Recent Innovations to keep membranes clean

Mr. Stephen Chesters
Managing Director
Genesys International Ltd
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

- Type of foulants
  - Biofilm & organic matter: 35%
  - Colloidal/particulate matter: 29%
  - Scales & Inorganic deposits: 29%
  - Not detected: 7%

- Scale & Inorganic Deposits
  - Ox. Fe/Mn: 33%
  - CaCO3: 13%
  - Ca -Phosphate: 2%
  - SiO2: 16%
  - CaSO4: 9%
  - Ba/Sr SO4: 27%
Membrane pressure damage
Autopsy results 2001 - 2009

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Scale & Inorganic Deposits:
- Ox. Fe/Mn: 16%
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- SiO2: 2%
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- Ba/Sr SO4: 13%
- 27%

- 33%
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 m³/day (IDA)
- Total 713 plants & increasing!
- Largest in Middle East (Sulaibiya 375,000 m³/day)
- New projects in Australia, Singapore & Europe
- WWRO approx 50% of cost of SWRO.
- Calcium phosphate Issues
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula</th>
<th>Abb. Name</th>
<th>Mineral Name</th>
<th>Structure</th>
<th>Solubility Product mol/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous calcium phosphate rock</td>
<td>Ca₉(PO₄)₆</td>
<td>ACP</td>
<td></td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Monocalcium phosphate</td>
<td>Ca(H₂PO₄)₂</td>
<td>MCP</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Dicalcium phosphate dihydrate</td>
<td>CaHPO₄·2H₂O</td>
<td>DCPD</td>
<td>Brushite</td>
<td>Amorphous</td>
<td>2.32 x 10⁻⁷</td>
</tr>
<tr>
<td>Dicalcium phosphate</td>
<td>CaHPO₄</td>
<td>DCP</td>
<td>Monetite</td>
<td>Amorphous</td>
<td>1 x 10⁻⁷</td>
</tr>
<tr>
<td>Tricalcium phosphate</td>
<td>Ca₃(PO₄)₂</td>
<td>TCP</td>
<td>Whitlockite</td>
<td>Amorphous</td>
<td>2.07 x 10⁻³³</td>
</tr>
<tr>
<td>Tetracalcium phosphate</td>
<td>Ca₄O(PO₄)₂</td>
<td>TTCP</td>
<td>Hilgenstockite</td>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Pentacalcium hydroxylapatite</td>
<td>Ca₅(PO₄)₃(OH)</td>
<td>HAP</td>
<td>Hydroxyapatite</td>
<td>Hexagonal</td>
<td>2.34 x 10⁻⁵⁹</td>
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<tr>
<td>Pentacalcium fluoroapatite</td>
<td>Ca₅(PO₄)₃(F)</td>
<td>FAP</td>
<td>Fluoroapatite</td>
<td>Hexagonal</td>
<td>3.16 x 10⁻₆⁰</td>
</tr>
<tr>
<td>Octacalcium phosphate</td>
<td>Ca₈(HPO₄)₂(PO₄)₄</td>
<td>OCP</td>
<td></td>
<td></td>
<td>2 x 10⁻⁴⁹</td>
</tr>
<tr>
<td>Calcium pyrophosphate</td>
<td>Ca₂P₂O₇</td>
<td>CPP</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hydroxyapatite Solubility

log ([HAP] / mol.L⁻¹)

pH

Solid titration

Moreno, 1968
Avnimelech, 1973
McDowell, 1977
Verbeek, 1980
Wier, 1971
Chuong, 1973
Bell, 1978
Levinskas, 1955
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

[Charts showing water analysis]

- Calcium: 140 mg/L
- Magnesium: 156 mg/L
- Sodium: 158 mg/L
- Bicarbonate: 225 mg/L
- Carbonate: 34.3 mg/L
- Chloride: 960 mg/L
- Fluoride: 0.5 mg/L
- Sulphate: 2148 mg/L
- Bicarbonate: 141.0 mg/L
- Nitrate: 10.0 mg/L
- Silica: 24.0 mg/L
- Phosphate: 0.0 mg/L

TDS: 4746.4 mg/L
Cations: 74.3 mg/L
Anions: 75.1 mg/L
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

<table>
<thead>
<tr>
<th>Total Cost Saving</th>
<th>Skid 1a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Saving, m³/annum</td>
<td>1,121,280</td>
</tr>
<tr>
<td>Energy Saving kWhr</td>
<td>857,000</td>
</tr>
<tr>
<td>Energy Costs Saving, US$/annum</td>
<td>$60,000</td>
</tr>
<tr>
<td>Membrane Replacement US$ pa</td>
<td>$39,000</td>
</tr>
<tr>
<td>Chemical Saving, US$ pa</td>
<td>$37,000</td>
</tr>
<tr>
<td>Total Saving, US$ pa</td>
<td>$136,000</td>
</tr>
</tbody>
</table>
Efficient operation at high silica levels

- Silicon Dioxide, SiO2. 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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Silica 60mg/l</td>
<td>Reject 256mg/l</td>
</tr>
<tr>
<td>pH 7.2 (reduced to 6.5 H₂SO₄)</td>
<td>Recovery rate Improved to 75%</td>
</tr>
<tr>
<td>4 skids – 2 stage 864 elements</td>
<td>3.8mg/l Genesys SI</td>
</tr>
<tr>
<td>Permeate 18,000 m³/day</td>
<td>Water saving 2,566,680 m³/year</td>
</tr>
<tr>
<td>Operating Recovery 60%</td>
<td>Energy Saving 3,836,160 kWhr/year</td>
</tr>
<tr>
<td>Silica fouling – 2 monthly cleaning</td>
<td>Energy Costs US$268,531</td>
</tr>
</tbody>
</table>
Cleaning Clay from Fouled membranes

Lead Elements 2001-2009  Source: GMP Laboratory Madrid
- Most common foulant in lead membrane elements
- Clay is colloidal alumino-silicates
- Source is erosion products in surface waters
- Reduction in flux and increases $\Delta P$
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.
• Particles <2µm pass through pretreatment 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.
• Cake layer continues to compress & becomes impermeable to water
• Permeate flow reduced
• Normal Cleaning solution can’t penetrate layer
• 1-3% solution of Genesol 703
• CIP 35-40°C
• <4 bar
Add Cleaning Solution

- 1-3% solution of Genesol 703
- CIP 35-40°C
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

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

- Flushing removes particles
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.
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 m³/day 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

<table>
<thead>
<tr>
<th>2005</th>
<th>SW Intake</th>
<th>Well SW</th>
<th>Raw Water</th>
<th>DMF effluent</th>
<th>CF Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>1.6</td>
<td>0.3</td>
<td>0.4-1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDI 3 min</td>
<td>18.3</td>
<td>7.1</td>
<td>11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDI 5min</td>
<td>13.2</td>
<td>5.4</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDI 15min</td>
<td>5.8</td>
<td>2.6</td>
<td>4.4</td>
<td>2.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>
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 become a valuable tool when designing, evaluating and optimizing filtration systems.
Particle counter
Optimizing coagulant and flocculant dosing using particle counter
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

Foulant is detected?

YES

Gravimetric Analysis

NO

Other tech.: SEM-EDX

Specific tests (*)

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

Microbiological counts

Conclusions and recommendations. Troubleshooting.

Membrane condition
Flux / Rejection %

(*) Cleaning test
Integrity / Oxidation test
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

Flux Recovery post cleaning
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