

Membrane filtration

Managing aluminum in membrane filtration



There is a growing amount of evidence that the simultaneous presence of Aluminum cations at low concentration and silicate species has a detrimental and costly impact on RO membranes. Dr. Jean Jacques Lagref and Ing. Ozgencil Haci look at the need to manage aluminum in membrane filtration processes for cost control by selectively sequestering dissolved Aluminum traces with chelating agents using the highest Antiscalant quality product.

Membrane technologies such as reverse osmosis, nanofiltration, ultrafiltration have found wider acceptance in recent years. Nowadays, the need to increase further the membrane performances is has emerged. The processing of recovery rate of 80% and above has become standard. The demand for higher productivity emphasized the membrane's fouling risks. The main concern is the precipitation or the scaling of mineral salts onto the membrane surface, leading to a progressive plugging of the pores, a flux reduction and higher operating pressure till the membranes are physically and irreversibly damaged. The scaling process also known as salt precipitation is a natural phenomenon which occurs when the solubility limit value is over-passed. Dissolved cations and anions then start to form layer by layer tiny crystallites which will progressively separate from water and fall out. The solubility limit value varies depending on the temperature, pH and the ionic strength of the water solution.

To prevent such scaling scenarios and costly cleaning operations, Antiscalant formulations have been developed. The Antiscalant active ingredients (phosphonates, polyacrylates...)

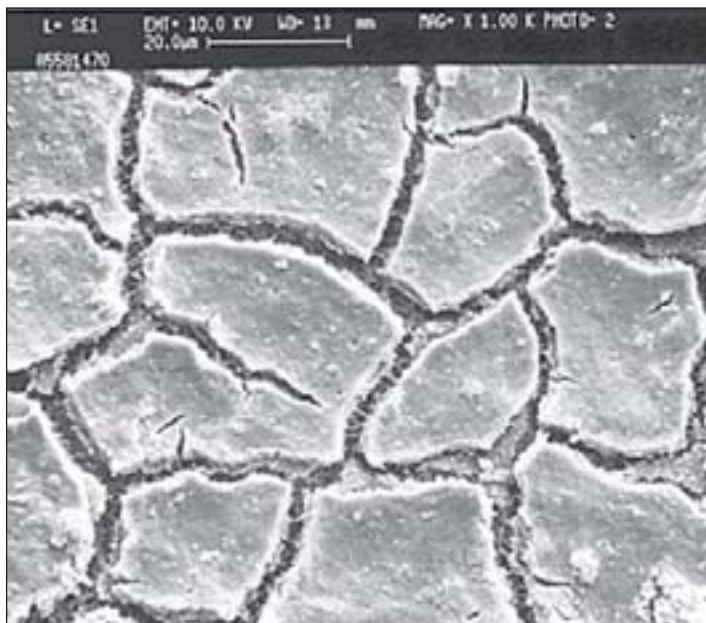
are acting on the crystal growth mechanisms and on the dispersion of the nano-sized forming crystals. Those substances will chemically and physically interact with soluble cations (complexation of elements) and with crystallite surfaces. As a result, because the crystallite growth is slowed down, the scaling event is delayed. The time-buying strategy will allow the super-saturated concentrate feed to pass through the RO unit safely.

Besides this well established knowledge, during the last 10 years, has been noticed a resurgence of heavy Silicate precipitation issues particularly in areas where the Silicate level is noticeable. The particularity of Silicate scaling is its ability to anchor metallic species and to catalyze further the Silicate precipitation when scale traces remain on the membrane. This after-cleaning drawback is getting more and more common as it follows the use-restriction, because of health associated risks, of cleaners based on Ammonium bi-Fluoride.

More surprising, the observation of Silicate scaling issues even with feed water having a moderate Silicate concentration triggered some

confusion. The emergence and democratization of RO membrane autopsies using X-Ray diffraction techniques revealed as expected the presence of Si-O elemental units but also the presence of un-expected Aluminum and Iron metal cations in most of the cases. Silicate scale was containing significant amount of Aluminum cations. It is known that Silicate solubility is influenced by multivalent ions like Fe^{2+} , Fe^{3+} , Mg^{2+} . However, no guideline to determine the silicate solubility in the presence of Aluminum exists.

Aluminium Silicates have been found deposited onto piping materials in distribution systems¹ in low pressure (MF/UF) and high-pressure water treatment processes installed in California², in hollow-fiber unit treating brackish water in Saudia Arabia...etc. For years, some plants on Djerba Island (Tunisia) suffered from Alumino-ferro Silicate scalings which are difficult to clean in comparison to $CaCO_3$ scale³. The investigations using X-Ray diffraction revealed also a strong correlation between Silicate fouling and the presence of traces of Aluminum cations (Al^{3+}). The more data are available the more it appears that this issue is common and encountered worldwide.



Scanning electron micrograph of aluminosilicate scale on a polyamide membrane surface. Courtesy from C.J. Gabelich, *Control of residual aluminum from conventional treatment to improve reverse osmosis performance, Desalination 190 (2006) 147-160.*

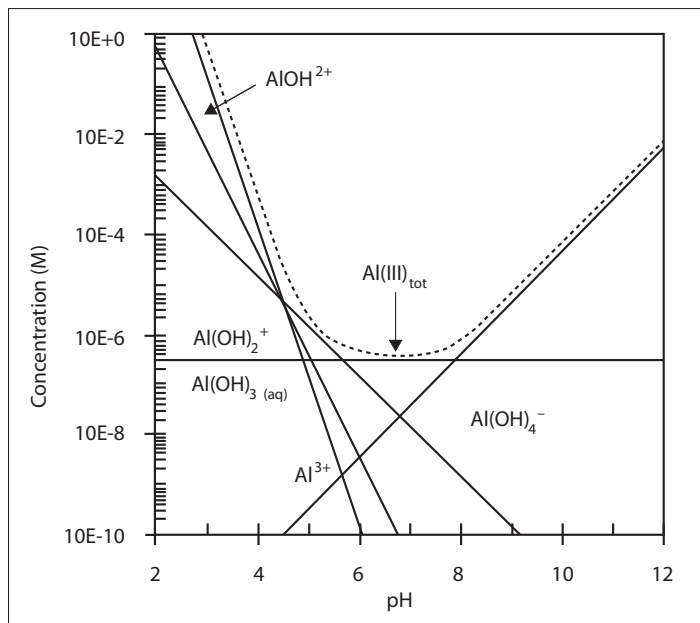


Figure 1. Solubility of monomeric aluminum. Figure courtesy from C.J. Gabelich et al./ *Desalination 180 (2005) 307-319.*

Discussion

Scientifically, such membrane fouling was theorized to occur through soluble Aluminum (Al^{3+}) reacting with ambient silica (H_4SiO_2) to form kaolinite ($Al_2Si_2O_5(OH)_4$) within the reverse osmosis unit⁴.

Despite the growing amount of new evidences, Aluminum is still considered as a “friendly” element and it is not cautiously handled from membrane engineering or Antiscalant chemistry point of view in most of Membrane projects. Toray Membrane Europe is part of the very few Antiscalant manufacturers worldwide to consider the

risk posed by Aluminum cations and to have developed a specific chemical solution to handle the risk.

Why is it serious?

Besides well-waters containing naturally Aluminum cations, the high frequency of Aluminosilicate fouling issues can be explained by the common use of Aluminum salts in membrane filtration pretreatment step. Aluminum sulfate (Alum) or Poly-Aluminum Chloride are for example used as a coagulation agent to remove natural organic matter such as humic acid. Non-optimum doses are likely to result in

increased residual Al in feed water to the membrane.

The severity of the scaling is explained by the low Aluminum concentration (<100 ug/L) needed to reduce drastically the silicate solubility, particularly at pH 7 (Fig.1 and Fig.2). At the same time, the Aluminum dose released during a classical Alum (Aluminum sulfate) pretreatment can reach 200 ug/L. In terms of process consequences, the RO salt rejection and the specific flux can start to decline after 300 hrs of operation only. Some specific flux decline has been measured up to 60% over 100 hrs of operation⁵.

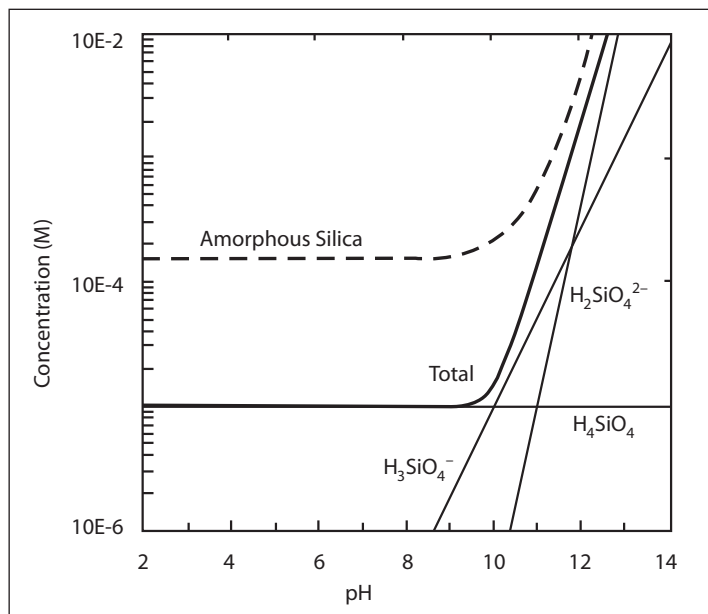


Figure 2. Concentration of dissolved silica species and their equilibrium with quartz (heavy line) and amorphous silica (dotted line) at 25°C. Figure courtesy from C.J. Gabelich et al./ *Desalination 180 (2005) 307-319.*

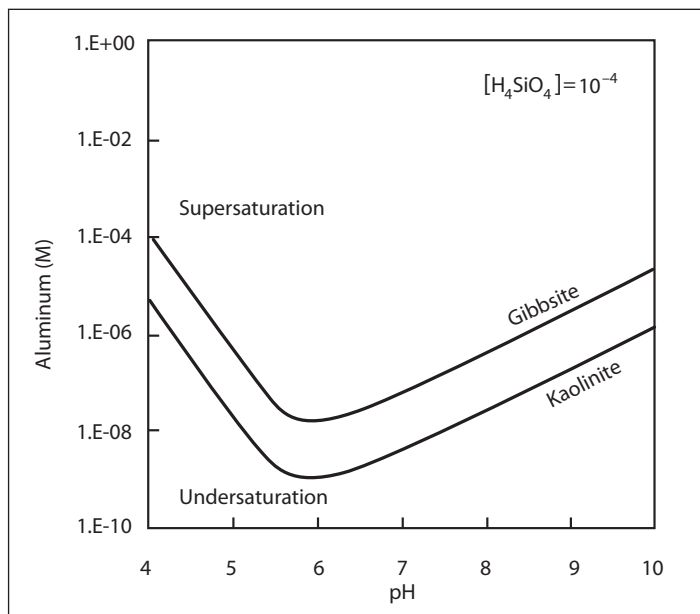


Figure 3. Solubility diagram of kaolinite and gibbsite at the H_4SiO_4 . Figure courtesy from C.J. Gabelich et al./ *Desalination 180 (2005) 307-319.* concentration of 10-4 mol/L.

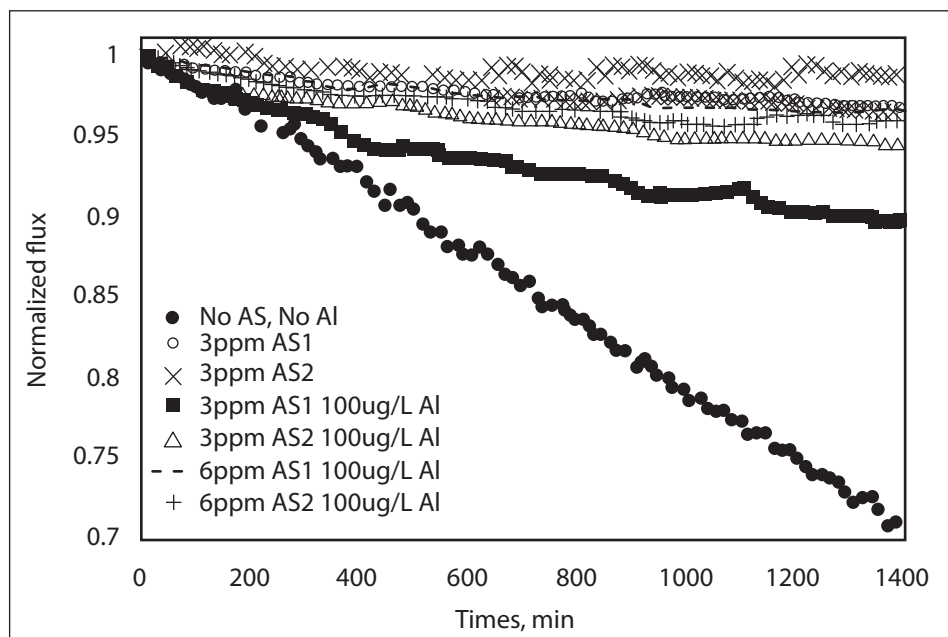


Figure 4. Impact of Antiscalant dosing on membrane flux decline due to gypsum scaling in a feed water containing aluminum (100ug/L). Courtesy from C.J. Gabelich et al./ *Desalination* 196 (2006) 280–292.

Aluminum and Silica Chemistry

Aluminum in water undergoes a series of hydration reactions that leads to insoluble metal hydroxides. However, based on the solution pH, various polymers and monomers are formed. If we take into account all the Aluminum possible species, the lowest solubility ranges from pH 5.7 to 7.8 (Figure 1)⁶. In the aluminum system the most common mineral phase is gibbsite $[Al(OH)_3]$. Between pH 7 to 9, the major dissolved species is $Al(OH)_4^-$.

For Silica the predominant dissolved species in equilibrium is silicic acid (H_4SiO_4) between pH 7 to 9. The major mineral-solution equilibrium would be from the dissolution of quartz. Below pH 8, the silica solubility is insensitive to pH values (Figure 2)⁷.

For a kinetic reason, the formation of Aluminum silicate will originate from the reaction between the dissolved species first. The most common species is the kaolinite $Al_2Si_2O_5(OH)_4$. According to Drever (1988) and Gabelich (2005), the solubility of kaolinite is minimal between pH 5.5 to 6.5. The lowest Aluminum concentration reachable is then of 10^{-9} mol/l (Figure 3).

Solutions

Gabelich (2005) reported that since several Aluminosilicate species are in equilibrium, the strategy is to act on these equilibria by reducing the concentration of either the anion or the cation of the species of concern. The complexation of Aluminum cations is an effective strategy. Gallup (1997) indicated that sequestering agents with carboxylate functional groups showed promise in achieving metal-silicate scale inhibition by complexing/

masking the Aluminum forming species which are less prone to react with silicic acid oligomers⁸. The use of Citrate and EDTA gave good inhibition results. To note, in the 90s, good inhibition results were obtained with the use of potassium tetrafluoroborate despite its corrosion side-effects.

Logically, better results were expected with the use of stronger complexing molecules like the Polyphosphonates. However, the performances seen with commercial Antiscalants based on Polyphosphonates or Polyacrylate were controversial. Gabelich (2005) reported negative results with some commercial well-known Antiscalant brands. A precipitation on the membrane surface was seen when the Aluminum concentration was ranging between 58ug/L and 200ug/L.

The surprise came from the X-Ray diffraction spectroscopy which revealed the presence of Aluminum Phosphate scale on the membrane. Phosphorous was detected in the colloidal phase during laboratory experiments. While high quality Antiscalant contains essentially Phosphonate or Polyphosphonate active ingredients, in the opposite some questionable quality Antiscalant products contain Phosphate (PO_4^-) anions.

When such questionable Antiscalant formulations are mixed with feed water containing Aluminum traces, a fast reaction occurs and forms Aluminum Phosphate which will immediately precipitate due to its very small solubility product K_{sp} (25°C) $9.84 \cdot 10^{-21}$. In a complementary study, Gabelich (2006) demonstrated that the dosing of high quality Antiscalants is always beneficial to prevent a membrane flux decline with feed water containing aluminum⁹ (Figure 4). Therefore, a specific

Antiscalant dose to sequester the Aluminum cation is necessary.

Conclusion

The growing amount of data and the clear evidence that the simultaneous presence of Aluminum cations at concentration as low as 100ug/L and silicate species has a detrimental and costly impact on RO membranes. The strategy to selectively sequester dissolved Aluminum traces with chelating agents like citrate, EDTA and Polyphosphonate proved its efficiency. The pre-requisite for a successful prevention with Polyphosphonate Antiscalants is to select the highest Antiscalant quality product. This selection will minimize operation cost and prevent from the opposite effect (scaling) encountered with low quality or aged Antiscalant. ●

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