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Reducing the Scaling Potential of Oil and Gas Produced Waters with Integrated Accelerated Precipitation Softening and Microfiltration

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Abstract

Development of unconventional oil and natural gas resources is inexplicitly tied to the generation of saline waste waters commonly referred to as produced water. Produced waters can contain high concentrations of sparingly soluble salts, making mineral scaling an important problem for desalination processes. This investigation evaluated the removal of dissolved and particulate forms of calcium, a common mineral scaling element, using accelerated precipitation softening (APS) combined with microfiltration (MF). Filtration of APS effluent produced filtrate with a 3% lower dissolved calcium concentration and 8xlower turbidity than filtrate from water softened without seeds. An optimum calcium carbonate seed concentration of 7 g/L was identified for the produced water. The particulate seeds are well-rejected by polymeric and ceramic membranes. In a cross-flow configuration the particulates did not significantly foul the ceramic MF membrane until a solids concentration of 15 g/L was reached indicating that the APS-MF system is capable of treating high-solids content water. In addition, it could be operated without settling the water after the APS reaction, while maintaining a reasonable operating filtrate flux and TMP.

Keywords

Produced Waters; Accelerated Precipitation Softening; Microfiltration

Introduction

The burgeoning development of domestic energy resources has been closely tied with the production of large volumes of saline water, termed produced water. As a matter of perspective, in 2007 roughly 21 billion barrels (1 barrel = 42 U.S. gallons) of produced water were generated in the U.S. from oil and natural gas extraction [1]. High concentrations of total dissolved solids (TDS) and sparingly soluble salts are characteristics that make produced water difficult to treat and reuse for beneficial purposes and has led to many stakeholders using deep well injection as their primary disposal strategy. Although desalination is not always required for produced water reuse, it is a necessity for many reuse options like stream flow augmentation, crop irrigation, livestock watering and cooling processes. While many options exist for water desalination, reverse osmosis (RO) is amongst the most popular and has been used in produced water treatment applications [2-4]. A common challenge for the application of RO processes for produced water treatment is mineral scaling, which often limits the achievable feed water recovery ration [5-7]. This challenge is exasperated for produced water applications as a result of their composition. Reducing the risks associated with mineral scaling are important to realizing the potential benefits of produced water reuse.

Mineral scaling results in the formation of relatively dense deposits on surfaces that ultimately affect process performance. For example, scale formation on heat exchangers reduces heat transfer efficiency, while on desalination membranes it results in reduced hydraulic permeability. Common mineral contaminants include calcium, barium, magnesium, iron and strontium that precipitate onto the RO membrane with sulfate and carbonate also present in the produced water [6]. A variety of factors determine the onset of scale formation, such as polyvalent cation concentration, solution pH and temperature. Commonly encountered types of mineral scales in RO systems are calcium carbonate, calcium sulfate and barium sulfate [6]. Development of new, or the refinement of existing, softening processes is further motivated by the emergence of wastewaters, like oil and gas produced waters, that can be highly saline and laden with sparingly soluble salts and minerals [2]. This presents challenges for treating produced waters or reinjecting produced waters as a result if scale formation on pipes or in the formation [8,9]. For membrane processes mineral scaling is a limiting factor that in many cases dictates the recovery ration for a given system [3]. Strategies like acidification and /or anti-scalant (dispersant) addition are widespread and relatively successful scaling mitigation strategies; however, reducing the concentrations of scale forming elements may extend the achievable recovery ration even further. This is particularly relevant for treating produced waters whose complex

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chemistries and comparatively high mineral concentrations make chemical pretreatment challenging.

Precipitation softening is a process by which scale-forming elements may be removed from water by adjusting (increasing) the pH to the minimum solubility point of the targeted cation(s). At this point the cation(s) form an insoluble compound, e.g., calcium carbonate and precipitates from solution. To improve the rate at which precipitation takes place the reaction may be seed with calcium carbonate particles. These particles serve as nucleation sites for precipitation to occur. This process is generally referred to as accelerated precipitation softening (APS) [10]. In the APS process, calcium carbonate seeds are dispersed in the source water before initiating precipitation with pH adjustment [10]. The calcium carbonate seeds enhance the kinetics of the reaction by providing a preferential surface area for nucleation and growth of precipitate crystals [14]. Calcium removal using APS from the reject stream produced by an RO system treating Colorado River water [10]. Calcium removal was 92% and 97% at pH 10.5 and 11.4, respectively [10]. Separately, Calcium and hardness removals of 92% and 58% [13], respectively when treating the concentrate from an RO process (total hardness = 471 mg/L as $CaCO_3$, Calcium = 118 mg/L) [11]. In this study an MF process was used to polish the APS effluent and authors observed improved performance of the downstream membrane distillation process relative to that observed in the absence of the APS process. Both studies claimed that calcite seeding increased precipitation kinetics by reducing the required reaction time from 30mins without seeds to 15 mins with seeds. Calcium carbonate seed size and mixing intensity have been found to affect the performance of APS systems. Seed size of 10 µm was ideal for particle growth [10]. Mixing must allow for seed growth by maintaining them in suspension, while also preventing shearing of the seeds as they grow [11]. It has been proven that other water constituents are removed in addition to sparingly soluble salts and minerals during APS treatment. These substances are removed through a combination of mechanisms including adsorption, co-precipitation, or as unique precipitates during the calcium carbonate precipitation reaction. For example, oxidized iron and manganese, silica, organics and free oils have been shown to be removed via adsorption onto calcium precipitates [10,12-14].

Liquid-solid separation is one outstanding area in APS systems that may be further improved. Gravity driven clarification systems are the most widely used processes for separating the calcium carbonate seeds and other particulates from the softened water; however, while effective these processes generally have large footprints and subject to effluent water quality upsets with changes in hydraulic loading rates and particulate characteristics, like size. Membrane filtration processes possess a number of characteristics that make them advantageous over clarification and media filtration processes, thereby making them an attractive option for integrated APS systems. Microfiltration (MF) using ceramic membranes have been shown to be an effective treatment option for APS processes. Calcium carbonate cake that formed on the membrane surface after filtering APS slurry, removed additional calcium compared to traditional APS treatment [15,16]. The authors claimed that the filter cake worked as a polishing step for calcium and particulate removal. This enhanced calcium and particulate removal through filtration after APS could lead to superior feed water for RO systems that may allow their application to produced water streams. Outstanding questions for the application of MF in APS systems center on how membrane fouling develops and affects the longer term operation of the process.

The objectives of this study were to evaluate the effectiveness of integrated APS-MF processes for treating produced water representative of that found in Wyoming, USA. Process effectiveness was evaluated in terms of calcium and turbidity removal in the filtrate flows. Membrane fouling and its subsequent effects on process performance, was also evaluated to establish the viability of the integrated process for full-scale applications. These evaluations were done using multiple membrane operation configurations, dead-end and crossflow, using polymeric and ceramic membranes. Performance results were compared and contrasted with conventional precipitation softening with and without the use of membrane filtration.

Experimental

Chemicals and reagents

All test solutions were made using ultrapure water having a resistivity of 18 mΩ-cm and an unbuffered pH of 7.5. All experiments were done using an electrolyte solution whose composition was made to be representative of concentrate coming from an RO system treating representative produced water in Wyoming, USA [22]. The solution had a TDS concentration of 15,600 mg/L. It was made by dissolving the following reagent grade salts into ultrapure water: 2.93 g/L calcium chloride, 5.05 g/L sodium sulfate, 1.72 g/L sodium bicarbonate and 5.90 g/L sodium chloride. All salts were acquired from Fisher Scientific (USA). The solution was mixed for a minimum of 1 hr to ensure complete dissolution of the salts. The pH of the mixture was 7.8 ± 0.25. Solution pH was adjusted in the various softening experiments using sodium hydroxide (10N, Fisher Scientific, USA) and sulfuric acid (1N, VWR Scientific, USA).

Membranes

This study included both polymeric and ceramic MF membranes to evaluate membrane fouling and suspended solids, namely calcium carbonate, as well as dissolved calcium removal. The polymeric MF membrane used was made of polyethersulfone (PES, Sterlitech Corporation, USA) and had a nominal pore size of 0.45 µm. The pure water specific flux for the PES membrane was 647 L/m^{2}hr bar at 20°C. The ceramic MF membrane used was constructed of titanium oxide (TiO_2, Sterlitech Corporation, USA) and had a nominal pore size of 0.45 µm. The tubular ceramic membranes were 250 mm long and were comprised of 7 tubular channels that were 2 mm in diameter. The pure water specific flux for the ceramic MF membrane was 37 L/m^{2}hr bar at 20°C.

Water quality analyses

Turbidity was measured using a Model HF Scientific Micro 100 turbidimeter (Fisher Scientific, USA). A minimum of three samples were analyzed to calculate an average turbidity value for a given sample. Total suspended solids (TSS) and total dissolved solids (TDS) were measured using ASTM method D5907-13. All tests were done in at least triplicate to establish repeatability. Statistical significance was assessed using an unpaired t-test for the comparison of two means. A criteria of $p < 0.05$ (95% confidence level) was used for determining statistical significance.

Conventional and accelerated precipitation softening tests

Precipitation softening experiments were carried out using a digital jar tester (Model 7790-711, Phipps & Bird, USA) and rectangular 2-L rectangular reactors. Conventional softening tests, those done without seeding, were done by adding sodium hydroxide to the test solution to reach a desired pH (7.9 to 11.6) to identify the optimal pH for calcium removal. The 1-L test solution was constantly mixed at 45 rpm, corresponding to a Camp-Stein mixing intensity or G value of 36 sec^{-1}, for 60 mins. At the completion of the mixing stage, agitation was ceased and the sample underwent clarification for 30 mins. All tests were done at ambient temperature (= 21°C). From these initial experiments calcium removal increased with pH, with maximum removal (≥97%) occurring at pH ≥ 10.5. All subsequent tests were therefore done at pH 10.5.

APS tests were done using calcium carbonate powder (ACROS Organics, USA). The calcium carbonate seeds and a mean measured diameter of 7.8 µm. The reported specific surface area for the calcium carbonate seeds of this size was 0.8 m^2/g [21]. Seeds were added to the test solution prior to raising the solution pH. Grab samples were taken from the reactor during mixing and after the clarification stage using a 10 mL syringe. The sample was filtered using a PVDF syringe filter (Millipore Corporation, USA) having a nominal pore size of 0.45

μm to remove the seeds prior to measuring the dissolved calcium concentration. The filtrate was analyzed to determine the dissolved calcium concentration. Calcium concentration was determined using an ion chromatograph (Model Dionex DX-120, ThermoFisher Scientific, USA), equipped with a cation separation column (Model CS12A Ion Pac Column, Thermo Fisher Scientific, USA), according to the ASTM method D6919-09.

Characterization of calcium carbonate seed growth

The evolution of calcium carbonate seed size under given reaction conditions was characterized using a granulometer (Malvern Mastersizer 3000, Malvern Instruments, UK). The Mastersizer 3000 is capable of measuring particles in a size range of 10 nm to 3.5 mm. Water samples were prepared having the same ionic composition as that used in the APS experiments. Particle size distribution was then measured as a function of time for two conditions. The first condition used a seed concentration of 7 g/L, while the second did not use any seeds. All measurements were done at a solution pH of 10.5 to simulate the softening conditions used in the APS experiments. All tests were done at 20°C and in triplicate to ensure the reproducibility of the results.

Calcium removal by microfiltration (MF) membranes coupled with precipitation softening

Removal of particulate and dissolved forms of calcium during MF of the decant from the precipitation softening experiments was assessed using a dead-end filtration apparatus. The flat-sheet membranes used in the dead end experiments had an active area of 14.6 cm^2. The MF tests were done in a variable flux, constant feed pressure (200kPa) configuration. Calcium removal and membrane fouling were assessed using three types of feed solutions: untreated or raw electrolyte, softened water without the use of calcium carbonate seeds and softened water using APS (Figure 1). The softened water in the absence of the seeds was made by adjusting the pH of the test solution to 10.5 using sodium hydroxide,while mixing in the softening reactor at 45 RPM (G = 38 sec^{-1}) for 10 mins. Subsequently, the entire solutionwas poured into the dead end filtration cell (Sterlitech Corporation, USA) and the experiment was begun. In this sequence, the membrane filtered out calcium carbonate and other insoluble mineral scales. For samples referred to as APS, 7 g/L of calcium carbonate seeds were added to the feed solution, in addition to adjusting their pH to 10.5. The seeded APS water sample with pH 10.5 was then stirred continuously at 45 RPM for 10 mins and poured into the filtration cell. Water flux was measured by collecting and measuring the mass of the permeate using a computer interfaced balance (Model XS6035, Mettler Toledo, USA). Grab samples were taken, using a 10 mL syringe, from the feed water and the filtrate and their turbidity and calcium concentration measured. All MF tests were done using a stirring speed of 150 RPM and at 21 ± 1°C in the dead end filtration cell.

Membrane fouling was assessed by measuring flux decline over time and through autopsy of the membranes after each test using scanning electron microscope (JEOL 5800 LV) with an Oxford Inca energy dispersive X-ray spectroscopy (SEM-EDS) analysis of the membrane surfaces. Cake hydraulic resistance and thickness values were calculated using Equation (1) & Equation (2), respectively.

$$\grave{U}R = \frac{180(1-e_c)^2}{d_p^2 e_c^3} \quad (1)$$

$$R_c = \grave{U}R_c d_c \quad (2)$$

Where $\grave{U}R_c$ was the specific resistance of the cake, e_c was the porosity of the cake structure (= 0.75), d_p was the average diameter of the particles that made up the cake structure (= 7.8 μm), R_c was the resistance of the cake and d_c was the average thickness of the cake structure. The calcium carbonate seeds were assumed to have a spherical geometry. The cake thickness, d_c was calculated according to Equation (3).

$$d_c = \frac{C_p V_f}{r_p A(1-e_c)} \quad (3)$$

Where C_p was the concentration of particles (seeds) in the feed solution (= 210 mg/L), V_f was the volume of water filtered or permeated, ρ_p was the particle density (= 480 kg/m^3) and A was the active membrane area (= 0.00146 m^2).

Integrated APS-MF performance analysis

The process flow diagram for the integrated APS-MF test unit is given in Figure 2. The APS reaction took place in a 5 L jacketed glass reactor (Prism Glass Research, USA). The water temperature was maintained at 20°C using a heat exchanger (Isotemp 3028P, Fisher Scientific, USA) that recirculated water through the jacketed reactor. A constant mixing speed of 45 RPM was maintained within the softening reactor. A calcium carbonate seed concentration of 7 g/L was used for all tests. After adding the seeds, the APS reaction was initiated by slow addition of sodium hydroxide until pH 10.5 was achieved. The reaction proceeded until a stable dissolved calcium concentration was achieved in the softening reactor, which remained continuously mixed. The slurry was then recirculated through the membrane module (Valisette Ceramic Test Cell, Sterlitech Corporation, USA), which contained the tubular ceramic MF membrane. The MF membrane was operated in an inside-out flow configuration, where the feed solution was introduced to the inside of the channels. Trans membrane pressure (TMP) was controlled using a diaphragm liquid backpressure valve (Model EB2NL2, Equilibar, USA). The APS-MF system was operated in the following modes: 1) Filtrate withdraw, which lead to a steady increase in the solids concentration in the

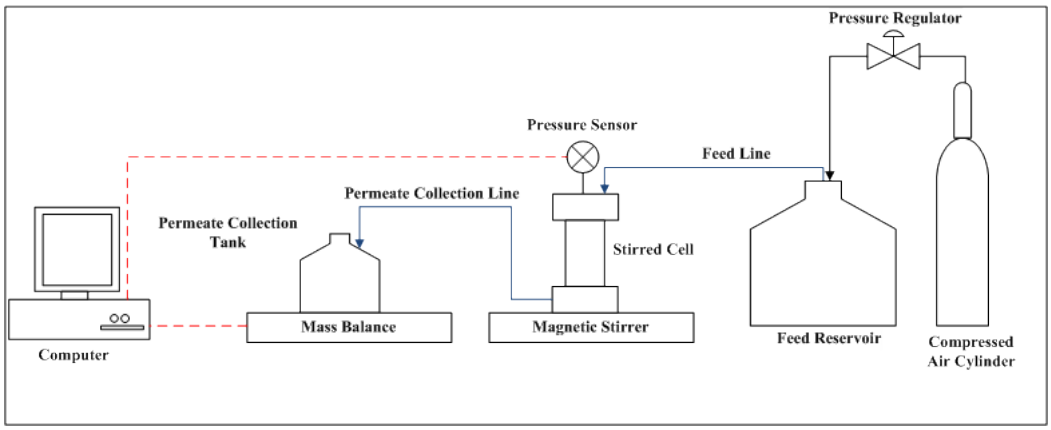

Figure 1: Process flow diagram for the dead-end filtration test apparatus used in the calcium removal and membrane fouling experiments

feed reservoir and 2) Filtrate return (closed loop) where the filtrate was returned to the feed reservoir, thus maintaining a relatively constant solids concentration in the feed. Throughout each test feed and filtrate samples were collected and analyzed for calcium concentration, turbidity, total solids and TDS. Membrane fouling was assessed in terms of changing TMP over time. The filtrate flux for all tests was maintained at a constant value of 200 LMH and a cross flow velocity of 0.45 m/sec.

Results and Discussion

Accelerated precipitation softening reaction kinetics and removal efficiency

The introduction of calcium carbonate seeds into the softening reactor resulted in increased precipitation kinetics (Figure 3) and greater calcium removal. The increase in precipitation kinetics was most notable for the seeded conditions at t ≤ 3 mins. After this point,

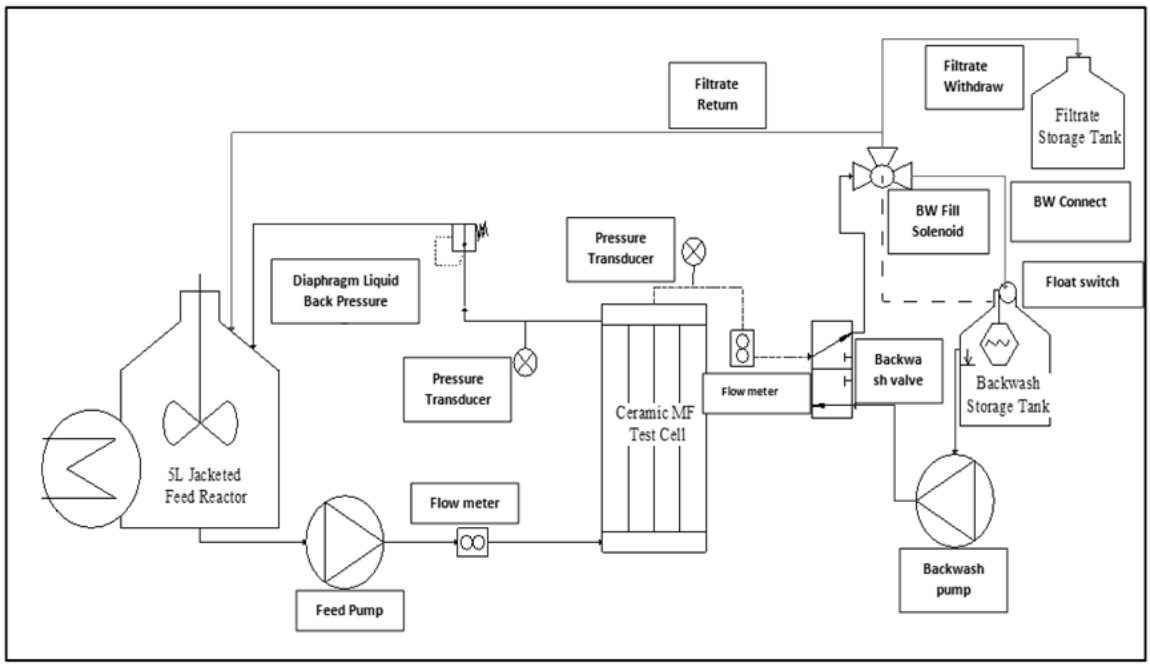

Figure 2: Process flow diagram of the APS-MF integrated test system

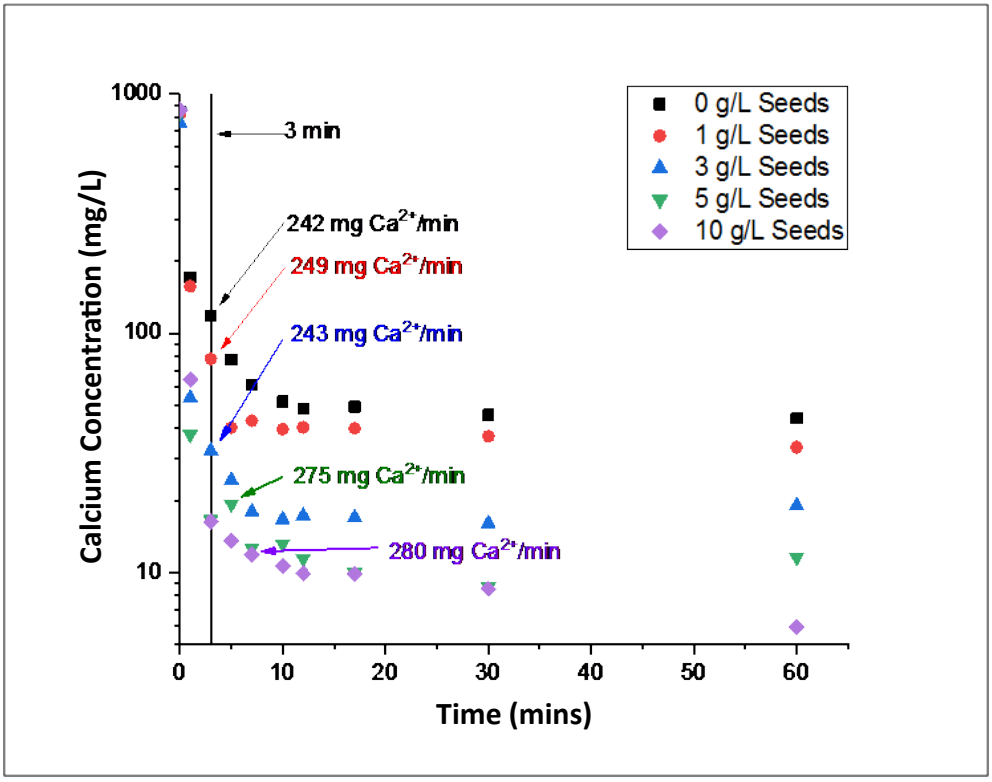

Figure 3: Calcium removal as a function of calcium carbonate seed concentration and time (initial calcium concentration = 800 mg/L, pH = 10.5, T = 25°C). The test solution was the synthetic produced water

there was a clear slowing in the kinetics for all seed concentrations. The rate of calcium precipitation did not change considerably from that in the absence of seeds until the seed concentration was ≥ 3 g/L. At this point the rate of calcium removal was 275 mg Ca^{2+}/min. This rate was approximately 15% greater than that measured in the absence of seeds (= 242 mg Ca^{2+}/min). Increasing the seed concentration to 10 g/L resulted in a minor improvement, to 280 mg Ca^{2+}/min, in the precipitation kinetics. Final calcium removal values reached 96% at a seed concentration of 5 g/L and 98% at 10 g/L. Previous works on precipitation softening have demonstrated that the practical minimum solubility limit for calcium at pH 10.5 is 10 mg/L as Ca^{2+} [20]. Differences between theoretical and practical solubility limits for calcium can occur as a result of variations in kinetics, competing ion effects and impacts of solution ionic strength on water activity and calcium solubility [19]. For this reason, higher or lower calcium removals may be achieved in complex mixtures like produced waters. Because the calcium concentrations at pH 10.5 and 11.6 were not statistically different within a 95% confidence level, all subsequent APS experiments were done at pH 10.5. In all cases, the reaction time required before the system reached a quasi-steady-state condition relative to calcium removal was 10 mins. Based on these results a seed concentration of 7 g/L and a reaction time of 10 mins were selected for subsequent testing.

Calcium removal and fouling of MF membranes

Calcium removal by the PES MF membrane varied depending on the type of pretreatment applied to the produced water (Figure 4a). In the absence of precipitation (no treatment), no calcium was removed by the PES MF membrane, as would be expected for a pure filtration process. In contrast, when softening of any type was used upstream of the PES MF membrane calcium removal was ≥ 6%. Removal was slightly improved over the other conditions when APS was done upstream of the PES MF membrane (Figure 4a). The 3% increase in calcium removal, relative to that achieved in the absence of seeding, was attributed to the fact that the seeds are larger than the membrane pore size (= 0.45 µm) and thus, were more effectively retained by the membrane. From Figure 4b the calcium carbonate seeds grew in size within 5 mins of the initiation of the reaction. The primary peak size shifted from 2 µm to 51 µm, with no appreciable growth afterwards. This agrees with the calcium removal kinetics shown in Figure 3 where the majority of the calcium was removed within 3 mins. Based on this, the calcium was removed by the MF membrane through filtration of the calcium carbonate seeds.

Amongst all the treatment scenarios, the APS and MF treatment produced filtrate having the lowest turbidity Figure 4a. When APS was followed by conventional clarification the effluent turbidity was 26×that for the APS and PES MF treatment train. The presence and growth of a cake structure on the PES MF membrane was evidenced by the observed flux decline when APS was used (Figure 5). APS resulted in rapid flux decline with continued filtration, which contrasts to those conditions when no softening was done or when conventional softening was done. No observed flux loss was observed for the non-APS pretreatments (Figure 5). This suggests that any solids retained by the membrane did not appreciably affect the composite hydraulic resistance of the membrane. Further, calcium removal in these processes occurred prior to membrane filtration, if applied. Clearly calcium was removed during conventional softening; however, the type(s) of membrane fouling that occurred was distinct from that which occurred with the APS treatment. From the turbidity results (Figure 4b) more particulates were present in the PES MF filtrate when conventional softening was used relative to that for the APS pretreatment. This implies that more particulates were in fact retained by the MF membrane following APS. In fact, the mass of calcium carbonate retained on the PES MF membrane (= 75.3 g/m^2) was an order of magnitude greater than that measured in the absence of softening (=1.0 g/m^2), or following conventional softening (= 3.4 g/m^2). The greater mass of solids retained following APS treatment was reflected in an exponential increase in cake resistance coefficient as filtration progressed, going from 3.60E10^{10} m^{-1} for the virgin PES membrane to 2.66E10^{10} m^{-1} after filtration of 500 mL of solution. Based on the particle size distribution in the feed (Figure 4a) and the resulting particle size to pore diameter ration, surface caking and complete pore blocking were the primary fouling mechanisms. These

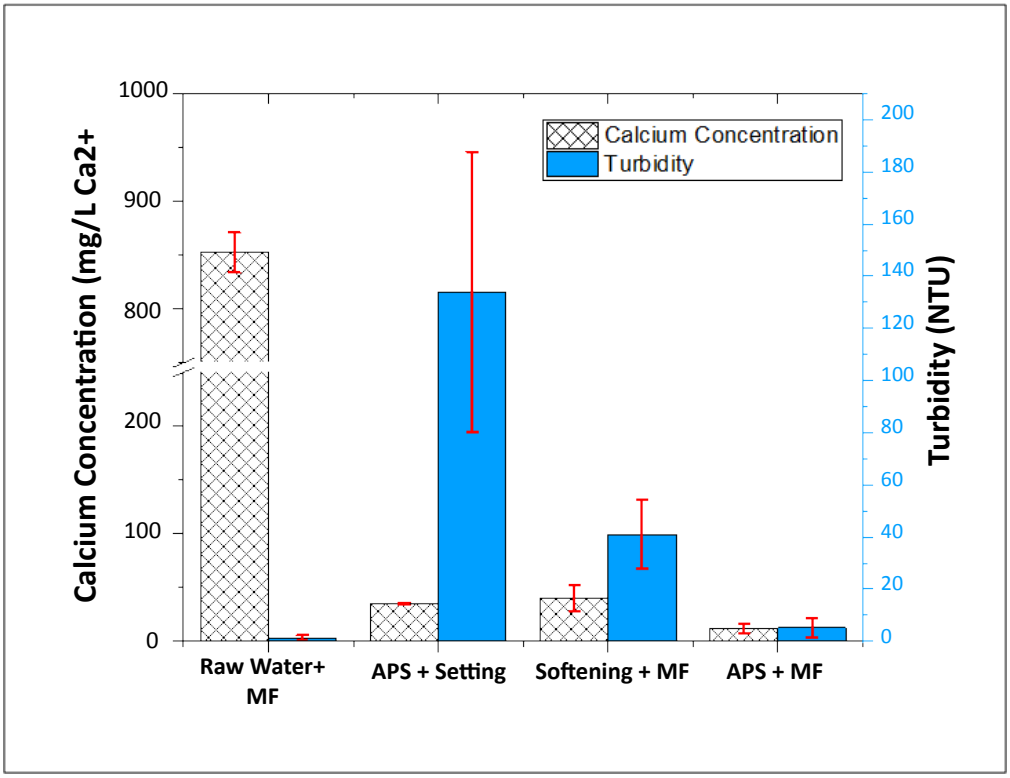

Figure 4a: Calcium concentration and turbidity of process flows subjected to varying treatment types (n = 3, initial calcium concentration = 800 mg/L, T = 25°C)

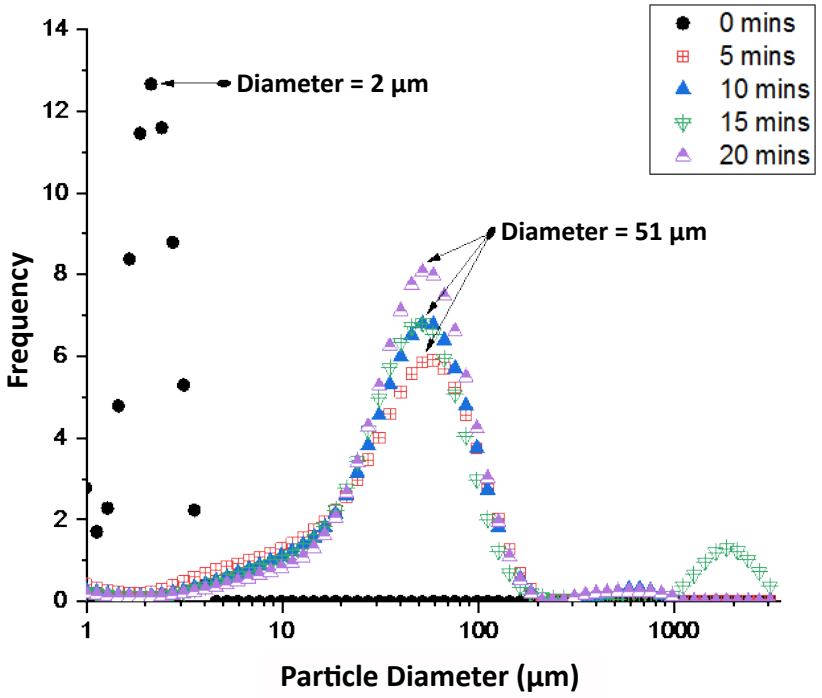

Figure 4b: Particle size distributions for the APS process at a seed concentration of 7 g/L at pH 10.5. The test solution was the synthetic produced water

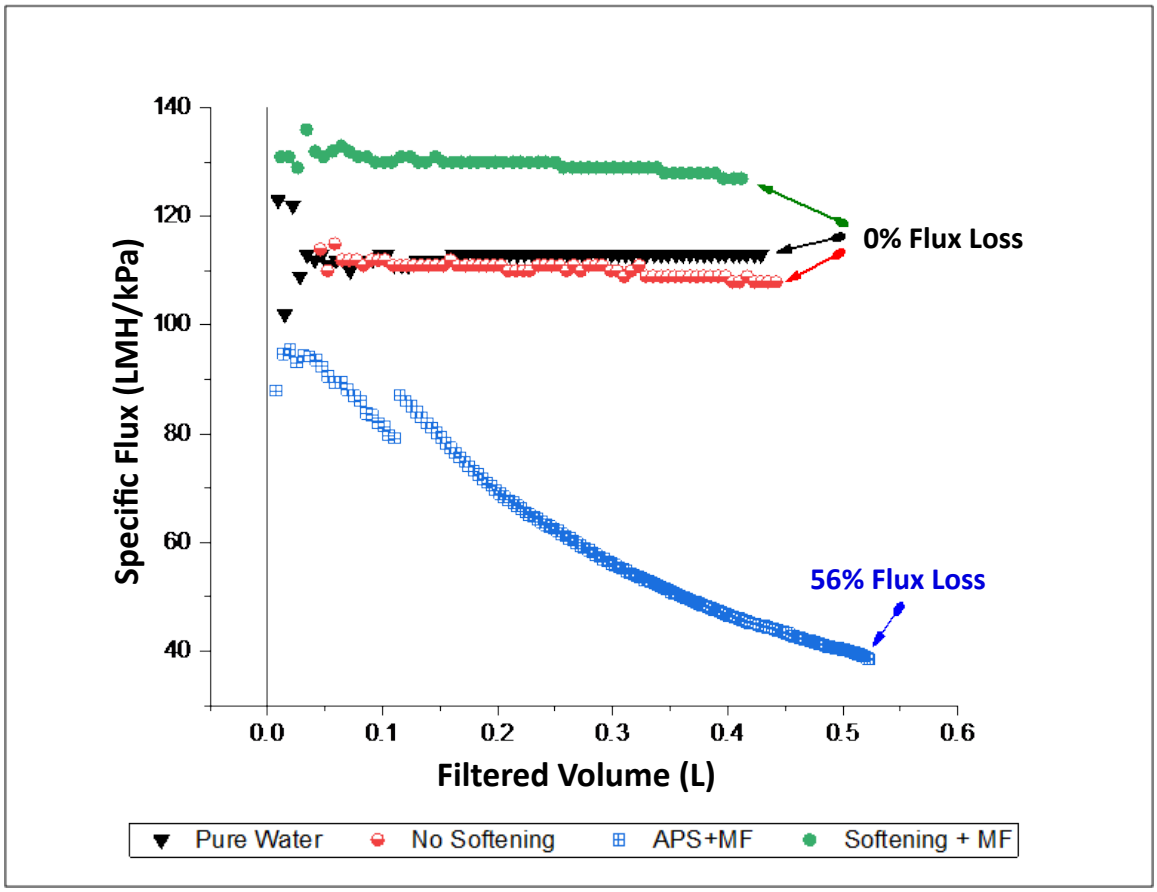

Figure 5: Specific water flux as a function of filtrate volume for the PES MF membrane where the feed flow was subjected to different types of pretreatment (n = 3, P_{NET} = 200 kPa, T = 25°C)

results are supported by SEM/EDS analysis of the PES MF membranes after each of the different treatment scenarios. From these analyses it was found that calcium carbonate cake formation was more prevalent after APS treatment, relative to the other conditions (Figures 6a-6c).

Integrated APS-MF system performance evaluation

Representative pictures of the feed water to the ceramic MF membrane and the MF filtrate are given in Figure 7a. The high turbidity of the feed water (>800 NTU) was due to the calcium carbonate seeds and the formation of precipitates during the APS reaction. No clarification was allowed after APS, as the APS reactor was continuously mixed, resulting in the highly turbid feed to the MF. From Figure 7b, the untreated water (prior to the initiation of the APS reaction) had a TSS concentration of zero. The TS were almost exclusively composed of TDS. Upon the initiation of the APS reaction the TSS concentration increased (= 9.0 ± 0.22 g/L) as a result of precipitate formation and seed addition. There was a 1.79 ± 1.0 g/L decrease in TDS for the APS effluent and MF filtrate due to removal of dissolved calcium and other co-precipitates like sulfate. Of note the turbidity of the MF filtrate was ≤ 0.18 NTU depending on the mode of operation and the sampling time during the test, representing an average turbidity removal of approximately 99.9%.

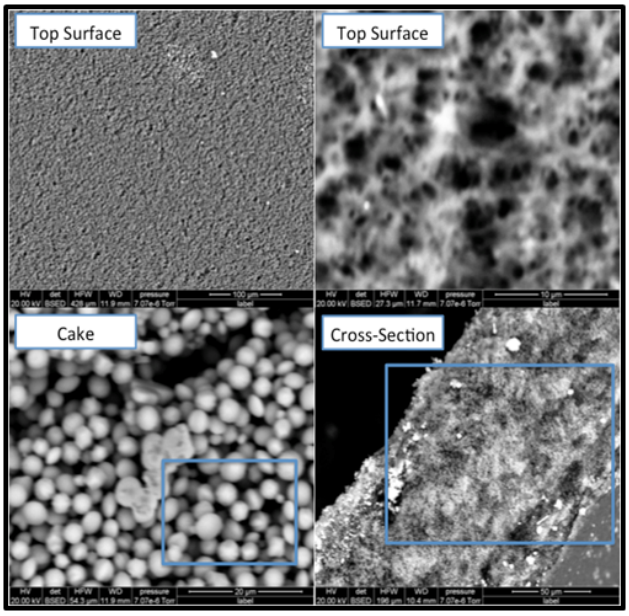

Figure 6a: Representative FESEM images of the PES-MF membrane surface with No softening

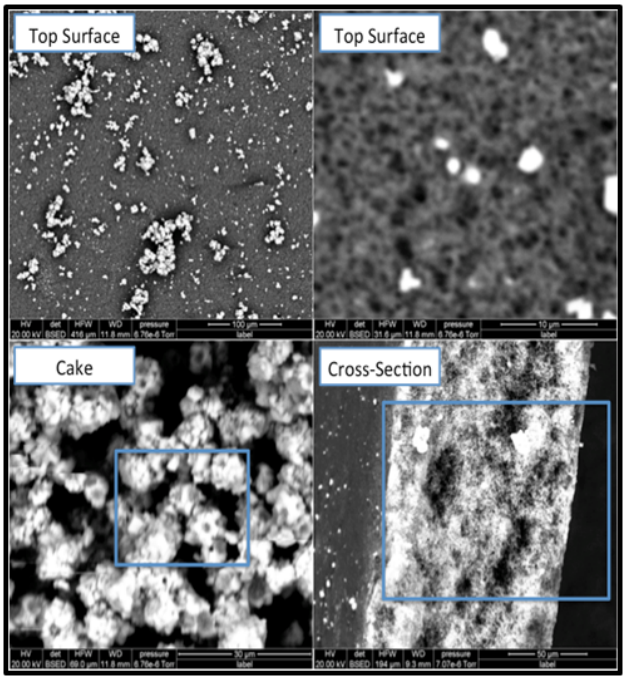

Figure 6b: Representative FESEM images of the PES-MF membrane surface with Conventional softening

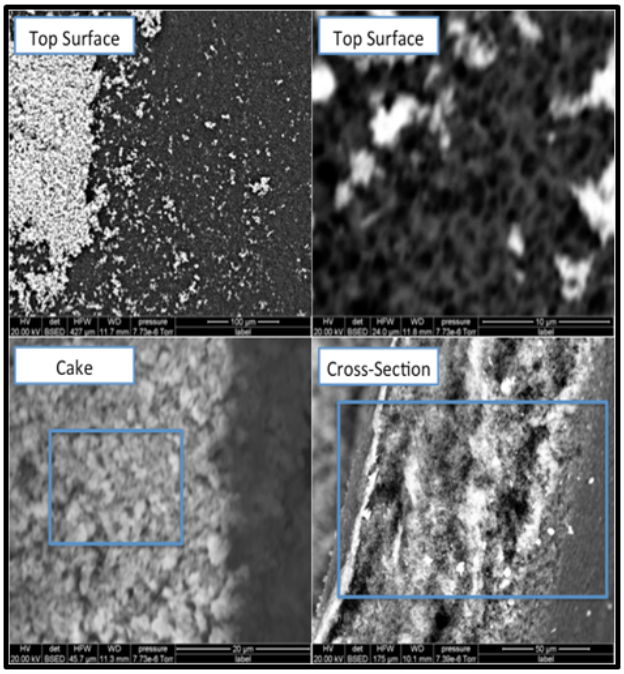

Figure 6c: Representative FESEM images of the PES-MF membrane surface with APS softening

Figure 7a: Representative picture of the ceramic MF feed (Turbidity > 800 NTU) following APS treatment and the ceramic MF filtrate (turbidity = 0.15 NTU)

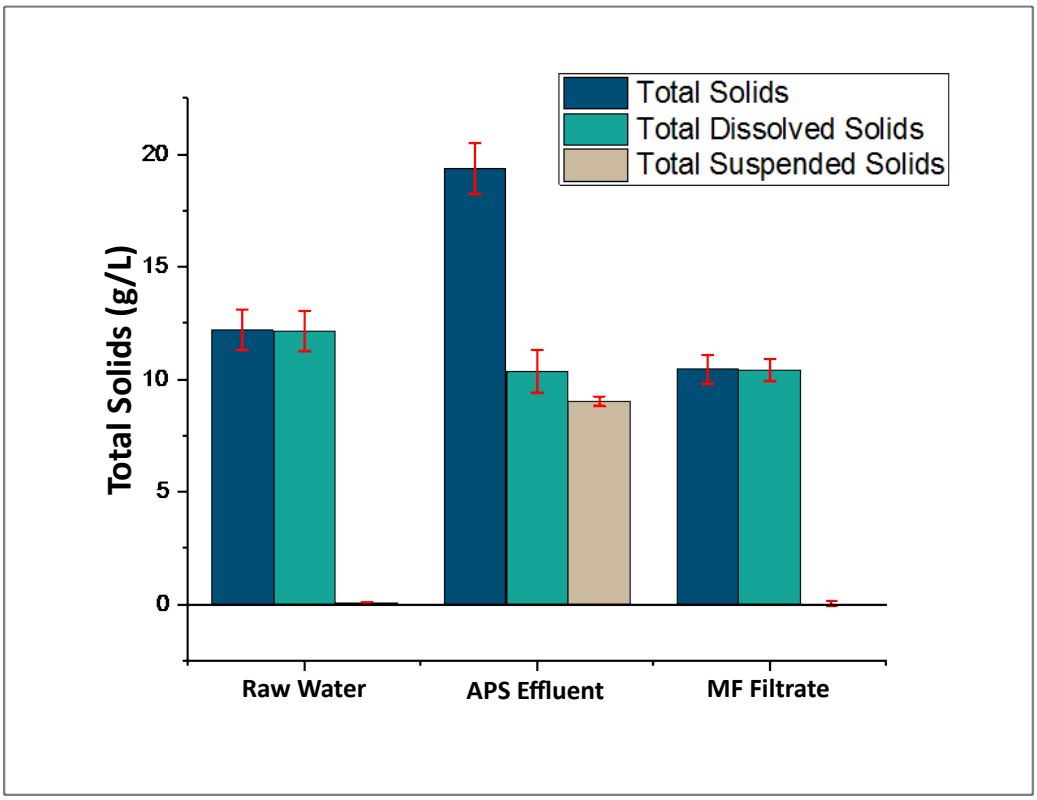

Figure 7b: Solids analysis of the untreated (raw), APS effluent and ceramic MF filtrate flows used in the integrated APS-MF test system (n = 3, T = 20° C). Samples for the MF filtrate were analyzed at the beginning of the filtration experiment

Compared to the dead-end filtration tests results for APS followed by MF, where 99% reduction in dissolved calcium was achieved (Figure 4a), the integrated APS-MF process achieved calcium removals between 96 to 98%. Here the filtrate calcium concentrations ranged between 16 to 35 mg/L as Ca^{2+}. Turbidity was reduced from 4.8 NTU to ≤ 0.18 NTU for both operation configurations (filtrate return and filtrate withdraw). Filtrate turbidity remained constant throughout the durations of all tests. The slightly lower calcium removal between the dead-end and cross flow tests may be attributed to the material differences in the PES and TiO_2 ceramic membranes, as well as to the relative lack of surface cake formation that was indirectly observed in the cross-flow system. The presence of calcium carbonate cake structures on membrane surfaces has been observed to result in greater calcium removal [15-17] due to improved precipitation conditions/kinetics within the cake structure. No significant decrease in calcium concentration, or turbidity, was observed overtime in the filtrate for either mode of operation in the cross flow tests. If a filter cake was forming or increasing overtime, filtration efficiency may improve and cause an improvement in filtrate quality (i.e., decreased calcium and turbidity) as has been observed in previous studies [15,16]. In addition, there was no appreciable change in membrane permeability over time. These observations were taken as indicators of a lack of appreciable cake formation on the membrane surface as was noted in the non-APS dead-end tests.

Marginal differences were observed between the two operational schemes in terms of the amount of calcium that was removed. Consistently, calcium removal was greater for the filtrate return mode (98% removal) when compared to the filtrate withdraw mode (96% removal). This is best attributed to the fact that the feed water chemistry and composition in the filtrate withdraw mode changed temporally (increased solids concentration) as a result of clean water being removed from this system. This had the effect of increasing the concentration of calcium carbonate and other particulate solids, in the feed water. It was postulated that this increase in particulate solids also resulted in an increase in the concentration of calcium, as small particulates, in the filtrate though no significant differences were observed in the turbidity values for the two configurations.

Membrane fouling in the integrated APS-MF process

Membrane fouling, measured in terms of TMP and filtrate quality, was assessed for both crossflow operational schemes. Because filtrate was not returned in the filtrate withdraw mode, the feed water quality changed over time. The TSS concentration increased time from 7.8 ± 1.5 g/L in the feed reservoir at the beginning of the tests to 59.1 ± 23.6 g/L at the end of the filtrate return tests. The increase in TSS concentration over time resulted in a corresponding increase in the solids loading rate on the MF membrane, going from roughly 1,560 to 11,820 g/m^{2}hr. Conversely, in the filtrate return mode the TSS concentration in the feed reservoir and solids loading onto the MF membrane remained relatively constant through each test at 8.0 ± 1.1 g/L and 1,600 g/m^{2}hr, respectively.

Representative water flux and TMP profiles for the cross flow MF process are reported in Figure 8 as a function of filtrate volume for both operational schemes. There was no change in TMP as filtration progressed for the filtrate mode of operation (constant feed water quality). This indicated that there was no appreciable accumulation of a cake structure on the membrane surface or pore blocking, which the two were fouling mechanisms expected for inorganic particle filtration. While a cake structure may have formed on the membrane surface, its hydraulic resistance was lower than the intrinsic hydraulic resistance of the virgin membrane. Therefore, the membrane may be said to have not fouled during filtration of ~200 L of the APS effluent (run time = 40 hrs). Notably no hydraulic backwashing, or pulsing, was used during this time and thus the only mechanism by which rejected solids were removed from the membrane surface was through the forces resulting from the cross flow shear. This result contrasts with what was observed in the dead end filtration experiments due to the cross flow shear that was present in the ceramic membrane tests. The shear forces continuously remove deposits from the membrane surface, where the interfacial conditions likely did not favor particle adhesion. This was due to the fact that both the membrane and calcium carbonate particles were hydrophilic and negatively charged at the pH condition used in the test. Another consideration was that the

process was operated below the critical flux [18] for the process. The critical flux is defined by a force balance between permeate/filtrate drag forces and the tangential (shear) forces acting on a particle as it approaches the membrane surface. Regardless of its origin, these results demonstrated a resistance to performance degradation by the ceramic membranes in treating the APS slurry.

In filtrate withdraw mode (Figure 8b) a rapid increase in TMP was observed after approximately 1.7 L of water had been filtered (run

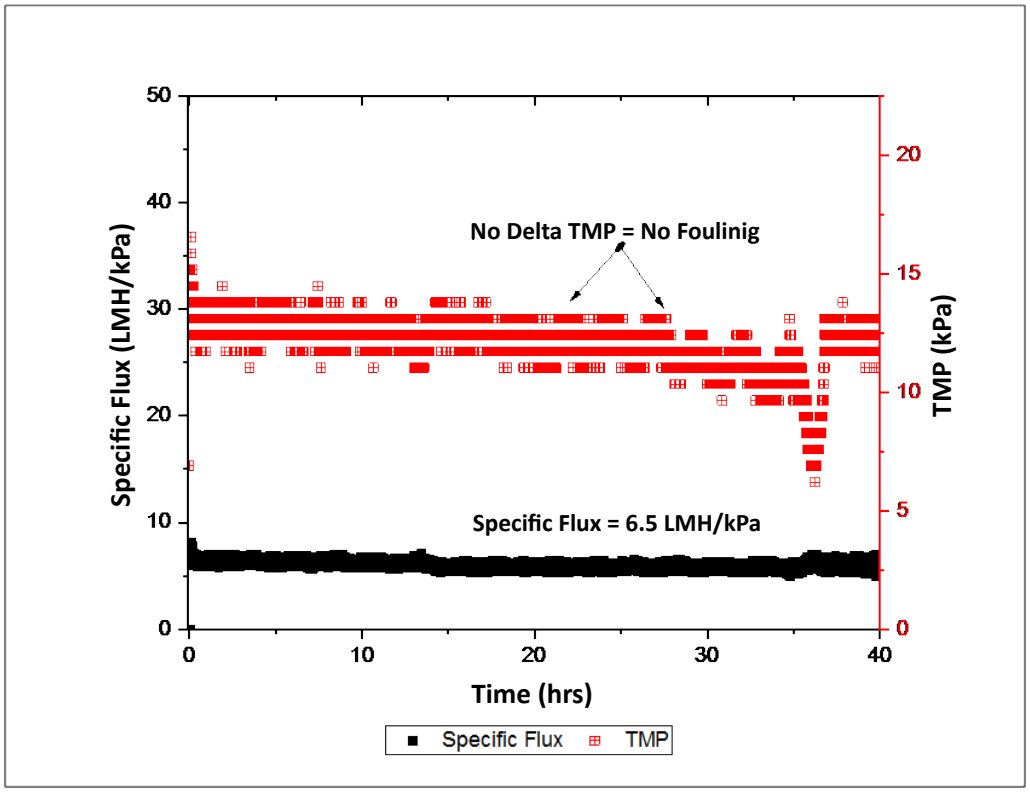

Figure 8a: Specific water flux and TMP as a function of volume of water filtered for the filtrate return. No backwashing or back pulsing was used in either mode of operation

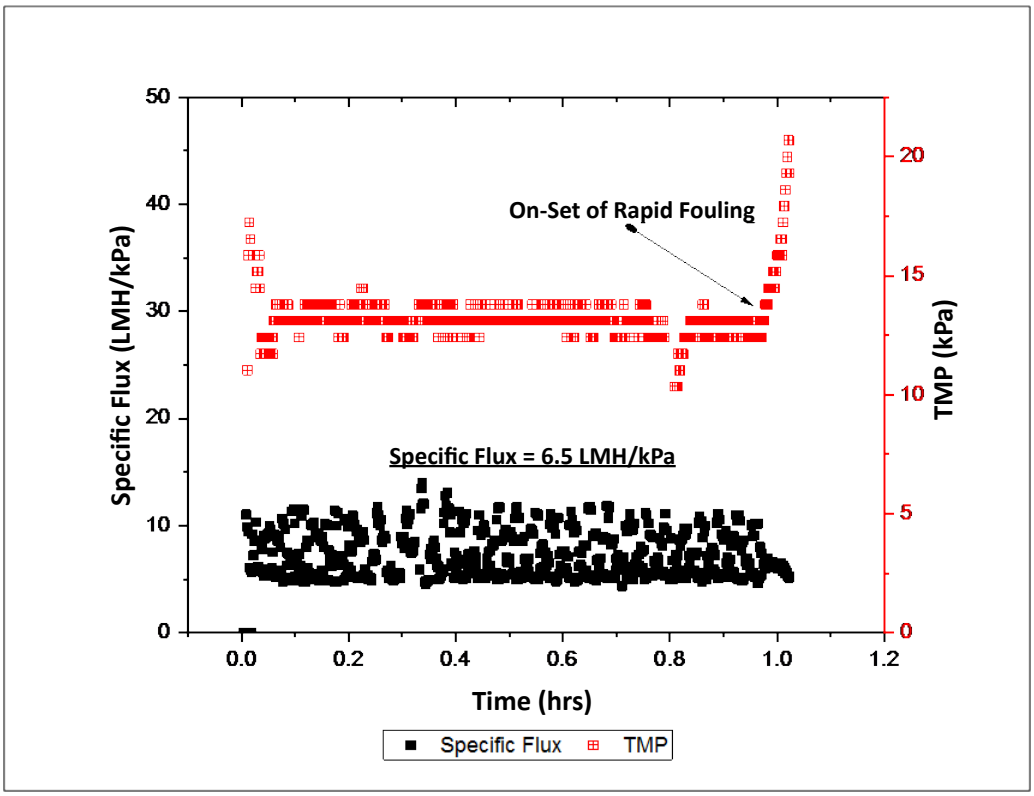

Figure 8b: Specific water flux and TMP as a function of volume of water filtered for the filtrate withdraw modes of operation. No backwashing or back pulsing was used in this operation

time = 1 hr). This point corresponded to a feed TSS concentration of around 15 g/L. Note that the starting TSS concentration in the feed was 8 ± 1.5 mg/L. Like the process when operated in filtrate return mode, the process demonstrated a resistance to fouling until a relatively high solids loading was reached. Several possibilities exist that may explain the rapid loss of permeability that occurred once the TSS concentration reached 15 g/L. These include the onset of particle aggregation and an associated change in the aforementioned force balance due and changes in solution viscosity due to the high solids concentration. Of note, membrane permeability was fully restored when the feed water was changed to pure water having the same pH. This implied that particle caking onto the membrane process was determined by physical and not chemical, processes. Therefore, increasing the cross flow shear action at the membrane surface (fluid flowrate) may extend the solids concentration in the feed flow that may be achieved during treatment. Additionally, the use of backwashing and or back pulsing during treatment would be expected to mitigate membrane fouling.

Conclusion

APS-MF treatment of representative produced water produces a superior product water quality in terms of turbidity and calcium concentration relative to that produced with conventional softening or APS/clarification. Filtration of APS effluent produced filtrate with a 3% lower dissolved calcium concentration and 8xlower turbidity than filtrate from water softened without seeds. An optimum calcium carbonate seed concentration of 7 g/L was identified for the produced water. The particulate seeds are well-rejected by polymeric and ceramic membranes. In a cross-flow configuration the particulates did not significantly foul the ceramic MF membrane until a solids concentration of 15 g/L was reached indicating that the APS-MF system is capable of treating high-solids content water. In addition, it could be operated without settling the water after the APS reaction, while maintaining a reasonable operating filtrate flux and TMP.

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