Evaluating Electrocoagulation and Chemical Coagulation for Removing Dissolved Silica from High Efficiency Reverse Osmosis (HERO) Concentrate Solutions

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ABSTRACT

High efficiency reverse osmosis (HERO) produces high pH concentrate streams that often contain high levels of dissolved silica. Removal of silica from these concentrate streams is desirable before brine concentration and crystallization. This research investigated removal of dissolved silica from simulated HERO concentrate solutions using electrocoagulation (EC) with mild steel anodes and chemical coagulation with FeCl_3 . At pH values of above 10, the mild steel anodes immediately passivated and were not able to deliver Fe^{2+} ions into the solution. This necessitated lowering the solution pH value via HCl or FeCl_3 addition prior to EC. At pH values ≤ 10 , iron dosing by EC was in agreement with that given by Faraday's law. The optimal initial pH value for operating the EC process was 8, which required addition of 17.8 mM HCl or 5.8 mM FeCl_3 . An EC iron dose of 4.0 mM resulted in 76-89% silica removal for solutions with initial pH values between 4 and 8. Higher dosing up to 9.3 mM increased silica removal by only 5%. Chemical coagulation was not as effective as EC, and was able to achieve a maximum removal of 64% with a 4.0 mM FeCl_3 dose. Solution ionic strength had no measurable impact on silica removal by EC, but did affect final solution pH values and silica removal by chemical coagulation. For both EC and chemical coagulation, the initial pH value of solution had greater impact on silica removal than the iron dose.

Keywords: High efficiency reverse osmosis (HERO) Concentrate, silica removal, electrocoagulation, chemical coagulation, iron

1 INTRODUCTION

High efficiency reverse osmosis (HERO) is becoming increasingly utilized for water desalination, especially for treating waters containing high levels of dissolved silica [1, 2]. In the HERO process, the feed water to the RO unit is raised to a pH value ≥ 9 . This has the effect of greatly reducing fouling of the RO membrane, and has been found to allow permeate recoveries as high as 99% [3]. The first step in a HERO process involves removal of Ca^{2+} and Mg^{2+} ions using weak acid cation exchange (WAC) media. The second step removes dissolved CO_2 . Decarbonation reduces the buffering capacity of the water, thereby decreasing the amount of NaOH required to raise the pH. Next, NaOH is added to raise the pH to ≥ 9 before it enters the RO unit. During the RO treatment step, the pH of the concentrate increases to ~ 11 - 11.2 , which is the highest pH allowable for continuous duty of most RO membranes [4, 5]. Because of high membrane rejection of ions, including OH^- , the permeate pH decreases to ~ 8.5 [3]. The softening of the water and decarbonation prevents carbonate scale from forming on the membrane. The elevated pH converts dissolved silica into anionic form (*e.g.*, H_3SiO_4^-), and also results in formation of a negative charge on the RO membrane surface. The negative charge on the membrane prevents fouling by colloidal material, dissolved silica and dissolved organic matter, which are also negatively charged at elevated pH values. In addition, the high pH on the concentrate side of the RO membrane prevents biofouling via both biocidal and electrostatic effects [6].

The HERO process was developed for treating groundwater containing high levels of dissolved silica, and HERO systems have been observed to operate with silica levels in the concentrate stream as high as 1500 mg/L without membrane fouling [2]. The high concentration of silica in HERO

concentrate solutions results in precipitation fouling of surfaces in piping systems and tanks when the high pH solutions are neutralized during brine treatment. Because of their unique properties, HERO concentrate streams are difficult to treat by conventional brine treatment methods, such as lime softening, brine concentrators or thermal crystallization [7]. HERO concentrate streams contain primarily alkali metal cations, mono- and divalent anions, and dissolved silica. Thus, the main challenge in treating these concentrates is removing high levels of dissolved silica from high pH solutions containing only monovalent cations. With only monovalent cations present, the electrical double layers on negatively charged flocculating particles are considerably expanded compared to those in solutions containing divalent and trivalent cations [8].

Commonly used methods for removing dissolved silica from solution include: adsorption on activated alumina, coagulation with iron and aluminum salts, and ion exchange, for high pH solutions. Adsorption and ion exchange produce regenerant brine solutions that would not solve the silica disposal problem. Thus, coagulation processes are the best treatment option for removing silica from HERO concentrate solutions. Several previous studies have found that dissolved silica can be removed from solution using either chemical coagulation or electrocoagulation (EC) using Fe^{3+} or Al^{3+} ions [9, 10, 11, 12, 13, 14, 15, 16]. Because Al^{3+} coagulation processes are less effective at pH values greater than 8, coagulation processes based on Fe^{3+} are preferred in high pH solutions [17]. Dissolved silica removal using iron coagulating agents can involve co-precipitation of ferric-silicate solids or involve silica adsorption to ferric hydroxide precipitates. Silica adsorption to ferric hydroxide is a chemical adsorption process where Fe-O-Si bonds form via a ligand exchange reaction [18]. These reactions involve replacement of -OH or $-(\text{OH})_2$ ligands bound to Fe(III) with a silicate

anion. Monodentate complexes involve formation of a single Fe-O-Si bond, and bidentate complexes involve formation of two Fe-O-Si bonds to a single Fe(III) atom (bidentate mononuclear), or to two adjacent Fe(III) atoms (bidentate binuclear) [18].

One challenge in using EC to treat HERO concentrate solutions is passivation of the anode at high pH values [19]. Passivation of iron anodes in highly alkaline solutions results from the low solubility of ferrous ions that result in an insoluble $\text{Fe}(\text{OH})_2$ layer on the anode surface that inhibits Fe^{2+} atoms from entering the solution. This causes an increase in the electrode voltage required to maintain the desired current density. At elevated anode voltages, water oxidation and evolution of O_2 gas become thermodynamically favorable, and O_2 evolution competes with iron oxidation as the anode reaction. This may result in iron dosing that is below that corresponding to Faraday's law. Thus, electrode passivation may cause problems with coagulant dosing when treating HERO concentrate solutions.

The goal of this research was to investigate the effectiveness of EC and chemical coagulation for removing dissolved silica from simulated HERO concentrate solutions. The effect of solution pH value on Fe^{2+} dosing was investigated to determine the ability of EC to deliver Fe^{2+} ions in accord with Faraday's law in high pH solutions. Batch experiments measuring dissolved silica removal were performed with varying doses of Fe^{3+} , delivered by EC or via addition of FeCl_3 . The effect of the initial solution pH value and solution ionic strength on silica removal was determined.

2 MATERIALS AND METHODS

Test solutions were prepared by dissolving sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, (Sigma-Aldrich) in simulated RO concentrate solutions or in ultrapure water (UPW) ($0.18 \mu\text{S}/\text{cm}$) to produce solutions

with ionic strengths (IS) of 55.6 and 16.7 mM. The compositions of the two test solutions are listed in Table 1. A dissolved silica concentration of 1000 mg/L as SiO_2 was selected to simulate a HERO process with 30 mg/L of silica in the feed water operated at a water recovery of 97%. The simulated RO concentrate was based on that produced in a previous investigation treating Central Arizona Project water, as delivered to Tucson, Arizona [20]. The test solutions prepared in UPW were used to investigate the effect of solution IS on silica removal. Natural organic matter was not included in the test solutions, since HERO is primarily used for treating groundwaters that often contain little or no organic matter. Prior to the chemical or electrocoagulation experiments, the initial solution pH values were adjusted to span the range from 12 to 2 by addition of analytic grade HCl or NaOH. Dissolved silica and iron concentrations were measured using an Agilent model 5100 synchronous vertical dual view inductively coupled plasma optical emission spectrophotometer (ICP-OES). Solution phase speciation of ions was modeled using the PHREEQC modeling package from the U.S. Geological Survey [21,22].

Chemical coagulation experiments were performed in 500 mL of solution contained in glass beakers using laboratory grade anhydrous powdered FeCl_3 (>98.5%, Science Company). A magnetic stir bar was used to stir the solutions at approximately 60 rpm during the FeCl_3 dosing. After dosing, the stirring was continued for a period of 2.0 hours. The supernatant solutions were sampled after 0.5 and 24 hours settling time. Except where indicated, samples were filtered using 0.1 μm syringe filters. To assess the amount of silica present in filterable colloidal species, selected samples were also taken without filtering.

Electrocoagulation experiments were performed in a rectangular flow-through reactor (Powell

Water Systems, Centennial Colorado) with nine mild steel electrodes in parallel plate configuration. The electrodes were $3.2 \times 34.0 \times 0.32$ cm with 0.4 cm interelectrode gaps. With all electrodes in place, the void volume of the reactor was 0.35 L with a total wetted anode surface area of 900 cm^2 . Before use, the electrodes were polished with 100 grit sandpaper. The test solutions were fed into the reactor at 0.5 L/min yielding a hydraulic detention time of 0.70 min. A current density of 8.0 mA/cm^2 was provided by a Protek model 3005B (30 V, 5 A) galvanostatic power supply. The samples were collected after 10 minutes of steady state operation, which was achieved after passage of 14 reactor volumes of solution through the reactor. Effluent samples from the EC reactor were collected in 125 mL vials and were shaken for 0.5 hours and then allowed to settle prior to sampling the supernatant solution. The effect of a cationic polymer clarifying agent (6505 HTH Super Concentrated Clarifier, Arch Chemicals, Inc.) on the settling properties of the flocs was investigated by dosing selected samples with concentrations ranging from 0.05% to 1%.

Iron dosing rates were measured by placing a single anode and single cathode in the EC reactor. Solutions with the desired pH value were circulated through the reactor while the electrodes were galvanostatically polarized at current densities ranging from 1.0 to 9.0 mA/cm^2 . The same set of two electrodes was used for all dosing rate experiments. Loss of iron from the anode was measured gravimetrically by weighing before and after polarization periods ranging from 1 to 5 hours.

Table 1. Composition of the low and high IS test solutions.

Feed water	Analyte	Concentration (mM)	Concentration (mg/L)
UPW	Na ⁺	33.3	766
	SiO ₂	16.6	1000
	Ionic strength (@pH=7)	16.7	
Simulated RO Concentrate	Na ⁺	64.7	1490
	SiO ₂	16.6	1000
	Cl ⁻	11.3	400
	SO ₄ ²⁻	10.1	967
	Ionic strength (@pH=7)	55.6	

3 RESULTS AND DISCUSSION

3.1 EC Dosing Experiments

The first objective of this research was to investigate the effect of solution pH value on the dosing of iron into the solutions. Figure 1 shows the iron dosing rate per unit area of anode surface as a function of the current density for solutions with pH values ranging from 5 to 12. The dosing rates (D_s) for solution pH values of 5, 7, 9 and 10 were in good agreement with that predicted by Faraday's law, as given by:

$$D_s \left(\frac{\mu\text{mol}}{\text{cm}^2\text{min}} \right) = \frac{i}{F \times z} \times \frac{1000 \mu\text{A}}{\text{mA}} \times \frac{60\text{s}}{\text{min}} \quad (1)$$

where F is the Faraday constant (96,495 C/mol), z is the charge on Fe²⁺, and i is the current density in mA/cm². This indicates that the reaction:

accounted for nearly all the anodic current. For pH values of 11 and 12, only trace amounts of iron were released into solution at any current density. Electrode passivation occurred immediately upon

anodic polarization, and is thereby different from slower passivation processes that are amenable to reversal via changing the electrode polarity [10]. Thus, in cases where HERO produces concentrate solutions with pH values of 11 or greater, the pH needs to be lowered in order to use EC for delivering the iron coagulant.

Figure 1. Iron dosing rate as a function of applied current density in solutions with pH values ranging from 5 to 12.

In order to allow Fe dosing via EC, the pH values of the simulated HERO concentrate solutions were lowered by adding either HCl or FeCl₃. Figure 2 shows how the dose of HCl and FeCl₃ affected the pH value of the test solutions. To lower the pH value from 11 to 8 required an HCl dose of 17.8 mM. This high dose can be attributed to the high buffering capacity of the solution. The dominant species of dissolved silica in the solution at pH=11 was the orthosilicate anion, H₃SiO₄⁻, since H₄SiO₄ has a pK_a value of 9.9 [23]. Given the total dissolved silica concentration of 16.6 mM, the stoichiometric amount of acid required to change the pH from 11 to 8 is 16.4 mM. This is close to the experimentally measured amount of 17.8 mM. The dose of FeCl₃ required to lower the pH from

11 to 8 was 5.83 mM, which is 5% greater than the stoichiometric amount of 5.53 mM if all the iron formed $\text{Fe}(\text{OH})_3$.

Figure 2. The effect of HCl or FeCl_3 addition on the pH value of 1000 mg/L SiO_2 solutions with $\text{IS}=16.7$ mM.

3.2 Electrocoagulation

The effectiveness of EC for removing dissolved silica from solutions with different initial pH values is shown in Figure 3a as a function of the initial pH value. Figure 3b shows the same silica removal data as a function of the final pH value. Except for the Fe dose of 9.8 mM, the initial pH values were adjusted down from 11 using HCl. For iron doses of 4.0 mM, SiO_2 removals between 76% and 89% were observed for initial pH values between 8 and 4 in both the low and high IS solutions. The similar removal in both the $\text{IS}=16.7$ and $\text{IS}=55.6$ solutions indicates that silica removal was not significantly affected by the solution IS. The ratio of Si atoms removed per Fe atom precipitated was 2.2 ± 0.1 for final solution pH values between 8 and 4.

The optimal initial pH range using a 4.0 mM Fe dose was 7-8. At this initial pH, a high level of silica removal was achieved (86-89%) while also minimizing the required HCl dose. The higher

silica removal at a final pH of 8 as compared to pH values of 9 and 10 can be attributed to electrostatic effects. At pH values of 9 and 10, the ferric hydroxide precipitate has a net negative charge [24]. This reduces adsorption of H_3SiO_4^- , which becomes the predominant silica species at pH values greater than 9.9. The decreasing silica removal with decreasing pH values below 6 can be attributed to decreasing precipitation of ferric hydroxide with decreasing pH. For the 4.0 mM Fe dose, the fraction of iron that remained dissolved was <0.1% at pH=6.1, 11% at pH=5.1, and 89% at a final pH value of 3.3

Figure 3a. Removal of silica by EC from solutions with different initial pH values after 24 hours of settling time.

Figure 3b. Removal of silica by EC from solutions with different final pH values after 24 hours of settling time.

The effect of iron dose is also shown in Figures 3a and 3b for the IS=16.7 mM solution. The 2.0 mM Fe dose resulted in 5-31% less silica removal than the 4.0 mM dose. Also shown in Figures 3a and 3b is an experiment where the initial pH value was adjusted to 8 using 5.8 mM FeCl_3 before adding a 4.0 mM Fe dose using EC. In this experiment the total Fe dose was 9.8 mM, but the silica removal was only 5% greater the 4.0 mM dose. This shows that the initial pH value affected silica removal by EC more than the Fe dose, and also shows that Fe doses greater than 4.0 mM did not significantly increase silica removal.

Iron dosing by EC had only a small impact on the solution pH values, as shown in Figure 4. The final solution pH values for the low ionic strength solutions were within 1 pH unit of the initial value. This can be explained by the fact that acid formed via precipitation of $\text{Fe}(\text{OH})_3$ was consumed in the cathode reaction of hydrogen gas evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). In the high IS solutions, the final pH values for solutions with initial pH values ≤ 4 were up to 2 pH units greater than the initial value. This can be explained by incomplete precipitation of Fe(III) at these pH values. Iron precipitation

ranged from 94% for an initial pH value of 4, to only 11% for an initial pH value of 2. For the lowest final pH value of 3.3, PHREEQC solution modeling indicated that the Fe(III) remained in solution as FeSO_4^+ (1.53 mM), $\text{Fe}(\text{OH})^{2+}$ (1.11 mM), $\text{Fe}(\text{OH})_2^+$ (0.38 mM) and Fe^{3+} (0.17 mM).

Figure 4. Final solution pH values versus initial pH value for Fe dosing via chemical coagulation (CC) and electrocoagulation (EC).

3.3 Chemical Coagulation

Silica removal by chemical coagulation is shown in Figure 5a for solutions with initial pH values ranging from 12 to 2. Figure 5b shows the same data as a function of the final solution pH values. Significant silica removal was observed for all experiments for an initial pH value of 10. For the 4.0 mM dose, high levels of silica removal were also observed for initial pH values between 9 and 5 for the IS=16.7 mM solution, but not for the IS=55.6 mM solution. This difference in performance can be attributed to final solution pH values in the higher ionic strength solution that were 0.4 to 0.5 pH units lower than those for IS=16.7 mM, as shown in Figure 4. Figure 5b shows that the final solution pH value had a significant effect on the level of silica removal, especially in the pH range from 2 to

3.

Figure 5a. Removal of silica by chemical coagulation from solutions with different initial pH values after 24 hours of settling time.

Figure 5b. Removal of silica by chemical coagulation from solutions with different final pH values after 24 hours of settling time.

Also shown in Figure 5a is silica removal from solutions where the initial pH was adjusted via FeCl_3 addition, rather than HCl addition. The solution with an initial pH value of 10, had 3.3 mM FeCl_3 added to reduce the pH from 11, followed by addition of a 4.0 mM FeCl_3 dose. The resulting FeCl_3 dose of 7.3 mM showed similar silica removal as the 4.0 mM dose. Similarly, a solution with a

total FeCl_3 dose of 9.3 mM was achieved via a 5.3 mM dose to reach pH 8, followed by a 4.0 mM dose. This resulted in similar removal as the solution with the 4.0 mM dose where the initial pH was lowered via HCl addition. These results indicate that the initial solution pH value had a greater effect on silica removal than the total FeCl_3 dose, and that FeCl_3 doses greater than 4.0 mM did not significantly increase silica removal over the 4.0 mM dose.

3.4 Floc Settling

The settling behavior of the flocs was investigated by taking filtered and unfiltered samples after 0.5 and 24 hours of settling time. Also investigated was the effect of cationic polymer addition on floc settling. The unfiltered supernatant samples are indicative of silica removal by settled solids. As shown in Figure 6, there was slightly more silica removal by settled solids after 24 hours than after 0.5 hours of settling for all clarifier doses. The difference in silica removal between filtered and unfiltered samples is indicative of filterable colloidal species. For the samples taken after 0.5 hours of settling time, up to 25% of the initial 1000 mg/L silica was present as filterable colloids. Combining the silica present as settled solids with the amount present as filterable colloids accounted for 70 to 94% of the silica. This indicates that there was very little silica present as dissolved silica. The optimal clarifier dose was 0.05%, which is equivalent to 500 mg/L.

Figure 6. Silica speciation after 0.5 and 24 hours settling time as a function of clarifier dose for a test solution with an initial pH value of 11 with an EC dose of 9.83 mM Fe.

4 CONCLUSIONS

This study indicates that both EC and chemical coagulation are effective for removing dissolved silica from HERO concentrate solutions. The major difference between EC and chemical coagulation was the effect of the coagulant on the final solution pH value. For EC, the initial solution pH value was the most important factor affecting the level of silica removal. Initial solution pH values of 10 or lower were required to avoid immediate passivation of the mild steel anodes. Iron doses of 4.0 mM were slightly more effective than 2.0 mM doses, and gave similar results as iron doses of 7.3 and 9.3 mM. The 4.0 mM dose was able to achieve silica removals ranging from 76 to 89% for final solutions pH values between 5 and 7.5. For chemical coagulation, the very high silica concentrations in the test solutions required high doses of FeCl_3 that resulted in final solution pH values that were too low to most effectively remove silica. For chemical coagulation, the optimal FeCl_3 dose was also

4.0 mM, with maximum silica removals ranging from 61-64% occurring at final solution pH values near 3.

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