GENESYS INTERNATIONAL

Application Guide 4

RO Pre-treatment - safe use of cationic flocculant

Extract from the paper "The safe use of a cationic flocculant with RO membranes", presented at the EDS Conference on Membranes in drinking water production and waste water treatment, Toulouse, France, October 2008

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Genefloc GPF is a membrane compatible low dose, poly amine cationic flocculant. The effectiveness of cationic flocculants is well known but due to the perceived danger of membrane fouling they are not widely used. This paper dispels some of the myths.

Membrane Compatibility

It is a widely held view that cationic flocculants can foul reverse osmosis membranes. This view is supported by three of the major membrane suppliers, as seen from their technical bulletins, product data sheets and web-sites.

Dow – Form No. 609-02027-1004
"The membranes in RO plants have been heavily fouled by a gel formed by the reaction between cationic poly-electrolytes and antiscalants."

"To minimise the risk of direct or indirect interference with RO membranes, anionic or non-ionic flocculants are preferred rather than cationic flocculants."

Form No. 609-02024-1004
"In addition cationic polymers may co-precipitate with negatively charged antiscalant and foul the membrane."

Hydranautics – TSB107.15 Page 2
"Common examples of foulants are: man made organic material (e.g.) antiscalant/dispersants, cationic poly-electrolytes."

Koch – TFC-HR8" Product data sheet
"TFC-HR membrane may be irreversibly fouled if exposed to cationic positively charged polymers or surfactants. Exposure to these chemicals during operation and cleaning is not recommended."

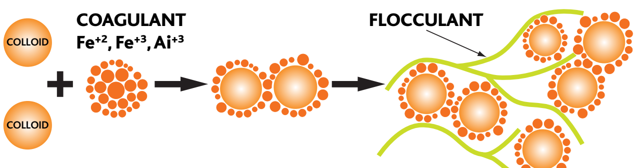

Fig 1: Flocculant bridging

Inorganic Coagulants/Flocculants

Inorganic coagulants are usually based on multivalent cations such as iron (ferric or ferrous) and aluminium salts. These positively charged molecules interact with negatively charged particles to assist in charge aggregation. At the correct pH, temperature and salinity these chemicals form insoluble hydroxides which, link together to form long chains or meshes, physically trapping small particles into the larger floc.

Organic Flocculants

Cationic polymers become positively charged when dissolved in water. They can be copolymers of acrylamide with a cationic monomer, cationically modified acrylamide or a polyamine. The cationic charge in these polymers is derived from nitrogen in the form of a secondary, tertiary or quaternary amine group. Those containing secondary or tertiary amines are sensitive to pH, and the charge on these polymers drops off at a pH >6.0. Polyquaternary amines are not pH sensitive and function well across a wide pH range. In these polymers, the charge can be located on a pendant group as shown in Figure 2.

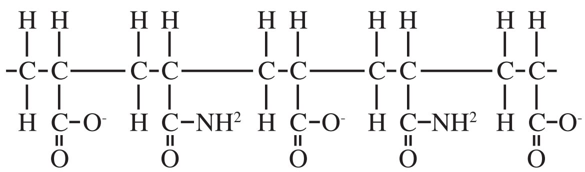

Fig 2: **Polyacrylamide molecular structure showing anionic sub branches.**

The pendant groups act like hooks trapping particles but also importantly potentially attaching to the anionically charged membrane surface rather like velcro. Once attached cationic polyacrylamides would be very difficult to remove.

Poly Quaternary Amines - are long and wrap flocs together. The cationic charge is positioned down a central backbone Figure 4. This means the molecule is much less likely to become permanently attached to the membrane surface.

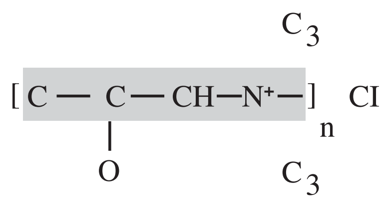

Fig 3: **Polyamine with charge on backbone**

Membrane Fouling

There are four primary mechanisms of coagulant and flocculant fouling:

- Any soluble iron or aluminium in the feed water present naturally or due to excess coagulant or flocculant dosing will oxidize to form iron and aluminium hydroxides and oxides on the membrane surface. This reaction can often be inhibited or retarded by using the chelating properties of phosphonate based antiscalant.
- An acrylic acid based antiscalant may react with iron and aluminium to form meta-acrylate salts which can irreparably foul the membrane as shown in Figure 5.
- Aluminium or iron based coagulants that do not form flocs are not soluble and will form preflocs which attach to any surface to neutralise its charge. This includes multi-media filters, cartridge filters and ultimately the membrane surfaces as well (Figure 4).
- Oil or latex present in some flocculants can cause direct adherence to the membrane surface.

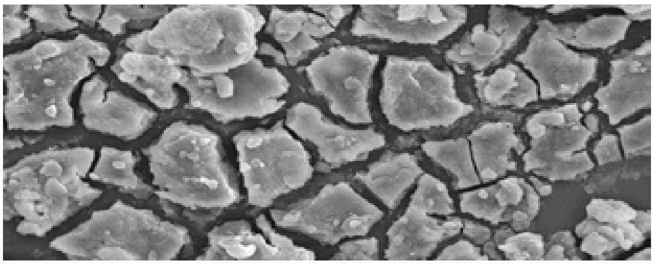

Fig 4: **Aluminium flocculant fouling on a membrane**

Fig 5: **Iron acrylate**

Genefloc GPF Compatibility

GPF has operated successfully in over 100 plants for five years despite being a cationic flocculant. This is due to:

- Molecular structure - the charged backbone means any excess flocculant reaching the membrane will straddle the pores and will be removed by shear forces
- Solubility - GPF will readily absorb on both filter media as well as being captured by flocs
- Antiscalant Pick-up - any residual flocculant will be neutralised with anionic phosphonate antiscalant

Case Study – Glen Rocky Gibraltar

This 1,400 m3/day sea water RO plant has a blended feed from open seawater and a seawater well supplying a feed tank with a 2-3 hour settling time to remove sand. Genefloc GPF flocculant is dosed at 0.5–2mg/l with 0.3mg/l of chlorine prior to three pressurised dual media filters with 90cm of sand and 30cm of anthracite. Sodium bisulphite for chlorine removal and Genesys LF antiscalant are dosed to a common manifold before the cartridge filters for each RO train. The results from a study conducted by Leparc et al concluded that: "Overall the pretreatment process appears to be effective to provide high water quality to the reverse osmosis units". The Silt Density Index measurements show a dramatic reduction after the dual media filters and cartridge filters with the use of Genefloc GPF.

21-24 June 2005	Sea intake	Well Sea-water	Raw water	DMF Effluent	Cartridge Filter Effluent
SDI15min	5.8	2.6	4.4	2.1	2.0

No major fouling events have occurred since the beginning of operation (September 2003). Satisfactory results have continued and a membrane autopsy conducted in 2008 showed there was no cationic flocculant present on the membrane. New particle counting techniques prove the effectiveness of the Genefloc GPF in increasing the particle size distribution.

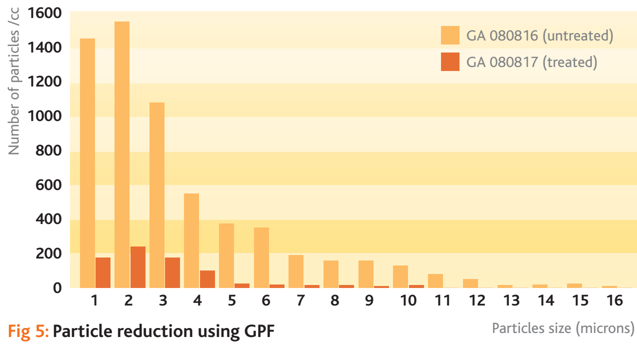

Fig 5: **Particle reduction using GPF**

Conclusions

- Although it is generally believed that the use of cationic flocculants pose a risk to membrane operation, long term practice indicates that certain cationic flocculants can be used safely
- There are several theories as to why some flocculants damage membranes and others do not. At the time of writing the authors feel a combination of factors are contributory
- Poly quaternary amine flocculants are safe to use
- Poly quaternary amine flocculants should be dosed early in the pre-treatment system prior to the filtration equipment
- The use of phosphonic acid based anionic antiscalant has always been used in conjunction with Genefloc GPF.

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