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CASE STUDY

UV15TK for 3-D Printing of Reverse Osmosis Feed Spacers with Reduced Scaling Effects

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Application

In the coming decades, global freshwater shortages will pose a significant hazard for humanity. Not only is clean, fresh water critical for essential human life, but our ever expanding industrial and agricultural footprint further increases the demand for freshwater. A combination of factors including population growth, the destruction of natural reservoirs, industrial pollution and the impacts of climate change will see water as one of the most important commodities of the 21st century. Reverse osmosis (RO) water treatment utilizes hydraulic pressure and a semipermeable membrane to separate 90-99% of the total dissolved solids (TDS) from the feed water supply.[1] Critically, reverse osmosis allows for the desalinization of brackish water and sea water; salt-laden water represents 97.5% of all water on earth, thus reverse osmosis treatment greatly increases the potential freshwater supply. Challenges with reverse osmosis include high energy costs and the deleterious effects of scaling that occur over the operating cycle. Scaling is a particular problem requiring chemical pre-treatment as well as costly chemical cleaning processes to extend the life of the membranes. **Figure 1** illustrates a schematic cut-away of a spiral-wound-element (SWE) reverse osmosis membrane. The design and construction of the feed channel spacer as well as the semipermeable membrane itself is critical to producing an efficient and long-lasting solution for water treatment.

The use of reverse osmosis treatment has tripled since 2000 with over 16,000 water treatment plants in operation worldwide.[2] Reverse osmosis now represents 65% of the desalinization market while consuming 90% less energy than desalinization via distillation. Osmosis is a spontaneous process wherein two solutions differing in concentration and separated by a semipermeable membrane experience diffusion of solvent molecules from the solution of lower solute concentration to the solution of higher solute concentration. Reverse osmosis utilizes hydraulic pressure on the feed solution to overcome the osmotic potential leading to the purification and diffusion of water molecules across the semipermeable membrane.

Fouling of the membrane is one of the key challenges of operating reverse osmosis treatment plants. Alleviation of fouling may require expensive chemical pre-treatment as well as costly cleaning procedures. Factors that contribute to fouling of the membrane include the concentration of the solution at the liquid-membrane interface as well as the design of the feed spacer. Constructed from a simple diamond-shaped mesh, the feed spacer separates the membrane leaves and guides the water flow as it diffuses through the membrane. The researcher, Jeremy Walker, as part of a doctoral thesis in civil engineering at Wayne State University, conducted a series of studies to improve the design of the feed channel spacer used in reverse osmosis membranes.

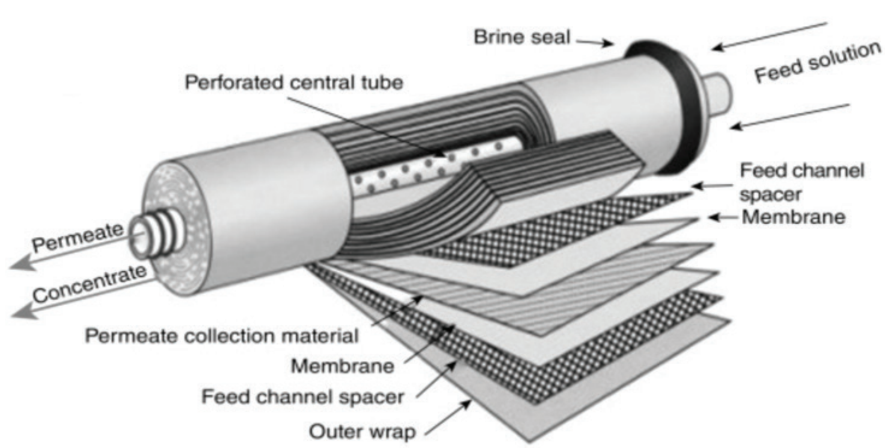

Figure 1. Spiral-Wound-Element (SWE) Reverse Osmosis (RO) membrane cross-section.[1]

The goal of these studies sought to design a feed spacer with reduced fouling and enhanced de-scaling properties during membrane cleaning.[2] Master Bond UV15TK, a UV-curable epoxy with a relatively high modulus, was chosen for use as a 3-D printing material to directly print micromixer elements of an optimal design onto the semipermeable membrane itself. Fluid dynamic modeling was performed to determine the optimal geometry of the chevron pattern. Optimal flow velocity and turbulent mixing decreases the tendency for scale formation, crystallization of solute species, and decreases the effects of fouling. **Figure 2** shows a standard industrial mesh feed spacer and the optimized 3-D printed micromixer elements comprised of UV-cured Master Bond UV15TK epoxy. Studies compared performance between the 3-D printed micromixer elements and the industry standard mesh with respect to fouling tendency and reverse-flow de-scaling.

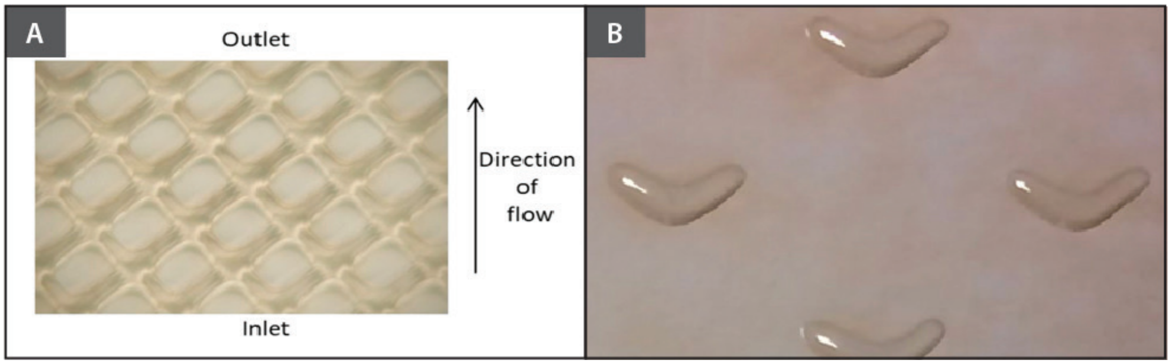

Figure 2. Feed channel spacers used in Spiral-Wound-Element (SWE) Reverse Osmosis (RO) water treatment. A) Industrial standard mesh feed spacer. B) Micromixer element with chevron design; directly 3-D printed using UV curable epoxy, Master Bond UV15TK, onto RO membrane.[2]

Key Parameters and Requirements

Reverse osmosis systems must withstand high pressures as well as harsh chemical environments. In addition to the corrosive salts present in the marine feedwater, the cleaning procedures require aggressive chemical solutions including strong acids and bases. As such, the printing media used in the construction of the chevron-shaped micromixer elements must have strong chemical resistance to concentrated salt solutions, acids, and bases. Further, a high strength and high modulus material is necessary to withstand the operating pressures[2] that may reach or exceed 1,200 psi. A high modulus material will also maintain good dimensional stability under these high pressures enabling the micromixer elements to guide the water-flow as intended. As the membrane materials are wound in the canister assembly, the 3-D printed chevrons must possess exception adhesion to the polyamide composite membrane film. Master Bond UV15TK has exceptional chemical resistance, possesses a high modulus, and has good adhesion to many substrates including polymers such as polyamides.

Of practical concern, the UV-curable printing material must also have a viscosity that is suitable to 3-D printing. The viscosity of the uncured epoxy must be low enough that it can be poured into a syringe and readily extruded as a thin bead during the 3-D printing process. The UV-curing mechanism is especially suitable for this as it allows for on-demand curing; the Master Bond UV15TK epoxy is a single-component product that requires no mixing prior to use and presents with no risk of premature gelling or pot-life concerns. Master Bond UV15TK has a viscosity of 6,000-12,000 cps at 75°F (24°C); it was successfully used in this study having been 3-D printed using a modified BioBots 3-D Printer with delivery through a 30-gauge needle prior to being cured with a 365 nm UV LED light source. The ideal cure occurs with a wide frequency flood lamp, but high intensity UV flashlights also work well to cure the UV15TK.

In addition to the epoxy selection, Walker performed fluid-flow dynamic modelling studies to determine the optimal geometry and orientation of the chevron-shaped micromixer elements.[2] Modelling was done with COMSOL Multiphysics to determine the optimal angle and geometry of the micromixers that were to be printed on the semipermeable membrane. An optimized microstructure design has the potential to maximize the membrane area that experiences optimal channel feed velocities of 0.2-0.3 m/s while minimizing velocities that are associated with fouling of the membrane. Velocities below 0.1 m/s and velocities greater than 0.3 m/s are known to encourage scaling and deterioration in the water flux through the membrane. **Figure 3** presents a visual summary of channel feed velocities determined from modelling the offset configured chevrons with interior angles: 60°, 90° and 120° with fixed parameters of 3 mm chevron length, 5.75 mm gap, and an inlet velocity of 0.104 m/s. A chevron interior angle of 90°was found to be optimal.

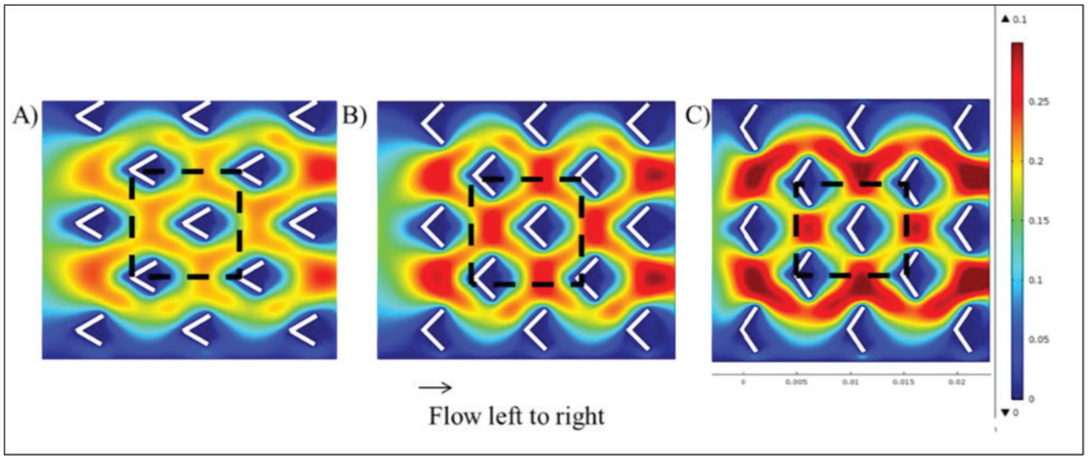

Figure 3. Design optimization modelling the fluid flow channel using COMSOL Multiphysics. Full velocity profile from 0-0.3 m/s varying the chevron angle of influence A) 60° B) 90° C 120°. Design constants: offset pattern, 3 mm chevron length, 5.75 mm gap, inlet velocity 0.104/m/s.[2]

Results

The impact of 3-D printing on membrane integrity and performance, specifically the exposure to high intensity UV radiation during cure, was assessed. The prepared control membrane, exposed to UV radiation but without deposited microelements, was found to be within 3% of the manufacturer's specification for water flux and salt rejection rate.[2] Analysis of the membrane surface with FT-IR did not indicate any adverse chemical changes to the polyamide surface.

After the design, optimization, 3-D printing and establishment of proof-of-concept, a scaling study and a reverse-flow, de-scaling study were conducted to assess the performance of the 3-D printed micromixer elements against the industry standard mesh feed spacers.[2] A protocol used to assess the tendency for scale formation and fouling first conditioned the membranes with deionized water and then 0.4M sodium chloride solution. During this conditioning phase, a baseline water flux rate is determined. The scaling solution, composed of 0.03M sodium sulfate and 0.03M calcium chloride was then passed through the membranes—this solution will have a strong tendency to induce scaling and fouling of the membranes with insoluble calcium sulfate precipitating out from the feed stock and depositing on the micromixer elements as well as the semipermeable membrane leading to reduced water flux.

Results of the scaling study are summarized in **Figure 4**. After introduction of the scaling solution, both the printed micromixer and the standard mesh feed spacer systems experienced a reduction in water flux of approximately 20% after ~7 hours. After ~10 hours, the water flux data diverges for the two test systems: the industrial standard mesh spacer system's water flux rate continued to deteriorate while the 3-D printed micromixer system maintained a stable water flux. After 12 hours of processing the scaling solution, the standard feed spacer saw a reduction of 78% in water flux whereas the micromixer element system experienced a reduced water flux of only 24%. This supports the hypothesis that the improved hydrodynamic open channel flow provided by the chevron-shaped micromixer elements minimized scale deposition and reduced the tendency for deleterious fouling when exposed to a solution with high-scaling tendency. Evaluation of the membranes by optical imaging and scanning electron microscopy (SEM) post-study supported the test data and reinforced the finding that the modified microelement system gave superior scaling resistance. Both systems indicated scaling through the bulk crystallization mechanism at the membrane interface; this occurs when calcium sulfate becomes supersaturated at the diffusion boundary and then deposits on the membrane and feed spacer. A visual comparison of the extent of scaling is shown in **Figure 5**.

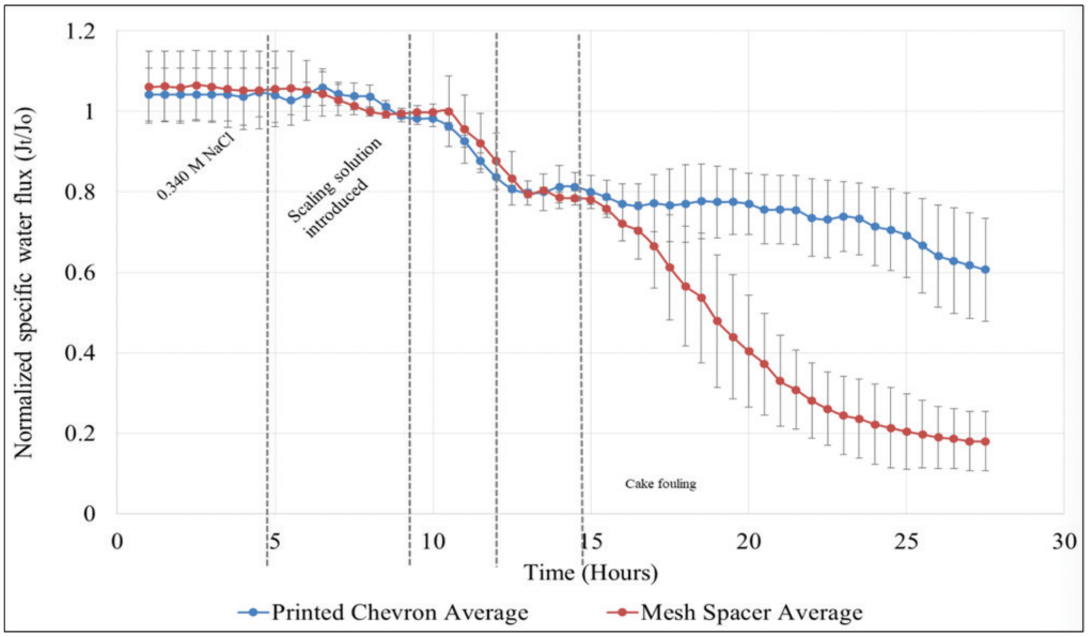

Figure 4. Scaling study comparing 3-D printed micromixer with Master Bond UV15TK (blue) and the standard industrial mesh feed spacer (red) monitoring normalized specific water flux through the RO system.[2]

In addition to the positive outcome of the scaling study, an interesting phenomenon was observed for the modified system. The process of printing the chevron-shaped elements on the semipermeable membrane has the effect of reducing the active membrane area—the unmodified membrane had an active membrane area of 140 cm^2; subtracting the area of the printed chevrons from the total area resulted in a theoretical active membrane area of 88 cm^2 for the modified construction. However, when the effective active membrane area was calculated using the average pure water flux data, it was found that the experimentally derived active area was 120 cm^2. It would not be expected that UV curing would increase the water flux; additionally, the salt rejection rate was not found to be different from either the standard membrane (<0.05% difference) or the manufacturer's specification (<3% difference) suggesting that no membrane damage had occurred during the UV curing process. It was hypothesized by Walker that this increase in effective active membrane area can be attributed to the ability of water to partially diffuse through the UV-curable epoxy material itself resulting in preservation of the total active membrane area. The impact of epoxy selection or modification of the cross-link density could potentially be used to further increase the efficiency of these designs. This can potentially be achieved by using higher intensities during the UV cure and/or post curing with some amount of heat. For example, adding heat to around 80-120°C for 1-2 hours could increase the cross linked density and glass transition temperature.

It was also hypothesized that the improved hydrodynamic conditions of the chevron-shaped micromixer elements would improve the ability to descale the membrane when run in reverse flow. It was found that during the first pulse of the reverse flow, the majority of the scale was removed from the modified system. This rapid descaling was observed with an acrylic transparent crossflow cell. Although spiral-wound-element RO membranes are generally not capable of being run in reverse flow, data from

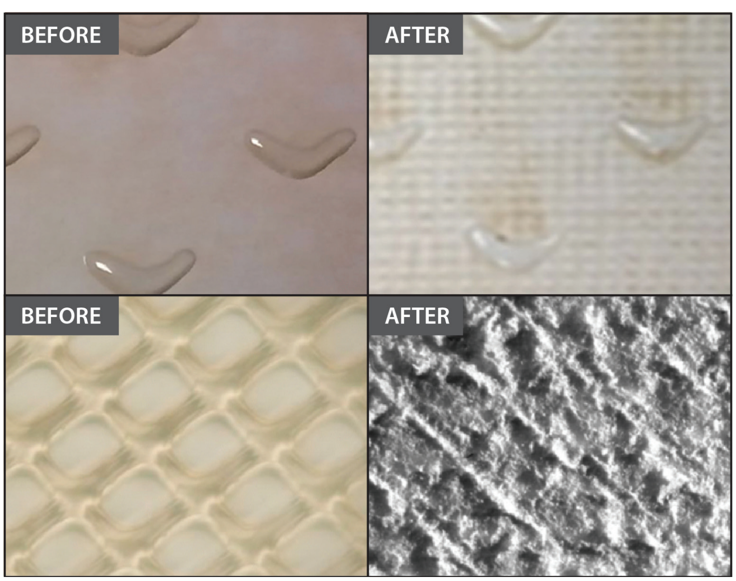

Figure 5. Optical imaging of 3-D printed micromixer (TOP) and standard industrial mesh feed spacer (Bottom) before and after the scaling study.

this study could prove useful in the design of next generation RO systems. As scaling and fouling problems are the Achille's heal of reverse osmosis treatment, the ability to quickly descale an RO system and without the use of hazardous and expensive chemical solutions would be a key advancement in the technology.

This work positively contributed to the field of engineering and to the development and advancement of reverse osmosis technology. It was demonstrated that 3-D printed micromixer elements can be optimized to reduce fouling and may also possess novel ability to readily clean and descale reverse osmosis membranes while reducing the necessity of expensive chemical pre-treatment and cleaning procedures. The use of UV-curable epoxy systems, like Master Bond UV15TK, opens up a variety of engineering possibilities. Modification of the geometric structure, size and arrangement of the 3-D printed microelements could be optimized for different feed stocks. The phenomenon observed wherein water was seemingly able to diffuse partially through the printed micromixer elements also opens the possibility of optimizing the epoxy chemistry and crosslink density to further improve water flux efficiency.

References

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[2] J. Walker. 2018. 'Analysis of Micromixers to Minimize Scaling Effects on Reverse Osmosis Membranes.' Doctor of Philosophy in Civil Engineering. Wayne State University. Detroit, Michigan. URL: https://digitalcommons.wayne.edu/cgi/viewcontent.cgi?article=3131&context=oa_dissertations Accessed: 08/20/2022.