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Silica Removal From Brine By Using Ion Exchange

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SILICA REMOVAL FROM BRINE BY USING
ION EXCHANGE

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2009

Dedication

To my wife, Sara Sanchez, for her love, patience and help
for the accomplishment of this work

To my father, Enrique Acevedo, for his support, guidance and
his example of endurance and perseverance

To my mother, Maria del Refugio Rodríguez
who always helped me with all of my decisions.

To my children, Carlos, Mayra, Pamela and Andrea,
who are the sources of my inspiration.

SILICA REMOVAL FROM BRINE BY USING
ION EXCHANGE

by

Carlos R. Acevedo, Chemical Engineer

THESIS

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Abstract

Local governments have been forced to look for additional water sources to satisfy the ever increasing demand for fresh water. Very often, the new water sources such as the underground water in continental territories have high salt content. Currently, reverse osmosis technology (RO) is one of the most common processes for water desalination. However, this process is limited by high silica and salt concentrations in water. At high concentrations silica clogs the membranes used in the RO process, reducing their life and increasing operational costs. In this study, quaternary ammonium resins and sulfonic acid resins were used to remove silica and hardness, respectively from brines of both a nano-filtration pilot plant and a synthetic silica solution. Experiments were performed under batch and flow conditions at neutral pH. For batch experiments two anionic quaternary ammonium resins and one cationic sulfonic acid resin were used at 0.02 to 10 g in 50 mL of solution to carry out equilibrium tests. The resins were also tested for silica removal from a synthetic solution (without hard cations) at pH values from 3 to 11 and from brines of a nano-filtration pilot plant (NFPP) at pH ranging from 8 to 10. For flow experiments, the resins were used at flow rates from 8.7 to 10.5 cm/min, and pH values from 8 to 10. In all cases the amounts of silica and hard cations were determined by inductively coupled plasma optical emission spectroscopy, or by the photometric determination of molybdate-reactive method or using the titrimetric method with EDTA. Results showed that pH highly influenced silica removal from water solutions using quaternary ammonium resins in the chloride form. For both resins, silica removal efficiencies were higher than 80 % at $\text{pH} > 9.0$ and less than 5% at $\text{pH} < 8.0$. Removal efficiency from the synthetic solution was about 62% and from the brine of the NFPP it was about 14%. The hardness of the brine from the NFPP was found to be about 700 mg/L, which suggests that hard cation complexes in solution limit the efficiency of silica removal using quaternary ammonium resins.

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Chapter 1: Introduction

Water demand worldwide has grown exponentially during the last decades due to the increase in human population. Potable water is scarce and new reliable techniques are needed to make potable undrinkable water. In coastal areas, where fresh water is insufficient, local water utilities have relied on desalination plants to manage the problem. In these regions, reverse osmosis (RO) techniques have been widely used to produce fresh water, generating brine that is returned to the ocean without environmental impact.

Brackish water is also found in several basins in continental territories. For instance, the Hueco Bolson in the City of El Paso, Texas has 600% more brackish water than potable water.¹ This water can also be changed to drinkable water using RO, but in this case, brine disposal is an issue that needs to be solved. The City of El Paso has the world's largest inland desalination plant. This facility produces 27.5 million gallons of fresh water daily (MGD). Brine disposal is being done by deep-well injection because it is the most viable alternative.²

Other alternatives for brine management are recycling and reduction. Recycling is mainly limited by salt concentrations and especially by silica concentration. Silica can precipitate and clog RO membranes, causing important economic losses. There are several ways to reduce the silica content in brine. This study focused on silica separation, using ion exchange processes. Both anionic and cationic resins were tested to determine the effectiveness of the process. The anionic resin was tested to reduce the silica content and the cationic resin to reduce hardness. (e.g. Mg^{2+} , Ca^{2+})

¹ El Paso Water Utilities - Public Service Board Desalination Plant.mht

² CDM Inc, Basis of Design Document, Brine Disposal, prepared for El Paso Water Utilities, April, 2002.

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Chapter 2: Literature Review

Water treatment is a complex process that sometimes is controlled by minor components. Silica (SiO_2) is one of those components that may control the treatment needed for a specific type of water. Silica can create problems with the feed water in cooling towers, boilers, and turbines because of its capability to vaporize and deposit into the turbines' blades, thus damaging them [1]. In the RO process, silica can clog the membranes, reducing their useful life and causing high operational costs [2, 3, 4, 5].

2.1 BASIC CHEMISTRY OF SILICA

Silica, in water supplies, is usually found in three different forms: reactive, colloidal and suspended particles [4]. Silica dissolves in water forming the very weak acids H_4SiO_4 or H_2SiO_3 , both of them present as non ionized species [1]. The reaction for silica solubilization is shown in Equation 2.1

Since silica dissolves in water at neutral pH, it basically appears in the form of non-ionized ortho or meta-silicic acid; this silica is known as reactive silica [1]. The equilibrium equation for monosilicic acid ionization is shown in Equation 2.2

$$\text{pKa} = \frac{[\text{H}_3\text{SiO}_4] [\text{H}^+]}{[\text{H}_4\text{SiO}_4]} = 9.9 \quad [\text{Eq. 2.2}]$$

In the hydrated state, monosilicic acid shows a structure formed by two water molecules, which are part of the original structure and four additional water molecules, to contain a total of six water molecules [4].

The structure of the monosilicic acid is shown in Figure 2.1

Figure 2.1 - Monosilicic acid structure [4]

If the silica concentration increases, it experiences polymerization. This phenomenon transforms soluble silica to an insoluble gel known as colloidal silica [4, 6]. Colloidal silica is generally assumed to be multiple polymerized units of silicon dioxide, or a complex of silicon that has reacted with organic or inorganic compounds, usually calcium and aluminum oxides [4].

There are several factors that affect silica solubility in water; the most important are temperature, pH, pressure and the nature of the solid phase [1, 6]. Silica solubility in nature is also affected by the presence of other ions in water. Iron, manganese, aluminum and even calcium and magnesium affect the equilibrium for silica [1, 6]. The formation of organic acids, as humic acid, increases the solubility of silica and once the pH decreases, it forms colloids that are present in many waters around the world [1, 4, 6].

Figure 2.2 shows the behavior of silica solubility in water at different pH values. It is observed that solubility increases at pH lower than 2 and higher than 8.5 [1, 4].

Figure 2.2 - Silica solubility in water at different pH values

The most common method to determine the concentration of silica in water is the formation of silicomolybdate complexes. This method applies only to soluble silica (reactive silica) at concentrations below 120 mg/L, at room temperature. Determinations for polymeric silica can be achieved by dissolving the polymer with hydrofluoric acid or by using the gravimetric method (D1428) of the American Society for Testing and Materials (ASTM). [1, 2]

2.2 NATURAL OCCURRENCE OF SILICA

Almost three quarters of the Earth's lithosphere is silica (SiO_2). The source of the silica present in water is the siliceous materials, but in general, its concentration is very low due to the low solubility of silicate minerals [1, 3]. The highest values for silica concentration in nature are found in well water supplies. Most silica is a result of dissolving rocks. On the other hand, surface water tends to contain a higher concentration of colloidal forms of silica [1, 3].

The chemistry of silica in surface water supplies becomes more complex since biological activity is involved in the process. Diatoms, a species of algae, assimilate reactive silica dissolved in water to create their protective shell, which is formed by silicon dioxide crystals. Silica, as the active form, is released into the environment once diatoms decompose. The ecological balance between dissolved silica and silicon dioxide structures is complex. Interaction with biological matter will also create the colloidal silica that is present in most surface waters [1, 3].

2.3 THE IMPACT OF SILICA ON WATER TREATMENT

As silica can create several problems in industrial operations such as cooling towers, boilers, turbines, and in processes such as RO or electrodialysis, it is important to remove silica from water in these and other industrial processes [1, 7]. There are several techniques to remove silica depending on the particular water application, the nature of the silica compounds, and the desired quality of the water. The most important are chemical precipitation, distillation, RO, ultra-filtration and ion exchange [1, 3, 8]. Chemical precipitation is based on the formation of ferric and magnesium silicates that can be further precipitated by adding lime. This process also removes calcium, magnesium and organic matter [1].

Distillation is used when high purity water and the elimination of pyroxenes are required [1, 3]. This process is applicable to pharmaceutical operations and related industries but the high cost of energy makes this process unviable for other applications [1]. RO is also applicable for silica removal, but once the resin is clogged by silica, it needs to be replaced [8, 9, 10]. This represents a very high operational cost. Ultra-filtration is sometimes used to remove colloidal silica [1, 3]. Ion exchange can be used to remove reactive silica under specific conditions [10, 11]. Silica is also found at the lower end of selectivity for anion resins, creating a scenario where silica breakthrough is one of the first to occur. As a result, silica can be effectively removed only if the ion-exchange resins are completely and properly regenerated.

The use of ion exchange to reduce or eliminate silica from the waste brine of an RO desalination plant can improve the efficiency of the process. As stated above, silica can clog membranes if its concentration is high enough to form a precipitate. Whether this occurs, membranes must be replaced making the process expensive and unfeasible.

2.4 ION EXCHANGE PROCESS

The ion exchange process consists of a chemical reaction between ions in a liquid phase and ions in a solid phase. Certain ions in the solution are preferentially sorbed by the ion exchanger solid, and because electroneutrality must be maintained, the solid exchanger releases ions back into the solution.

Ion exchange (IE) resins consist of an organic or inorganic network structure with attached functional groups. Most are synthetic resins made by polymerization of organic compounds into a porous three-dimensional structure. The functional ionic groups are introduced by reacting the polymeric matrix with a chemical compound containing the desired group. IE resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Also, IE resins are often classified by the nature of their functional group as strong acid, weak acid, strong base or weak base. Strong acid resins are made of styrene and divinylbenzene by sulfonation of the copolymer; weak acid resins contain a carboxyl group ($-\text{COOH}$). Strong base has quaternary ammonium groups ($-\text{R}_3\text{N}^+\text{OH}^-$) and weak base amine groups ($-\text{NH}_2$ or $-\text{RNH}$). These resins have been previously used to remove silica

from aqueous solutions [6, 11]. Among the most widely used quaternary ammonium resins are Dowex 21K XLT and Dowex Marathon MSA [6]. Dowex G26 and Bayer Ionac C-249 were used as cationic resin.

Equation 2.3 shows the basic adsorption process between a cationic resin containing sodium and calcium salts

The reverse (regeneration) process is shown in equation 2.4

Within the ionic exchange process, the water to be treated is passed through the resin until available exchange sites are filled and the contaminant appears in the effluent (breakthrough); once the resin is exhausted, the bed is backwashed, regenerated and rinsed with water to begin another cycle [12]. Reports indicate that silica can be virtually completely removed from water [1, 4]. However, characteristics of ion exchange process to remove silica from brines in inland desalination plants were not found in the literature.

2.5 OBJECTIVE

The main objective of this research was to use an ion exchange process to remove silica from reverse osmosis concentrate so that additional water could be recovered through second-pass RO.

2.5.1 Specific objectives

The specific objectives of this study were:

1. To test the efficiency of anionic quaternary ammonium resins and cationic resins to remove silica from a nano-filtration concentrate, under batch conditions and neutral pH (equilibrium capacity studies).
2. To test the efficiency of anionic quaternary ammonium resins and cationic resins to remove silica from a synthetic silica solution, under batch conditions and neutral pH (equilibrium capacity studies).

3. To evaluate the effect of pH on the silica removal efficiency, for ion exchange process.
4. To test the performance of the silica removal using ion exchange and column methods.
5. To carry out test for hardness removal and subsequent silica removal from a concentrate of the nano-filtration plant (cationic and anionic treatment trains).
6. Another objective was to test the regeneration of cationic resins, using salt from an evaporation pond utilized to concentrate the brines of a nano-filtration plant.

Chapter 3: Procedure

3.1 RESIN SELECTION

This research was performed to determine the type of resin suitable for silica and hardness removal. After reviewing the uses and characteristics of different resin manufacturers, Dowex 21 K XLT and Dowex Marathon MSA, were selected to remove silica, whereas cationic resins Dowex G-26 and Bayer Ionac C-249 were used to remove hardness. Characteristics of these resins are shown in appendix D.

3.2 SILICA REMOVAL FROM CONCENTRATE GENERATED IN A NANO-FILTRATION PILOT PLANT

The first approach for the present work was to directly test the resins with a concentrate solution, similar to the brines from a RO desalination plant, without changing the resin or water conditions.

Equilibrium tests were performed, using three different types of resins, to evaluate silica, calcium and magnesium removal from a concentrate generated in a nano-filtration pilot plant. Characteristics of the concentrate were: Silica content (as SiO_2) 110 mg/L; calcium 6.17 mg/L; magnesium 4.82 mg/L.

Different amounts of resins (from 0.02 g to 0.5 g) were added to 30 mL plastic tubes that were filled with the concentrate. Equilibrium distribution tests were performed for a period of 24 hours for the Dowex resins 21KXLT, Marathon MSA and G-26 using a Speci-Mix Thermolyne model M26125 (Barnstead International, Dubuque IA). Liquid phase samples were filtered through 0.45 μm Whatman filters. Initial and final concentrations of silica, calcium, and magnesium were determined by using inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Perkin-Elmer, Optima 4300 DV, Shelton, CT).

3.3 SILICA REMOVAL FROM A SYNTHETIC SILICA SOLUTION USING ANIONIC EXCHANGE RESINS

Silica solutions with a concentration of 30 mg SiO₂ /L were prepared using a soluble salt of sodium metasilicate (Na₂SiO₃ · 9H₂O) and deionized RO water, to perform batch equilibrium distribution tests using anionic resin Dowex 21 K XLT. Amounts of resin ranging from 0.34 to 1.05 g were added to 50 mL plastic tubes that were filled with the silica solution and agitated for 24 hours to allow equilibrium. Tests were carried out without controlling the pH of the equilibrium solutions.

Liquid phase samples were pulled at the completion of the tests and filtered through 0.45 µm Whatman filters. The concentration of SiO₂ was determined using the photometric determination of molybdate-reactive method³ [6] and a spectrophotometer HACH model DR4000U (Loveland, CO). Tests were repeated four times with the same previously used resin, with new aliquots of SiO₂ solution to evaluate the behavior of the process in the sequential batches.

3.3.1 Influence of pH upon equilibrium

Tests were performed to determine changes in the pH of the solution associated with changes in the amount of resins. Additional equilibrium tests were carried out using the same technique but adjusting the pH from 11.1 to 3.27 with sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄). For this study, an initial concentration of 31 mg SiO₂ /L was used, resin was weighted directly in the tubes and 50 mL of sample were added. The pH was adjusted with NaOH /H₂SO₄ and mixed for 24 h. Two series of experiments were run using two samples of resins and one sample of water for each pH value.

3.4 REMOVAL OF SILICA USING QUATERNARY AMMONIUM RESINS UNDER FLOW CONDITIONS

As part of this research, silica removal using an ion exchange column was also performed. For this experiment, a solution using deionized RO water and sodium metasilicate with a silica concentration of 40 mg/ L was prepared. The pH was adjusted to 8.5 using a solution 0.1 M of sodium hydroxide. This

³ Method ASTM 4500-SiO₂ C.

pH was initially selected to test the silica removal efficiency at a moderately high pH without adding large amounts of basic that make this process expensive and prohibiting for industrial use.

A glass tube was cleaned with diluted acid solution and rinsed with deionized water. Subsequently, it was filled with quaternary ammonium anionic resin Dowex 21 K XLT to make an anionic exchange column. The minimum recommended height of the column, according to the Dowex resin data sheet was 80 cm. The resin was washed with deionized RO water before beginning the test to reduce the effect of the free acidity in the resin. Characteristics of the column are summarized in Table 3.1. The flow rate was adjusted using a peristaltic pump, as shown in figure 3.1. Flow rates from 1.8 to 5 mL/min were tested; samples were collected approximately every 10 minutes, and the silica concentration was measured using a spectrophotometer Hach-DR4000U.

Table 3.1 - Anionic exchange column characteristics

Anionic Exchange Column	
Anionic exchange resin volume	29.4 mL
Column diameter	0.604 cm.
Bed height	102.5 cm.
Detention time with void bed	11.18 min
Average flow	2.5 mL/min
Type of flow	Ascendant

Figure 3.1 - Ion exchange column test

Other experiments were performed using the concentrate of the nano-filtration process to test the efficiency of silica removal from these kinds of solutions. The methodology used to perform the tests was the same as described above. In these experiments, 15 g of Dowex 21 KXLT anionic exchange resin with average ascendant flow of 3.5 mL/min was used. The initial SiO_2 concentration was 153.6 mg/L and total hardness was 730 mg/L. The pH was adjusted to 8.08 using sodium hydroxide, because at higher pH precipitation of calcium and magnesium occurred.

3.5 HARDNESS REMOVAL

3.5.1 Ion exchange columns

Hardness removal using ion exchange has been successfully used for many years. In this study, tests for hardness removal were carried out to prove the effectiveness for this method, to remove cations, and subsequently, remove silica.

For this experiment, a solution from the nano-filtration pilot plant (NFPP) with an initial hardness of 690 mg/L (measured using the EDTA method) was used. A glass tube was filled with

cationic resin Bayer Ionac C-249 to make an exchange column. The resin was washed with RO/deionized water before the beginning of the test. The characteristics of the column are summarized in Table 3.2. A flow rate of 20 mL/min was tested and samples were collected approximately every 50 mL.

Table 3.2 - Cationic exchange column characteristics

Anionic Exchange Column	
Cationic resin volume	30 mL
Column diameter	0.604 cm
Bed height	104 cm
Detention time with void bed	1.49 min
Average flow	20 mL/min
Type of flow	Ascendant

3.5.2 Equilibrium tests for hardness removal

For these tests, samples from the NFPP were set in 50 mL plastic tubes filled with resin Bayer Ionac C-249. Equilibrium distribution tests were performed using a mixing device for a period of 24 hours. Liquid phase samples were filtered through 0.45 µm Whatman filters and hardness was measured by titrimetric method with EDTA.

3.5.3 Tests for the use of recovered salt as regenerant for cationic resins

Besides the tests for silica and hardness removal, another test to find out the possibility for the use of salt recovered from evaporation ponds, used in another research for brine disposal alternatives, was performed.

For this test, a saturated solution was prepared using the recovered salt sample, and distilled water. This solution was passed through a column containing previously used cationic resin Bayer Ionac C-249.

Hardness of the salt solution after passing the column was tested using the titrimetric method with EDTA. Regeneration solution flow was continued until reaching a concentration lower than 40 mg/L in the effluent.

Chapter 4: Results and Discussions

4.1 SILICA AND HARDNESS REMOVAL FROM THE CONCENTRATE OF A NANO-FILTRATION PILOT PLANT: BATCH EXPERIMENTS

4.1.1 Silica removal from concentrate generated in a nano-filtration pilot plant

To determine silica, calcium and magnesium concentrations in the nano-filtration concentrate, tests with diluted 1:10 samples in distilled water were performed. The data showed that the nano-filtration concentrate had the following concentrations: $[\text{SiO}_2] = 125 \text{ mg/L}$, $[\text{Ca}] = 6.2 \text{ mg/L}$, $[\text{Mg}] = 4.8 \text{ mg/L}$.

Results for silica removal from the concentrate generated in the NFPP, after a mixing period of 24 h, using the resin Dowex 21KXLT are shown in Table 4.1.

Table 4.1 - Removals of Si, Ca, and Mg (mg/L) from a nano-filtration pilot plant concentrate using the resin Dowex 21K XLT

Sample Number	Amount of resin (g)	Si (mg/L) 212*	Ca (mg/L) 228*	Mg (mg/L) 279*
1	0.022	100	N.D.	4.56
2	0.046	102	5.96	4.61
3	0.066	102	5.96	4.63
4	0.082	102	6.08	4.68
5	0.108	104	6.18	4.72
6	0.500	105	6.24	4.80
7	0.022	105	6.30	4.76
8	0.046	105	6.23	4.74
9	0.062	105	6.29	4.79
10	0.086	104	6.25	4.86
11	0.104	104	6.24	4.81
12	0.500	103	6.33	5.66

*wavelength for the ICP Test

Samples from 7 to 12 were duplicates of sample 1 to 6, respectively. The data showed that silica concentrations remained very similar. Furthermore, a faintly backward behavior was observed. Slightly more silica was removed with less amounts of resin. As seen in Table 4.1, there was not a clear trend for

the amount of resins and the silica removed from the liquid phase. The lowest silica concentration corresponded to the smaller amount of resin (0.022), but the highest silica concentration corresponded to several resin samples. Values for calcium and magnesium remained approximately constant. It is very likely that the neutral pH of the water avoided the dissociation of the metasilicic acid to form the ion $[\text{H}_3\text{SiO}_4]^-$; thus the un-dissociated form of this compound did not have the capacity for ionic attraction to the binding site of the resin. Additionally, the presence of anions such as sulfate, chloride or phosphate in solution, with higher affinity for the anionic resin, prevented the attraction of the ion $[\text{H}_3\text{SiO}_4]^-$.

The first dissociation of the metasilicic acid is shown in the equation 4.1:

In this process, the presence of OH^- displaces the equilibrium of the dissociation to the right, while the free acidity in the resin reduces the concentration of OH^- ions. Therefore, the equilibrium of the dissociation is displaced to the left. This could explain the backward behavior of the equilibrium between the amount of resin and the silica removed (Table 4.1). From these results, it can be assumed that the effect of the acidity was more important than the amount of resin. The concentrations of calcium and magnesium remained almost constant because the resin had no attraction for cations.

Removals of silica by the quaternary ammonium resin (resin Dowex Marathon MSA) are shown in Table 4.2.

Table 4.2 - Removals of Si, Ca, and Mg (mg/L) from a nano-filtration pilot plant concentrate using the resin Dowex Marathon MSA

Sample Number	Amount of resin (g)	Si as SiO_2 (mg/L) 212	Ca (mg/L) 228	Mg (mg/L) 279
13	0.505	102	6.11	4.86
14	0.025	104	6.12	4.86
15	0.044	104	6.09	4.85
16	0.062	104	6.12	4.87
17	0.083	104		

As seen in this table, the concentration of silica, calcium, and magnesium remained approximately constant.

Figure 4.1 shows results for the anionic resin Dowex 21 K XLT. In this figure the “y” axis represents the remained concentration of silica in the solution and the “x” axis represents the amount of resin added. As shown in this figure there was no clear relationship between the amount of resin utilized and the silica concentration.

Figure 4.1 - Silica removal by using anionic resin Dowex 21 K XLT

For this test, concentrations of calcium and magnesium remained approximately constant as shown in Figure 4.2. Since the anionic resin has no influence on the cations, no changes were experienced in both calcium and magnesium concentrations.

Figure 4.2 - Hardness removal by using anionic resin Dowex 21K XLT

Results for the use of the resin Dowex Marathon MSA at < 0.1 g showed values of silica concentration approximately constants (104 mg/L), while at 0.505 g the results was about 102 mg/L (Figure 4.3).

Figure 4.3 - Silica removal by using anionic resin Dowex Marathon MSA

4.1.2 Hardness removal from concentrate generated in a nano-filtration pilot plant

The use of the cationic resin G-26 to remove silica from salt solutions is mentioned in the technical information of the Dowex ion exchange resins. This resin was also tested in conjunction with the two anionic resins to evaluate the possibility for silica removal, besides the effectiveness for hardness removal. For this test, results showed significant removal of calcium and magnesium. In this case, higher removal corresponded to higher amounts of resin.

The DOWEX resin G-26 did not show any effect on silica removal; however, as shown in Figure 4.4, calcium and magnesium concentration confirmed the effectiveness of resin for hardness removed.

Figure 4.4 - Hardness removal by using cationic resin Dowex G-26

Figure 4.4 shows that Dowex G-26 resin used at > 0.06 g removed all calcium and most of magnesium.

4.1.3 Overall results for silica and hardness removal from concentrate generated in a nano-filtration pilot plant

Results of the tests can be summarized as follows:

- Maximum silica removal corresponds to the sample No. 1, (using the smallest amount of resin) and was only 9 % removal.
- Silica removal efficiency was very low for the three resins used in the tests.
- Backward behavior was observed for silica removal and the amount of resin; more removal was obtained with less resin.
- Calcium and magnesium removal was successfully done by the cationic resin.
- Both anionic resins showed similar results.

In order to evaluate the behavior of the silica removal without the interference of other ions dissolved in the concentrate of the nano-filtration pilot plant, other series of experiments were performed, using pure water and sodium metasilicate to prepare a silica solution.

4.1.4 Silica Removal from a synthetic solution of sodium metasilicate

Due to the fact that the SiO_2 removal from the nano-filtration using the anionic resins was very low, new experiments were performed using the synthetic solution described in Section 3.3. This solution was deprived of the hard cations Ca and Mg. In these experiments, SiO_2 concentrations were determined using the molybdate method [6]. Tests were performed in duplicate and repeated four times with the same resin. Results for the first of the four cycles showed a backward behavior in which higher amount of resin corresponded to smaller silica removal (Table 4.3). This result supported the hypothesis that the free acidity of the resin affected the dissociation of the silicic acid, thus the ion exchange performance. Results for the test are summarized in Table 4.3.

Table 4.3 - Removal of silica from a synthetic solution by Dowex 21K XLT (quaternary amine type) in the first cycle

Amount of Resin (g)	Final Concentration (mg/L of SiO_2) First cycle	Removal efficiency (%)	Amount of Silica Removed (mg)
0.34	6	80.0	1.19
0.34	6.1	79.7	1.18
0.67	7.2	76.0	1.12
0.67	7.3	75.7	1.11
5.03	17.5	41.7	0.53
5.03	16.7	44.3	0.57
10.05	23.3	22.3	0.23
10.05	24.2	19.3	0.20

As stated above, tests were repeated four times with the same resin using new aliquots of SiO_2 solution. Results for the second cycle of the tests were reported in Table 4.4

Table 4.4 - Silica removal from a synthetic solution and anionic (quaternary amine type) resin test (second cycle)

Amount of Resin (g)	Final Concentration (mg/L of SiO ₂) Second cycle	Removal efficiency (%)	Amount of Silica Removed (mg)
0.34	7.7	74.3	1.1
0.34	7.5	75	1.11
0.67	7	76.7	1.13
0.67	7.3	75.7	1.11
1.68	8.4	72	1.03
1.68	8.4	72	1.03
3.35	6	80	1.08
3.35	6	80	1.08
5.03	8.8	70.7	0.9
5.03	9.2	69.3	0.88

For the second cycle, the silica removal efficiency ranged between 70 and 80 %, reducing the slope of the backward behavior; equilibrium silica concentration ranged between 7 and 9.2 and the amount of silica removed ranged from 0.88 to 1.11.

A third and fourth test were repeated in the same manner of the second test. Results showed again a reduction of the backward behavior. Table 4.5 and 4.6 report the values for the final silica concentration, removal efficiency and the amounts of silica removed during the third and fourth cycles, respectively.

Table 4.5 - Silica removal from a synthetic solution and anionic (quaternary amine type) resin test (third step)

Amount of Resin (g)	Final Concentration (mg/L of SiO ₂) Third cycle	Removal efficiency (%)	Amount of Silica Removed (mg)
1.68	7.0	76.7	1.09
1.68	7.6	74.7	1.06
3.35	7.1	76.3	1.03
3.35	7.2	76.0	1.03
5.03	9.3	69.3	0.88
5.03	9.2	69.0	0.88

For the third cycle, silica removal efficiency ranged between 69 and 77 %, very similar to the second cycle and still presented a slightly backward behavior.

Table 4.6 - Silica removal from a synthetic solution and anionic (quaternary amine type) resin test (fourth cycle)

Amount of Resin (g)	Final Concentration (mg/L of SiO ₂) Fourth step.	Removal efficiency (%)	Amount of Silica Removed (mg)
1.68	6.4	78.7	1.06
1.68	6.5	78.3	1.06
3.35	6.6	78.0	1.11
3.35	6.7	77.7	1.11

The range for silica removal efficiencies in the fourth cycle were even smaller; removal efficiencies ranged from 77.7 %, using 3.35 g of anionic resin to 78.7 %, using 1.68 g of anionic resin. The backward behavior was diminished in each of the four tests. This may be explained by the dilution of the acidity present in the resin, which influences the silica dissociation.

Overall results for the four cycles are shown in the Figure 4.10.

Figure 4.5 - Equilibrium test for silica removal from a synthetic solution and anionic resin

The amount of silica removed during each test was calculated and is shown in Figure 4.11.

Figure 4.6 - Amount of silica removal from a synthetic solution using anionic resin (batch test)

During the first cycle, a variation of approximately 1 mg (maximum and minimum) was observed; whereas the variation for the third cycle was less than one mg. Figure 4.6 and Figure 4.7 show the amounts of silica removed from solution (raw data and percentages, respectively). As shown in these figures the backward behavior and the range of concentrations were reduced in every cycle. In addition, the percentage data showed that the slope for the third and fourth cycle were positive, indicating that the backward behavior was almost eliminated, probably due to the dilution of the free acidity of the resin.

Figure 4.7 - Percentages Amount of silica removal from a synthetic solution using anionic resin (batch test)

Overall results for these series of equilibrium tests indicated that the effectiveness of ion exchange for silica removal need pH controlled conditions. Since the results for silica removal under the initial conditions were not as expected, new series of tests were performed under controlled pH conditions. As reported by Ben Sik Ali et al [6] equilibrium tests may be improved if the resin is previously preconditioned by increasing pH [6].

4.1.5 Effect of pH in the efficiency of silica removal using ionic exchange

New series of tests were developed adjusting the pH with 0.1 M of NaOH or H₂SO₄ solutions, and using the same technique for the equilibrium capacity study. For these tests, three 50 mL tubes were filled with aliquots of silica solution. In two of them, the same amount of resin was added and the third one was used as a control sample.

The results are summarized in Table 4.12. In this table the weight of resin per milliliter of solution is included in column III, the mass in column (IX), and the relationship between the mass sorbed per mass of resin is reported in column (XI). This table shows that at pH values higher than 10, the ration of silica removed: resin was in the order of 1×10^{-3} , and the percentages removed were around 50%. These results suggest that at pH >10, silica can be effectively removed from water using resin Dowex 21 K XLT. The decision to use this technique for silica removal from brines requires an economical evaluation that is beyond the scope of this work.

Table 4.7 - Results for silica removal from a synthetic solution and anionic resin Dowex 21 K XLT at different pH values

(I) Sample	(II) Water volume (mL)	(III) Weigh of resin (g)	(IV) (m) (g/l)	(V) pH	(VI) Initial SiO ₂ (mg/L)	(VII) Final SiO ₂ (mg/L)	(VIII) SiO ₂ removal (g)	(IX) (x)	(X) SiO ₂ removal %	(XI) X=x/m
1	50	1.03	20.6	11.1	32.9	16.1	8.40E-04	0.0168	51.06	8.16E-04
2	50	1.04	20.8	11.1	32.9	15.7	8.60E-04	0.0172	52.28	8.27E-04
3	50	0	0	11.1	32.9	32.9	0		0	
4	50	1.04	20.8	10.29	32.1	15.5	8.30E-04	0.0166	51.71	7.98E-04
5	50	1.04	20.8	10.29	32.1	14.9	8.60E-04	0.0172	53.58	8.27E-04
6	50	0	0	10.29	32.1	32.1	0		0	
7	50	1.04	20.8	9.22	31.7	30.2	7.50E-05	0.0015	4.73	7.21E-05
8	50	1.04	20.8	9.22	31.7	29.2	1.25E-04	0.0025	7.89	1.20E-04
9	50	0	0	9.22	31.7	31.7	0		0	
10	50	1.04	20.8	8.52	32.1	30.7	7.00E-05	0.0014	4.36	6.73E-05
11	50	1.04	20.8	8.52	32.1	31.6	2.50E-05	0.0005	1.56	2.40E-05
12	50	0	0	8.52	32.1	32.1	0		0	
13	50	1.04	20.8	7.61	29.8	29.7	5.00E-06	0.0001	0.34	4.81E-06
14	50	1.04	20.8	7.61	29.8	29.8	0	0	0	0
15	50	0	0	7.61	29.8	29.8	0		0	
16	50	1.04	20.8	6.28	29.6	29.5	5.00E-06	0.0001	0.34	4.81E-06
17	50	1.04	20.8	6.28	29.6	29.4	1.00E-05	0.0002	0.68	9.62E-06
18	50	0	0	6.28	29.6	29.6	0		0	
19	50	1.04	20.8	5.41	30.3	29.5	4.00E-05	0.0008	2.64	3.85E-05
20	50	1.04	20.8	5.41	30.3	30.2	5.00E-06	0.0001	0.33	4.81E-06
21	50	0	0	5.41	30.3	30.3	0		0	
22	50	1.04	20.8	3.27	26.5	26.5	0	0	0	0
23	50	1.04	20.8	3.27	26.5	26.5	0	0	0	0
24	50	0	0	3.27	26.5	26.5	0		0	

4.2 TEST FOR SILICA REMOVAL USING AN ANIONIC EXCHANGE COLUMN

4.2.1 Silica removal from a synthetic solution using an ionic exchange column

Results for silica removal using the resin Dowex 21K XLT under flow conditions are shown in Table 4.8. As shown in this table, the highest removal (73 %) was obtained at a flow rate of 2.9 mL/min after 175 min. By the time when the breakthrough occurred, approximately 50% of the total content of silica was removed. Taking into consideration the pKa of the silicic acid and the pH of the solution (8.5), the percent of ion $[H_3SiO_4]^-$ present in solution may be similar to the percent of silica removed. Silica dissolved in water creates the monosilicic acid (H_4SiO_4) as shown in Equation 4.1

In this form, silica is generally un-ionized at most natural pH levels. At pH 8.5, only 10% of the monosilicic acid is ionized, and if the pH reaches 9 to 10, only 50% of the monosilicic acid is ionized (Equation 4.2).

$$pKa = \frac{[H_3SiO_4] [H^+]}{[H_4SiO_4]} = 9.9^* \quad [Eq. 4.2]$$

*concentration dependent

The data sheet for the anionic resin reports an interchange capacity of 1.3 equivalents of silica per liter of resin. Assuming that only 10 % of the SiO_2 can be removed by the anionic resin, the theoretical amount of this compound silica to be removed is 0.13 equivalents per liter of resin. This value corresponds to 7.8 grams per 1 liter of resin. In this experiment the amount of resin used was 29.4 mL; thus the amount of silica that can be theoretically removed is $(29.4/1000) (7.8) = 0.23$ grams = 230 milligrams. The total silica removed by this test was 13.64 mg. Taking in account that the SiO_2 content in solution was 22.2 mg ($0.562 \text{ L} \times 39.5 \text{ mg/L}$), the efficiency of this process was $62.2\% [(13.64)/(22.2) 100 = 62.2]$

Table 4.8 - Results for silica removal from a synthetic solution using anionic resin Dowex 21 K XLT under flow conditions

Time	Volume	Flow	SiO ₂ initial	SiO ₂ final	Variation.	Amount of Silica removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
0	0	0	39.5			
25	45	1.80	39.5	12.7	26.8	1.21
35	25	2.50	39.5	11.6	27.9	0.70
45	28	2.80	39.5	15.4	24.1	0.67
55	25	2.50	39.5	19.4	20.1	0.50
65	26	2.60	39.5	19.5	20	0.52
75	25	2.50	39.5	16.6	22.9	0.57
85	25	2.50	39.5	14.5	25	0.63
95	27	2.70	39.5	13.1	26.4	0.71
105	26	2.60	39.5	12.2	27.3	0.71
118	25	1.92	39.5	11.5	28	0.70
130	25	2.08	39.5	11.5	28	0.70
140	25	2.50	39.5	12.2	27.3	0.68
152	25	2.08	39.5	11.7	27.8	0.70
165	25	1.92	39.5	12.7	26.8	0.67
175	29	2.90	39.5	10.4	29.1	0.84
182	26	3.71	39.5	12.6	26.9	0.70
188	30	5.00	39.5	16.5	23	0.69
194	25	4.17	39.5	19.5	20	0.50
199	25	5.00	39.5	22.0	17.5	0.44
205	25	4.17	39.5	21.6	17.9	0.44
211	25	4.17	39.5	25.4	14.9	0.45

The percent of silica removed (62.2%) could be explained by the kinetic of the dissociation of the silicic acid. By the time the breakthrough occurred, the amount of ions $[\text{H}_3\text{SiO}_4]^-$ in solution was very low, and the velocity of the dissociation was not high enough to compensate the equilibrium of ions attached to the resin and ions in solution. Even though the resin had enough capacity to accept more $[\text{H}_3\text{SiO}_4]^-$, it is hypothesized that the amount of ions in solution was not high enough to fill all the binding sites.

Additional tests were performed using similar conditions, but with the concentrate of the nano-filtration plant. As previously stated, the solution pH could not be raised higher than 8.5 without observing calcium and magnesium precipitation. Tests carried out, at pH values ranging from 8.2 to 8.5 showed low silica removal efficiency. Wilmarth et al. [11] working under similar conditions, reported a

low efficiency for quaternary ammonium resins. Additional research is needed to analyze the best conditions for silica removal besides increasing the pH value.

4.2.2 Silica removal from the concentrate of a nano filtration plant using an IE column

In order to determine the efficiency of the anionic column for silica removal from the concentrate of the nano-filtration plant, an experiment was carried out using an initial silica concentration of 153.6 mg/L. The sample had a pH of 8.08 and a total hardness of 730 mg/L. 15 g of Dowex 21 KXLT anionic exchange resin were used under an average ascendant flow of 3.5 mL/min. The results are reported in the Table 4.9.

Table 4.9 - Results for silica removal from a concentrate of a NFPP using anionic resin Dowex 21 K XLT under flow conditions

Volume (mL)	Flow (mL/min)	SiO ₂ initial	SiO ₂ final	Variation.	Amount of silica removed (mg)
25	3.5	153.6	87.2	66.4	1.66
50	3.5	153.6	119.8	33.8	0.85
75	3.5	153.6	134.8	18.8	0.47
100	3.5	153.6	135.6	18.0	0.45
125	3.5	153.6	138.4	15.2	0.38
150	3.5	153.6	140.6	13.0	0.33
175	3.5	153.6	150.4	3.2	0.08
200	3.5	153.6	153.6	0.0	0.00

The data showed a total removal of 4.2 mg of silica and a ratio of 0.281×10^{-3} g silica per g of resin. The mass of silica in solution was calculated using the volume and the concentration of silica in solution; this was found to be $200 \text{ mL} \times 153.6 \text{ mg}/1000\text{mL} = 30.7 \text{ mg}$.

The removal efficiency was calculated using the mass of silica removed and the mass in solution. As shown below, the efficiency was 13.7%. This value is low and should be economically evaluated to be considered for an industrial process.

$$\text{Removal efficiency} = [(4.2) / (30.7)] \times 100 = 13.7 \%$$

Since the pH value for this experiment (8.08) was lower than the one described in the previous section (8.5), it was expected that less ions would be present in the solution and, therefore lower efficiency was also expected. Additionally the presence of other anions such as sulfates and chlorides, with higher affinity to the resin, limited the removal of ions $[\text{H}_3\text{SiO}_4]^-$. In this experiment, the removal of silica was almost negligible after an effluent of 200 mL.

4.3 HARDNESS REMOVAL

4.3.1 Hardness removal from a nano-filtration concentrate using cationic resin Bayer Ionac C-249 under flow conditions

Results for hardness removal from the concentrate of the NFPP using cationic resin are shown in Table 4.10. As shown in this table, the total hardness removal calculated using a flow rate of 20 mL/min was 1,042 mg that represents a hardness removal efficiency of 51%. Efficiency was calculated using the total amount of hardness in solution (2,035 mg) and the hardness removed, as shown below

$$\text{Efficiency removal} = ((1,042) / (2,035)) 100 = 51 \%$$

The final hardness concentration of treated water can be controlled by managing the breakthrough point for the process or adjusting the flow rate.

For the test reported in Appendix B, Table B.2, the removal efficiency was 66% using a flow rate of 11 mL/min. It can be observed that the breakthrough, under lower flow conditions, as is the case of the experiment shown in Table 4.10 was reached after more time (about 100 minutes) than the corresponding for this test (about 50 min), in which the flow rate was higher.

For both tests, in order to obtain any desired hardness, the efficiency can be improved by controlling the flow rate and the final breakthrough point, before the resin regeneration.

Table 4.10 - Results for hardness removal from a nano-filtration concentrate using cationic resin Bayer Ionac C-249 under flow conditions

Time	Volume	Flow	Hardness initial	Hardness final	Variation.	Amount of Hardness removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
0	0	0	690			
12.5	250	20	690	10	680	170.00
25.0	250	20	690	35	655	163.75
27.5	50	20	690	50	640	32.00
30.0	50	20	690	55	635	31.75
32.5	50	20	690	60	630	31.50
35.0	50	20	690	65	625	31.25
37.5	50	20	690	80	610	30.50
42.5	100	20	690	100	590	59.00
47.5	100	20	690	110	580	58.00
60.0	250	20	690	170	520	130.00
72.5	250	20	690	265	425	106.25
85.0	250	20	690	380	310	77.50
97.5	250	20	690	470	220	55.00
110.0	250	20	690	580	110	27.50
122.5	250	20	690	600	90	22.50
135.0	250	20	690	640	50	12.50
147.5	250	20	690	680	10	2.50

As part of this research, salt with high Na content, recovered from evaporation ponds for brine disposal alternatives, was tested for cationic resin regeneration.

Results show that salt treatment regenerated the resin after 30 bed volumes (Appendix B, Table B.3). As mentioned above, this may be an option to make these processes “*environmentally friendly*”.

4.3.2 Equilibrium tests

Equilibrium test were performed for hardness removal, using cationic resins. Results are shown in Table 4.11

Table 4.11 - - Equilibrium test results for hardness removal

Test for Concentrate Treated With Cationic Resin								
mass of resin	Humidity	dry mass (m)	volume	m	Co	Ce	Delta C, x	X=x/m
g	%	g	L	g/L	g/L	g/L	g/L	g/g
0.050	50.00	0.025	0.050	0.500	0.690	0.530	0.160	0.320
0.230	50.00	0.115	0.050	2.289	0.690	0.260	0.430	0.188
0.370	50.00	0.185	0.050	3.673	0.690	0.160	0.530	0.144
0.490	50.00	0.245	0.050	4.852	0.690	0.120	0.570	0.117
0.890	50.00	0.445	0.051	8.744	0.690	0.060	0.630	0.072
1.070	50.00	0.535	0.051	10.476	0.690	0.045	0.645	0.062
1.430	50.00	0.715	0.051	13.902	0.690	0.030	0.660	0.047

The relationship between the equilibrium concentration and the amount of hardness removed by the resin was evaluated using the Freundlich equation

$$\frac{x}{m} = X = KC_e^{1/n} \quad [\text{Eq. 4.3}]$$

where:

x= mass of solute adsorbed

m= mass of adsorbent

X= mass ratio of the solid phase –that is, the mass of adsorbed solute per mass of adsorbent

C_e= equilibrium concentration of solute, mass/volume

K, n= experimental constants.

This equation can be converted to a linear equation by using logarithms, thus the equation 4.3 is transformed to:

$$\text{Log } \frac{x}{m} = \text{Log } K + \frac{1}{n} \text{Log } C_e \quad [\text{Eq. 4.4}]$$

The graphical representation of the equation 4.4 is identified as a *Freundlich isotherm*. In this graph, the value of “n” is obtained by the slope of the line; “K” is the value of the intersection of the line with the y axis.

Experimental values are shown in the Figure 4.17

Figure 4.8 - Freundlich Isotherm (Cationic resin and concentrate).

Final equation for the ion exchange of this solution and the cationic resin is:

$$\frac{x}{m} = X = 0.464 C_e^{1/1.587} \quad [\text{Eq. 4.5}]$$

The calculated correlation for the points in the figure is: 0.999; therefore, the results have an almost perfect match to the Freundlich equation.

Chapter 5: Conclusions

The results of this research has corroborated that the effectiveness for silica removal using ion exchange resins highly depends on pH. Monosilicic acid must be dissociated to release the silica and this only effectively happens at pH values higher than 9.0.

The presence of anions with higher affinity for the quaternary-ammonium resins affects silica removal.

Dowex 21K XLT and Dowex Marathon MSA resins showed similar behavior for silica removal.

In the case of the silica removal from the concentrate of the nano-filtration pilot plant, which contained high concentrations of calcium and magnesium, pH increase was not feasible because the calcium and magnesium precipitate as insoluble hydroxides. These precipitates physically interfered in the ion exchange process, clogging the resin column.

Results have shown that high values of hardness, calcium, magnesium and even barium must be removed before the removal of silica from brine. This can be done by precipitation using lime or sodium hydroxide to increase the pH, thus precipitating the carbonates and hydroxides, or using a cationic exchange process.

Positive results were obtained for hardness removal from the concentrate of the NFPP using the cationic exchange resins Dowex G-26 and Bayer Ionac C-249.

Additional work needs to be developed in order to make a mass balance for the process described above and determine the economic feasibility for this process, comparing the process cost and the cost for disposal of the additional un-recovered water.

Recovered salt from the brine evaporation process can be used to regenerate the exhausted resin, making the process environmental friendly (See Appendix B).

Additional research is needed to test the effectiveness for silica removal from this concentrate using a combined process of cationic exchange, pH increase, and anionic exchange (See Appendix B).

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Appendix A

A.1-SILICA REMOVAL REPORT

A.1.1-Silica removal from prepared solutions of SiO₂

Experiment A.1

A silica solution was prepared with deionized RO water and sodium metasilicate to obtain a concentration of 40 mg/L of silica. The pH was adjusted to 8.5 using sodium hydroxide. A glass tube was filled with quaternary ammonium anionic resin to make an anionic exchange column. The minimum recommend height for the column was 80 cm. The resin was washed with deionized RO water before the beginning the test. The characteristics of the column are summarized in Table A.1.

Table A.1 -Anionic exchange column characteristics

Anionic Exchange Column	
Anionic exchange resin volume	29.4 mL
Column diameter	0.604 cm.
Bed height	102.5 cm.
Detention time with void bed	8.9 min
Average flow	3.3 mL/min
Type of flow	Ascendant
Resin	Dowex 21KXLT

Flow rates from 1.9 to 4.2 were adjusted using a peristaltic pump. Silica concentration and the net amounts of silica removed were reported in the Table A.2.

Table A.2- Silica removal results using an ionic exchange column and anionic resin

Time	Volume	Flow	SiO ₂ initial	SiO ₂ final	Variation.	Amount of Silica removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
0	0	0	39.5			
13	25	1.92	39.5	11.5	28.0	0.70
12	25	2.08	39.5	11.5	28.0	0.70
10	25	2.50	39.5	12.2	27.3	0.68
12	25	2.08	39.5	11.7	27.8	0.70
13	25	1.92	39.5	12.7	26.8	0.67
10	29	2.90	39.5	10.4	29.1	0.84
7	26	3.71	39.5	12.6	26.9	0.70
6	30	5.00	39.5	16.5	23.0	0.69
6	25	4.17	39.5	19.5	20.0	0.50
5	25	5.00	39.5	22.0	17.5	0.44
6	25	4.17	39.5	21.6	17.9	0.45
6	25	4.17	39.5	25.4	14.1	0.35

Results showed that the lowest value of silica concentration was 10.4, equivalent to 73 % of the initial silica content. The total amount of silica removed was calculated adding the corresponding amounts from each sample. It is assumed that only 10% of the SiO₂ dissociate at pH 8.5

The total amount of silica removed in this experiment was 7.42 mg, while the total amount of silica in the solution was 12.24 mg. The calculated efficiency was

$$\text{Removal efficiency} = ((7.42) / (12.24)) 100 = 61 \%$$

A.1.2-Silica removal from a concentrate from a nano-filtration pilot plant using anionic resin

Dowex 21 K XLT

Experiment A.2

A concentrated solution from the nano-permeate pilot plant was treated with cationic resin to reduce the hardness to 15 mg/L. The solution had a concentration of 146 mg/L of silica after the hardness removal. The pH was adjusted to 10.79 from an original value of 8.08 using sodium hydroxide. A glass tube was filled with quaternary ammonium anionic resin (Dowex 21 KXLT) to make an anionic

exchange column. The resin was washed with deionized RO water before beginning the test. The characteristics of the column are summarized in Table A.3

Table A.3- Anionic exchange column characteristics

Anionic Exchange Column	
Anionic exchange resin apparent volume	14 mL
Anionic exchange resin weight (g)	11.15
Column diameter	0.541 cm.
Bed height	15.2 cm.
Detention time with void bed	4 min
Average flow	3.5 mL/min
Type of flow	Ascendant

The flow rate was adjusted by gravity to 3.5 mL/min and samples were collected every 50 mL. Silica concentration was measured using a spectrophotometer Hach-4000. Silica concentrations and the net amounts of silica removed are shown in Table A.4

Table A.4- Results for silica removal using resin 21 K XLT under flow conditions

Time	Volume	Flow	SiO ₂ initial	SiO ₂ final	Variation.	Amount of Silica removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
0	0	0	146			
14.3	50	3.5	146	135.4	10.6	0.53
28.6	100	3.5	146	136.8	9.2	0.46
42.9	150	3.5	146	142.6	3.4	0.17
57.1	200	3.5	146	144.8	1.2	0.06
71.4	250	3.5	146	146	0	0

For this test, the total amount of silica removed was 1.22 mg, total amount of silica in the solution was 36.5 mg and the efficiency was found to be very poor (3.3%)

$$\text{Removal efficiency} = ((1.22) / (36.5)) 100 = 3.3 \%$$

Experiment A.3

A concentrated solution from the nano-permeate pilot plant was treated with cationic resin to reduce the hardness to 40 mg/L. The solution had a concentration of 149 mg/L of silica after hardness removal. The pH was adjusted to 10.16 from an original value of 8.47 using sodium hydroxide. A glass tube was filled with quaternary ammonium anionic resin (Dowex Marathon MSA) to make an anionic exchange column. The resin was washed with deionized RO water before beginning the test. The characteristics of the column are summarized in Table A.5

Table A.5- Anionic exchange column characteristics

Anionic Exchange Column	
Anionic exchange resin apparent volume	25 mL
Anionic exchange resin weight (g)	15
Column diameter	0.541 cm.
Bed height	15.2 cm.
Detention time with void bed	4 min
Average flow	3.3 mL/min
Type of flow	Ascendant

The flow rate was adjusted by gravity to 3.3 mL/min and samples were collected every 25 mL. Silica concentrations were measured using a spectrophotometer Hach-DR4000U. Silica concentrations and the net amounts of silica removed were reported in the Table A.6.

Table A.6- Silica removal results using an ionic exchange column and anionic resin

Time	Volume	Flow	SiO ₂ initial	SiO ₂ final	Variation.	Amount of Silica removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
7.6	25	3.3	149	60.4	88.6	2.22
15.2	50	3.3	149	117	32.0	0.80
22.7	75	3.3	149	122.2	26.8	0.67
30.3	100	3.3	149	135	14.0	0.35
37.9	125	3.3	149	126.4	22.6	0.57
45.5	150	3.3	149	132.4	16.6	0.42
53.0	175	3.3	149	129	20.0	0.50
60.6	200	3.3	149	133.2	15.8	0.40
68.2	225	3.3	149	134.8	14.2	0.36
75.8	250	3.3	149	132.2	16.8	0.42
83.3	275	3.3	149	136.8	12.2	0.31

For this test, the total amount of silica removed was 7.0 mg and the amount of silica in solution was 41.0 mg. The calculated efficiency was 17%.

$$\text{Efficiency removal} = ((7.0) / (41.0)) 100 = 17 \%$$

Appendix B

B.1-HARDNESS REMOVAL REPORT

B.1.1-Hardness removal from a concentrated solution of a nano-filtration pilot plant

Experiment B.1

In this experiment, a cationic resin was used to reduce the hardness of a solution from the NFPP (initial hardness of 690 mg/L). A glass tube was filled with the cationic resin Bayer Ionac C-249 to make an ion exchange column. The resin was washed with deionized RO water before beginning the test. The characteristics of the column are summarized in Table B.1

Table B.1 -Anionic exchange column characteristics

Anionic Exchange Column	
Cationic resin volume	30 mL
Column diameter	0.604 cm
Bed height	104 cm
Detention time with void bed	1.49 min
Average flow	11 mL/min
Type of flow	Ascendant

The flow rate was adjusted to 11 mL/min using a peristaltic pump. Samples were collected approximately every 50 mL, and the hardness was measured using the EDTA titrimetric method. Final hardness and the net amounts of hardness removed were reported in the Table B.2.

Table B.2- Results for hardness removal results using cationic resin Bayer Ionac C-249 under flow conditions

Time	Volume	Flow	Hardness initial	Hardness final	Variation.	Amount of Hardness removed
(min)	(mL)	(mL/min)	mg/L	mg/L		mg
0	0	0	690			
17.3	190	11	690	0	690	131.1
35.5	200	11	690	0	690	138.0
62.7	300	11	690	25	665	199.5
90.0	300	11	690	60	630	189.0
127.3	410	11	690	140	550	225.5
148.2	230	11	690	240	450	103.5
170.0	240	11	690	360	330	79.2
191.8	240	11	690	460	230	55.2
213.6	240	11	690	520	170	40.8
238.2	270	11	690	600	90	24.3

The total amount of hardness removed (1042 mg) was calculated adding the corresponding amounts of each sample and the removal efficiency (66%) was calculated as shown below

$$\text{Efficiency removal} = ((1186) / (1808)) 100 = 66 \%$$

B.2- CATIONIC RESIN REGENERATION

Experiment B.2

The cationic resin Bayer Ionac C-249 was regenerated with a saturated solution of the recovered salt from an evaporation pond containing sodium chloride. The results are reported in Table B.3.

Table B.3- Regeneration of the cationic resin Bayer Ionac C-249 using recuperated salt from an evaporation pond

Time	Volume	Flow	Hardness	Hardness removed
(min)	(mL)	(mL/min)	mg/L	mg
0	0	0		
5.0	100	20	650	65.0
9.5	190	20	4070	366.3
15.5	310	20	1875	225.0
20.5	410	20	1100	110.0
25.5	510	20	750	75.0
35.5	710	20	400	80.0
45.5	910	20	300	60.0
55.5	1110	20	200	40.0
68.0	1360	20	90	22.5
80.5	1610	20	70	17.5
88.0	1760	20	50	7.5
101.0	2020	20	50	13.0
108.5	2170	20	40	6.0
116.0	2320	20	30	4.5
131.0	2620	20	30	9.0
146.0	2920	20	20	6.0

Appendix C

FLOW CALCULATION FOR IONIC EXCHANGE ACCORDING TO THE PRODUCT INFORMATION

Flow Calculations		
Column 0.604 cm diameter		
Column height	76 cm	
Diameter	0.604 cm	
Area	0.287cm ²	
Recommended flow	5-60 m/h	
Equivalent flow (mL/hr)	143.4	1721.1
Equivalent flow (mL/min)	2.4	28.7
Backwash (mL/min)	0.5	4.8
Counter current regeneration (mL/min)	2.4	9.6
Regeneration 4-8 BV (mL)	87.2	174.4
Regeneration time (min)	36.5	18.2
Rinse Volume (mL)	87.2	174.4
Rinse time (hr)	2.4	9.6

Appendix D

RESIN CHARACTERISTICS

DOWEX™ 21K XLT

Product Name	Type	Matrix	Functional Group
DOWEX 21K XLT	Type I Strong Base Anion	Styrene-DVB, Gel	Quaternary Amine

Specifications	Unit	Cl ⁻ Form
Total Exchange Capacity, min.	eq/L	1.3
Water Retention Capacity	%	50 - 60
Uniformity Coefficient		1.1 max.
Particle Size Distribution		
Volume Median Diameter	µm	525 - 625
Whole Uncracked Beads, min.	%	90
Total Swelling (Cl ⁻ → OH ⁻), approx.	%	18 - 20
Particle Density	g/mL	1.08
Shipping Weight**	g/L	670
Shipping Weight**	lbs/ft ³	42

** As per the backwashed and settled density of the resin, determined by ASTM D-2187.

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DOWEX™ MARATHON™ MSA

Product Name	Type	Matrix	Functional Group
DOWEX MARATHON MSA	Type I Strong Base Anion	Styrene-DVB, Macroporous	Quaternary Amine

Specifications	Unit	Cl ⁻ Form
Total Exchange Capacity, min.	eq/L	1.1
Total Exchange Capacity, min.	kg/ft ³ as CaCO ₃	24.0
Water Retention Capacity	%	56 - 66
Uniformity Coefficient		1.1 max.
Whole Beads	%	95 - 100
Mean Particle Size	µm	640 ± 50
Total Swelling (Cl ⁻ → OH ⁻), approx.	%	15
Particle Density	g/mL	1.06
Shipping Weight**	g/L	670
Shipping Weight**	lbs/ft ³	42

** As per the backwashed and settled density of the resin, determined by ASTM D-2187.

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DOWEX™ G-26 (H)

Product Name	Type	Matrix	Functional Group
DOWEX G-26 (H)	Strong Acid Cation	Styrene-DVB, Gel	Sulfonic Acid

Specifications	Unit	H ⁺ Form
Total Exchange Capacity, min.	eq/L	2.0
Water Retention Capacity	%	45 - 52
Uniformity Coefficient		1.1 max.
Particle Size Distribution (Mean Particle Size)	μm	650 ± 50
Whole Uncracked Beads, min.	%	95
Crush Strength (Average, min.)	g/bead	500
Total Swelling (Na ⁺ → H ⁺)	%	7
Particle Density	g/mL	1.22
Shipping Weight**	g/L	800
Shipping Weight**	lbs/ft ³	49
Trace metals, ppm dry resin, max	Na Fe Cu Al 100 50 50 50	Heavy Metals (as Pb) 20
Ionic conversion, min.		H ⁺ 99.7

** As per the backwashed and settled density of the resin, determined by ASTM D-2187.

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(BAYER) SYBRON IONAC C249

Product Name	Type	Matrix	Functional Group
SYBRON IONAC C249	Strong Acid Cation	Styrene-DVB	Sulfonic Acid

Specifications	Unit	Na ⁺ Form
Total Exchange Capacity, min.	eq/L	1.9
Water Retention Capacity	%	45 - 48
Physical form		Black spherical beads
Particle Size Distribution (Mean Particle Size)	mesh	16 - 40
pH range stability		0 - 14
Total Swelling (Na ⁺ → H ⁺)	%	5
Shipping Weight**	lbs/ft ³	52
Maximum Free Chlorine	mg/L	1

Vita

Carlos Acevedo, son of Enrique Acevedo and Refugio Rodriguez, was born in 1966, in the City of León, Guanajuato, México. He got his Bachelor in Science in Chemical Engineering, in 1989 (Thesis: Improvements to the Wastewater Treatment Plant for “Química Central de México” (QCM)). From 1989 to 1997, he worked at QCM as coordinator of environmental projects for water, sewer and air pollution. Another position he occupied in the company was Industrial Safety Manager; his role in this position was to coordinate safety and environment projects. While working at this company, he also designed and built wastewater treatment plants, improved the industrial wastewater treatment plant for chromium recovery, designed a hazardous waste landfill, and managed projects for polluted areas remediation and chromium recovery processes.

He began working as a consultant and contractor for environmental projects in 1997, on his own company, Ingeniería y Proyectos Ecológicos, Sociedad Anónima (IPESA). Working in IPESA, he managed environmental projects for the tanning industry in Leon, Guanajuato. Designed and built wastewater treatment plants for domestic and industrial wastes; designed hazardous waste landfills, and advised many companies on environmental improvements and the compliance with environmental rules and regulations.

He worked as a mathematics and physics teacher in the “Universidad Anahuac” in Leon, Guanajuato from 1997 to 1999 and as teaching assistant at UTEP from 2001 to 2002.

In 2001 he moved to El Paso, TX and worked for the Lower Valley Water District, as New Installations Coordinator for one year. In 2001 he started his graduate program in Chemistry at the University of Texas at El Paso. In 2002 he was recruited by the Border Environment Cooperation Commission (BECC). At BECC he manages environmental projects along the USA-Mexico Border, having certified ten projects for water distribution, wastewater collection and treatment, and solid waste disposal. Currently he works at BECC as Project Engineer.

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This thesis was typed by Carlos R. Acevedo.