NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: A Novel Brine Precipitation Process with the Aim of Higher Water Recovery

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Overview:

This Accelerating Innovation Research-Technology Translation (AIR-TT) project will develop a proof-of-concept for a new treatment process that removes water contaminants that may foul reverse osmosis (RO) or nanofiltration (NF) membranes used for producing potable-quality water. In contrast to commercialized pretreatment processes for RO and NF that remove only particulate contaminants, the proposed process removes dissolved contaminants and particulates larger than 5 µm.

This new treatment process involves the use of a fluidized bed crystallization reactor (FBCR) to precipitate scale-forming mineral solids, dissolved organic matter, and dissolved silica. Scale forming mineral solids are precipitated as $CaCO_3$ and $Mg(OH)_2$. Dissolved silica is precipitated as $MgO(SiO_2)x\cdot(H2O)x$, and organic matter and microbial contaminants are removed via adsorption onto, and incorporation into, the crystallizing mineral solids. Effluent from the reactor is fed into a coarse microfilter to remove particulates larger than 5 µm. The pH value of the effluent of the FBCR is adjusted to 11 using the base line of the BMED which also results in bacteria and virus inactivation.

There are two effluent lines per membrane. The clean and treated water is permeate water and the polluted and contaminated side named concentrate, rejected water or brine. The acids and bases used to adjust pH are generated from the NF concentrate solutions using bipolar membrane electrodialysis (BMED). The treatment process will be used on municipally treated secondary effluent wastewater prior to treatment via NF. A two-stage NF system will be used, and will be operated at a pH value of 11 on the concentrate side of the membranes. Operating the NF at high pH will greatly reduce membrane fouling due to electrostatic effects. At high pH, the NF membranes will be negatively charged, as will dissolved silica, natural organic matter, and colloidal particulates. Removal of most of the dissolved foulants prior to NF will greatly increase NF permeate recovery, and decrease the volume of concentrated brine solution that is produced by one order of magnitude.[1,2] Although the proposed treatment process seems more complex than conventional pretreatment using 0.1 µm microfiltration (MF) or ultrafiltration (with even smaller pore sizes), the process will actually be less

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[1] Badruzzaman, M.; Oppenheimer, J.; Adham, S.; Kumar, M. Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electrodialysis and electrochlorination processes. J. Membr. Sci. 2009, 326, 392−399.

[2] Giesen, A.; Erwee, H.; Wilson, R.; Botha, M.; Fourie, S. Experience with crystallization as sustainable, zero-waste technology for treatment of wastewater. In Proceedings of the International Mine Water Conference; Pretoria, South Africa, Oct 19−23, 2009; International Mine Water Association: Granada, Spain, 2009.

expensive due to the much smaller size of the MF process that only requires removal of particulates larger than 5 µm. Allowing particulates as large as 5 µm is made possible by uniquely designed NF modules by EconoPure Water Systems, LLC. The proposed treatment system is highly scalable, and thus applicable to both large and small-scale industrial and municipal water treatment operations. The project will be performed at the Water and Energy Sustainable Technologies (WEST) Center using secondary effluent wastewater.

Broader Impacts:

The technology to be developed here will enable large-scale inland desalination using RO and NF. Currently, large scale RO and NF are not commonly practiced in non-coastal areas due to the high costs of brine disposal. Decreasing the volume of brine production by one order of magnitude will make inland RO and NF cost-effective. This will enable both municipally treated wastewater and brackish groundwater to be used as sources of potable or industrial water. These two new sources of water will increase the available water resources and reduce the imposed restrictions on economic development in arid regions of the country.

Progress to Date:

Through past NSF-sponsored research we developed a process that eliminates the production of waste brine streams when regenerating ion exchange media used for water softening. The process operates as a closed-loop system and has zero-liquid-discharge. Acids and bases for regenerating ion exchange media are made from dilute, reusable, brine solutions and a bipolar membrane electrodialysis (BMED) stack. The repeating unit cell in a BMED stack consists of an anion exchange membrane (AM), a bipolar membrane (BPM), and a cation exchange membrane (CM), as illustrated in Figure 1.

BMED stacks may contain up to 300 of these repeating unit cells. The BPM consists of a strong acid cation exchange membrane (CM), a transition layer containing a weak base catalyst, and a strong base anion exchange membrane (AM)[3]. The weak base layer between the AM and CM promotes the splitting of water into H^+ and OH^- ions[4]. With only 1 volt of applied polarization, the rate of water splitting is more than 7 orders of magnitude greater than the rate in bulk water. The electric field also promotes electromigration of H^+ towards the cathode, and OH towards the anode. The H^+ get trapped in the acid chamber by an AM, and the OH^- get trapped in the base chamber by a CM. Electroneutrality is maintained in the acid and base chambers by electromigration of anions and cations, respectively, from the diluate solution.

[3] Strathmann, H. Ion-Exchange Membrane Separation Processes; Elsevier: Amsterdam, 2004.
[4] Onsager, L. Deviations from Ohm's law in weak electrolytes. J. Chem. Phys. 1934, 2, 599−615.

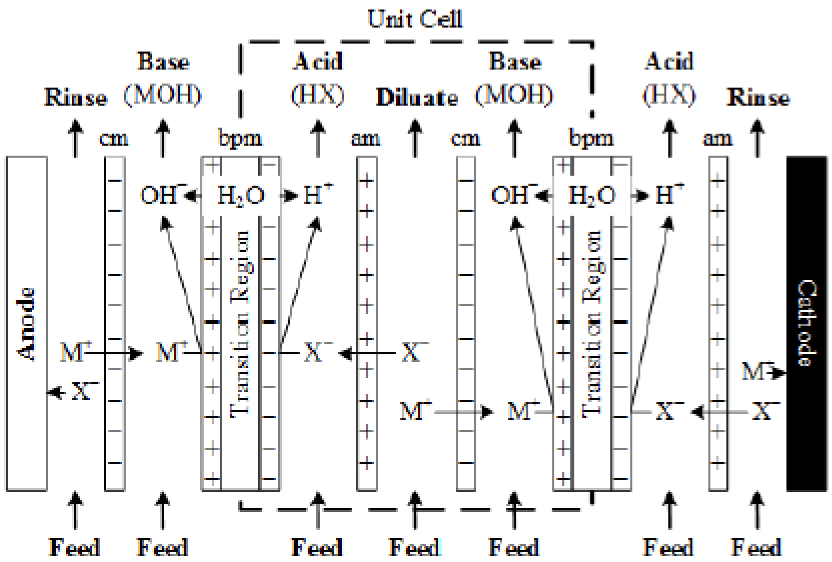

Figure 1 Schematic drawing illustrating the production of acids and bases from the corresponding salts by electrodialysis with bipolar membranes. (Davis, J. R.; Chen, Y.; Baygents, J. C.; Farrell, J. Production of acids and bases for ion exchange regeneration from dilute salt solutions using bipolar membrane electrodialysis. ACS Sustainable Chem. Eng. 2015, 3 (9), 2337–2342.)

The acid is used to regenerate weak acid cation (WAC) exchange media loaded with Ca^{2+} and Mg^{2+} ions, as illustrated in Figure 2. The base solution is used to regenerate a weak base anion (WBA) exchange media. A fraction of the base solution is passed through a hollow fiber membrane contactor that is used to saturate the solution with CO_2 to provide a source of CO_3^{2-} anions. Effluent solutions from the base chamber of the BMED cell, the ion exchange canisters, and the membrane contactor are fed into a fluidized bed crystallization reactor (FBCR) that operates at a pH value of ~11. The FBCR contains sand grains to serve as heterogeneous nucleation sites for $CaCO_3$ and $Mg(OH)_2$ precipitation. Over time, the seed grains become coated with the crystallized minerals and the suspended particles grow in size. When the diameters of the crystallized mineral particles exceed ~2 mm, the particles are discharged from the bottom of the reactor. Liquid effluent from the FBCR is fed through a ceramic microfilter and back into the brine tank, thereby completing the closed-loop. Further details on the process can be found in two recent publications[5,6].

[5] Davis, J. R.; Chen, Y.; Baygents, J. C.; Farrell, J. Production of acids and bases for ion exchange regeneration from dilute salt solutions using bipolar membrane electrodialysis. ACS Sustainable Chem. Eng. 2015, 3 (9), 2337−2342.

[6] Chen, Y.; Davis, J. R.; Nguyn, C. H.; Baygents, J. C.; Farrell, J. Electrochemical Ion-Exchange Regeneration and Fluidized Bed Crystallization for Zero-Liquid-Discharge Water Softening. Environ. Sci. Technol. 2016, 50, 5900−5907

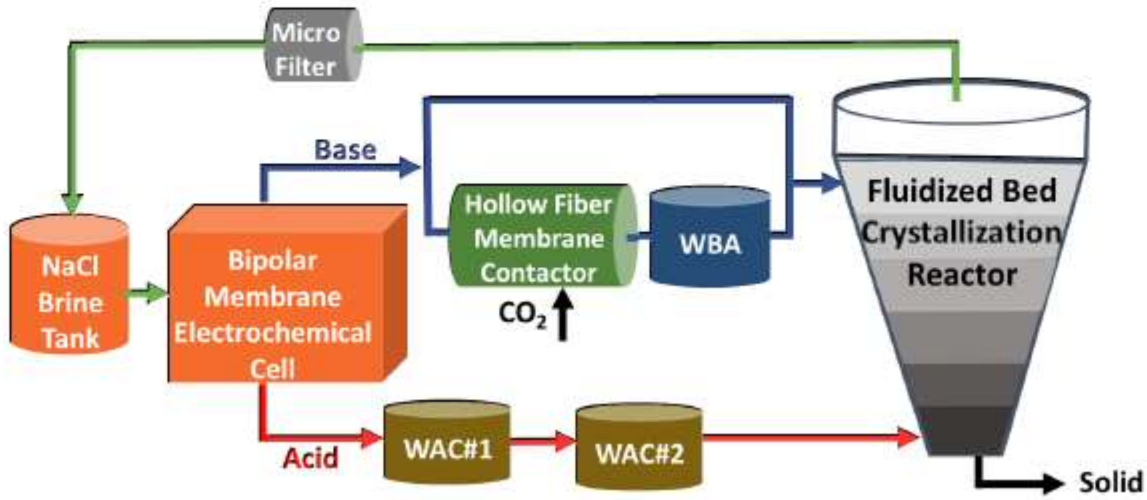

Figure 2 Closed-loop system for regenerating ion exchange media and crystallizing hardness minerals. Half-of the base stream is contacted with CO_2 and is used to regenerate WBA media into HCO_3^- form. During the water softening step (not shown), the WBA media provides a source of alkalinity for removing permanent hardness by the WAC media. (Chen, Y.; Davis, J. R.; Nguyn, C. H.; Baygents, J. C.; Farrell, J. Electrochemical Ion-Exchange Regeneration and Fluidized Bed Crystallization for Zero-Liquid-Discharge Water Softening. Environ. Sci. Technol. 2016, 50, 5900−5907)

Purpose of this Research:

The goal of the proposed research is to extend the use of BMED and FBCRs to converting municipally treated wastewater or brackish groundwater into potable water. The BMED/FBCR technology will be used to treat these water streams prior to nanofiltration (NF) or reverse osmosis (RO) treatment. The proposed process is expected to increase water recovery by reducing membrane fouling. The higher permeate recoveries are expected to reduce the volume of brine concentrates by more than a factor of 10. This is important because it is more cost effective to treat smaller volumes of concentrated than to treat a large volume of dilute brine.

Figure 3 illustrates one example of the proposed process where NF is used for producing potable water. The water to be treated is fed into a FBCR maintained at a high pH using base produced by a BMED stack. In the FBCR, hardness minerals are removed from solution and precipitate as $CaCO_3$ and $Mg(OH)_2$ on seed particles suspended in the fluidized bed. Dissolved silica is removed as $MgO(SiO_2)_x{\cdot}(H_2O)_x$, and organic matter and microbial contaminants are removed via adsorption onto, and incorporation into, the crystallizing mineral solids. Effluent from the reactor is fed into a coarse microfilter to remove particulates larger than 5 µm in diameter. The filtered water containing micron and submicron particulates are then fed into a NF module. The feed to the NF is maintained at a high pH, and the NF elements are specially designed to accommodate particulates (details in next section). Concentrate from the primary NF (1°NF) is fed into a secondary NF (2°NF) for further concentration. Concentrate from the 2°NF is fed into a BMED stack and is used to produce acids and bases. The base from the BMED stack is used to maintain a high pH in the FBCR. Acid from the BMED stack is used to lower the pH of the NF feed solutions, neutralize the pH of the permeate solutions, and is also used to acidify the feed solution to the BMED stack. The crystallized mineral solids in the FBCR grow over time, and once large enough settle out of reactor as pellets with diameters larger than 2 mm. Because of their large size and high density, the pellets are easily dewatered via gravity drainage to more than 99% solids, and can be sold for use in making cement.

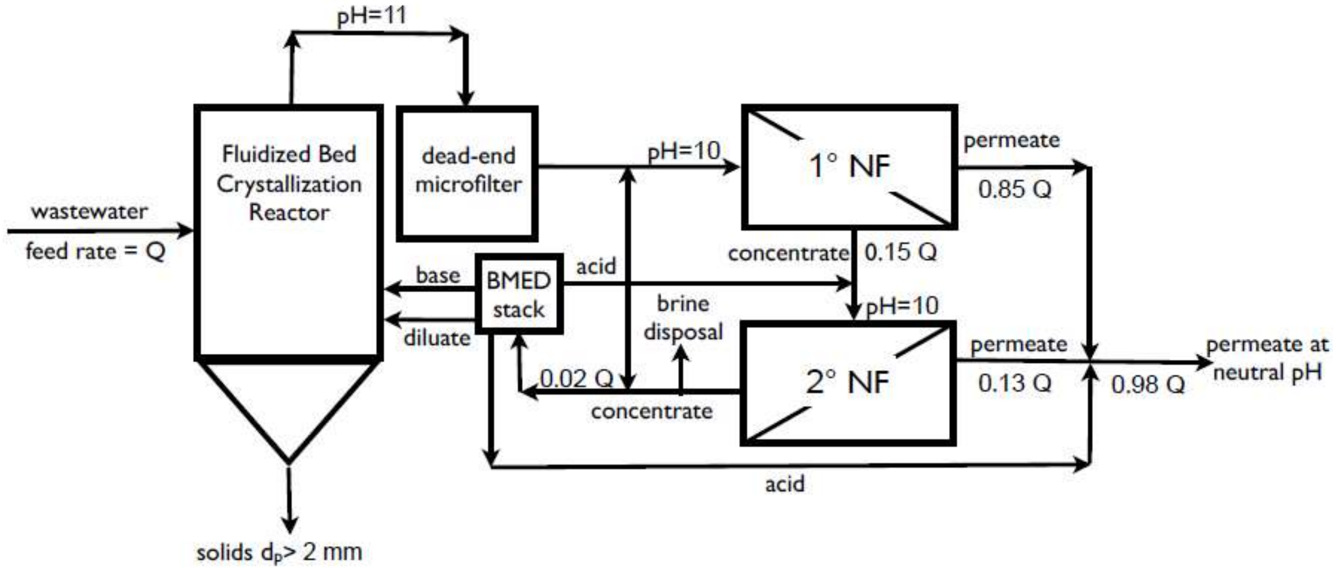

Figure 3 Schematic diagram of proposed treatment process. Approximate volumetric flow rates for different streams are denoted by the fraction of the influent feed rate, Q. Also shown are approximate pH values for different streams.

Conclusion:

Based on the previous research and preliminary results, it has been proven that BMED is able to treat synthetic brine and provide the base solution that is needed to increase the pH value to 11 in the FBCR. Furthermore, BMED provides an acid line that can be used for lowering the pH value of the first membrane influent and concentrate stream of first membrane. In order to reach a broader conclusion, membranes are going to be used to produce real brine from secondary effluent of a wastewater plant in Tucson, Arizona.

Next steps:

This project started in September 2016 and the literature review and process design for this project was completed in November 2016. The equipment has been procured and the pilot plant will be set up in WEST by January 30, 2017. The system is divided into sections including FBCR, membranes, and BMED. The next step will be to reach a steady state in these individual sections, which means to reach almost stable effluent for them. Samples will be taken three times a day from the inlet and outlet of these sections to verify the steady state condition.