PRACTICAL EXPERIENCE WITH HIGH SILICA CONCENTRATION IN RO WATERS

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ABSTRACT

Silica chemistry is very complex. Silica can be found on the surface of reverse osmosis membranes in a polymeric or crystalline form, and can also reach the membranes as colloidal particles.

Due to a shortage of good quality water in many regions of the world, reverse osmosis plants are forced to operate with very high levels of silica. Operating with high silica concentration will cause membrane fouling which is very difficult to clean and can cause irreversible membrane damage of the polyamide rejection layer. In order to avoid membrane fouling and control costs there is a choice of operating the reverse osmosis plant at low recoveries, or improving the plant pretreatment, membrane treatment and cleaning practices.

This paper describes three case studies demonstrating significant improvements in the operation of reverse osmosis systems for potable, agricultural and mining purposes. Recovery rates have been safely increased and the plant operated with silica levels of up to 340 mg/L of silica in the concentrate and fouling/scaling problems have been solved.

Keywords: Reverse osmosis, membranes, deposits, scale, fouling, silca, antiscalant, scale inhibitor, cleaners, flocculant

INTRODUCTION

Obtaining potable, irrigation and high quality industrial waters from high salinity water sources using reverse osmosis is technically and economically feasible. Nevertheless some of the ions that are present on the water can be limiting factors for applying this technology. This paper describes operational practices in those plants where silica is the limiting factor for increasing recovery rates.

Silicon is a very common element in nature, as earth crust contains approximately 25% of this element. Silica (SiO_2) content in natural waters usually varies between 10-40 mg/L, but in some places (Chile, México, Canary Islands) concentrations can reach up to 100 mg/L.

METHODOLOGY

The research conducted in this paper is based principally on the operation of pilot plants and field plants using sacrificial membranes and various antiscalant and cleaning chemicals. . Membrane autopsies have been carried out which are a unique tool for characterizing the state of membranes and it is fundamental to guarantee the efficiency of chemical treatments.

The results that are presented in this paper refer to diverse studies related to problems with dissolved silica (also called "reactive silica") and not to alumino-silicates (clays in colloidal form) also called "non-reactive silica".

RESULTS AND DISCUSSION

Fouling processes on membrane surface: Silica deposits.

Fouling is the most common problem in membrane separation processes, affecting parameters like flow rate and salt rejection. Some ions dissolved in the water; calcium, bicarbonates and sulphates can form crystalline scales on the membrane surface that will rapidly affect the process of osmosis. These scales will initially affect last elements from last stage, the membranes that are in contact with the most concentrated water, with a higher scaling potential.

Other ions dissolved in water; iron, manganese and aluminium will form amorphous deposits on the membrane surface, reducing membrane performance. These deposits will affect all membrane elements in the plant the same way. Fouling occurs because the concentration of ions is exceeded and because they are cationic and have an affinity for the weak anionic charge of the membrane surface.

The scaling and fouling behaviour of silica is varied. In those plants operating with high silica concentrations of over 200 mg/L as SiO_2 in the reject, scaling will occur in the rear elements unless specific silica antiscalants are dosed. In most cases silica deposits are amorphous due to the dosage of polymeric based dispersants. Figure 1 & 2 Both amorphous and crystalline scales will cause a decrease in output as well as a decrease in salt rejection and often result in irreversible damage of the membrane salt rejection layer.

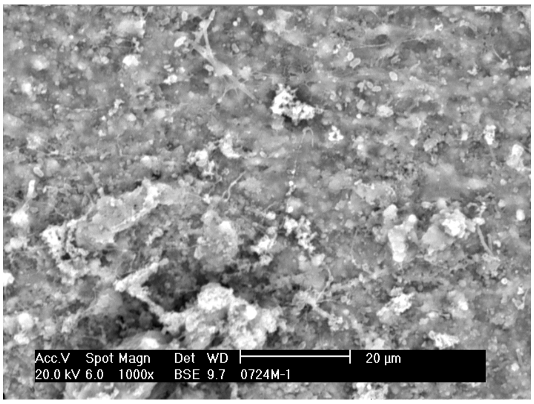

Figure1.- SEM Micrograph. Silica deposit on membrane surface.

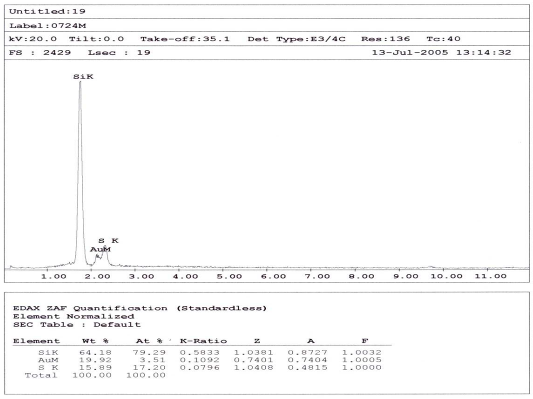

Figure 2.- EDX spectrum – deposit detected on Fig. 1

In some plants silica deposits have been identified on the lead membrane elements. In these cases silica comes already formed (suspended) in raw water. These deposits also result in a flow rate decrease in the first stage. Furthermore an increase in salt passage can also be observed not only by deposits on the membrane surface but also by abrasion processes as shown in Figure 5.

Silica can also be present on the membrane surface due to the presence of aluminosilicates (clays in colloidal form) Figures 3 & 4 and diatoms and algae in raw water caused by poor pre-treatment.Figure 6 In order to avoid these silica deposits, plant pretreatment should be optimized.

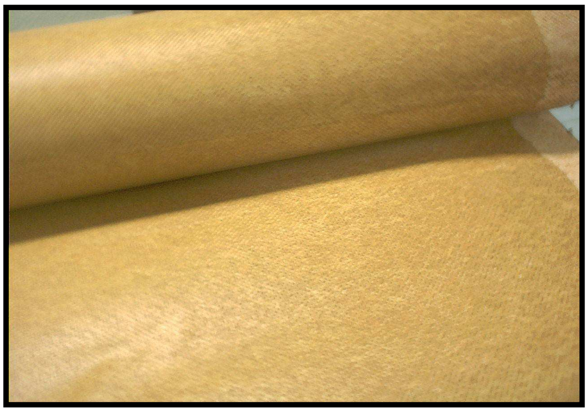

Figure 3: Aluminosilicates detected on membrane surface.

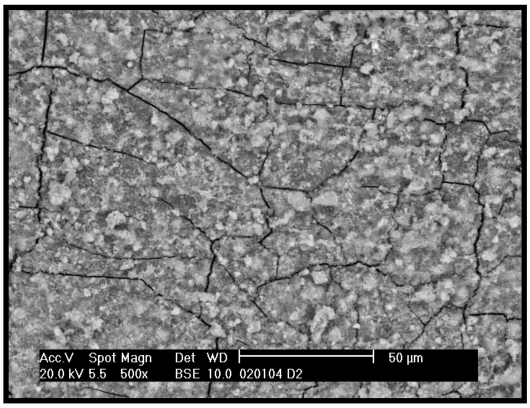

Figure 4: SEM-EDX Micrograph. Aluminosilicates on membrane surface.

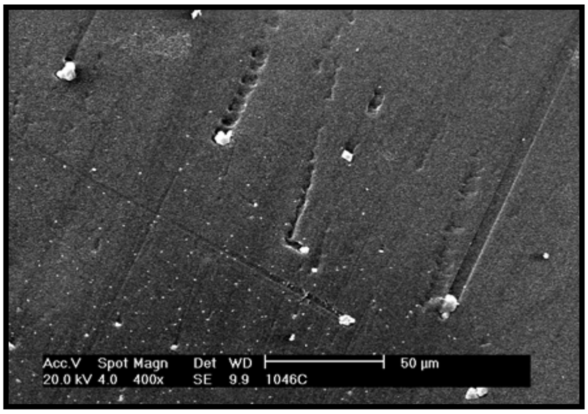

Figure 5: Silica particles on a membrane surface (abrasion). SEM-EDX Micrograph.

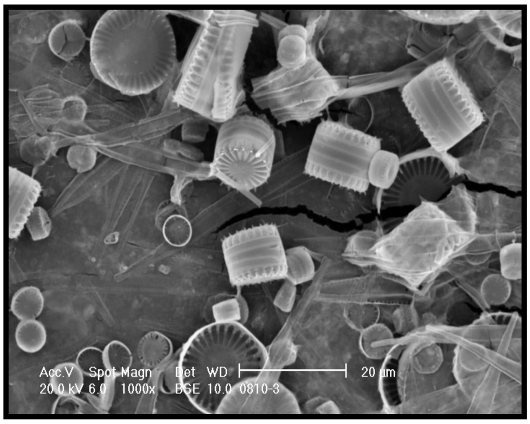

Figure 6: Diatoms on a membrane surface. SEM-EDX Micrograph.

Silica scale inhibition mechanisms

Traditionally the ways to avoid silica precipitation, as other scales, were:

- Mixture of polymers, mainly coming from acrylic and maleic acids, using crystal distortion and dispersion properties of polymers. As these products are limited to disperse already precipitated existing particles, modified crystals can still be found on membrane surface. The mechanism of crystal distortion is shown in Figure 7.

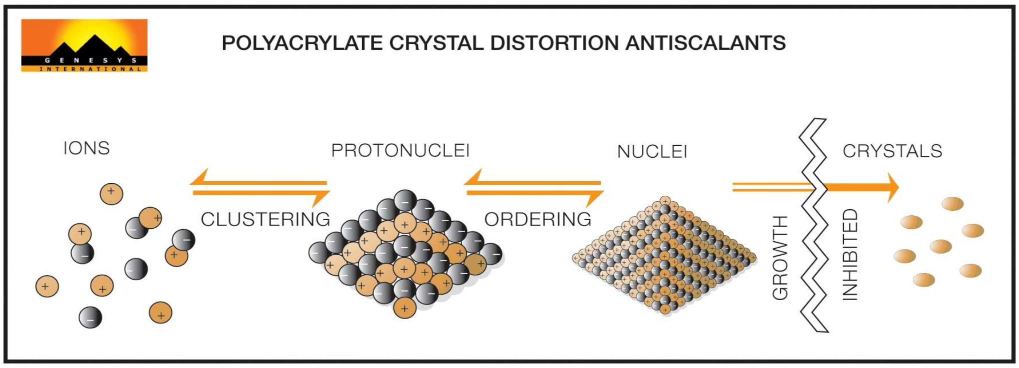

Figure 7: Crystal distorsion mechanism

- Mixtures of phosphonates that use the threshold inhibition effect of these products to inhibit precipitation and crystal formation. Antiscalants act in the reversible stage of crystal formation reaction inhibiting crystal formation as shown in Figure 8.

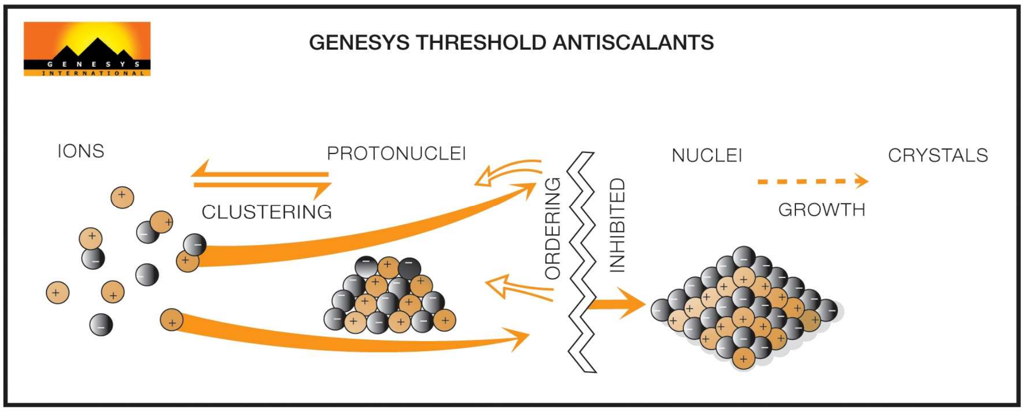

Figura 8: Esquema del mecanismo de inhibición de formación de cristales (efecto umbral)

The objective is to avoid scaling formation and to increase recovery rate. For this purpose a complete water analysis of raw water is needed, and critical parameters to be considered are silica, calcium, bicarbonates, iron, aluminium, magnesium and the water pH. Analysis of these parameters and using specialised scaling prediction software allows the optimum product and dosage rate to be calculated. Raw water acidification should be avoided as in many cases this can reduce silica solubility.

It is also crucial to prevent iron, aluminium and manganese from reaching the membranes as even at very low concentrations (0.05 mg/L) they have a high antiscalant demand which acts as a sequestrant.

Our product investigation line is concentrated on a synergistic blend of both phosphonate based broad spectrum antiscalants and polymers specially formulated against silica. This product combines threshold inhibiting effect with crystal distortion and dispersant properties.

Silica deposit prevention

In order to avoid the formation of colloidal silica it is very important to pipe water directly from the wells to the filters, avoiding intermediary tanks. If colloidal particles are detected, jar tests can be carried out to determine the optimum dose of membrane compatible flocculant which will improve particle retention in the filtration systems. The efficiency of this treatment can be evaluated and improved using the silt density index test on samples taken after the sand filters.

Particles which escape pre-treatment must be retained by the cartridge filters so the installation of expanded propylene cartridge filters is required. Experiences from in the field recommend installing 1 micron units.

The cleaning of silica deposits

Ammonium biflouride has been traditionally used in cleaning silica scales and deposits, as fluorine is generated in an acidic medium. Fluorine can dissolve silica crystals but its use has important disadvantages related to handling by operators and oxidative properties. Fluorine can also oxidize the polyamide layer even faster then chlorine.

Specialty chemicals have been formulated to replace the use of ammonium bifluoride. These products have been specially developed to be compatible with polyamide membranes and prevent the formation of volatile hazardous compounds. These products are a combination of surfactants, polyphosphates and chelating agents that rapidly remove silica scales and colloidal matter (aluminosilicates) from the membrane surface.

For a successful cleaning of silica 4 parameters must be considered:

- Flow rate: At least 8 m^3/h per 8” pressure vessel is needed.
- pH: Its a crucial parameter to be considered in silica cleaning. Commonly chemicals used for cleaning (detergents) silica work at pH between 10.5-11.5.
- Temperature: Although in other scales cleaning is not a critical parameter, temperature is important when dissolving silica deposits. Cleaning at 35-40ºC is strongly recommended.
- Chemical product: To use a detergent able to rapidly dissolve silica is important but special care must be taken to prevent polyamide damage. Cationic surfactants must be avoided.

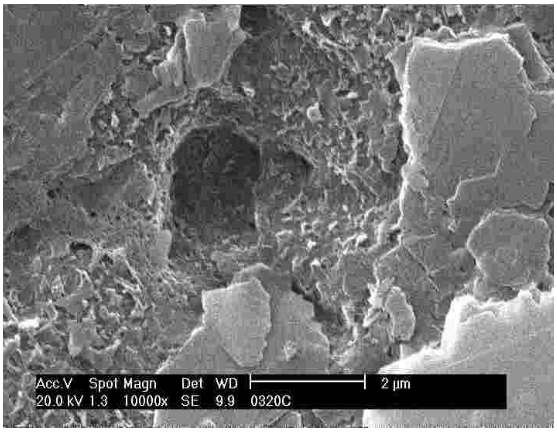

Figure 9: SEM Micrograph. Membrane partially covered by a silica deposit.

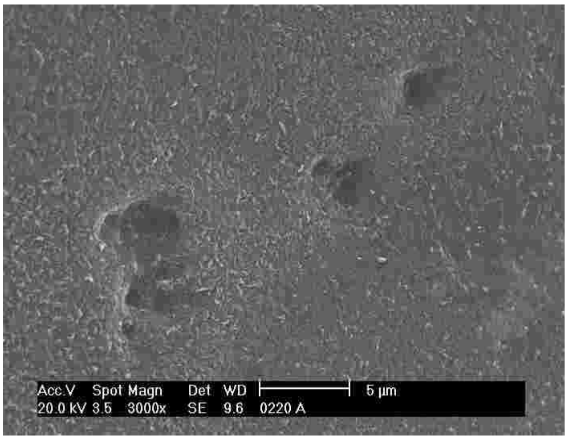

Figure 10: SEM Micrograph. Damaged membrane shown in Fig. 9 after chemical cleaning.

In some cases although chemical cleaning of silica deposits are successful, salt rejection decreases after cleaning due to irreversible damage on the polyamide layer by the pressurised partial penetration of scale into the membrane surface as shown in Figure 9 and 10..

Case studies

Case study 1: RO unit for irrigation water production

The plant is sited in a volcanic area in Spain. The feed water silica concentration is very high at 115 mg/L high pH value of 7.8, very high temperature of 35ºC and Iron and Manganese concentrations of lower than 0,02 mg/L. The scaling potential of this water was very high for silica and calcium carbonate as shown by Figure 11. The scaling prediction software Figure 12 indicated that by using a silica specific antiscalant Genesys Si and without acid dosing of the feed water this plant could operate at a recovery rate of 70%. A product water output of 450 m^3/h at a recovery rate of 70% has been achieved since November 2002.

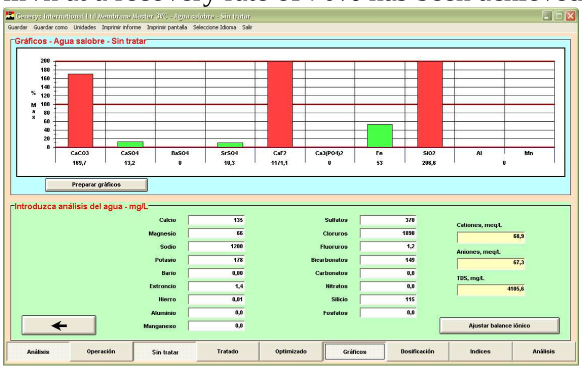

Figure 11: Scaling potential Case study 1 untreated.

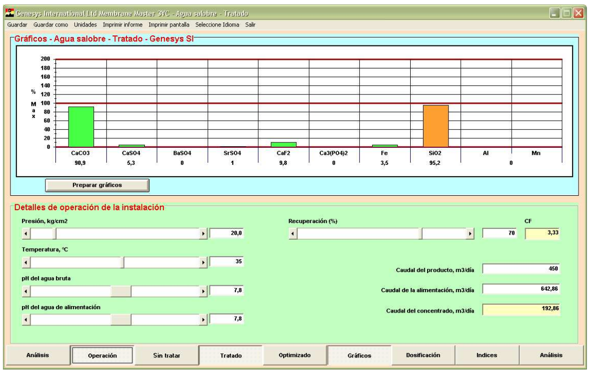

Figure 12: Scaling potential case 1 treated with a specific antiscalant.

For operational safety the membranes have been flushed with permeate daily and a preventative membrane clean has been conducted annually. The original plant design was to operate with acid and recovery rate of 50-55% Using the silica specific antiscalant has meant the plant recovery has increased by 20% giving substantial operational savings.

Case study 2: RO unit for potable water production

The reverse osmosis plant is located in Gran Canaria Island (Spain), and it has been in operation since 2004. The plant feed water supply is well water with a silica concentration of 64 mg/L, a low pH of 6.8, gaseous carbon dioxide and the presence of iron at 0.04 mg/L and manganese 0.16 mg/L.

The plant was designed to operate at a recovery rate of 75%. The maximum operational recovery rate achieved was 64%. Operating at higher recoveries than 64% lead to a loss in product output due to rapid catastrophic silica scaling which irreparably damaged the membranes which required replacement.. Using an accurate feed water analysis the untreated software projection figure 13 showed silica, iron, manganese and calcium carbonate fouling were likely. The treated projection in figure 14 indicated that the plant could operate safely at a recovery rate of 75% when using a silica specific antiscalant.

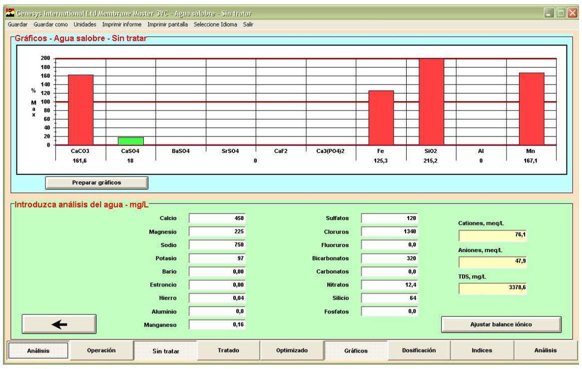

Figure 13: Scaling potential Case study 2 untreated.

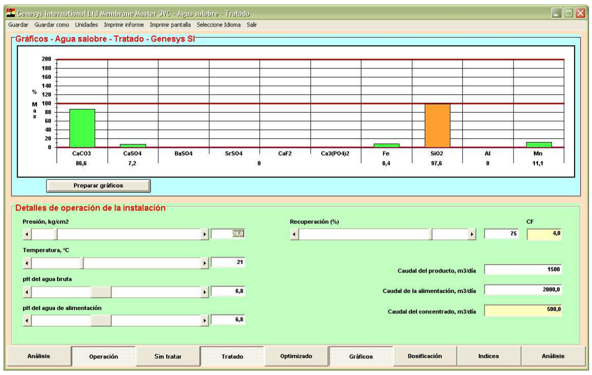

Figure 14: Scaling potential case 1 treated with a specific antiscalant.

The Genesys Si antiscalant has been dosed since January 2005, and the plant has been operating at 75% recovery. As a safety precaution, flushing the membranes with permeate water is done daily, and once per year a preventative clean of the membranes is conducted. During this period, a failure in the dosing pump was registered, resulting in a massive silica scaling in the second stage. All the membranes from the second stage needed to be replaced. First stage membranes were scaled, but it was possible to clean them up to an acceptable value of salt rejection. This episode clearly demonstrates the effectiveness of the antiscalant to control silica scaling with up levels of silica of 250-300 mg/labove in the concentrate.

Case study 3: RO unit for mining

The studied plant is sited in a mining area in Chile, and has been in operation since 1999. The plant suffered severe fouling problems of both stages. The membranes were cleaned every fifteen days in order to remove silica deposits and maintain the product water flowrate. The silica scaling and the frequent membrane cleanings resulted in the membranes being replaced twice a year. The annual cost of the cleaning process and replacement membranes was xxxxxxx

Several membrane autopsies and water analyse were conducted to investigate the source and process of scale formation., Detailed feed water analysis was also conducted and the effectiveness of the sand filters and cartridge filters assessed. The studies show the presence of silica particles in the feed water. These particles affected the lead membranes. The last stage membranes were affected by silica scales. In addition manganese oxide was found in the sand filters, micro filters and membranes.

The plant is fed from several wells, with an average silica concentration of 75 mg/L and pH of 7.4. The feed water was acid dosed to reduce pH to 6.5. of the presence of iron 0.03 mg/L, aluminium 0.37 mg/L and manganese 0.55 mg/L was also detected. The system was designed to achieve recovery rates of 75%, but actual plant operation was lower than 60%, and the membranes had to be cleaned twice per month.

The results from the studies suggested the following improvements:

- Dosage of a flocculant before the sand filters to prevent silca particles reaching the membranes.
- Replace the sand in the filters, and clean the sand periodically with disinfectant agents and manganese cleaners, to avoid channelling.
- To use spun 1 micron micro filters in order to remove clay and silica particles.
- Dosage of a silica specific antiscalant and stop acid dosing.

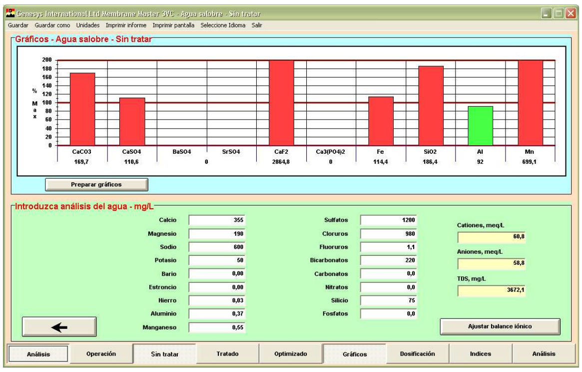

Figure 15: Scaling potential Case study 3 untreated.

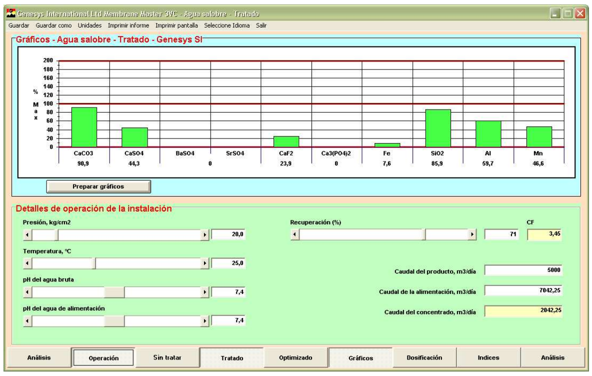

Figure 16: Scaling potential case 1 treated with a specific antiscalant.

Figure 15 shows the untreated situation for this feed water with silica, manganese, iron, calcium carbonate and calcium sulphate fouling a major concern. The treated version using a silica specific antiscalant is shown in figure 16. The plant has been operating with a much improved recovery rate of 71% versus the historical rate of only 60%. The first stage membranes are cleaned every two months, due to the on-going deposition of silica particles from the feed storage tank, and due to the variability of water turbidity. The main short term goal is to optimize the flocculant dosage to reduce turbidity and particulate matter, and increase the recovery rate further to 75%. Current water savings at 71% recovery are xxxxxx and could rise to xxxxxxx if 75% recovery is achieved.

CONCLUSIONS

- Dosing a silica specific antiscalant prevents silica scale and deposits on membrane surfaces without having to reduce the feed pH through acid dosing.
- It is possible to increase recovery rates and make substantial savings in water and energy consumption.
- The silica specific antiscalant has been operating successfully in both pilot plant and fully operational plant with continuous levels of silica in the reject water of 240mg/L. In optimum conditions feed water without iron, aluminium, manganese and with a high pH and temperature values up to 375 mg/L of silica in the reject can be reached.
- Using specific flocculants and improving the efficiency of the filtration systems it is possible to reduce the amount of colloidal silica reaching the membrane system.This allows continuous operation and minimises downtime for membrane cleaning.
- For a successful removal of silica scales and deposits, specialty chemicals must be used. These products must be polyamide membrane compatible to avoid oxidation problems.