MEMBRANES

THE IRON SILICA AND ORGANIC POLYMER TRIANGLE

Reverse osmosis (RO) (1) is a process of using trains of semipermeable membrane elements for filtering water under pressure to remove solutes. It is a work horse for generating high-purity water needed for the production of steam and power.

Typically the feedwater stream separates into a 60% to 90% stream of purified water, the balance being a waste stream of concentrated brine. During this concentration of water 3 to10 fold, solubilities of solutes in the feedwater can be exceeded, and may crystallize or coagulate during passage through the RO elements causing fouling. Iron, silica and organic matter are three common constituents of RO membrane foulants (2), this being especially prevalent in the arid southwestern areas of the United States.

An interesting case-history at the Nevada Cogen plants in North Las Vegas, Nevada, led us to review the chemistry of the interaction of iron, silica, and organic polymers that led to fouling of RO prefilters and the membrane itself. Frequent and rapid fouling of filters and membranes led us to perform chemical analyses on the foulants. Elemental composition of the typical light- brown colored gels found on the filters indicated the predominant presence of silica, iron, and organic material. Laboratory demonstration is possible of the complete incorporation of low levels of iron added to a polymerizing solution of silicic acid. This released a suspension of light yellow silica gel that showed the facile and visually complete incorporation of iron in the formation of colloidal ferric silicate in the RO feedwater. Further, incipient ferric silicate precipitate could be shown to precipitate upon the addition of a polymer used in certain proprietary anti-scalant formulations. Replacement of the anti-scalant with one not containing the implicated polymer resolved the problem.

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In this article, we will document this case study, and review the literature surrounding the ternary interaction of silica, iron and organics.

Iron, Silica, and Organic Foulants

Iron, silica, and organic matter are abundant components of the crust and surface of the earth. They are found in various concentrations in dissolved or sub-visible colloidal forms in natural waters. Organic materials are ubiquitous on the surface and deep in the ground, transformed by cycles of living organisms and geochemistry. Each by itself, ferric oxide/hydroxides, silica gels and organic polymers such as humic acids (from decayed plants), bacterial slime and synthetic polymers used in water treatment have been found as foulants on RO membranes (1, 2, 3). More commonly, these foulants are seen in binary forms of varied compositions (2). The frequent occurrence of iron silicates (1, 4, 5-7) points to the facile dehydration polymerization reaction of ferric hydroxide with silicic acid as monomers in unlimited proportions. Binary interactions of iron or silicates each with organic polymers is the basis of the development of various synthetic organic polymers as dispersants for iron or silica (8, 9). The intimate association of silica with organic material occurs in the formation of microscopic algae called diatoms. Silica condensation into biological organism (10) is an extensive process in natural waters. The incorporation of iron into organic material by ion-exchange or chelation is well known. Soluble polyacrylates and acrylate copolymers can be readily precipitated by the addition of ferric ions. River-borne ferric oxides are mainly colloidal particles stabilized by humic or fulvic acids (11). Organic polymers of all sorts, natural or synthetic, adsorb readily to surfaces of particles and is an important factor in the dispersion (12, 13) or deposition of particles in waters (14).

It is evident from this survey of the literature that iron, silica, and organic polymers each has an affinity to associate either chemically or physically with the other. When present together in the same water, ternary ("triangular") interactions occur, and precipitation or deposition on surfaces may occur, which is the subject of our interest. The mechanisms, the kinetics, and structural requirements by which these interactions occur are beyond the scope of this article. We wish however to document a case history of such an occurrence that fouled membranes. The recognition of

TABLE A
Elemental Analysis

Element	*% by Weight (absolute)*
Carbon	11.85%
Hydrogen	2.05
Nitrogen	1.94
Iron	7.00
Silicon	20.45 (equiv to 43.74% SiO_2)
Phosphorous	0.80
Copper	<0.05
Elements not tested for	55.91
Total	100%

the process taking place allowed us to solve an anti-scalant application problem with a specific type of RO feedwater.

Nevada Cogen Case Study

The use of several anti-scalants appeared to be associated with the frequent (2 to 4 days) clogging of RO prefilters and noticeable buildup on the RO elements. The foulant is visible as a brownish gel/slime. The use of anti-scalant was temporarily suspended in Plant 1 RO unit, pending the outcome of the investigation. A spent pre-filter cartridge was shipped to the laboratory for analyses.

Sample preparation. The spent filter was placed over a 2-liter beaker. Light brown colored gel was washed off the filter cartridge with a jet of RO permeate water, and allowed to settle. The gel was washed by decantation, then collected on a paper filter. The compacted gel was transferred to dry filter paper, pressed dry, then finally dried in an oven at 130 °C. A light brown amorphous solid was obtained. The following tests were performed.

Qualitative tests. The solid was insoluble in dilute hydrochloric acid and sodium hydroxide. Some charring occurred on heating in crucible in air. After carbon was burned away, red iron oxide-like powder remained.

Elemental analysis. The absolute percent by weight of the following seven elements were determined gravimetrically. The results are here tabulated. Due to cost limitations, only seven likely elements were tested (Table A).

Energy dispersive X-ray analysis (SEM-EDX). By this analysis, X-ray emission energies between 1 to 20 kiloectron volt (keV) were scanned. Elements with increasing atomic numbers between (not including) sodium (atomic number 11) and molybdenum (atomic number 42) would be detected and relative amounts quantitated. This covers the range of light and heavy metals commonly seen in water supplies. Since the lighter elements (hydrogen, carbon, nitrogen, and oxygen) are not measured, the values reported here are *relative weight percentages* and not absolute values done by weighing samples as was done for the elemental analyses reported above. The relative weight percentages are given in Table B both for the elements as well as for the assumed compound forms in which these elements are likely to exist in the foulant.

TABLE B
Elemental Analysis by SEM-EDX

Element	*Relative wt*	*Compound (assumed)*	*Relative wt*
Silicon	52%	SiO_2	57%
Iron	25	Fe_2O_3	18
Aluminum	7.0	Al_2O_3	8.0
Potassium	6.0	K_2CO_3	4.8
Phosphorous	4.2	PO_4	4.7
Calcium	2.6	$CaCO_3$	3.1
Sulfur	2.1	SO_4	2.2
Magnesium	0.8	MgO	1.6
Titanium	0.7	TiO_2	0.6
Total	100.4%		100.0%

Conclusions on foulant analysis. The light brown colored gel is silica which contains in its polymeric matrix a high level of iron (about 18% by weight as iron oxide), and lower levels of aluminum, calcium, magnesium, and titanium. This iron-rich silica is complexed with about 15% of nitrogen-containing organic polymer(s) with affinity for silica. The source of this organic polymer can be either microbial or chemical (anti-scalant) in origin, or both.

Laboratory confirmations of source of foulant. With the insight on the composition of the foulant, we were able to simulate in the laboratory the formation of gel with similar appearance. The following were the findings in several qualitative experiments:

1. Yellow ferric silicate gel could be induced to separate from aqueous solution under the following conditions: To a 20 milliliter (mL) flask, add 1.00 mL of a sodium silicate solution (20 g $Na_2SiO_3 \cdot 9H_2O$ in 100 mL RO permeate water), 6 drops of 5 normal (N) nitric acid with mixing, then immediately 15 mL of RO permeate water. The pH is 10. Add 0.5 mL of a ferric chloride ($FeCl_3$) solution (1.0 gram [g] of $FeCl_3$ in 50 mL of water). A hazy solution forms with pH of 2 to 3. Drops of aqueous trisodium phosphate ($Na_3PO_4 \cdot$) (1.0 g $Na_3PO_4 \cdot 12H_2O$ in 25 mL of water) are added to a pH of 7. A heavy gel with all the iron color settles in minutes.

2. A stock solution of ferric silicate prepared as above, but without complete final precipitation with trisodium phosphate, was used in testing flocculation/precipitation actions of polymers in various anti-scalant formulations. It was found that a single polymeric ingredient of the anti-scalants used at Nevada Cogen had flocculation activity significantly more than others.

3. A replacement anti-scalant was found with no ferric silicate flocculation activity.

The solution. A replacement antiscalant selected from the laboratory tests was installed in the RO plant. The prefilter fouling problem immediately disappeared, and the RO system performance stabilized and improved over time.

Concluding Comments

The binary interactions between iron, silica, and organic polymers have been reviewed, and a case study on a foulant resulting from a ternary interaction of these three types of foulants is documented in this article. While much has been accomplished in the formulation of anti-scalants for controlling single-entity foulants, the complex binary and multiple interactions of incipient foulants during passage through an RO system presents real challenges to the design and operation of RO systems. The facile incorporation of not only iron, but other ubiquitous cations such as aluminum, calcium, and magnesium in nearly unlimited proportions into dissolved polymeric or colloidal silica structures present a great variety of structures for consideration. In the prediction of fouling potentials of feedwaters to the RO system, the complexities of the silicate colloid structure and properties are magnified by equal or greater complexities of the structure and properties of the natural and synthetic organic polymers that they interact with. To develop better antiscalants/antifoulants for the RO system, inhibition of the interactions between incipient foulant species need to be examined at both the level of molecular chemistry and interactions at the surface of growing particles. Progress in this field would lead to reduction in plant downtime, improvement in RO efficiency, and prolonging membrane service life.■

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