Chemical control of colloidal fouling of reverse osmosis systems

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Abstract

Fouling of membranes by colloidal organic and inorganic particles continues to be documented as the most common and challenging obstacle in attaining stable continuous operation of reverse osmosis (RO) and ultrafiltration (UF) systems. Much current research is being conducted on physical parameters to mitigate such fouling. The focus has been on membrane synthesis and element design; microfiltration and ultrafiltration pretreatment; electromagnetic devices; correlation with physical factors such as Silt Density Index, zeta potential and critical flux; technique of direct observation of fouling process through a membrane; and classification of macromolecular organics for correlation with fouling characteristics. We report initial successes with chemical control of colloidal fouling. Through screening with a large number of observable coagulations of natural colloids, we have developed a group of proprietary anticoagulants and dispersants that would, at less than 10 ppm dosage to the RO feedwater, control various classes of colloidal foulants. Case studies of the control of humic matter, elemental sulfur and colloidal silicate in problematic RO systems that became stabilized are briefly presented. We conclude that a great need and potential exists in economically controlling the myriads of fouling interactions of colloidal particles during concentration within the brine channels of RO membrane elements. Low dosages of antifoulants can in many cases obviate the need for installation and maintenance of pretreatment unit or operations designed to remove such colloidal foulants from the process stream.

Keywords: Colloidal fouling; Colloids; Ultrafiltration; Reverse osmosis; Membrane fouling; Humic matter; Elemental sulfur; Colloidal silica; Anti-coagulant; Dispersant; Antifoulant

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1. Introduction

Fouling of membranes by colloidal organic and inorganic particles continues to be documented as the most common and challenging obstacle in attaining stable continuous operation of reverse osmosis (RO) [1–9] and ultrafiltration (UF) [10–13] systems. Much current research is being conducted on physical parameters to mitigate such fouling. The focus has been on membrane synthesis and element design [14,15]; microfiltration and UF pretreatment [16,17]; electromagnetic devices [18–20]; correlation with physical factors such as Silt Density Index (SDI) [21–24], zeta potential [25, 26], and critical flux using a technique of direct observation of the fouling process through a membrane [27–29]; and classification of macromolecular organics for correlation with fouling characteristics [30–33]. We report the initial successes with chemical control of colloidal fouling.

2. Chemical approach

Colloids that can affect the operation of membrane systems are finely dispersed solid particles or liquid droplets that escape filtration by sand, multimedia and 5 or 1 micron guard filters. They range in size from 0.1 to 0.005 microns, just above molecular dimensions, exhibiting physicochemical properties that differ from those of both the constituent molecules and the macroscopic material. Colloids have high surface-area-to-volume ratios giving them singular, diverse and often curious properties [34]. They generally coagulate at increased concentration and salinity as found in the processing conditions of membrane systems. A vast body of literature documents the complexity of colloidal interactions and changes in properties by surface modifications of particles through adsorption or reaction with ions, molecules or other particles.

Through screening of a large number of observable coagulations of natural colloids that are present in surface waters, we have developed a group of proprietary anticoagulants and dispersants that would, at less than 10 ppm dosage to the RO feedwater, control various classes of colloidal foulants. We present brief case studies of the control of humic matter, elemental sulfur and colloidal silicate in problematic RO systems that became stabilized.

3. Case study on humic matter

A large paper pulp facility on Lake Superior, Canada, draws water from a bay with floating logs and much humic matter from decaying wood. It has three RO trains, each designed to be fed at 400 gallons per minute (gpm) (91 m³/h), producing 300 gpm (68 m³/h) each of permeate to provide boiler feedwater and water for manufacturing processes. Each train is in an 8:4 array of six-element vessels with a total of 72 8" membrane elements. The raw lake water is chlorinated, filtered through a multimedia filter (MMF), dechlorinated with bisulfite, and treated with 2–6 ppm of antiscalant, and passed through 5-micron cartridge filters before the RO trains. The SDI of the raw water varies with the season, averaging about 13.0. Dissolved iron concentration was about 0.03 ppm.

When started up in May, 1999, the 5-micron filter cartridges lasted for 3 days, and for the following year required changing every 3–7 days, despite the upgrading of the MMF packing and introduction of air-scouring. Fouling of the membranes was severe, requiring cleaning every 5 days on average. Over the first year, membrane flux loss was severe. The differential pressure (ΔP) of the first stages of all three trains increased to about 150 psi (10.5 kg/cm²), crushing about 30 membrane elements that had to be replaced. System down-time and cleaning chemical supply to this relatively remote plant site became a problem.

At this point a full investigation was conducted and a monitoring for process improvement

Table 1
Elemental composition of a coagulate of humic matter with colloidal clay

Absolute percentage by weight (gravimetric):	
Carbon	41.76
Hydrogen	6.11
Nitrogen	4.55
Ash	20.48

Relative percentage by weight (SEM-EDX; inorganics)	
Silicon (Si)	52
Aluminum (Al)	19
Sulfur (S)	7.8
Phosphorous (P)	5.0
Sodium (Na)	5.0
Magnesium (Mg)	4.9
Potassium (K)	3.3
Calcium (Ca)	2.1
Iron (Fe)	1.0
Total	100.1

was instituted. The fact that 5-micron guard filters and the first stages of the RO trains were fouled are clear indications of fouling by colloidal particles. Membrane autopsies and elemental composition analyses of the light-brown rubbery foulants scraped off membrane surfaces showed that the foulant was a coagulate of humic matter (73–80%) and colloidal clay (20–27%). The typical elemental analysis of a dried foulant sample is shown in Table 1.

For controlling colloidal fouling, an anti-coagulant/dispersant Protec RO-C (35) at 5.0–7.0 ppm was added in addition to a reduced dosage to 1.0 ppm of a similar antiscalant. The result was dramatic. The filter cartridge replacement rate decreased several fold. Cleaning frequency was extended from an average of 5 days to 5 weeks, and membrane life expectancy increased substantially. From calculations of the plant management, the overall operating cost of

the RO system was reduced by approximately $250,000 (Canadian) per year.

4. Case study on elemental colloidal sulfur

Colloidal sulfur, a product of air-oxidation of sulfide ions, is a lipophilic, water-insoluble, slightly yellow to colorless powder in aggregated form. It is prevalent in some oil-bearing aquifers in the Middle East and in wells that are affected by the actions of sulfate-reducing bacteria. We first encountered a severe colloidal sulfur fouling problem in an RO system in Bahrain.

Two 175 gpm (40 m³/h) permeate RO systems were designed to operate with water from the local aquifer with a SDI ranging from 3.5 to 6.5. Colloidal sulfur at the 5 ppm level had been detected in the raw water. No pretreatment was designed for the system except for 5-micron and 1-micron guard filters. Within 2 days of the start-up, both the 5-micron and 1-micron filters as well as the RO membranes were severely fouled. Chemical analyses confirmed that the foulant on the guard filters and the RO membrane was elemental sulfur powder. Following cleaning with a sulfur-specific membrane cleaner, Protec RO-C [35] was put on line as a dispersant at a 5 ppm dosage. In conjunction with monitoring the performance of the system and fluctuating sulfur influx, the dosage of Protec RO-C was adjusted in the range of 2 to 7 ppm.

Following cleaning, the flux and permeate conductivity improved by 10% but did not appear complete. It is expected that the waxy nature of sulfur powder is refractory to aqueous cleaning solutions. With the Protec RO-C dispersant on line, however, not only was the fouling arrested, but also the flux continued to gradually improve. The most dramatic improvements were that the frequencies of cartridge filter changes and membrane maintenance cleanings became better than what is normally acceptable.

The benefits of the ability to control colloidal sulfur fouling chemically in this situation is to

allow for reliable RO operation in desert regions where the supply of product water is critical to life. Significant savings in operation were accrued from preserving the service life-spans of cartridge filters and minimizing the need for maintenance cleaning of the refractory sulfur foulant.

5. Case study on colloidal silicate

Silicates represent a wide composition of matter, ranging from pure silica to complex silicates that constitute much of the crust of the earth. In the colloidal form, they have a high affinity for heavy metals such as iron and for organic polymers [3,4]. In the complex environment of RO feedwaters, their fouling potentials are expected to be difficult — if not impossible — to predict.

We encountered an opportunity to observe the fouling pattern and the positive response to chemically controlling colloidal silicate in a bottling water plant RO system. This is a two-pass RO system with a 2:2:1 array in the first pass and a 1:1:1 array in the second pass of vessels with three 8"×40" spiral-wound membrane elements each. Recoveries are 80% and 85%, respectively. A 900-ft-deep well, supplying about 66 gpm (15 m³/h) of water, was filtered through a 5-micron filter, blended with 9 gpm (2 m³/h) of second pass reject, and dosed with 1 ppm of antiscalant, which is pumped through the system, producing 50 gpm of two-pass permeate and 15 gpm (3.4 m³/h) of first pass reject, which is discharged.

A full study was performed when severe flux reduction was observed in the first pass array. Off-line single element testing and cleaning showed that fouling was most severe in the lead elements, less severe in the elements in position 2, and only slight fouling in position 3. The casing of a lead element was carefully opened for inspection and sampling of foulant for chemical analyses. The surface of the membrane was found

Table 2
Elemental composition of a colloidal silicate RO foulant

Absolute percentage by weight (gravimetric):	
Carbon	10.59
Hydrogen	1.36
Nitrogen	0.36
Ash	75.79

Relative percentage by weight (SEM-EDX; inorganics)	
Calcium (Ca)	46
Silicon (Si)	40
Manganese (Mn)	4.3
Iron (Fe)	3.2
Sodium (Na)	1.7
Copper (Cu)	1.4
Sulfur (S)	1.2
Aluminum (Al)	1.0
Magnesium (Mg)	0.5
Phosphorous (P)	0.4
Total	99.7

to be clean to the eyes, unstained, though slightly gritty to touch. A foulant sample harvested from several pages of membranes was washed with RO permeate water and dried at 120–130°C for analyses of elemental composition. The results are shown in Table 2. In the cleaning study, membrane flux was fully restored by a single cleaning with a silicate-specific cleaner. Our conclusion was that the fouling was due to a colloidal form of mixed calcium, manganese iron silicate coated with some bacterial slime, but with positively charged surface properties that localized it to the lead RO elements.

Protec RO [35], an anti-deposition agent specially effective for silica and silicates, was prescribed for simultaneous dosing with the antiscalant. A drop in the fouling rate was immediately observed, even at a low dosage of 1 ppm. Due to a fluctuating colloidal load in the

incoming water and the need for adjusting the antifoulant dosage, careful monitoring by trend-charting of normalized permeate flow, differential pressure and salt passage is being implemented in this system for maintenance cleaning and anti-foulant dosage adjustments.

6. Conclusions

Among many cases of effective chemical control of colloidal fouling in RO systems, we presented three examples here. Due to the com-plexities of colloidal systems and RO fouling tendencies, the selection of antifoulants and their dosages are currently largely empirical. We have found, however, that within the affordable dosages in the range of 1 to 10 ppm, significant control can be attained.

For designing RO processes, chemical control with antifoulants offers the attractive possibility that one does not have to remove the objection-able colloidal foulants by pretreatment, but simply with minimal intervention, allow the col-loids to pass harmlessly through the RO system and be naturally discharged with the brine. The antifoulant injection alternative is also attractive given the difficulties encountered with the clari-fication of low-turbidity waters; the carry-over of coagulants that severely foul membranes; bio-fouling of activated carbon towers; and colloidal fouling of UF, MF and NF membranes used in pretreatment. In existing RO systems, antifoulants can be used to overcome certain difficiencies in installed pretreatment units pertaining to colloidal foulant control.

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