

Case Study: Excessive Sulfuric Acid Dosing Resulting in Irreversible Scale Formation

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Abstract

Many consultants in the RO water treatment industry recommend sulfuric acid dosing into the feed water as a safety measure. This case study reviews a situation where acid dosing was used with the intention of improving system performance but resulted in severe sulfate scaling. The difficulties in cleaning sulfate scales are discussed and after numerous lengthy trials, an effective cleaning procedure is found and implemented.

Introduction:

One of the “rules of thumb” recommended by most industry experts is the dosing of sulfuric acid into RO feed-water as a precautionary measure. Many caution to always dose enough acid to maintain a reduced pH. They argue that sulfuric acid will act as a back-up scale inhibitor should the antiscalant dosing pump fail. While pH reduction provides excellent control for calcium carbonate and calcium phosphate scale formations, both are reversible scales that are among the easiest to clean. The advantages provided by sulfuric acid dosing have to be weighed against the risks of introducing excess sulfates into the feed water. Sulfates at high concentrations can combine with certain cations to form sparingly soluble salts at levels beyond their saturation limits. Sulfate scales are not pH dependent; they are formed by irreversible reactions which make them very difficult if not impossible to clean.

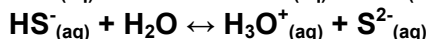
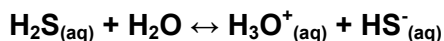
Background

When a recently commissioned RO plant in Southwest Florida could not achieve design permeate the head operator contacted the system manufacturer. The plant had been in operation for only 6 months.

AWC’s services were solicited and a field service engineer was sent out to investigate. He discovered that a prominent scale had formed on the tail-end elements of the second stage. When he applied a few drops of hydrochloric acid to a small piece of the scale, it did not dissolve or bubble. Sulfate scaling was immediately suspected and the plant’s log sheets were reviewed.

Apparently the plant had been experiencing heavy elemental sulfur precipitation in the clearwell after degassification. The operators were advised by their counterparts in neighboring municipal RO plants to further depress the feed pH to 5.4 in order to maintain H₂S solubility in water (See Fig.1)

Acid addition drives the equilibrium to the left thereby maximizing H₂S formation. H₂S gas is removed by the degassifier at very high efficiency



Sulfide ions when exposed to oxygen in the degassifier oxidize to form elemental sulfur

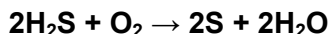
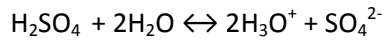


Fig.1: Formation of elemental sulfur in permeate water after degassifier

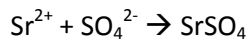
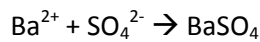
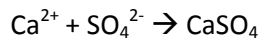
In doing so, the plant operators overlooked the manufacturer’s recommendation to maintain a pH of 7 or to avoid acid dosing at all. The reason this recommendation had originally been implemented was because of extremely high sulfate and strontium levels in the feed water (see Table 1).

A dosage of about 100 ppm Sulfuric acid (93%) is required to reduce the pH from 7.4 to 5.4. This increased the sulfates in the tail end elements by about 420 ppm, raising the total sulfates to 3046 ppm.

Sulfuric acid dissociates into hydronium ions and sulfate ions once it is dosed into water:



The sulfate anions can combine with Calcium, Barium and Strontium cations to form sparingly soluble salts that can result in irreversible adhesive scales. Sulfate scales can be impossible to clean leaving no choice but to replace the tail-end membranes.



Feedwater Evaluation:

In order to further investigate, a new feedwater sample was collected and analyzed. The water chemistry had not changed. The analysis was entered into an antiscalant projection program to review the saturations of the various scalants (Table 2). Calcium Sulfate and Strontium Sulfate were well above their saturation limits but within the limits of the antiscalant being used.

Feed-water Parameters	Mg/L (as ions)
Calcium	350
Barium	0.04
Strontium	30
Iron	0.06
Manganese	ND
Sulfate	525
Bicarbonate	120
Carbonate	0.11
Silica	17
pH	7.4

Table 1: Feed water analysis

For further verification, a lab study was conducted. The water chemistry in the reject was reconstituted and testing was performed on a control sample vs. a sample containing antiscalant. It was confirmed that the antiscalant was able to control all scalants including strontium sulfate at levels far higher than those which had resulted in scaling at the RO plant.

Potential Scalants	Calculated Saturations
Calcium Carbonate (LSI)	-0.56 (index value)
Calcium Sulfate	233%
Barium Sulfate	2066%
Strontium Sulfate	782%
Silica	56%

Table 2: %Saturation of various scalants at 80% recovery with sulfuric acid dosing to reduce pH to 5.4

Design and operational flaws contributing to the problem

It is always good practice to look beyond the obvious when trying to find the cause of a problem. In this case, the system could not be operated at full design capacity because of feed well limitations. Each 2.5MGD train was only provided with enough feedwater to produce 2 MGD. The reduced cross-flow may have resulted in a larger boundary layer area, consequently contributing to the scaling potential. The ‘boundary layer’, also known as concentration polarization, describes a phenomenon where ions exist at higher concentration levels at the membrane boundary than the general body of the outgoing concentrate stream; this region experiences a less turbulent flow providing a better environment for precipitated salts to settle.

The plant had been designed with flow meters on the total permeate and concentrate streams only, with no flow meters on the feed side. Monitoring of the individual stages was not possible due to the absence of flow meters to measure the first stage permeate or second stage feed. If a flow meter was giving incorrect readings, it would have gone unnoticed because simple mass balance calculations could not be performed with the limited flow data available.

When the existing flow meters were calibrated using portable magnetic flow meters, they were all found to be out of calibration. This may have led to the operation of the plant beyond its design recovery.

Upon reviewing plant data, the service engineer found that it was being collected on a daily basis but not plotted or normalized. Without a normalization curve, scaling may have been overlooked for quite some time; the problem would not become apparent until the scaling was at an advanced enough stage to cause a drastic decrease in permeate productivity.

It was also found that the antiscalant dosing pumps were not being regularly calibrated; As with any other equipment, regardless of technology or sophistication, dosing pump calibration is an absolutely necessary practice and should be performed weekly.

Based on all the projections which were later verified by lab tests, the antiscalant was fully capable of preventing strontium sulfate scale formation well beyond the design parameters. This leads us to believe that a system upset may have occurred that was further exaggerated by the increased sulfates introduced through the sulfuric acid dosing.

Membrane Evaluation:

In order to test the membrane in an off-site facility, the service engineer replaced one of the tail element membranes with a membrane spacer. Due to the size of the system, the absence of a single membrane element for a short period of time did little to affect the total water quality.

A small piece of protruding scale was scraped off and an SEM / EDS analysis was performed to determine its elemental constituents (Fig 2,3). The scale was determined to be mostly strontium sulfate with traces of calcium sulfate.

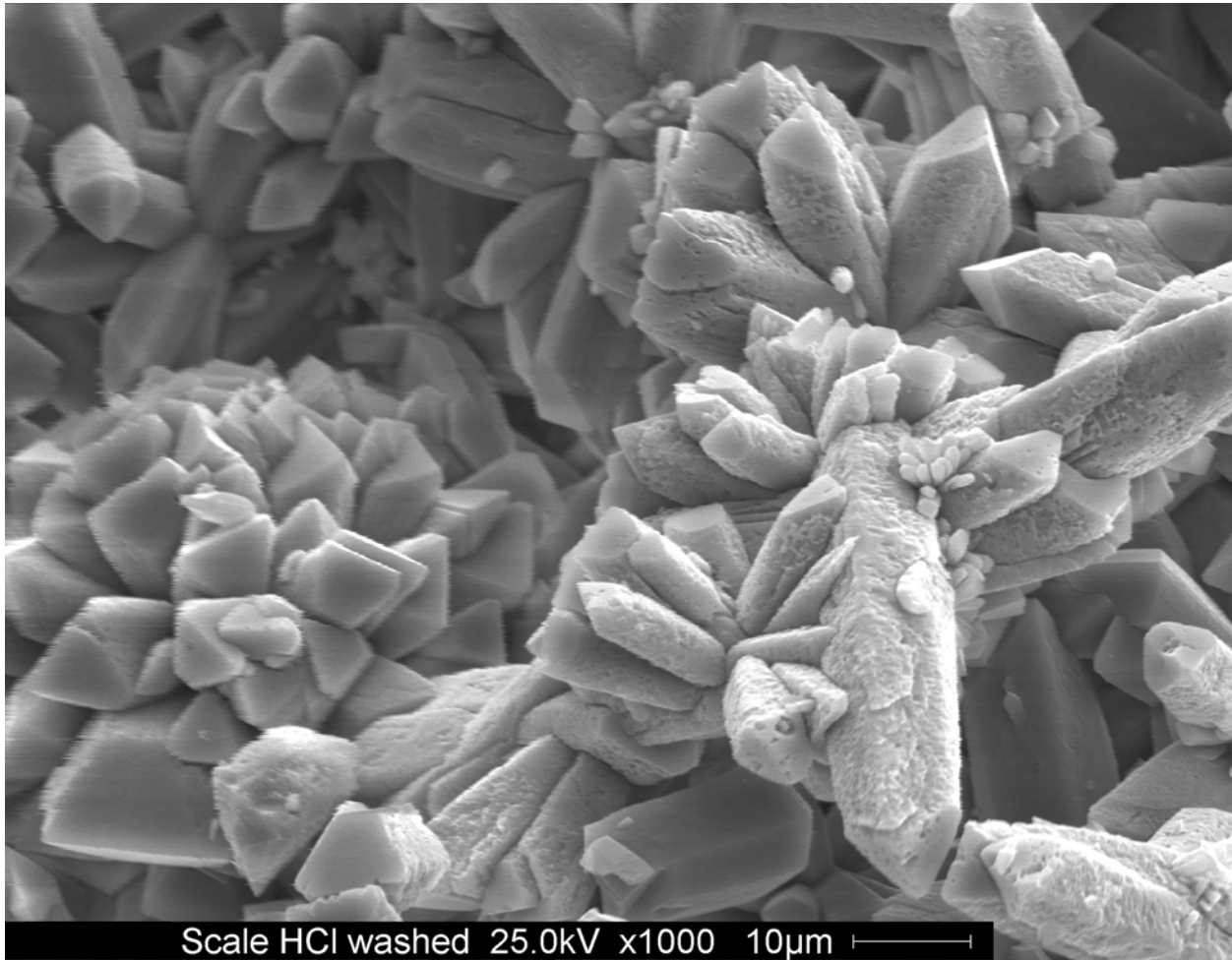


Figure 2: Strontium Sulfate Scale on membrane surface at 1000 times magnification

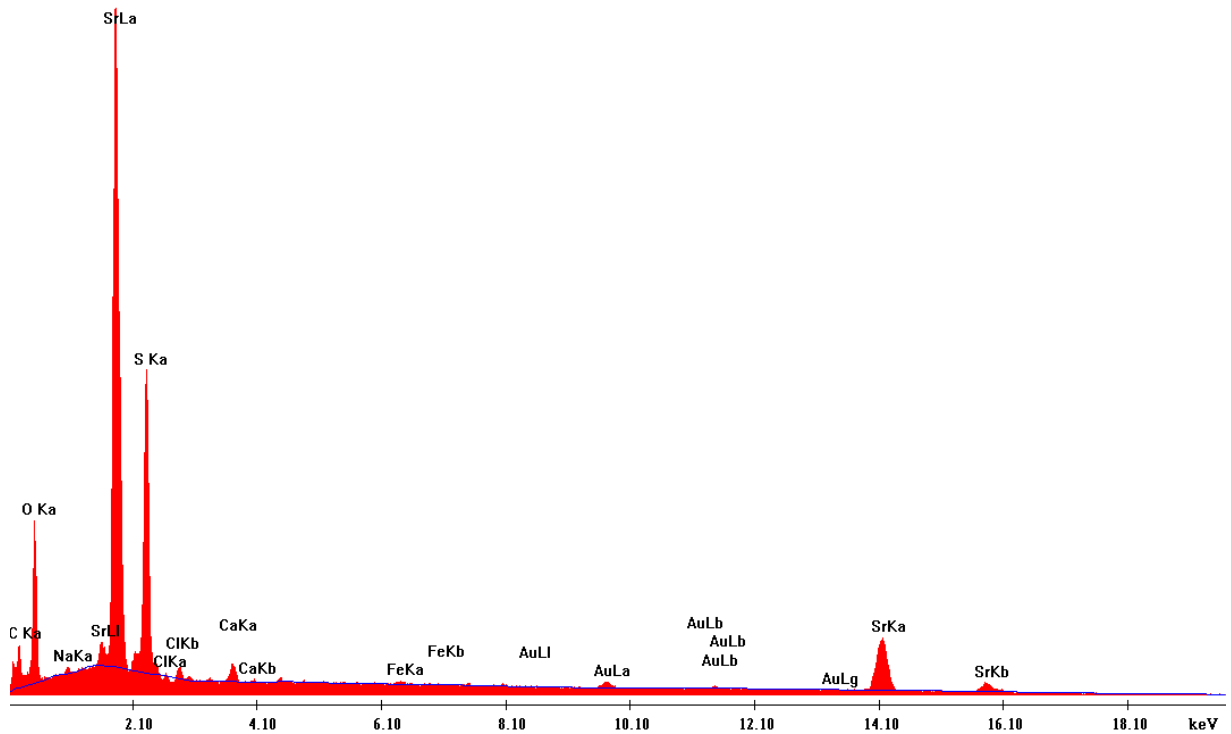


Figure 3: Energy Dispersive Spectroscopy showing elemental make-up of the scale on the membrane surface consisted mainly of strontium and sulfur.

The membrane was weighed and found to be 43 LBS, about 9 LBS heavier than a new element. The element was a Toray membrane, TMG20-430. It was evaluated by performing a wet test identical to the protocol provided by the membrane manufacturer. The membrane was only capable of a 3.5% recovery (Table 3) compared to 15% recorded by the membrane manufacturer. This indicated the extent of the scale formation.

Date	June 02, 2008	June 23, 2008
Type of Membrane	TMG20-430 (membrane 1)	TMG20-430 (membrane 2)
Feed temperature, °C	29.6	28.8
Permeate flow, gpm	0.778	0.44
Differential pressure, psi	5	10
% Recovery	3.49	2.06
% Salt rejection	81.9	52.8
Comments/Remarks	Weight of membrane before cleaning at 43 lbs	Weight of membrane before testing at 41 lbs

Table 3: Results of performance test of scaled membrane prior to cleaning.

Various chemicals were tested in an attempt to clean the membrane. These included EDTA and various blends of EDTA, Tri-sodium phosphate and sodium tripolysphosphate as recommended in widely available literature. Recovery only improved by 1% despite continuous recirculation at maximum temperature for about 18 hours.

Two proprietary products were then tested, AWC C-237 and then AWC C-239 (Table 4).

Chemical used	AWC C-237 (2% solution by vol) – Membrane 1	AWC C-239 (2% solution by vol) – Membrane 2
Date	June 18, 2008	July 24, 2008
Type of Membrane	TMG20-430	TMG20-430
Feed temperature, °C	28.3	28.9
Permeate flow, gpm	2.1	5.656
Differential pressure, psi	0	0
% Recovery	9.0	22.6
% Salt rejection	94.8	94.7
Comments/Remarks	Weight after cleaning at 38 lbs	Final weight of membranes after cleaning = 34 lbs

Table 4: Results of performance test of scaled membrane after cleaning.

The C-237 gave partial cleaning results while the C-239 gave excellent cleaning results, completely removing the scale. For both chemicals, temperature had maintained at 122°F and a total recirculation time of 48 hours was required. The low salt rejection, which is typically after a high pH cleaning, partially recovered after the membranes were placed on line for a few days. However, the formed scale had been thick enough to pry the membrane leaves apart, probably causing some irreversible structural tearing.

The successful results with the single element cleaning prompted an attempt at a full scale cleaning. The AWC C-239 was circulated through the second stage for only 12 hours because the municipality had to cater to water demands and could not shut down their system for a longer period of time. The desired solution temperature could not be achieved because the plant did not have a heater in their mixing tank. Furthermore, the flow rates across the membrane surface were not comparable to those achieved in a single element cleaning. Feed pressures to achieve design permeate flow rates were not reduced and there were no improvements in the pressure drops across the second stage of either train. It was decided that the elements would all be cleaned off-site at the RO maintenance company's facility.

The tail end elements were taken out six at a time and temporarily replaced with membrane spacers until off-site cleaning could be completed. The scale removal was extremely successful with results similar to those in table 4.

Conclusion:

There appear to be many factors which contributed to the scaling at this RO plant. The low feed flow and the consequently reduced cross flow may have played a significant role. The flow meters which were out of calibration were giving incorrect readings which could have led to operation at higher than design recoveries. But most importantly, the sulfuric acid dosing raised the sulfate ions in the tail end elements to extremely high levels creating an environment that was favorable for scale formation. When operating at such borderline conditions, the slightest system upset can result in disaster. Moving the acid dosing point to the permeate side can eliminate the scaling problems while resolving the elemental sulfur precipitation issues in water containing high H₂S levels. The cost of reducing the pH in the permeate is also much lower than doing so in the feed – alkalinity is rejected by the membranes leaving the permeate without a buffering capacity so that a fraction of the acid dosage will result in maximal pH reduction.

When cleaning an RO membrane, the temperature, cleaning time and flow rate are all equally as important as the cleaning chemical used for removing sulfate scales. In this case, it was found that cleaning for 12 hours at low flow rates and near ambient temperatures was ineffective despite great success using the same chemical off-site. Cleaning off-site allowed for higher flow rates and was most effective at 122°F for 48 hours, returning the membranes to acceptable operating conditions. EDTA, trisodium phosphate, sodium tripolyphosphate combinations were found to be ineffective at removing strontium sulfate scale despite continuous circulation at elevated temperatures for several days. By contrast, the specialty chemicals AWC C-237 and AWC C-239 resulted in measurable improvements, substantially removing strontium sulfate scales, and returning differential pressures and permeate flow rates to near original design conditions.

Selection of the correct cleaning chemicals and procedures can result in great savings for RO plants that have experienced heavy sulfate scales. Inadequate chemicals or procedures can result in the costly replacement of all tail element membranes – the larger the plant the higher the cost. Regardless, sulfate scale removal can only be accomplished through single element cleaning and the structural damage caused by the formed scale can never be reversed. The best approach to cost effective plant operation is always prevention. The feed water analysis should always be carefully studied and a qualified water chemistry expert should always be consulted prior to making changes to chemical dosages or operational parameters.