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An automated lab-scale flue gas permeation membrane testing system at the National Carbon Capture Center

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ABSTRACT

A constant pressure, mixed gas permeation testing skid was deployed at the National Carbon Capture Center to test membrane performance when continuously exposed to slipstream post-combustion flue gas. Small, laboratory scale membranes can be loaded for testing and the degree of automation allowed the skid to be run unattended for several weeks at a time. In this report, we share our experience in commissioning the skid and quantifying CO_2, N_2 and O_2 permeances of several membranes during the first round of testing. Dense films of polydimethylsiloxane and poly(bistrifluoroethoxyphosphazene) were tested with flue gas for approximately 20 h each. In addition, we successfully tested four thin film composite hollow fiber membranes made by a dip coating process, consisting of porous Torlon hollow fibers coated with a selective layer of poly(bistrifluoroethoxyphosphazene) or its mixed matrix with a metal organic framework SIFSIX-Cu-2i filler particles. Initial results suggest the polydimethylsiloxane showed comparable results to the literature data, but the coated hollow fiber membranes have lower CO_2 permeances relative to N_2 or O_2 permeances compared to their performance under idealized, dry, contaminant-free mixed gas conditions. While quantification of H_2O permeance was performed, we found it was affected by concentration polarization even with small membrane area and a low stage cut.

1. Introduction

The Carbon Capture R & D program conducted by U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL) is aimed toward accelerating the development of cost-effective CO_2 emission mitigation technologies. An important part of this program is the DOE's National Carbon Capture Center (NCCC)'s Post Combustion Carbon Capture Center (PC4) facility, where a pulverized coal flue gas slipstream supplied by the E.C. Gaston steam plant operated by Alabama Power is made available for various technology partners to demonstrate their carbon capture technologies in field trials [1–3]. Most of these partners constructed purpose-built testing skids aimed toward testing their own technology, typically at advanced bench or small pilot scale. For instance, Membrane Technology Research (MTR) recently completed a two year, 1 t/day post-combustion flue gas test with their Polaris™ membrane modules [1]. While the capability for testing membranes with real flue gas at NCCC-PC4 is attractive to many research programs in the US, the large scale and often specific or proprietary nature of these developer skids make it difficult for smaller research groups to test their most promising membranes without constructing their own testing skids, which takes significant time, expense and expertise. In 2014, when our team at NETL decided to construct a lab-scale membrane testing skid to be installed at the NCCC-PC4, we recognized that such a skid could be useful not only as part of our own membrane development effort [4], but also to provide a universal membrane testing platform at NCCC-PC4 that could help accelerate technology development for many other research groups.

This paper describes our successful effort to develop the NETL Post-Combustion Membrane Testing Skid (PCMS), the experimental challenges and considerations, and the promising initial results from our membranes. Despite the short-term and unoptimized nature of these demonstration tests, the PCMS was ultimately designed for long term minimally attended operation. Seven membranes, in both flat sheet film and hollow fiber formats, were successfully tested over short

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periods using flue gas supplied by NCCC. For all these membranes, CO_2, O_2, N_2 and water vapor permeance were quantified over a period between 15 and 22.5 h. The results generally agreed well with literature data or experiments performed using other permeation instruments at NETL but did hint of potential performance reduction even in pre-conditioned flue gas. This report of the experience gathered in constructing the PCMS will help the broader research community interested in undertaking a similar effort using real or simulated flue gas to accelerate carbon capture technology development.

2. Theory

The PCMS is a constant pressure (isobaric) mixed gas permeation system with a basic design that has been widely used and reported by many membrane research groups, including ours [5–9], emphasizing experiment automation to allow unattended operations for an extended period. Briefly, a membrane is sealed in a specialized pressure cell which isolates the feed (upstream) from the permeate (downstream) side, allowing gas exchange between the two sides to happen only by diffusion through the membrane. For a mixed-gas permeation measurement, it is important to minimize gas composition change over time on both sides that result from diffusion through the membrane. This is achieved by constantly flowing the feed gas at a particular flowrate and pressure on the upstream side to sweep the entire membrane face, and to do the same on the downstream side using a sweep gas. The experiment is typically set up such that the feed flow is much greater than the amount of gas permeating through the membrane to minimize compositional changes on both feed and sweep streams: the stage cut (i.e. ratio of transmembrane gas flow to the feed flowrate) is typically less than 1% [10]. The permeances of the individual components can be calculated by measuring the permeate stream (i.e. the stream consisting of sweep gas plus permeating components) flowrate and its composition. In the PCMS, because the major flue gas components are present cumulatively less than 1% in the permeate stream, we used a gas chromatograph (GC) to perform the analysis: therefore, the sweep gas chosen is the same as the GC carrier gas.

The permeance of a particular gas component A through the membrane is defined as the gas flux normalized by the partial pressure differential between the upstream or downstream side, or mathematically [11]:

$$Q_A = \frac{N_A}{p_{2,A} - p_{1,A}} \tag{1}$$

where Q_A is the permeance of component A (in this study, expressed in terms of gas permeation unit, or GPU, 10^{-6} cm^3(STP)/cm^2 s cmHg), N_A is the transmembrane gas flux, $p_{2,A}$ and $p_{1,A}$ are the upstream and downstream partial pressures of A, respectively. In this measuring scheme, the gas flux is defined in terms of the permeate flowrate and gas composition by:

$$N_A = \left(\frac{\dot{v}_l}{A}\right) x_{1,A} \tag{2}$$

where $\dot{v}_l$ is the permeate stream flowrate, A is the membrane area and $x_{1,A}$ is the mole fraction of component A in the permeate stream. Combining Eqs. (1) and (2), therefore, yields:

$$Q_A = \frac{\dot{v}_l x_{1,A}}{A(P_2 x_{2,A} - P_l x_{1,A})} \tag{3}$$

where P_2 and P_1 denote feed and permeate stream pressures, respectively, and $x_{2,A}$ is the mole fraction of component A in the feed stream. Whenever the selective layer thickness is known definitively, i.e. in the case of homogeneous thin film membranes, gas permeability (here given in the customary unit Barrer, 10^{-10} cm^3(STP) cm/cm^2 s cmHg) can be calculated by multiplying the individual permeance Q with the membrane thickness.

Table 1
Operation parameters for membrane testing during our December 2015 testing period (cf. Fig. 5).

Membrane temperature	40 °C
Initial argon purge time	45 min
Time to first sample	30 min
Sampling frequency	30 min
Sampling pattern	4 permeate to 1 retentate
Feed pressure	18.7 psia (1.27 bar)
Feed flowrate	10 cm^3/min
Sweep pressure	18.7 psia (1.27 bar)
Sweep flowrate	10 cm^3/min

Eq. (3) has an inherent assumption that the gas compositions on either side of the membrane are near constant throughout, i.e. the partial pressures of gaseous components of the feed stream are not significantly changed in the retentate, the partial pressures of permeated gases are very low in the permeate stream, and pressure drop along the length of the hollow fiber membranes is negligible. By keeping the experiment at low stage cut (< 1%), this condition was met for most components in the PCMS. However, it is worth paying special attention to water vapor, which typically has very high permeance through a membrane and is present at low concentrations in the feed stream. Thus, even a relatively small membrane area is sufficient to deplete water vapor content between the feed stream and the retentate stream significantly. In the case of hollow fiber membranes, water vapor concentration could also vary significantly along the membrane length [12,13]. Since we performed our hollow fiber experiments in a counter-current flow configuration with approximately equal pressure and flowrates between the upstream and downstream sides (cf. Table 1 in a latter section), the compositional change on the two sides were approximately balanced. Therefore, we still can use Eq. (3) to calculate the water vapor permeance in the hollow fiber membranes as a first approximation. Later we will show that the concentration polarization effect was significant enough anyway to prevent determination of the true water vapor permeance for these membranes.

3. Equipment design

3.1. Flow design

The PCMS was designed to test membranes using treated post-combustion flue gas from a pulverized coal combustion plant as the only expected feed stream. The flue gas from the Unit 5 boiler was pre-treated by, in order, hot-side electrostatic precipitation (particulate removal), selective catalytic reduction (NO_x removal), and flue gas desulfurization (SO_2 removal) before passing into the PC4's caustic scrubber and then into the PCMS. These pre-treatments removed most of the common minor contaminants: the SO_2 level was expected to be no more than 1 vppm and NOx was expected to be at trace levels, leaving CO_2, O_2, H_2O and inerts (N_2 and Ar) as the only components of interest in the flue gas from an analytical standpoint. The flue gas is introduced to the PCMS at ambient temperature, close to atmospheric pressure, and is always fully saturated with water. Accordingly, the PCMS was designed to draw the flue gas using a pump, partially dehumidify it, and then send a portion of this gas into the membrane feed side. Fig. 1 shows the flow diagram of the PCMS and Fig. 2 shows the PCMS as installed at the NCCC. Reducing the feed gas dew point helps to avoid water condensation in the system without heating it, preventing damage to our sensitive electronic flow components. The sweep gas chosen was argon, based on both cost consideration and the fact that quantifying argon permeance is not generally important in