Dissolved CO_2 – An Alternative for Cleaning Inorganic Scale from RO Membranes

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Background

Membrane fouling is a major operational issue in reverse osmosis desalination plants. In particular, plants treating brackish groundwater can encounter troublesome inorganic scales that cling to membranes and are difficult to remove.

While many efforts focus on methods to prevent fouling, it often continues to occur. Here, dissolved CO_2 is proposed as a novel cleaning method to remove scales from inorganically fouled membranes.

Theory

The use of gas for membrane cleaning involves contact between the bubble surface and foulants to shear material from the membrane. Air flowing over and through membranes have previously been applied to cleaning micro- and ultrafiltration membranes.[1]

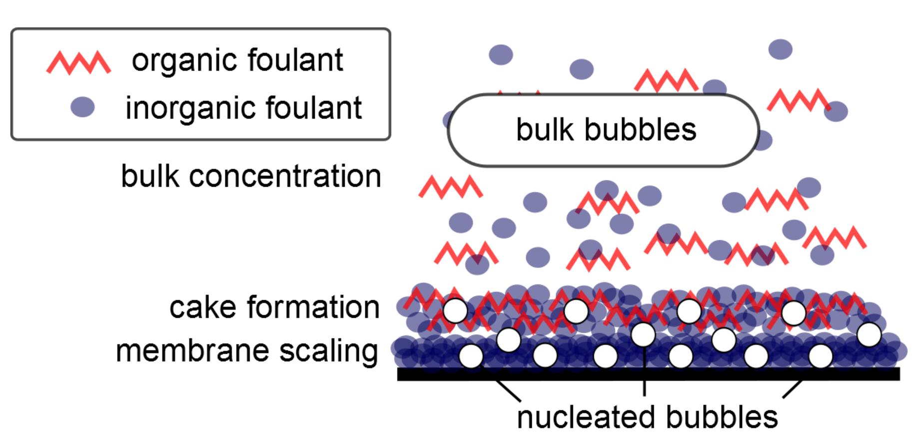

Figure 1: Depiction of gas cleaning mechanism for fouled membranes. Nucleated bubbles form on the membrane and particulates while gas phase bubbles stay in the bulk.

The hypothesis with dissolved CO_2 is that it is not present in a gas phase until it reaches the membrane. The membrane surface provides nucleation sites for bubbles to form. This produces bubbles that are smaller and in closer contact with the scales than any type of two-phase air cleaning. This method was shown to be effective in removing biofilms from reverse osmosis membranes by Vitens Water Technology, a company in the Netherlands.[2]

Materials and Methods

- CPA2 Hydranautics Low-pressure Reverse Osmosis Membrane
- Crossflow membrane cell (GE SEPA II)
- Synthetic scaling solutions with background sodium chloride
  - $CaCO_3$ solution: 200 ppm $CaCl_2$, 200 ppm Na_2CO_3, 10 g/L NaCl
  - Silicate solution: 400 ppm $CaCl_2$, 300 ppm SiO_2, 10 g/L NaCl
- Two cleaning procedures:
  - Dissolved gas cleaning – bubble gas into vertical pressure vessel filled with DI water (7.5 L) until pressure is 500 psi. Release solution through membrane cell under headspace pressure.
  - Chemical cleaning – circulate chemical cleaning solution for 30 minutes without added pressure.

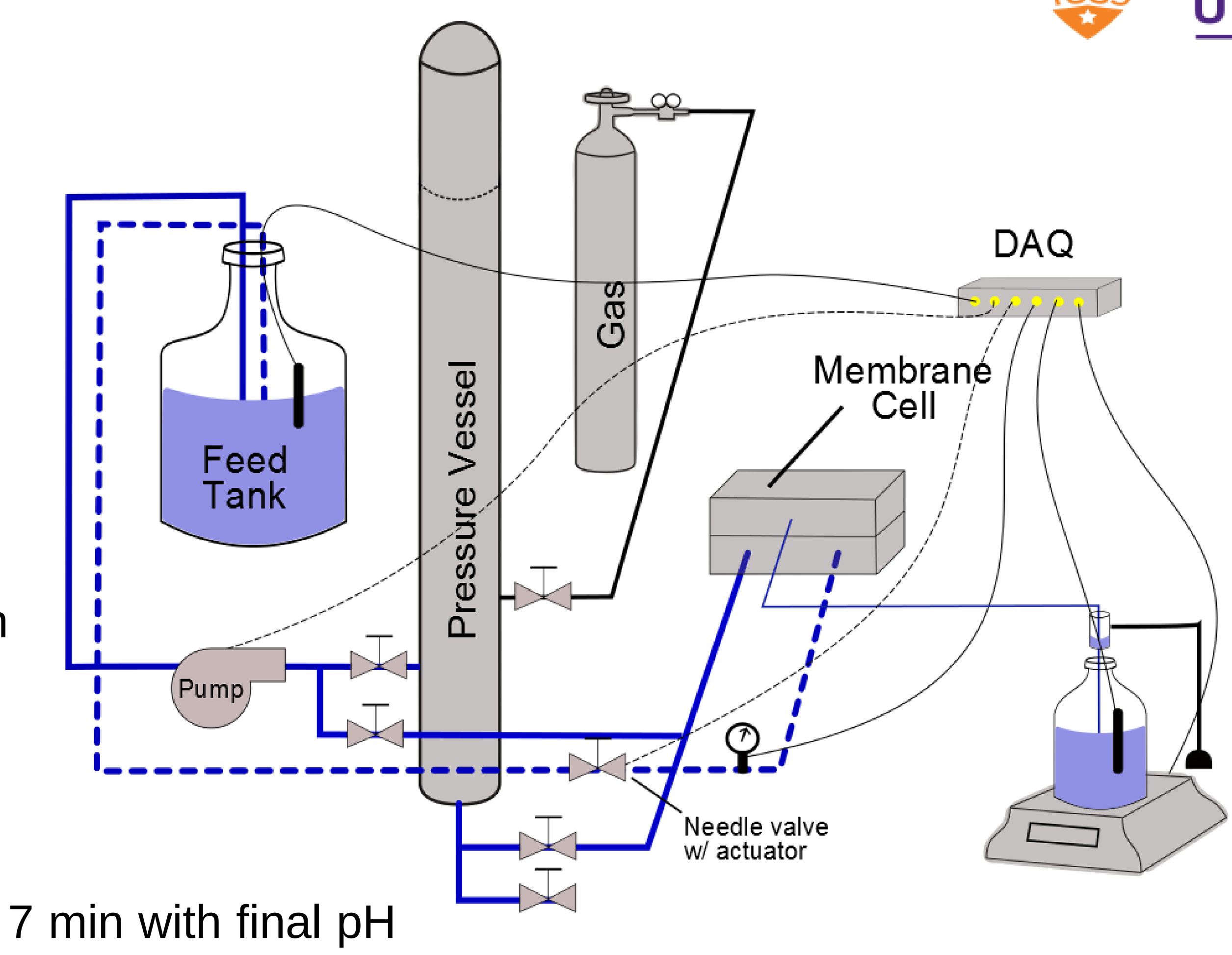

Figure 2: Sketch of bench-scale testing apparatus.

Results

Calcium Carbonate The best cleaning resulted from dissolved CO_2 – a cleaning run of 7 min with final pH 4.5. Similar cleaning was achieved with pH 3 for 30 min, an industry standard. Cleaning with pH 4, N_2 instead of CO_2, acidified N_2, and DI water produced minimal cleaning. Scanning electron microscope (SEM) images of cleaned membranes at 1000 times magnification show changes in scale morphology when cleaned with dissolved CO_2 and pH 4 solution.

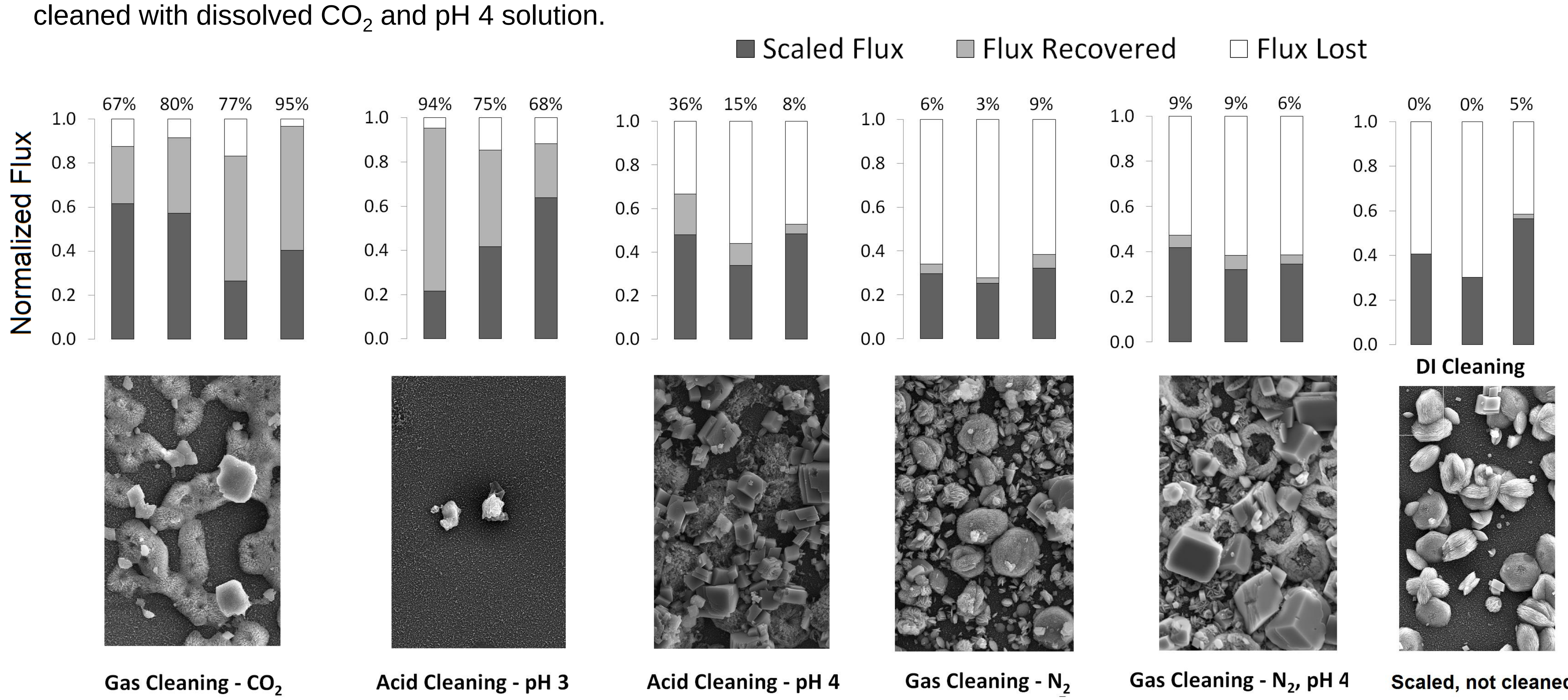

Figure 3: Results of each cleaning trial to remove calcium carbonate scale. Dark bars are normalized flux after scaling; light bars show recovered flux after cleaning. Flux recovery percentages are shown above each trial.

1. Dissolved CO_2 *- high flux recovery and morphological change in scale*

2. pH 3 *– nearly complete flux recovery, little scale remaining*

3. pH 4 *– moderate recovery, some morphological scale change*

4. N_2 Gas *– limited flux recovery, no scale change*

5. N_2 Gas/pH 4 *– limited flux recovery, some morphological change*

6. DI/not cleaned *- no flux recovery*

Calcium Silicates None of the attempted cleaning solutions were able to significantly remove silicate scale. A high pH solution containing the surfactant sodium dodecyl sulfate produced the best results. Silica is known to be problematic and typically handled with pretreatment to reduce feed concentrations.

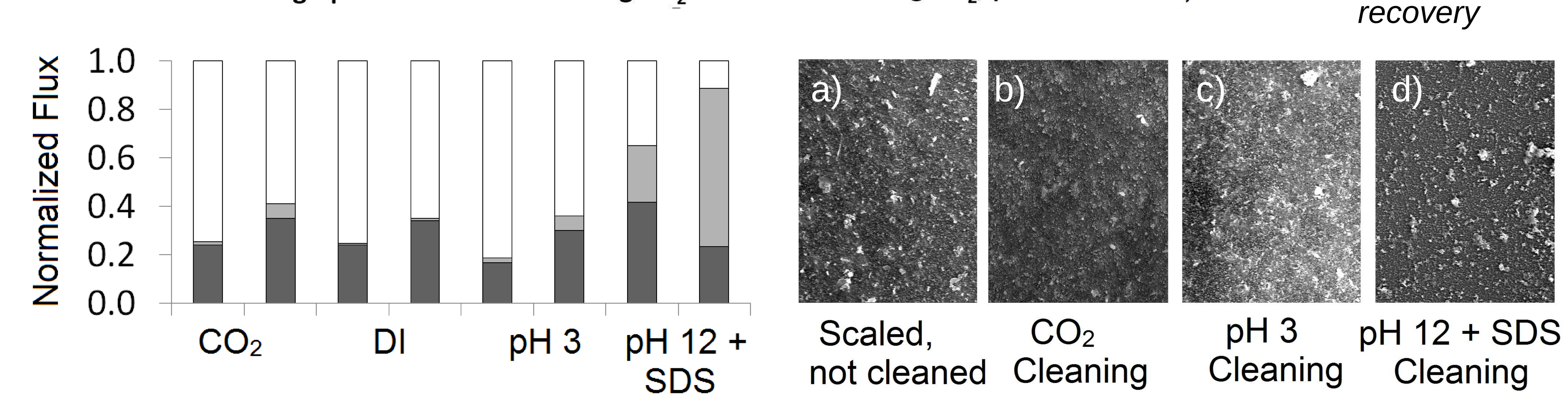

Figure 4: Results of cleaning calcium silicate scale. a) an uncleaned membrane, b) cleaning with CO_2 – little result in scale buildup and flux recovery, c) cleaning with a pH 3 solution – also limited scale removal and flux recovery, d) cleaning with sodium dodecyl sulfate in pH 12 produced the best results – high flux recovery and visible scale removal.

Discussion

Dissolved CO_2 was effective at removing calcium carbonate scale from reverse osmosis membranes. The pH of the solution after carbonation was 4.5. Controls for pH show that pH 3 cleans well, but not pH 4. Therefore, pH was not the dominant factor in CO_2 cleaning. Controls with N_2 gas show limited flux recovery in both adjusted and unadjusted pH solutions; bulk phase bubbling is therefore ruled out as a cleaning mechanism.

CO_2 and N_2 gas cleaning runs exhibited significant operational differences. Dissolved CO_2 solutions exited from the membrane cell at a much higher velocity than N_2 solutions, despite identical driving pressure and total run times. Therefore, it is likely that CO_2 is exsolving at the membrane while N_2 remains in gas phase throughout. Overall, the data are consistent with the hypothesis that CO_2 bubble nucleation at the fouled-membrane surface induces a cleaning effect.

Applications

Green Alternative Dissolved CO_2 can replace costly conventional antiscalants and/or chemical cleaning solutions. Cleaning solutions are often prepared on site and require storage of hazardous chemicals. CO_2 naturally volatilizes, leaving no residual chemical in the wash water.

Carbon Sequestration For an in-line application with concentrate disposal through underground well injection, this process could have the added benefit of carbon sequestration. This use of CO_2 helps increase its market value and encourage progress in carbon capture.

References

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2. Ngene, Ikenna S., et al. "CO2 nucleation in membrane spacer channels remove biofilms and fouling deposits." *Industrial & Engineering Chemistry Research* 49.20 (2010): 10034-10039.
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