703 Cleaning low pressure



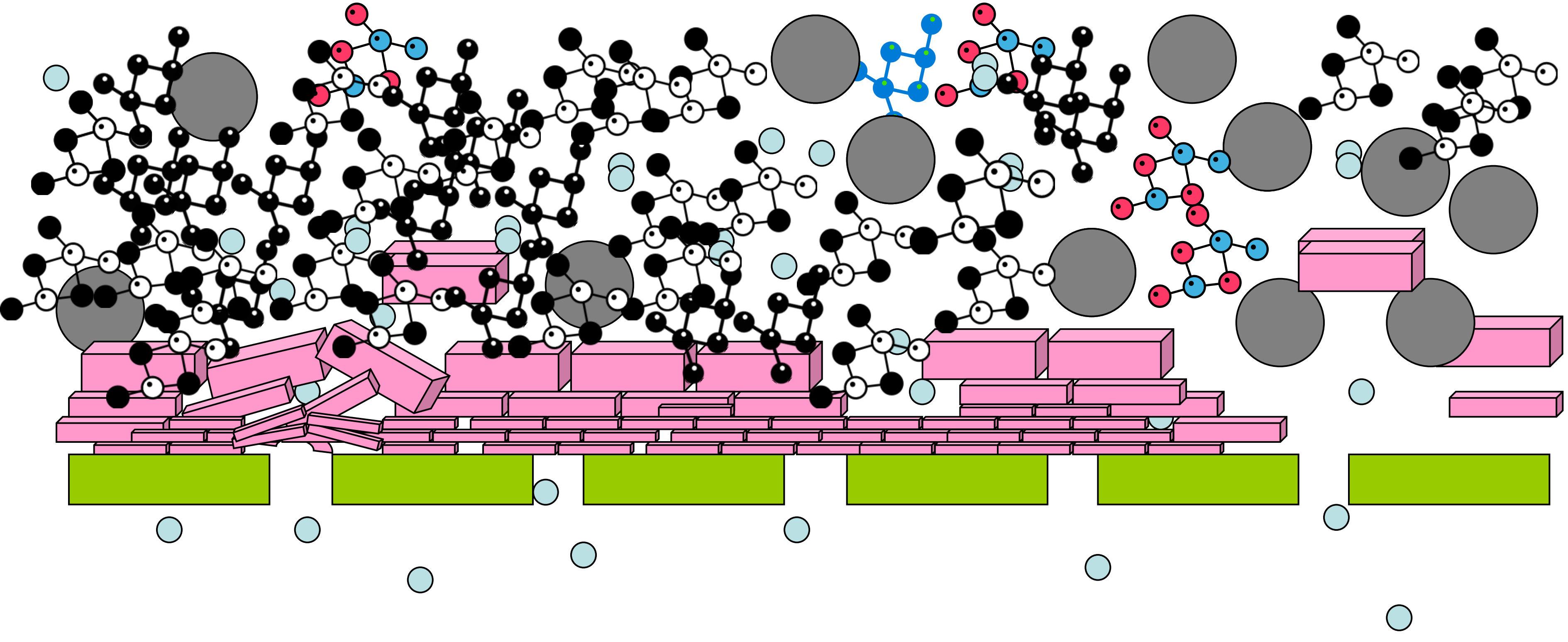
- 1-3% solution of Genesol 703
- CIP 35-40ºC
- <4 bar

Add Cleaning Solution



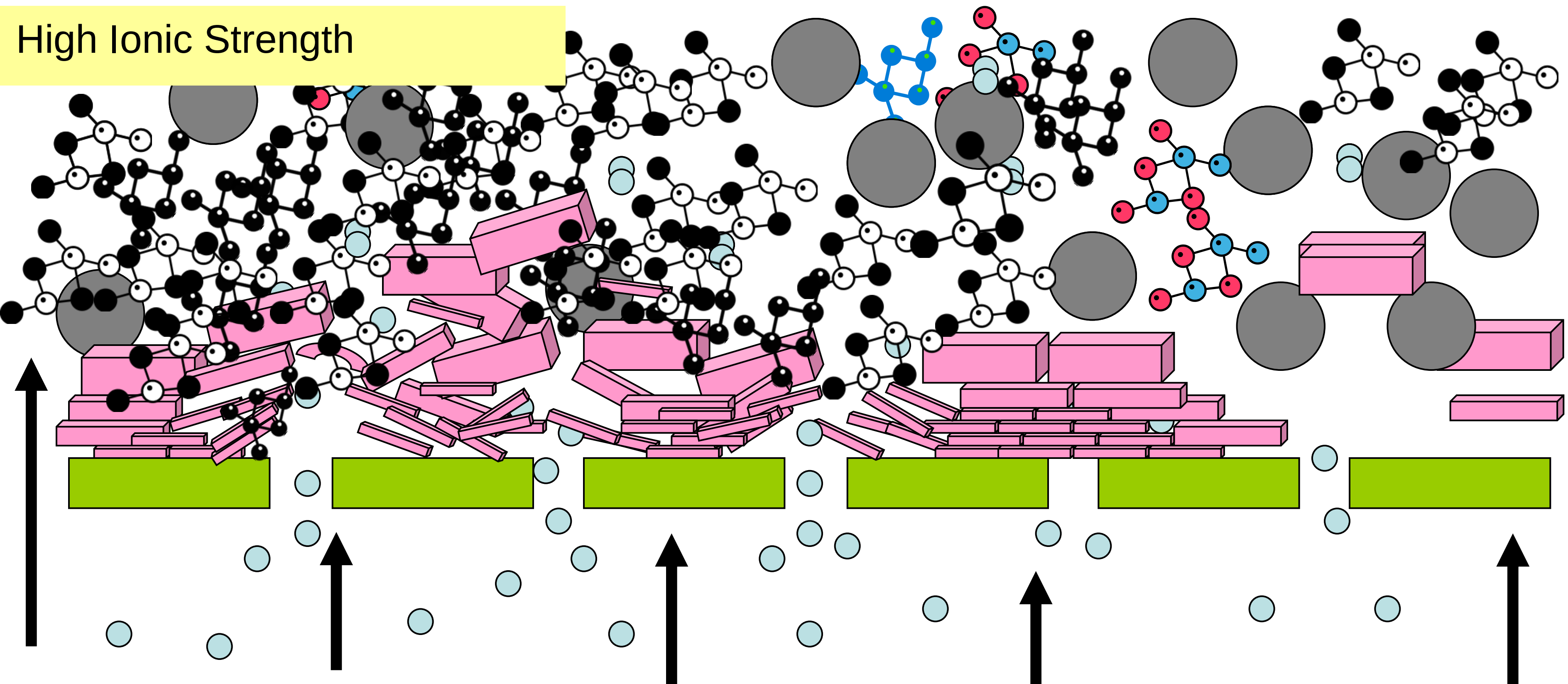
- 1-3% solution of Genesol 703
- CIP 35-40ºC

Mode of Action – surface tension



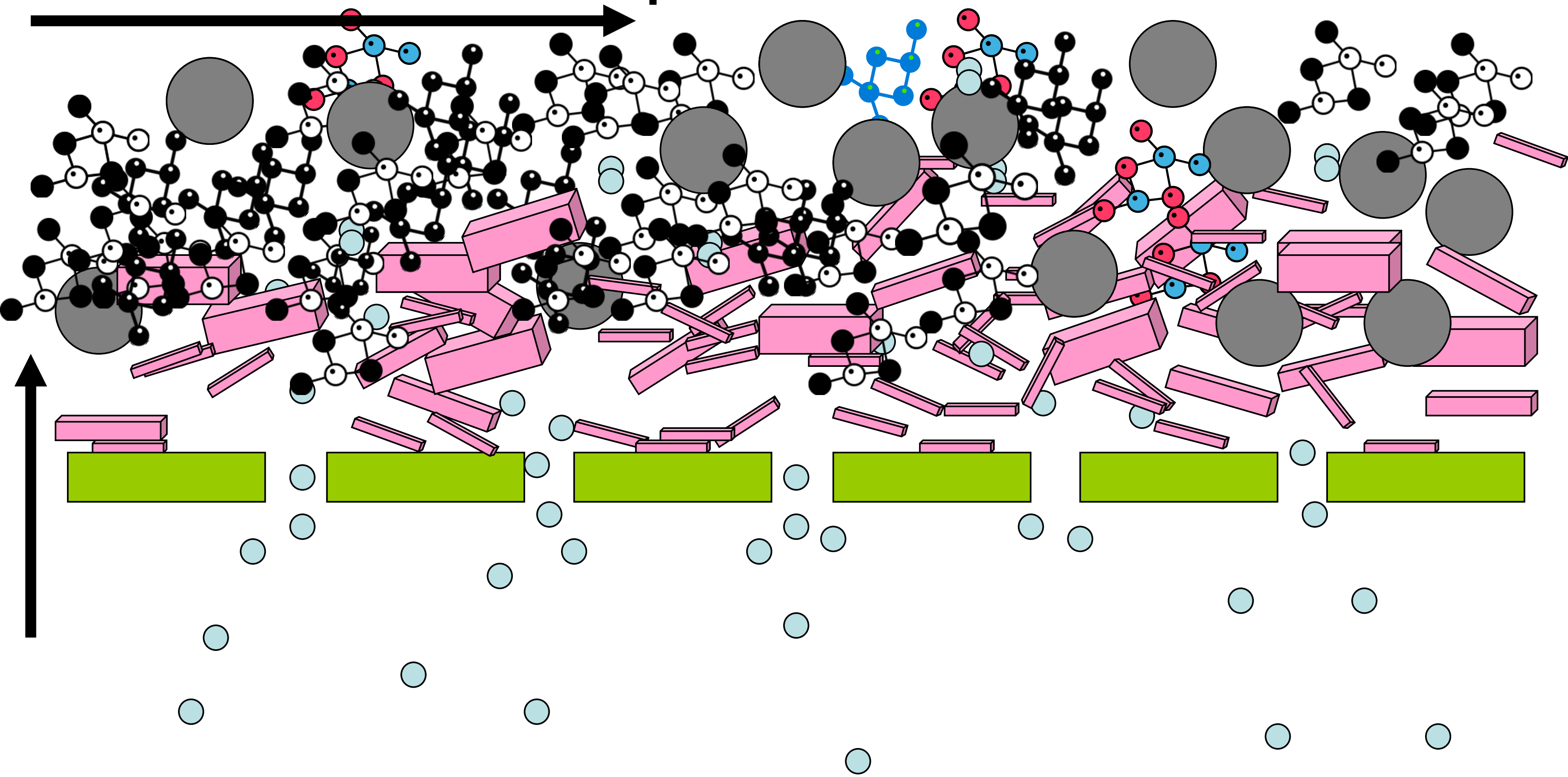
- Water/surface inter-phase – surface tension reduced, surfactant penetrates deposit
- Deposit becomes more permeable allowing G703 to penetrate

Mode of Action – deposit removal



- High Ionic Strength
- Osmotic pressure reverses flow
- Deposits “lifted” away from surface
- Minimises abrasion

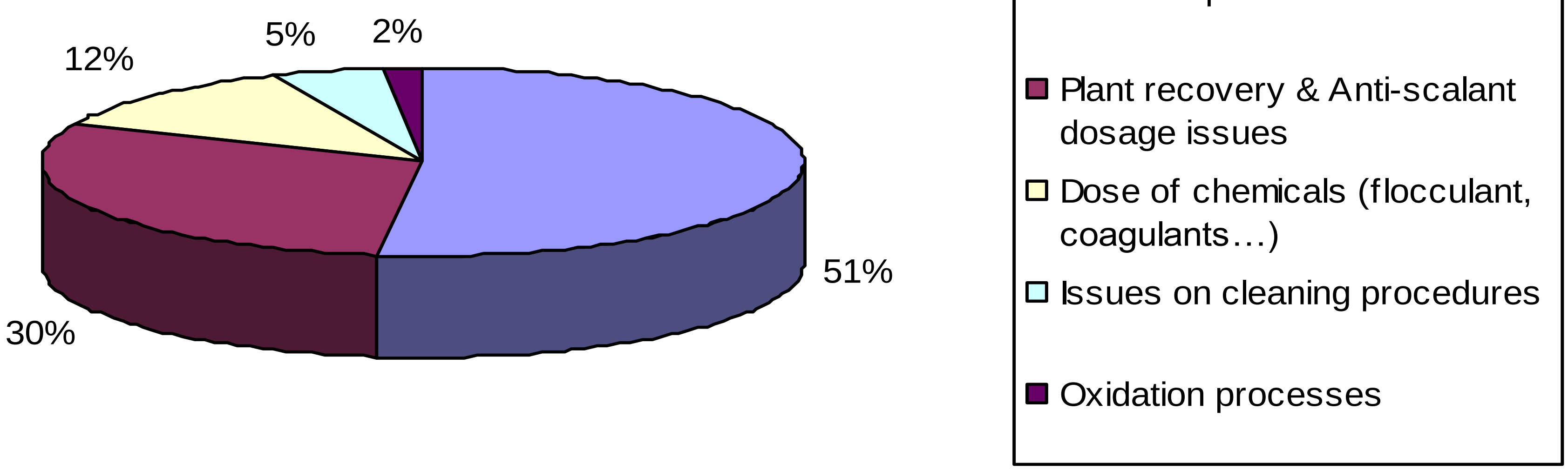
Low pressure flush



•Flushing removes particles

Fouling prevention – pre-treatment optimisation

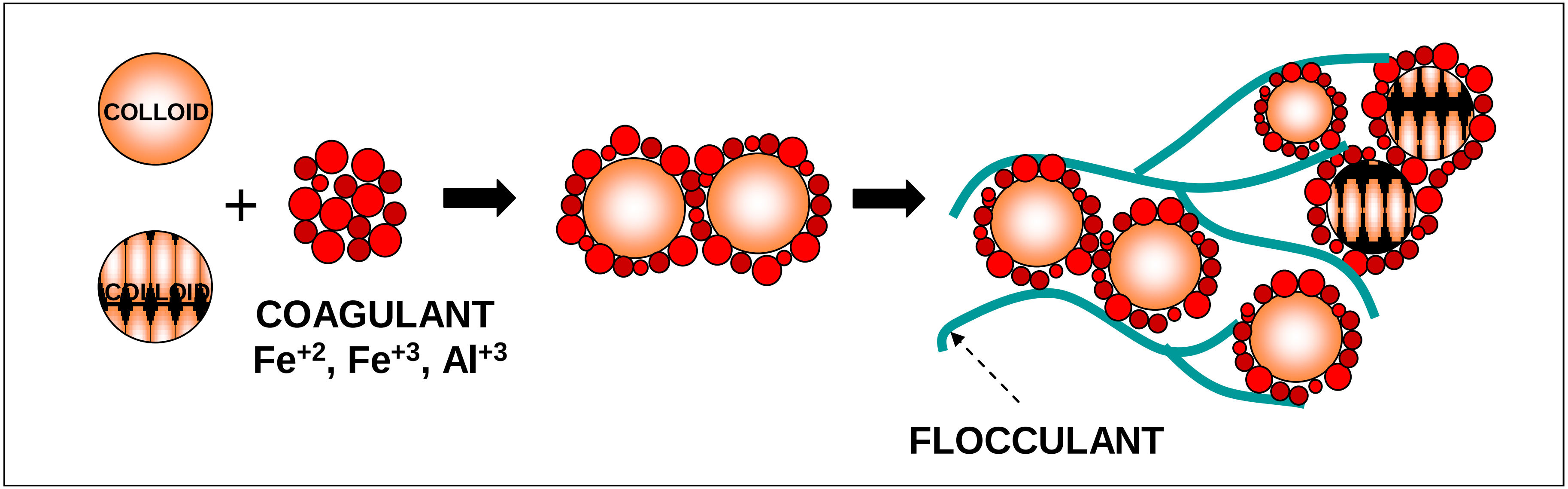
Membrane Autopsies 2001-2006. Main cause of failures detected.



63% of RO membrane failures are caused by inefficient pre-treatment or coagulant/flocculant fouling

Chemical Pre-treatment Mechanisms

- **Flocculation –** bridging of particles by polymer chain forming flocs
- Particle agglomeration allows mechanical removal



Flocculant Bridging

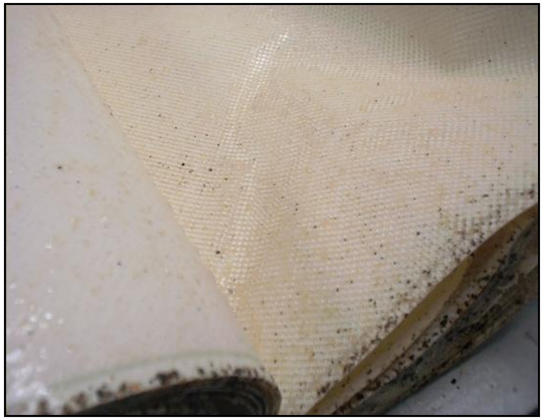
Cationic & Anionic Flocculants

- **Cationic Flocculants:**
  - Acrylamide copolymers with cationic monomer
  - Polyquaternary amines are pH insensitive
  - Chlorine resistant
  - Inorganic suspended solids removal
  - High molecular weight effective at removing large amounts of solids.
- **Anionic Flocculants:**
  - Acrylamide copolymers contain 2 types of monomer unit
  - pH sensitive functions best > pH 6
  - Target Organic removal

Pre-treatment & membrane fouling

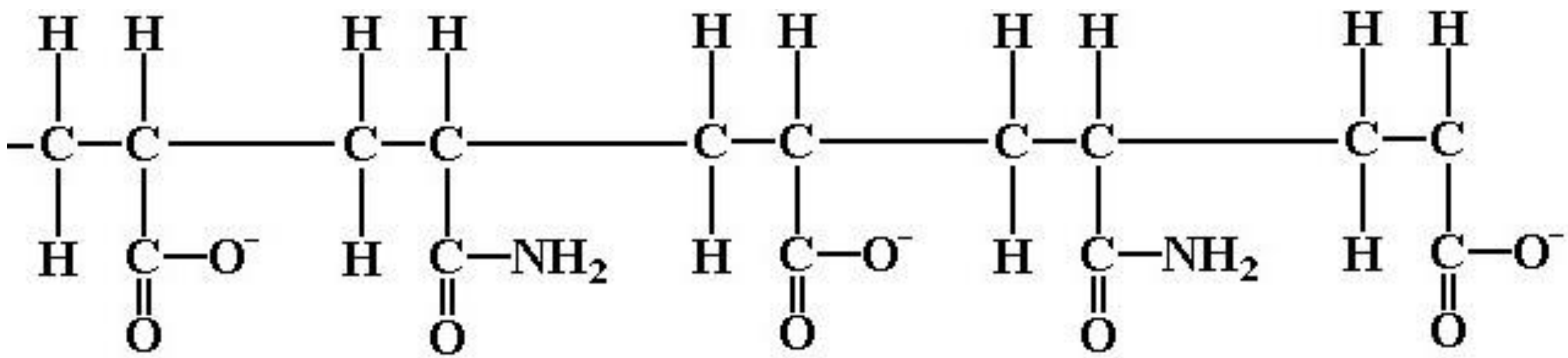
- **Established view that despite the advantages of cationic flocculants they are incompatible with RO & NF membranes:**
  - Soluble Fe^{3+} or Al^{3+} form hydroxides fouling membrane surface
  - Acrylate antiscalent reaction fouls membranes
  - Aluminium & iron based coagulants may attach direct to membrane surface
  - Oil or latex in some flocculants may adhere to membrane surface.

Iron Acrylate Fouling

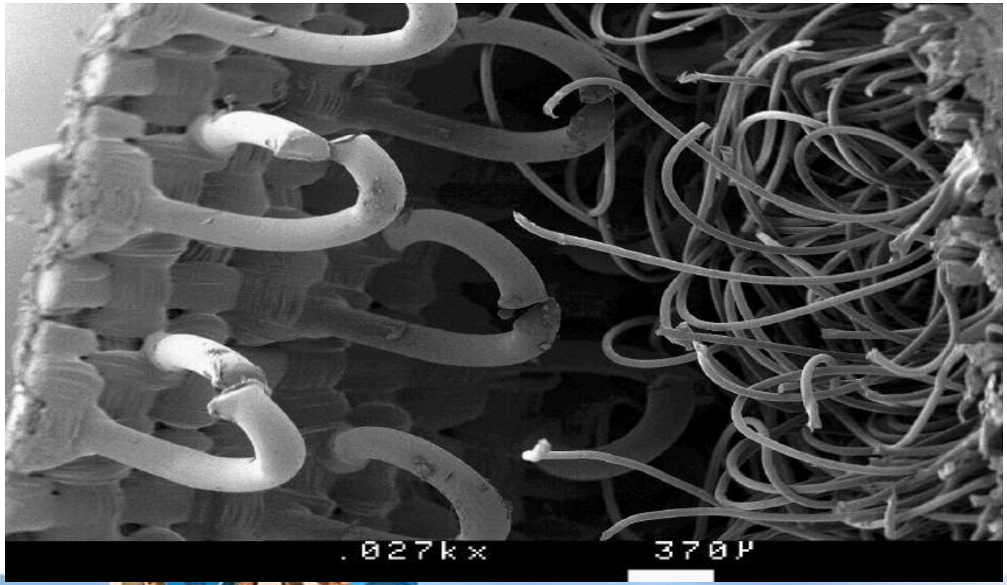


Aluminium Fouling

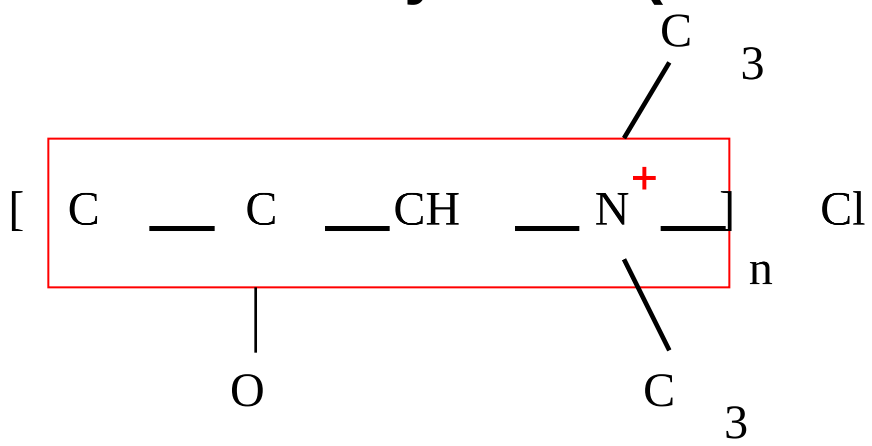
Polyacrylamide



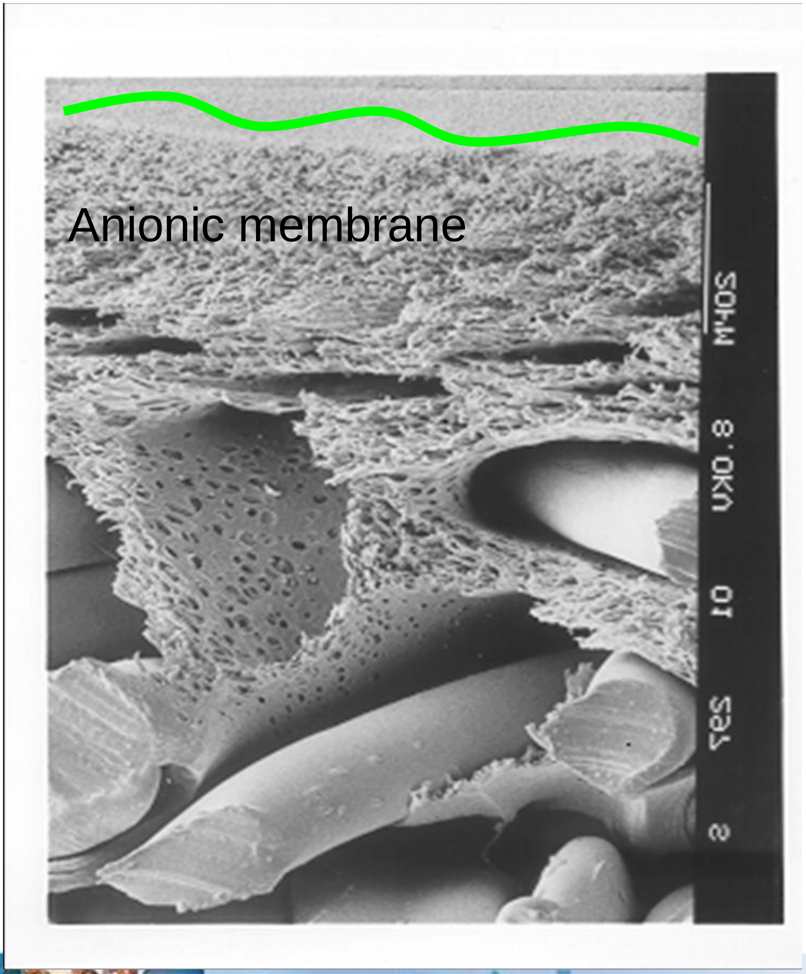
- Pendular branches
- Hook on to membrane
- Oil or latex suspensions



Polyamine (Genefloc GPF) flocculant



- Charge on molecule backbone
- Loose attraction on membrane
- Subject to shear forces
- Cationic charge neutralised by anionic phosphonate antiscalant



Genefloc GPF – Case Study

- 1,400 m^3day SWRO plant
- Feed tank 3 hour residence time.
- Genefloc GPF dosed at 2mg/l with 0.3mg/l sodium hypochlorite
- 3 dual media filters sand & anthracite
- 5 µm cartridge filters
- Sodium bisulphite dosage & Genesys LF antiscalent
- 2 trains of 56 DOW SWHR 380 RO membranes
- Plant operational with the same membranes since September 2003

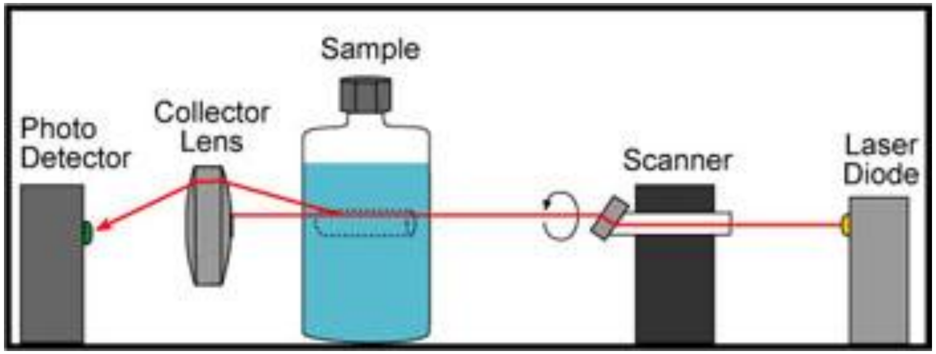
GPF feed water treatment – Leparc et al 2005

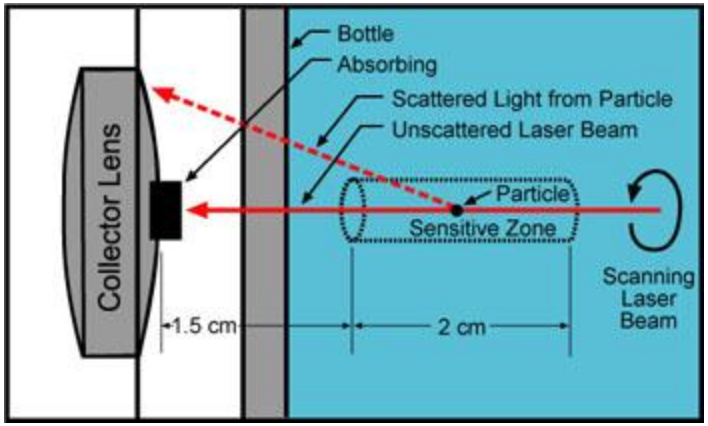
2005	SW Intake	Well SW	Raw Water	DMF effluent	CF Effluent
Turbidity (NTU)	1.6	0.3	0.4-1.1		
SDI 3 min	18.3	7.1	11.8		
SDI 5min	13.2	5.4	9.0		
SDI 15min	5.8	2.6	4.4	2.1	2.0

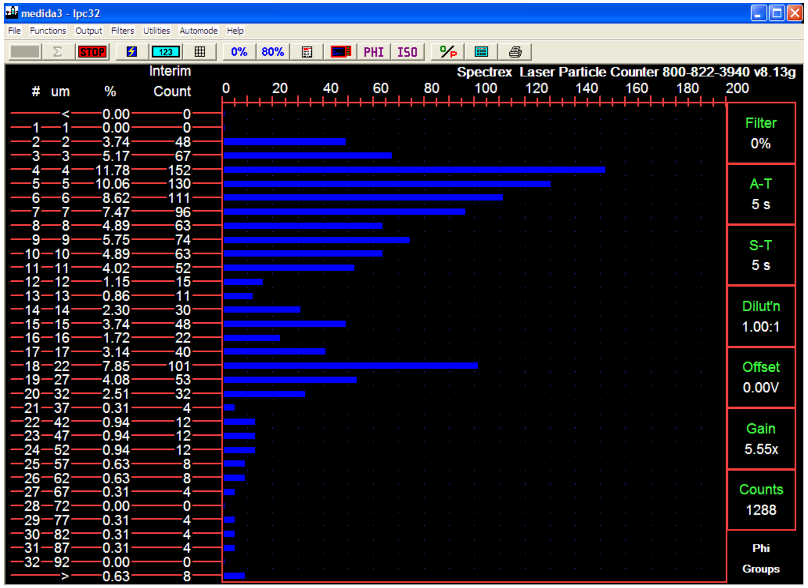
Genefloc GPF – Conclusions

- **Cationic charge** – located on backbone not pendular sub branches preventing irreversible membrane attachment
- **Molecular Size** – long chains prevent pore attachment allowing easy removal by shear forces
- **Solubility** – dilution & low dose rate allows easy absorption onto media filter surface

Optimising pre-treatment – reducing membrane fouling



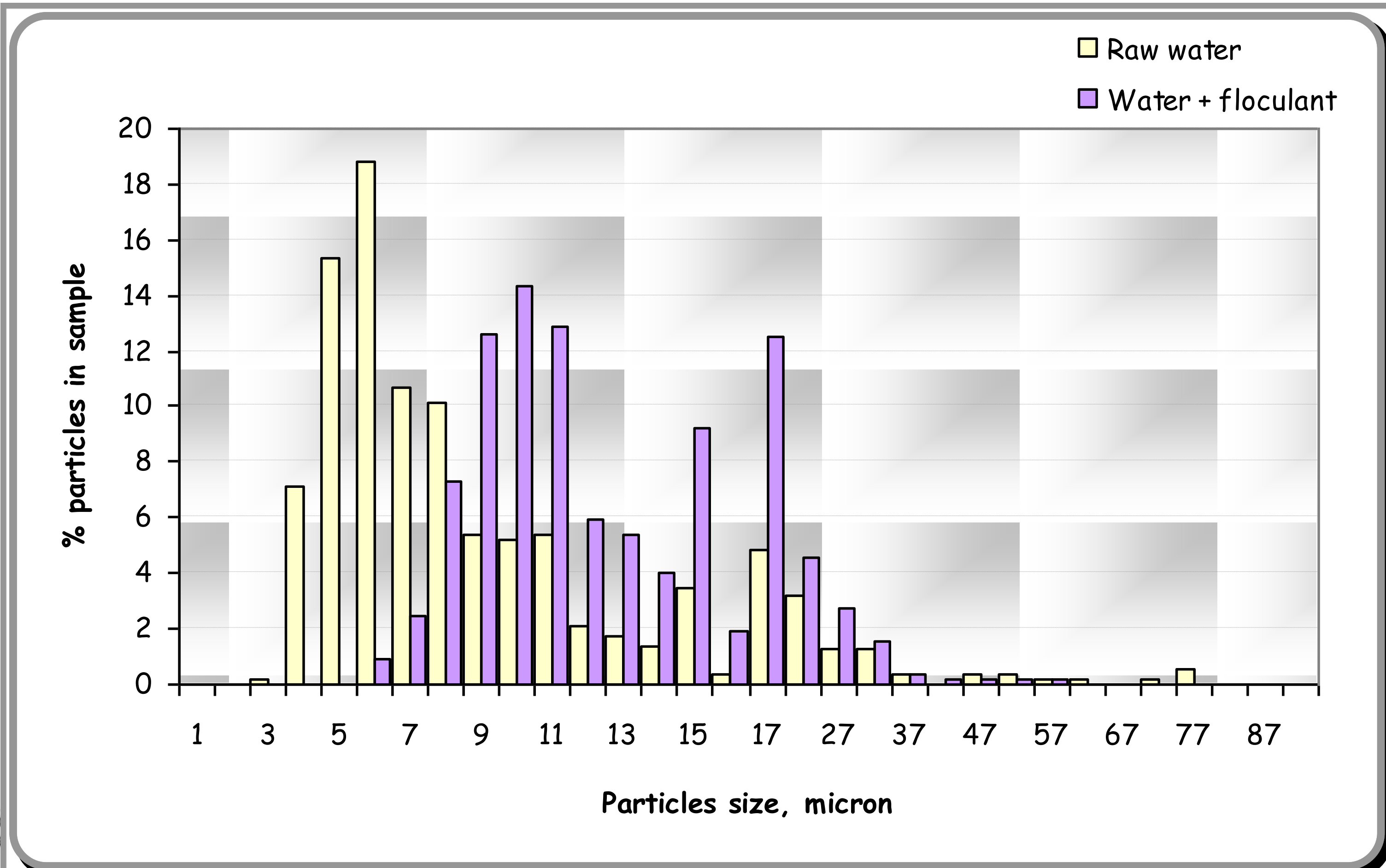




Particle counting instruments have became a valuable tool when DESIGNING, EVALUATING and OPTIMIZING FILTRATION SYSTEMS.

Particle counter

Optimizing coagulant and flocculant dosing using particle counter



Cleaning Frequency & Efficiency

DOW FILMTEC*“….. the correct pH is critical for optimum foulant removal. If a foulant is not successfully removed, the membrane system performance will decline faster ….. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs”*

Hydranautics:

“The appropriate solution to use can be determined by chemical analysis of the fouling material. A detailed examination of the results of the analysis will provide additional clues as to the best method of cleaning”

Membrane Autopsy Methodology

External inspection

Internal inspection

Specific tests (*)

Foulant is detected?

YES

NO

Gravimetric Analysis

Other tech. : SEM-EDX

ATR-FTIR/RMN Dif. R-X, etc.

Microbiological counts

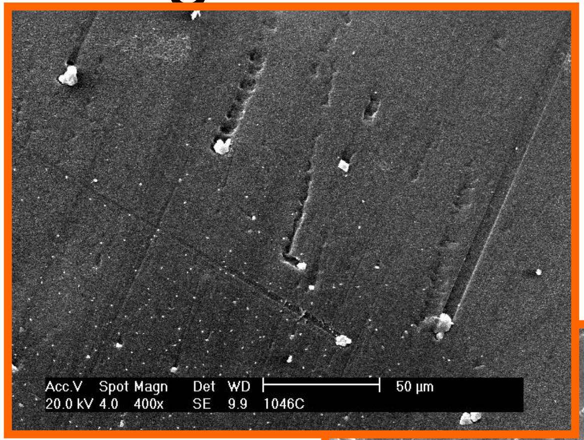
Membrane condition
Flux / Rejection %

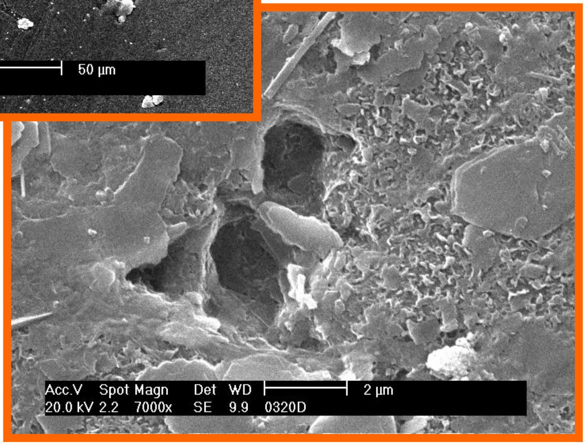
(*) Cleaning test
Integrity /Oxidation test

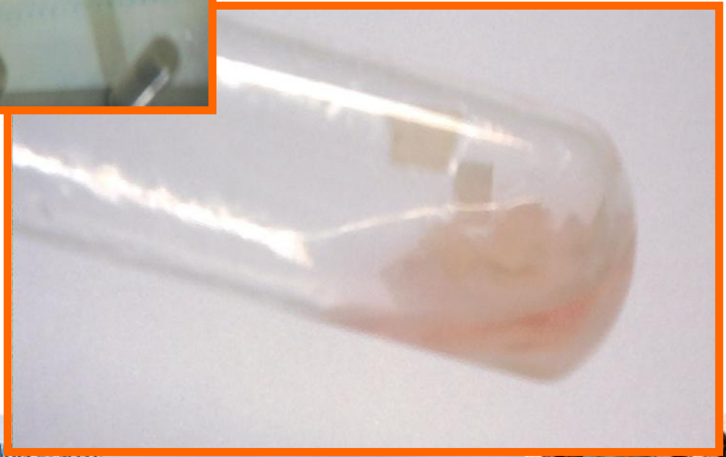
Conclusions and recommendations. Troubleshooting.

Membrane Autopsy

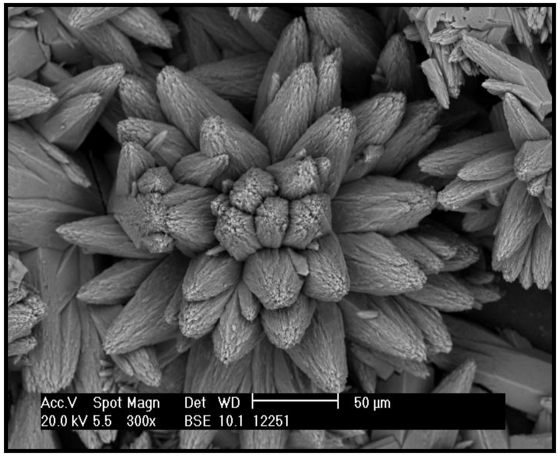
Chemical & Physical Damage

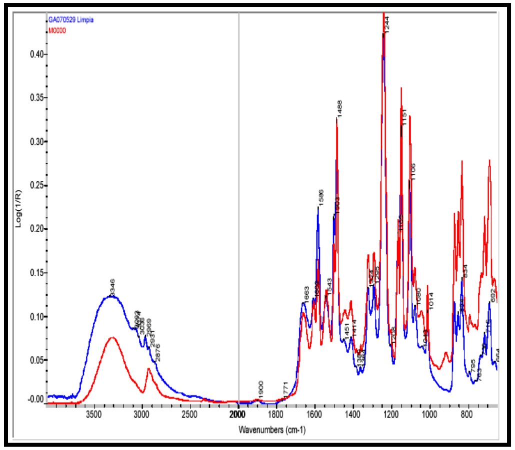


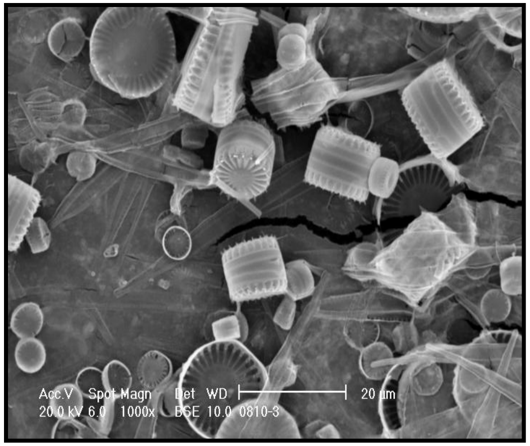




Foulant Identification – GMP Madrid







Foulant Identification:

- Scanning electron microscopy (SEM-EDAX)
- Infrared Spectroscopy (ATR-FTIR)
- X-Ray Diffraction analysis ATR
- Nuclear Magnetic Resonance (NMR)

Membrane Autopsy

Genesol Product Selection

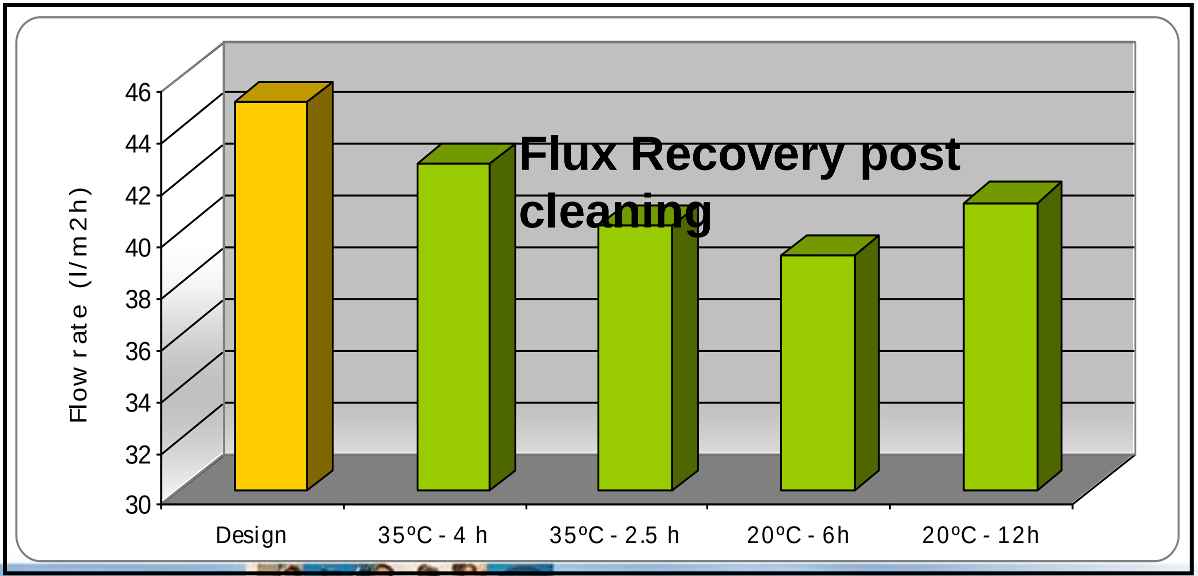
- Genesol products tested against the foulant under different conditions

- Product selected based on recovery of membrane to design flux and salt rejection

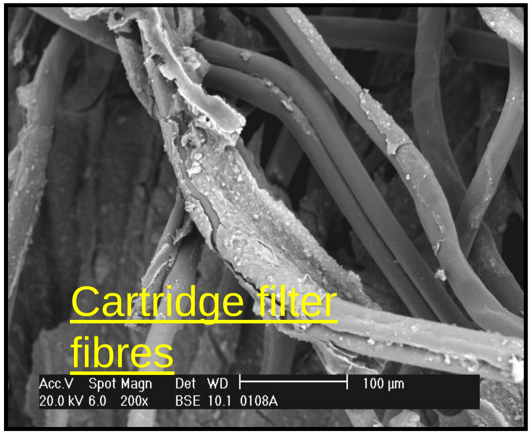
- SEM-EDAX comparison of membrane surface before and after cleaning procedure


Cleaned Membrane Section


Flat sheet cleaning rig

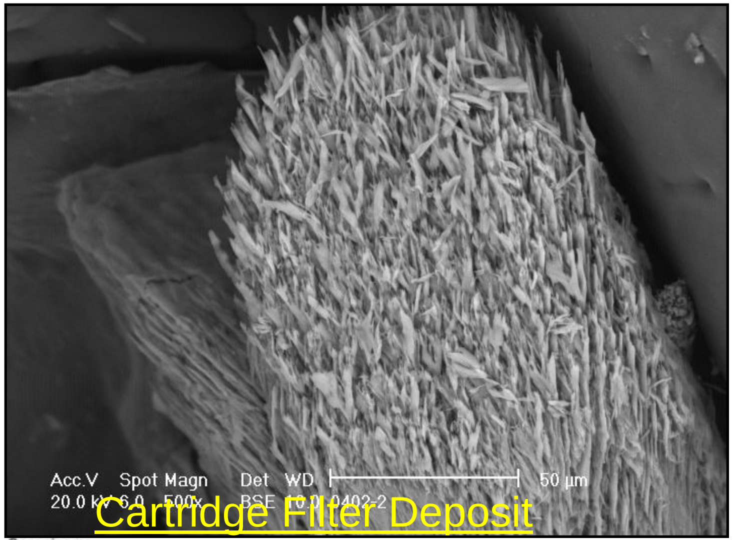


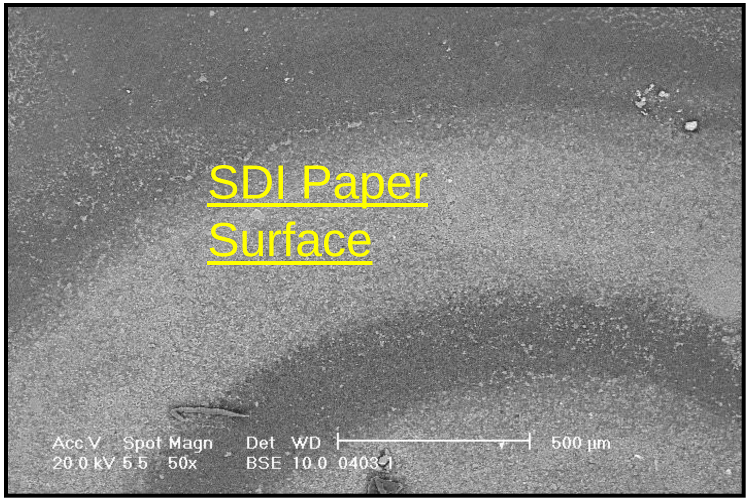
Membrane Autopsy alternatives



Cartridge Filter:
- SEM-EDAX identification of foulants on cartridge filter

SDI Filter Paper:
SEM-EDAX of 0.45 µm SDI filter paper deposit identification





Membrane Autopsy

- Monitoring of Membrane condition helps prevent problems.
- Process gives positive answers in event of failure.
- Ensures optimum cleaning programme application.
- Scientifically based answers in event of membrane issues.

Conclusions

- RO engineers design innovations
- Chemists help make the plant work
- Lab techniques help improve operation