Characterization of Fouling with Hygroscopic and Non-hygroscopic Aerosols in Composite Polymer Membranes for Water Vapor Transport Applications

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Overview

Composite membranes using a thin vapor-permeable polymer layer over a structural substrate are used in gas dehydration, food-packaging, and humidity control of indoor spaces. One application of such membranes is in enthalpy exchanger cores used in Energy Recovery Ventilators (ERV) of building HVAC systems.

There are many studies of membrane fouling from liquids (e.g. reverse osmosis [1]) and gases (e.g. micro- and ultra-filtration [2]) but we have found only one study for composite membranes in HVAC-relevant conditions. Charles & Johnson [3] characterized the air-side particulate fouling of a hollow-fiber membrane during a membrane evaporative cooling process. They found significant biological growth, but only minor impacts on water vapor transfer – not surprising because the fouling was from clean air (~3000 particles/cc) over only 120 hours.

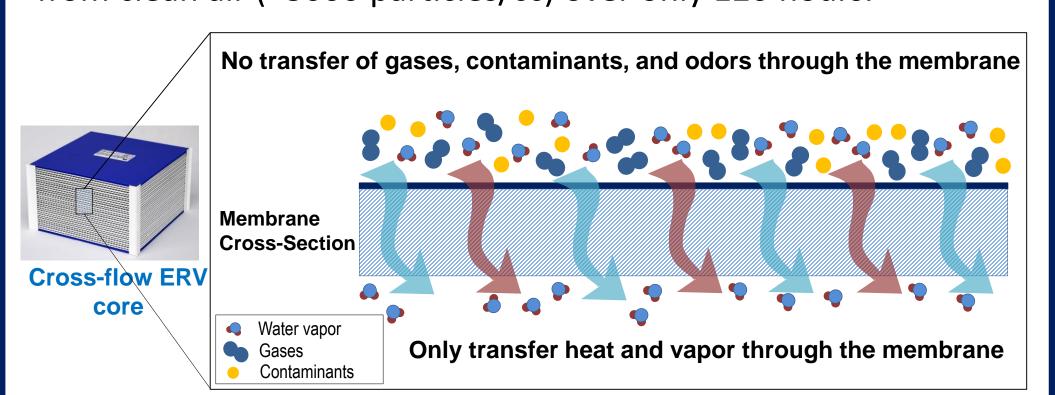


Figure 1: Ideal Membranes for building ERV application

In our work, the impact of accelerated exposure to air pollution on the water vapor flux through commercial membrane media is investigated to develop an understating of potential air-side particulate fouling mechanisms and resulted performance degradation during membrane lifetime in the field.

Experimental Methodology

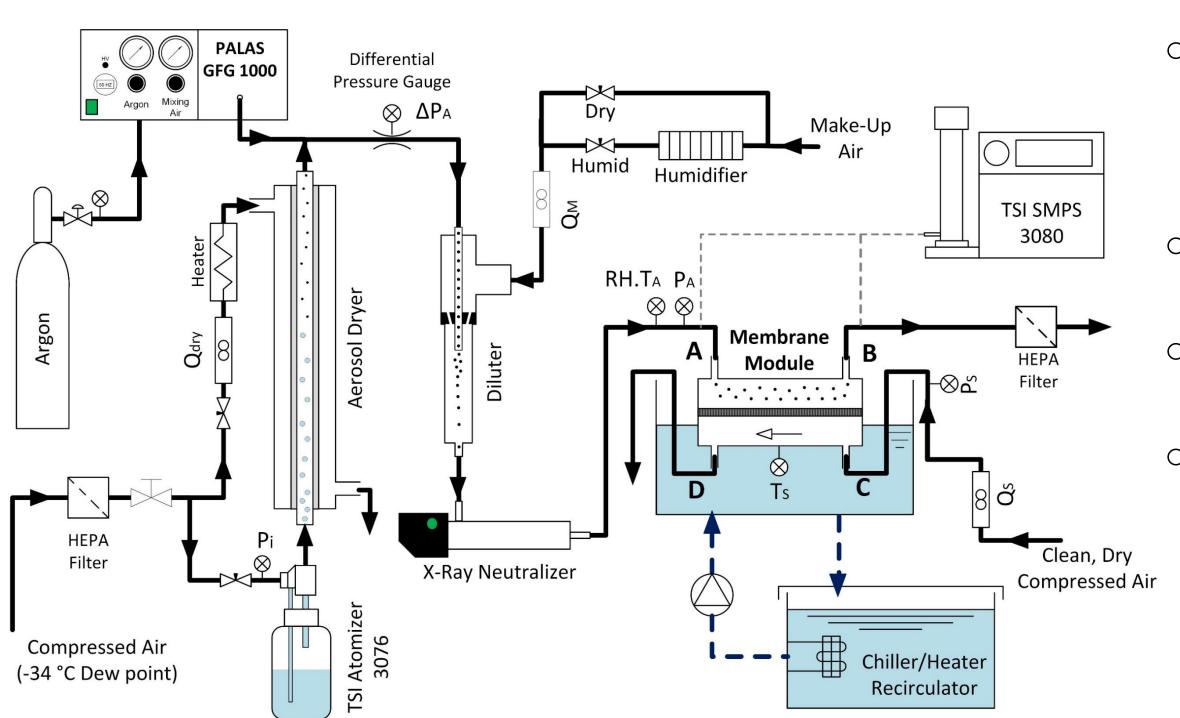


Figure 2: Experimental schematic

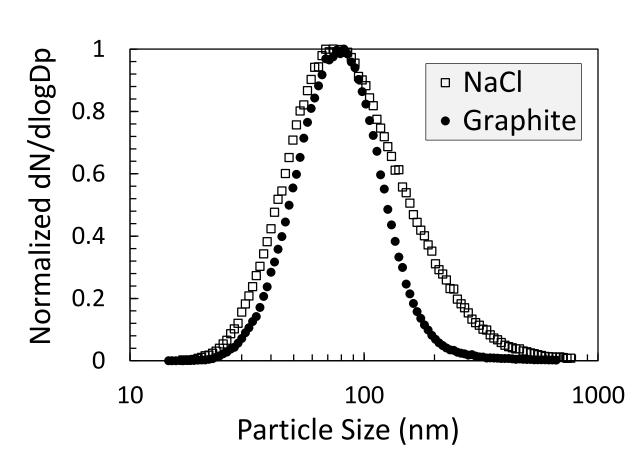


Figure 3: Particle mobility size distribution

- Two aerosol types:
- Hygroscopic salt (NaCl, Dg=88nm) from TSI 3076 atomizer
- Non-hygroscopic soot-like spark-generated graphite (SGG) (Dg=82nm) from a PALAS GFG 1000
- Upstream/downstream size distributions by TSI SMPS 3080 (used in deposition calculations)
- Membrane surface charge removed by immersion for 30 minutes in isopropyl alcohol
- Membrane samples are placed inside a counter-flow test module (active area of 456 mm2) that passes two air streams on opposing sides of the membrane:
- A-to-B: particle-laden airstream flowing in a circuit that allows for control of the size and concentration of aerosol, the RH and the flowrate
- C-to-D: sweep dry, HEPA-filtered airstream that allows control of the flowrate and temperature.
- Cumulative exposure is approximately that of one year of exposure in a heavily polluted environment.

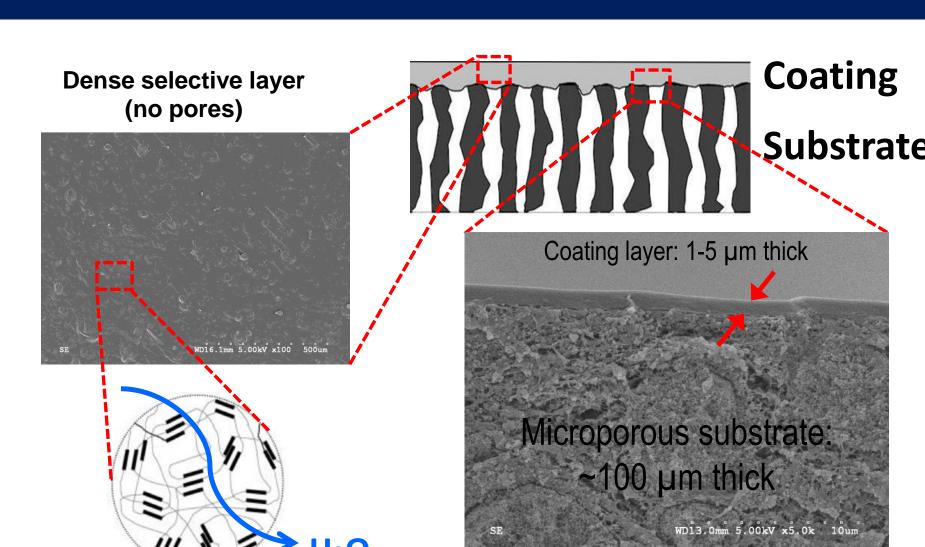


Figure 4: Composite Polymer membranes

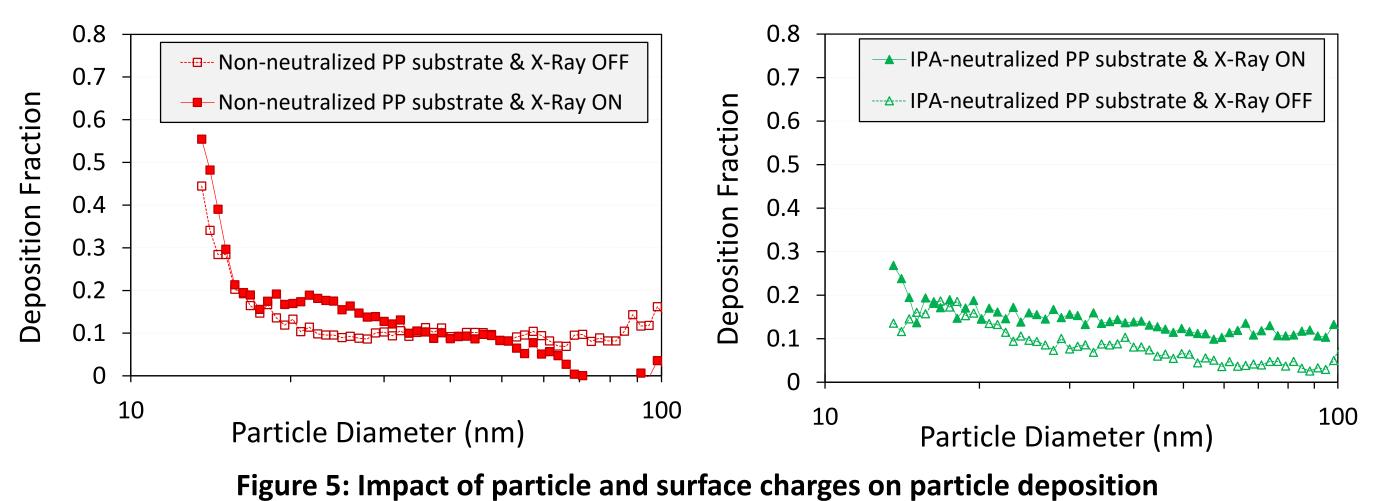
Membrane Cross Section [4]

- Composite membranes are composed of a dense polymer film coated on the surface of a porous polymer substrate.
- The dense coating layer (<10μm) provides a water- vapor-selective barrier and the porous substrate layer provides the mechanical strength of the membrane.
- The two sides of the membrane are referred to as 'coated' and 'uncoated' sides.

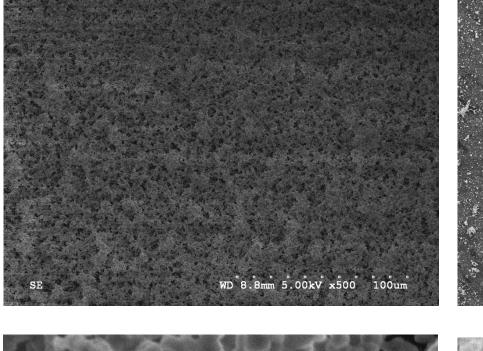
Table 1: Properties of membrane samples

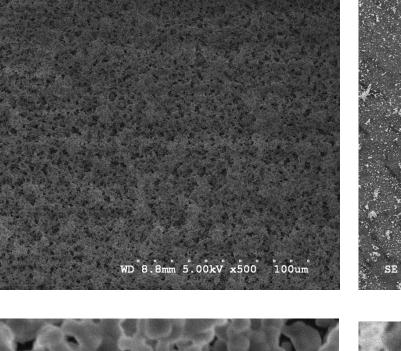
| Coating Material | Substrate | Thickness | Water Vapor Flux at 50°C |
|-------------------------|--|--|---|
| | | (μm) | (kg/m2/day) |
| hydrophilic PEO-based | Coated on a hydrophobic | 105-115 | 22 ± 4 |
| block co-polymer film | PE-based substrate | | |
| hydrophilic cellulosic- | Coated on a hydrophobic | 35-50 | 30 ± 3 |
| based polymer film | PP substrate | | |
| | | | |
| k \ | hydrophilic PEO-based lock co-polymer film hydrophilic cellulosic- | hydrophilic PEO-based Coated on a hydrophobic PE-based substrate hydrophilic cellulosic- Coated on a hydrophobic | hydrophilic PEO-based Coated on a hydrophobic PE-based substrate hydrophilic cellulosic- Coated on a hydrophobic Special Coated On Coat |

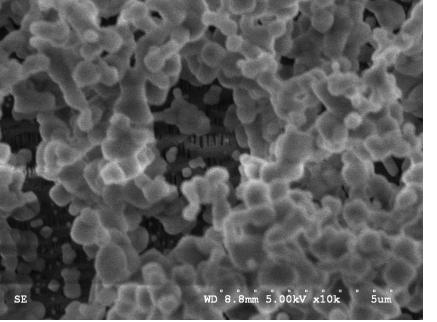
Particle Deposition on Membrane Surfaces



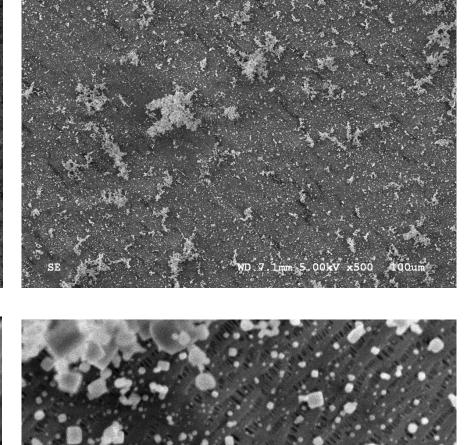
- The effects of particle charge distribution, number concentration, temperature-gradient (Thermophoresis), and membrane surface on the rate of particle deposition were investigated using a TSI SMPS 3080.
- Neutralization of surface charge by IPA reduces deposition of the smallest particles.
- Aerosol particles neutralized with a soft x-Ray neutralizer (TSI 3088) showed a tendency to form uniform, compact deposit layers leading to cake layer formation on membrane surfaces and flux reductions of up to 5% of the clean membrane value.
- Although the state of the aerosol and surface charges influence the deposition fraction and the deposit morphology, it is shown through vapor flux measurements that they have little direct influence on the degradation of membrane permeability.







Uniform, compact deposit formed from neutralized particles



Sparse aggregates formed from non-

neutralized particles

Figure 6: Effect of particle charge on deposit formation patterns on membrane surfaces

Membrane Fouling Mechanisms

1) Dry loading with RH<20% for the aerosol airstream

Performance Testing of Membranes includes [5]:

Particle deposition fraction measurement

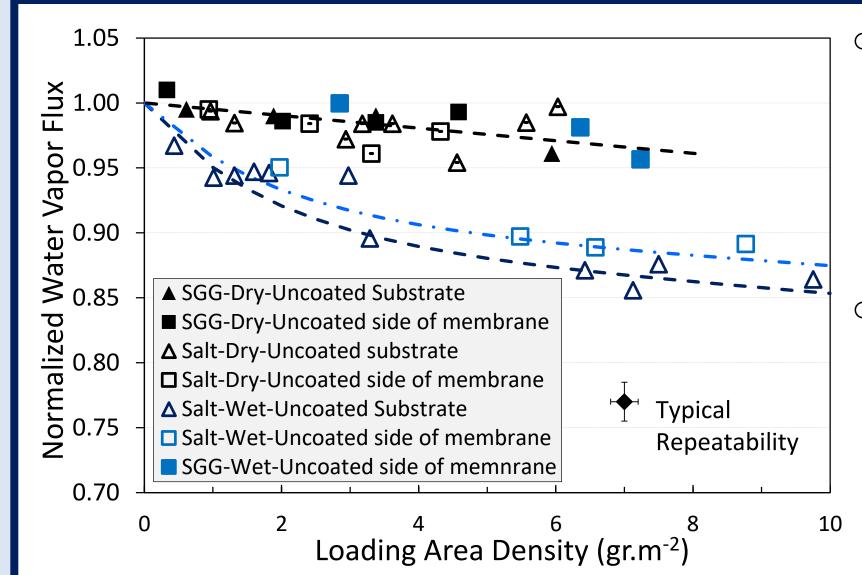
Pressurized air crossover leak rate (at 1 PSI)

Water Vapor flux (pre- and post-loading)

leading to surface condensation

2) Wet loading cycles in which dry loaded samples are

exposed to intermittent humid conditions (RH~75%)

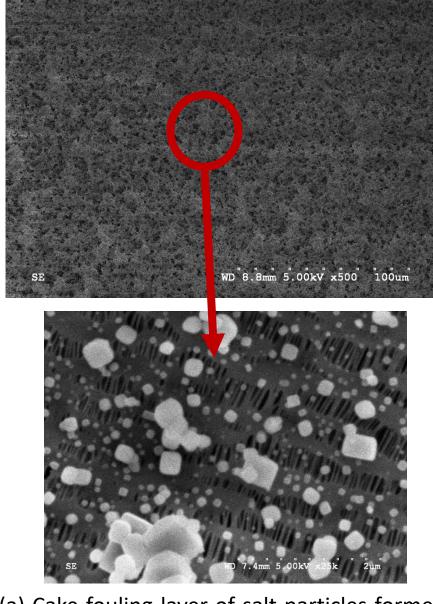


Loading conditions:

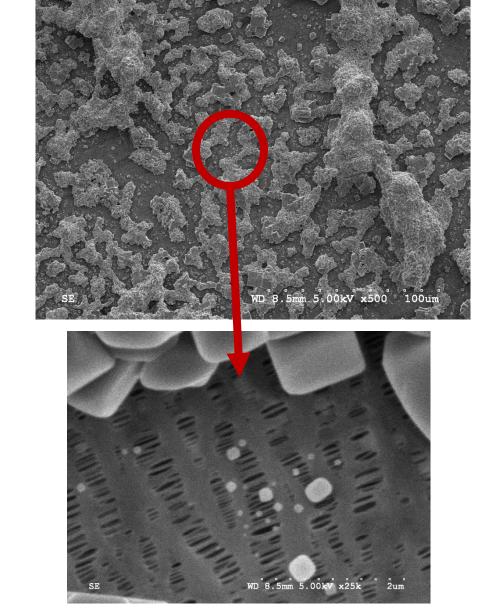
Figure 7: Changes in membrane flux resulted from particle loading

- Membranes wet-loaded with hygroscopic particles on the 'uncoated' side (Fig. 7) showed vapor flux decline up to 15%, whilst membranes loaded on the 'coated' side did not show a significant flux decline under similar wet loading conditions.
- Uncoated substrate samples show a consistently higher flux decline compared to membranes under similar wet loading. This supports the hypothesis that observed flux decline is caused by increased resistance of the microporous membrane substrate due to a pore-narrowing process.

o SEM images, as well as the fact that the loaded membrane flux can be restored to its preexposure value by a simple wash, imply that re-crystallization of salt ions dissolved in condensed water onto the pores of membrane substrate is a potential explanation for the changes.



(a) Cake fouling layer of salt particles formed at low RH (<20%) does not affect the pores of membrane substrate.



(b) Individual sub-micron particles grow and form super-micron crystals and aggregates at elevated RH (50%), but do not affect the substrate pores.



(c) Salt particles dissolve in water droplets, nucleated on the membrane surface, and reach pores in aqueous form. These ions re-crystalize in dry condition resulting in pore-narrowing.

Figure 8: Structural Changes of hygroscopic salt particles deposited at different RH.

Conclusions

- Moderate membrane fouling by both hygroscopic and non hygroscopic particles in dry conditions (i.e. no condensation occurs) has minimal impact on water vapor flux of membrane samples.
- Heavy loadings of such particles on both 'coated' and 'uncoated' sides that form a thick cake layer (≥membrane thickness) can result in a slight flux decline (<5%) due to the added resistance of the cake layer.
- Deposition of hygroscopic nanoparticles on the 'uncoated' side of microporous substrate of membrane, in the presence of condensation, could significantly decrease water vapor transport through membrane samples (up to 15%)
- Air-side particulate fouling of composite membranes can be controlled and minimized by measures such as: (1) Exposing coated side of membrane to the stream with more nanoparticles; (2) Membrane module installations such that any potential condensation occurs on the coated side; (3) Periodic membrane cleaning (e.g. washing with distilled water)

References

[1] Goosen, M. F. A., et al. "Fouling of reverse osmosis and ultrafiltration membranes: a critical review." Separation Science and Technology 39.10 (2005): 2261-2297.

[2] Guo, Wenshan, Huu-Hao Ngo, and Jianxin Li. "A mini-review on membrane fouling." Bioresource technology 122 (2012): 27-34.

[3] Charles, N. & Johnson, D., 2008. The occurrence and characterization of fouling during membrane evaporative cooling. Journal of Membrane Science, 319(1-2), pp.44-53.

[4] Huizing, 2010. Coated membranes for enthalpy exchange and other applications, US20120061045.

[5] Sylvester, A., et. Al. "Impact of Environmental Tobacco Smoke on Membrane-Based Energy Recovery Ventilators", AAAR 35th Annual Conference, October 17 - 21, 2016, Portland, Oregon, USA.





