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pH modification for silica control

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ABSTRACT

Lowering solution pH slows the polymerization of silica and formation of silica scale. In batch systems, lowering the pH of approximately 200 ppm silica solutions prevents scale formation for over 300 h. Silica scale forms most quickly near pH 8. Solutions with pH 3.6–3.7 can maintain silica levels of 1,000–3,000 ppm for roughly 90 h. Bench-scale membrane testing showed that silica scale formation lag times of approximately 72 h were achievable after lowering the pH to 4.5–4.7, which might allow flushing of silica-laden solutions through, for example, flow reversal, before scale formation occurs during water treatment.

Keywords: Silica; Scale formation; Nanofiltration

1. Introduction

Better silica control methods are needed to desalinate impaired waters for power plant cooling, steam production, and drinking water. Many impaired waters, such as saline ground waters and waste waters, contain high dissolved silica levels and require only minor concentration to form silica scale [1]. Silica scale is hard and resistant to most forms of chemical attack (e.g. acid washing) and far harder to remove from towers, boilers, and membranes than other mineral scales. The low thermal conductivity of silica scale disproportionately decreases boiler output. Antiscalant precipitation inhibitors that work by blocking specific sites on growing well-ordered crystals are less effective on amorphous silica [2]. Silica can be coagulated with metal salts such as alum or ferric chloride [3], or selectively precipitated through warm lime softening [4], although large amounts of sludge are produced in the process. Silica scale can also be prevented by raising the pH to greater than 10 and removing divalent cations (through, for example, ion exchange [5]) that otherwise nucleate scale).

Feedwater acidification is an attractively simple way to prevent silica scale [6–10]. Low pH slows the polymerization of monomeric silica to silica polymers, then silica scale [11] in silica oversaturated solutions. Once silica polymers reach a certain size, termed a "critcal nucleus," they rapidly form silica scale, ultimately leaving behind equilibrium levels of silica monomers in solution. The formation rate of critical nuclei—the slow rate-limiting step in the polymerization/nucleation/scale formation cascade—depends on pH and the presence of other ions. At 25°C, nucleation is rapid at pH 8 and occurs in minutes; nucleation is slower in solutions more acidic and basic. Increased total dissolved solids accelerates polymerization and nucleation by compressing the electric double layer and shielding silica charge. Treatment methods can

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take advantage of the low pH polymerization lag time by periodically discharging oversaturated, silica-laden waters before the scale is able to form, for example during membrane filtration [8].

Critical unknowns are the scale formation lag time, the extent of the pH effect, and the impact of other ions. Long time lag would allow higher concentration of feedwaters, hence greater water utilization. Our goal is to experimentally establish the time limits on dissolved silica stability in low pH nanofiltration concentrate such as might be generated by sidestream nanofiltration of cooling tower water. Sidestream nanofiltration of scale-forming ions inhibits scale formation in cooling towers [12] but relocates potential scale formation from the cooling tower to the nanofiltration membranes. Batch and membrane testing establishes the extent of low pH inhibition of silica scaling.

2. Experimental methods

Three experimental efforts were carried out: batch testing of scale inhibition using evaporated blowdown (Silica > 200 ppm); batch testing of scale inhibition from ultra-high silica solutions (Silica approximately 1,000–2,000 ppm); and bench testing of scale inhibition during multistage nanofiltration. The cooling tower blowdown was from Sandia National Laboratories Building 518 or the Center for Integrated Nanotechnology (CINT) and is evaporatively concentrated groundwater. Table 1 gives the major element composition of CINT cooling tower blowdown [12].

2.1. Blowdown batch testing

Five separate volumes of CINT blowdown were processed:

1. water was acidified to pH approximately 5 (5.1) to prevent polymerization;
2. water was evaporated to half its volume to increase the silica concentrations;
3. water was cooled to 25°C;
4. pHs of water were adjusted by adding NaOH; and
5. dissolved monomeric silica concentrations were then monitored over time.

Four solutions were adjusted upwards to pHs of 6, 7.1, 8.2, and 9.1; the pH 5.1 solution was used as is. The pH was measured using an electrode standardized at pH 4 and 10. Monomeric silica was measured using the Hach Silica test (Cat No. 14554), which relies on the molybdate blue reaction [11], and later with an inductively coupled plasma mass spectrometer (ICP-MS).

Because of the pre-evaporation step, silica monomer concentrations (and that of the other conservative ions) were twice the levels in Table 1 ($SiO_{2,aq} \sim 220$ ppm). Amorphous silica saturation at this temperature and these pHs is approximately 120 ppm, which means that the starting solutions were over saturated with respect to amorphous silica and thermodynamically favored to polymerize and form scale. Polymerization and scale formation would be indicated by a decrease in dissolved monomeric silica concentration over time.

Table 1
Major element composition of CINT cooling tower blowdown [from 12]

Ion	Concentration (ppm) [mol/l]
Na^+	152 [6.6e−3]
Ca^{+2}	163 [4.1e−3]
Mg^{+2}	27 [1.1e−3]
Cl^-	105 [3.0e−3]
SO_4^{2-}	139 [1.4e−3]
HCO_3^-	374 [6.1e−3]
K^+	25 [6.3e−4]
$SiO_{2,aq}$	109 [1.8e−3]
pH	8.9

2.2. Ultra-high silica batch testing

Two test fluids were prepared (see Table 2) by sequential addition of salts, concentrated HCl, sodium silicate, followed by pH adjustment to pH 3.6–3.7 using potassium hydroxide. The test fluids were designed to be rich in non-silica salts, and hence, representative of saline reverse osmosis (RO) concentrate streams. All salts except sodium silicate were first dissolved in either 60 ml of deionized water (Run A) or 90 ml of deionized water (Run B). Concentrated HCl (38% w/w; 12 M) was then added in quantity sufficient to assure that a pH of approximately 2.4 would be maintained once more basic sodium silicate had been added subsequently. Trial and error indicated the needed mass of concentrated HCl to be 80% that of sodium silicate. Sodium silicate was dissolved in 15 ml of deionized water and added dropwise to the acidified salt solution over the span of about 4 min while the solution was stirred vigorously. No solution cloudiness was observed when the sodium silicate was added, suggesting that no silica-bearing colloids or solids formed. The solutions were diluted up to approximately 100 ml, and 1 N KOH was added manually to raise the pH to the desired experimental range of 3.6–3.7.

Table 2
Initial compositions of ultra-high silica test solutions

	A (g)	B (g)		A (mg/kg)	B (mg/kg)
$CaCl_2$	0.3719	0.772	Ca	1,355	2,462
$MgSO_4$	0.1148	0.2263	Mg	234	404
K_2SO_4	0.0462	0.1011	Na	1,641	3,581
NaCl	0.2317	0.6452	SiO_2^{aq}	962	1,926
$Na_2SiO_3 \cdot 9H_2O$	0.4790	1.0123	K	209	401
Mass (salts + H_2O)	99.0	113.1	Cl	3,821	7,831
pH	3.7	3.6	SO_4^{2-}	1,182	2,091

Each of the test fluids was periodically sampled after stirring over a period of approximately 90 h and samples analyzed for monomeric silica, total silica, and pH. In sampling, approximately 0.5 ml of solution was extracted, two small drops (approximately 0.03 g) of concentrated HCl were added, and then, the sample diluted to a total volume of 11–13 ml. All weights were recorded so that the silica analyses could be corrected for dilution. Duplicate analyses were conducted once at the time of sampling (early) and again four hours later (late) using the molybdate blue method (Hach method 8185 using the Hach DR/2400 Portable Spectrophotometer), which measures monomeric silica, but also measures small oligomers (e.g. dimers, trimers, and tetramers). Parallel ICP-MS analyses of total silica (monomers + polymers + suspended colloids) were also carried out. All samples were diluted 0.5–10 ml with plasma grade water. The calibration curve used six points and had a correlation coefficient of 0.9998. All samples were weighed to four places and the dilutions input manually into the ICP software. Each analysis involved an average of four sweeps. The associated standard deviations were compared to assure accuracy. The pH electrode was calibrated (one point) against a pH 4 buffer.

2.3. Bench-scale membrane testing

Bench-scale membrane testing used cooling tower water with initial silica concentrations of approximately 100 mg/l lowered to a pH to 3.6–3.7 with HCl (This is the same cooling tower water used by Altman et al. [12]). Six spiral wound membranes were set up in series such that concentrate flow stream from the first membrane was treated by the second membrane and so on (Fig. 1).

A recirculating system returned the permeate water and concentrate from the final membrane back to the tank. Spiral wound nanofiltration membranes (Osmotik® Part N112–75 XX) were used. The membranes are approximately 1.75 inches diameter × 11.75 inches long and are designed to run at 75 gallons per day at 60 psi. They are rated to have an 85% rejection rate with typical rejections of 89–92%. These membranes were selected as they most closely matched those used in the study described by Altman et al. [12].

3. Results

3.1. Blowdown batch tests

Fig. 2 shows batch-measured pH-dependent silica scale formation. Over time, dissolved silica decreased from its initial value of 220 ppm at all pHs. Note though that rapid decreases in silica—hence rapid scale formation—is confined to the pH 8 run. Lowering the pH of the CINT Cooling Tower Water apparently inhibits the kinetics of silica scale formation for several dozen hours. The results in Fig. 2 are consistent with previous observations of pH-dependent kinetic inhibition of silica polymerization noted in the Introduction.

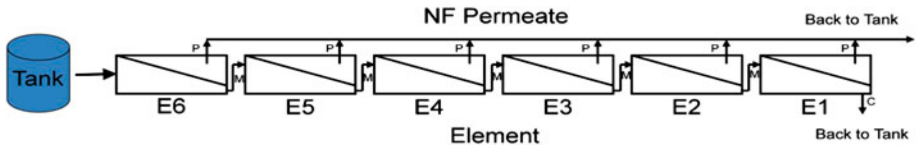

Fig. 1. Schematic of membrane filtration setup.
Note: Order of flow is from element 6 to element 1. E = Element, P = Permeate, M = Makeup, and C = Concentrate.

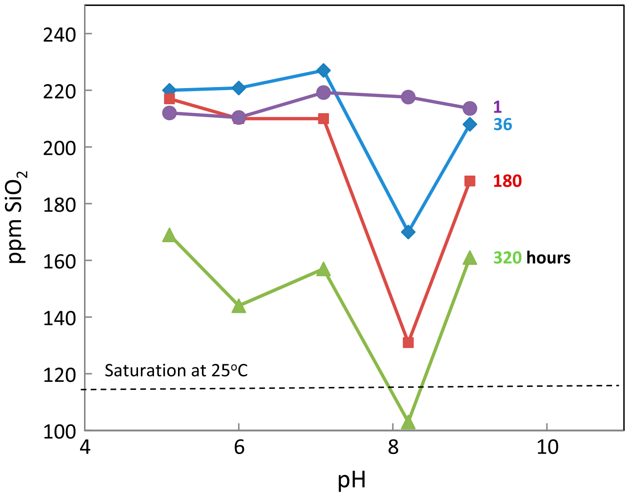

Fig. 2. pH dependence of silica scale formation from evaporatively concentrated CINT water.

3.2. *Ultra-high silica batch results*

Much higher silica levels and lower pH (3.6–3.7) were used to establish the upper limits of the scale inhibition effect. Results are presented in Table 3 and Figs. 3 and 4. First, note that between approximately 4–35% of dissolved silica in Run A ($SiO_{2,t=0} = 962$ ppm) was non-monomeric, and presumably a polymer (The sample at 2.33 h is an outlier at 45 and 46%). There was no trend in the ratio of silica monomers to polymers with time in Run A. Within approximately the first 2 h of Run B ($SiO_{2,t=0} = 1962$ ppm) approximately 11–54% of dissolved silica was non-monomeric. Over time, the non-monomeric fraction increased to as high as 66%.

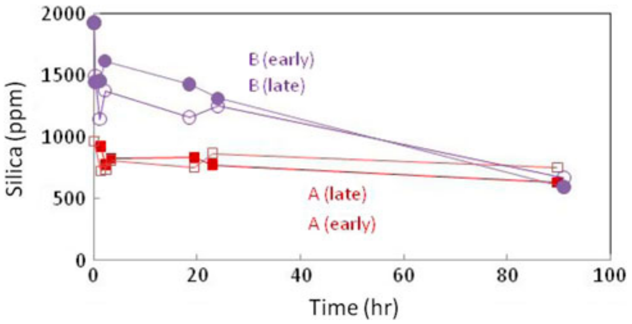

Fig. 3. Silica levels (monomer) over time. Squares—Run A. Circles—Run B. Open symbols are late analyses. Filled symbols are early analyses.

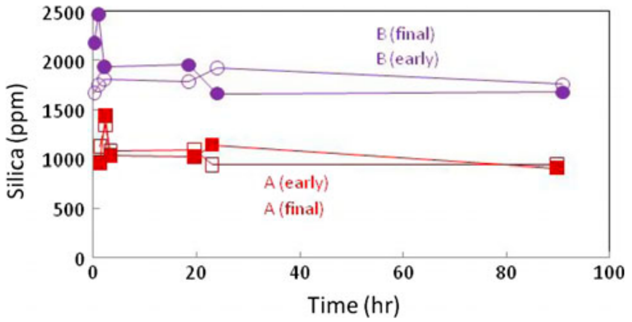

Fig. 4. Total Silica levels over time. Squares—Run A. Circles—Run B. Open symbols are late analyses. Filled symbols are early analyses.

Fig. 3 plots dissolved monomeric silica over time. A systematic decrease in monomeric silica levels was not observed in the first 18 h for both Run A and Run

Table 3
Silica analyses results (ppm)

	Elapsed time (h)	SiO_2 monomer (early)	SiO_2 total (early)	SiO_2 monomer (late)	SiO_2 total (late)
A	0	$SiO_{2,t=0} = 962$ ppm			
	1.33	923	961	726	1,128
	2.33	776	1,436	739	1,345
	3.33	824	1,034	812	1,081
	19.50	837	1,022	749	1,089
	23.00	774	1,141	867	943
	89.75	633	910	754	937
B	0	$SiO_{2,t=0} = 1926$ ppm			
	0.25	1,497	2,178	1,447	1,671
	1.08	1,145	2,467	1,456	1,752
	2.15	1,377	1,936	1,618	1,811
	18.50	1,160	1,955	1,426	1,783
	24.00	1,251	1,662	1,313	1,924
	90.92	670	1,677	597	1,757

B (Table 3, Fig. 4). Clear removal of monomeric silica only occurred after roughly a day and only from the more concentrated solution (Run B). Physical examination of the experiments indicated silica precipitates after 3 days (A). A small amount of solid initially formed in B that did not visibly increase until 3 days had elapsed. Fig. 4 plots total dissolved silica over time. Note that total concentrations remain relatively stable, explaining the increase in the ratio of silica monomers to polymers at late time in Run B.

The possible existence of colloidal silica is consistent with the generally high scatter of the dataset. The scatter cannot be explained by the analytic technique since replicate measurements on a 50 ppm silica standard made using a stock solution were repeatable.

The key observations from the ultra-high silica experiments are as follows:

(1) Concentrations of monomeric silica a little below 1,000 ppm were able to stay in solution over the duration of the experiments of almost four days.

(2) Polymerization of silica dissolved in solution was not observed for the experiment starting with silica concentrations a little below 1,000 ppm (though silica precipitation was observed after three days).

(3) Polymerization of silica was observed at starting concentrations near 3,000 ppm. However, polymerization did not occur until after the first day.

Acid control is effective in allowing high levels of silica (1,000–2,000 ppm) to remain in solution without serious precipitation problems for more than one day and up to three days. This is substantially less than the typical residence time of water in a filtration system. Although some monomeric silica polymerized after three days, it did not form a macroscopic colloidal precipitate or scale. A complicating factor is that synthesizing the test fluids initially produces some silica polymers.

3.3. Bench-scale membrane results

pH and silica results of the low pH bench-scale membrane testing are shown in Fig. 5. The pH of the

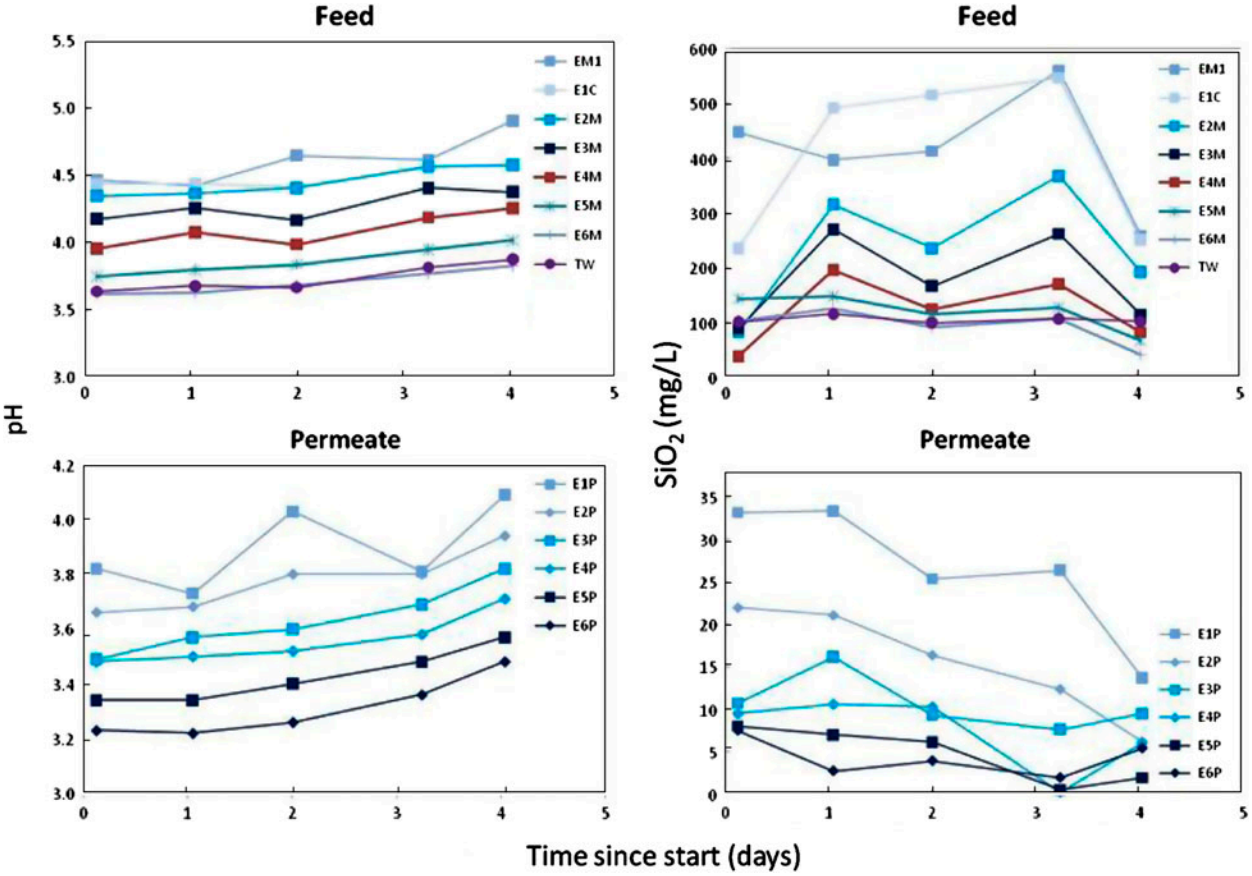

Fig. 5. pH and silica measurements from the test run at low pH. Key: TW = tank water; E = element; M = makeup; C = concentrate (see Fig. 1 for setup and locations of samples).

feed for the last module (EM1) was 4.6–4.9; permeate pHs were from 3.2 to 3.6. Silica in the feed solution and concentrate of the last membrane module was approximately 500 ppm and well above the level needed for equilibrium precipitation of silica scale at 25°C (approximately 120 ppm). Permeate silica levels never exceeded 35 ppm. The high silica levels in the feedwaters to the last modules dropped at 4 days, though not to equilibrium levels, suggesting that after 3 days dissolved silica polymerized to form scale, although the process did not go to completion. One key point of Fig. 5 is that lowering the pH prevents silica scale formation on membranes for at least 72 h. Reversing the flow [13] and/or flushing the membranes with low silica solutions to remove any silica scale nuclei should therefore be an effective means for preventing silica scale formation if it is performed within 72 h windows.

Fig. 6 shows base case results for the same membrane train (though new membrane elements) but using non-acidified, higher pH tank water (base case). With one exception, feedwater pHs were 8.4–8.7. The feedwater silica level was approximately 100 ppm and typically below 300 ppm in the later modules.

Fig. 7 compares the specific conductivity of the low pH run to that of the base case. The base case, high pH, conductivities on the downstream elements were roughly half to one-third that seen in the low pH runs (2,000 vs. 4,000–6,000 µS/cm). A possible explanation for the drop in conductivity in the high pH runs is the formation of calcite which would have decreased both Ca^{2+} and HCO_3^- levels (neither was measured).

Base case, high pH silica levels remained relatively constant over time, similar to what was seen in the low-pH experiment over the first 72 h, albeit with lower starting silica levels. The original expectation was for silica scale formation to cause dissolved silica levels to rapidly reach equilibrium values of approximately 120 ppm. One explanation for the lack of complete equilibration in the base case is the relatively

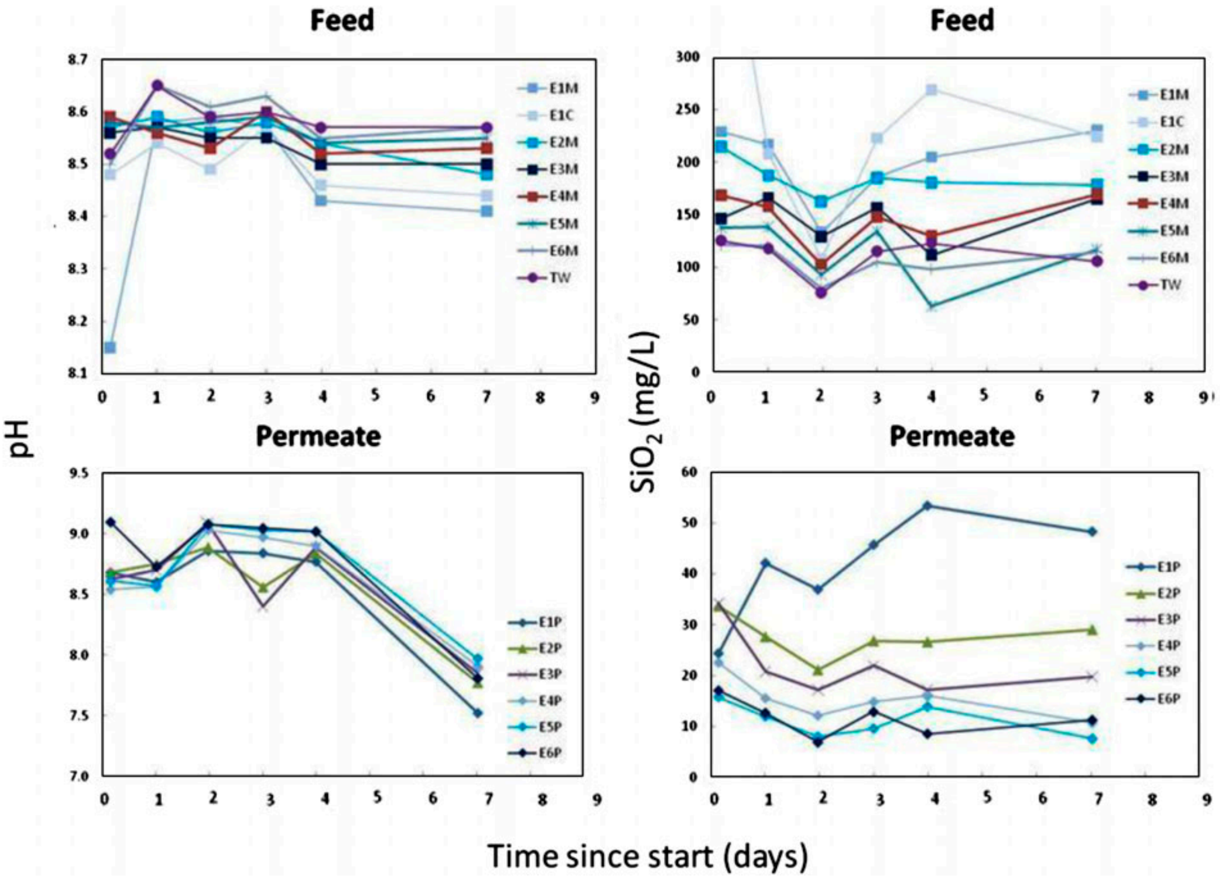

Fig. 6. pH and silica measurements for base case (pH 8.4–8.7). Key: TW = tank water; E = element; M = makeup; C = concentrate (see Fig. 1 for setup and locations of samples).

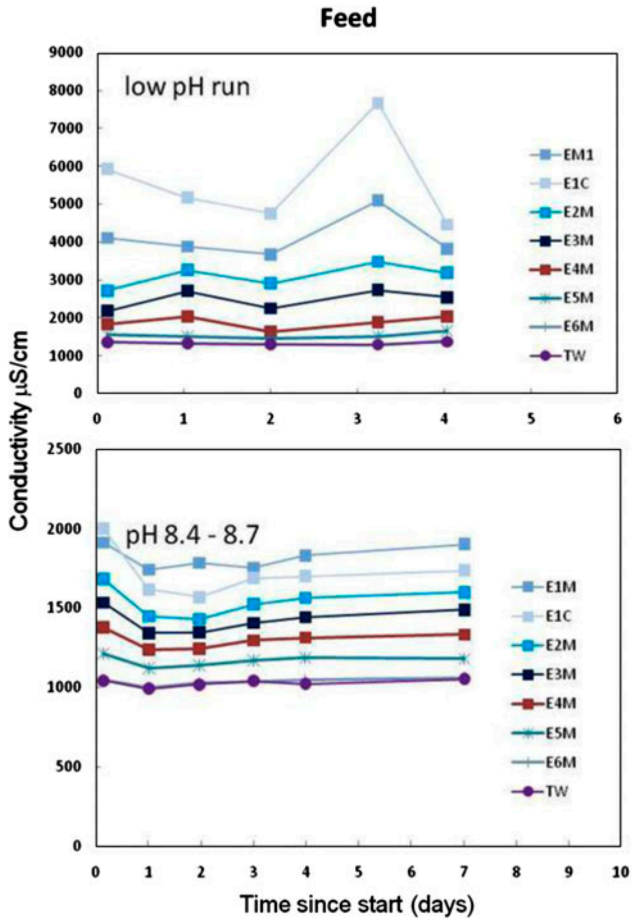

Fig. 7. Specific conductivity of feedwaters for low pH and base case runs. Key: TW = tank water; E = element; M = makeup; C = concentrate (see Fig. 5 for setup and locations of samples).

high pH of the feedwaters (pH 8.4–8.7); at higher and lower pH, silica polymerization and scale formation are slowed. Increasing pH above pH 8 also increases the solubility of silica. Lastly, silica polymerization and formation rates are higher at higher initial silica levels. The incomplete silica scale formation in the base case is therefore thought to be caused by the combination of decreased polymerization rate, lower silica levels, and (possibly) higher silica solubility.

4. Discussion

Lowering the pH of silica-rich solutions can prevent silica scale formation for considerable periods of time which might allow oversaturated silica concentrate to be periodically flushed from membrane trains. The process works at the molecular level by the following steps: (1) Lowered pH slows the formation of silica scale nuclei, and (2) Flow reversal removes nascent scale nuclei immediately before they are able to enter their fast growth phase. Lowered pH will also prevent formation of calcite scales and make less necessary the use of anti-scalants that specifically prevent calcite formation [14]. The next most likely scale to form in low pH solutions over short periods of time is then likely to be calcium sulfate (For this reason, sulfuric acid should not be used to lower the pH). The performance of calcium sulfate anti-scalants at low pH is therefore likely to be a concern.

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