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The safe use of cationic flocculants with reverse osmosis membranes

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ABSTRACT

Flocculants are used in combination with coagulants to agglomerate suspended particles for removal by filtration. This technique is used extensively in all types of surface waters to reduce the silt density index (SDI) and minimise membrane fouling. Although organic cationic flocculants are particularly effective, their widespread use in membrane applications is limited because of perceived problems with flocculant fouling at the membrane surface causing irreparable damage. Reference material from some of the major membrane manufacturers on the use of flocculants is given.

Autopsies show that more than 50% of membrane fouling is caused by inadequate, deficient or poorly operated pre-treatment systems. The Authors suggest that if the correct chemistry is considered, the addition of an effective flocculant can be simple and safe. The paper discusses the use of cationic flocculants and the fouling process that occur at the membrane surface. The paper explains the types of coagulants and flocculants used and considers cationic flocculants and the way they function.

Operational results when using a soluble polyquaternary amine flocculant (Genefloc GPF) developed by Genesys International Limited is presented. Genefloc GPF has been in extensive use for several years and a review of the results clearly shows no detrimental effect on membrane performance.

A case study shows the effectiveness of Genefloc GPF in reducing SDI and increasing particle size prior to filtration. In every case a significant improvement in plant performance is seen with a reduction in cleaning frequency and extended membrane life. New particle counting techniques [1] have assisted us in optimising flocculant dosage rate and monitor on-going performance.

Keywords: Reverse osmosis; Membrane; Fouling; Cationic flocculant; Polyamine; Polyquaternary amine; Coagulation; Flocculation

1. Introduction

It is a widely held view that the use of cationic polymers/flocculants can be (and is) detrimental to membrane operation. Consequently the water treatment service companies have been cautious about the use of such chemicals, which is inevitable considering the views of three of the major membrane suppliers, as seen from their technical bulletins, product data sheets and web-sites.

1.1. Dow – Form No. 609-02027-1004

> ''Coagulants and flocculants may interfere with an RO membrane indirectly or directly.''

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> "Nearly all antiscalants are negatively charged and will react with cationic coagulants and flocculants present in the water."
>
> "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."

1.2. Form No. 609-02024-1004

> "In addition cationic polymers may co-precipitate with negatively charged antiscalants and foul the membrane."

1.3. Hydranautics – TSB107.15 Page 2

> "Common examples of foulants are: man made organic material (e.g.) antiscalants/dispersants, cationic poly-electrolytes."

1.4. 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."

2. Membrane cleanliness

To reduce the membrane fouling tendency it is important to have feed water with low suspended solids. Coagulants and flocculants are used to increase particle size so they can more easily be removed by subsequent filtration processes. The results of numerous membrane autopsies clearly show that most membrane fouling in lead elements is caused by deficiencies in coagulation/flocculation and subsequent filtration [1]. This report confirmed an earlier study by Darton and Fazel [2].

3. Coagulants and flocculants

Coagulation is the destabilisation of anionically charged suspended colloidal materials to prevent mutual repulsion. Ferric chloride and aluminium sulphate are examples of trivalent cations used for coagulation.

Flocculation is the bridging of particles by a polymer chain, causing them to form flocs or larger aggregates. These flocs will either float (flotation) or sink (sedimentation), making them easier to remove from the system.

Electrolytes are molecules that, when dissolved in water, ionize and carry a positive (cationic) or negative (anionic) charge.

Poly-electrolytes are electrolytes which have more than one charge-bearing atom in the molecule. Examples are acrylamide copolymers and polyaluminium chloride.

4. Inorganic coagulants and 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. Many of these chemicals, under appropriate pH, temperature and salinity conditions, react with water to form insoluble hydroxides which, on precipitation, link together to form long chains or meshes, physically trapping small particles into the larger floc. Van der Waals attraction and/or the use of polymeric coagulants complete the process, forming larger aggregates which can be further flocculated or separated from the waste stream. Commonly used coagulants are shown in Table 1.

5. Organic flocculants

There are many linear and branched polymers with high molecular weights and variable charge densities. Non-ionic polymers have no charge-bearing groups and are typically homopolymers of acrylamide. Anionic polymers, when dissolved in water, are negatively charged and are usually copolymers (polymers containing two types of monomer) of acrylamide and acrylic acid, sodium acrylate or another anionic monomer. The charge is located on a pendant group protruding from the polymer chain backbone. The charge on these polymers is pH sensitive and they function best above pH 6.0.

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 or may be in the backbone of the polymer chain.

Table 1
Common inorganic coagulants

Product	Description and application
Ferric chloride [$FeCl_3$]	Phosphate removal, sludge conditioning and dewatering, trace metals removal, and odour control
Ferrous chloride [$FeCl_2$]	Phosphate removal, odour control, heavy metals removal, controls toxic sulphide generation in anaerobic digesters, oil and grease removal, and sludge conditioning
Ferric sulphate [$Fe_2(SO_4)_3$]	Water clarification, decolourising surface water, sludge conditioning and dewatering, trace metals removal, organics removal (including trihalomethanes), sulphide control, phosphate removal, oil and grease separation and dissolved air floatation (DAF)
Ferrous sulphate [$FeSO_4$]	Phosphate removal, trace metals removal, and odour control
Aluminium chloride [$AlCl_3$]	Metals removal, oil and grease separation and water clarification
Aluminium sulphate [alum, $Al_2(SO_4)_3$]	Most widely used inorganic coagulant. Metals removal, oil and grease separation and water clarification
Polyaluminium chloride [PAC]	Metals removal, oil and grease separation and water clarification
Sodium aluminate	Colour removal, phosphorus removal, lime softening, pH control and silica reduction

High molecular weight polymers form as in coiled chains. When dissolved in water, the charged areas on the chain repel each other and force the chain to uncoil which increases the viscosity of the solution. It is important to know that this process takes time, so more reaction time is needed for high molecular weight polymers to function effectively. Since the charge affects the speed at which the chain uncoils, higher charged polymers uncoil faster than low charged polymers so it is important to allow an ageing period before polymers are used. Non-ionic polymers may never fully uncoil since they carry no charge.

There are several factors affecting the dissolution of polymers, especially those of high molecular weight. Dissolved solids, hardness, and other impurities inhibit complete dissolution because they shield the polymer's charged groups from repelling each other, so softened or deionized/distilled water is the preferred polymer solvent.

Polymers typically come in three physical forms: dry powdered or granular solids, liquids and emulsions. Some commonly used organic flocculants are shown in Table 2.

6. Reaction mechanisms

Most water-borne contaminants carry a negative surface charge which stabilises them causing electrostatic repulsion. This includes emulsified oil and grease and finely divided solids suspensions. Inorganic coagulants and polymeric flocculants neutralise this charge which allows the particles to come closer together and which destabilises the suspension as shown in Fig. 1. In addition, charged polymers (polyelectrolytes) can agglomerate the stabilised particles through the ''charge patch'' or ''bridging'' mechanisms as shown in Fig. 2. The particles then sink or float (depending on the relative density of the solute and the

Table 2
Common organic flocculants

Product	Description	Application
Quaternised polyacrylamide copolymers	Copolymers of acrylamide with a cationic monomer	Insensitive to pH below 10
Quaternised Mannich polymers	Highly charged, high molecular weight cationic homopolymer of acrylamide	Short shelf life, viscous, unpleasant odour, not chlorine resistant or pH insensitive
Polyamines	Cationic medium molecular weight, linear or branched polyquaternary amines	Soluble, long shelf life, no odour chlorine resistant and pH insensitive
Poly (diallyl dimethyl ammonium chloride) polymers (DADMAC)	Similar to polyamines can be copolymerized with acrylamide monomers	High charge densities located in branches
Natural polymers	Starches, tannins, alginate	Prone to fermentation and short shelf life, used with aluminium

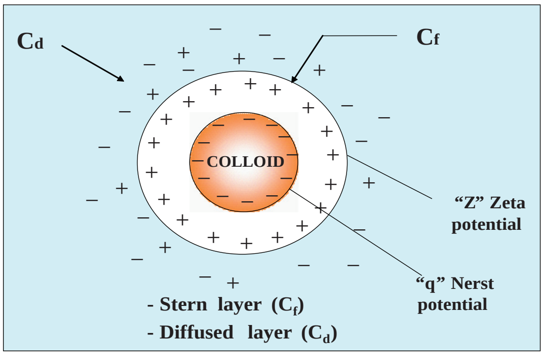

Fig. 1. Flocculant destabilisation.

contaminant) and are removed. In a typical treatment, a low molecular weight cationic polymer is often used in conjunction with an inorganic coagulant such as alum, aluminium chloride or ferric chloride, to generate small flocs known as ''pinfloc''. This is usually followed by treatment with a high molecular weight anionic polymer which attaches to the now cationic particles and causes even bigger flocs. These larger flocs are easy to remove. In RO feed waters with low levels of contaminants the water is often treated only with high molecular weight anionic or cationic polymers. Practical experience has shown that anionic compounds are better at removing organics and cationic compounds for inorganic suspended solids removal. Long-chain polymer flocculants, such as modified polyacrylamides can be supplied in dry or liquid form. The most common, polyacrylamide solution is supplied as a 10–40% active emulsion in a carrier fluid, with surfactants, oil and latex. The oil and latex can cause membrane damage by filming on the polyamide membrane surface. There are many flocculants which vary in molecular weight, charge density, solubility and charge position. All these factors affect the likelihood of membrane fouling and hence compatibility.

High molecular weight flocculants have a long-chain length which improves bridging, or attaching to a greater numbers of particles. Charge weight is measured in milliequivalent/gram and is a function of charge density and molecular weight. High charge weight is important for the activity of particular chemical products. For instance polyacrylamide has a high molecular weight with a large number of cationically or anionically charged sub branches attached to a central non-ionic backbone see Fig. 3.

Most RO systems operate with a raw water relatively colloid free but with a small and variable but potentially damaging amount of suspended solids. In this case it is preferable to use polyamines which are a large molecule that is cationically charged throughout its entirety down a central backbone as shown in Fig. 4. The polyamine molecule due to its length tends to wrap flocs together. The structures described above are important in their ability to irreversibly foul the membrane surface. Cationic polyacrylamides will tend to attach the cationic sub branches to the anionically charged membrane surface and membrane pores rather like velcro hooks attaching to the recipient surface.

Polyamines alternatively with a central charge on a long backbone are less likely to become permanently attached to the membrane as they are long molecules which straddle multiple membrane pores where shear forces at the concentration polarisation surface are more likely to cause detachment. This is important when considering flocculant fouling mechanisms.

7. 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 antiscalants.
- An acrylic acid based antiscalant may react with iron and aluminium to form meta-acrylate salts which can irreparably foul the membrane.

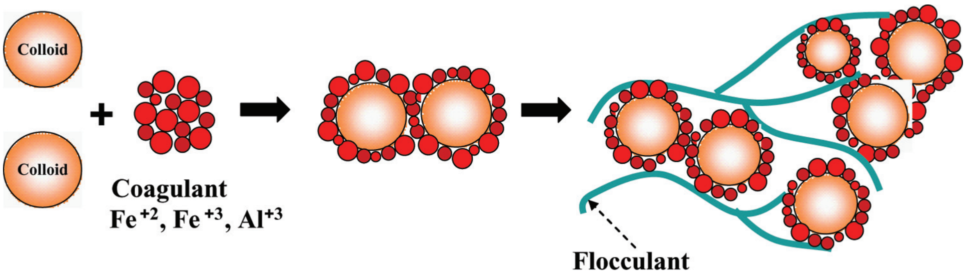

Fig. 2. Flocculant bridging.

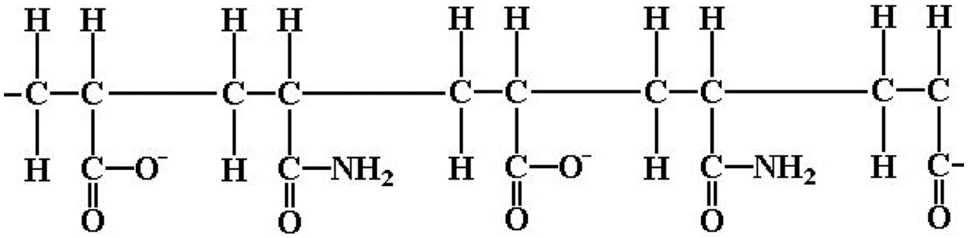

Fig. 3. Polyacrylamide molecular structure showing anionic sub branches.

- 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.
- Oil or latex present in some flocculants cause direct adherence to the membrane surface.

7.1. Aluminium

Aluminium salts are amphoteric in nature and it is important that the pH of the water within the membrane itself has greater aluminium solubility than the part of system where aluminium coagulation occurs. Aluminium hydroxide can function as a base neutralising an acid, as $Al(OH)_3 + 3HCl >> AlCl_3 + 3H_2O$, or as an acid neutralising a base, as $Al(OH)_3 + NaOH >> Na[Al(OH)_4]$. Any excess aluminium in the feed water (even small amounts ~50 ppb) can cause membrane fouling. Aluminium can react with low silica levels 10 mg/L resulting in ortho-rhombic crystalline aluminium silicate fouling as shown in the micrograph in Fig. 5 and fouled membrane sample in Fig. 6.

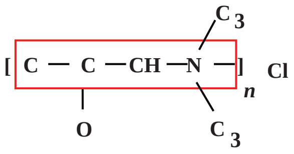

Fig. 4. Polyamine cationic backbone.

7.2. Iron

Iron fouls similarly to aluminium but iron is easier to remove so iron compounds are the preferred coagulants. Excess iron chloride is insoluble and will readily foul the membrane if not removed by filtration. The choice of antiscalant is also important as some polymer based antiscalants can react with iron to form iron acrylate which fouls the membranes as shown in Fig. 7. Particulate and preflocs can also deposit on the membrane.

7.3. Oil and latex

Some flocculants use emulsions of oil and latex to maintain stability before application and are therefore not recommended in membrane applications. Fig. 8 shows the image of a severely oil damaged membrane from a large plant in Germany. Following a detailed autopsy the source of the oil was found to be the commodity flocculant that was in use in the pre-treatment system. Oil on the membrane surface can dissolve the polyamide layer causing irreparable damage.

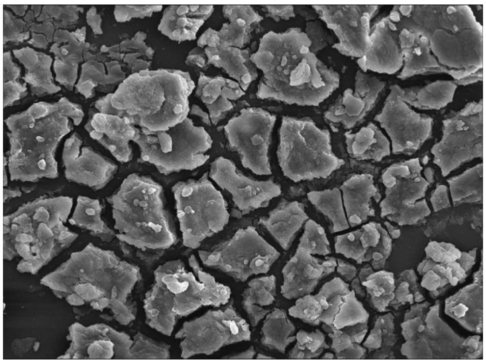

Fig. 5. Aluminium fouling SEM.

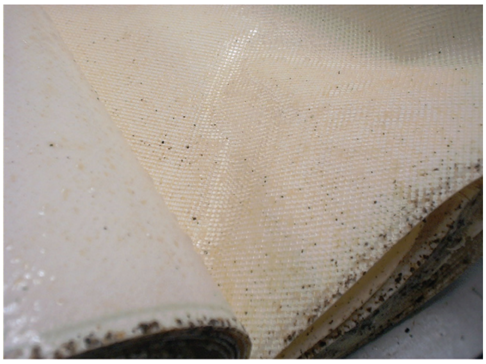

Fig. 6. Aluminium fouling membrane.

Fig. 7. Iron polymer fouling.

8. Genefloc GPF, a membrane compatible flocculant

The importance of reducing suspended solids in the feed water to RO and NF membrane plant was the driving force behind Genesys International Ltd. developing an easy to apply, soluble cationic polyquaternary amine flocculant called Genefloc GPF. Since inception Genefloc GPF has been used in more than one hundred surface water RO and NF plants around the world. Flocculant fouling has never been reported nor has Genefloc GPF ever been found on an autopsied membrane. The case study in Section 9 demonstrates the effectiveness of Genefloc GPF and the excellent membrane condition even after 5 years exposure to the flocculant. The authors feel that the molecular structure, solubility and antiscalant reactivity of polyquaternary amines are features that minimise the risk of membrane fouling when compared with many other cationic polymeric flocculants.

8.1. Molecular structure

The polyamine molecule is positively charged along its backbone and not in pendular sub branches. Consequently excess flocculant reaching the membrane surface will adhere across its length rather than adhering by its sub branches as is the case with polyacrylamide based flocculants. The molecule structure is such that numerous membrane pores are likely to be straddled and shear forces are likely to remove the adhering molecule.

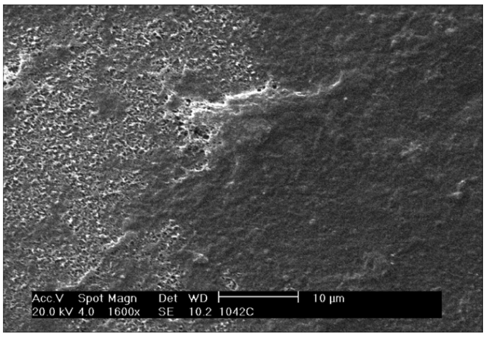

Fig. 8. Oil damaged membrane

8.2. Solubility

Even though Genefloc GPF is applied as a dilution it will readily absorb on both filter media as well as flocs. The effectiveness of Genesys GPF is in part due to coating of filter media, such as sand, which significantly improves media performance.

8.3. Antiscalant pick up

Any residual flocculant will readily react with anionic antiscalants. Flocculants are therefore dosed early in the pre-treatment system, whilst antiscalants are dosed just prior to the membrane itself. Care must always be taken to ensure that there is sufficient active antiscalant present to inhibit scale formation as a proportion of the anionic antiscalant will react with any excess cationic flocculant. The idea of using a phosphonic acid antiscalant with the polyamine flocculant ensures there is an inbuilt safety mechanism to remove residual flocculant prior to the membrane.

9. Case study

The case study demonstrates the effectiveness of Genefloc GPF and shows that a cationic flocculant can be used safely.

Glen Rocky. This plant is a 1400 m^3/day sea water RO plant in Gibraltar. Feed water is a blend of open seawater and a seawater well which supplies a feed tank with 2–3 h settling time to remove sand. Genefloc GPF flocculant is dosed at 2 mg/L with 0.3 mg/L of chlorine prior to three pressurised dual media filters with 90 cm of sand and 30 cm 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. [3] are summarised in Table 3. The results are an average of samples taken over a 4 day period. Leparc et al. also found a substantial reduction in algal and bacteria content and concluded that:

> ‘‘Overall the pre-treatment process appears to be effective to provide high water quality to the reverse osmosis units’’ ‘‘No major fouling events have occurred since the beginning of operation’’ (September 2003).

Table 3
Turbidity and SDI measurements

21st–24th June 2005	Seawater intake	Well seawater	Combined raw water	DMF effluent	Cartridge filter effluent
Turbidity (NTU)	1.6	0.3	0.4–1.1		
SDI_{3min}	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

The plant has operated successfully for five years without any membrane problems and with continuous dosage of a cationic flocculant at 2 mg/L. In August 2008 a membrane from the lead element of the plant was removed for membrane autopsy. Key points from the report are summarised below:

- The membranes were in good general condition after 5 years of continuous service.
- A very thin light brown deposit was found on the membrane surface.
- Scanning electron microscopy and energy dispersive spectroscopy (EDAX) techniques showed the deposit consisted of alumino-silicates and iron.
- More detailed analysis using internal reflection spectrometry and attenuated total reflectance infra-red spectrometry confirmed the deposit composition and did not show the presence of any organic compounds and specifically polyquaternary amine compounds which would have indicated floccuulant fouling.
- Marks from the spacer were observed on the membrane surface which had caused some physical damage.

Additional data was gathered using a particle counter which showed over a 90% reduction in the number of particles less than 5 μm in treated water samples taken after flocculant dosage and the media filters (Fig. 9).

10. Conclusions

- Although it is a 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.
- Polyquaternary amine flocculants are safe to use.
- Polyquaternary amine flocculants should be dosed early in the pre-treatment system prior to the filtration equipment.

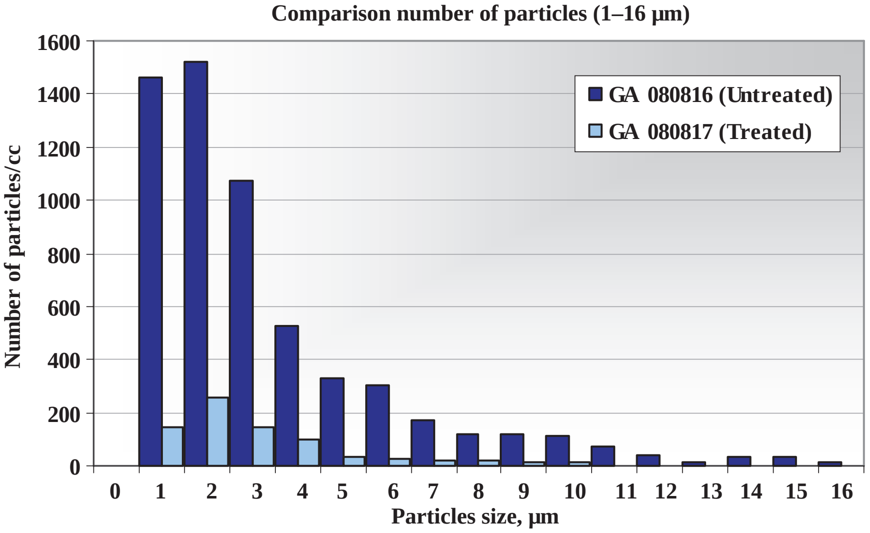

Fig. 9. Particle counter results.

- The use of phosphonic acid based anionic antiscalants has *always* been used in conjunction with Genefloc GPF.

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