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Restoration of "dead" clay fouled membranes

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ABSTRACT

Without doubt, the membrane is the key component of a Reverse Osmosis (RO) system, but the pretreatment system is often the most important contributor to the smooth and efficient operation of a membrane plant. This is especially true when treating challenging source waters such as highly turbid surface waters from open canals, rivers, and lakes. These are often contaminated with a variety of organics that have complex and variable chemistries and can carry large loads of suspended solids. Amongst these are the clay minerals, (alumino-silicates), derived from the weathering of rocks and the entrainment of soils, which create a particularly difficult fouling. Over 100 RO plants in the Karachi area are affected by this type of fouling which is characterized by high 1st stage differential pressure (ΔP) and loss of flux. The clay forms a layer on the membrane surface which is impervious to water and so feed pressures are increased to maintain permeate flow, resulting in increased energy costs due to higher consumption of electricity. Permeate quality is also affected by impregnated clay interfering with the salt rejection properties of the membrane. This article presents the results of cleaning experiments conducted on completely fouled membranes and to all intents 'Dead' membranes from a system treating such canal water. Cleanings were performed with conventional commodity chemicals, a series of proprietary products, and finally with a specialist product (Genesol-703) specifically designed for the removal of clay fouling. In conducting the experiments, a specific method of application was derived which gives extremely good results.

Keywords: Membranes; Clay; Fouling; Restoration; Flux; Cleaning

1. Case history

A sugar and ethanol production plant in Sindh Province of Pakistan was using a reverse osmosis desalination plant to purify water for use in various stages of the industrial process. The raw water is abstracted from a nearby Canal and has the following characteristics:

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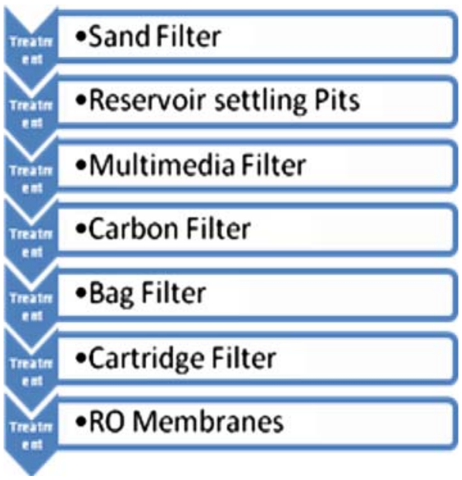
The plant has the following pretreatment program:



Reverse Osmosis (RO) Systems design

Feed capacity	–	40 m^3/h
Product flow	–	25 m^3/h
No. of stages	–	02
Array	–	5 × 3
No. of membranes	–	32
Model of membranes	–	BW30 400, Filmtec USA
No. of vessels	–	08
Feed water type	–	Canal Water
Feed TDS	–	400–600 ppm
COD	–	60–90
BOD	–	15−25
Design feed pressure	–	150 psi

1.1. Issues

Silt Density Index after cartridge filters: unlimited

Membranes choke within one week, feed pressure doubles to maintain permeation but despite this, flux decreases resulting in product flow decreasing by 60% against the original design specification.

1.2. Cause

Clay and organics ingested into the membranes are severely restricting permeation.

1.3. RO membranes

The membrane is the heart of the RO plant and is constructed of a thin, semipermeable, polyamide film cast onto a relatively thick, Polysulphone support with an integral fabric weave to give strength. The whole thickness is being in the range of 160 μm. Membranes are characterized by their unique properties of high water permeation, very low salt passage, and dimensional and chemical stability. In spite of their small sizes and high solubility in water, salts, even those with low molecular weights, do not pass through the membrane at a significant rate. Their passage is held to a very low level e.g. less than 1% using this thin film composite (TFC) arrangement. Passage of larger size colloidal and suspended solid particles is completely prevented by the membrane's closed structure. This is also true of micro-organism such as bacteria which, when present in the feed, will be trapped on the membrane surface causing it to foul. Membrane fouling is also introduced by the presence of scaling and corrosion products in the feed. The presence of any of the above in the feed water will cause membrane fouling and reduce RO plant efficiency; hence, effective feed pretreatment is essential. This must address the specific issues of removing suspended solids, capturing dissolved metal ions, and preventing the ingress of biological or organic matter which will be present in the source water. Appropriate anti-scalants must also be used to prevent the precipitation of sparingly soluble salts which can exceed their saturation limits.

In this instance, the biggest contributor to the fouling problems was the presence of clay minerals.

2. Clay history

Clay is a general term including many combinations of one or more clay minerals such as kaolinite and montmorillonite with traces of metal oxides and organic matter. Clay deposits are mostly composed of phyllosilicate minerals containing variable amounts of water trapped in the mineral structure.

Clay minerals are hydrous aluminum phyllosilicates, sometimes, with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations. Clays have structures similar to the micas and therefore, form flat hexagonal sheets. Clay minerals are common weathering products of rocks (including weathering of Feldspar) and low temperature hydrothermal alteration products. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone, and siltstone and in fine grained metamorphic slate and phyllite.

Structurally they are composed of tetrahedron rings linked by shared oxygen atoms to other rings in a two-dimensional plane forming a sheet-like structure. These sheets are connected to each other by weakly bonded layers of cations which often have water and other neutral atoms or molecules trapped between the sheets giving clay its soft compressible nature. The resultant crystal structure is flat and plate like. According to Swaddle, we refer to them as Aluminosilicates when some of the Si^{4+} ions in the silicates structure are replaced by Al^{3+} ions. For each Si^{4+} ion replaced by an Al^{3+}, the charge must be balanced by having other positive ion such as Iron, Magnesium, alkali metals, alkaline earths, and other cations.

Aluminosilicate minerals are minerals composed of aluminum, silicon, and oxygen, plus counter cations. They are a major component of kaolin and other clay minerals.

Silt is granular material of a size somewhere between sand and clay. Silt may occur as a soil or as suspended sediment (also known as suspended load) in a surface water body. It may also exist as mud deposited at the bottom of a water body. Silt is easily transported in water. Silt and clay contribute to turbidity in water. Silt is transported by a stream that is why surface water (canal water, river water, and seawater) is enriched with silt.

2.1. Operational effects of clay fouling:

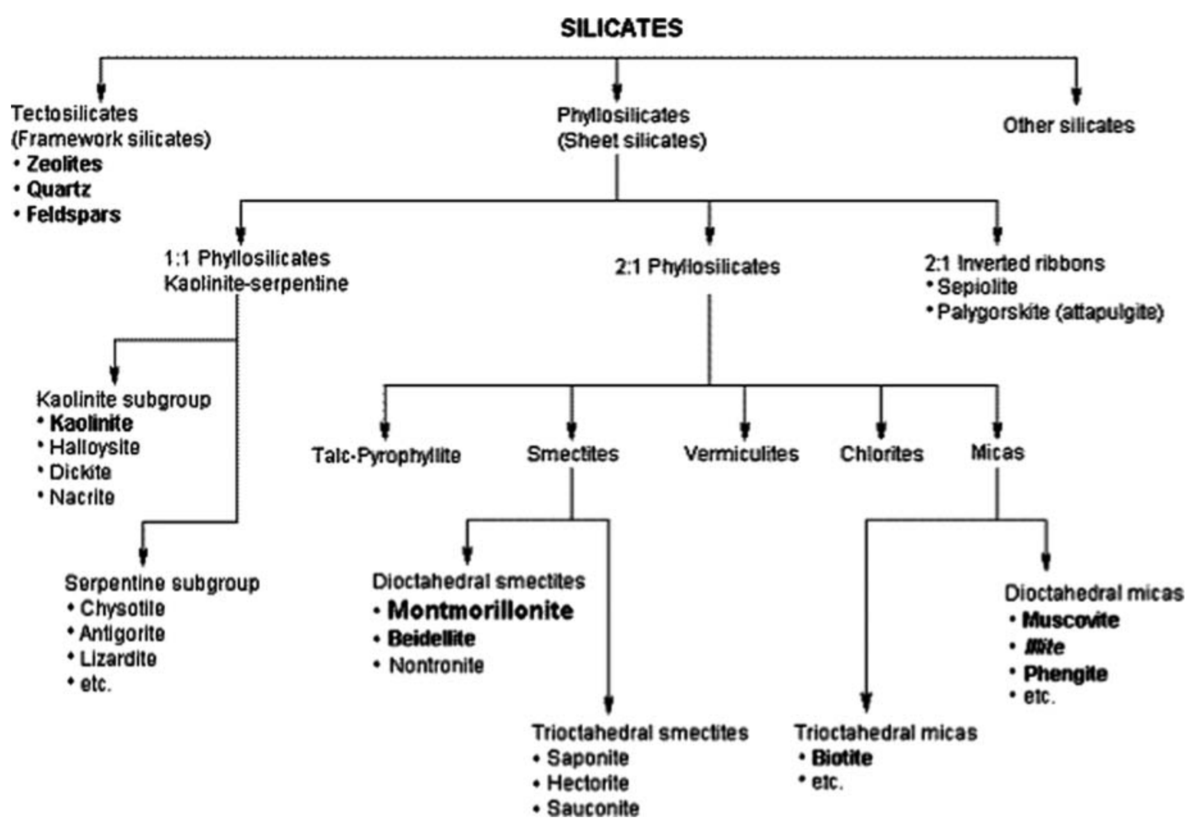
Due to its flat, plate-like structure, clay tends to form layers on the surface of the membrane. These layers will build, one on top of the other, as the colloidal clay particles enter the membrane environment under pressure. Clay has the property of plasticity and will both compact, impregnating into the membrane surface, and spread across the sheet. It is also hydrophobic and so will tend to reject water from its surface. The result is the gradual coating of the membrane with a water impervious layer of Clay which reduces the area available for permeation and acts as a hydraulic barrier to the passage of water along the feed–brine channels.

In operational terms, this results in loss of flux (reduction of permeate flow at the same feed pressure) and an increase in the differential pressure along the feed–brine channel, (ΔP).

And so the feed pressure is increased to maintain permeation resulting in increased consumption of electricity.

When differential pressures exceed 4 Bar, there will be irreversible mechanical damage to the membranes themselves, potentially including telescoping, brine spacer extrusion, and fracture of the outer fibreglass jacket.

Eventually, permeate quality deteriorates as the salt rejection properties of the membrane are compromised by the impaction of clay particles.



2.2. Why failed prefiltration

The use of highly turbid canal water as a raw water source for RO Membranes is a major problem in the world of water treatment. Many RO plants have failed because of this.

It is very difficult to handle such aggressive water by conventional pretreatment (sand filter, carbon filter, or cartridge filter).

Such surface waters (River, Sea, Canal, and Lake) are highly enriched with high turbidity, silica, clay, inorganic, and organic particles. All of these types of suspended materials are mutually dangerous for RO membranes. Because of its colloidal size, clay is very difficult to trap by simple filtration and this is the principle cause of it reaching the membranes. Conventional prefiltration does not have the ability to act as a barrier for such small size particles and so requires specially enhanced measures to ensure removal. These would include the use of "Active" media which interacts with the particles to effect their removal plus the use of "Filter Aids" which destabilize the interparticle, repulsive forces and allow the agglomeration of colloids into larger, filterable particles.

Full remedial treatment must therefore include a revision of the pretreatment system to prevent further fouling.

2.3. Cleaning of membranes, art, or science

The cleaning of membranes is not a defined formula, not a thumb rule, and not $2+2=4$. Chemical cleaning of membranes is an art, which gives different and amazing behavior and results in different styles, in different places, and at different times. The more you practice, the better you get.

The cleaning procedure has a very profound and prominent role in cleaning the membrane and obtaining the optimal results:

- Sufficient and calculated quantity of chemical solution for the number of membranes to be cleaned.
- Proper ratio of solvent and solute.
- Correct selection of cleaning chemicals for the type of foulant present.
- Establishing and maintaining correct parameters such as pH, pressures, temperatures, flows, etc.
- Proper design of the CIP system (pump, filtration, and piping).

2.4. Cleaning chemical selection

The cleaning chemicals and cleaning method play a major role in restoring membrane performance and the correct selection of cleaning chemicals is vital in achieving the desired results. If the cleaning chemicals are not appropriate, the membrane may be damaged or not work effectively after cleaning.

Cleaning agents can affect fouling materials present on a membrane surface in three ways:

(i) Foulants may be removed.
(ii) Morphology of foulants may be changed (swelling and compaction) and/or surface chemistry of the deposit may be altered, such that the hydrophobicity or charge is modified [1].
(iii) Reported foulant-cleaning agent reactions are hydrolysis, peptization, saponification, solubilization, dispersion (suspension), and chelation.

If an inappropriate cleaning agent is chosen, negative effects can appear and membrane performance can be adversely affected. Membrane manufacturers clearly warn about the consequences of applying inefficient cleaning techniques:

> If foulant is not successfully removed, the membrane system performance will decline faster, as it is easier for the foulant to deposit on the membrane surface area. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs. Most effective cleaning allows longer system operating time between cleanings and results in the lowest operating costs [2].

In order to provide an effective cleaning compound for the removal of clay deposits, Genesys International Ltd. formulated Genesol 703 [3].

Genesol-703 is a 100% active, powder form product composed of a combination of alkalinity builder to provide high pH, a surfactant for surface wetting, and to aid penetration, a chelating agent to aid the breakdown of biofilms and sequester metallic ion fouling, and an ionic strength builder to promote the generation of normal osmotic effects during the soaking phase of the washing cycle. The product is approved under NSF/ANSI 60 guidelines. This combination of products has a detergent and surfactant effect on the colloidal clay fouling and creates a high ionic strength at the membrane surface.

The Genesol-703 mode of action can be described as follows: the first stage of attack occurs at the water surface interphase of the clay deposit and it is due to the synergistic mode of operation of the specialized chemical combination. The process starts by reducing the surface tension of the deposit and by increasing the effectiveness of the surfactant which overcomes the impermeability of the foulant to allow the cleaning solution to penetrate into the interlayer spaces of the clay structure. The clay then becomes more porous, increasing the permeability to water and consequently increasing the surface area of the deposit in contact with the active chemical. The wash solution is then able to penetrate and disrupt the “body” of the deposit.

The unique formulation of Genesol 703 provides a secondary physical action which increases cleaning efficiency at the membrane surface allowing a “double edged” approach to deposit removal. This action also removes blockages from the membrane pores caused by the swelling effect of the hydrated clay particles.

During the normal operation of an RO system, pressure is provided by the high pressure pump (HPP) to overcome the osmotic pressure of the salty feed water and to force water from the feed/brine side of the membrane into the low salinity permeate side.

During normal cleaning, the wash solution is introduced to the feed/brine side of the membrane by a low pressure circulation pump which will normally maintain a pressure less than 4 Bar. Nevertheless, even at this low pressure there are still permeation and a tendency for the production of permeate during the circulation phase. Circulation is necessary to provide the purging effect which removes released foulant and to provide shear forces which rip foulant from the membrane surface when the cleaning agents have worked to weaken any attractive forces chemically.

In the past, soaking was normally provided merely to allow contact time for the wash solution chemicals to react. However, with Genesol 703, the soaking phase takes on more significance while the circulation pump is switched off, and the system pressure falls to zero, the high ionic strength of the wash solution induces the effect of normal osmosis and promoting the migration of low ionic strength solution from the permeate side to the wash solution side of the membrane. In doing so, it encourages the release of foulant from the membrane surface. It also assists in unblocking the membrane pores which become filled with swollen clay particles. Once foulant is removed from the membrane surface into the body of the wash solution, the dispersing effects of the detergent prevents redeposition and is likely to prevent membrane abrasion.

In addition to the effectiveness of Genesol 703 in removing clay deposits, its application also serves as a means of “shock treatment” to reduce the bio fouling potential through lysis of micro-organisms; in turn, this helps to prevent further system contamination. Cell lysis occurs due to the semipermeable nature of the membrane surrounding the micro-organism; the cleaning solution creates the movement of water from the cell cytoplasm resulting in the eventual removal of the membrane from the cell wall.

This case study (as indicated below) proved this product together with the new cleaning technique is much more effective at removing clay mineral deposits than conventional acid and alkaline cleaning products and routine cleaning practice.

3. Remedies and results

Various remedies were applied to try to cope with this:

3.1. First remedy

3.1.1. Membrane cleaning with conventional chemicals

First wash: Recirculate the alkaline solution of EDTA (ethylene diamine tetraacetic acid) and sodium dodecyle benzene sulphonate (a surfactant) through the membranes by keeping the following parameters to maintain:

Description	Value	Units
Recirculation flow (single vessel cleaning)	9	m^3/h
Solution strength	2–3%	W/W %
pH of solution	11.5	
Recirculation time	4–6	h
Solution temperature during cleaning	40	°C

Maintain high pH with caustic soda and then flush with fresh water for 30 min.

Second wash: Recirculate the acidic solution of hydrochloric acid (HCL) or sulphamic acid and citric acid.

Description	Value	Units
Recirculation flow (single vessel cleaning)	9	m^3/h
pH of solution	2–3	
Recirculation time	2–3	h

This wash produced no significant result in increasing flux.

3.2. Second remedy

3.2.1. Membrane cleaning with branded chemicals

Many different imported branded proprietary cleaning chemicals were used to try to restore flux, with the same cleaning procedure as mentioned before. These produced unremarkable results for both high and low pH chemicals.

3.3. Third Remedy

3.3.1. Cleaning with Genesol 703

After continuously cleaning the membranes on weekly or bi-monthly basis using many different cleaning chemicals, Genesol 703 was selected for testing.

Description	Value	Units
Recirculation flow (single vessel cleaning)	9	m^3/h
Solution strength	2%	W/W %
pH of solution	11	
Recirculation time	4–6	h
Solution temperature during cleaning	40	℃

This product showed some improved results for clay removal from membranes and restored the membranes flux to 50–60% of design.

After 10 months of difficult and hectic operation, however, the product flow came down to only $5m^3/h$ and cleaning with Genesol 703 no longer gave significant results. At this point, it was decided further operation was not feasible and so the membranes should be replaced.

Because of fouling, the membranes were giving only 20% of the design product flow and high energy costs resulting from the excessive consumption of electricity had rendered the plant uneconomic. Also, due to high pressure, some of the membranes had compressed physically.

3.4. New treatment regime: Step-1

Fifteen days after stopping the RO plant, we applied a new experiment on membranes with Genesol 703. The membranes were soaked with a 4% solution of 703 under 10–20 psi pressure.

After 24 h of soaking, the elements were flushed with fresh water and the solution which came out contained a large quantity of clay/silt and was a muddy colour.

3.5. New treatment regime: Step-2

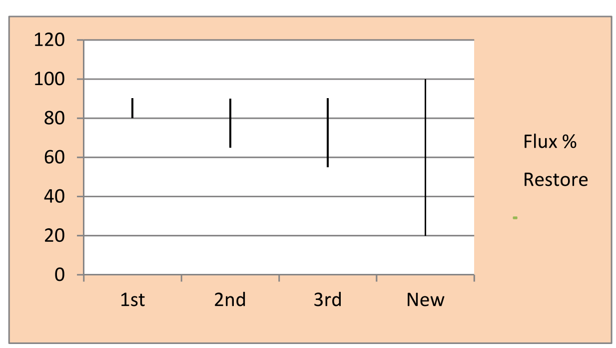
Again the membranes were soaked, with a 4% solution of Genesol 703 under 10–20 psi pressure. After 72 h, the membranes were flushed and the solution which came out was like sludge. After 30 min, settling time over 200 g clay was found in one litre of flushing water.

Output from Step 2, before and after settling

4. Results

The results were amazing, membranes flux was restored to the original design specification at the design feed pressure on membranes that were going to be thrown away and there was no loss of salt rejection.

	Cleaning results		Total Flux Restoration
	From	To	
1st Remedy	80%	90%	10%
2nd Remedy	65%	90%	25%
3rd Remedy	58%	90%	32%
New treatment Regime	20%	100%	80%



5. Conclusions

- Genesol 703 was effective at removing clay and slit from fouled membranes in a conventional cleaning protocol.
- In extreme fouling conditions and when left to soak for 1–3 days, Genesol 703 had a surprising and dramatic effect on removing clay and silt deposits bringing membranes back from the dead and restoring flux and salt rejection performance.
- Further work is in progress on this site to improve the pretreatment process with specific emphasis on measures to remove more of the silt load before the RO membranes.

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