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**CONTROL OF SILICA SCALING PHENOMENA IN
REVERSE OSMOSIS SYSTEMS**

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**CONTROL OF SILICA SCALING PHENOMENA IN
REVERSE OSMOSIS SYSTEMS**

by

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To my parents, Carlos and Idalia, for all their support and guidance throughout my life .

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Industrial development in the Border region of Mexico and Texas depends on the availability and quality of water; several industries require high quality process water. Reverse osmosis systems achieve that quality, but high concentrations of silica in the local water supplies limit the recovery. Silica is problematic in membrane systems due to its complicated chemistry. Silica may induce both scaling and fouling, causing decline in the water production rate, reduced water product quality and permanent damage to membranes. The objective of this research was to develop pretreatment strategies for RO systems subject to silica fouling and scaling.

To accomplish this objective required a thorough investigation of processes to remove silica prior to membrane treatment with softening and adsorption/precipitation. This investigation included chemical equilibrium modeling of possible treatment schemes, and subsequent bench-scale batch experiments of the most promising treatments identified by that modeling. A bench-scale RO system was then operated with and without pretreatment to test

the efficacy and potential benefits of the best treatments identified in the batch experiments.

Lime softening proved to be an effective method to reduce silica concentration. Results show that addition of magnesium chloride (35 mg/L of Mg^{+2}) and 165-180 mg/L lime plus soda ash for calcium control (160-190 mg $\text{Na}_2\text{CO}_3/\text{L}$) dramatically decreased the silica concentration from 28 mg/L as Si to approximately 5 mg/L as Si. According to Mineql simulations, the precipitated compound is chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). RO experiments with both synthetic Rio Grande water (*i.e.*, water made to mimic the chemical composition) and Rio Grande water were performed with and without influent water pretreatments. Operational conditions were 1550 kPa, and cross-flow velocity of 3.6 cm/s at 25 °C. Untreated Rio Grande water presented a specific flux decline of 53 %. Pretreated water presented a lower flux decline at the same conditions, 7 %. SEM and XPS analysis showed less amount of silica fouling over the membranes. Pretreatment of silica-bearing waters before entering an RO unit dramatically improved the flux behavior, which is the main parameter describing membrane system performance.

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CHAPTER 1. INTRODUCTION

Membrane processes, especially high-pressure membrane processes, are now frequently applied in the production of high quality water. Causes for the expansion of membrane use in environmental applications are improvements in the underlying technology, a more competitive market, a more demanding regulatory environment, a broader range of membrane processes, and the availability of materials from which they can be fabricated. The finest of membrane filtration, reverse osmosis (RO), effectively removes all types of contaminants (particles, pathogens, microorganisms, colloids and dissolved inorganics). When properly designed and operated, RO is a very efficient drinking water and ultrapure water treatment process. The system complies with the recent and expected changes in regulations that guide the water industry, as well as with the water specifications required by some industries.

A reverse osmosis system must be well maintained to ensure reliable performance by meeting the water quality requirements with the lowest capital and operating costs. The performance of an RO system is influenced mainly by the feed water quality, feed pressure, temperature, level of recovery and membrane characteristics. The quality of the feed water is the single most important factor to be considered in ensuring the technical and economic viability of a membrane plant (Gabelich, 2002). RO systems are typically comprised of several modules in series, with the concentrate of one becoming the feed stream for the next. With this arrangement, the recovery (*i.e.*, the fraction of the influent

water volume that becomes product water) is increased considerably from what could be achieved in a single unit.

In a reverse osmosis system, the concentration of suspended and dissolved particles increases on the reject side of the membrane. As materials accumulate near, on and within the membranes, they produce two of the most important problems in a RO unit: scaling and fouling. Scaling of RO membranes occurs when the concentration of the inorganic constituents of the concentrate stream exceeds saturation and precipitate as solids over the membrane surface. Scaling is most likely to occur in the last stages of an RO system because the concentration of salts increases as water is removed through the membranes. Typical scalants are calcium carbonate, sulfates and silicates. Scales are very difficult to remove without damaging the membranes.

Fouling refers to accumulation of materials on the surface or within the pores of a membrane. These materials include clay minerals, colloidal silica, iron and aluminum oxides (particle fouling), microbes (biofouling), and humic acids and residual polymers (organic fouling). These materials typically foul the first stages of the system and may be removed by cleaning. Scaling and fouling decrease the system productivity by adversely affecting both the quantity (product water flux) and quality (product water concentration) of the permeate stream. If scaling and fouling are controlled and slowed down, it is possible to achieve a good system performance, with long membrane life and low operating costs.

1.1 PROBLEM STATEMENT

Industrial development in the Border area of Mexico and Texas is dependent on many factors; one of the most important factors is the availability and quality of water. Several industries established along the Mexico/Texas border region require a very high level of quality for their process water. Reverse osmosis is a membrane-based process used by several industries that yields water with the required level of quality.

A characteristic of the water in this area is its relatively high concentration of silica; of the few measurements available, several at both ends of the Rio Grande in Texas are in the range of 20-26 mg/L as SiO_2 , more than double the values common in the rest of the State and the nation (Water and Sustainable Development in the Binational Lower Rio Grande/Rio Bravo Basin, TNIRIS, 2001). Comb (1996) reported that, throughout Mexico, most well water supplies contain 50 to 100 mg/L as SiO_2 . Even though it is not a human health problem at any concentration, silica at such high concentrations represents a severe problem in membrane-based water treatment processes.

Reverse osmosis systems are arranged in series and parallel to maximize water recovery. Since the reject stream of each membrane element is the influent for the next element in series, the stream becomes more concentrated as the water flows through the system. At recovery levels of 95%, the concentration of silica in the feed/concentrate stream of the last elements is approximately 20 times that of the original influent. Because RO removes most species similarly, most species have concentrations that are increased by approximately this same factor. The high concentrations of several cations and anions might exceed the solubility

limits of some salts, and precipitation might occur. If salts precipitate on the surface of membranes, the scale decreases the flux of water product. Colloidal particles may also foul the membrane pores, blocking the passage of water through the membrane. Silica compounds may produce both scaling and fouling on a reverse osmosis system; these compounds have been reported to be difficult, costly, and sometimes impossible to remove without damaging the membranes.

Although a considerable amount of literature on silica chemistry exists along with practical knowledge on silica problems in the geothermal industry, the conditions of that industry are high temperatures and high silica supersaturation values. Conditions of high temperatures and high silica concentrations are not representative of the reverse osmosis systems used for water treatment, where ambient temperatures and lower silica concentrations are usually found. The complexity of silica chemistry has been proven by different practical studies, since researchers have encountered unexplainable results, while similar works studying other scalants are free from those complications (Sheikholeslami and Zhou, 2000; Bremere *et al*, 2000; Sjoberg, 1996). There are very few practical and theoretical analyses with respect to silica chemistry in membrane systems. This research was designed to help fill that gap.

1.2 OBJECTIVE

The potential for scaling and fouling in reverse osmosis systems could be reduced by silica control in high silica bearing waters. Silica control may be achieved by operational strategies (*e.g.*, recovery level control, pH adjustment) and pretreatment for silica removal in the influent water. Some pretreatment possibilities are precipitation with magnesium and calcium, (*i.e.*, within a softening process) and precipitation and/or simultaneous adsorption with aluminum or iron salts.

The objective of this research was to investigate combinations of pretreatment and RO operational strategies that optimize the production of clean industrial process water for water quality conditions that include the presence of high silica concentrations. This objective was accomplished with a combination of experimental work (on synthetic as well as natural waters from the Border region) and mathematical modeling. Controlling and diminishing the scaling and fouling potential of silica compounds should improve the performance and perhaps the economic viability of the reverse osmosis process.

1.3 APPROACH

To achieve the objectives of the research, bench scale softening jar tests and membrane filtration were performed. Two possible processes for silica removal were investigated experimentally: (i) precipitation with magnesium and calcium, *i.e.*, within a softening process and (ii) precipitation and/or simultaneous adsorption with aluminum and iron.

Two different waters were used: (i) Rio Grande water from the Laredo area and (ii) a synthetic water with the characteristics of Rio Grande water to analyze the influence of the specific ions studied (Si^{+4} , Ca^{+2} and Mg^{+2}) and avoid interference of other constituents present in natural water.

For the softening precipitation of silica, jar tests were performed for each water with a systematic variation of conditions for calcium (including lime addition), magnesium (including MgCl_2 addition), silica (including sodium silicate addition), and pH (controlled by lime dose and sodium carbonate).

For the jar tests with iron to allow precipitation and/or adsorption, the iron was added as FeCl_3 at several doses and pH values (defining the behavior throughout the reasonable pH/Fe concentration space) to allow the precipitates to form. After appropriate mixing, settling and filtration in these small scale batch tests, several analyses were performed on both the solids and the solutions. The processing of samples after solid/liquid separation was essentially identical for the two types of jar tests. For the softening tests, the residual Si, Ca, and Mg were determined via Inductively Coupled Plasma Spectroscopy (ICP). Various other chemical analyses, including pH and alkalinity were performed. For the iron tests, Fe, Si and pH were measured on the solutions. A similar set of experiments with aluminum was performed; the fact that Al(III) is more soluble than Fe(III) at high pH makes it a less likely adsorption surface.

The solid phases formed at the conditions for optimal silica removal were tentatively identified by Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS). Morphological characteristics were studied with a Scanning Electron Microscope (SEM); the identification should help identify the chemical conditions required for maximum precipitation. Exact

conditions for the jar tests were chosen for the specific water after preliminary experiments and after mathematical modeling using raw water chemistry.

A precipitation process leaves the water saturated or supersaturated with respect to the solid phase. Hence, the precipitation itself is only one step of the pretreatment; a solid/liquid separation process (settling, depth filtration, or ultrafiltration) is required, as is a subsequent chemical adjustment prior to application of the water to the membrane. Settling is likely to yield an acceptable degree of solid/liquid separation. Chemical adjustment has to be made to prevent further precipitation. For the softening process, reducing the pH is common, and this step was applied here as well. For the iron and aluminum precipitation, increasing the pH was sufficient, because the iron, aluminum, and silica are all more soluble at high pH.

The solutions after optimizing the treatment and post-treatment from the jar tests were put into a batch laboratory membrane system (flat sheet membranes) to study the flux decline (*i.e.*, fouling) of the membranes. In each case, the decline in the specific flux (flux per unit pressure) was measured over a substantial loading (measured as volume of water processed per unit area). Comparisons of these runs under various conditions allowed measurement of the accomplishment of the pretreatment schemes.

Two types of mathematical modeling were performed and used together: equilibrium chemistry modeling to understand the driving force for precipitation at two points in the treatment scheme (pretreatment and on the membranes) and a model of full-scale membrane processes to track the concentrations of all relevant species through a membrane system at steady state. The first is a commercial program, Mineql®, which is useful to predict the degree of supersaturation at any

point in the system, and is used to study the speciation of silica and possible solid phases that could be formed in developing this research. It was used throughout the research to influence experimental conditions and interpret experimental results. The second was developed in this research, and is a relatively straightforward, mass balance approach, done separately for all major constituents in the water. The combination of the two programs enabled one to study mathematically the tradeoffs between various degrees of treatment and the yield in the membrane system that can be achieved without silica fouling.

CHAPTER 2. LITERATURE REVIEW

2.1 WATER ISSUES IN THE MEXICO - TEXAS BORDER REGION

The U.S.-Mexico border extends approximately 2,000 miles from the Pacific Ocean in the west to the Gulf of Mexico in the east. This region lies within the political jurisdiction of four U.S. States and six Mexican States. Although each of these states has their own political and geographical conditions, both countries share common air and water resources. Responsibility for resource management falls in the political authority of two nations with different legal systems, national objectives and different priorities and levels of development.

Several agreements, such as the Border Environmental Cooperation Agreement and the Water Treaty of 1944, have attempted to solve sanitation problems and requirements for industry, as well as settle disputes between the two nations. These commissions have also planned, built, and managed water works.

Organizations such as the Border Environment Cooperation Commission (BECC), the International Border Water Commission and the Border Information Center, a sector of the Texas Natural Resources Information System, have published studies that revealed the major environmental problems in the Border Area are the poor quality of surface and underground water and the shortage of water for both domestic and industrial use. Water has been defined as the border's scarcest, most precious and most fragile resource.

Two-thirds of the Mexican *maquiladoras* (manufacturing plants that use American input materials) are located in the Border area. More than 1500 of these

assembly companies with operations mainly related to food processing, beverage, textiles, electronics and auto equipment production exist along the Texas/Mexico border. These industries require high quality process water. Reverse osmosis is a membrane-based process that yields water with the required specifications, although some characteristics of the Border water interfere and cause problems to this type of system.

2.2 SILICA OCCURRENCE

High silica values are reported in the Border area of Mexico/US; of the few measurements available, several at both ends of the Rio Grande in Texas are in the range of 20-26 mg/L as SiO_2 , more than double the values common in the rest of the State (HARC and ITESM, Water and Sustainable Development in the Binational Lower Rio Grande/Rio Bravo Basin, 2001).

According to the Middle Rio Grande Basin Study (2001), concentrations of dissolved silica are typically 20-23 mg/L (as SiO_2) along the basin margins and markedly elevated (50-70 mg/L) in a north-south zone throughout the center part of the basin. The elevated silica concentrations probably reflect reactions with siliceous clay minerals associated with fluvial sediment, and possibly weathering of volcanic glass. Alkalinity is less than 200 mg as CaCO_3 /L throughout most of the basin. The reported median alkalinity is 165 mg/L for all basin waters.

High values of silica concentrations are also found in North America in the Great Basin region of the West and in the California Central Valley in the United States, and throughout Mexico, where most well water supplies contain 50 to 100

mg/L (Comb, 1996). Since silica found in well waters is typically a result of the dissolution of silica containing rocks, it is mostly reactive (monomeric) silica. Surface waters contain both reactive and colloidal forms, although the most abundant species is still reactive silica. Sjöberg (1996) reported that concentrations of silica in some natural waters range from 36 to 70 mg/L. Higher concentrations ranging from 30 mg/L to 180 mg/L are also found.

In the production of ultrapure water for the power, microelectronics, and other industries, the reverse osmosis process is commonly the major step in the reduction of dissolved and suspended matter, either as the final step or before polishing by ion exchange. With the diverse locations of industries requiring ultrapure water around the world, silica concentration in source waters can range between 1 to 60 mg/L, and even 300 mg/L in some volcanic regions. Some industries require water containing less than 1 µg Si/L (Ning, 2003).

2.3 SILICA CHEMISTRY

2.3.1 SILICA CHARACTERISTICS

Silicon dioxide or silica, SiO_2 , is widely distributed in the environment. Next to oxygen, silicon, Si, is the most abundant (29.5% wt) element on the Earth's crust. In natural waters, silica comes from the weathering of minerals, rocks, soils, sands, and clays. Second only to carbon, silica forms the largest number of compounds with other elements. Unlike the common C-C-C chains of carbon chemistry, the magnitude of the bond energy of the Si-O is considerably higher than that of the Si-H bond and more than twice that of the Si-Si bond. As a

consequence, chains of the type Si-O-Si-O are the skeletons of silica chemistry (Ning, 2003).

Many crystalline forms exist, the most common of which is quartz, but invariably, silica is found in the +IV oxidation state. Silica is a general term that comprises silicon dioxide (SiO_2) in its crystalline, amorphous, hydrated and hydroxilated forms. It can be classified, depending on its size, as soluble, colloidal or suspended particles. Soluble silica presents diameters below 0.001 micrometers, colloidal and supra-colloidal particles are in the range of 0.001 to 1 and 1 to 10 micrometers, respectively, and suspended particles are those particles with diameters above 10 micrometers. Silicon content is commonly given in terms of the mass of silicon dioxide.

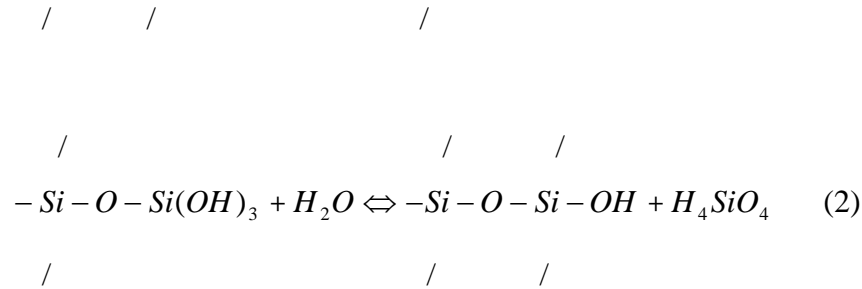
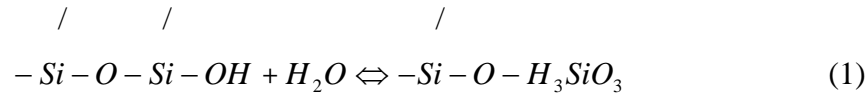
Different processes regulate silica-water interactions. These processes include dissolution, dissociation, precipitation, polymerization, complexation with metals forming silicates, adsorption and desorption (Sjoberg, 1996).

2.3.2 SILICA-WATER CHEMISTRY

Silica, as SiO_2 , may be found in two solid forms, amorphous and crystalline. Some of the crystalline silica compounds are quartz, cristobalite and tridymite. Amorphous silica is a general term for solid silica lacking the crystal structure. Amorphous silica may exist in monomeric silica, polymeric silica and granular silica forms. Once hydrolyzed monomeric silica, also known as dissolved, soluble or reactive silica, forms silicic acid. Polymeric silica is also known as colloidal silica. Granular silica is also called suspended silica (Sheikholeslami and Tan, 1999).

The dissolution process of amorphous silica in water occurs when the silica-oxygen-silica bonds hydrolyze. The hydration number of silica is 2, forming the weak tetrameric silicic acid ($\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or H_4SiO_4).

A mechanism for the dissolution of silica was proposed by Fleming (1986), and it is still well accepted. The dissolution proceeds in two steps: (1) formation of chemisorbed silicic acid on the hydroxylated silica surface and (2) the further reaction of the chemically adsorbed silicic acid with water to give H_4SiO_4 and again, the hydroxylated silica surface.



Silica solubility is influenced mainly by temperature, pH, and the presence of another ions and organic compounds. The effect of pressure on silica solubility at values up to a few hundred bars and at temperatures below 100 °C has been shown to be negligible (Sheikholeslami *et al.*, 2000).

Silica solubility as a function of temperature

The equilibrium constants for silica-water interactions are a function of temperature and the chemical structure of the silica (Iler, 1979). The equilibrium constants for four crystalline structures (-quartz, -cristobalite, -cristobalite and chalcedony) and for amorphous silica are shown in Table 2.1 for various temperatures.

Table 2.1 Log K for the Hydrolysis of SiO₂ Crystal Structures and Amorphous Silica (P=100 kPa)

T (°C)	-quartz	-cristobalite	-Cristobalite	chalcedony	amorphous silica
0	-4.502	-3.891	-3.372	-4.206	-2.994
25	-3.999	-3.449	-3.005	-3.728	-2.714
50	-3.627	-3.128	-2.743	-3.377	-2.506
75	-3.335	-2.879	-2.54	-3.102	-2.304

The values shown in Table 2.1 refer to the reversible reaction of SiO₂ to form the monomeric silicic acid written as follow:



The notation for the formation constants is stated as K_{pq} , where q is the number of silicon atoms in the hydrolyzed form and p is the valence number of the compound.

From the previous chemical equation,

$$K_{eq} = 10^{-2.714} = \frac{[H_4SiO_4]}{[SiO_2(s)]}$$

since the activity of a pure solid is one (*i.e.*, $[SiO_2(s)]=1$), $[H_4SiO_4]=1.93 \times 10^{-3}$ mol/L. In terms of SiO_2 , the solubility limit is 116 mg/L. Amorphous silica presents the highest solubility.

Silica dissociation and solubility as a function of pH

The amorphous silica solubility is strongly pH dependent. The previous silica solubility limit of 116 mg as SiO_2 /L is valid for neutral pH values (6-8). Generally, solubility of silica increases as pH increases. The pH value has no effect on the solubility of silica at low pH values.

Comb (1996) stated that pK values are slightly concentration dependent. Reported pK values for $SiO(OH)_3^-$ are between pH 9 and 10. However, it is generally accepted in the literature that pK for $SiO(OH)_3^-$ is approximately 9.5, independent of the total concentration of silica.

Sjoberg (1996) reported that, below pH 9, silica is dissolved in water mainly in the form of monosilicic acid (nonionic); although the dimeric silicic acid complex (two Si atoms in the molecule) also forms, it never exceeds 5% of total silica in silica saturated solutions on this pH range. Above pH 9, the monosilicic acid increasingly dissociates into the bisilicate anions ($SiO(OH)_3^-$, $pK_1=9.47$ and $SiO_2(OH)_2^{-2}$, $pK_2=12.65$) and polysilicates.

The monomeric species dominate at all environmental concentrations and pH values. Monosilicic acid remains in the monomeric form for long periods at 25 °C, if the concentration remains below 120-200 mg as SiO₂/L (Iler, 1979). The speciation of aqueous silica in solution (at 25 °C) under conditions where no polymerization occurs is shown in Table 2.2 (Sjoberg, 1996).

Table 2.2 Formation Constants for the Hydrolysis of Monomeric Products of Silicic Acid

P,q	Chemical reaction	Formation Constants (Log K _{pq})
-1,1	$H_4SiO_4 \Leftrightarrow SiO(OH)_3^- + H^+$ (4)	-9.47
-2, 1	$H_4SiO_4 \Leftrightarrow SiO_2(OH)_2^{-2} + 2H^+$ (5)	-22.12

To plot these equations on a pC-pH diagram requires that they be expressed in terms of soluble silica species, H⁺, and SiO₂(s). The equations must be rearranged so that each species is in equilibrium with SiO₂(s). By adding equation (3) and (4) we obtain the equation of the first silicate ion, SiO(OH)₃⁻, in equilibrium with the solid, SiO₂(s). Equation (6) presents this equilibrium.

$$\text{Log K} = -12.18 \quad (6)$$



From here,

$$[SiO(OH)_3^-][H^+] = 10^{-12.184} \quad \text{or}$$

$$\log[SiO(OH)_3^-] = -12.184 + pH \quad (7)$$

By adding equations (3), (5) and the water equilibrium equation (8), the reaction for the second bisilcate ion, $SiO_2(OH)_2^{-2}$, in equilibrium with the solid, $SiO_2(s)$, is obtained. Equation (9) shows this equilibrium.



From here,

$$\frac{[SiO_2(OH)_2^{-2}]}{[OH^-]^2} = 10^{3.166} \quad \text{or}$$

$$\log[SiO_2(OH)_2^{-2}] = 2pH - 24.834 \quad (10)$$

The concentration of silicic acid is obtained from equation (3) as follows,

$$\log[H_4SiO_4] = -2.714 \quad (11)$$

The silica solubility line is represented by the following equation (12):

$$\log[Si]_{\max} = \log\{[H_4SiO_4] + [SiO(OH)_3^-] + [SiO_2(OH)_2^{-2}]\} \quad (12)$$

By plotting equations (7), (10), (11) and (12), the silica speciation and solubility diagram is obtained (Figure 2.1).

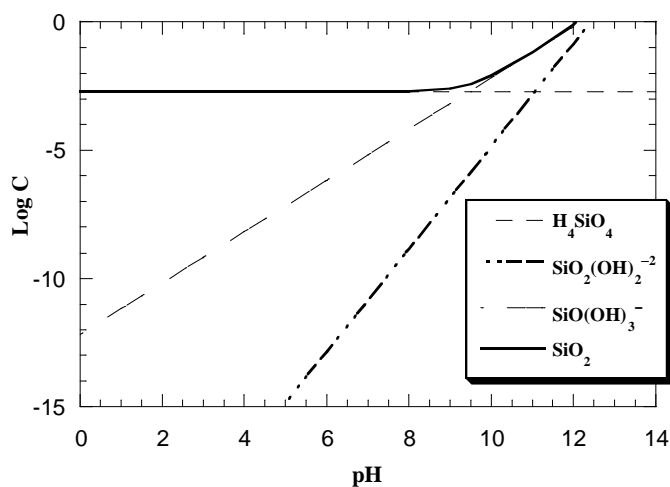


Figure 2.1 Silica Solubility Diagram

Silica solubility values are still not well defined and different values have been reported especially for pH values above 9 (Table 2.3). The higher solubilities reported by Al-Mutaz (1999) and Iler (1979) than those obtained from Equation 12 suggest that the pK_1 value could be slightly less than 9.47.

Table 2.3 Solubility of Amorphous Silica (mg SiO₂/L) at 25 °C

pH	Values from equation (12)	Reported by Al-Mutaz (1999)	Reported by Iler (1979)
6	120	126	120
7	120	120	120
8	124	120	120
9	159	236	138
9.5	244	317	180
10	514	419	310

When a solution of monomeric silicic acid has concentrations greater than 120-200 mg/L, that is, greater than the amorphous silica solubility at the

conditions in the solution, and in the absence of a solid phase on which the soluble silica might be deposited, the monomer polymerizes.

2.3.3 SILICA POLYMERIZATION

Silica polymerization requires ionized (OH^- and $\text{SiO}(\text{OH})_3^-$ groups), as well as unionized silica. This implies that the rate of silica polymerization depends on the extent of ionization of the silica. Solutions with pH less than 8 are weakly ionized. At pH less than 6.5 there is virtually no ionization and no singly ionized ion can polymerize with unionized silicic acid. Above the pK_1 value, the ionization of monosilicic acid increases and, the solution mostly has the silicate ions ($\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{-2}$), and very low amounts of silicic acid.

Therefore, the pH range to minimize the rate of silica polymerization is below pH 6.5 or above pH 10. Both conditions may present disadvantages in a reverse osmosis system. Some RO membranes are intolerant to low pH values. On the other side, a high pH value creates a potential for the precipitation of highly insoluble calcium and magnesium silicates

Information obtained from Si nuclear magnetic resonance (NMR) spectroscopy has provided a picture of the speciation in silicate solutions. Works by Engelhardt (1983) and Harris (1986) have shown the identification of 19 different silicate species, from dimers to decamers.

The polymers have few silanol groups ($=\text{Si-OH}$) inside, whereas the surface has many. Above neutral pH, the surface silanols are ionized, giving the polymer a negative charge. The large polymers form colloidal particles. Colloids can also be formed by silica bonding loosely with organic compounds or with

inorganic compounds (Comb, 1996). Colloidal silica has very little charge at low pH and is negatively charged at neutral pH or higher. Results from experiments (Iler, 1979) have shown that silica colloids may be stable and do not aggregate easily even at high salt concentrations. This stability is attributed to repulsive forces and hydration of colloids. The isoelectric point of the colloidal silica is approximately at pH 3. At solution pH above 3, silica colloids possess a net negative charge. However, at higher ionic strengths, the particles are less stable due to the double layer compression. At ionic strengths typical of natural waters, silica colloids are negative charged and very stable particles. Even if the stability of colloidal silica is high, in the presence of polyvalent metals it may precipitate (*e.g.*, the addition of Al^{+3} to an undersaturated silica solution has been known to cause polymerization (Iler, 1979)).

Sjoberg (1996) performed potentiometric and Si NMR measurements to determine thermodynamic data with respect to polysilicate formation. The species mainly formed were dimers, trimers (linear and cyclic trimers) and tetrameric species. After the polymer grows to about three or four linear units, it takes a cyclic form and eventually cross links internally. Although species with higher nuclearities were formed in minor amounts, within the concentration studied ($\text{Si} \leq 0.05 \text{ M}$, that is, 1400 mg/L), the prevailing polysilicate was the tetrameric species.

The formation constants for the polymeric compounds are presented in Table 2.4 (Sjoberg, 1996).

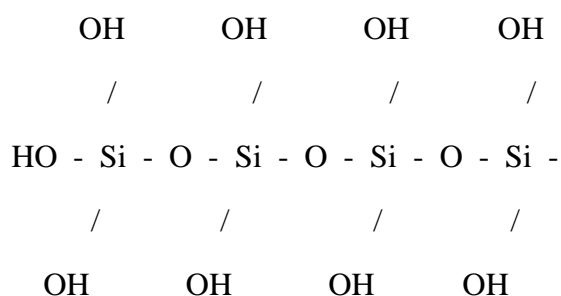
Table 2.4 Formation Constants for the Hydrolysis of Polymeric Products of Silicic Acid

p,q	Chemical reaction	Formation Constants (Log K_{pq})⁺
0,2	$2H_4SiO_4 \Leftrightarrow Si_2O(OH)_6 + H_2O$	8.95
-1,2	$2H_4SiO_4 \Leftrightarrow Si_2O_2(OH)_5^- + H^+ + H_2O$	10.25
-2,2	$2H_4SiO_4 \Leftrightarrow Si_2O_3(OH)_4^{-2} + 2H^+ + H_2O$	-18.00*
-3,3	$Si_3O_6(OH)_3^{-3}$ cyclic form	-26.43*
-3, 3	$Si_3O_5(OH)_5^{-3}$ linear form	-25.40*
-4,4		-32.81*
-5,5		< -41.5*

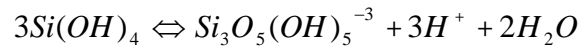
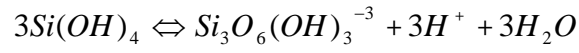
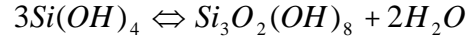
+The notation for the formation constant, is stated as K_{pq}, where p is the number of valence of the compound and q is the number of silicon atoms in the hydrolyzed form.

*The formation constants, K_{pq}, are defined according to the reaction $pH^+ + qSi(OH)_4 \Leftrightarrow H_p(Si(OH)_4)_q^{p+}$.

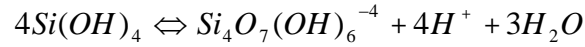
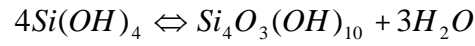
The reaction for the trimers and tetramers were deduced from the polymeric silica model presented below,



Trimeric polymer and its dissociation:



Tetrameric polymer and its dissociation:



The polymerization reactions proceed more easily with already polymerized species, as dimers, rather than with other monomers, and they slow down as the concentration of monomer decreases (Iler, 1979). The reaction has slow kinetics at values of supersaturation less than twice the solubility limit since the induction period is long. At supersaturation levels of three times the solubility limit, the polymerization reaction presents a very fast kinetics.

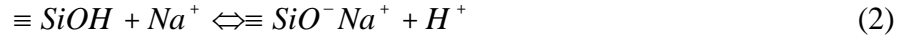
2.3.4 SILICA SURFACE CHEMISTRY

Silica, as the primary oxide component of the earth's crust, is one of the most common surface functional groups in aqueous environments. It is important to determine surface complexes because the fundamental chemistry that controls interfacial reactions may depend on the types and concentrations of surface species.

Carroll *et al.* (2002) combined nuclear magnetic resonance (NMR) spectroscopy and surface complexation modeling to evaluate amorphous silica reactivity as a function of solution pH and reaction affinity in NaCl and CsCl solutions. The NMR studies suggested that changes in surface speciation are driven by pH and to a lesser extent alkali concentrations, and not by reaction time or the saturation state. Basically, the silica-water interface consists of silanol (Si-OH) complexes that deprotonate to form negatively charged complexes with increasing pH and increasing ionic strength. Thus, cation adsorption is favored with increasing pH. Positively charged complexes from adsorption of protons to silanol sites are negligible over the normal pH range. Reactions (1) and (2) proceed in the absence of any salt, and in the presence of NaCl, respectively (Carroll *et al.*, 2002):



$$K_{\equiv \text{SiO}^-} = \frac{[\equiv \text{SiO}^-][\text{H}^+]}{[\equiv \text{SiOH}]} * 10^{-\left(\frac{F\psi_o}{2.303RT}\right)} \quad \text{Log K} = -7.5 \pm 1$$



$$K_{\equiv SiO^- Na^+} = \frac{[\equiv SiO^- Na^+]\{H^+\}}{[\equiv SiOH]\{Na\}} * 10^{-\left(\frac{F(\psi_B - \psi_o)}{2.303 R_g T}\right)} \quad \text{Log K} = -6.5 \pm 0.4$$

where,

$$\sigma_o = C_1(\psi_o - \psi_\beta), \text{ for reaction (1)}$$

$$\sigma_o = \frac{F}{A}(-[\equiv SiO^-] - [\equiv SiO^- Na^+]), \text{ for reaction (2)}$$

$$\sigma_d = C_2(\psi_d - \psi_\beta)$$

$$\sigma_\beta = \frac{F}{A}(-[\equiv SiO^- Na^+])$$

$$\sigma_o + \sigma_\beta + \sigma_d = 0$$

$$[\equiv SiOH]_{T,pH} = [\equiv SiOH] + [\equiv SiO^-] + [\equiv SiO^- Na^+]$$

{ } = activity of the aqueous species

[] = concentration of surface species

F= Faraday constant

R_g= Ideal gas constant

T=Temperature

_o = Electrical potential for the O-plane (O-plane is the surface)

_β = Electrical potential for the β-plane (β-plane is a plane proposed in Triple Layer Models)

_d = Electrical potential for the diffuse plane

C₁= Inner layer capacitance

C₂= Outer layer capacitance

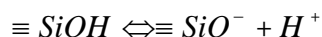
σ = Surface charge

Note that all nomenclature is collected in Appendix A.

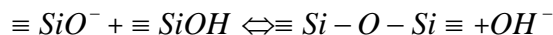
The Na and Cs NMR results show that the cations form outer sphere surface complexes and that the concentration of these complexes increases with increasing pH due to electrostatic attractions.

NMR studies have also shown that the concentration of silanol sites may polymerize to form siloxane bonds (Si-O-Si) with increasing pH. Mechanistically, polymerization is promoted by the deprotonation of $\equiv SiOH$ complexes to form siloxane bonds at the silica-water surface, yielding a net reaction that does not generate or consume protons (Iler, 1979). Polymerization, as stated before, is independent of solution pH and it is a function of silica solution concentration.

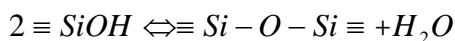
Deprotonation reaction:



Polymerization reaction:



Net Reaction:



2.3.5 SILICA CHEMISTRY INVOLVING METAL IONS

Silica interactions with the surface hydroxyl groups and metal ions affect its solubility, making that solubility difficult to predict. A study made by Badruk *et al.* (2001) showed that the electrolytic constituents in solution can notably decrease silica solubility. Metal ions can react with or adsorb on solid silicates, monomeric silica, and polymeric silica. The compounds formed by monovalent ions and silica are not a concern as they are quite soluble (*e.g.*, sodium and

potassium silicates). However, multivalent metal ions catalyze silica precipitation reactions.

The intensity of the interactions presents the following trend for silica precipitation (Sjoberg, 1996):



The number of charged sites on the silica surface is small at pH 5 and zero at pH 2, yet the surface adsorbs certain polyvalent cations very strongly at low pH, such as iron and aluminum (Iler, 1979). However, the mixture of silica and different salts makes the prediction more difficult, since the type of silica and salts present may allow the precipitation to take place at the pH at which the metal hydroxide would be precipitated.

Silica chemistry: divalent ions

Although the mechanism for silica removal with magnesium hydroxide has not been proven, it is thought to be a process in which the silica, either as a molecular acid or as the silicate ion, is adsorbed on the surface of the floc and/or a magnesium-silicate compound is formed (Knight, 1981). As stated before, above pH 9, the monosilicic acid increasingly dissociates into the bisilicate anions ($\text{SiO}(\text{OH})_3^-$, $\text{pK}=9.47$ and $\text{SiO}_2(\text{OH})_2^{-2}$, $\text{pK}=12.65$) and polysilicates.

Therefore, alkaline environments favor the formation of silicate ions, which react with the metal ions and form insoluble metal silicates.

In waters with calcium and magnesium (and many Texas waters have high concentrations of these metals), it is thermodynamically possible for silica to form such solids as tremolite ($2\text{CaO}\cdot 5\text{MgO}\cdot 8\text{SiO}_2\cdot \text{H}_2\text{O}$), forsterite ($2\text{MgO}\cdot \text{SiO}_2$), and several others.

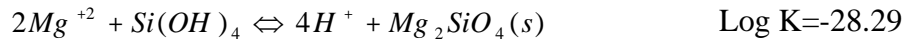
Magnesium precipitation is greatly increased at a pH of approximately 10.0 (below the pH where $\text{Mg}(\text{OH})_2$ precipitates) when additional silica is added to the water. This behavior is an indication of a magnesium silicate precipitation. However, very little is now known about these precipitates and how one might use them to control silica concentrations.

Observations made by Trofe (1985) tend to support a chemical reaction mechanism for the removal of silica in softeners. Formation of a magnesium-silicate-hydroxide solid of the general form $\text{Mg}(\text{SiO}_4)_x(\text{OH})_{2-x}$ was postulated. The composition of the precipitated magnesium-silicate-hydroxide is dependent on the relative concentrations of those species in the solution. This theory goes in opposition to more conventional precipitation mechanisms where solids are formed based on fixed stoichiometric ratios of the constituents, as occurs, for instance, with calcium carbonate. The presence of these solids and their composition is a function of the softener operating conditions and solution composition. Different studies have shown that the efficiency of magnesium for removing silica increases as silica concentration increases. Reported thermochemical constants for the different reactions of silica were compiled for this research as shown below (Bard, 1985; Cox 1989; NIST Critical Stability Constants of Metal Complexes Database, 1997; Dietzel, 1998; Nordstrom, 1990; Sillen, 1971 and Mineql®, 1999). Possible magnesium silicate compounds that can be formed are presented in Table 2.5.

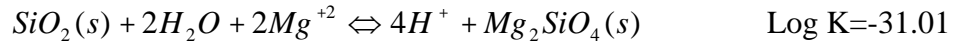
Table 2.5 Magnesium-Silicate Chemical Reactions

Species	Reaction	Log K
Forsterite	$2Mg^{+2} + Si(OH)_4 \Leftrightarrow 4H^+ + Mg_2SiO_4(s)$	-28.29
Sepiolite	$2Mg^{+2} + 3Si(OH)_4 \Leftrightarrow$ $0.5H_2O + 4H^+ + Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O(s)$	-15.76
Sepiolite (A)	$2Mg^{+2} + 3Si(OH)_4 \Leftrightarrow$ $0.5H_2O + 4H^+ + Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O(s)$	-18.78
Talc	$3Mg^{+2} + 4Si(OH)_4 \Leftrightarrow$ $4H_2O + 6H^+ + Mg_3Si_4O_{7.0}(OH)_2(s)$	-23.05
Clinoenstite	$Mg^{+2} + Si(OH)_4 \Leftrightarrow H_2O + 2H^+ + MgSiO_3(s)$	-11.33
Chrysotile	$H_2O + 3Mg^{+2} + 2Si(OH)_4 \Leftrightarrow$ $6H^+ + Mg_3Si_2O_5(OH)_4(s)$	-32.20

To plot these equations on a pC-pH diagram requires that all the reactions be expressed in terms of the concentrations of the silicate formed, H^+ , Mg^{+2} and $SiO_2(s)$. The equations must be rearranged so that each species is in equilibrium with $SiO_2(s)$. For example, to obtain the line corresponding to forsterite on a pC-pH diagram, the forsterite reaction must be combined with equation (3), as follows.



By adding the previous equations, the reaction of forsterite, Mg_2SiO_4 , in equilibrium with the solid, $SiO_2(s)$, is obtained. The next equation shows this equilibrium.



$$\frac{[\text{Forsterite}] * [\text{H}^+]^4}{[\text{SiO}_2(s)] * [\text{H}_2\text{O}]^2 * [\text{Mg}^{+2}]^2} = 10^{-31.01}$$

From the previous equilibrium equation, and assuming that the activity of the water and the solid, $\text{SiO}_2(s)$, is the unity, the forsterite line of a pC-pH diagram is obtained.

$$\log[\text{Forsterite}] = -31.012 + 2\log[\text{Mg}^{+2}] + 4\text{pH}$$

Calcium silicates are also likely to form under certain conditions. Silica-calcium reactions along with the equilibrium constants corresponding to each reaction are presented in Table 2.6.

Table 2.6 Calcium-Silicate Chemical Reactions

Species	Reaction	Log K
Ca₃SiO	$3\text{Ca}^{+2} + \text{Si}(\text{OH})_4 + \text{H}_2\text{O} \rightleftharpoons 6\text{H}^+ + \text{Ca}_3\text{SiO}_5(s)$	-73.86
Wollastonite	$\text{Ca}^{+2} + \text{Si}(\text{OH})_4 \rightleftharpoons \text{H}_2\text{O} + 2\text{H}^+ + \text{CaSiO}_3(s)$	-12.99
p-Wollastonite	$\text{Ca}^{+2} + \text{Si}(\text{OH})_4 \rightleftharpoons \text{H}_2\text{O} + 2\text{H}^+ + \text{CaSiO}_3(s)$	-13.84
Larnite	$2\text{Ca}^{+2} + \text{Si}(\text{OH})_4 \rightleftharpoons 4\text{H}^+ + \text{Ca}_2\text{SiO}_4(s)$	-39.14
Ca-Olivine	$2\text{Ca}^{+2} + \text{Si}(\text{OH})_4 \rightleftharpoons 4\text{H}^+ + \text{Ca}_2\text{SiO}_4(s)$	-37.64

Interactions of silica with both magnesium and calcium ions may also occur. The chemistry of these interactions is presented in Table 2.7.

Table 2.7 Calcium-Magnesium-Silicate Chemical Reactions

Species	Reaction	Log K
Akermanite	$2Ca^{+2} + Mg^{+2} + 2Si(OH)_4 \Leftrightarrow H_2O + 6H^+ + Ca_2MgSi_2O_7(s)$	-47.47
Tremolite	$2Ca^{+2} + 5Mg^{+2} + 8Si(OH)_4 \Leftrightarrow 8H_2O + 14H^+ + Ca_2Mg_5Si_8O_{22}(OH)_2(s)$	-56.54
Merwinite	$3Ca^{+2} + Mg^{+2} + 2Si(OH)_4 \Leftrightarrow 8H^+ + Ca_3MgSi_2O_8(s)$	-68.54
Monticellite	$Ca^{+2} + Mg^{+2} + Si(OH)_4 \Leftrightarrow 4H^+ + CaMgSi_2O_4(s)$	-30.27

Silica chemistry: trivalent ions

Precipitates with aluminum, iron, or both are thermodynamically possible, although little is known about these interactions. It is believed that the tendency of silica to complex trivalent ions is due to the high charge densities of the trivalent ions (*i.e.*, small size yet high charges). Unlike most of the metal ions, aluminum and iron present interactions with silica in the range of pH 4 to 8 (Mickley, 1981).

Aluminum-Silica Chemistry

Aluminum atoms can substitute for silicon in the colloidal silica structure (Okamoto *et al.*, 1996). The difference in valence (+3 vs. +4) creates negatively charged groups. The negative charge created by the different valences of Al and Si must be compensated by hydrogen ions or other cations; this produces

aluminosilicate compounds. The solubility of the Si-O-Si bond in the mineral solution depends on the kind of metallic ions adjacent in the silicate lattice. The solubility increases in the order $K < Na < Ca < Mg$.

Sugita (1999) showed that the presence of aluminum and silica in geothermal brines formed aluminosilicates ($xAl(OH)_3 \cdot ySiO_2 \cdot nH_2O$). Silica–aluminum chemistry is complex and many reactions may proceed. Table 2.8 is a compilation of these reactions.

Table 2.8 Aluminum-Silicate Chemical Reactions

Species	Reaction	Log K
Anorthite	$2Al^{+3} + Ca^{+2} + 2Si(OH)_4 \Leftrightarrow$ $8H^+ + Al_2CaSi_2O_8(s)$	-25.43
Laumontite	$2Al^{+3} + Ca^{+2} + 4Si(OH)_4 \Leftrightarrow$ $8H^+ + Al_2CaSi_4O_8(OH)_8(s)$	-14.46
Phlogopite	$2Al^{+3} + K^+ + 3Mg^{+2} + 3Si(OH)_4 \Leftrightarrow$ $10H^+ + AlKMg_3Si_3O_{10}(OH)_2(s)$	-66.3
Kalsilite	$Al^{+3} + K^+ + Si(OH)_4 \Leftrightarrow$ $4H^+ + AlKSiO_4(s)$	-12.83
Muscovite	$3Al^{+3} + K^+ + 3Si(OH)_4 \Leftrightarrow$ $10H^+ + Al_3KSi_3O_{10}(OH)_2(s)$	-12.99
Nepheline	$Al^{+3} + Na^{+1} + Si(OH)_4 \Leftrightarrow$ $4H^+ + AlNaSiO_4(s)$	-14.21
Ca-Nontronite	$0.33Al^{+3} + 0.17Ca^{+2} + 2Fe^{+3} + 3.67Si(OH)_4 \Leftrightarrow$ $2.68H_2O + 7.32H^+ +$ $Al_{0.33}Ca_{0.17}Fe_2Si_{3.67}(OH)_2(s)$	20.88
Leonhardite	$4Al^{+3} + 2Ca^{+2} + 8Si(OH)_4 \Leftrightarrow$ $H_2O + 16H^+ + Al_4Ca_2Si_8O_{17}(OH)_{14}(s)$	-16.49
Wairakite	$2Al^{+3} + Ca^{+2} + 4Si(OH)_4 \Leftrightarrow$ $2H_2O + 8H^+ + 1Al_2CaSi_4O_8(OH)_6(s)$	-18.87

Table continues on next page.

Table continued.

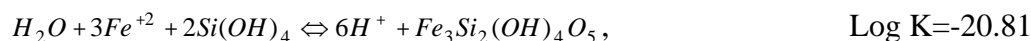
Gehlenite	$3H_2O + 2Al^{+3} + 2Ca^{+2} + Si(OH)_4 \Leftrightarrow$ $10H^+ + Al_2Ca_2SiO_7(s)$	- 56.82
Mg-Nontronite	$0.33Al^{+3} + 2Fe^{+3} + 0.17Mg^{+2} + 3.67Si(OH)_4 \Leftrightarrow$ $2.68H_2O + 7.32H^+ +$ $1Al_{0.33}Fe_2Mg_{0.17}Si_{3.67}(OH)_2(s)$	20.58
Montmorillonite	$1.71Al^{+3} + 0.22Fe^{+3} + 0.49Mg^{+2} + 3.81Si(OH)_4 \Leftrightarrow$ $3.24H_2O + 6.76H^+ +$ $Al_{1.71}Fe_{0.22}Mg_{0.49}Si_{3.81}O_{6.76}(OH)_2(s)$	-2.67
Na-Nontronite	$0.33Al^{+3} + 2Fe^{+3} + 0.33Na^+ + 3.67Si(OH)_4 \Leftrightarrow$ $2.68H_2O + 7.32H^+ +$ $Al_{0.33}Fe_2Na_{0.33}Si_{3.67}(OH)_2(s)$	14.50
Leucite	$Al^{+3} + K^+ + 2Si(OH)_4 \Leftrightarrow$ $2H_2O + 4H^+ + AlKSi_2O_6(s)$	-6.42
Microcline	$Al^{+3} + K^+ + 3Si(OH)_4 \Leftrightarrow$ $4H_2O + 4H^+ + AlKSi_3O_8(s)$	-0.61
Sanidine	$Al^{+3} + K^+ + 3Si(OH)_4 \Leftrightarrow$ $4H_2O + 4H^+ + AlKSi_3O_8(s)$	-1.06
Low Albite	$Al^{+3} + Na^+ + 3Si(OH)_4 \Leftrightarrow$ $4H_2O + 4H^+ + AlNaSi_3O_8(s)$	-2.59
Analbite	$Al^{+3} + Na^+ + 3Si(OH)_4 \Leftrightarrow$ $4H_2O + 4H^+ + AlNaSi_3O_8(s)$	-3.50
Analcime	$Al^{+3} + Na^+ + 2Si(OH)_4 \Leftrightarrow$ $H_2O + 4H^+ + AlNaSi_2O_5(OH)_2(s)$	-6.72
Pyrophyllite	$2Al^{+3} + 4Si(OH)_4 \Leftrightarrow$ $4H_2O + 6H^+ + Al_2Si_4O_{10}(OH)_2(s)$	1.59
Halloysite	$H_2O + 2Al^{+3} + 2Si(OH)_4 \Leftrightarrow$ $6H^+ + Al_2Si_2O_5(OH)_4(s)$	-9.57
Kaolinite	$H_2O + 2Al^{+3} + 2Si(OH)_4 \Leftrightarrow$ $6H^+ + Al_2Si_2O_5(OH)_4(s)$	-7.43

Iron-Silica Chemistry

Ferrous (II) and ferric iron (III) have a strong tendency to react with silica through the addition of lime or sodium hydroxide to a pH of minimum solubility. Silica may interact with iron in two ways: (1) precipitation as an iron silicate and (2) adsorbed to the $\text{Fe}(\text{OH})_3$ surface.

(1) Precipitation as an Iron Silicate

Gallup (1998) showed that iron silicate is less soluble than aluminum silicate, which in turn is less soluble than amorphous silica. Both ferrous, Fe^{+2} , and ferric, Fe^{+3} , ions in brine may react with silicic acid to form precipitates. Ferric ion has been shown to be the more reactive form of iron in the silica precipitation reaction, and ferric silicate is less soluble than ferrous silicate (Gallup 1998). The reaction of ferrous iron with silica has been reported as follows.



The mechanism of removal is thought to be hydrolyzed iron species reacting with silica monomers to form a salt where iron is integrally incorporated in the precipitate structure. However, the exact mechanism by which silica is removed by the hydroxides is not sufficiently clear. The amount of hydroxide required for removing silica increases with silica concentration, but not in direct proportion.

(2) Iron Adsorption

Adsorption is a possibility for treatment of silica. Iron is known to adsorb onto amorphous silica, and the reverse is also true—that soluble silica can adsorb onto ferric hydroxide (Anderson and Benjamin, 1985). Further, adsorption onto preformed iron hydroxides (*e.g.*, ferrihydrite) also has been demonstrated as a side effect (competition) during arsenic treatment.

Fe-O-OH phases have high specific surface areas and a high reactivity with respect to dissolved components, including silicic acid. This affinity is documented, for example, by the relatively high silica content of many sedimentary iron ores. Different ferrous solids, such as goethite, lepidocrocite, hematite, magnetite and ferrihydrite, may present interactions with silica compounds.

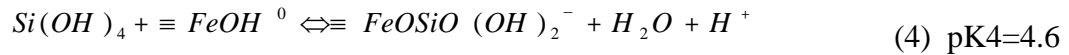
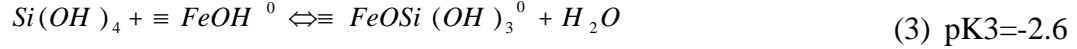
The adsorption of H_4SiO_4 onto ferrihydrite was determined as a function of pH with a wide range of silicic acid and iron, $\text{Si/Fe}=0.26\text{-}1.8$ (Swedlund, 1999). Maximum adsorption occurred between pH 8 and 10 and the percentage of silicic acid adsorbed increased with decreasing Si (Total)/Fe. The interaction between the acid and the ferric solid involves both adsorption and polymerization.

In experiments done by Dietzel (1998), the concentration of silicic acid decreased continuously as a function of reaction time via adsorption at the surface of the ferrous solid, following a first order law. Three stages could be distinguished. The first stage is finished within some minutes, the second one within hours, and the third one within about 15 days. The values of the reaction rate constants are similar for all the above iron oxides.

The adsorption equilibrium may be described by the interaction of silicic acid with surface hydroxyl groups and the formation of specific surface complexes. In a simple approach, three different kinds of surface hydroxyl groups may be distinguished according to the reactions shown below (Dietzel, 1998). For the compound studied, goethite, the following constants were obtained.



Following this approach the adsorption of silicic acid onto the surface of iron oxides may be described by a surface complexation according to the following reactions (Dietzel, 1998):



The incorporation of silica into the solids, essentially ferrihydrite, results in Si/Fe ratios of the iron oxides of about 0.13. According to these studies, it may be concluded that the silica content of sedimentary iron oxide ores is directly related to the adsorption of silicic acid onto the primary precipitates via the formation of the above surface complexes (Dietzel, 1998).

2.4 REVERSE OSMOSIS SYSTEM

Membrane filtration plays an increasingly important role as a unit operation for resource recovery, pollution prevention, separation applications and water quality control. The expansion of membrane applications reflect improvements in the underlying technology, a more competitive market, a more demanding regulatory environment, a broader range of membrane processes and the availability of materials from which they can be fabricated (Wiesner, 1999).

Membrane filtration is the separation of the components of a pressurized fluid effected by polymeric or inorganic membranes. There are four commonly accepted categories of pressure-driven membranes. The classification is based on the size of the material they are capable of removing from the feed stream. From the smallest to largest pore size, these are reverse osmosis, nanofiltration, ultrafiltration, and microfiltration.

Natural osmosis is the process by which living beings can absorb pure water from the environment. It occurs when solutions with two different concentrations are separated by a semi-permeable membrane. When the system is set, a fundamental scientific principle comes into play: the liquids try to reach equilibrium (*i.e.*, the same concentration of contaminants) on both sides of the membrane. Thus, pure water passes through the membrane to the salt water side in an attempt to dilute the salt solution. This attempt to reach equilibrium is called osmosis.

Reverse osmosis (RO) is the reversal of the natural flow of osmosis in order to separate pure water from the salt and other contaminants. RO systems are

able to provide water with the more stringent requirements to several different types of industries, such as pharmaceuticals, electronics, medical, food and beverages, cosmetics and many others.

The reverse osmosis system operates in the crossflow design, that is, the feed water runs parallel to the membrane and it is separated into two effluent streams: permeate and concentrate. Permeate is the fraction that has passed through the semi-permeable membrane while the concentrate (or reject stream) is the stream that carries the solutes and suspended solids. Hydraulic pressure is applied to the concentrated side of the stream, allowing water to diffuse through the membrane pores, rejecting practically all particles, bacteria and inorganic and organic compounds. Reverse osmosis membranes effect filtration with chemical-physical rejection mechanisms (rejection of particles and molecules depends upon their size and charge). The greater the charge and the size, the greater the rejection.

The membrane pore sizes range from 5 to 15 angstroms, effecting separation of the solute down to 150 molecular weight and often lower. On the size range, RO is effective for removing compounds in between 0.0001 to 0.1 microns. With respect to the particles charges, RO membranes reject nearly all (>99%) strongly ionized polyvalent salts and only around 95% of the weakly ionized monovalent salts. Neutral compounds are rejected on the basis of their size (typical percentage of rejection is approximately 95%). The reject ratio changes over the life of the membrane. Each time a membrane is cleaned its properties slightly change. After years of operation, the ability to reject some compounds or elements may drop to such a level that it is necessary to replace it. The basic

reverse osmosis system is shown in Figure 2.2 (Filmtec Membrane Technical Manual, 2002).

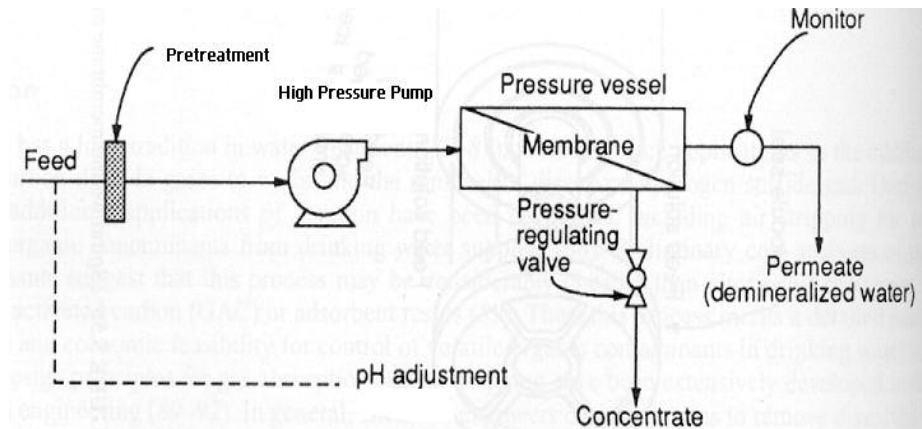


Figure 2.2 Diagram of a Reverse Osmosis System

2.4.1 REVERSE OSMOSIS SYSTEM PERFORMANCE

A reverse osmosis system must be well maintained to ensure reliable performance meeting the water quality required with the lowest capital and operating costs. The performance of an RO system is influenced mainly by six factors (1) feed water quality, (2) level of recovery, (3) pressure, (4) temperature, (5) pH and (6) membrane characteristics (material and configuration). The performance of the system is mainly evaluated through two categories: permeate flux (or filtrate flux) and permeate quality (degree of rejection). These characteristics that affect or describe performance are described below.

(1) Feed water quality

The quality of the feed water is the single most important factor to be considered in ensuring the technical and economic viability of a membrane plant (Gabelich, 2002). Feed water, depending on the source, can contain different concentrations of suspended matter and dissolved solids. On a reverse osmosis system, as water passes through the membranes, the volume on the concentrate channel decreases, and the concentration of suspended and dissolved particles increases. As materials accumulate near, on, and within the membranes, they usually reduce the permeability of the membrane to the water flow by blocking the pores. Therefore, the feed water must undergo adequate pretreatment to ensure the process of material accumulation on the membranes is delayed as much as it is technically and economically possible.

(2) Recovery Level

Reactive silica and colloidal silica concentrations increase on the feed stream of a reverse osmosis unit as water diffuses through the membranes to the permeate side. Along with the silica, all other ion concentrations also increase. To delay precipitation (scaling) and accumulation (fouling) of ions and other compounds on the membrane surface, only a percentage of the feed is collected as permeate. The recovery level of the RO unit is the ratio of the permeate flow to the feed flow, as follows:

$$\text{Recovery Level} = \frac{Q_{\text{permeate}}}{Q_{\text{feed}}} * 100$$

The concentration of the reject stream increases dramatic as the percentage of recovery increases. Figure 2.3 shows the concentration factor as a function of the percentage of recovery.

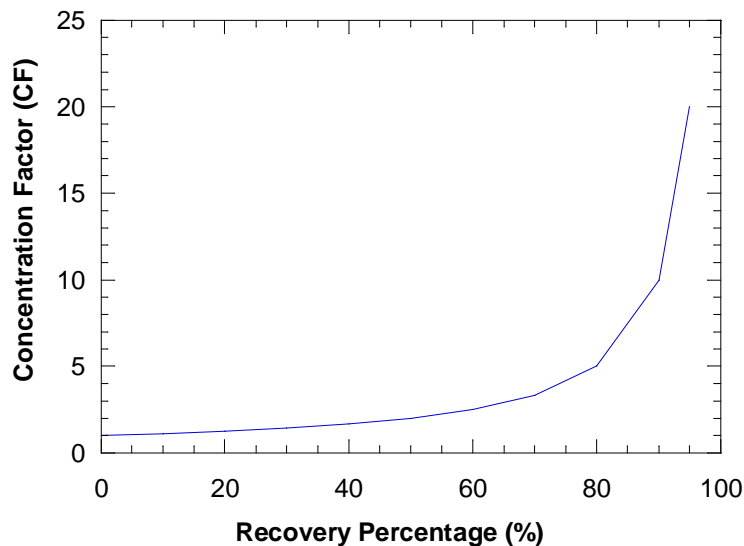


Figure 2.3 Concentration Factor of Reject Stream as a Function of Recovery

An adequate recovery level is dependent on membrane material and geometry, feed water composition and cleaning procedures. The amount of water that can be recovered from the influent stream is one of the main factors that determine the economic viability of a reverse osmosis system. Though it would seem that a high a recovery is the best option, a balance has to be established. At high recovery levels, scaling and fouling are more likely to occur and the permeate quality becomes poorer. The challenge in the desalting of water by RO units is to increase the recovery by retarding the processes of scaling and fouling, without increasing the burden of chemicals added.

The concentration factor (CF) is described as the ratio of the concentration of the concentrate stream (C_c) and the concentration of the feed stream (C_f):

$$CF = \frac{C_c}{C_f}$$

The CF is a function of the recovery level (R) of the RO unit and the membrane rejection (Y) for the ion or compound, as follows,

$$CF = \frac{1}{1 - R * Y}$$

(3) Pressure

The pressure required is dependent on the concentration of the salt solution on the reject side of the membrane. The higher the concentration of the reject stream, the higher the osmotic pressure that has to be overcome. Reverse osmosis membranes are typically operated from 700 to 7000 kPa. At high operating pressure conditions, membranes may undergo mechanical compression (or compaction). The result of this compaction is an irreversible loss of permeate rate, so it is not recommended to work near the higher theoretical pressure limits.

(4) Temperature

Crossflow membrane separations are currently operated at a temperature range from 0 to 85 °C. Membrane cleaning can occur at 110 °C and even higher. The operating pressure decreases 4% for each increment of 1 °C on the feed water, but it is often uneconomical to raise the temperature of the influent water.

(5) pH

Basic solutions represent a problem for cellulose acetate membranes since the rate of hydrolysis increases exponentially with increasing pH values. The accepted pH range for cellulose membranes is 2 to 8, although higher or lower values are acceptable if the economics of the application allow more frequent membrane replacement. Polyamide type membranes generally stand pH up to 12.

(6) Membrane Material and Configuration

The type of membrane that best fits the specific situation depends upon the characteristics of the feed water, since no polymer and configuration can withstand the environments of all possible water recovery applications.

Membranes are manufactured from cellulose acetate (CA), aromatic polyamide (PA) or polyamide thin-film composites (TFC). A polymeric membrane generates charges and leads to an electric potential near the surface when it is in contact with an electrolyte solution. Each polymeric membrane contains ion groups (such as $-\text{SO}_3^-$) or ionizable functional groups ($-\text{NH}_2$ and $-\text{COOH}$). These groups present certain charges under specific conditions of the solution. The surface tends to be positive at low pH and negative at high pH values. The points of zero charge of most membranes occur between pH 3 and pH 5.5. Thus, membrane surfaces have negative charges in natural waters. Colloids with negative charges tend to be repelled from the membranes, although other mechanisms are responsible for fouling and attachment of these colloids to the membrane surfaces.

The configuration has to be set in a way that produces a compact module (a high surface area for water passage per unit of volume), avoids leaks between

the feed and the permeate compartments, presents ease of cleaning and ease of assembly and disassembly. Membrane material can be spiral-wound around a tube, or hollow fibers can be bundled together, providing a very high surface area or packing density (m^2/m^3) for water treatment inside a compact cylindrical element. Spiral-wound membranes may tolerate waters with relative high concentrations of scaling salts, silica and colloidal material. Other less used configurations are tubular and plate and frame. Membranes account for 15 to 40% of the price of an RO installation. Since they must be replaced periodically, careful membrane selection is essential.

Permeate Flux

A loss of permeate flux may be due to an increase in the feed total dissolved solids (that is, an increase in the osmotic pressure that has to be overcome to permeate water through the membranes). Permeate flux may also decrease due to fouling of the membrane surface, fouling of the feed spacer, increase in the recovery rate without increasing the feed pressure and decrease in feed water temperature with no change in feed pump pressure.

Permeate Quality

A decrease in the rejection of ions and compounds, measured as an increase in permeate conductivity, may be due to fouling of the membrane surface. Permeate conductivity may also increase due to damage on the membrane surface (such as exposure to chlorine or another oxidizing chemical) which allows more salts to pass, increase in the feed TDS (since the system rejects a set percentage of the salt) and damaged seals.

2.4.2 PREDICTION OF THE PERMEATE FLUX OF A REVERSE OSMOSIS SYSTEM

Different approaches may be considered to predict the permeate flux given the operating parameters. Each theory makes the prediction of flux and particle transport based on mechanisms of transport phenomena. Mass transport mechanisms that carry potential scaling/fouling materials toward the membrane include convection (permeation drag) by applied transmembrane pressure. Transport mechanisms that carry materials away from the membrane on crossflow mode include Brownian diffusion, shear-induced diffusion, and inertial lift (Belfort *et al.* 1994). The magnitude of each mechanism in back transport is a function of particle size. The relative importance of each mechanism can be expressed as velocities. The velocities of particle transport by the Brownian diffusion, v_B , the shear induced diffusion, v_s , and the inertial lift, v_L , can be estimated as follows (Wiesner and Chellam, 1992; Wiesner and Aptel, 1996).

$$v_B = \frac{kT}{3\pi\mu R d_p} \quad v_L = \frac{u_o^2 d_p^3 \rho}{32\mu R^2} \quad v_s = 0.05 \frac{u_o d_p^2}{4R^2}$$

where k =Boltzmann constant; μ =viscosity of water; R =radius of hollow fiber or capillary membrane; d_p =particle diameter; and u_o =centerline maximum velocity.

The Brownian diffusion is inversely proportional to particle diameter whereas the shear-induced diffusion and the inertial lift are proportional to the second and third orders of particle diameter, respectively. Therefore, small particles are transported predominantly by Brownian diffusion. As particles

become bigger, the velocity by Brownian diffusion diminishes, and the velocities by shear-induced diffusion and inertial lift increase, making them the dominant transport mechanism.

Another important factor that most of the permeate flux prediction theories consider as central in modeling the performance of an RO unit is the concentration polarization (CP) phenomena. Concentration polarization refers to the development of concentration gradients close to the membrane surface. This is due to different rates of transport of various components across the membrane. CP is a detrimental phenomenon for RO membranes since it exposes the membrane surface to even higher solute concentrations than the average values of the reject stream calculated above. This high concentration layer acts to further decrease permeate flux by reduction of the pressure driving force through the increase in the counteracting osmotic pressure. The most deleterious effect of concentration polarization is that it aggravates the risk of precipitation of a sparingly soluble salt by enhancing its concentration level on the membrane surface. The concentration polarization phenomena should be taken into account when establishing the recovery level of an RO system.

The standard film theory and the thin film theory are often used. More recently, the real permeability approach was developed by Sutzkover *et al.* (2000). These theories are explained below.

Standard Film Theory

The standard theory is a derivation from Darcy's law, which makes the prediction of flux based on hydraulic resistances from the membrane and from fouling layers (Wiesner *et al.*, 1996). The theory describes the relationship between transmembrane pressure and filtrate flux.

The flux of clean water through a membrane without any scaling or fouling is:

$$J = \frac{\Delta P - \sigma_K * \Delta \pi}{\mu * R_m}$$

where J is the permeate volumetric flux, ΔP is the transmembrane pressure drop, σ_K is an empirical constant, $\Delta \pi$ is the change in osmotic pressure near the membrane, μ is the absolute viscosity of the water, and R_m is the hydraulic resistance of the clean membrane.

As material starts to accumulate over the membrane surface and pores, resistance increases over time. The reduced permeate flux is then calculated as follows,

$$J = \frac{\Delta P_{net} - \sigma_K * \Delta \pi}{\mu(R_m + R_c + R_{cp} + R_a)}$$

where R_c , R_{cp} and R_a are hydraulic resistances due to a cake layer, a concentration polarization layer, and solute adsorption in the membrane pore, respectively.

Thin Film Theory

The thin film theory is used to predict filtrate flux when the flux is limited by mass transfer of the solute and is not dependent on the pressure. The theory assumes advection and diffusion are the two mechanisms for solute transport and the permeate flux is at steady state (Chang, 1996).

The thickness of the concentration polarization layer is a function of the relative magnitude of advective flow and diffusive transport of the solutes. The mass balance in the boundary layer is expressed with the following equation:

$$J * C = J * C_p - D \frac{dC}{dx}$$

where J is the permeate flux, C is the concentration of the solute, C_p is the concentration in the permeate, D is the diffusion coefficient of the solute and dC/dx is the concentration gradient between the bulk and the surface. The boundary of the concentration polarization layer is from the edge of the bulk flow to the membrane surface. Integration of the differential equation across the boundary layer gives the following expression.

$$J = \frac{D}{\delta} * \ln\left(\frac{C_w - C_p}{C_b - C_p}\right)$$

where δ is the thickness of the concentration polarization layer, so that D/δ is a mass transfer coefficient, k . C_b , C_w and C_p are the concentrations in the bulk, at the wall and in the permeate, respectively.

Real Permeability Approach

Real permeability decline measurements are useful tools in determining silica scaling phenomena and in characterizing anti-scalant effectiveness.

Permeate flux decline may be caused by two factors: scaling and an increase in osmotic pressure due to the withdrawal of permeate. According to this theory, the shortcoming of the permeate flux decline curve is that it does not distinguish between flow decline due to scaling and flow decline due to an increase in osmotic pressure. This last effect is eliminated in the real permeability curve and the flux decline registered is caused only by scale deposition (Sutzkover, 2000).

The analysis is based on the examination of the decay in real permeability (L_p). The validity of the real permeability parameter was supported by comparison of the measured mass transfer coefficient given by developed generalized correlations in fully developed flow with expected theoretical values. The calculation of the real permeability parameter involves the following steps (Sutzkover, 2000).

1. Calculation of Reynolds number and Schmidt number

$$Sc = \frac{\mu}{\rho^* D_v}$$

S_c = Schmidt number

μ = fluid viscosity

D_v = solution diffusivity

ρ = fluid density

$$Re = \frac{\rho * v * d}{\mu}$$

Re = Reynolds number

v = velocity of fluid

d = diameter of tube

2. Calculation of the mass transfer coefficient (K_D)

$$Sh = \frac{K_D * d}{D_v} = 0.023 * Re^{0.875} * Sc^{0.25} \quad \text{for turbulent flow conditions}$$

$$Sh = \frac{K_D * d}{D_v} = 1.61 * (Re * Sc * \frac{d}{L})^{\frac{1}{3}} \quad \text{for laminar flow conditions}$$

Sh = Sherwood number

3. Calculation of the concentration polarization factor

$$CP = e^{\frac{J_v}{K_D}} = \frac{C_m - C_p}{C_f - C_p}$$

CP = concentration polarization factor

J_v = volumetric flux through the membrane

C_p = concentration of salt in the permeate stream

C_f = concentration of salt in the feed stream

C_m = concentration of salt in the membrane surface

4. Real Permeability (L_p)

In the absence of scale deposition, the permeate flux at increasing water recovery percentages should be a constant value $L_p = L_{po}$. L_{po} is the intrinsic membrane permeability of a clean, unfouled membrane.

$$L_p = \frac{J_v}{\Delta P - \pi_m} = \frac{J_v}{\Delta P - CP^* \pi_f}$$

π_m = osmotic pressure on the membrane

π_f = solution osmotic pressure

2.5 SILICA IN REVERSE OSMOSIS SYSTEMS

The presence of silica in its diverse forms in water is one of the main problems in industrial processes, since it causes many problems in boilers, pipes, turbines and membrane based processes. The conditions of the majority of the silica related studies are temperatures in the range of 60-120 °C, pH values from 3 to 9, and high silica concentrations, which represent conditions typically found in the geothermal industry. These conditions are not representative of RO systems, where ambient temperatures, pH close to neutral, and lower silica concentrations are usually found. Silica is considered to be the major unresolved scaling inorganic in membrane systems due to its very complicated chemistry, speciation and complex polymerization behavior (Koo, 2002). There are very few practical and theoretical analyses with respect to silica in membrane systems.

2.5.1 SILICA PRESENCE IN A REVERSE OSMOSIS UNIT

Each type of silica can produce problems while operating a reverse osmosis system. Monomeric or soluble silica, along with silicates, may precipitate over the membrane surface producing the phenomenon named scaling. Polymeric or colloidal silica may create gel deposits of dimers, trimers and higher level silica polymers over the membranes, a phenomenon named fouling. Even though colloidal silica may be removed by washing the membranes with a solution of phosphonated detergent, continuous cleaning procedures decrease the membrane life.

Scaling and fouling cause decline in the water production rate, reduced water product quality, unsteady-state operation conditions and serious damage to the membranes. To compensate for the decline in the water production rate, the operating pressure needs to be increased. To compensate for the lower water product quality, significantly shorter runs between cleanings have to be done. Scaling, fouling and repeated cleaning damage the membranes irreversibly. All of these possibilities cause an increase in the operating costs

The standard industry guideline establishes the maximum silica concentration in RO systems on the concentrate stream as 120 mg/L as SiO_2 at 25 °C (ASTM, Practice D4993-89). However, this standard limit varies depending on the specific conditions of the system, because silica solubility is influenced by a large number of parameters. The concentration polarization effect causes silica concentrations to be higher near the membrane surface than at the bulk of the solution, enhancing the possibility of fouling and scaling occurrence. To avoid such deposits, it is necessary to control all these processes simultaneously.

2.5.2 SCALING ON REVERSE OSMOSIS SYSTEMS

Scaling of RO membranes occurs when the concentration of the inorganic constituents of the concentrate stream exceeds saturation and precipitate as solids over the membrane surface. Scaling reduces the capacity of the membrane to reject solutes; therefore, the permeate stream is of a lesser quality, and the recovery of the product water is limited. Due to the low solubility of most scales, they are very difficult and sometimes impossible to remove. In addition, existing scales on a membrane provide nucleation sites that can decrease the effectiveness of antiscalant chemicals and increase the rate of formation of additional scales. Therefore, it is of paramount importance to slow down, as far as it is economically and technically possible, the process of scaling on membranes.

Scaling is most likely to occur in the last elements in series of an RO system, because the concentration of salts increases as water is removed through the membranes. Typical scalants are calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, and silicates. Table 2.9 indicates general guidelines for preventing scaling on RO units (Filmtec Membrane Elements Technical Manual, 1995).

Table 2.9 General Guidelines for Preventing Scaling on RO Membranes

Parameter	Value
*LSI (TDS<5,000 mg/L)	<1.0 with antiscalant <0 without antiscalant
*SDSI (TDS>5,000 mg/L)	<0.5 with antiscalant <0 without antiscalant
**Barium	<0.005 mg/L
**Strontium	<0.1 mg/L
***Silica	60-150 mg/L

*The Langelier Saturation index determines the potential for forming calcium carbonate scales. This index is usually applied to RO waters with less than 5,000 mg/L of total dissolved solids. The Stiff-Davis Saturation Index is used when the total dissolved solids exceeds 5,000 mg/L of total dissolved solids.

**Barium and strontium present a very low solubility and their sulfate scales are difficult to remove.

***The solubility of silica is a function of temperature, pH, as well as the chemical composition of the feed water.

Prediction of silica deposition is neither easy nor exact, since it depends on feed water chemistry, pH and time. As noted above, silica itself can be present in many forms and also forms magnesium silicates, alumino-silicates and other metal silicates if the concentrations of the ions exceed the solubility equilibrium product of the corresponding salts at the temperature and pH of the solution. Silica is typically one of the major constituents of scales formed on RO membranes (Kronmiller, 1994).

If conditions of polymerization are present, colloidal silica may also form. It is difficult to determine if the silica attached to a membrane is of the colloidal or molecular type.

Work done by Sheikholeslami, *et al.* (1999) has shown that scaling may occur by one or more of the following processes.

- 1) Scaling may be produced by direct deposition of monosilicic acid that reacts with a solid surface. Possible solid surfaces include a silica surface itself, metal hydroxides surfaces, colloidal matter, pre-existing scales and metal corrosion products. This form of scaling can occur even if no colloidal silica, metals, or previous scales exist. The resultant scale is non-porous and usually very difficult or impossible to remove.
- 2) Precipitation of silica with polyvalent ions, such as iron, aluminum, calcium and magnesium. Silicic acid and polysilicic acid react in the presence of metals and suitable pH to form silicates even at silica concentrations below the solubility limit of amorphous SiO_2 . Polymerization reactions in the presence of metals may also take place. Silicates form as a viscous material, but as they dehydrate, they become harder and more difficult to remove.
- 3) Polymerization of silica monomers at high concentrations may cause fouling. At low initial values of supersaturation, the polymerization reaction occurs very slowly, and the monomeric silica concentration remains almost unchanged. At higher values of supersaturation, approximately twice or more the solubility limit, the scales formed are soft and porous because the polymers (colloids) have few internal cross-links. With time, the scale becomes harder as cross-linking and dewatering occur and more monomeric silica deposits, filling the porous sections. Polymerization seems to increase with temperature, salt concentration, and

low alkaline pH values since the hydroxyl ions catalyze the reaction. The surface area of the polymers might become enough large that monomeric silica can deposit directly on the polymers, causing an increment in the colloids' size. Low amounts of polymeric silica typically found in natural waters suggest that the phenomenon of fouling due to polymerization may be less important than other scaling mechanisms in membrane systems with recoveries up to 80% (Bremere *et al.*, 2000).

2.5.3 FOULING ON REVERSE OSMOSIS SYSTEMS

A major obstacle for the widespread use of RO technology is the problem of colloidal fouling. Fouling refers to colloid accumulation of materials on the surface or within the pores of a membrane. These materials include clay minerals, silica, iron and aluminum oxides (particle fouling), microbes (biofouling) and humic acids and residual polymers (organic fouling). These materials typically foul the first elements in series of an RO system. Fouling adversely affects both the quantity (product water flux) and quality (product water concentration) of the permeate stream. It is important to identify the fouling as soon as possible, since some fouling is irreversible if not detected until an advanced stage (Huiting, *et al.*, 2001).

Silica colloidal species are thought to be monosilicic acid that has polymerized with multiple units of silicon dioxide, or monosilicic acid that has formed loose bonds with organic compounds or other inorganic constituents,

usually aluminum and calcium oxide structures (Bremere *et al.*, 2000). The polymer attaches to the membrane surface, plugging its pores and blocking the feed channel spacer. Although attached colloidal silica may be removed from RO membranes using caustic soda at pH around 11.5 or a phosphonated solution, the system efficiency decreases due to pressure drops, and consequently, the energy cost increases. Fouling also increases the cost of running the system due to time spent on the cleaning procedure and the cost of the cleaning solution. Water production also decreases due to the system shut down, and in the long run, membranes are damaged by the cleaning chemicals. Table 2.10 presents general guidelines to minimize the fouling of RO membranes (Filmtec Membrane Elements Technical Manual, 1995).

Table 2.10 General Guidelines for Preventing Fouling on RO Membranes

Parameter	Value
*SDI ₁₅	< 4
**Turbidity	< 1
***Iron	< 0.05 mg/L
***Manganese	< 0.5 mg/L
***Hydrogen Sulfide	< 0.1 mg/L
****Organics	< 10 mg/L

* Silt Density Index (SDI) is one of the most important parameters in the RO feed water. SDI indicates the level of contaminants (suspended or colloidal impurities and other foulants) in the raw water, and therefore, it represents the fouling potential of the water. It is obtained by manually measuring the reduction in filtration rate through a membrane filter with specified pore size in a 15 minute test.

**Turbidity is measured in Nephelometric Turbidity Units (NTU). Some equipment manufacturers recommend that turbidity be less than 0.2 NTU.

***Iron and manganese are considered as suspended solids, since under most operating conditions, both metals oxidize and deposit on the surface of the membranes. Hydrogen sulfide is readily oxidized, usually by oxygen or chlorine, and precipitates sulfur at the pH of typical feed water sources. Hydrogen sulfide is found almost only in well water sources.

****Feed water organic levels, measured as total organic carbon (TOC), have to be low to prevent fouling with organic molecules as well as to minimize the potential for microbial fouling, since these molecules are nutrients that support microbial growth.

Scaling and fouling processes are likely to eventually occur in any system; however, if these processes are controlled and slowed down, it is possible to achieve better system performance by maximizing membrane life and reducing operating costs.

2.6 PRETREATMENT PROCESSES

Temperature, pH, percentage of recovery, cross flow velocity conditions and feed water pretreatment are the main operational factors that control silica precipitation (scaling) and polymerization (fouling) in reverse osmosis systems. Silica increases its solubility at high temperatures (Comb, 1996). However, increasing the temperature of the feed stream may be impractical when considering the energy costs and the tolerance of some membranes to high temperatures. By increasing the water pH, amorphous silica solubility also increases. Although it is possible to process high silica waters with an elevated feed water pH, control of other ions should be carefully controlled since precipitation of other salts may occur, particularly, calcium carbonate, calcium sulfate and magnesium hydroxide. Alkaline environments also favor the formation of the silicate ion which can react with metal ions and form insoluble metal silicates. The pH values have to be controlled since membranes are susceptible to extreme pH values. Control of scaling and fouling of silica compounds has been traditionally managed by limiting the recovery level of the system. Restricting the recovery percentage is not always a good solution. If a high recovery is used in

silica bearing waters without proper pretreatment, the result could be a costly membrane cleaning operation or replacement of membranes.

Pretreatment processes help to control the chemical behavior of the feed/concentrate stream, but due to the many factors that affect silica solubility, the chemistry of these processes has not been completely understood. Techniques to minimize silica scaling and fouling of membranes include water treatment processes such as silica seeds, ion exchange units, coagulation processes, softening, and addition of chemical compounds such as commercial antiscalants and antifoulants. The selection of the technologies is feed water specific. A brief description of the methods is presented below.

Silica seeds

The use of silica seeds to adsorb silica has been extensively studied (Bremere *et al.*, 2000). The conditions of the studies are very high levels of silica concentrations typically present in geothermal brines, unlike reverse osmosis feed streams, where much lower silica concentrations are usually present. An experiment done by Bremere, *et al.* (2000) intended to remove polymeric silica by silica seeds, showed a low silica deposition rate. At concentrations of approximately 200 mg/L as Si, a reduction to approximately 150 mg/L as Si was achieved after 4 hours. At higher silica concentrations, 530 mg/L as Si, silica deposited more rapidly, but the final concentration was still too high to be fed to a RO unit. One cause of the low removal is that the surface silanol groups of the polymeric silica in water cause it to have a negative charge; therefore they remain stable in solution since the silica gel seed surface is also negatively charged. The addition of iron (III) made to subsequent studies showed a better silica removal.

Ion Exchange Unit

Reactive silica dissociates in water forming a weak acid whose slight negative charge results in an affinity to strong base anion resins and, therefore, it can be partially removed using ion exchange units. However, the colloidal silica is difficult to remove with this technique and in some cases has a negative impact on the ion exchange unit. Silica is one of the first ions to break through in the anion resins, and therefore is effectively removed only if the ion exchange resin is completely regenerated (Comb, 1996).

Commercial Chemicals

Recently, antiscalants or dispersants have been introduced to the market to allow the system to operate at higher recoveries without experiencing the problems of scaling or fouling (typically carbonate or sulfate based scales). Weng (1995) stated that dispersion of colloidal particles occurs through electrostatic repulsion and steric repulsion. Electrostatic repulsion occurs when the polymer adsorbs to the particle, increasing the negative charge and thus repelling other negatively charged particles. Steric repulsion acts when the adsorbed polymers repel each other due to osmotic effects or entropy/volume restriction effects.

Commercially available inhibitors, as Hypersperse SI 300 (Argon Scientific), claim to increase silica solubility, while cleaners as MT3100 and MT5010 (BFGoodrich) may help in restoring the flux. At the present moment, there are no specific inhibitors that can be used to prevent silica fouling/scaling (Koo *et al.*, 2001). The difficulty in inhibiting silica stems from its changeable

nature. The effectiveness of the cleaners depends on the deposit structure, but for silica, the structure differs with solution pH, presence of other ions, and the process which forms the precipitated particles.

It is important to be aware that the addition of these chemicals is not always safe as they are a potential cause of precipitation of other salts over the membranes. The discharge of membrane concentrate stream containing these chemicals may be restricted due to environmental laws.

Softening

The effectiveness of lime softeners in silica removal has been recently studied but still not fully understood (Sheikholeslami, *et al.*, 1999, Sheikholeslami, *et al.*, 2000). Softening reduces hardness and alkalinity, and it significantly reduces silica in water. Usually, in order to increase silica solubility, the pH has to be increased. However, this condition causes the precipitation of other species, especially calcium carbonate and magnesium hydroxide. Softening offers advantages as pH can be increased because of the low concentration of hardness ions. Also, the low concentration of the divalent ions may decrease the potential for silica precipitation in the concentrate stream, since these cations can serve as a precipitation nuclei. Softening may be carried out in a hot or cold environment. The addition of magnesium oxide is most often the best method in hot lime softeners (Nalco Chemical Company, 1997). Anionic polymers are used to minimize carryover after the hot softening. The use of the hot processes is not typically used in RO systems, unless heat exchangers and extra heat are available. Also, the stream has to be cooled down, to avoid damaging either the membranes

or the materials used to seal the different sheets of the RO elements. Studies are more focused on the evaluation of softening processes at ambient temperature.

Lime and/or soda ash are used to precipitate calcium and magnesium hardness in cold lime softeners. Sodium aluminate is also effective in the cold softening process. Some studies have established that magnesium oxide only increases total hardness in cold softening without significantly reducing silica (Nalco Chemical Company, 1997), even though it is the best option in hot softening processes. It is suggested that softening be followed by filtration to remove any solids prior to the membranes.

Coagulation

Some studies have considered the possibility of using a coagulation process as a silica removal treatment. The most commonly used coagulants are aluminum salts and iron salts.

The use of aluminum salts prior to reverse osmosis treatment has been shown to be problematic (Gabelich, 2002). Membrane fouling was theorized to occur through soluble aluminum reacting with silicic acid to form kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) within the RO unit. Chelating agents (as citrate at 34 mg/L and EDTA at 16 mg/L) have been tested for their efficacy in controlling aluminum silicate fouling. The results of bench scale testing demonstrated that citrate controls the formation of aluminum-silicates, although the presence of another antiscalant (as a phosphonate-based antiscalant used to control another type of scaling) may react with the aluminum despite the presence of citrate.

The risk of using a coagulant chemical should be weighed against the risk of fouling the membrane because even small amounts of metals left in the stream

may exacerbate fouling. If operating conditions are properly controlled, problems caused by coagulants can be minimized.

In summary, from the literature review it can be stated that softening, coagulation or a combination of both pretreatments may help to decrease the processes of scaling and fouling of silica in a reverse osmosis system. More studies are required in this area since very few have been carried out.

CHAPTER 3. EXPERIMENTAL METHODS AND MATHEMATICAL MODELING

3.1 OVERVIEW

The objective of this research is to investigate combinations of pretreatment and RO operational strategies that optimize the production of clean industrial process water for water quality conditions that include the presence of high silica concentrations. The objective was accomplished with a combination of experimental work and mathematical modeling.

The experimental protocol for this research was designed to simulate a pretreatment step (softening or coagulation with aluminum or iron) followed by a reverse osmosis bench-scale system to investigate effects and best conditions of pretreatment to defer the process of scaling / fouling over reverse osmosis membranes.

Different waters were considered to understand effects of the specific pretreatment on the behavior of silica bearing waters fed to membrane process. The source waters were synthetic waters with inorganic constituents only (emulating Rio Grande water composition) and natural water collected from the Rio Grande at the border area between Texas and Mexico.

In this research, efficient pretreatments were selected on the basis of lowering concentrations of silica and other common scaling and fouling ions down to levels that did not theoretically reach saturation levels once the feed water stream becomes concentrated in the reverse osmosis unit. After selection of the adequate pretreatment, the waters were pretreated and introduced to a laboratory

scale reverse osmosis unit to explore effects of the pretreatment on RO performance.

The solid phases formed at the conditions for optimal silica removal were identified by Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS). Morphological characteristics were studied with a Scanning Electron Microscope (SEM); the identification should help identify the chemical conditions required for maximum precipitation. Exact conditions for the jar tests were chosen for the specific water after preliminary experiments and after mathematical modeling using raw water chemistry.

Two types of mathematical modeling were performed and used together; equilibrium chemistry modeling to understand the driving force for precipitation at two points in the treatment scheme (pre-treatment and membrane) and a mass balance model of full-scale membrane processes to track the concentrations of all relevant species through a membrane system at steady state.

An overview of the research design is shown in Figure 3.1.

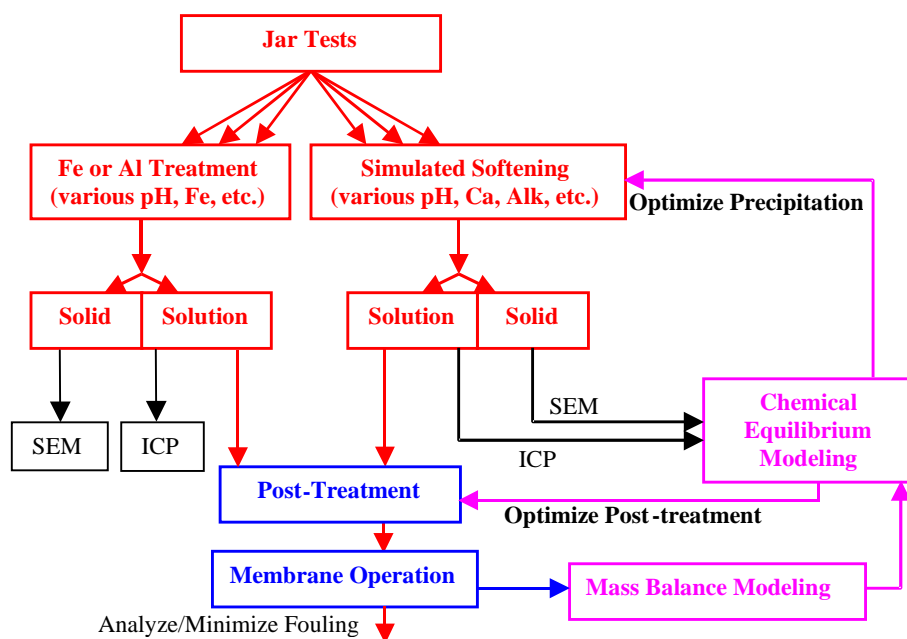


Figure 3.1 Overview of Research Design

3.2 MATERIALS

3.2.1 MEMBRANE MATERIAL

Cellulose acetate membranes have silica rejections of approximately 85 to 90%. Thin film polyamide membranes present higher silica rejections, approximately 96%. Polyamide membranes present a silica rejection of approximately 94% (Sheikholeslami and Zhou, 2000). Although thin film polyamide membranes present a higher silica rejection than polyamide membranes, they have more tendency to be fouled by silica. More often, polyamide membranes are considered a good option when treating high silica bearing waters.

3.2.2 WATERS

Different waters (synthetic and real) were considered to understand effects of the specific pretreatment on the behavior of silica-bearing waters fed to the membrane process.

Natural Water

River water, which was brought from the Laredo area in the Mexico/Texas border region, allowed the analysis of the effectiveness of the previously selected silica removal treatments. Untreated water from the river was treated in the university laboratory under the best silica removal conditions (to emulate an industry taking raw water directly from the river or a changed operation of a municipal plant to achieve silica removal in the central plant).

To characterize natural waters, analyses on calcium, magnesium, silica, iron and aluminum concentrations were carried out. Also, pH and alkalinity were measured.

Synthetic Water

Synthetic waters allow investigation of the effects of specific components that might cause silica precipitation. This water contained only inorganic constituents to avoid organic material interference. The water resembles the concentrations of inorganic constituents of Rio Grande waters. The calculation of concentrations of each constituent is shown in Table 3.1.

Table 3.1 Calculations for each Constituent Concentration in Synthetic Water

Constituent	Calculation
Si^{+4}	$4 \text{ meq/L} = 1 \text{ mmol/L} = 28 \text{ mg Si}^{+4}/\text{L}$ $= 283 \text{ mg Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}/\text{L}$
Ca^{+2}	$3.75 \text{ meq/L} = 1.875 \text{ mmol/L} = 75 \text{ mg Ca}^{+2}/\text{L}$ $= 275.03 \text{ mg CaCl}_2 \cdot \text{H}_2\text{O}/\text{L}$
Mg^{+2}	$1.64 \text{ meq/L} = 0.82 \text{ mmol/L} = 20 \text{ mg Mg}^{+2}/\text{L}$ $= 167 \text{ mg MgCl}_2/\text{L}$
Na^{+}	$\text{Alkalinity} - (2 \cdot [\text{Ca}^{+2}] + 2 \cdot [\text{Mg}^{+2}] - [\text{Cl}^-])$

The synthetic water was used for different scenarios of softening pretreatment (lime softening, lime softening plus addition of a magnesium salt, lime softening with addition of soda ash) and coagulation pretreatments (aluminum and iron coagulation).

3.3 BATCH EXPERIMENTS: SOFTENING AND COAGULATION

Batch tests help to gain insight into the specific effects that one or more components have on silica and how they interact at different system conditions. Although the batch tests give indications of expected behavior of silica in RO systems, they do not simulate exactly the chemistry behavior of the constituents of a reverse osmosis feed water, since hydrodynamic effects, filtering and concentrating factors (concentration polarization phenomena) play an important role on the physical and chemical interactions of molecules.

Alkaline environments favor the formation of silicate ions, which react with the metal ions and form insoluble metal silicates. According to this, the treatments studied considered the addition of a base (softening) and a metal. Softening and coagulation were investigated by conducting jar tests using a six-place gang-stirrer jar tester. The jars are square (11.5 cm inside) with floating covers to prevent carbon dioxide from being dissolved into the water during tests, therefore affecting pH and precipitation of Ca^{+2} and Mg^{+2} . Jar tests were performed on one liter of water. The measured mass of each chemical was mixed with 5 mL of distilled deionized water to make a slurry in a beaker. Using a 30 mL syringe, the slurry was drawn and injected into the softening jars. Separate syringes were used for magnesium, soda ash, aluminum or iron slurries. Rapid mixing was initiated at 150 rpm and the lime and magnesium (or the coagulant) slurries were added to the six jars simultaneously. Rapid mixing continued after lime and magnesium addition for two minutes. Soda ash injection was conducted after one minute of lime addition during the rapid mixing. The rapid mixing lasted three minutes in the case of soda ash addition. After rapid mixing, each experiment had 30 minutes of slow mixing followed by 30 minutes of settling. Supernatant was drained from the jar tests using the port that is 2.2 cm from the bottom. Liquid analyses on ICP were preceded by filtration through 0.22 μm filter. Solids were collected and air-dried. Analyses in electronic microscopes (SEM, EDS and XDS) were performed to determine the solids' composition.

The treatments studied included the addition of different bases. Since silica-magnesium compounds and silica-magnesium-calcium compounds are the most likely precipitates from a viewpoint of thermodynamic stability, a magnesium salt was added. The initial treatments that were chosen to investigate

were: (1) addition of a base (lime) in a wide range of doses and (2) addition of a base (lime) followed by a magnesium salt.

Calcium carbonate starts to precipitate at the calcium concentration at which the product of calcium and carbonate ions exceeds the solubility product. Thus, with increasing addition of lime, the calcium concentration in the solution decreases until the carbonate ion is exhausted. Further addition of lime, after the dose that yields the minimum calcium concentration, increases the calcium in the solution. Silica precipitation as a silicate compound or silica adsorption onto $\text{Mg}(\text{OH})_2$ solids usually occurs at a high pH (>10.5). Thus, it is likely that the required lime to induce silica removal would produce high calcium concentrations for the conditions of the waters studied. The addition of sodium carbonate, to supply the carbonate necessary to react with calcium to precipitate calcium carbonate was studied. Thus, the third softening treatment was the addition of two bases (lime and sodium carbonate) followed by a magnesium salt.

Although addition of sodium hydroxide for pH increase is expensive, this compound was considered since lime addition increased calcium concentrations to high values. The effect of calcium carbonate precipitation on silica removal was also analyzed by comparison of the results of sodium hydroxide experiments with results given by lime and sodium carbonate addition. Thus the fourth softening treatment was the addition of two bases (lime and sodium hydroxide) followed by a magnesium salt.

Precipitates of silica with aluminum, iron, or both are also thermodynamically possible, although little is known about these interactions. Unlike most of the metal ions, aluminum and iron present interactions with silica in the range of pH 4 to 8. Therefore, addition of different bases (or no addition of

a base) was studied for each metal. The bigger particles formed by coagulation enhance the mass transport away from the membrane, *i.e.*, the back transport mechanism in crossflow operation. The back transport velocities reduce accumulation of particles near the membrane surface. A study by Braghetta *et al.* (1997) showed that although the flux decline of pretreated water may be similar to raw water, the flux recovery by surface wash was greater with the coagulation pretreatment. The results implied that aggregating fine particles increased the possibility of removing them from the membrane surface.

Different aluminum salts (aluminum sulfate and aluminum chloride) were studied to establish if the corresponding anions have any effect on the removal of silica. The aluminum treatments that were tested are: (1) addition of an aluminum salt followed by sodium bicarbonate, (2) addition of an aluminum salt followed by sodium carbonate, and (3) addition of an aluminum salt followed by calcium hydroxide. The iron treatments that were tested are addition of an iron salt with adjustment of feed water to different initial pH values.

To assess the scaling and fouling propensity of water, it is not sufficient to monitor only the concentration and level of saturation of the main foulant in the feed water of a RO unit (silica in this case). The presence and interactive effects of other feed constituents (even in minute amounts) could produce pore blockage in the membranes. Thus, the concentration of other important ions (*e.g.*, Ca^{+2} , Mg^{+2} , Al^{+3} , Fe^{+3}) as well as silica concentrations were measured.

3.4 DYNAMIC EXPERIMENTS: REVERSE OSMOSIS UNIT

A laboratory membrane system (with flat sheet membranes) was used. Flat sheet configurations include the spiral wound design. The flat sheet configuration was selected since spiral wound design affords the best characteristics of high packing density, low cost and high pressure operation for typical RO applications. With the recent advent of specialized feed channel spacer materials, a very wide range of applications now employs the spiral design. Production of drinking water and high purity water is typically accomplished by spiral wound design (Paulson, 1990).

Following the selected pretreatment, water was fed to the reverse osmosis unit. The maximum allowed silica concentration value in the feed stream of a reverse osmosis unit (before the saturation limit for amorphous silica is reached) depends on the percentage of recovery desired for the system. The standard industry guideline establishes the maximum silica concentration in RO systems on the concentrate stream as 120 mg/L as SiO_2 at 25 °C (55.2 mg/L as Si) (ASTM, Practice D4993-89). However, this standard limit varies depending on the specific conditions of the system, because silica solubility is influenced by various parameters. For instance, certain ions present in the feed stream may interact with silica and induce its precipitation before reaching the solubility limit, as explained in Chapter 2.

Taking into account the standard industry guideline for RO units of the ASTM, 120 mg SiO_2 /L (55.2 as mg Si/L), Table 3.2 indicates the maximum silica

(mg Si/L) allowed in the feed stream as a function of the recovery established for the particular system.

Table 3.2 Maximum Silica Allowable in a Reverse Osmosis Feedstream

Recovery percentage	Concentration Factor	Maximum [Si⁺⁴] in feed water (mg/L)
50	2	27.6
67	3	18.4
75	4	13.8
80	5	11.0
83	6	9.2
88	8	6.9
90	10	5.5
95	20	2.7

3.4.1 PROCEDURE FOR RUNNING RO EXPERIMENTS

At the beginning of each test, a new membrane sheet was thoroughly cleaned with distilled water to prevent any compound, such as preservatives used by the manufacturer, to leach into the system. After rinsing with distilled deionized water, the membrane sheet was installed in the reverse osmosis system. Each experiment consisted of 3 stages.

The first stage of the experiment was the conditioning of the membrane. A sodium chloride solution was circulated for approximately 2.5 hours. The circulation of a sodium chloride solution allows one to account for variations in pore area between the membranes in the laboratory unit, *i.e.*, it tests the reproducibility of the membranes, as well as to test if the membrane is in good condition. The

concentration of the sodium chloride solution depends on the specifications given by the manufacturer for each specific membrane. According to the manufacturer, the sodium rejection for AG membranes with 2000 mg/L NaCl in the feed solution at 1550 kPa and 25 °C is 99.2%, while the rejection for AK membranes with 500 mg/L NaCl in the feed solution at 790 kPa and 25 °C is 98%. The membrane sodium rejection was determined at the end of the conditioning period measuring the sodium concentration in the collected permeate water via an Inductively Coupled Plasma Spectroscopy (ICP). The membranes that did not meet the specified requirements were discarded and a new membrane was tested. Only membranes that met the sodium specifications were used for the experiments with Rio Grande water.

Filtrate flow was recorded every 30 seconds by a Data Acquisition System (Labtech Software®). This value was converted to specific flux by dividing by the membrane area and applied transmembrane pressure as follows.

$$\bullet = \frac{V(mL)}{t(sec)} * \left(\frac{L}{1000mL} \frac{3600s}{hr} \right) / A(m^2) * P(psi) \left(\frac{100kPa}{14.5psi} \right)$$

where

\hat{J}_v = Specific volumetric permeate flux (L/m²/hr/kPa)

V= Permeate volume

A= Membrane area

P = Pressure

The second stage involved the addition of the feed solution. The procedure consisted of recycling the feed solution while continuously withdrawing the permeate water. The increasing concentration induced by permeate withdrawal progressively enhances the scaling potential. The membrane is now exposed to a recycling solution that represents a concentrate of a higher water recovery level. By repetition of this cycle of operations, the membrane is exposed for fixed periods of time to solutions of progressively increasing concentration. The objective of this type of operation is to emulate a real reverse osmosis system where there are as many as six membrane elements connected in series that are exposed to progressively increasing solution concentrations. Each membrane element is called a stage. The initial water volume in the feed tank was sufficient to prevent any minor loss of materials in a fouling layer during a total recycling period to have any measurable effect on the influent concentration.

The operational period in this research was 60 hours for each experiment. A sharp drop in membrane permeability suggests the onset of scaling and is an indicator of the limiting fractional water recovery. The concentration of Si^{+4} , Mg^{+2} and Ca^{+2} as well as pH on the feed tank water and product water were measured at different recovery levels. Membrane surface analysis, including Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscope (SEM), were conducted after the conclusion of the experimental period. The third stage of experiment involves cleaning of the membranes. The feed solution is drained and the feed tank is filled with deionized water which is pumped through for a few hours (the water temperature may be raised). If the flux is not restored, the deionized water is drained and replaced by an acid solution (in full-scale membrane plants the acid solution is typically citric acid

at pH about 3 with the solution made up with soft water). If the acid cleaning is successful, then the problem is probably inorganic. If the acid cleaning is not successful, a caustic cleaning is followed (may be caustic alone, or caustic and hypochlorite, or caustic and detergent).

If the surface wash has a negligible effect it may imply that particulate matter is mostly precipitated solids, which are difficult to remove. It may also be organic or inorganic dissolved material interacting with the membrane.

Membranes should be cleaned when the normalized product flow decreases by 10% or the pressure drop increases by 10%. Sometimes cleaning can be used as an indirect indicator of the source of fouling or scaling.

3.4.2 MEASUREMENTS ON DYNAMIC EXPERIMENTS

Two main parameters are measured to evaluate the performance of the system: specific flux behavior and quality of permeate.

Specific flux decline has been used as an indicator of scaling or fouling over the membranes. Water flux can be expressed in different ways, including (1) the specific flux and (2) the percent of the clean water specific flux or specific flux of reference solution given by manufacturer (typically a sodium chloride solution.)

(1) The specific flux is the flux divided by the applied transmembrane pressure. This normalization is valuable since water flux, *i.e.*, the water production increases with TMP. If the system is operated at a constant pressure, the decline of the specific flux is identical to that of the water flux.

(2) The clean water specific flux is the specific flux of the distilled/deionized water of a clean membrane. Each membrane sheet presents a different initial flux due to different pore densities in the various sheets, even though if they are made from the same material by the same manufacturer and has the same nominal molecular weight cut-off (MWCO). Thus, the decline of the specific flux in a certain experimental condition is monitored relative to the initial specific flux of clean water. The percent of clean water specific flux is useful to compare the flux decline behavior in different experiments based on the initial specific flux from the clean water.

$$\% \text{ of clean specific flux} = \frac{\text{Specific Flux}_{\text{at certain condition}}}{\text{Clean water specific flux}} * 100$$

3.4.3 MEMBRANE ANALYSIS

It is important to know the type and characteristics of the precipitated solids at different influent silica, calcium and magnesium concentrations, since RO performance is dependent of the type of precipitate (some of them are easier to be removed).

As stated before, SEM and spectroscopy analysis (EDS, XPS) were conducted. Images from SEM allow comparison of the surfaces of clean and fouled membranes and indicate the presence and morphological aspects (qualitatively) of foulants or scalants over membranes. EDS provides an elemental analysis of the fouling materials and determines the chemical composition of the outer membrane

layer. XPS analysis is more accurate on the metal part, because the probing depth is only few nanometers, while EDS reaches a few microns. The type and characteristics of the precipitated solids formed under different treatments influence RO performance since some solids are easier to be removed. The exact nature of the scales formed has been reported to be difficult to determine.

SEM Operation

Images of membranes are usually taken under an acceleration voltage of 5 kV, which allow magnifications of 500 to 10,000 times. In general, magnifications of the order of 500 to 1000 were used to investigate overall images of materials fouling the membranes.

The membrane sample for SEM and EDS analysis were prepared by cutting a small piece of membrane and attaching it to an aluminum mount by graphite tape, with no coating applied to the sample.

EDS Analysis

The composition of the outermost few nanometers of the membrane surface was analyzed by energy dispersive spectroscopy (EDS). EDS is useful to identify and quantify the elemental and functional groups on the membrane surface. The EDS data are given in percent weights for detected elements.

The EDS data are obtained using a LEO-SEM 1530 scanning electron microscope. The LEO 1530 is an ultra-high resolution field emission SEM utilizing the GEMINI field emission column with a thermal field emitter. The system is equipped with an Al monochromatic source (Al K α radiation at 1486.6 eV. Scans

are obtained with a step size of 1 eV and pass energy of 93.3 eV. High resolution scans may be obtained with a step size of 0.1 eV and pass energy of 11.75 eV).

XPS Analysis

The elemental composition of the solids precipitated can be quantitatively analyzed using X-ray photoelectron spectroscopy (XPS). XPS technique has been little used in analyzing membrane elements, although its benefits are important as they show the main fouling components. XPS surface analyses results have an accuracy within 10% (Sun, 2005).

The main constituents of an XPS are a vacuum chamber, an X-ray gun, a sample manipulator and an electron energy analyzer. The base pressure in the XPS ultra-high vacuum chamber is 1×10^{-10} torr. When a sample is irradiated with soft X-rays, photoelectrons are emitted from either the valence or core level. An electron from a higher level then fills the vacancy created from the emitted photoelectrons. The energy released in filling the core vacancy results in the emission of an X-ray, which is collected by a lens system and focused into an energy analyzer. The conservation of energy law allows the binding energy of the emitted photoelectron to be calculated. This binding energy of core electrons is characteristic of individual elements and thus the elements become identifiable. Results from elemental composition analysis help to determine the potential main fouling/scaling component.

3.4.4 MEMBRANE CLEANING

The third stage of the experiments involved the cleaning stage (after preconditioning of the membrane and the addition of the feed solution). Cleaning of the RO membranes is recommended when the RO unit shows evidence of fouling, prior to a long-term shutdown, or as a matter of scheduled routine maintenance (Filmtec Membrane Elements Technical Manual, 1995). Fouling characteristics that signal the need to clean are a 10-15% decrease in permeate quality and/or a 10-15% increase in pressure to maintain the same flow. Although cleaning of a membrane may restore some of the original flux, the process of cleaning presents a risk of damaging the membrane.

The feed reservoir was drained and filled with deionized water which was pumped through for a few hours. If flux was not restored, the deionized water was drained and the membranes were soaked in a cleaning solution. The selection of the proper cleaning solution depends on the fouling compounds. There are three major groups of RO membrane foulants, as explained in Chapter 3: hardness/metal oxides, colloidal/silica and alum/polymers. These potential problems can exist independently, but can also occur together resulting in a mixed fouling. These are the three most common problems that have been encountered by the operators of industrial RO systems. It is usual to have to use a number of different cleaning chemicals to achieve the optimum cleaning. The time required to clean a membrane can take from 4 to 8 hours.

The cleaning procedure may be helpful to evaluate if a chemical bonding is occurring between the scaling compounds and the membrane. Usually if the compound is deposited over the membrane (without a chemical bonding), a cleaning

procedure either with deionized water or an acidic solution restores the flux substantially, otherwise cleaning becomes very difficult.

After the cleaning period, the membranes were placed in the RO unit and the tank was again filled with deionized water. The water flux was then monitored and compared with the initial stage. If there was no improvement, a more concentrated cleaner solution was used. This stage of experiment was not carried out on one of the three membranes, since a study on fouling and scale morphology was done on one of the membranes.

Possibly, the silica scaling process may involve both metal-silicates and polymeric depositions. If the silica has polymerized in the bulk and then deposited as colloidal fouling over the membrane, cleaning of the membrane may restore the flux to almost the initial value.

Specific solutions have been recommended for polyamide membrane elements. If the material is an inorganic mineral some generic cleaning solutions that may be used are (Madaeni, 2001):

1. Phosphoric acid addition to water until a pH of 2-2.5 is reached.
2. A mixture of a 1% (by weight) solution of tetra-sodium EDTA in dechlorinated water. pH must be measured before introducing the solution into the system. The maximum allowable cleaning solution pH is 11.5.

For specifically silica-based foulants, recommended solutions for polyamide membranes are:

1. A mixture of a solution that contains 2.4% of ammonium bifluoride and 2.4 % (by weight) of citric acid. Addition of citric acid to adjust the solution's pH to 2.0-2.5 is required.

2. A tetra-sodium EDTA solution as stated in the cleaning of inorganic foulants. The clean water flux measurements after each cleaning method was intended to evaluate the efficiency of each cleaning process and hence determine the nature of the attached compounds (fouling or scaling).

3.4.5 LIQUID SAMPLE ANALYSIS

After pretreatment and solid-liquid separation, each liquid sample was characterized to determine the removal of silica and other ions. In addition, liquid samples from the membrane, *i.e.*, feed, permeate and concentrate samples were also characterized.

An Inductively Coupled Plasma (ICP) was used to measure total silica concentrations. Calcium, magnesium, aluminum and iron were also measured by means of an ICP.

Alkalinity was measured by titration with 0.01 N H_2SO_4 . pH was measured with an Orion Research Model 701A with Orion Sureflow Ross Combination pH probe.

3.4.6 MATHEMATICAL MODELING

Two mathematical approaches were used as a complement to experimental analysis: a mass balance and equilibrium chemistry modeling.

Mass Balance

To assess if a constituent is precipitating, a comparison between the real concentrations in the recycling solution and the expected theoretical values can be done. If the measured concentration in the recycling solution is lower than the expected theoretical values for a specific species, precipitation is occurring. The mass balance over a membrane is as follows,

$$Q_f C_f = Q_p C_p + Q_c C_c$$

Considering that the membrane is not perfect, it allows the passage of some materials. If Y is the rejection fraction of a certain salt, then $(1-Y)$ is the amount of salt that is allowed to pass. Therefore, the concentration of the salt in the product, C_p , is expressed as,

$$C_p = (1 - Y) * C_c$$

Substituting C_p in the mass balance,

$$Q_f * C_f = Q_p * (1 - Y) * C_c + Q_c * C_c$$

$$C_c = \frac{Q_f * C_f}{Q_p * (1 - Y) + Q_c}$$

Dividing the previous equation by Q_f and considering that $R = Q_p/Q_f$ and $Q_f = Q_p + Q_c$, the theoretical concentration of the salt in the concentrate stream is obtained:

$$C_c = C_f * \left(\frac{1}{1 - R * Y} \right)$$

where,

C_c = Concentration of the salt in the concentrate stream

C_f = Concentration of the salt in the feed stream

R = Recovery level set for the RO unit

Y = Membrane rejection for an specific salt

Chemistry Equilibrium Simulator

The equilibrium commercial program Mineql[®] is useful to understand the driving force for precipitation. Mineql[®] indicates the most likely precipitate from a viewpoint of thermodynamic stability, under the different conditions of the system.

CHAPTER 4: PRETREATMENTS FOR SILICA REMOVAL

The presentation of the results is divided into two chapters. The first chapter includes characteristics of the natural source water chosen for the study and the determination of the specific conditions of softening and coagulation pretreatments for the reverse osmosis treatment.

The two pretreatment processes for silica removal that were investigated are:

- (i) precipitation with magnesium and calcium, *i.e.*, within a softening process,
- (ii) precipitation and/or simultaneous adsorption with iron and aluminum.

The next chapter presents results of the reverse osmosis unit when either softening or coagulation is used as pretreatment.

4.1 WATER CHARACTERISTICS

Water with the characteristics of Rio Grande water (median values) was reproduced in the laboratory to analyze the influence of the specific ions studied (Si^{+4} , Ca^{+2} and Mg^{+2}) and avoid interference of other ions and particles present in natural river waters. Rio Grande water chemical composition is presented in Table 4.1.

Table 4.1 Rio Grande Water Chemical Composition

Compound	River Water (mg/L)*		River Water (mol/L)
	Range	Median	
Alkalinity	150-180	165 (as CaCO_3)	1.87×10^{-3} 8.23×10^{-4}
Calcium	50-100	75	
Magnesium		20	
Total Hardness	200-400	300 (as CaCO_3)	
pH		8.02	
Silica (center part of the basin)	50-70 (as SiO_2)	60 (as SiO_2) 28 (as Si)	1.0×10^{-3}
Silica (typical)	20-26 mg SiO_2/L	23 (as SiO_2) 11 (as Si)	3.92×10^{-4}
Silica (Mexico, most well water supplies)*	50 to 100 (as SiO_2)	75 (as SiO_2) 35 (as Si)	1.25×10^{-3}

*Data: Water and Sustainable Development in the Binational Lower Rio Grande/Rio Bravo Basin, Final Report.

4.2 PRETREATMENT MODELING ON MINEQL SOFTWARE

Theoretical analyses were run using the Mineql software. Mineql is a water equilibrium chemistry simulation program that indicates the most likely precipitate from a viewpoint of thermodynamic stability. Several reactions involving silica compounds were added to the Mineql database. Thermochemical constants for the different reactions of silica were compiled from Bard, 1985; Cox 1989; NIST Critical Stability Constants of Metal Complexes Database, 1997; Dietzel, 1998; Nordstrom, 1990; Sillen, 1971 and Mineql® Manual, 1999. The objective of running simulations in Mineql was to determine the conditions of pH and addition of different chemicals (*i.e.*, different water treatments) that theoretically reduce silica and hardness ions considerably. The results given by Mineql helped in narrowing the range of conditions tested in the laboratory.

Mineql indicates the precipitated solids at different silica, calcium, magnesium and carbonate concentrations. It is important to know the type of solids that are forming since RO performance is dependent on the type of precipitate (since some solids are easier to be removed). The exact nature of the scales formed during silica removal is difficult to determine in a real system.

The three modeling treatments done for Rio Grande water conditions were softening, aluminum treatment and iron treatment.

4.2.1 SIMULATION NO.1: SOFTENING SIMULATION OF RIO GRANDE WATER

Softening offers the advantage that pH can be elevated with the result that metal-silicates are more likely to precipitate and calcium and magnesium concentrations decrease. After softening and subsequent pH reduction, compounds such as metal-silicates, calcium carbonate, calcium sulfate or magnesium hydroxide are less likely to precipitate in the membrane system.

Simulation No.1 was done considering addition of a base (calcium hydroxide which is commonly called hydrated lime) to Rio Grande water. Two simulations were done for different river water concentrations: (1) Simulation of Rio Grande water with a silica concentration of the typical value (23 mg SiO_2/L) and (2) Simulation of Rio Grande water with a high silica concentration (60 mg SiO_2/L). The reactions that may proceed are stated in Chapter 2.

Table 4.2 shows the results for the modeling of case (1), that is, Rio Grande water with average silica concentration of 23 mg SiO_2/L (11 mg as Si/L). The pH, the solid compounds formed, and the remaining ions in the water are the results given by the modeling program. The first row of the table shows Rio Grande water without any treatment. The pH was calculated by the program based on the electroneutrality principle. At the initial pH calculated (pH=7.97), the program finds that the water is already supersaturated and precipitation of solids has already started. Thus, the initial concentrations of ions in water in the simulation are lower than the actually found in the Rio Grande. The results indicate that silica should be almost completely removed by addition of approximately 130 mg CaO/L. pH values near 9 allow the removal of silica along with low calcium and magnesium concentrations. Tremolite is the silica-containing compound that is mainly formed

under the simulation condition that lowers silica to a near zero value. Chrysotile is formed at higher pH values and it is the main silica-containing compound at pH values of 9.30 and higher. Results indicate that brucite ($\text{Mg}(\text{OH})_2$) starts forming at pH 10.5. Magnesium is removed by formation of tremolite and chrysotile, according to Mineql. Calcium is mainly removed by formation of calcite and tremolite.

Table 4.2 Softening Simulation of Rio Grande water at 23 mg SiO_2/L

TREATMENT	pH	SOLIDS					IONS IN WATER		
CaO (mg/L)		CAL (mg/L)	DOL (mg/L)	BRU (mg/L)	TRE (mg/L)	CHRY (mg/L)	TOT Si ⁺⁴ (mg/L)	TOT Ca ⁺² (mg/L)	TOT Mg ⁺² (mg/L)
0	7.97	102.0	56.6	0.0	26.4	0.0	3.7	19.4	9.9
105	8.08	120.0	59.9	0.0	30.2	0.0	2.7	17.1	8.7
113	8.22	137.0	64.5	0.0	33.4	0.0	1.8	14.6	7.5
122	8.39	155.0	70.4	0.0	36.0	0.0	1.1	12.0	6.1
130	8.63	172.0	77.4	0.0	38.0	0.0	0.5	9.2	4.7
139	8.97	189.0	85.5	0.0	39.2	0.0	0.2	6.4	3.3
147	9.29	215.0	76.9	0.0	30.8	11.9	0.1	4.8	2.4
156	9.29	256.0	39.1	0.0	7.1	44.3	0.1	4.8	2.4
164	9.73	279.0	31.1	0.0	0.0	54.3	0.0	3.6	1.8
173	10.30	294.0	29.1	0.0	0.0	54.3	0.0	3.9	2.1
181	10.50	319.0	8.4	5.7	0.0	54.3	0.0	4.5	2.5
190	10.60	330.0	0.0	10.7	0.0	54.3	0.0	7.5	1.4
198	10.80	332.0	0.0	12.4	0.0	54.3	0.0	12.8	0.6
207	11.00	332.0	0.0	12.9	0.0	54.3	0.0	18.4	0.3

*TRE=tremolite, DOL=dolomite, CAL=calcite, CHRY=chrysotile, BRU=Brucite (solid compounds).

Note: The values for total silica, total calcium and total magnesium are the ionic concentrations remaining in water.

The next modeling is case (2) Rio Grande water with average silica concentration of 60 mg SiO₂/L (28 mg as Si/L). The condition of Rio Grande River without any treatment (first row of the table) shows a slightly lower pH than previous simulation, due to a higher silica concentration. Again, the program calculates that raw water is at supersaturated conditions and the precipitation of solids already started. Table 4.3 indicates that silica should be almost completely removed by addition of approximately 150 mg CaO/L. Tremolite is the silica-containing compound that is mainly formed under the simulation conditions that removes silica almost completely. Chrysotile is formed at higher pH values (pH 9.34 and above). Magnesium is precipitated as tremolite and dolomite, while calcium is removed as calcite. Mineql indicates that calcium and magnesium ions are present in low concentrations under the conditions where silica is removed.

Table 4.3 Softening Simulation of Rio Grande water at 60 mg SiO₂/L

TREATMENT	pH	SOLIDS				IONS IN WATER		
CaO (mg/L)		CAL (mg/L)	DOL (mg/L)	TRE (mg/L)	CHRY (mg/L)	TOT Si ⁺⁴ (mg/L)	TOT Ca ⁺² (mg/L)	TOTMg ⁺² (mg/L)
0	7.68	101.0	0.0	66.3	0.0	9.7	28.2	11.6
105	7.74	119.0	0.0	71.8	0.0	8.2	26.4	10.6
113	7.81	137.0	0.0	77.2	0.0	6.7	24.4	9.7
122	7.89	156.0	0.0	82.0	0.0	5.3	22.3	8.8
130	7.99	175.0	0.0	87.6	0.0	3.9	19.9	8.0
139	8.11	196.0	0.0	91.7	0.0	2.7	17.2	7.2
147	8.27	217.0	2.9	95.8	0.0	1.6	14.1	6.6
156	8.47	237.0	10.5	98.2	0.0	0.8	11.0	5.6
164	8.74	254.0	18.8	99.8	0.0	0.4	8.2	4.2
173	9.15	271.0	0.0	100.6	0.0	0.1	5.4	2.8
181	9.34	301.0	0.0	86.8	19.9	0.1	4.7	2.1
190	9.78	318.0	0.0	80.2	28.8	0.0	4.4	0.5
198	10.40	329.0	0.0	78.6	31.0	0.0	6.2	0.1
207	10.70	331.0	0.0	78.5	31.3	0.0	11.0	0.0
216	10.90	332.0	0.0	78.5	31.3	0.0	16.6	0.0

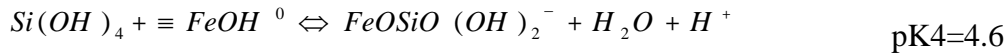
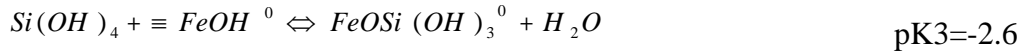
*TRE=tremolite, DOL=dolomite, CAL=calcite, CHRY=chrysotile (solid compounds).

Note: The values for total silica, total calcium and total magnesium are the ionic concentrations remaining in water.

4.2.2 SIMULATION NO.2: IRON TREATMENT SIMULATION OF RIO GRANDE WATER

Simulation No.2 was performed considering addition of ferric iron (Fe^{+3}) to Rio Grande water at the high silica concentration (60 mg SiO_2/L). The reactions that may proceed are stated in Chapter 2. Table 4.4 shows the results for the modeling of this case.

Results of Table 4.4 show that the iron-silicate compound formed is $FeSi(OH)_4$. $FeSi(OH)_4$ chemistry was presented in Chapter 2 where the adsorption of silicic acid onto the surface of the iron oxide is described by a surface complexation reaction, as follows:



According to Mineql, silica is mainly removed by precipitation of sepiolite ($Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O(s)$) and by adsorption onto ferric oxides ($FeSi(OH)_4$). Chrysotile ($Mg_3Si_2O_5(OH)_4(s)$) precipitates at pH values above 8.2 and thus it contributes to silica removal only at low doses of iron addition. Magnesium is mainly removed by precipitation of sepiolite and chrysotile while calcium is removed by calcite precipitation. The pH value for the lowest concentrations of silica, magnesium and calcium is approximately 8.3.

Table 4.4 Iron Treatment Simulation of Rio Grande water at 60 mg SiO₂/L

TREATMENT	pH	SOLIDS				IONS IN WATER			
Fe ⁺³ added (mg/L)		FeSi(OH) ₄ (mg/L)	CAL* (mg/L)	CHRY (mg/L)	SEP (mg/L)	TOT Si (mg/L)	TOT Ca (mg/L)	TOT Mg (mg/L)	TOT Fe (mg/L)
0	8.32	31.2	132.0	75.9	0	6.9	22.0	0.0	2.98E-06
2.1	8.29	27.9	92.9	23.7	47.6	5.7	37.8	6.6	4.60E-08
4.3	8.26	26.4	90.6	16.0	53.7	5.9	38.8	7.7	4.48E-08
6.4	8.23	24.0	88.5	8.1	59.9	6.4	39.6	8.9	4.38E-08
8.6	8.2	24.3	86.5	0.1	66.3	6.8	40.4	10.0	4.31E-08
	8.14	23.6	82.0	0	60.8	7.8	42.4	10.9	4.23E-08
10.7									
12.8	8.09	22.9	77.4	0	55.0	9.5	44.0	11.7	4.18E-08
15.0	8.04	22.7	73.0	0	49.5	10.9	45.6	12.6	4.15E-08
17.1	8	22.3	68.7	0	43.7	12.5	47.6	13.4	4.14E-08
19.3	7.95	21.9	64.3	0	38.2	14.0	49.2	14.3	4.14E-08
21.4	7.90	17.3	60.3	0	33.2	15.5	50.8	14.7	4.14E-08
23.5	7.86	14.9	56.3	0	28.2	16.9	52.4	15.3	4.14E-08
25.7	7.81	12.1	52.3	0	23.5	18.3	54.0	15.8	4.14E-08
27.8	7.76	9.5	48.2	0	17.6	19.9	55.7	16.4	4.14E-08
30.0	7.72	5.7	44.1	0	13.4	21.4	57.3	16.7	4.14E-08

*CAL=calcite, CHRY=chrysotile, SEP=sepiolite (solid compounds).

4.2.3 SIMULATION NO.3: ALUMINUM TREATMENT SIMULATION OF RIO GRANDE WATER

For the simulation of the aluminum treatment, the presence of potassium (5.12e-5 mol/L, *i.e.*, 2 mg K⁺/L) and sodium (1.3810⁻³ mol/L, *i.e.*, 30 mg Na⁺/L) at the conditions reported for Rio Grande water were considered. The addition of potassium and sodium ions to the modeling program was due to the several reactions that alumino-silicates present with these ions. Possible reactions for silica-aluminum interaction are shown in Chapter 2.

Table 4.5 shows the results for the modeling of case (2), that is, Rio Grande water with average silica concentration of 60 mg SiO₂/L (28 mg as Si/L). The initial pH of water calculated by Mineql based on the electroneutrality principle is 8.29, as shown in Table 4.5.

At the initial pH, silica in water was already lower (15 mg as Si/L) than the initial 28 mg as Si/L since silica containing compounds had already precipitated. To lower the silica concentration even further, an addition of 8-13 mg Al⁺³/L is needed. Silica is removed mainly by the precipitation of sepiolite and the aluminosilicate leonhardite ($Al_4Ca_2Si_8O_{17}(OH)_{14}(s)$). Dolomite and calcite allow for magnesium and calcium removal. The best pH range for silica removal by using an aluminum treatment is 8.0-8.1.

Table 4.5 Aluminum Treatment Simulation of Rio Grande water at 60 mg SiO₂/L

TREATMENT	pH	SOLIDS					IONS IN WATER			
Al ³⁺ added (mg/L)		CAL (mg/L)	DOL (mg/L)	LEO (mg/L)	CHRY (mg/L)	SEP (mg/L)	TOT Si (mg/L)	TOT Al (mg/L)	TOT Ca (mg/L)	TOT Mg (mg/L)
0	8.29	172.0	30.0	0.0	30.2	25.5	15.3	0.0	6.2	2.7
2.1	8.26	153.0	50.9	0.0	16.0	41.9	13.9	0.0	7.3	3.2
4.3	8.17	136.0	71.3	0.0	0.0	56.0	13.4	0.0	9.2	4.0
6.4	8.13	120.0	95.7	36.9	0.0	57.5	4.1	0.0	11.1	4.9
8.6	8.11	103.0	96.8	32.6	0.0	61.6	4.1	0.0	12.8	5.7
10.7	8.08	93.6	79.8	29.9	0.0	72.9	1.8	0.0	16.4	7.2
12.9	7.96	90.2	63.2	25.4	0.0	73.6	2.7	0.0	21.4	9.5
15.0	7.82	86.8	47.0	25.1	0.0	0.0	21.9	0.0	26.4	11.7
17.1	7.71	83.5	31.0	0.0	0.0	0.0	28.0	0.0	31.2	13.8
19.3	7.61	80.1	15.4	0.0	0.0	0.0	28.0	0.0	36.0	15.9
21.4	7.52	76.9	0.2	0.0	0.0	0.0	28.0	0.0	40.8	18.0
23.6	7.45	73.7	0.0	0.0	0.0	0.0	28.0	0.0	45.2	20.0
25.7	7.36	55.5	0.0	0.0	0.0	0.0	28.0	0.0	52.8	20.0
27.8	7.29	37.5	0.0	0.0	0.0	0.0	28.0	0.0	59.6	20.0
30.0	7.22	20.0	0.0	0.0	0.0	0.0	28.0	0.0	66.8	20.0
32.1	7.17	2.7	0.0	0.0	0.0	0.0	28.0	0.0	73.6	20.0
34.3	6.96	0.0	0.0	0.0	0.0	0.0	28.0	0.0	74.8	20.0
36.4	6.79	0.0	0.0	0.0	0.0	0.0	28.0	0.0	74.8	20.0
38.6	6.64	0.0	0.0	0.0	0.0	0.0	28.0	0.0	74.8	20.0

*CHRY=chrysotile, SEP=sepiolite, LEO=leonhardite, DOL=dolomite, CAL=calcite (solid compounds).

Note: The values for total silica, total calcium, total aluminum, and total magnesium are the ionic concentrations in water.

4.3 EXTENT OF SOFTENING FOR SYNTHETIC RIO GRANDE WATER

Silica is removed to some extent along with calcium and magnesium compounds when water undergoes softening, according to previous literature. Mineql results confirmed the precipitation of silica during softening treatment. This

investigation is tailored toward the pretreatment stage and addresses the chemistry of silica removal in the presence of calcium and magnesium and at various pH values in batch tests. Two different silica concentrations were tested within the range reported for silica concentration in the Rio Grande River.

Batch tests were run under different conditions of treatment. The concentration range of the chemical additions was in accordance with the results given by the modeling program. Lime softening has proven to be an effective method to reduce silica concentration, even if its primary objective is to control water hardness. Therefore, lime was the main base selected for the investigation. Other bases were also investigated to allow comparisons of the effectiveness of each base, *i.e.*, sodium hydroxide and sodium carbonate. Sodium hydroxide presents the advantage over lime in respect to its soluble form (easier and more accurate working dosages) although it is considerably more expensive. According to previous experiments and Mineql results, enough magnesium has to be present to achieve silica precipitation, as the main compounds formed are magnesium-silicates. Rio Grande water contains magnesium; thus, experiments were initially run without any further magnesium addition. To evaluate the influence of higher concentration of magnesium on silica removal, experiments were also done with addition of a magnesium salt. Two magnesium salts were evaluated, magnesium chloride and magnesium sulfate. Table 4.6 shows the different softening treatments studied.

Table 4.6 Softening Treatments in Batch Experiments

Softening Treatment	Chemical Addition
Treatment 1	Lime addition
Treatment 2	Mg ⁺² salt addition
Treatment 3	Lime + Mg ⁺² salt
Treatment 4	Lime + Mg ⁺² salt + Soda Ash
Treatment 5	Lime + Another base + Mg ⁺² salt

In general, use of glassware was minimized to avoid the possibility of silica leaching from glass into solutions. Analytical grade chemicals and reagents were used in this study. Silica solutions were prepared using a soluble salt of metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). Magnesium and calcium initial concentrations were obtained by addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Sodium bicarbonate was also added to attain the initial alkalinity conditions. After each treatment, all samples were filtered using a 0.22 μm Millipore filter before being analyzed for the metal constituents by an Inductively Coupled Plasma Spectrophotometer (ICP).

For the softening precipitation of silica, jar tests were performed for each water with a systematic variation of magnesium (added as MgCl_2) and pH (controlled by lime dose and sodium carbonate). It is important to distinguish between the solubility of silica in pure water and its solubility in the presence of other substances or the effect of pH on it. Effect of pH on silica solubility is discussed through its dissociation constants in Chapter 2. Although the solubility of silica increases with pH, the solubility of the alkaline silicates decreases with increasing pH. Therefore, the presence of other potentially precipitating ions, such as calcium and magnesium, can help precipitate silica in the form of metal-silicates. The effect of reaction time on the removal of silica has been studied. Silica removal

increased with increasing reaction time, although a reaction time of 20-30 min has been accepted as optimum (Badruk et al. 2001).

4.3.1 SOFTENING TREATMENT 1: ADDITION OF LIME

The first set of experiments was run with addition of different lime concentrations to synthetic Rio Grande water. Silica initial concentration was 44 mg SiO₂/L (corresponding to 20.5 mg as Si⁺⁴/L) since this a value encountered in some regions of the Rio Grande river. Table 4.7 shows that, as the lime dose increased and the pH rose, the Mg⁺² and Si⁺⁴ concentrations were reduced; it is clear that, as the magnesium present in the water ran out, the silica precipitation stopped. The Mineql simulation indicated that silica reacts with magnesium to form different compounds. Silica may also be adsorbed by magnesium hydroxide solids. The main compounds formed according to Mineql under the conditions studied were magnesium-silicates (tremolite and chrysotile).

**Table 4.7 Batch Treatment of Synthetic Rio Grande water at 44 mg/L SiO₂:
Lime Softening**

TREATMENT	RESULTS		
CaO (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
0	21.2	20.5	8.2
125	3.3	12.2	10.95
170	1.6	12.4	11.10
230	0.0	12.1	11.41

Silicon has a high propensity to interact with magnesium hydroxide due to larger surface areas and positive charges on the surface of this solid, although precipitation of $\text{Mg}(\text{OH})_2$ is not common in real softening systems due to the voluminous sludge produced.

Batch tests were done at twice the magnesium concentration of Rio Grande, 38 mg/L, to investigate the effect of magnesium on silica removal. The results in Table 4.8 show that silica decreased from a concentration of 23.8 mg/L to a concentration of 4.8 mg/L as a result of a higher initial magnesium concentration. This result is considerably better than the 12.1 mg/L achieved without the extra magnesium addition. The increase in the calcium concentration at the highest lime dose was due to the addition of lime; calcium precipitated to form CaCO_3 up to the point where carbonate was exhausted. After this point, calcium increased its concentration since there was not sufficient carbonate present for calcium to react with.

**Table 4.8 Batch Treatment of Synthetic Rio Grande water at 44 mg/L SiO_2 :
Lime Softening with Higher Initial Magnesium Concentration**

TREATMENT	RESULTS			
	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	pH
0	62	37.9	23.8	8.3
125	17	20.9	10.1	10.4
170	22	4.8	8.0	10.85
230	65	0	4.8	11.37

4.3.2 SOFTENING TREATMENT 2: MAGNESIUM SALT ADDITION

According to the previous experiments, the presence of magnesium is critical to achieve silica precipitation. A magnesium salt, $\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$, was added to synthetic Rio Grande water with an initial silica concentration of 44 mg SiO_2/L , without the addition of a base. The magnesium treatment without a base was considered since Mineql results indicated low values of silica at a pH around 8.3, which is the pH of Rio Grande water. The removal of silica on the modeling program was by precipitation of tremolite starting at a pH of 7.5. Table 4.9 shows just an infinitesimal decrease of silica concentration. This experiment indicates that, in the actual system, silica is not removed at low pH values (below 9), even if sufficient amounts of Mg^{+2} and Ca^{+2} ions are present to theoretically form metal silicates.

Table 4.9 Batch Treatment of Synthetic Rio Grande water at 44 mg/L SiO_2 : Magnesium Addition

TREATMENT		RESULTS		
Jar Test	Mg^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	pH
0	0	19.4	19.5	8.3
1	12	31.2	19.2	8.9
2	18	36.7	19.1	8.88
3	35	51.6	19.0	8.87
4	70	87.2	18.7	8.82

4.3.3 SOFTENING TREATMENT 3: ADDITION OF LIME AND A MAGNESIUM SALT

Synthetic Rio Grande water at 44 mg SiO₂/L

In this experiment, both previous treatments were combined. Lime and a magnesium salt were added simultaneously to synthetic Rio Grande water with an initial silica concentration of 44 mg SiO₂/L. Lime was added at two different doses, 75 mg CaO/L and 130 mg CaO/L while different amounts of a magnesium salt were added. The results in Table 4.10 indicate that, at a lime dose of 130 mg CaO/L and addition of 12 mg Mg⁺² / L, silica and hardness ion concentrations all decreased to low values.

**Table 4.10 Batch Treatment of Synthetic Rio Grande water at 44 mg/L SiO₂:
Lime Softening with Magnesium Addition**

TREATMENT			RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
0	0	0	61.7	19.4	20.5	9.1
1	12	75	5.5	22.6	13.2	10.00
2	18	75	3.5	22.6	13.1	10.11
3	35	75	4.0	38.6	13.7	10.01
4	70	75	4.3	68.5	11.4	10.18
5	90	75	5.2	81.8	10.6	10.22
6	120	75	5.5	102.2	10.2	10.18
7	12	130	16.3	2.8	4.9	10.86
8	18	130	14.2	7.0	4.8	10.75
9	35	130	13.7	25.8	6.3	10.55
10	70	130	21.6	53.9	5.5	10.22
11	90	130	22.9	64.8	4.6	10.23
12	120	130	23.0	87.9	4.4	10.15

Experiments were carried out to compare the effectiveness of different magnesium salts: magnesium sulfate versus magnesium chloride. No significant differences on the precipitation results were found between the two salts, as expected. Magnesium chloride was selected to run the next experiments, because addition of magnesium sulfate may induce precipitation of sulfates while running the reverse osmosis unit if control of sulfates is not carefully undertaken.

Synthetic Rio Grande water at 60 mg SiO₂/L

A higher initial silica concentration was studied, 60 mg SiO₂/L (corresponding to 28 mg as Si/L). The treatment consisted of a simultaneous addition of a base (lime) and magnesium chloride, as this is the treatment that has proven to yield good silica removal.

Lime doses were selected considering the results given by Mineql. Mineql stated that good results for silica removal (at 28 mg as Si⁺⁴/L) were achieved by addition of 150 mg CaO/L. Two lime doses lower than this value were studied (80 and 130 mg CaO/L) and some doses above this value were also studied (165, 180, 210 and 260 mg CaO/L). Table 4.11 and Figure 4.1 show that low additions of lime (80 and 130 mg CaO/L) removed silica at approximately 46% and 55% at the highest magnesium dose (30 mg Mg⁺²/L). At higher doses of lime, 150 mg CaO/L and 165 mg CaO/L, silica was removed up to 75%. With the addition of 180 mg CaO/L, silica was removed up to 83%. Further additions of lime, and thus, further increase in pH, seemed to redissolve some of the silica precipitates. At doses of 210 mg CaO/L and 260 mg CaO/L, silica was reduced by 79%.

**Table 4.11 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂:
Lime Softening with Magnesium Addition**

TREATMENT			RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
1	5	80	21.3	15.1	17.9	10.35
2	10	80	10.6	17.9	17.2	10.20
3	15	80	9.3	21.9	16.5	10.21
4	25	80	8.9	29.9	15.3	10.18
5	30	80	8.6	33.8	15.1	10.15
6	5	130	39.4	6.6	15.7	10.80
7	10	130	44.1	11.2	14.4	10.72
8	15	130	41.5	11.9	12.7	10.64
9	25	130	36.3	22.6	13.4	10.48
10	30	130	41.6	26.1	12.6	10.46
11	5	150	55.3	1.6	12.4	11.05
12	10	150	52.8	1.9	10.6	10.97
13	15	150	54.3	4.2	9.8	10.86
14	25	150	43.8	12.1	8.7	10.74
15	35	150	46.5	17.4	7.7	10.59
16	45	150	42.1	18.1	6.9	10.50
17	5	165	44.2	2.0	11.1	10.88
18	10	165	49.2	3.7	9.9	10.79
19	15	165	51.2	5.0	7.7	10.75
20	20	165	53.7	6.5	7.7	10.93
21	25	165	49.7	6.8	7.1	10.75
22	30	165	48.9	9.3	6.2	10.69
23	35	165	53.6	14.5	6.9	10.66
24	45	165	56.2	17.1	6.3	10.54
25	5	180	59.4	0.24	10.8	11.06
26	10	180	54.6	1.1	9.5	10.95
27	15	180	59.0	2.8	6.9	10.88
28	25	180	56.8	2.3	6.1	11.00
29	30	180	58.7	3.8	4.9	10.95
30	35	180	58.1	8.7	4.7	10.69
31	40	180	53.4	13.0	4.9	10.56
32	45	180	55.5	12.6	4.8	10.53
33	5	210	67.7	0.15	10.9	11.21
34	10	210	72.5	0.14	9.6	11.24
35	15	210	69.7	0.28	6.7	11.08
36	25	210	81.3	0.40	7.5	11.40
37	30	210	80.5	0.60	5.9	11.33
38	5	260	97.8	1.02	10.9	11.79
39	15	260	113.1	0.34	9.8	11.73
40	25	260	101.5	0.20	9.1	11.7
41	30	260	102.2	0.20	7.0	11.70
42	35	260	106.9	0.76	6.0	11.52
43	45	260	104.5	1.7	5.9	11.36

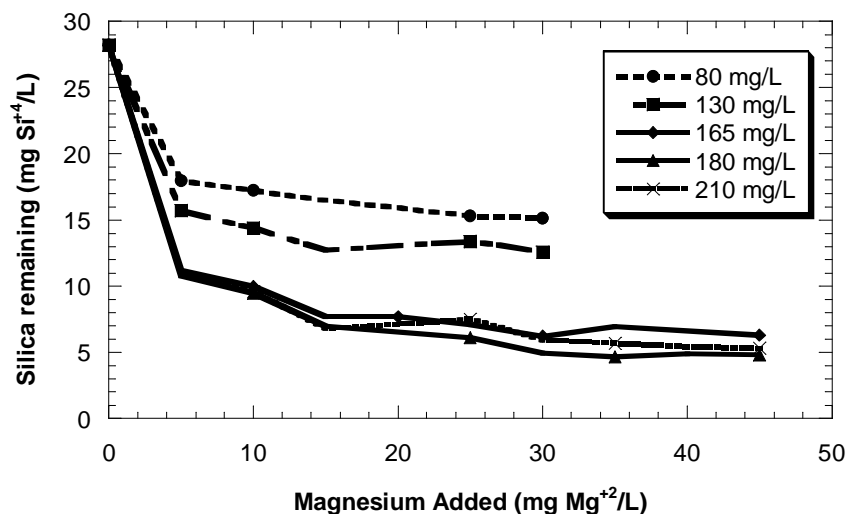


Figure 4.1 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂: Lime Softening with Magnesium Addition

In summary, the experiments showed that silica is best removed by addition of 180 mg CaO/L. Considering both the silica and magnesium results, the best condition was the jar with a dose of 30 mg/L Mg²⁺ and 180 mg CaO/L.

Calcium concentrations increased as lime was added. At low additions of lime (80 mg CaO/L), calcium decreased as it reacted with the carbonate present in water and formed calcium carbonate. At higher lime additions, it seemed that carbonate ions were depleted and calcium ions remained in water. This high calcium concentration (approximately 55 mg Ca²⁺/L) may induce precipitation of calcium compounds on reverse osmosis membranes; thus, it would need to be reduced before entering the RO unit.

The adequate treatment depends on the required specifications of the product water. This set of experiments showed low concentrations of silica and magnesium

by addition of 180 mg CaO/L and 15-30 mg as Mg^{+2} /L. pH was high; therefore, a pH adjustment must be made before running the membrane system with this water.

4.3.4 SOFTENING TREATMENT 4: ADDITION OF LIME, A MAGNESIUM SALT AND SODA ASH

Soda ash, along with lime and a magnesium salt, was added to control calcium concentrations. By the addition of soda ash, sufficient carbonate should be present to allow for the precipitation of calcium carbonate. The required amount of soda ash was determined based on the point that carbonate ions were limited. Therefore, the required amount of sodium carbonate added was calculated with the following formula:

$$Na_2CO_3 = (\text{Lime Dose}_{\text{desired CaO}} - \text{Lime Dose}_{\text{depletion of carbonate}}) * \frac{1 \text{ mmol } Na_2CO_3}{1 \text{ mmol excess Lime(CaO)}} *$$

$$\frac{106 \text{ mg/mmol } Na_2CO_3}{56 \text{ mg/mmol CaO}} * 1L \quad (4.1)$$

Earlier experiments showed that the lime dose where carbonate was exhausted under the conditions studied was 80 mg CaO/L; this value was used for the lime dose at the point of depletion of carbonate in the equation.

Synthetic Rio Grande water at 60 mg SiO_2 /L

The next set of experiments was run under the better conditions for silica removal attained on the previous set of experiments for synthetic Rio Grande water

at 60 mg SiO₂/L. Table 4.12 shows that, by addition of Na₂CO₃ the calcium concentration was substantially lowered, achieving a reduction of the calcium concentration of approximately 85% with respect to the experiments without soda ash addition. The magnesium concentration was also slightly reduced due to a slight increase in pH.

**Table 4.12 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂:
Lime Softening with Magnesium and Na₂CO₃ Addition**

TREATMENT				RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
0	0	0	0	50.0	19.9	28.0	8.03
1	5	165	161	6.8	1.3	14.6	11.27
2	10	165	161	7.8	1.9	12.8	11.17
3	15	165	161	4.8	1.8	9.5	11.02
4	25	165	161	7.0	6.6	6.9	10.82
5	35	165	161	12.3	13.0	5.8	10.60
6	45	165	161	12.5	20.1	5.5	10.52
7	5	180	189	5.9	0.9	15.2	11.43
8	10	180	189	6.3	1.2	13.7	11.31
9	15	180	189	8.7	8.3	5.4	10.83
10	25	180	189	7.3	8.0	9.9	10.74
11	35	180	189	17.7	2.7	5.3	11.12
12	45	180	189	10.3	16.2	6.3	10.76
13	5	210	246	3.9	0.4	17.1	11.58
14	10	210	246	8.5	1	15.9	11.51
15	15	210	246	3.6	0.5	12.0	11.49
16	25	210	246	4.4	1.2	9.1	11.31
17	35	210	246	6.2	3.7	6.5	11.08
18	45	210	246	6.5	7.5	5.1	10.94

Table 4.13 presents the treatments that gave the better results for removing silica, magnesium and calcium concentrations at synthetic Rio Grande initial silica concentration of 60 mg SiO₂/L. These treatments were selected as the pretreatments for synthetic Rio Grande water before entering the RO unit.

Table 4.13 Best Softening Treatments: Synthetic Rio Grande water at 60 mg SiO₂/L

TREATMENT				RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
3	15	165	161	4.8	1.8	9.5	11.02
4	25	165	161	7.0	6.6	6.9	10.82
9	15	180	189	8.7	8.3	5.4	10.83

Synthetic Rio Grande water at 23 mg SiO₂/L

Another set of experiments was run according to Mineql results for an initial silica condition of 23 mg SiO₂/L. Mineql indicated that the range of calcium oxide that gave good ion removal was between 130-150 mg CaO/L added. Addition of a magnesium salt was also considered since it has previously been demonstrated that enough magnesium has to be present to induce silica precipitation. To control calcium concentrations, sodium carbonate was added according to Equation 4.1. Table 4.14 shows that experiments made with synthetic Rio Grande water with a silica concentration of 23 mg SiO₂/L showed good silica removal at 15 mg Mg⁺²/L and addition of lime between 130-155 mg CaO/L. At an addition of 130 mg CaO/L, a silica removal of 42% was achieved while an addition of 155 mg CaO/L achieved a silica removal of 66%.

**Table 4.14 Batch Treatments of Synthetic Rio Grande water at 23 mg/L SiO₂:
Lime Softening with Magnesium and Na₂CO₃ Addition**

TREATMENT				RESULTS				
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	Alk (mg CaCO ₃ /L)	pH
0	0	0	0	38.3	17.1	11.5	169.0	8.23
1	15	130	95	14.3	16.8	6.7	104.0	10.81
2	25	130	95	14.6	23.9	6.4	75.2	10.70
3	35	130	95	14.0	32.0	6.2	60.0	10.61
4	45	130	95	15.4	40.1	5.9	56.0	10.53
5	15	155	142	11.1	6.8	3.9	74.0	10.96
6	35	155	142	20.4	20.7	4.7	68.0	10.86
7	45	155	142	22.6	29.4	4.5	77.0	10.77
8	15	180	189	11.2	4.2	5.9	130.0	11.32
9	25	180	189	14.6	6.9	4.7	102.0	11.16
10	35	180	189	17.2	11.5	4.0	80.0	11.03
11	45	180	189	19.4	19.1	3.5	60.0	10.87

Table 4.15 presents the treatments that gave the better results for removing silica, magnesium and calcium concentrations at synthetic Rio Grande initial silica concentration of 23 mg SiO₂/L. Addition of a lime dose of 180 mg CaO/L did not increase substantially the amount of silica removed; thus, the lower doses of 130 and 155 mg CaO/L were selected.

Table 4.15 Best Softening Treatments: Synthetic Rio Grande water at 23 mg SiO₂/L

TREATMENT				RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
1	15	130	95	14.3	16.8	6.7	10.81
5	15	155	142	11.1	6.8	3.9	10.96

Softening Treatment 5: Addition of a Magnesium Salt + Lime + Sodium Hydroxide

This treatment consists of addition of sodium hydroxide (NaOH) along with lime and a magnesium salt. Even though addition of sodium hydroxide for pH increase is expensive, this compound was added for the purpose of research; to investigate the effect of calcium concentrations and calcium carbonate precipitation on silica removal by addition of base different than lime.

The amount of lime added plus the sodium hydroxide added were in amounts equivalent to the lime added in previous successful experiments. Addition of 75 mg CaO/L plus 107 mg NaOH /L is equivalent to the addition of 150 mg CaO/L. Addition of 90 mg CaO/L plus 129 mg NaOH /L is equivalent to the addition of 180 mg CaO/L. Table 4.16 shows that even though the pH reached values that induced silica precipitation when lime was added as the only base, silica removal in the case of lime and NaOH addition was lower. Calcium and magnesium concentrations were slightly lower when both bases were added due to a slight increase in the pH value with respect to the addition of lime alone. These results

indicate that the addition of lime alone is better in terms of decreasing the silica concentrations in water than the addition of sodium hydroxide along with lime.

**Table 4.16 Batch Treatments of Synthetic Rio Grande water at 60 mg/L SiO₂:
Lime Softening with Magnesium and NaOH Addition**

TREATMENT				RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	NaOH (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
0	0	0	0	55.2	19.0	28.2	8.01
1	15	75	107	8.8	8.0	12.5	10.80
2	20	75	107	8.6	10.4	12.0	10.75
3	25	75	107	9.6	13.7	11.4	10.67
4	15	90	129	6.7	2.8	9.7	11.04
5	20	90	129	8.4	3.3	9.0	11.03
6	25	90	129	8.4	5.5	8.3	10.81

4.3.5 SELECTION OF SOFTENING DOSES FOR SYNTHETIC RIO GRANDE WATER

A selection of treatments for water at initial conditions of 23 mg SiO₂/L and 60 mg SiO₂/L was made based on low concentration of Mg⁺², Ca⁺² and Si⁺⁴ achieved. As stated before, the median silica concentration on regions of typical silica values in the Rio Grande River is 23 mg SiO₂/L and on regions of high silica values the median concentration is 60 mg SiO₂/L.

Table 4.17 shows the treatments selected to be applied to synthetic Rio Grande water before entering the RO unit.

Table 4.17 Selection of Softening Treatments of Synthetic Rio Grande water to test on the RO unit

	Part A: 60 mg SiO₂/L			Part B: 23 mg SiO₂/L		
	Softening Treatment 1	Softening Treatment 2	Softening Treatment 3	Softening Treatment 4	Softening Treatment 5	
TREATMENT						
Lime addition=	165	165	180	130	155	mg CaO/L added
Mg addition=	15	25	15	15	15	mg as Mg ⁺² /L added
Soda Ash Addition=	161	161	189	95	142	mg Na ₂ CO ₃ /L added
RESULTS						
Si ⁺⁴ =	9.5	6.9	5.4	6.7	3.9	mg/L
Mg ⁺² =	1.8	6.6	9.3	16.8	6.8	mg/L
Ca ⁺² =	4.8	7	8.7	14.3	11.1	mg/L
Alk=	87.4	72	77	104	74	mg CaCO ₃ /L
pH*	11.02	10.82	10.83	10.81	10.96	

*pH was adjusted to 8 before the membrane treatment.

4.3.6 SIMULATION OF CHEMICAL BEHAVIOR OF WATER ENTERING A RO UNIT

To simulate in the Mineql software the likely precipitates formed over the membranes, it is necessary to know the theoretical expected concentration of the feed/concentrate stream at a certain recovery level. The concentrations expected on the feed/concentrate stream for the pretreated water entering the RO unit after two typical recovery levels of drinking water (88% and 90%) are shown in Table 4.18 for the two different influent silica concentrations. The criterion to select the pretreatments that were tested on the RO unit was based on silica and hardness concentration removal, as well as the lowest amount of precipitate expected over the membranes. The Mineql program identified the likely precipitates over the membrane at the conditions of concentration of the concentrate/feed stream and pH.

**Table 4.18 Expected Concentrations of Synthetic Rio Grande water
Feedstream at Two Recovery Levels**

	Part A: 60 mg SiO₂/L			Part B: 23 mg SiO₂/L	
	Softening Treatment 1	Softening Treatment 2	Softening Treatment 3	Softening Treatment 4	Softening Treatment 5
Recovery = 88% (CF=8)					
Si ⁺⁴ (mg/L)=	76	55.2	43.2	53.6	31.2
Mg ⁺² (mg/L)=	14.4	52.8	74.4	134.4	54.4
Ca ⁺² (mg/L)=	38.4	56	69.6	114.4	88.8
Alk (mg CaCO ₃ /L)=	699.2	576	616	832	592
Recovery = 90% (CF=10)					
Si ⁺⁴ (mg/L)=	95	69	54	67	39
Mg ⁺² (mg/L)=	18	66	93	168	68
Ca ⁺² (mg/L)=	48	70	87	143	111
Alk (mg CaCO ₃ /L)=	874	720	770	1040	740

CF=Concentration Factor

Mineql gives the expected silica values that remain soluble in the concentrate/feed stream and the amount of silica that may precipitate in a solid.

Mineql uses the thermodynamic data provided for several chemical reactions involving the formation of silicates and magnesium and calcium containing compounds.

Results in Tables 4.19 show that the best pretreatment according to Mineql (the one that would give the lowest amount of precipitates over the membranes) is the softening treatment No 1. Results of the simulation indicate that, for a recovery water percentage of 88%, the water pretreated with softening treatment 1 would theoretically precipitate approximately 164 mg/L while pretreated water with softening treatment 2 and 3 would precipitate 341 and 433 mg/L, respectively. Mineql simulations predicted that the precipitated solids may be the magnesium-

calcium-silicate tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2(\text{s})$), calcium carbonate, and dolomite ($\text{CaMg}(\text{CO}_3)_2(\text{s})$).

Table 4.19 Expected Precipitates of Pretreated Synthetic Rio Grande water at 60 mg SiO_2/L

Part A: Recovery Level = 88%	Softening Treatment 1	Softening Treatment 2	Softening Treatment 3
Silica behavior			
Silica in concentrate stream=	75.5	55.2	42.0
Si^{+4} (mg/L) remains in water=	49.3	10.4	5.9
Si^{+4} (mg/L) precipitated in a solid=	26.2	44.8	36.2
Solids Formed			
Tremolite (mg/L)=	94.9	162.2	0.0
Calcite (mg/L)=	69.3	0.0	0.0
Dolomite (mg/L)=	0.0	179.0	311.5
Talc (mg/L)=	0.0	0.0	122.4
Total solids (mg/L)	164.2	341.2	433.9
Part B: Recovery Level = 90%			
Silica behavior			
Silica in concentrate stream=	95.2	69.8	53.2
Si^{+4} (mg/L) remains in water=	51.8	13.0	6.9
Si^{+4} (mg/L) precipitated in a solid=	43.4	56.9	46.4
Solids Formed			
Tremolite (mg/L)=	111.1	206.0	0.0
Calcite (mg/L)=	86.4	0.0	0.0
Dolomite (mg/L)=	0.0	234.1	403.6
SiO_2 (am) mg/L	27.4	0.0	0.0
Talc (mg/L)=	0.0	0.2	156.9
Total solids (mg/L)	224.9	440.3	560.5

These simulations show that the lowest concentration of silica on the feed stream might not be the condition that produce the lowest amount of precipitates

while running an RO system (softening treatment No. 1 was a better option with a silica concentration on the feed stream of 9.5 mg Si/L while softening treatments 2 and 3 had silica concentration of 6.9 and 5.4 mg Si/L, respectively). Concentration levels of other ions, in this case magnesium and calcium, also determine the pretreatments that should be selected.

Table 4.20 shows the results of the simulations for Rio Grande water at an initial silica condition of 23 mg SiO₂/L. According to Mineql, for the condition of Rio Grande water at 23 mg SiO₂/L, softening treatment No. 5 would give a lower amount of precipitates over the membranes.

Table 4.20 Expected Precipitates of Pretreated Synthetic Rio Grande water at 23 mg SiO₂/L

Part A: Recovery Level = 88%	Softening Treatment 4	Softening Treatment 5
Silica		
Silica in concentrate stream=	53.2	30.8
Si ⁺⁴ (mg/L) remains in water=	3.8	14.2
Si ⁺⁴ (mg/L) precipitated in a solid=	49.5	17
Solids Formed		
Tremolite (mg/L)=	0.0	60.0
Calcite (mg/L)=	0.0	188.0
Dolomite (mg/L)=	532.6	324.4
SiO ₂ (am) (mg/L)	0.0	0.0
Talc (mg/L)=	167.5	0.0
Magnesite (mg/L)	38.4	0.0
Total solids (mg/L)=	700.1	572.4
Part B: Recovery Level = 90%		
Silica behavior		
Silica in concentrate stream=	67.2	39.2
Si ⁺⁴ (mg/L) remains in water=	4.4	17.2
Si ⁺⁴ (mg/L) precipitated in a solid=	62.8	22.0
Solids Formed		
Tremolite (mg/L)=	0.0	79.7
Calcite (mg/L)=	0.0	26.5
Dolomite (mg/L)=	661.6	414.7
SiO ₂ (am) mg/L)	0.0	0.0
Talc (mg/L)=	212.6	0.0
Total solids (mg/L)=	874.2	520.9

4.3.7 SUMMARY OF SOFTENING TREATMENTS FOR SYNTHETIC RIO GRANDE WATER

Batch tests were carried out to determine the precipitation characteristics of silica at different initial SiO_2 concentrations, pH values, and in the presence of calcium and magnesium. All the experiments were carried out at 25 °C.

The silica concentrations that were evaluated for synthetic Rio Grande water are (1) 23 mg SiO_2/L , corresponding to the median of the typical range reported, 20-26 mg SiO_2/L , (2) 44 mg SiO_2/L , condition reported as present in the medium zone of the basin and (3) 60 mg SiO_2/L , corresponding to the median of the range reported for places with high silica concentrations in the river, 50-70 mg SiO_2/L .

The softening treatment that better fits the influent stream of a reverse osmosis unit depends on the feed water quality and the desired recovery percentage. The equilibrium chemistry program Mineql was used to narrow the range of chemical additions that were studied on batch experiments. Mineql results indicate that an increase in pH is necessary to start metal-silicates precipitation. In order to raise pH, two bases were studied, lime and sodium hydroxide.

The treatments that were studied included the following: (1) Lime addition, (2) Magnesium addition, (3) Lime and magnesium additions, (4) Lime, magnesium and soda ash additions and (5) Sodium hydroxide, lime and magnesium additions.

Lime showed to be a better base than sodium hydroxide in removing silica. The amount of lime needed is a function of the initial silica concentration and the amount of silica that needs to be removed. A magnesium salt, $\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$, was added simultaneously in some experiments to allow the formation of silica-magnesium compounds. Additions of magnesium in the range of 5-45 mg as Mg^{+2}/L

were studied. To control calcium concentrations, sodium carbonate was added to provide enough carbonate for calcium to react with and precipitate as calcium carbonate.

For water with an initial silica concentration of approximately 23 mg SiO₂/L, simultaneous addition of 130 mg CaO/L, 15 mg as Mg⁺²/L, and 95 mg Na₂CO₃/L may be a good treatment previous to a reverse osmosis unit. This treatment gives low concentrations of silica, magnesium and calcium ions. For achieving even lower ion concentrations, higher amounts of chemical must be added: 155 mg CaO/L, 15 mg Mg⁺²/L, and 142 mg Na₂CO₃/L. These two pretreatments were selected to be evaluated in the RO unit.

For water with an initial silica concentration of 60 mg SiO₂/L, simultaneous addition of 165 mg CaO/L, 15 mg as Mg⁺²/L, and 160 mg Na₂CO₃/L may be a good treatment. Other treatments that also allowed for good ion removal were 165 mg CaO/L plus 25 mg as Mg⁺²/L and 160 mg Na₂CO₃/L and 180 mg CaO/L plus 15 mg as Mg⁺²/L and 190 mg Na₂CO₃/L. These three pretreatments were also tested on the RO unit.

As can be seen from previous results, the amount of hydroxide required for removing silica increases with the silica concentration, but not in direct proportion. Adsorption, chemical reaction or a combination of both processes are responsible for silica removal. The optimal pH for silica removal by a softening treatment is between pH 10.5-11, which coincides with the conditions created during lime softening.

4.4 EXTENT OF ALUMINUM TREATMENT FOR SYNTHETIC RIO GRANDE WATER

Aluminum salts present interactions with silica in water. Sugita (1999) showed that the presence of aluminum and silica in geothermal brines formed aluminosilicates ($x\text{Al}(\text{OH})_3 \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$), as explained in Section 2.3.5. Two aluminum salts, aluminum sulfate and aluminum chloride, were investigated to evaluate the effect of the anions SO_4^{-2} and Cl^- on the removal of silica. According to Mineql, aluminum salts give good silica removal by addition of approximately 10-13 mg Al^{+3}/L , in the pH range of 7.8-9.

4.4.1 ALUMINUM CHLORIDE TREATMENT

The first set of experiments consisted of the addition of aluminum chloride alone. Table 4.21 shows that silica concentrations were still high even with high doses of aluminum chloride. It is clearly observed that aluminum chloride alone was not able to reduce silica content significantly. The aluminum addition dropped the pH outside the range of silica-aluminum interaction; thus, the addition of a base was tested.

**Table 4.21 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂:
Addition of an Aluminum Salt**

TREATMENT		RESULTS				
Jar Test	Al ⁺³ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	Al ⁺³ (mg/L)	pH
0	0	55.2	19.0	27.9	0.0	8.01
1	12	39.4	15.0	16.9	0.0	6.94
2	20	46.8	14.7	14.5	0.0	6.64
3	27	54.2	15.0	18.2	13.2	6.82
4	36	56.4	15.4	20.5	24.7	5.87
5	54	65.6	15.5	22.2	43.6	4.20
6	68	67.9	15.4	22.2	55.6	4.07

Three bases, along with an aluminum salt addition, were studied to analyze the effectiveness of each base:

- (1) Aluminum treatment 1: Aluminum salt and NaHCO₃ addition
- (2) Aluminum treatment 2: Aluminum salt and Na₂CO₃ addition
- (3) Aluminum treatment 3: Aluminum salt and Ca(OH)₂ addition

4.4.2 ALUMINUM TREATMENT: ALUMINUM SALT AND NAHCO₃ ADDITION

Aluminum Sulfate followed by sodium bicarbonate

According to Mineql simulations, the addition of 8-13 mg Al⁺³/L, lowers silica, magnesium and calcium concentrations to very low values at a approximately pH of 8.1. According to literature, aluminum presents interactions with silica in the pH range of 7-9. Thus, the experiments were run trying to mitigate

the drop in pH, by addition of sodium bicarbonate, according to the following reaction:

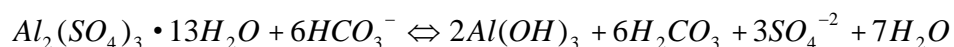


Table 4.22 presents the results of aluminum addition in the range of 20-45 mg Al^{+3} /L along with the stoichiometric values of sodium bicarbonate required to avoid a drop on pH due to the acidic nature of aluminum salts. An addition of 20 mg Al^{+3} /L gave a silica removal of 35% at pH around 7.6. Slightly lower concentrations of silica were reached at higher aluminum doses.

Table 4.22 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO_2 : Addition of Aluminum Sulfate and Na_2HCO_3

TREATMENT			RESULTS				
Jar Test	Al^{+3} (mg/L)	$NaHCO_3$, (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	Al^{+3} (mg/L)	pH
0	0	0	55.2	19.0	27.9	0.0	8.01
1	20	186.7	31.1	15.0	13.0	0.5	7.56
2	25	233.3	34.2	15.2	12.9	0.4	7.33
3	30	280.0	33.3	14.7	12.4	0.9	7.28
4	35	326.7	32.9	14.7	12.2	0.7	7.3
5	40	373.3	32.8	14.8	12.4	0.9	7.3
6	45	420.0	33.7	14.5	11.7	1.0	7.16

Aluminum chloride followed by sodium bicarbonate

Aluminum chloride was studied to investigate the effect of another aluminum salt on silica removal. The amount of sodium bicarbonate was added according to the following reaction.

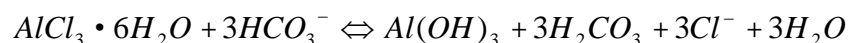


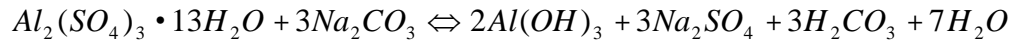
Table 4.23 shows that by addition of 25 mg/L as Al^{+3} and 233 mg/L of $NaHCO_3$, a silica removal of 35% was achieved. Further increases in aluminum dose did not improve the results considerably. The results obtained with aluminum sulfate and aluminum chloride were very similar. It can be assumed that the sulfate and chloride ions did not interfere in the process of silica precipitation.

Table 4.23 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO_2 : Addition of Aluminum Chloride and Na_2HCO_3

TREATMENT			RESULTS				
Jar Test	Al^{+3} (mg/L)	$NaHCO_3$ (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	Al^{+3} (mg/L)	pH
0	0	0.0	55.2	19.0	27.9	0.0	8.01
1	20	186.7	29.6	15.7	13.8	0.8	7.12
2	25	233.3	32.0	15.8	13.4	0.5	6.88
3	30	280.0	38.9	14.9	12.7	1.0	7.25
4	35	326.7	42.3	15.0	12.3	0.6	7.1
5	40	373.3	33.1	15.6	12.8	0.5	6.6
6	45	420.0	37.9	15.7	12.4	0.3	6.3

4.4.3 ALUMINUM TREATMENT: ALUMINUM SALT AND Na_2CO_3 ADDITION

A set of experiments with increasing aluminum doses and sodium carbonate was done. The reaction of an aluminum salt and sodium carbonate proceeds as follows,



Sodium carbonate was added in equivalent doses to the calcium hydroxide that gave good silica removal. The doses of sodium carbonate 215, 245, 275, and 303 mg $\text{Na}_2\text{CO}_3/\text{L}$ are equivalent to 115, 130, 145 and 175 mg CaO/L .

Table 4.24 indicates that, at a high sodium carbonate dose, a high pH was reached and silica removal increased. Magnesium concentrations decreased from 19 mg Mg^{+2}/L to approximately 13 mg Mg^{+2}/L at pH values below 9.30. The precipitation of silica, magnesium and aluminum compounds at this pH value indicates that the thermodynamically possible compounds that may be formed according to Mineql are the silicates sepiolite ($\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O}(s)$) and leonhardite ($\text{Al}_4\text{Ca}_2\text{Si}_8\text{O}_{17}(\text{OH})_{14}(s)$).

**Table 4.24 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂:
Addition of Aluminum Chloride and Na₂CO₃**

TREATMENT			RESULTS				
Jar Test	Al ⁺³ (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	Al ⁺³ (mg/L)	pH
0	0	0	55.2	19.0	27.9	0.0	8.01
1	15	215	20.4	13.2	10.9	0.29	8.32
2	20	215	24.6	13.3	10.8	0.26	8.1
3	25	215	31.3	13.6	11.7	0.16	7.59
4	15	245	18.0	12.5	9.3	0.43	8.68
5	20	245	24.3	13.6	10.8	0.26	8.21
6	25	245	24.4	13.6	10.9	0.17	7.74
7	15	275	14.5	13.8	8.9	0.40	9.03
8	20	275	27.9	14.8	9.3	0.28	8.48
9	25	275	37.2	14.0	9.9	0.30	7.77
10	15	303	11.4	13.1	8.8	0.50	9.30
11	20	303	23.3	13.7	9.2	0.30	8.48
12	25	303	33.2	14.2	9.3	0.00	7.82

The following experiments evaluated the effectiveness of an aluminum treatment along with calcium hydroxide as the base that allows the control of pH.

4.4.4 ALUMINUM TREATMENT 3: ALUMINUM SALT AND Ca(OH)₂ ADDITION

Metals precipitate as hydroxides through the addition of lime or caustic soda to a pH of minimum solubility (Iler, 1979). Also, metals are coprecipitated with calcium carbonate. A stronger base, calcium hydroxide, was added to increase pH to higher values than in previous experiments.

Table 4.25 shows that, by addition of 25 mg as Al^{+3}/L and 130 mg CaO/L , silica removal was 84% (from 20 mg as Si^{+4}/L to 3.1 mg as Si^{+4}/L). A higher dose of calcium oxide, 175 mg /L, and 25 mg as Al^{+3}/L , gave a slightly better result. According to these experiments, pH values that give good silica removals are in the range of 8.5-9.2.

Table 4.25 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO_2 : Addition of Aluminum Chloride and CaO

TREATMENT			RESULTS				
Jar Test	Al^{+3} (mg/L)	CaO (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	Al^{+3} (mg/L)	pH
0	0	0	55.2	19.0	27.9	0.0	8.01
1	25	130	59.1	13.1	3.1	0.9	8.5
2	40	130	102.8	14.9	3.8	0.3	7.47
3	50	130	129.0	15.3	5.0	0.0	7.21
4	60	130	131.0	15.6	6.7	0.0	7.02
5	70	130	142.0	16.0	10.8	0.0	6.55
6	80	130	146.0	16.1	12.0	0.0	6.26
7	25	175	48.5	11.8	1.8	2.9	9.16
8	40	175	90.8	13.3	1.0	0.7	8.34
9	50	175	125.7	14.4	1.9	0.8	8.18
10	60	175	143.9	15.5	5.1	0.2	7.4
11	70	175	151.6	15.5	8.6	0.4	6.82
12	80	175	157.0	15.7	9.8	0.3	6.57

Figure 4.1 shows a comparison of the three types of aluminum treatments explained before. For additions of aluminum ranging from 0 to 30 mg Al^{+3}/L , the addition of 4.6 meq of $\text{Na}_2\text{CO}_3/\text{L}$ or 4.6 meq of CaO/L greatly affected silica removal.

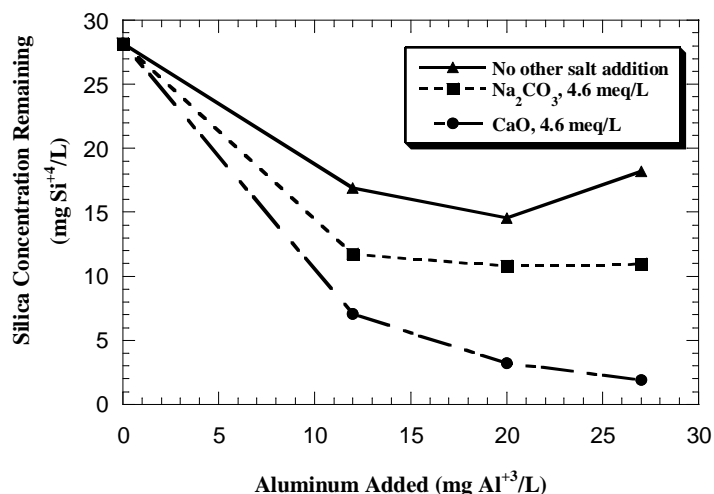


Figure 4.2 Silica Removal at Different Aluminum Treatments

Although the addition of calcium oxide achieved a good silica removal, a drawback of this treatment was the high concentration of calcium that remained in the water. In the presence of carbonate or sulfate ions, calcium compounds may cause scaling problems in an RO unit. Thus, calcium concentrations in the solution have to be controlled before entering an RO unit.

4.4.5 ALUMINUM TREATMENT 4: ALUMINUM SALT, $\text{Ca}(\text{OH})_2$ AND Na_2CO_3 ADDITION

A series of experiments were carried out to lower calcium concentration by addition of soda ash. The best treatments of addition of aluminum and lime given by the previous experiments were considered for this set of experiments. Table 4.26

shows that calcium concentrations were substantially reduced when soda ash was added. Since good silica removals were achieved by addition of 15-25 mg Al^{+3}/L these aluminum doses were tested. Lime and soda ash were added to control pH and calcium concentration.

Table 4.26 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO_2 : Addition of Aluminum Chloride, CaO and Na_2CO_3

TREATMENT				RESULTS				
Jar Test	Al^{+3} (mg/L)	CaO (mg/L)	Na_2CO_3 (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	Al^{+3} (mg/L)	pH
0	0	0.0	0	55.2	19.0	27.9	0.0	8.01
1	15	130	95	11.7	10.9	8.7	0.97	8.35
2	15	140	114	10.9	5.7	6.9	0.96	8.44
3	15	150	133	8.7	1.5	6.4	0.34	8.72
4	25	130	95	20.4	10.6	3.2	0.90	8.15
5	25	140	114	22.2	12.6	1.5	0.61	8.22
6	25	150	133	16.2	11.4	3.9	0.60	8.35

4.4.6 SELECTION OF ALUMINUM DOSES FOR RIO GRANDE SYNTHETIC WATER

Addition of sodium bicarbonate to compensate for the low pH induced by aluminum salt addition did not remove enough silica to consider it a possible treatment. Addition of doses of aluminum around 25 mg as Al^{+3}/L along with calcium hydroxide (approximately 130 mg CaO/L) increased pH values up to 9.2 and yielded good silica removal. Silica was lowered from concentrations of approximately 20 mg/L to approximately 2-3 mg/L as Si^{+4} . Addition of soda ash

allowed for good calcium removal. Table 4.27 shows the pretreatments selected to test on the RO unit.

Table 4.27 Best Aluminum Treatments: Synthetic Rio Grande water at 60 mg SiO₂/L

TREATMENT			RESULTS				
Al ⁺³ (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	Al ⁺³ (mg/L)	pH
0	0	0	55.2	19.0	27.9	0.0	8.01
15	150	133	8.7	1.5	6.4	0.34	8.72
25	130	95	20.4	10.6	3.2	0.90	8.15

4.5 EXTENT OF IRON TREATMENT FOR SYNTHETIC RIO GRANDE WATER

Iron, as stated in Chapter 2, presents strong interactions with silica in the range of pH 4 to 8 (Mickley,1981). Dissolved silica may be absorbed onto a surface such as ferric hydroxide, rather than precipitate as a discrete compound. Iron may also react with silica monomers to form iron-silicates. The solubilities of iron-silicates in water are approximately 10 mg/L at 25°C, much lower than amorphous silica which presents a solubility of 120 mg/L at 25°C (Gallup, 1998.)

Iron should be monitored before entering the RO unit, as it is a common membrane foulant. In its ferrous state (Fe⁺²), it is soluble. However, when it is oxidized to its ferric state (Fe⁺³), it is insoluble and forms a precipitate. Oxidation may occur when oxygen or an oxidizing agent, as chlorine, is introduced. If iron is not removed in a prefiltration step, it fouls and stains the surface of the membrane, reducing both flux and rejection performance.

4.5.1 RESULTS OF FERRIC CHLORIDE TREATMENT

Iron is added as FeCl_3 at several doses and pH values (defining the behavior throughout the reasonable pH/Fe concentration space) to allow the precipitates to form. Water was adjusted so that its initial pH was 6, 7, 8 and 9 with either HCl or NaOH.

After appropriate mixing, settling, and filtration with a 0.22 μm membrane filter, analyses of the solution were performed on an ICP. Table 4.28 shows that a better silica removal was achieved when raw water was adjusted to a basic pH (pH=9). Metal ions in water solution (such as iron) tend to be more soluble at higher hydrogen ion concentration (lower pH). The best silica removal was just above 50% by addition of 25 mg Fe^{+3}/L at pH 9. The experimental results were unexpected due to the strong silica-iron interactions reported in the literature.

**Table 4.28 Batch Treatment of Synthetic Rio Grande water at 60 mg/L SiO₂:
Addition of Ferric Chloride**

TREATMENT		RESULTS					
Jar Test	Fe ⁺³ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	Fe ⁺³ (mg/L)	pH	% silica removal
Initial pH=6							
0	0	66.2	19.8	28.4	0	6.02	0.0%
1	15	66.1	17.1	22.5	0.04	6.12	19.7%
2	20	75.1	18.7	24.1	0.07	5.92	13.8%
3	25	71.9	17.1	21.8	0.13	5.63	22.2%
Initial pH=7							
4	15	42.7	15.0	19.8	0.02	6.56	29.3%
5	20	48.8	14.7	21.1	0.02	6.26	24.6%
6	25	51.4	14.9	19.4	0.01	6.30	30.8%
Initial pH=8							
7	15	37.9	13.9	17.9	0.10	7.59	36.1%
8	20	36.5	14.2	18.6	0.06	7.29	33.7%
9	25	38.2	14.4	18.1	0.02	7.07	35.4%
Initial pH=9							
10	15	14.2	14.8	17.6	0.0	9.43	37.1%
11	20	15.7	14.9	17.8	0.0	9.1	36.4%
12	25	21.6	14.7	13.2	0.0	8.79	52.8%

The type of silica present in the water may explain the low silica removal in the experiments. As explained in Chapter 2, silica in water may be in the dissolved, colloidal or suspended state. Polymerization reactions of monomeric silica to form polymeric silica (colloidal silica) occur at concentrations approximately twice the saturation level of soluble silica (120 mg SiO₂/L). Due to the much lower Rio Grande silica concentrations (up to 60 mg SiO₂/L), the predominant type of silica in natural waters is monomeric. On the other side, both aluminum and iron are coagulants mainly used to remove colloidal particles. Therefore, the low silica

removals may be due to the silica being mainly in the dissolved or monomeric state. Literature reports on iron-silica interactions are mainly related to the geothermic industry where much higher silica concentrations are found (approximately 700 mg SiO₂/L).

4.6 EXTENT OF SOFTENING FOR ACTUAL RIO GRANDE WATER

Water from the Rio Grande in the Laredo area was collected in a single large batch. The collection of raw water in a large volume was intended to allow all the tests to be conducted from a single batch, thus avoiding source water variability, which may cause complications in data interpretation. The raw water was stored in a 4 °C refrigerator to avoid changes in water quality over time. Table 4.29 shows the chemical analysis of the actual Rio Grande water. Calcium and magnesium concentrations were lower than the reported concentrations used in the Mineql simulations and the synthetic water experiments.

Table 4.29 Chemical Composition of Actual Rio Grande water

	Concentration (mg/L)
Si⁺⁺⁴	28.7
Mg⁺²	16.2
Ca⁺²	23.3
Alkalinity (mg CaCO₃/L)	158
pH	8.02
Turbidity (NTU)	7
Dissolved Organic Carbon (DOC)	1.97
Total Organic Carbon (TOC)	2.42

A series of jar tests was conducted with the best pretreatments previously selected for synthetic Rio Grande water. As shown in Table 4.30, the highest addition of magnesium (35 mg/L of Mg^{+2}) dramatically decreased both the silica and magnesium concentrations at both levels of lime and soda ash addition.

Table 4.30 Batch Treatment of Rio Grande water at 60 mg/L SiO_2 : Lime Softening with Magnesium and Na_2CO_3 Addition

TREATMENT				RESULTS			
Jar Test	Mg^{+2} (mg/L)	CaO (mg/L)	Na_2CO_3 (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	pH
0	0	0	0	23.3	16.2	28.7	8.02
1	15	165	161	24.1	0.7	14.1	10.25
2	25	165	161	29.9	1.3	8.4	10.74
3	35	165	161	30.1	1.1	5.3	10.81
4	15	180	189	13.2	0.4	13.2	10.05
5	25	180	189	14.6	0.7	8.5	10.69
6	35	180	189	15.1	0.6	6.1	10.75

Mineql was run with the previous conditions to make a comparison with the real results. A comparison of the Mineql modeling in Table 4.31 to the experimental results of Table 4.30 shows that silica and magnesium concentrations after the softening treatments were similar for the simulation and the real experiment. According to Mineql, calcium is precipitating as calcium carbonate and silica and magnesium as chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$).

Table 4.31 Mineql Simulation of Rio Grande Softening Pretreatments

TREATMENT				MINEQL RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH
1	15	165	161	22.5	0.0	15.9	10.80
2	25	165	161	22.5	0.0	7.8	10.90
3	35	165	161	22.5	0.0	0.0	11.00
4	15	180	189	8.9	0.9	13.2	10.25
5	25	180	189	8.9	0.7	7.9	10.45
6	35	180	189	8.9	0.5	0.0	10.60

It is clear that silica removal was a function of the magnesium added.

Calcium removal is a function of the sodium carbonate added and thus, the pH.

Calcium concentrations are predicted to be lower than they are in the real system.

Pretreatments of Jar 3 and Jar 6 were selected, due to the final low concentration of silica and magnesium, to be run in the Reverse Osmosis unit. Softening as a pretreatment for Rio Grande river water before reverse osmosis was conducted in a batch mode; a large amount of water (15 L) was softened in a 20 L cylindrical plastic reservoir at the specified softening conditions. The softening batch test was performed in the same way as the softening jar tests. It consisted of 2 minutes of rapid mixing (3 minutes in the case of soda ash addition), 30 minutes of slow mixing, followed by a 30 minute settling period. The supernatant from the softening was used as the feed water for the subsequent softening operation. An XPS analysis of the precipitated solids was performed.

XPS analysis

The elemental composition of the precipitated solids was quantitatively analyzed using XPS analysis. The nature of the solids formed is critical to the reverse osmosis system performance. Table 4.32 shows that the precipitated solids are composed of silica, magnesium and calcium. Although calcium-silicates are quite insoluble, these compounds do not form rapidly except at very high temperatures (Meyers, 1999). Compounds that are more likely to be formed are magnesium-silicates and calcium carbonate. Si/Mg mass ratios of the precipitated solids are 0.61 and 0.65 for pretreatments 1 and 2, respectively. Chrysotile has a Si/Mg ratio of 0.76. These results suggest that chrysotile probably was formed, but was supplemented with another magnesium precipitate.

Table 4.32 XPS Analysis of Solids from Softening Pretreatments of Rio Grande water

Element/ Weight percentage	Pretreatment 1 (%)	Pretreatment 2 (%)
Calcium	8.2	14.0
Oxygen	64.3	62.6
Silica	10.4	9.2
Magnesium	17.0	14.0

4.7 SUMMARY OF SILICA REMOVAL TREATMENTS

The economic viability of adding a pretreatment stage prior to a reverse osmosis unit varies from case to case. However, the main advantage of pretreatment is the reduced membrane fouling costs and operation with higher recovery levels. The optimum dose of pretreatment depends on the quality of the

feed water and the recovery desired. It may not be necessary to remove the ions to a very low level.

Softening was found to be a better silica removal treatment than coagulation for Rio Grande water, as can be seen with the much better results given by softening experiments in comparison with ferric and aluminum salts. Between a lime dose of 150 mg CaO/L to 180 mg CaO/L, each increase in lime addition increased silica reduction. At higher doses of 180 mg CaO/L, silica starts to redissolve in the solution. A magnesium salt is necessary to induce silica precipitation. A dose of 35 mg/L of Mg^{+2} dramatically decreased both the silica and magnesium concentrations. Compounds that are most likely to be formed are magnesium-silicates and calcium carbonate. According to Mineql, the magnesium-silicates chrysotile and tremolite precipitated out of the solution. Si/Mg ratios of the precipitated solids, given by XPS analyses, are 0.61 and 0.65 for the pretreatments analyzed. Chrysotile has a Si/Mg ratio of 0.76. These results suggest that chrysotile probably was formed, but was supplemented with another magnesium precipitate, perhaps $\text{Mg}(\text{OH})_2$. The optimal pH for silica removal within a softening treatment is approximately 10.5 to 11.

CHAPTER 5: BENCH SCALE REVERSE OSMOSIS EXPERIMENTS

5.1 REVERSE OSMOSIS SYSTEM

5.1.1 REVERSE OSMOSIS UNIT

The reverse osmosis system used in this research is a bench-scale membrane apparatus with a plate and frame module. This module simulates the spiral wound behavior in a real treatment plant. The system is operated in a cross-flow mode. A schematic diagram is shown in Figure 5.1.

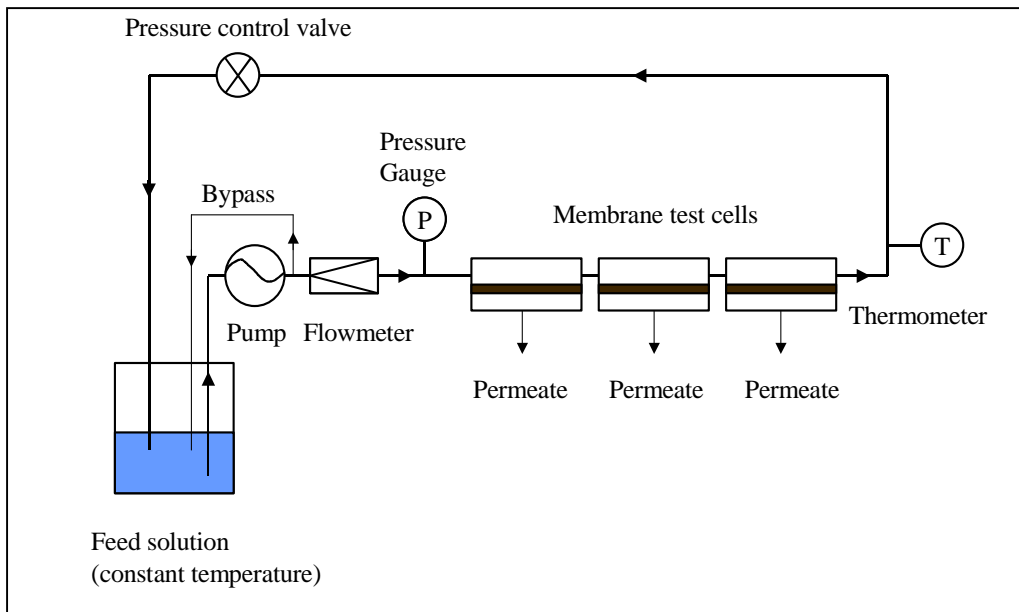


Figure 5.1 Schematic Diagram of the Experimental Reverse Osmosis Unit

The system has a 30 L feed tank and consists of 60 cm² of filter area and three lines: feed, permeate and concentrate lines. The transmembrane pressure of the system was indicated on a pressure gauge. Heat generated by the pump was removed from the recycling solution by a water-cooled heat exchanger. The temperature of the circulating solution was controlled at 25°C. After each experiment was finished, deionized water was pumped through the system during 4 hours to clean the pipes.

5.1.2 MEMBRANES

Two polyamide membranes manufactured by Osmonics (AK and AG membranes, as named by Osmonics) were used to run the experiments. The nominal molecular weight cut-off of the membranes is 100 daltons. The influence of various pretreatment schemes and transmembrane pressure on flux behavior and on permeate quality were investigated.

AK membranes are recommended for silica-bearing waters and were used at a transmembrane pressure of 790 kPa. The manufacturer claims a rejection of 98% at 500 mg/L NaCl at 25 °C. AG membranes are also recommended for silica-bearing waters and work at a transmembrane pressure of 1550 kPa. The theoretical rejection is of 99.2 % at 2000 mg/L NaCl at 25 °C. Both membranes can be used over a pH range between 4 and 11.

Energy dispersive spectroscopy (EDS) was conducted on a LEO-SEM 1530 (Zeiss and Leica, Thornwood, New York) to know the elemental composition of the clean membranes. An accelerating voltage of 10 kV was chosen to determine the elemental analysis of the membranes. The voltage determines the energy and wavelength of electrons in the electron beam. An accelerating voltage of 10 kV

allows for a good penetration of the electrons through the samples, thereby allowing a magnified image of the specimen that shows details not visible with a light microscope. This accelerating voltage also allows for a detailed information about the surface structure, differences of atomic number within the sample and information about the elemental content since it allows a resolution of 2 nm at 2 mm of working distance (WD). The EDS data are given in percent weights of detected elements. Table 5.1 shows the results given by EDS analyses for the clean membranes. The intensity measures photons per second (or counts per second). Since each element has its own unique set of energy levels, the emitted photons are indicative of the element that produced them. The atomic concentration in the sample is also reported.

Table 5.1 Elemental Composition of the Experimental Membranes

AK Membrane			
Element	Intensity (c/s)*	Atomic Concentration (%)	Weight (%)
C	45.1	88.8	85.1
O	19.0	10.6	13.5
S	6.5	0.50	1.3
Total		100.0	100.0
AG Membrane			
C	136.1	83.2	78.4
O	102.1	16.2	20.38
S	17.31	0.41	1.03
Mg	1.4	0.03	0.05
Si	0.32	0.007	0.015
Ca	0.71	0.02	0.083
Total		100.0	100.0

*kV=10

Analysis of a clean AK membrane detected the presence of carbon (C), oxygen (O) and sulfur (S). AG membrane analysis also detected the presence of carbon (C), oxygen (O) and sulfur (S) as the main elements of the polymer, similar to AK membranes, but trace amounts of magnesium (Mg), silica (Si) and calcium (Ca) were also detected.

A SEM image of an AK clean membrane was taken and is shown in Figure 5.2. Figure 5.2 shows that even clean membranes present some imperfections at a resolution of 10 μm .

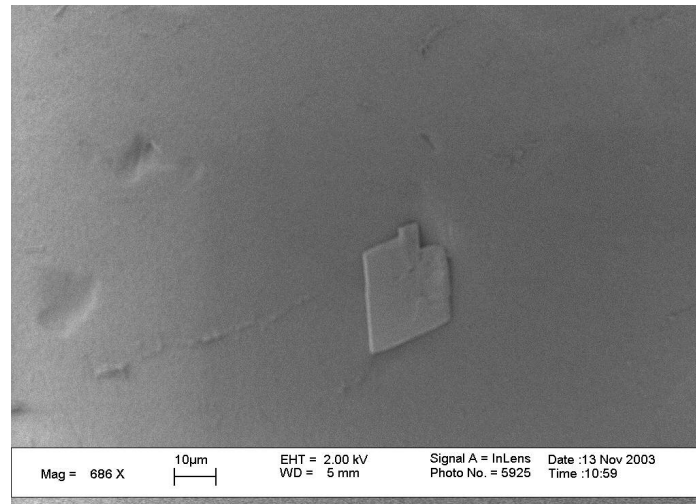


Figure 5.2 Image of AK Clean Membrane

Salt Rejection

The NaCl rejection was determined for AG and AK membranes after a preconditioning period with deionized water. The rejection for AG membranes with 2000 mg/L NaCl feed solution at 1550 kPa and 25 °C was 97.4%. For AK membranes with 500 mg/L NaCl feed solution at 790 kPa and 25 °C was 96.4%.

These values are somewhat lower than the reported by the manufacturer, 98% for AK membranes and 99.2% for AG membranes, but both results indicate that the membranes and the entire experimental apparatus were working well. Appendix B presents the calculations for the membrane rejection percentages.

5.2 SELECTION OF CONDITIONS OF RO EXPERIMENTS

The general objectives of the laboratory tests were to characterize the role of some major parameters on the performance of an RO unit such as (1) feed silica concentration and quality of feed water (2) transmembrane pressure and (3) crossflow velocity in RO systems in general and in Rio Grande water in particular. The experiments were conducted at a constant temperature of 25 °C and initial pH of 8. A sodium chloride solution was circulated before each experiment for approximately 150 minutes to stabilize the membrane and to evaluate if the quality of the membrane was adequate. Water flux during the NaCl feed should be between 0.075 to 0.1 L/m²-h-kPa for AK membranes and 0.04 to 0.055 L/m²-h-kPa for AG membranes.

5.2.1 QUALITY OF FEED WATER

The effects of initial silica, calcium and magnesium concentrations on fouling were investigated. These studies allowed the investigation of the influence of ionic composition on the silica deposition process.

Seven different water conditions were investigated. Two experiments were run with synthetic Rio Grande water, to establish a baseline from which to evaluate the effectiveness of the pretreatments. The two baseline experiments were for an initial silica concentration of 23 mg SiO₂/L (typical concentration of Rio Grande water) and 60 mg SiO₂/L (median concentration on the zones of higher silica of the Rio Grande River.) For water with an initial silica concentration of 23 mg SiO₂/L, two pretreatments were selected, as established in Chapter 4, to evaluate its effectiveness when used before a reverse osmosis unit. For water with an initial silica concentration of 60 mg SiO₂/L, three pretreatments were selected. Table 5.2 shows the seven feed water conditions of the reverse osmosis experiments. For each condition of river water, the treatment that gave the better results in terms of lower decline of flux across the membrane was selected. The selected treated water was then run at different operating conditions of the RO unit, *i.e.*, crossflow velocity and pressure.

Table 5.2 Chemical Composition of RO Feed water

	Si⁺⁴ (mg/L)	Mg⁺² (mg/L)	Ca⁺² (mg/L)	pH*
Baseline 1 (Rio Grande water)	28.1	20.1	75.0	8.03
Softening Treatment 1	9.5	1.8	4.8	11.02
Softening Treatment 2	6.9	6.6	7.0	10.82
Softening Treatment 3	5.4	9.3	8.7	10.83
Baseline 2 (Rio Grande water)	10.7	20.1	75.0	8.05
Softening Treatment 4	6.7	16.8	14.3	10.81
Softening Treatment 5	3.9	6.8	11.1	10.96

*pH was adjusted to 8 before entering the RO unit.

5.2.2 TRANSMEMBRANE PRESSURE

The effect of transmembrane pressure on permeation flux of water at a temperature of 25 °C was studied. The two pressures studied were 790 kPa using AK membranes, and 1550 kPa using AG membranes.

5.2.3 CROSSFLOW VELOCITY

Most crossflow systems, including those with a spiral-wound configuration, require turbulent flow conditions to decrease the fouling process over the membranes. Thus, a reasonably high crossflow velocity across the membrane is needed. Because pure water is continuously pulled away from the feed stream, contaminant concentration increases across the length of the membrane element. When the crossflow velocity is too low, the contaminants are not flushed away from the membrane surface.

To study the effect of crossflow velocity on fouling, experiments were carried out at two different flow rates: 1.13 L/min and 4.16 L/min, corresponding to 0.98 cm/s and 3.6 cm/s of crossflow velocity. Considering the density and viscosity of the solution as $\rho=0.99 \text{ g/cm}^3$ and $\mu=0.89 \text{ cP}$, the Reynolds number for a flow rate of 1.13 L/min was $Re=2586$ which is on the limit of laminar conditions. For the flow rate of 4.16 L/min, the Reynolds number was 9659, so that turbulent conditions were present.

Table 5.3 shows the conditions of each of the 19 experiments carried out in the RO unit with softening pretreatment of the influent water.

Table 5.3 Design of RO Experiments with Softening Pretreatments

Pressure/Crossflow velocity	790 kPa		1550 kPa	
	0.98 (cm/s)	3.6 (cm/s)	0.98 (cm/s)	3.6 (cm/s)
Synthetic Rio Grande water (SiO₂=60 mg/L)	Run 1	Run 2	Run 3	Run 4
Softening Treatment 1*	Run 5	Run 8	Run 9	Run 10
Softening Treatment 2	Run 6			
Softening Treatment 3	Run 7			
Synthetic Rio Grande water (SiO₂=23 mg/L)	Run 11	Run 12	Run 13	Run 14
Softening Treatment 4	Run 15			
Softening Treatment 5*	Run 16	Run 17	Run 18	Run 19

*Softening treatments 1 and 5 had the lowest flux decline under the baseline pressure and velocity conditions. Thus, these pretreatments were applied to the feed water of the RO unit at different operational conditions.

5.3 RESULTS OF RO EXPERIMENTS: SYNTHETIC RIO GRANDE WATER WITH SOFTENING PRETREATMENT

5.3.1 INFLUENCE OF QUALITY OF WATER ON A RO UNIT PERFORMANCE

Synthetic Rio Grande water with an initial silica condition of 60 mg SiO₂/L

The objective of this set of experiments was to evaluate the influence of the quality of water (*i.e.*, total hardness and silica, magnesium and calcium concentrations) on the performance of the system. Three different pretreatments were applied to laboratory-made Rio Grande water (with an initial silica condition of 60 mg SiO₂/L) that was further treated in a reverse osmosis unit, at the same

operating conditions: 790 kPa and 0.98 cm/s for 60 hours. The description of the selection of the pretreatments is shown in Section 4.3.5. The criterion to select the pretreatments that were tested on the RO unit was based on silica and hardness concentration removal, as well as the lowest amount of precipitate expected over the membranes. Table 5.4 shows the composition of the three treated waters that were fed to the RO unit. All waters were analyzed with Inductively Coupled Plasma (ICP) spectroscopy. To avoid precipitation of metal silicates at high pH, 1N HCl was added to bring solution pH down to 8.

Table 5.4 Chemical Analysis of Water Tested on the RO Unit at 60 mg SiO₂/L

	Rio Grande water	Treatment 1*	Treatment 2*	Treatment 3*
Si⁺⁴ (mg/L)	28	9.5	6.9	5.4
Mg⁺² (mg/L)	20	1.8	6.6	9.3
Ca⁺² (mg/L)	75	4.8	7.0	8.7
Total Hardness (mg CaCO₃/L)	220	19.4	44.7	60
Alk (mg CaCO₃/L)	164	87.4	72.0	77.0
pH	8.03	11.02	10.82	10.83

*Treatment 1: Addition of 15 mg/L of Mg⁺², 165 mg/L lime and 160 mg Na₂CO₃/L.

Treatment 2: Addition of 25 mg/L of Mg⁺², 165 mg/L lime and 160 mg Na₂CO₃/L.

Treatment 3: Addition of 15 mg/L of Mg⁺², 180 mg/L lime and 190 mg Na₂CO₃/L.

All tests at 790 kPa and 0.98 cm/s.

Figure 5.3 shows the specific flux decline for untreated synthetic Rio Grande water during 60 hours of operation of the RO unit. The three lines represent the flux behavior of the three membranes of the system. The three membranes had very nearly the same flux as one another throughout the experiment, and this type of result was found in all experiments. Therefore, in the subsequent presentation of the flux results, only an average of the three results is shown. The flux decline was quite

dramatic in this experiment with untreated water, with the flux at the end of the 60 hours being approximately half of the initial flux and the total volume treated being approximately $1.6 \text{ m}^3/\text{m}^2$.

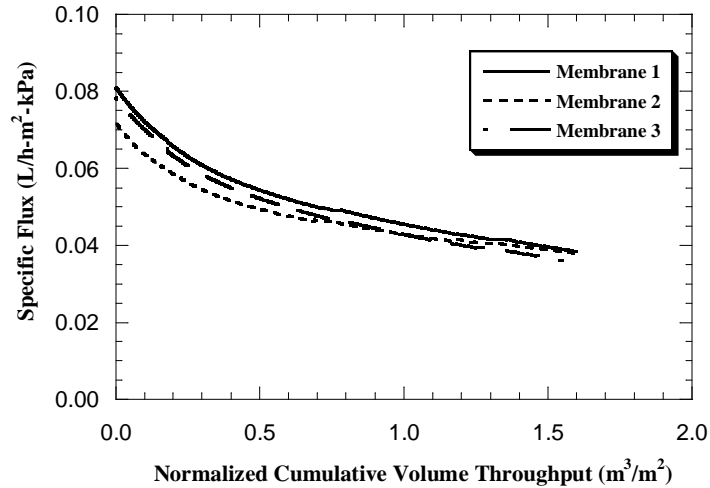


Figure 5.3 Influence of Feed water Quality on Specific Flux Decline
(Synthetic Rio Grande water at 790 kPa and 0.98 cm/s)

Synthetic Rio Grande water was then pretreated with the three chosen softening treatments. Figure 5.4 shows that the specific flux decreased as a function of time (or as the cumulative volume throughput increased), but that the pretreatments had a dramatic effect on the flux behavior. Rio Grande water had the greatest flux decline at the end of the operation period; it showed a constant decline of the specific flux over the entire period studied. Feed waters that were pretreated before entering the RO unit showed a much lower decline of the specific flux over time.

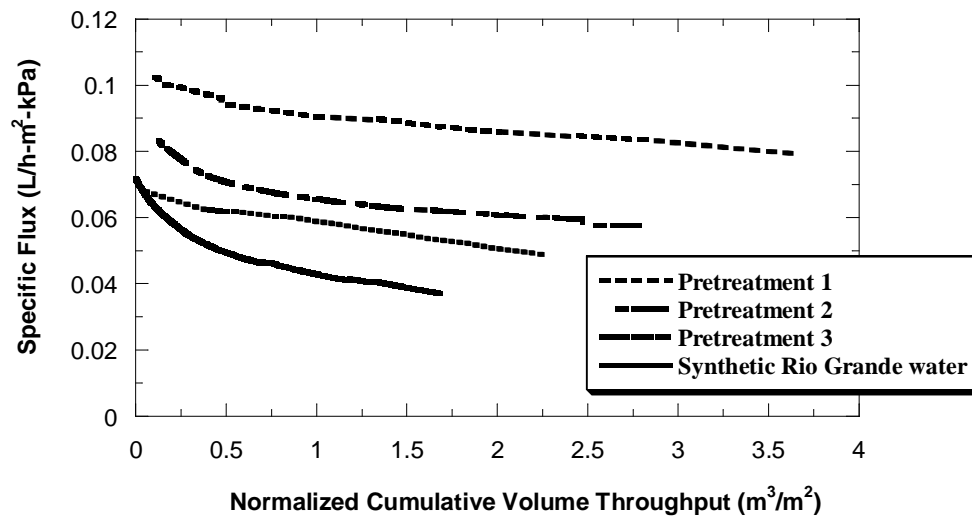


Figure 5.4 Influence of Feed water Quality on Specific Flux Decline: Pretreated Synthetic Rio Grande water at 790 kPa and 0.98 cm/s

The lowest flux decline was for Softening Treatment 1. The volume of feed water recovered increased from 32 % for synthetic Rio Grande water without pretreatment to 70 % for pretreated synthetic Rio Grande water. The increase in recovery percentage is clearly due to a lower amount of material deposited over the membrane and to a lower osmotic pressure that the high pressure pump has to overcome to allow water to diffuse through the membrane pores.

Table 5.5 shows the specific flux decline and the normalized cumulative volume throughput for the membrane at 15 and 60 hours of operation. Rio Grande untreated water had a higher rate of flux decline over time. From 15 to 60 hours of operation, the flux decline for untreated water increased 64%, while for pretreated waters, it increased 48% for pretreatments 1 and 2 and 29% for pretreatment 3.

Table 5.5 Membrane Performance at 60 mg SiO₂/L

	Average Flux Decline*		Volume Throughput (% of recovery)	
	At 15 hours	At 60 hours	At 15 hours	At 60 hours
Rio Grande Water	31.9 %	52.5 %	3.2 L (10.6%)	9.8 L (32.6%)
Softening Treatment 1	13.1 %	19.5 %	6.0 L (20.2%)	21.1 L (70.3%)
Softening Treatment 2	22.6 %	33.6 %	4.7 L (15.7%)	16.5 L (55.0%)
Softening Treatment 3	29.7 %	38.4 %	3.7 L (12.3%)	13.5 L (45.0%)

*The average is calculated from the flux decline of each of the three membranes of the RO unit; all tests at 790 kPa and 0.98 cm/s.

The decline of flux seems to follow a similar pattern over time for all of the conditions tested. At 15 hours of operation, untreated water had a 2.4 times the flux decline of pretreated water with treatment 1. At 60 hours of operation, untreated water had 2.7 times the flux decline of pretreated water. The same behavior was present for the two other pretreatments.

To analyze the nature and morphology of the material deposited on the membranes, SEM and EDS analysis were performed at the end of each experiment.

SEM Analysis

A scanning electron microscope LEO-SEM 1530 was used to evaluate structural and morphological features of scale deposits. Figures 5.5 shows membrane images at the end of the experiment with synthetic Rio Grande water without any pretreatment. The membrane surfaces present uniform aggregates of deposited material covering almost the entire membrane area studied. Particles shown on the second image (1240 X) appear to be square-type. As can be seen from the images, severe fouling occurred, which induced a specific flux decline of 52.5%.

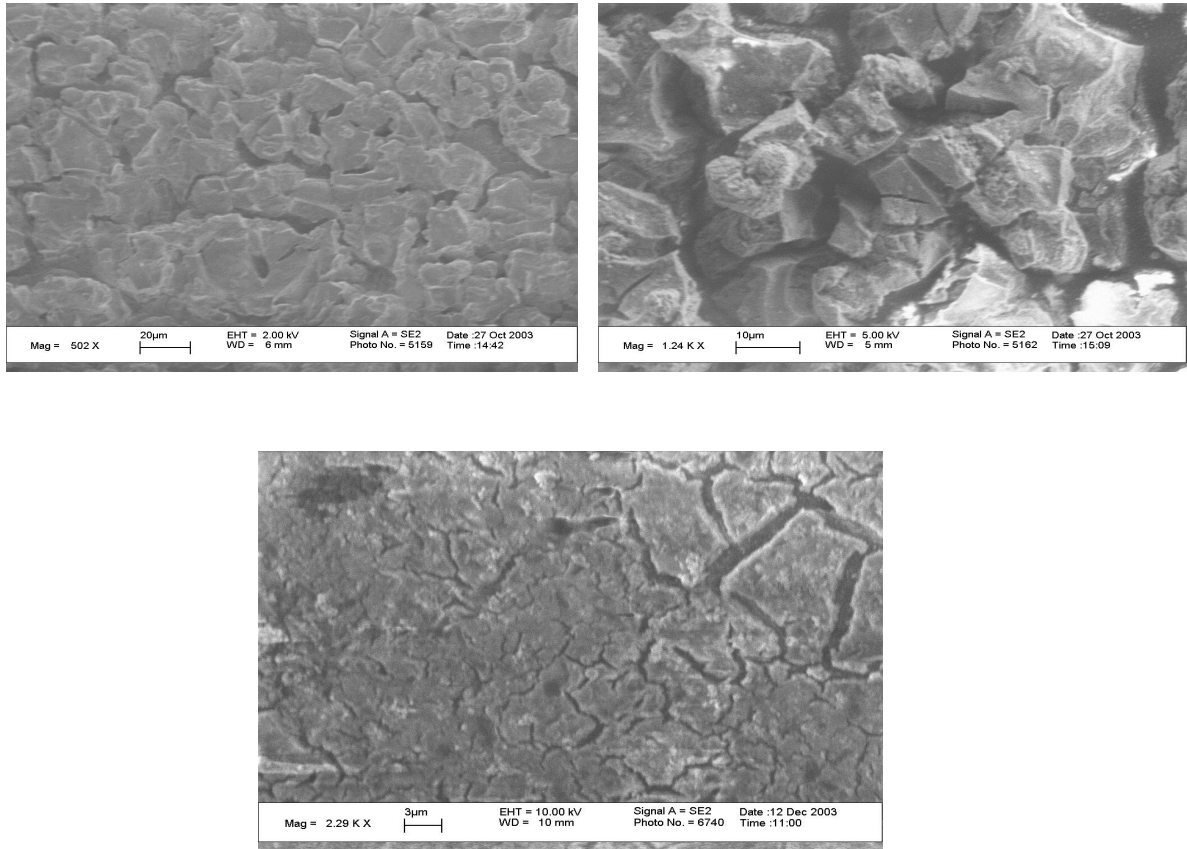


Figure 5.5 SEM Images of RO Membranes: Synthetic Untreated Rio Grande water (502, 1240 and 2290X)

Membrane images at the end of the experiment with pretreated Rio Grande River with the best pretreatment, Softening Treatment 1, presented some particles attached to the membrane, although they were more scattered and did not cover the entire surface. The specific flux decline was 19.5 %. Figure 5.6 shows these images.

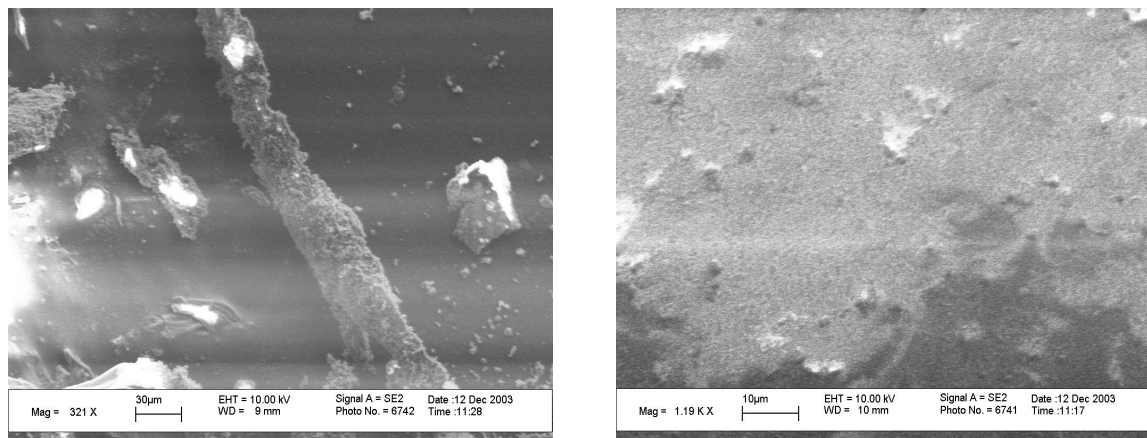


Figure 5.6 SEM Images of RO Membranes: Synthetic Pretreated Rio Grande water (321 and 1190X)

The experiments with different quality of feed water (but same conditions of operation) show that softening treatments allow for a better performance of the RO unit, *i.e.*, a lower flux decline occurs (52.5% vs. 19.5% of specific flux decline) as a result of a less amount of particles deposited over the membrane surface. Even though the three feed waters that underwent pretreatment allowed for a better performance of the RO unit than synthetic Rio Grande water without pretreatment, the Softening Treatment 1 proved to be the best treatment, as it induced the lowest specific flux decline. These results are in accordance with Mineql simulations (Table 4.22) where the program showed that the amount of precipitates that may be formed after concentration of the feed stream is lower for water pretreated with softening treatment 1.

EDS Analysis Results

Energy dispersive spectroscopy (EDS) analyses were conducted to identify the elements in the precipitates on the membranes. The results of the analysis are shown in Table 5.6. EDS analyses revealed the presence of silica as the major component of the scales while running synthetic Rio Grande water as feed water. Carbon and oxygen are the main elements of the polymer polyamide and were present at 85% and 13 % respectively on the analysis of a clean membrane. The only other element identified in a substantial percentage was magnesium, 9.03%. The analysis suggests that magnesium and silica are precipitating together as a magnesium silicate, as batch tests also suggested.

Table 5.6 EDS Analysis of RO Membranes for Synthetic Rio Grande water at 60 mg SiO₂/L

Element	Weight Percentage of Elements				
	AK Membrane	Rio Grande water	Pretreated water: ST 1*	Pretreated water: ST 2	Pretreated water: ST 3
Carbon	85.1	63.3	85.6	84.0	80.5
Oxygen	13.5	9.5	12.8	14.7	19.4
Sulfur	1.3	0.26	0.27	0.14	0.20
Magnesium	0.0	9.03	0.08	0.28	0.45
Silica	0.0	11.8	0.23	0.79	1.23
Calcium	0.0	5.94	0.0	0.0	0.00
Total	100.0	100.0	100.0	100.0	100.0

*ST=Softening Treatment; all tests at 790 kPa and 0.98 cm/s.

Mineql simulations, as well, showed that the main compounds formed were the magnesium silicates, tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2(s)$) and chrysotile ($Mg_3Si_2O_5(OH)_4(s)$). From the SEM images, it appears that the particles deposited over the membranes were in the size range of 10 to 100 microns. Apparently, some precipitate agglomeration and growth processes of silicate compounds could occur at the membrane-solution interface.

The EDS analysis of the scales deposited over the membranes indicated that a silica level of less than 10 mg as Si/L (pretreated waters) in an RO feed water caused no scaling at a water recovery rate up to 70% (as seen in softening treatment 1). At higher recovery rates, scaling problems may still be absent, but the experiments presented here were run up to that percentage of recovery.

Feed water pretreated with softening treatment 1, which had the highest silica concentration of the pretreated feed water (9.5 mg Si/L), presented the lowest flux decline over time. This feed water had a very low magnesium concentration. From these results, it can be said that silica concentration by itself is not the only parameter to predict if scaling occurs over the membranes. The concentration of both silica and magnesium seemed to determine the extent of scaling over the membranes for water with the make up of the Rio Grande River. It seems that a magnesium-silica compound deposition was induced rather than a monomeric deposition of silica (deposition of silica as silicon dioxide). Magnesium and calcium ionic concentrations were both below 10 mg/L for pretreated water. Even though magnesium was present as a scale over the membrane, it was below 1 % of the elemental composition of the membrane. Calcium was not a scale problem for pretreated water.

Based on the low residence time of the concentrate stream in an industrial RO system and the low silica concentrations when water is pretreated, it seems that the only condition likely to result in membrane scaling is adsorption or reaction of silica with other ions, mainly the magnesium ion. Homogeneous reactions, *i.e.*, polymerization of silica with other silica molecules, forming colloidal particles, is less likely to occur since this reaction occurs at high silica supersaturation values, a condition that is not likely to occur at the low initial feed water silica concentration of the pretreated waters. Water pretreated with the softening treatment 1 confirmed that, even though silica concentration is relatively high (in comparison to the other two pretreated waters), precipitation of silica is not likely to occur if calcium and magnesium concentrations are low.

Even though the scaling problem on pretreated waters seems to be low, the flux decline in the three experiments with pre-treated water was still considerable, 19.5%, 33.6% and 38.4%, for pretreatments 1, 2 and 3 respectively.

Synthetic Rio Grande water with an initial silica condition of 23 mg SiO₂/L

Two different pretreatments were applied to synthetic Rio Grande water (with an initial silica condition of 23 mg SiO₂/L) that was further treated in a reverse osmosis unit at 790 kPa and 0.98 cm/s for 60 hours. Experiments made with Rio Grande water with a silica concentration of 23 mg SiO₂/L showed good silica removal at 15 mg Mg⁺²/L and addition of lime between 130-155 mg CaO/L. At an addition of 130 mg CaO/L (Treatment 4) a silica removal of 42% was achieved while an addition of 155 mg CaO/L (Treatment 5) achieved a silica removal of 66%.

Table 5.7 shows the composition of the three treated waters that were fed to the RO unit. As before, pH was adjusted to 8.0 prior to the membrane treatment.

Table 5.7 Chemical Analysis of Water tested on the RO Unit at 23 mg SiO₂/L

	Rio Grande water	Treatment 4	Treatment 5
Si⁺⁴ (mg/L)	11	6.7	3.9
Mg⁺² (mg/L)	20	16.8	6.8
Ca⁺² (mg/L)	55	14.3	11.1
Alk (mg CaCO₃/L)	164	104	74
pH	8.03	10.81	10.96

All tests at 790 kPa and 0.98 cm/s.

As stated before, the main parameter that characterizes the performance of the system is the specific flux behavior. Figure 5.7 shows the flux decline over 60 hours of operation of the RO unit for Rio Grande water (23 mg SiO₂/L) and two pretreated feed waters. As expected, Rio Grande water presented the highest specific flux decline (35%) at the end of the operation period and thus, the lowest cumulative volume. The specific flux of the Rio Grande water presented a sudden decline in the specific flux in the early part of the experiment. This sudden decline of the flux may be an indication of a scale precipitation which was not so porous and thus blocked the water passage through the membrane. Usually, carbonate precipitation, especially calcium carbonate, induces a sudden decline of specific flux and it is a scale difficult to be removed without damaging the membrane.

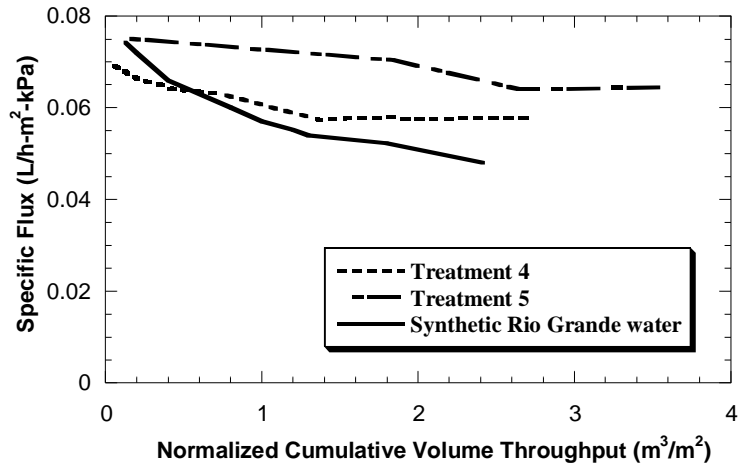


Figure 5.7 Influence of Feed water Quality on Specific Flux Decline: Synthetic Rio Grande water at 23 mg SiO₂/L, 790 kPa and 0.98 cm/s

Table 5.8 shows the average specific flux decline at 15 and 60 hours of operation as well as the normalized cumulative volume throughput for the membrane. Flux decline for untreated water increased 84% from 15 to 60 hours of operation, while for the best treatment, softening treatment 5, the flux decline increased 51%. As can be seen, flux declines more rapidly at the beginning of the experiments. After a few hours of operation, flux presents a lower rate of decline, especially for pretreated waters.

Table 5.8 Membrane Performance at 23 mg SiO₂/L

	Average Flux Decline*		Volume Throughput (% of recovery)	
	At 15 hours	At 60 hours	At 15 hours	At 60 hours
Rio Grande Water	19.0 %	35.0 %	4.8 L (16.0%)	14.9 L (49.6%)
Softening Treatment 4	9.5 %	23.9%	5.4 L (18.0%)	17.3 L (61.2%)
Softening Treatment 5	9.4 %	14.2 %	7.6 L (25.4%)	20.2 L (67.5%)

*The average is calculated from the three membranes of the RO unit ; all tests at 790 kPa and 0.98 cm/s.

Softening treatment 5 presents the lowest percentage of specific flux decline. Pretreated water with softening treatment 5 had very low silica and magnesium concentrations, 3.9 mg Si⁺⁴ /L and 7 mg Mg⁺²/L. The results are in accordance to Mineql simulations (Table 4.24). The program predicted that lower amount of precipitates may occur during RO operation if feed water underwent softening treatment 5.

EDS analysis

Energy dispersive spectroscopy analyses were conducted on the membranes after their use to determine the nature of the precipitates on the membranes. EDS analyses shown in Table 5.9 revealed the presence of calcium and silica as the major components of the scales while running synthetic Rio Grande water as feed water. Carbon and oxygen are the main elements of the membrane polymer (polyamide). The only other element identified in a considerable amount was magnesium, 3.5%.

Table 5.9 EDS Analysis of RO Membranes: Synthetic Rio Grande water at 23 mg SiO₂/L

Element	Weight Percentage of Elements		
	Rio Grande water	Pretreated water: ST 4*	Pretreated water: ST 5
Carbon	63.95 %	72.27 %	86.6 %
Oxygen	20.56 %	25.16 %	12.81 %
Magnesium	3.53 %	0.42 %	0.078 %
Silica	4.74 %	1.89 %	0.23 %
Sulfur	0.26 %	0.24 %	0.27 %
Calcium	6.93 %	0.00 %	0.00 %
Total	100.0 %	100.0 %	100.0 %

*ST=Softening Treatment; all tests at 790 kPa and 0.98 cm/s.

The analysis suggests that calcium is precipitating as calcium carbonate and/or as a magnesium-calcium-silicate. The pH at the end of the experiment was 8.4. Mineql predicts that, at this pH and the final ionic concentration of the feed water, the most likely compounds to be formed are calcite and tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2(s)$).

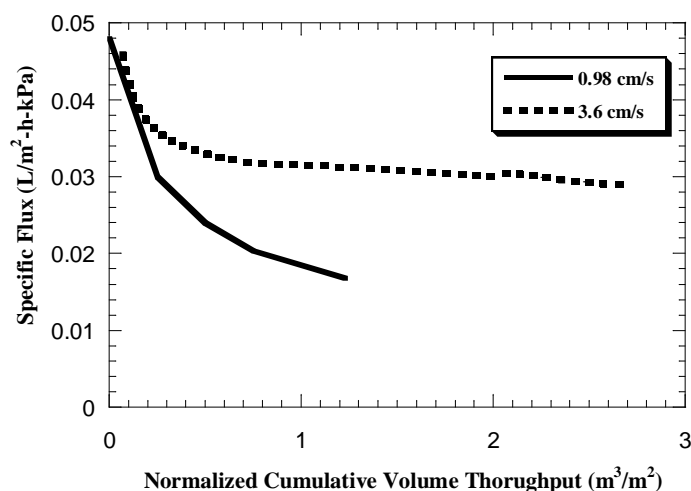
EDS analyses of the scales deposited over the membranes indicated that a silica concentration of less than 7 mg as Si/L (pretreated waters) in an RO feed water causes no scaling at a water recovery rate up to 68% (softening treatment 5).

5.3.2 INFLUENCE OF CROSSFLOW VELOCITY ON A RO UNIT PERFORMANCE

Most crossflow systems, including the spiral-wound configuration, require turbulent conditions to decrease the fouling process over the membranes. Since pure water is continuously pulled away from the feed stream, contaminant concentration increases across the length of the membrane element. If the crossflow velocity is too low, the contaminants are not flushed away from the membrane surface, but as the crossflow velocity increases, the cost of pumping the fluid is higher. The influence of flow is analyzed on untreated and pretreated water in this section. For each water, the flux behavior, an EDS analysis and a concentration polarization analysis are presented below.

Influence of Crossflow on Untreated Synthetic Rio Grande River water

To study the influence of crossflow velocity on fouling for untreated synthetic Rio Grande water, experiments at two crossflow velocities, 0.98 cm/s and 3.6 cm/s, were carried out. The operational period was 60 hours. Figure 5.8 shows that, for crossflow velocity of 3.6 cm/s, the specific flux decline was 37.6%; for crossflow velocity of 0.98 cm/s, the flux decline was 65%, at otherwise same conditions of feed water, temperature and pressure.



**Figure 5.8 Influence of Crossflow Velocity on Specific Flux Decline:
Untreated Synthetic Rio Grande water at 23 mg SiO_2/L and 1550 kPa**

EDS analyses of the experimental membranes were carried out to investigate the elements deposited on the membranes. Table 5.10 shows that, at the same feed water conditions and operational pressure, calcium deposits do not occur at high crossflow velocities (0.98 cm/s vs. 3.6 cm/s). This result was present in both pair of experiments, at 790 kPa and at 1550 kPa. Magnesium and silica deposits occurred at slightly lower percentage at higher crossflow velocities. It seems that the main factor inducing a higher specific flux when higher cross flow velocities are applied is the absence of calcium compounds scaling the membranes, although silica and magnesium were also deposited in lower amounts at higher crossflow velocities.

Table 5.10 EDS Analysis of RO Membranes: Untreated Synthetic Rio Grande water at 60 mg SiO₂/L

	Weight Percentage of Elements			
	790 kPa		1550 kPa	
Conditions of Operation	0.98 cm/s	3.6 cm/s	0.98 cm/s	3.6 cm/s
Carbon	65.3 %	72.26 %	65.61 %	70.61 %
Oxygen	9.5 %	10.28 %	13.66 %	13.68 %
Magnesium	9.03 %	7.15 %	6.73 %	6.26 %
Silica	11.8 %	9.94 %	10.15 %	8.88 %
Sulfur	0.26 %	0.35 %	0.31 %	0.35 %
Calcium	3.94 %	0.0 %	3.52 %	0.0 %
Total	100.0 %	100.0 %	100.0 %	100.0 %

An analysis of the concentration of salts near the membrane surface might explain these results. Such analysis is presented in the next section.

Concentration Polarization Analysis

The method used to estimate the concentration polarization value was proposed by Sutzkover (2000), and was explained in Chapter 2.

Concentration Polarization at 790 kPa and 0.98 cm/s

At 790 kPa, for a crossflow velocity of 0.98 cm/s, the velocity is 23.3 cm/s for the system tube diameter of 1 cm. Considering the density and viscosity of the solution as $\rho=0.99 \text{ g/cm}^3$ and $\mu=0.89 \text{ cP}$, the Reynolds number

can be calculated to be $Re=2590$. The average diffusivity of the solution is $D_v=1.3 \times 10^{-5} \text{ cm}^2/\text{s}$, since the main ions reacting with silica are calcium and magnesium. For these values the Schmidt number is $Sc=692$.

With the Reynolds number and Schmidt number, the value of the Sherwood number can be calculated, $Sh=44$. With the Sherwood number and the chemical properties of the solution, the value of the mass transfer coefficient is $K_D= 5.68 \times 10^{-4} \text{ cm/s}$. With a maximum flux of $J_v=0.001 \text{ mL/cm}^2\text{-s}$, the value of concentration polarization (CP) can be calculated as follows:

$$CP = e^{\frac{J_v}{K_D}}$$

Thus $CP= 5.8$.

If the ionic concentration of the feed water is already high, the continuous increase in concentration of the feed-concentrate stream during the experiment, along with the concentration polarization phenomenon developed on the membrane surface, may lead to precipitation of salts over the membranes. Previous analysis of concentration polarization values reported values ranging from 1.4 to 4.2 for crossflow velocities ranging from 0.11 cm/s to 5.1 cm/s (Koo, 2002).

To analyze the scenario with the recovery level achieved in the Rio Grande water experiment, the expected ion concentration near the membrane was calculated as follows:

$$C_{feed-concentrate} = C_{feed} * (\frac{1}{1 - R * Y})$$

where,

$C_{feed-concentrate}$ = Concentration of the ion in the concentrate stream

C_{feed} = Concentration of the ion in the feed water

R = Recovery level set for the RO unit

Y = Membrane rejection for an specific ion

Calcium concentration near the membrane surface

The calcium concentration in the feed stream was approximately 45 mg Ca^{+2} /L. The recovery level was 32.6% and the average rejection of the calcium ion was approximately 97% (an average value of 1.35 mg Ca^{+2} /L was measured in the permeate stream via an ICP spectrophotometer). For these values, the concentration in the feed-concentrate stream near the end of the experiment was $C_{feed-concentrate} = 66$ mg Ca^{+2} /L. Thus, the concentration of calcium in the membrane surroundings can be calculated as follows:

$$C_{membrane} = CP * (C_{feed-concentrate} - C_{product}) + C_{product}$$

From the previous equation, $C_{membrane} = 376$ mg Ca^{+2} /L. At this high value, it is possible for calcium carbonate or calcium-silicates to precipitate.

Silica concentration near the membrane surface

The silica concentration in the feed stream was 28 mg Si/L and the recovery level was 32.6%. The average rejection of silica ion was approximately 96% (an average value of 1.05 mg Si/L was measured in the permeate stream via an ICP).

For these values, the concentration in the feed-concentrate stream near the end of the experiment was $C_{\text{feed-concentrate}} = 40.9$ mg Si/L. Thus, the concentration of silica in the near membrane surroundings is $C_{\text{membrane}} = 232.4$ mg Si/L, *i.e.*, 498 mg SiO_2/L .

The silica concentration value near the membrane surface is as much as 4.1 times the saturation value that allows polymerization reactions to develop. Thus, silica may be causing a flux decline both by precipitation as metal-silicates and by fouling the membranes with colloidal silica.

Concentration Polarization at 790 kPa and 3.6 cm/s

At the same pressure, 790 kPa, a crossflow velocity of 3.6 cm/s yields a velocity of 87 cm/s. The Reynolds number is 9660 and the Schmidt number is 692. The mass transfer coefficient can then be calculated, $K_D = 4.69 \times 10^{-3}$ cm/s. The maximum flux is 1.5×10^{-3} mL/cm²-s. From here, a value of CP=1.37 is calculated.

For this experiment, the concentration in the feed stream was also 45 mg Ca^{+2}/L . At the same recovery level of previous experiment, $C_{\text{feed-concentrate}} = 66$ mg Ca^{+2}/L , giving a $C_{\text{membrane}} = 90$ mg Ca^{+2}/L . The silica concentration in the feed stream was 28 mg Si/L. For this value, $C_{\text{feed-concentrate}} = 40.9$ mg Si/L. Thus, $C_{\text{membrane}} = 55.6$ mg

Si/L, *i.e.*, 119 mg SiO₂/L. At these much lower values, scaling of calcium salts is not likely to occur while silica is likely to be precipitating with magnesium, since at the low concentration of 119 mg SiO₂/L, it is unlikely that precipitation of silicon dioxide or polymerization reactions would occur.

As can be seen from the previous analysis of concentration polarization phenomena between the two experiments, silica concentration near the membrane wall is a function of crossflow velocity (and other parameters as feed water concentration). The higher the crossflow velocity, the lower the accumulation of particles and materials occur at the membrane surface, leading to a lower degree of fouling (accumulation of material) and possibly scaling (precipitation of salts).

Influence of Crossflow velocity on synthetic Rio Grande pretreated water

The influence of crossflow velocity conditions if water is pretreated and has a considerably lower concentration of ions and particles may be different than that of untreated water. Figure 5.9 shows the specific flux decline over 60 hours of operation for pretreated water (with Softening Treatment 1) at different crossflow velocities. Figure 5.9 shows that, the higher the feed water crossflow velocity, the lower the flux decline at the same conditions of pressure and feed water concentrations. The specific flux decline for crossflow velocity of 0.98 cm/s was approximately 18.2 %, while for a crossflow velocity of 3.6 cm/s, it was approximately 7.3 %.

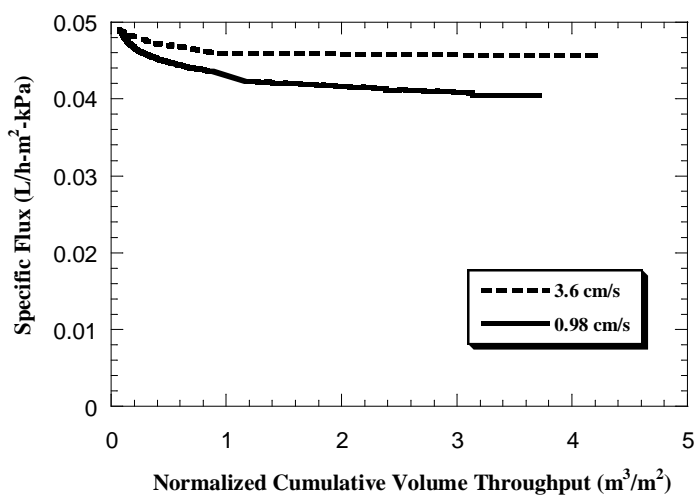


Figure 5.9 Influence of Crossflow Velocity on Specific Flux Decline for Pretreated Synthetic water at 1550 kPa

EDS Analysis Results of RO Membranes EDS analyses of the previous experiments were carried out to investigate the precipitation of particular ions at different crossflow velocities. Table 5.11 shows that the percentage of the Mg^{+2} and Si^{+4} elements deposited on the membranes is low at both crossflow velocity conditions for the two different pressures for the pretreated waters. Calcium scales are not present according to the EDS analysis. Even though the analysis of membranes gave a low weight percentage of deposited material in both experiments, the higher the crossflow velocity, the lower the specific flux decline.

Table 5.11 EDS Analysis of RO Membranes for Pretreated Synthetic water at 1550 kPa

	Weight Percentage of Elements			
	790 kPa		1550 kPa	
Conditions of Operation	0.98 cm/s	3.6 cm/s	0.98 cm/s	3.6 cm/s
Carbon	83.6 %	85.2 %	83.6 %	71.33 %
Oxygen	13.8 %	13.7 %	14.6 %	27.7 %
Magnesium	0.45%	0.123 %	0.16 %	0.32 %
Silica	1.88 %	0.56 %	0.68 %	0.35 %
Sulfur	0.108 %	0.203 %	0.358 %	0.107 %
Calcium	0.0 %	0.0 %	0.0 %	0.0 %
Total	100.0 %	100.0 %	100.0 %	100.0 %

In summary, the experiments with both pretreated and untreated laboratory-made Rio Grande water presented a lower specific flux decline at higher crossflow velocities. Crossflow velocity has proven to be critical in the performance of an RO system, since the formation of concentration gradients close to the membrane surface (concentration polarization phenomena) is influenced by the crossflow velocity conditions. A concentration polarization mathematical analysis with the method reported by Sutzkover (2000) indicated that, at a crossflow velocity of 3.6 cm/s, the concentration polarization value is as low as 1.3 (*i.e.*, the concentration near the membrane surface is 1.3 times the concentration in the bulk solution) while at a low crossflow velocity, 0.98 cm/s,

CP is as high as 5.8, mainly due to the lack of turbulent conditions that allow particles to be swept away. At these high concentrations, it is much more likely that silica could polymerize to form colloidal silica that could deposit over the membrane surface, and more importantly, silica (and other ions) exceed their solubility limit and precipitate as silicates which are hard to remove without damaging the membrane. Experiments showed that at the same pressure and feed water quality, the higher the crossflow velocity, the lower the flux decline.

5.3.3 INFLUENCE OF TRANSMEMBRANE PRESSURE ON A RO UNIT PERFORMANCE

The effect of transmembrane pressure on flux decline was studied at two pressures, 790 kPa (AK type membranes) and 1550 kPa (AG type membranes). The operational time was 60 hours.

Table 5.12 shows that, for synthetic Rio Grande water at a crossflow velocity of 3.6 cm/s, the higher the pressure, the lower the flux decline. For instance, for pretreated water at 790 kPa the flux decline was 20.6% while at a pressure of 1550 kPa, the flux decline was 7.3%. The specific flux increased as the TMP increased at the higher crossflow velocity studied. This is an expected result as pressure is the driving force allowing water molecules to diffuse through the membrane pores.

At the lower crossflow velocity, an increase in TMP increased the flux decline for untreated water, while the flux decline was very similar for the pretreated waters at the two pressures. This behavior for the untreated water can be explained by an increase in scaling and fouling over the membrane surface at the higher pressure due to the high concentration of salts at the membrane wall; as explained above, the concentration at the membrane surface is high because of the high influent concentrations and the high concentration polarization at the low crossflow velocity. This phenomenon allows a higher particle deposition rate due to the higher particle flux towards the membrane as a result of the increased permeate flux due to the higher pressure. The treated water, with its much lower influent concentrations, was not nearly so susceptible to scaling.

Table 5.12 Influence of Transmembrane Pressure on Flux Decline for Synthetic Rio Grande water

	Crossflow velocity=3.6 cm/s	
	790 kPa	1550 kPa
Synthetic Rio Grande water (60 mg SiO₂/L)	46.9%	37.6%
Softening Treatment 1	20.6%	7.3%
Synthetic Rio Grande water (23 mg SiO₂/L)	34.2%	30.7%
Softening Treatment 4	18.2%	7.1%
	Crossflow velocity=0.98 cm/s	
Synthetic Rio Grande water (60 mg SiO₂/L)	52.5%	65.0%
Softening Treatment 1	19.5%	18.2%
Synthetic Rio Grande water (23 mg SiO₂/L)	35.0%	43.5%
Softening Treatment 4	23.9%	21.9%

5.4 RESULTS OF RO EXPERIMENTS: SYNTHETIC RIO GRANDE WATER WITH ALUMINUM PRETREATMENT

As explained on Chapter 2, silica presents interactions with aluminum salts in the pH range of 8 to 9. Alumina, Al_2O_3 , has been reported to be an adsorbent for dissolved silica. Best results can be obtained if alumina is produced in the solution. The formation of fresh alumina in the presence of dissolved silica leads to hydrolysis, formation of Al_2O_3 precipitate and silica adsorption onto the precipitate. In addition, reaction of sodium aluminate with water produces OH^- ions that further promotes precipitation of magnesium hydroxide and hence enhancement of silica reduction (Sheikholeslami, 2000). The aluminum-silica reactions were shown on Chapter 2.

The pretreatments selected on Chapter 3 to be tested before the RO unit are shown on Table 5.13

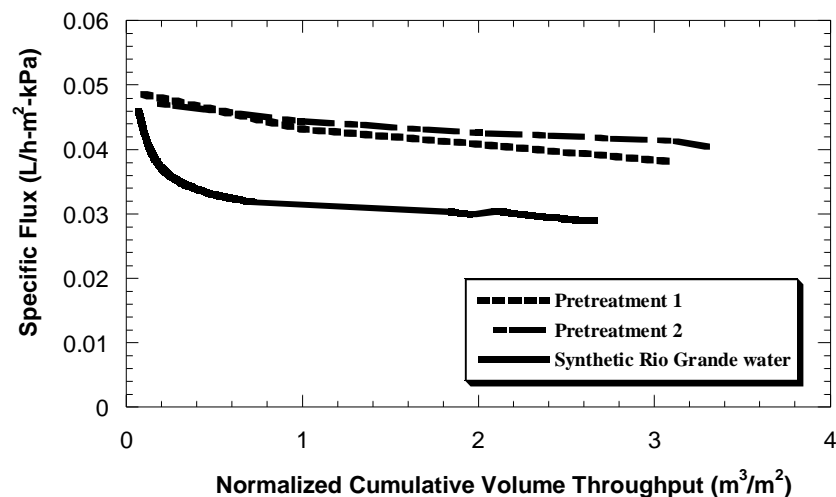
Table 5.13 Selection of Aluminum Pretreatments to test on the RO Unit

	TREATMENT			RESULTS				
	Al^{+3} (mg/L)	CaO (mg/L)	Na_2CO_3 (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)	Si^{+4} (mg/L)	Al^{+3} (mg/L)	pH
Synthetic Rio Grande water	0	0.0	0	55.2	19.0	28.2	0	8.01
Aluminum Treatment 1	15	150	133	8.8	1.5	6.4	0.3	8.72
Aluminum Treatment 2	25	130	95	20.4	10.6	3.2	0.9	8.15

Coagulant residuals from the pretreatment process may negatively affect reverse osmosis membrane performance since minor amounts of aluminum (and/or iron) cause silica precipitation. Thus, it is important to lower aluminum

concentration below 1 mg/L before entering the RO unit. pH was adjusted to 7.5 with 1N HCl to avoid further interactions of silica with aluminum.

The better conditions of operation for the RO unit, according to the previous softening experiments were at higher pressure and crossflow velocity, *i.e.*, 1550 kPa and 3.6 cm/s; thus, these were the conditions applied to the next RO experiments. The experiments were run for 60 hours. Figure 5.10 shows a lower decline of the specific flux if feed water is pretreated. For untreated synthetic water, the average specific flux decline was 38.8%. Water pretreated with aluminum treatment 1 had a specific flux decline of 21.5%, while pretreated water with aluminum treatment 2 had a specific flux decline of 15%. Even though the concentrations of calcium, magnesium and aluminum ions were slightly higher in the second pretreated water in comparison to the first pretreated water, the silica concentration was only half as great. This condition seems to outweigh the slightly higher concentrations of the other ions and produced a lower specific flux decline. Although the specific flux decline was much lower after an aluminum pretreatment was applied in comparison to untreated Rio Grande water, water pretreated with softening treatments had a better performance at the same conditions of operation (flux decline was 8% with a softening pretreatment, while flux decline was 15% with an aluminum pretreatment).



**Figure 5.10 Influence of Feed water Quality on Specific Flux Decline:
Aluminum Pretreatments on Rio Grande Synthetic water at 60 mg
SiO₂/L, 1550 kPa and 3.6 cm/s**

5.5 RESULTS OF RO EXPERIMENTS: RIO GRANDE WATER WITH SOFTENING TREATMENTS

The objective of this set of experiments was to evaluate the influence of the quality of water on the performance of the RO unit, *i.e.*, the effect of two softening pretreatments on Rio Grande River water. Softening pretreatments were selected over coagulation pretreatments to test on river water since softening pretreatments proved to have a better performance of the RO system than coagulation pretreatments for experiments with laboratory-made Rio Grande River water as feed water.

5.5.1 ANALYSIS OF RIO GRANDE WATER WITHOUT PRETREATMENT

The first experiment was run with Rio Grande water from the Laredo area (with an initial silica condition of 60 mg SiO₂/L) to establish a baseline of comparison. The operational conditions of the system included a pressure of 1550 kPa and a crossflow velocity of 3.6 cm/s for 15 hours. After preconditioning of the membranes, Rio Grande water ran for 15 hours and flux was recorded over time. Flux declined more rapidly at the beginning of the experiment, and continued to decline steadily for the entire operation period. At the end of the experiment, flux decline was approximately 56.3%, *i.e.*, the flux was 43.7% of the initial value. The substantial flux decline is a sign of the heavy fouling of the membranes. The system was stopped and the experimental solution was drained. One of the membranes was taken out to make a morphological and elemental analysis while the other two remained in place. The feed tank was filled again with deionized water as a cleaning solution at approximately 27-28 °C and it was pumped through the system during 4 hours. Flux reported an increase from 43.7% of the initial value after the experimental solution to 59.0% of the original value after the deionized water cleaning. Flux increase by membrane cleaning with deionized water is an indication that at least part of the material is deposited over the membrane surface without forming chemical bonds with the outer membrane ionic groups. Fouling is typically a result of suspended solids, colloidal silica, microbes and organic material, particularly long-chained species that deposit on the surface of the membrane. Flux may have not been restored up to a higher level due to scaling over the membranes. Scaling in this experiment may be due to soluble metal-silicates and other compounds as calcium carbonate. An element that was

not measured in this study was sulfur. Colloidal sulfur can seriously foul the membranes.

A stronger cleaning solution was prepared to clean the membranes. The membranes were taken out from the RO unit and were soaked in a cleaning solution of 2.4% of ammonium bifluoride and 2.4% (by weight) of citric acid. The pH was adjusted to 2.0-2.5 by addition of citric acid. After a cleaning period of 6 h, the membranes were placed in the RO unit and the tank filled with distilled water. The water flux was then monitored and compared with the initial stage. Final flux for the membranes was 0.03 L/h-m²-kPa, *i.e.*, flux was recovered up to a 73% of the original value. Although the membranes were soaked in a strong acid cleaning solution, the flux could not be totally recovered. Figure 5.11 shows the four stages of the experiment (cleaning 1 refers to cleaning with deionized water and cleaning 2 refers to membrane soaking in the acidic solution).

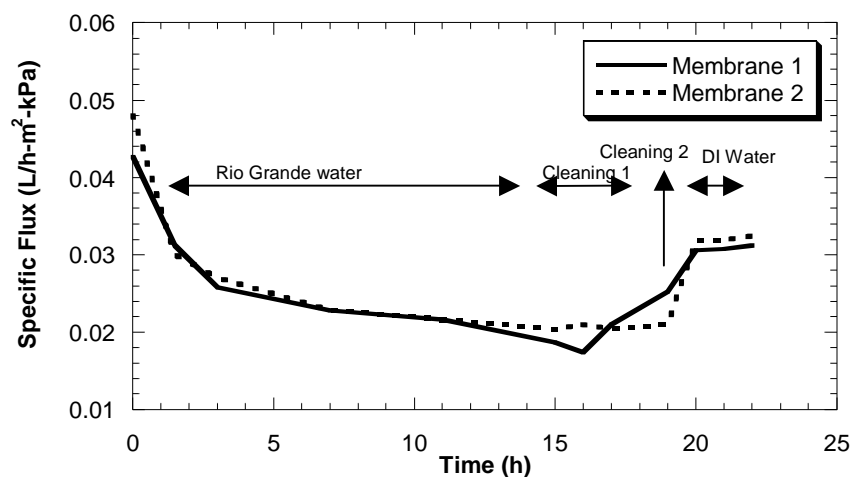


Figure 5.11 Influence of Feed water Quality on Specific Flux Decline:
Untreated Rio Grande water at 60 mg SiO₂/L, 1550 kPa and 3.6 cm/s

The operating period was relatively short, 15 h, in comparison to the runs with Rio Grande simulated water. Flux decline for Rio Grande synthetic water was approximately 44% for 60 hours of operation (*i.e.*, 56% of the initial flux). Thus, it can be seen that other material, as ions, sediments, natural organic matter, silt and particles present in the real water were causing additional fouling.

Table 5.14 shows the results of a XPS analysis. The main fouling elements are magnesium, calcium and silica. The Si/Mg ratio of the precipitated solids on the membranes after the experimental solution was 2.1. Tremolite, the magnesium-silicate likely to precipitate according to Mineql, has a Si/Mg ratio of 1.84. The results suggest that, as Mineql predicted, tremolite was probably formed, but was supplemented with another silica precipitate.

Table 5.14 XPS Analysis of RO Membranes for Untreated Rio Grande water

Weight Percentage of Elements	XPS analysis after experimental solution*	XPS analysis after cleaning solutions*
Carbon	63.5 %	70.5 %
Oxygen	15.5 %	14.5 %
Magnesium	5.14 %	3.14 %
Silica	10.9 %	6.8 %
Sulfur	0.0 %	0.0 %
Calcium	4.84 %	4.81 %
Total	100.0 %	100.0 %

*Tests at 1550 kPa and 3.6 cm/s.

Particles of different sizes covered the membrane surface in isolated patches of deposits which appeared to be amorphous in nature. No crystalline substance was evident. It seems particles tend to agglomerate in some areas rather than forming an even layer. Even after cleaning the membranes with an acid solution, some compounds remain attached, indicating that precipitation and chemical bonding to the membranes is a possibility. Scaling of the membranes in this case seems irreversible. A stronger chemical solution may be used, although it carries a risk of damaging the membrane or shortening its life.

Concentration Polarization Analysis

An analysis of the concentration polarization phenomenon, as proposed by Sutzko (2000) was done to investigate the development of concentration gradients close to the membrane surface.

Considering the values of $\rho=0.99 \text{ g/cm}^3$, $\mu=0.89 \text{ cP}$ and $v= 87 \text{ cm/s}$ for the system tube diameter of 1 cm, $Re=9660$. Using a diffusivity of $D_v= 1.3 \times 10^{-5} \text{ cm}^2/\text{s}$, the Schmidt number is $Sc=692$. The mass transfer coefficient can then be calculated, $K_D= 4.69 \times 10^{-3} \text{ mL/cm}^2\text{-s}$. The flux is $1.25 \times 10^{-3} \text{ mL/cm}^2\text{-s}$. From here, a value of $CP=1.30$ is calculated. For this experiment, the concentration in the feed stream was 28 mg Si/L. with a recovery level of 33.8%. For these values, the concentration in the feed-concentrate stream was $C_{\text{feed-concentrate}}=41.4 \text{ mg Si/L}$. Thus, the concentration of silica in the near membrane surroundings is $C_{\text{membrane}}=53.5 \text{ mgSi/L}$, *i.e.*, 116 mg SiO_2/L .

The concentration of silicon dioxide near the membrane is very near its solubility value of 120 mg SiO_2/L in a silica-water system, but it would seem

unlikely that silica could precipitate. Therefore, one might expect a low specific flux decline. However, XPS analysis showed that metal-silicates are likely to be precipitating on the membranes. This river water is likely to have included other elements not analyzed that may have interactions with silica, substantially lowering its solubility value. Ions that may act to decrease the solubility limit are aluminum and/or iron, even at very low concentrations.

Precipitation of metal-silicates is the more likely reaction to occur, as silicon dioxide has a lower kinetics of precipitation. The fact that silica precipitates were only partially removed from the membrane surface after a chemical cleaning is an indicator of the nature of particle deposition that is occurring. Colloidal fouling, *i.e.*, polymerized silica attached to the membrane surface is easier to be removed and it usually comes off the membrane surface after a few hours of cleaning, unlike deposited silicates which usually form strong bonds with the chemical groups on the membrane surface.

5.5.2 ANALYSIS OF RIO GRANDE WATER WITH PRETREATMENT

Analysis of Rio Grande River water with Pretreatment 1

Two pretreated waters were selected to analyze the effect of the pretreatment stage in an RO unit with real waters. The description of the selection of the pretreatments is shown in section 4.6. Table 5.15 shows the treatments and composition of the two waters that were fed to the RO unit.

Table 5.15 Chemical Analysis of Rio Grande water Tested on the RO Unit

TREATMENT				RESULTS			
Jar Test	Mg ⁺² (mg/L)	CaO (mg/L)	Na ₂ CO ₃ (mg/L)	Ca ⁺² (mg/L)	Mg ⁺² (mg/L)	Si ⁺⁴ (mg/L)	pH*
0	0	0	0	23.3	16.2	28.7	8.50
3	35	165	161	30.1	1.1	5.3	10.81
6	35	180	189	15.1	0.6	6.1	10.75

* pH was adjusted to 8 before entering the RO unit.

Pretreated Rio Grande water ran for 15 hours and flux was recorded over time. The flux decline was slight and steady for the entire operation period. At the end of the experiment, flux decline was approximately 8.6 %, *i.e.*, it was 91.4 % of the initial value. This low value of flux decline proves that the softening treatment applied to the influent water substantially improves the performance of the RO system. The system was stopped and the experimental solution was drained. The feed tank was filled again with deionized water as a cleaning solution at approximately 27-28 °C and it was pumped through for about 4 hours. Flux reported a very slight increase up to 92.4% of the original value after the deionized water cleaning. Again, a stronger cleaning solution of 2.4% of ammonium bifluoride and 2.4% (by weight) of citric acid was prepared to soak the membranes in. pH was adjusted to 2.0-2.5 by addition of citric acid. After a cleaning period of 6 h, the membranes were placed in the RO unit and the tank filled with distilled water. The water flux was then monitored. Final flux for the membranes was 0.00079 L/min-m²-kPa, *i.e.*, flux was recovered up to a 97.5%.

From visual inspection, membranes appeared to have a white and opaque thin film of particles when dried. This film is an indication of particle and colloidal deposition, rather than a chemical precipitation of amorphous silica,

which has a more glasslike film appearance. Membranes were analyzed by XPS spectroscopy after the experimental solution and after the cleaning solution to investigate what chemicals were fouling the membranes.

Table 5.16 shows the results of the XPS analysis. The low flux decline was due to substantially lower hardness and silica compounds attached to the membranes. Cleaning of the membranes slightly decreased the already low amounts of calcium, magnesium and silica ions deposited on the membrane surface.

Table 5.16 XPS Analysis of RO Membranes for Rio Grande water with Pretreatment 1

Weight Percentage of Elements	XPS Analysis after experimental solution*	XPS analysis after cleaning solutions*
Carbon	76.6 %	78.6 %
Oxygen	19.57 %	19.5 %
Magnesium	0.32 %	0.08 %
Silica	0.96 %	0.23 %
Sulfur	0.29 %	0.27 %
Calcium	1.26 %	0.96 %
Total	100.0 %	100.0 %

*Tests at 1550 kPa and 3.6 cm/s.

The examination of the scale structure confirmed previous findings that the solution concentration affects the scale structure. According to some studies (Koo, 2001), surface structure of precipitated particles differ with solution pH, presence of ions and the process which forms the precipitated particles. A morphological study of these membranes showed a whiter and much thinner layer of deposits in comparison to the membranes of the experiment with untreated Rio Grande water. Particles size was on average smaller. No specific crystalline form was found.

For this experiment, the concentration in the feed stream was 5.3 mg Si/L. with a recovery level of 68 %. For these values, the concentration in the feed-concentrate stream was $C_{\text{feed-concentrate}} = 15.26 \text{ mg Si/L}$. Thus, the concentration of silica in the near membrane surroundings is $C_{\text{membrane}} = 19.5 \text{ mg Si/L}$, *i.e.*, 42.4 mg SiO₂/L. The low silica concentration near the membrane explains the low flux decline of this experiment.

Analysis of Rio Grande River water with Pretreatment 2

A second experiment was run for 15 hours with real pretreated Rio Grande water to have a comparison of the quality of pretreatments. This water contained half the calcium concentration as the first pretreated water. The silica concentration was similar and magnesium concentration was, as in the previous experiment, very low. The flux decline was low, approximately 7.2%, *i.e.*, it was 92.8% of the initial value. The system was stopped and the experimental solution was drained. The feed tank was filled again with deionized water as a cleaning solution at approximately 27-28 °C and it was pumped through for about 4 hours. Deionized water cleaning did not improve the flux, since the recorded flux was

still 93% of the original value after the 4 hour cleaning. After this cleaning, the procedure was the same than in previous experiments. An acid solution was prepared to soak the membranes in. After a cleaning period of 6 h, the membranes were placed in the RO unit and the tank filled with distilled water. Final flux for the membranes was 0.00078 L/min-m²-kPa, *i.e.*, flux was recovered up to a 96.5%.

Membranes were analyzed by an XPS spectroscopy after the experimental solution and after the cleaning solution. Table 5.17 shows a similar elemental analysis than experiment with pretreatment 2.

Table 5.17 XPS Analysis of RO Membranes for Rio Grande water with Pretreatment 2

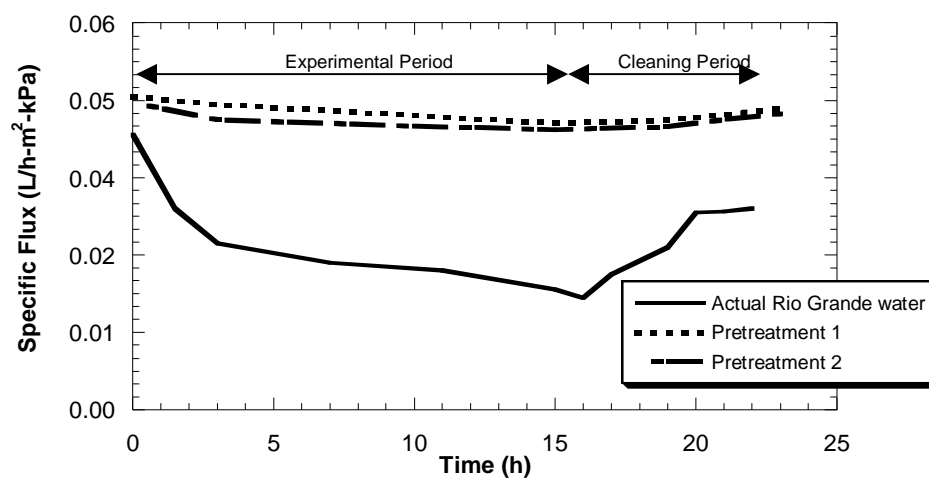
Weight Percentage of Elements	XPS Analysis after experimental solution*	XPS analysis after cleaning solutions*
Carbon	76.4 %	77.6 %
Oxygen	21.69 %	20.5 %
Magnesium	0.22 %	0.19 %
Silica	0.67 %	0.58 %
Sulfur	0.12 %	0.08 %
Calcium	0.53 %	0.52 %
Total	100.0 %	100.0 %

*Tests at 1550 kPa and 3.6 cm/s.

5.5.3 COMPARISON OF UNTREATED AND PRETREATED RIO GRANDE RIVER WATER IN REVERSE OSMOSIS EXPERIMENTS

Flux decline was substantially lower in the experiments with pretreated water. Both experiments with pretreated water had a very similar flux behavior over the operational period. Even though the second pretreated water contained twice as much calcium, it seems that the concentration value, 15 mg Ca⁺²/L, was still too low to induce a substantial flux decline.

The cleaning solutions in the pretreated water recovered the flux almost to the original value. It is worth noting that the experimental unit was not equipped with feed spacers which are used in large-scale systems to help optimize crossflow velocity characteristics. Thus, the flux decline in a real system equipped with the spacers and carriers may be even lower or may occur at much longer times of operation. Figure 5.12 shows the flux behavior for untreated and pretreated waters, both before and after cleaning.



**Figure 5.12 Influence of Feed water Quality on Specific Flux Decline:
Pretreated Rio Grande water at 60 mg SiO₂/L, 1550 kPa and 3.6 cm/s**

Table 5.18 presents a summary of flux behavior at the end of the experimental solution and after cleaning of the membranes.

Table 5.18 Percentage of Initial Specific Flux after Membrane Cleaning for Rio Grande water

	Untreated water (%)	Treatment 1 (%)	Treatment 2 (%)
Flux at 15 hours	43.7	91.4	91.3
Flux after water cleaning	59.0	92.4	92.4
Flux after acid solution cleaning	73.1	96.3	96.5

5.5.4 SUMMARY OF REVERSE OSMOSIS EXPERIMENTS

Bench scale reverse osmosis experiments with synthetic Rio Grande water were performed for 60 hours and experiments with actual Rio Grande River water were performed for 15 hours. Three parameters were tested: feed water quality, crossflow velocity and transmembrane pressure.

Softening and coagulation treatments were investigated as a way to reduce silica and other ions in the feed waters of the reverse osmosis system and thus induce a lower flux decline. Rio Grande laboratory-made water that underwent a softening pretreatment presented a flux decline of 7.3%, while untreated water had a flux decline of 37.6% at the same operational conditions (crossflow velocity of 3.6 cm/s and 1550 kPa). Influent water that was pretreated with an aluminum treatment (addition of lime and aluminum chloride) presented a flux decline of 15.0%. Softening pretreatments of the feed water proved to be a better option than coagulation pretreatments of feed water. Untreated Rio Grande River water presented a specific flux decline of 56.3% at the end of the experiment while a softening pretreatment of the influent water lowered the flux decline to 8.6%.

SEM and XPS analyses of the membranes showed less silica, calcium and magnesium deposited on the membrane surface when water underwent a pretreatment step. XPS analysis showed that silica is the major foulant of the RO membranes if water from the Rio Grande River is left untreated. Tremolite is the likely metal-silicate precipitating on the membrane surface, according to Mineql simulations and to the Mg/Si ratio of the XPS analysis of the membranes.

The effect of crossflow velocity was studied applying two different conditions, 0.98 cm/s and 3.6 cm/s. Untreated Rio Grande laboratory-made water had a flux decline of 65% at a crossflow velocity of 0.98 cm/s while the flux decline was 37.6% at a crossflow velocity of 3.6 cm/s. Pretreated Rio Grande laboratory-made water had a flux decline of 18.2% at 0.98 cm/s while it was 7.3% at 3.6 cm/s. Crossflow velocity has proven to be critical in the performance of an RO system, since the formation of concentration gradients close to the membrane surface (concentration polarization phenomena) is influenced by the crossflow velocity conditions. At the low crossflow velocity studied, concentration polarization was high, $CP=5.8$, inducing a high flux decline. At the high crossflow velocity studied, concentration polarization was $CP=1.37$, allowing for a much lower flux decline.

The effect of pressure was examined at 790 and 1590 kPa. Untreated Rio Grande water had a flux decline of 46.9% at 790 kPa while it was 37.6% at 1550 kPa. Pretreated Rio Grande water had a flux decline of 20.6% at 790 kPa while it was 7.3% at 1550 kPa. Thus, higher pressure (AG Osmonics membranes at 1550 kPa) allowed for a better recovery of product water in comparison to lower pressures (AK Osmonics membranes at 790 kPa).

Cleaning of membranes was studied using deionized water and an acidic solution (citric acid and ammonium bifluoride). Flux reported a low increase when deionized water was run through the system. A stronger cleaning solution (2.4% of ammonium bifluoride and 2.4 % (by weight) of citric acid) allowed for higher flux recoveries.

CHAPTER 6: CONCLUSIONS

6.1 INTRODUCTION

The objective of this research was to investigate combinations of pretreatment and RO operational strategies that optimize the production of clean industrial process water from water with high silica concentrations. This objective was accomplished with a combination of experimental work (on synthetic as well as natural waters from the U.S.-Mexico Border region) and mathematical modeling. To accomplish this objective required a thorough investigation of processes to remove silica prior to membrane treatment; the processes investigated included precipitation of silica associated with softening (removal of calcium and magnesium by lime addition) and adsorption/precipitation in coagulation systems with alum and iron. A bench-scale RO system was operated under different conditions with and without pretreatment to demonstrate directly the value of pretreatment. The investigation was carried out using synthetic water mimicking the makeup of Rio Grande river water, and then real water from that river was used to confirm the earlier results. Softening and coagulation pretreatments were investigated as means to reduce silica and hardness concentration and thereby decrease membrane fouling; the research included mathematical modeling of silica chemistry using Mineql®.

Softening pretreatments consisted of addition of lime, magnesium salts, and soda ash to precipitate magnesium-calcium silicates and control calcium concentration. Coagulation pretreatments consisted of addition of aluminum or iron salts as it has been reported that silica presents interaction with these trivalent ions forming alumino-silicates and iron-silicates. A bench-scale flat sheet membrane system was used to test the synthetic water and field water with and without pretreatment.

6.2 CONCLUSIONS

The conclusions of this research are presented below.

1. Lime softening has proven to be an effective method to reduce silica concentration, even if its primary objective is to control water hardness. Addition of magnesium salts is necessary to induce silica precipitation, as was evidenced by the series of pretreatments investigated and by Mineql simulations. Addition of soda ash is necessary for calcium control. Specific results with the Rio Grande water show that addition of magnesium chloride (35 mg/L of Mg^{+2}) and 165-180 mg/L lime (CaO) plus soda ash for calcium control (160-190 mg $\text{Na}_2\text{CO}_3/\text{L}$) dramatically decreased the silica concentration from 28 mg/L as Si^{+4} to approximately 5 mg/L as Si^{+4} , while simultaneously reducing the magnesium ion to approximately 1 mg Mg^{+2}/L and calcium ion to as low as 15 mg Ca^{+2}/L .

According to Mineql simulations, the precipitated compounds are calcium carbonate and the magnesium-silicates chrysotile ($Mg_3Si_2O_5(OH)_4(s)$) and tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2(s)$). Results from an XPS analysis of the precipitated solids indicate that Si/Mg ratios of the precipitated solids are between 0.61 and 0.65. Chrysotile has a Si/Mg ratio of 0.76. The results suggest that, as Mineql predicted, chrysotile was probably formed, but was perhaps supplemented with another magnesium precipitate.

2. The formation of fresh amorphous $Al(OH)_3(s)$ by the addition of alum provides a large surface area for the adsorption of silica. Some aluminum-silicates might also precipitate. Addition of lime and two aluminum salts (sulfate and chloride) were investigated. The thermodynamically possible compound that could be formed according to Mineql simulations under the conditions studied is the alumino-silicate leonhardite ($Al_4Ca_2Si_8O_{17}(OH)_{14}(s)$). Specific results for synthetic RIO Grande water indicate that addition of 15 mg as Al^{+3}/L and 150 mg CaO/L achieved a silica removal of 77%, as silica went down from 28 mg/L to 6.4 mg/L. A higher dose of aluminum, 25 mg as Al^{+3}/L and 130 mg CaO/L gave a better result, a silica removal of 88%, as silica decreased from 28 mg/L to 3.2 mg/L. Addition of soda ash in the range of 95 to 130 mg Na_2CO_3/L

allowed for good calcium control. pH values that give good silica removals with aluminum treatments are in the range of 8-9.

3. Iron was added as FeCl_3 at several doses and pH values (defining the behavior throughout the reasonable pH/Fe concentration space) to allow the precipitates to form. Synthetic Rio Grande water was adjusted so its initial pH was 6, 7, 8 and 9 with either HCl or NaOH. Better silica removal was achieved when raw water was adjusted to a basic pH (pH=9). Silica removal percentage was just above 50% by addition of 25 mg Fe^{+3}/L . The experimental results were unexpected due to the strong silica-iron interactions reported in the literature. An explanation for the low silica removals achieved in this research may be the form of silica that is being removed. Polymerization reactions of monomeric silica to form polymeric silica (colloidal silica) occur at concentrations approximately twice the saturation level of soluble silica (120 mg SiO_2/L). Due to the much lower Rio Grande silica concentrations (up to 60 mg SiO_2/L) the predominant type of silica in natural waters is monomeric. On the other side, iron is a coagulant mainly used to remove colloidal particles. Therefore, the low silica removals may be due to the silica being mainly in the dissolved or monomeric state. Literature reports on iron-silica interactions are mainly

related to the geothermic industry were much higher silica concentrations are found (approximately 700 mg SiO₂/L).

4. Bench scale RO experiments with Rio Grande laboratory-made water were performed for 60 hours and experiments with Rio Grande River water were performed for 15 hours. Three parameters were tested: feed water quality, crossflow velocity and transmembrane pressure. Operational conditions were pressure of 1550 kPa and crossflow velocity of 3.6 cm/s at a constant temperature of 25 °C. Untreated Rio Grande water presented a specific flux decline of 53% at the end of the experiment. Water pretreated with the best softening conditions presented a much lower flux decline at the same conditions and time of operation, 7 %. SEM and XPS analysis showed less silica fouling the membranes for pretreated water. XPS analysis showed that silica is the major foulant of RO membranes, if Rio Grande water is left untreated. Pretreatment of silica bearing waters to lower silica values down to approximately 5 mg Si/L before entering an RO unit made a dramatic improvement in flux behavior, which is the main parameter describing system performance.

5. Running of the RO system with softening and coagulation pretreatments indicated that softening pretreatment is a better option than aluminum or iron pretreatment. Even though coagulation pretreatments showed good silica control, they proved to be less effective than softening treatments when running the RO unit, apparently because very low amounts of aluminum or iron are likely to foul the membranes.

6. The effect of pressure was examined using polyamide membranes manufactured by Osmonics, operating at 790 and 1590 kPa. For pretreated Rio Grande water, the higher the pressure, the lower the flux decline, at otherwise same conditions of feed water quality and crossflow velocity. For example, at a crossflow velocity of 3.6 and 790 kPa the flux decline was 18%, while at a pressure of 1550 kPa, the flux decline was 8.2%. Transmembrane pressure of an RO system is the driving force that allows water to diffuse through the membrane. Nevertheless, very high pressures may induce membrane compaction and further flux decline. At 1550 kPa, this phenomenon is not occurring as evidenced by the low flux decline behavior. Thus, higher pressures (AG-type Osmonics membranes at 1550 kPa) allow for a better recovery of product water in comparison to lower pressures (AK-type Osmonics membranes at 790 kPa).

7. The effect of crossflow velocity was studied applying two different values, 0.98 cm/s and 3.6 cm/s. Crossflow velocity has proven to be critical in the performance of an RO system, since the formation of concentration gradients close to the membrane surface (concentration polarization phenomena) is influenced by the crossflow velocity conditions. A mathematical analysis of concentration polarization indicated that, at the crossflow velocity of 3.6 cm/s, the concentration polarization value is as low as 1.3 (*i.e.*, the concentration near the membrane surface is 1.3 times the concentration in the bulk solution). At the low crossflow velocity of 0.98 cm/s, CP is as high as 5.8. At the high concentrations of several ions near the membrane, induced by a high CP value, it is likely that silica polymerizes, forming colloidal silica that may deposit over the membrane surface, and more importantly, silica (and other ions) exceeds their solubility limit and precipitate as metal-silicates which are hard to remove without damaging the membrane. Reverse osmosis experiments showed that at the same pressure and feed water quality, the higher the crossflow velocity, the lower the flux decline.
8. Cleaning of membranes was studied using deionized water and an acidic solution (citric acid and ammonium bifluoride). The flux slightly increased when deionized water was run through the system. Flux increase by means

of membrane cleaning with deionized water is an indication that at least part of the material is deposited over the membrane surface without forming chemical bonds with the outer membrane ionic groups. A stronger cleaning solution (2.4% of ammonium bifluoride and 2.4% by weight of citric acid) was prepared to clean the membranes. After a cleaning period of 6 h, 73% of the flux was recovered for untreated water and up to 96% for pretreated Rio Grande water. Although the membranes were soaked in a strong acid cleaning solution, the flux could not be totally recovered. Flux may have not been restored up to a higher level due to scaling over the membranes. Scaling may be due to soluble metals as calcium and magnesium reacting with silicon ions, or soluble metals as small traces of iron and/or aluminum forming metal-silicates.

6.3 RECOMMENDATIONS

Some recommendations for future investigations may focus on the following aspects:

- Adjustment of pH of the influent stream, after softening pretreatment, with an acid other than hydrochloric acid, for example, citric acid. The citrate ion might act as a complexing agent and further prevent precipitation on the membrane surface.

- Addition of seed crystals in the pretreatment step to enhance the precipitation process.
- Measurement of fouling/scaling indicative indexes such as the Langelier Saturation Index (LSI) and Silt Saturation Index (SDI) to establish maximum limits of these indexes in RO silica containing influent water at different silica concentrations. Perhaps an index that is more specifically related to silica precipitation could be developed.
- Studies on silica scaling/fouling at RO operational conditions besides those studied in this research (TMP at 790 and 1550 kPa and crossflow velocities at 0.98 and 3.6 cm/s). Different hydrodynamic conditions of the flow may improve the results found in this research.
- The efficacy of various cleaning solutions other than those studied in this research may be tested. Membranes scaled with inorganic materials, including silica, may also be cleaned with a solution of 1% tetra-sodium EDTA or a phosphoric acid solution. Commercial available cleaners for silica containing deposits may also be studied, such as MT3100 and MT5010 (BFGoodrich).
- Studies on specific silica inhibitors may be looked at to control formation of scales. Some of the commercial available silica inhibitors are Acume 500 (multi-polymer), Hypersperse SI 300 and Permatreat 510 (blend of

polymers and phosphonates provided by Argon Scientific), Aquafeed EX-105 (anionic polyelectrolyte).

- Finally, the operational period in this research was relatively short in comparison to the operation in a real system. Therefore, investigation of the efficacy of the best treatments studied in this research over much longer periods might be necessary before results of this research can be applied to a industrial-size reverse osmosis system.

APPENDIX A: SYMBOLS

A = Membrane area

C_1 = Inner layer capacitance

C_2 = Outer layer capacitance

C_c = Concentration of salt in the concentrate stream

C_f = Concentration of salt in the feed stream

C_m = Concentration of salt in the membrane surface

C_p = Concentration of salt in the permeate stream

CP = Concentration polarization factor

d = Diameter of tube

D_v = Diffusivity

F = Faraday constant

J_v = Volumetric permeate flux ($L/m^2 h$)

\hat{J}_v = Specific volumetric permeate flux ($L/m^2 h \text{ kPa}$)

K = Equilibrium constant

K_d = Mass Transfer Coefficient

R_g = Ideal gas constant

R = Recovery level

Re = Reynolds number

S_c = Schmidt number

Sh = Sherwood number

T =Temperature

V =Permeate volume

Y = Membrane rejection for an specific salt

ϕ_o = Electrical potential for the O-plane (O-plane is the surface)

ϕ_d = Electrical potential for the d-plane (d-plane is a plane proposed in Triple Layer Models)

σ = Electrical potential for the diffuse plane

σ = Surface charge

μ = Fluid viscosity

ρ = Fluid density

v = Velocity of fluid

π_m = Osmotic pressure on the membrane

π_f = Solution osmotic pressure

$\{ \}$ = Activity of the aqueous species

$[]$ = Concentration of surface species

APPENDIX B: MEMBRANE SALT REJECTION

The concentrations in both the feed stream and permeate for all of the relevant ions were measured at various times throughout the experiment. The feed concentrations gradually increased as the concentrate was recycled. The permeate concentrations for each ion were quite consistent among the three permeate streams for each time, but rose slightly over time along with the feed concentration. For each time, therefore, an average concentration was considered and the membrane ionic rejection was calculated as follows:

$$\% \text{ Rejection} = 1 - \frac{\text{Concentration of permeate}}{\text{Concentration of feed}}$$

Table B.1 shows the ionic concentrations at different times for each of the three cells of the RO unit for one experiment. The data indicate that the rejection of all of the ions was quite high, and also that the rejection was quite constant over time.

All of the experiments exhibited the same trends of rising concentrations in both the feed and permeate, but nearly constant % rejection over the entire experiment. Therefore, a single value of the % rejection for each ion was calculated for each of the experiments; these values are reported in Table B.2. The data in the table indicate that excellent rejection of silica, magnesium, and calcium was achieved in all of the experiments. These data are further evidence that the RO experiments were performed well.

Table B.1

	Concentration (mg/L)					Rejection (%)
	Feed stream	Permeate Cell 1	Permeate Cell 2	Permeate Cell 3	Permeate Average	
Sample @ 14 h						
pH	8.3	8.3	8.3	8.32		
Si	30.6	1.6	1.56	1.63	1.60	94.3
Mg	21.2	0.11	0.15	0.14	0.13	99.3
Ca	47.2	1.1	1.02	0.99	1.0	97.7
Sample @ 30 h						
pH	8.34	8.35	8.35	8.39		
Si	32.6	1.65	1.67	1.66	1.7	94.6
Mg	24.8	0.16	0.15	0.16	0.2	99.3
Ca	52.2	1.2	1.03	0.98	1.1	97.7
Sample @ 44 h						
pH	8.3	8.34	8.37	8.37		
Si	37.2	1.68	1.69	1.7	1.7	94.8
Mg	28.5	0.15	0.28	0.17	0.2	99.2
Ca	62.3	1.22	1.06	1.01	1.1	97.9
Sample @ 60 h						
pH	8.36	8.35	8.38	8.38		
Si	45.9	1.72	1.61	1.69	1.7	95.5
Mg	33.9	0.16	0.14	0.18	0.2	99.4
Ca	74.8	1.23	1.08	1.03	1.1	98.2

Table B.2

AK Membranes

Experiment	Si ⁺⁴	Mg ⁺²	Ca ⁺²
1	94.9%	97.4%	96.6%
2	94.8%	99.3%	97.8%
5	96.0%	97.0%	95.6%
6	94.2%	98.9%	96.8%
7	94.6%	98.2%	95.6%
8	94.5%	97.7%	95.5%
11	94.2%	99.2%	96.4%
12	94.6%	99.0%	96.9%
15	95.7%	99.3%	96.2%
16	95.8%	98.5%	97.1%
17	95.1%	98.2%	96.1%

AG Membranes

Experiment	Si⁺⁴	Mg⁺²	Ca⁺²
3	95.3%	98.3%	97.8%
4	95.8%	98.6%	97.9%
9	95.9%	97.8%	97.9%
10	96.4%	98.7%	97.4%
13	96.9%	98.2%	96.2%
14	96.0%	96.9%	97.6%
18	97.2%	97.9%	97.6%
19	96.4%	98.7%	97.3%

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