

Elevated Test Pressure Significantly Reduces Dynamic Accumulation Oxygen Transmission Rate (ASTM F3136) Measurement Time for Barrier Packaging Films

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ABSTRACT

Measurement of gas transmission rates of materials is important for successful package design. The dynamic accumulation (DA) method (ASTM F3136) is becoming increasingly popular for measuring oxygen transmission rate (OTR) due to its simplicity and low cost. However, measurement time increases with barrier properties of materials, limiting measurement throughput. A dynamic accumulation measurement prototype capable of operating up to 1,000 psig was developed in order to accelerate gas transfer by boosting concentration gradients via elevated absolute pressures. Results show that measurement results were independent of test pressure while measurement times were substantially reduced. These results also suggest that gas transmission rate testing using the steady state approach (e.g. ASTM D3985) will also benefit from tests performed at elevated pressures by boosting signal and/or expanding the range of measurement, permitting measurement of higher barrier films than are currently possible.

Key Words:

Permeation, Gas, Oxygen, Oxygen Transmission Rate OTR, Pressure, Packaging, Modified Atmosphere Packaging, MAP, Dynamic Accumulation

INTRODUCTION

Gas transmission through packaging materials occurs by the process of permeation. Rates of transmission for specific packages or packaging materials are most often reported as a gas transmission rate in terms mols or milliliters of gas (at standard temperature and pressure, STP) per square meter of packaging/material per day (mol/m²/day or ml (STP)/m²/day). For the case of oxygen, the rate is referred to as the oxygen transmission rate (OTR). OTR specifications for packaging films are often reported at 23°C and normalized to a partial pressure difference of 1 atm.

Two approaches are commonly used to measure OTR and are referred to as dynamic accumulation (DA) (unsteady state approach described by ASTM F3136-2015) and coulometric method (steady state approach described by ASTM D3985-05). Recently, studies comparing these methods have been reported (Siro et al., 2010; Abdellatief and Welt, 2013). Siro et al. (2010) found fairly good agreement, while Abdellatief and Welt (2013) found no significant differences in results between the methods.

Limitations of both OTR methods potentially limit their applicability to specific OTR ranges. For the case of DA, as barrier properties of materials increase, time required to accumulate appreciable amounts of gas also increases, resulting in long test times. For the coulometric method, as barrier increases signal-to-noise ratio decreases, making it difficult for instruments to deliver dependable results.

The purpose of this work was to attempt to mitigate these limitations by exploiting elevated absolute pressures to amplify concentration gradients and accelerate gas transfer. Accelerating gas transfer should help to reduce measurement time for the DA method (unsteady state – ASTM F3136) and boost signal for the coulometric method (steady state – ASTM D3985).

THEORY

Abdellatief and Welt (2008, 2013) provided the derivation of the differential equation and analytical solution that describes the process used to obtain OTR by dynamic accumulation. In doing so, they described the Accomplished Oxygen Ratio (AOR) as:

$$AOR = \frac{(p_{O_2}^{ambient} - p_{O_2}^t)}{(p_{O_2}^{ambient} - p_{O_2}^0)} \quad [1]$$

Where p_{O_2} is the partial pressure of oxygen. Superscripts “ambient,” 0 and t refer to the oxygen rich side of the dynamic accumulation chamber, the initial partial pressure of oxygen in the accumulation chamber at the start of a test (usually zero if the accumulation chamber is completely flushed with an inert gas such as nitrogen) and the time of the experiment, respectively.

A simplified version of the resulting solution to the differential equation is:

$$-\ln(AOR) = OTR \frac{A}{V_{total}} \cdot t \quad [2]$$

Where A is the test gas transfer area through the sample (typically in m²), V_{total} is the volume of the accumulation chamber (typically in cm³) and t is time (typically in days). OTR can be determined from the slope of the line created by plotting $-\ln(AOR)$ versus time as follows:

$$OTR = |Slope| \frac{V_{total}}{A} \quad [3]$$

Measurement time of traditional DA operating at normal atmospheric pressure can be predicted using Equations 2. Consider an accumulation chamber with volume, V_{total} 8 cm³, and sample gas transfer area, A, of 0.002027m², testing packaging films with OTR values of 1, 10, 100 and 1000 ml/m²/day using both air and oxygen as the oxygen rich, ambient gas.

Table 1 shows that for films with an OTR of 100 ml/m²/day, test times would be expected to be around 1 day when testing with air and about 5 hours when testing with oxygen. However, for barrier films with OTR of 1 ml/m²/day, test times would be almost 100 days using air and several weeks using oxygen. While there is no theoretical limit to the level of barrier that can be measured using DA, test time can become a practical limitation as barrier increases.

OTR (ml/m ² /day)	Air	Oxygen
	p _{ambient} (atm)	
	0.209	1.000
1	2263	469
10	226	46.9
100	22.6	4.69
1000	2.26	0.469

Table 1—Test time in hours predicted using Equation 2 (excluding conditioning time) for films with various OTR values, where all tests are deemed to end when accumulation chamber oxygen partial pressure reaches 5 mbar.

One possible approach to reducing DA test time is to use gas sensors with greater sensitivity in order to discern accumulation rates of smaller quantities of oxygen. Work on improving sensor performance is ongoing by a number of researchers using ruthenium, platinum and palladium based materials (Cheng-Shane et al, 2011; Balezao, et al., 2008). Another way to reduce test time, however, is to increase the rate of gas transfer by increasing the concentration gradient and thereby increasing the driving force for mass transfer. With gasses, such as oxygen and nitrogen, concentration gradients are expressed as partial pressure differences. For the case of the typical DA test cell, the difference in partial pressure of oxygen is created across the material being tested (Figure 1).

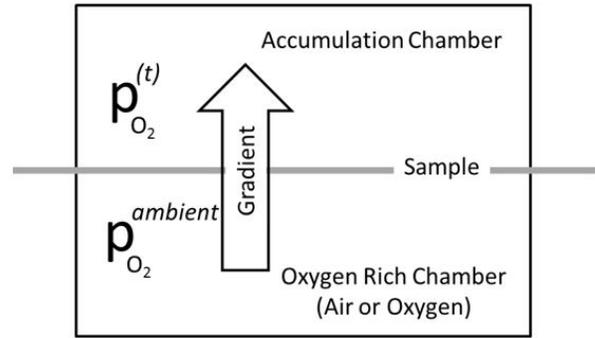


Figure 1--Simplified Dynamic Accumulation OTR Test Cell.

Typically, such tests have been performed at atmospheric pressure. When air ($p_{O_2} = 0.21$ atm) is used in the oxygen rich chamber and the accumulation chamber is initially flushed completely with nitrogen, the greatest partial pressure difference occurs at the beginning of the test, where

$$p_{O_2}^{(t)} = p_{O_2}^0 \quad \text{and} \quad (p_{O_2}^{ambient} - p_{O_2}^0) = (0.21 - 0) = 0.21 \text{ atm}$$

Similarly, when pure oxygen ($P_{O_2} = 1.0$) is used in the oxygen rich chamber, the greatest partial pressure difference is 1 atm. Equations 1-3 and Table 1 show that for the same material (constant OTR), use of oxygen instead of air reduces test time by a factor of approximately 5 (determined by the ratio of the partial pressures of oxygen in the oxygen rich gas, $1.0/0.21 = 4.76$).

Application of Dalton's Law suggests that performing DA tests at pressures above atmospheric pressure will increase partial pressure gradients, increasing gas transfer rates and reduce test times further, in sympathy with the ratio of partial pressures. Therefore, the same test acceleration as achieved by using pure oxygen instead of air at atmospheric pressure should be achievable by using air at an elevated absolute pressure of 4.76 atm, where the partial pressure of oxygen is 1 atm ($4.76 \text{ atm} \times 0.21 = 1 \text{ atm}$). To avoid stretching or damaging

samples, however, the accumulation chamber should be flushed, pressurized and purged with nitrogen at the same elevated pressure as the gas in the oxygen rich chamber to avoid differences in pressure across the sample. Therefore, high pressure DA is best performed with both chambers operating at matching elevated pressures.

Figure 2 shows expected time savings offered by DA operated at elevated pressures up to about 50 atm (750 psia) for a barrier film of 1 ml/m²/day.

Therefore, the purpose of this work was to (1) design, fabricate and test a dynamic accumulation cell capable of operating at elevated pressures up to 1,000 psig, (2) perform OTR measurements on a test barrier film at 200, 400 and 700 psig and (3) evaluate effects of test pressure on OTR measurement and measurement time.

While this work focused on effects of elevated pressure on DA measurements and test time, it is expected that effects of elevated pressure on steady state gas transmission measurements will similarly boost signal strength, thus expanding the range of measurement for the steady state method, permitting measurement of barrier materials that are not presently measurable.

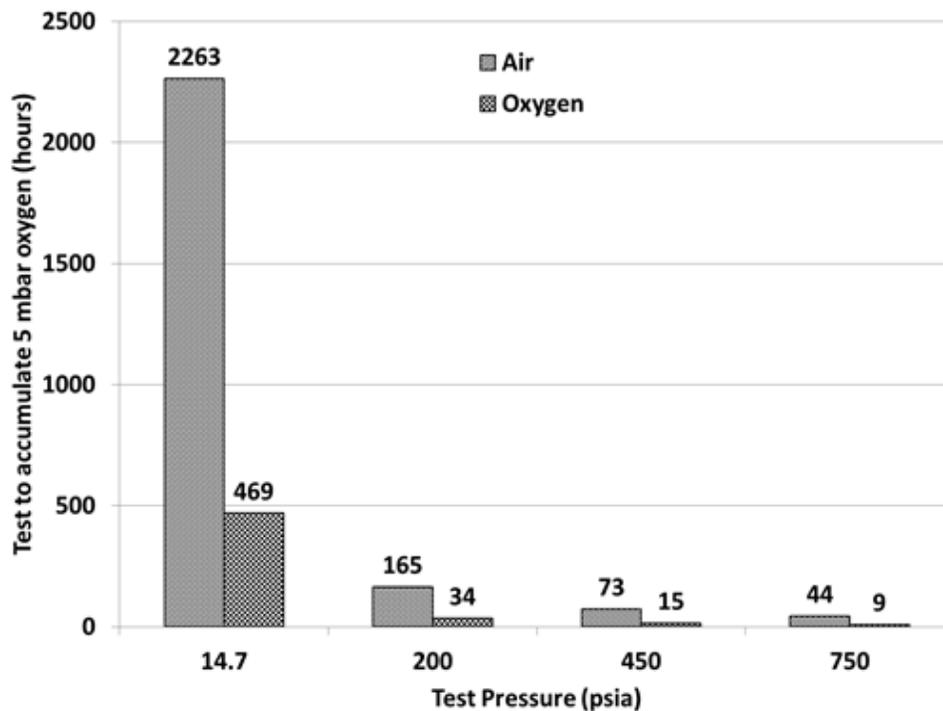


Figure 2--Test times in hours predicted using Equation 2 (excluding conditioning time) for a barrier film with OTR = 1 ml/m²/day, where tests assumed to end when accumulation chamber oxygen partial pressure reaches 5 mbar

MATERIALS AND METHODS

Design and Operation

A key consideration in designing a DA system that employs elevated oxygen pressure is safety. Specifically, all materials should be oxygen compatible and specially cleaned for use with pressurized oxygen. While higher pressures are possible, practical and safety considerations suggest an upper limit for high pressure OTR systems of 1000psig. Reasons for this practical design limit include:

- Typical oxygen and nitrogen compressed gas cylinders are filled to about 2000-2400 psig. Testing at any pressure requires supply gas at higher pressures. Since DA uses relatively little gas (Abdellatif and Welt, 2009), a reasonable number of measurements are possible when testing up to 1,000 psig using typical commercially supplied cylinders.
- The safety regime for compressed oxygen is viewed to change above 1,000 psig. While care should be exercised at any elevated oxygen pressure, extra special care must be taken when operating above 1,000 psig (Stoltzfus et al., 1996; Rosales et al., 2007).
- Many off-the-shelf components such as regulators, tubing, valves, fittings, gauges, etc. may be easily and cost effectively procured that are rated to operate at 1,000 – 3,000 psig, providing good safety margins when normally operating up to 1,000 psig. Testing at higher pressure will likely requires more costly specialized components.

Therefore, we chose to design our prototype system with an upper operating limit of 1,000psig. A schematic of our system is shown in Figure 3.

The high pressure DA system was designed to be operated in a particular manner in order to accomplish the following:

1. Purge the entire system, including both chambers with nitrogen.
2. Pressurize both chambers simultaneously to desired test pressure.
3. Isolate the accumulation chamber in order to commence a test.
4. Flush/exchange the oxygen rich chamber with pressurized oxygen or air supplied at the same absolute pressure as contained in the accumulation chamber so as to not stretch the sample.
5. Depressurize system without damaging the sample.

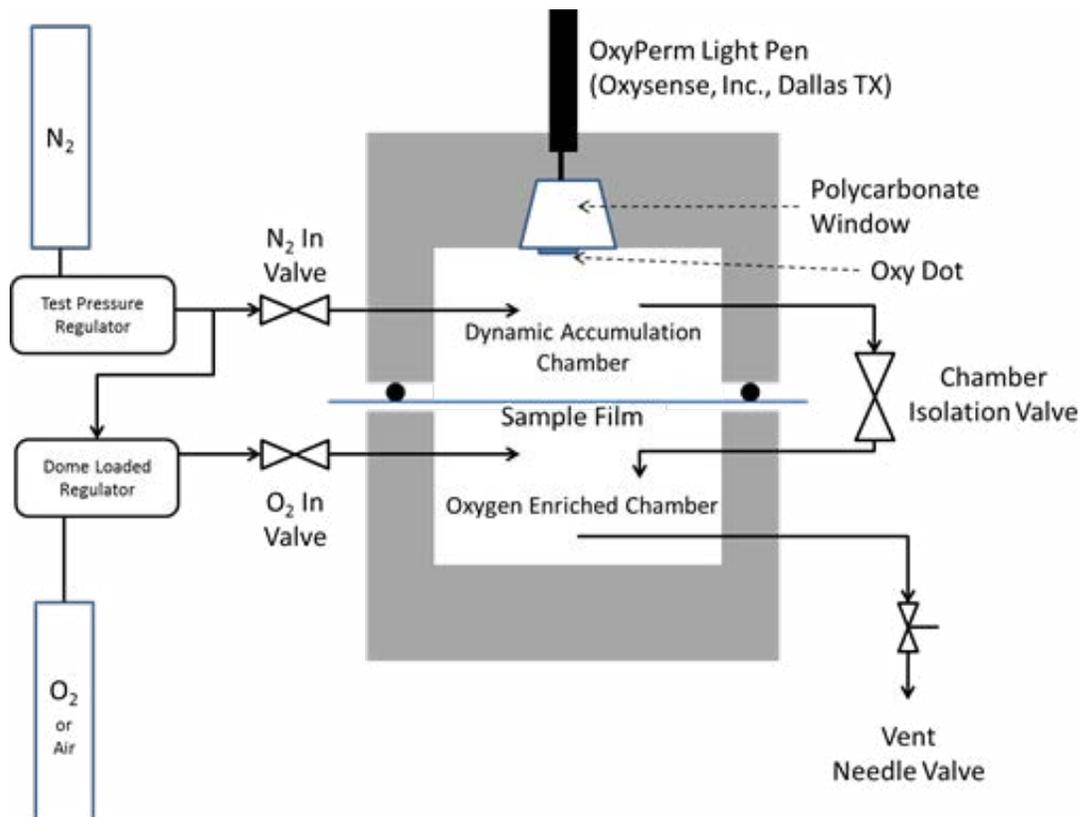


Figure 3--Schematic of high pressure dynamic accumulation system for measuring gas transmission rate

A key component of the high pressure OTR system is the Dome Loaded Regulator (Model RDN2-02-VVK-L, Swagelok, Inc., Solon, OH) used to supply oxygen at a pressure that matches the pressure set for nitrogen. The dome of the regulator is pressurized by pressurized nitrogen, providing automatic pneumatic-mechanical matching of oxygen to nitrogen pressures.

All tubing and compression fittings were made with 1/8" stainless steel and/or 1/16" NPT. The OTR test cell was machined from 3" 316 stainless rod.

All oxygen concentration measurements were made using a fluorescence based, optical oxygen analyzer ("Oxysense Analyzer") (Model 310, Oxysense, Inc., Dallas TX). Test samples were mounted on the flange surface of the Oxygen

Enriched Chamber (bottom chamber in Figure 3) using silicone grease. If necessary for the Oxysense Analyzer, a "high" oxygen calibration data point in air ($p_{O_2} = 0.21$) was obtained just prior to sealing samples between chambers. Prior to sealing the system, the chamber isolation (Model SS-41S2 Ball Valve, Swagelok, Inc. Solon, OH) and vent valves (Model SS-ORS2 Needle Valve, Swagelok, Inc., Solon, OH) were opened to avoid any possible pressurization that might occur simply from sealing the sample between chambers. Both gas inlet valves (Model SS-41S2 Ball Valve, Swagelok, Inc. Solon, OH) were closed. The nitrogen supply regulator (Victor Model SR4-0781-1448, ESAB, Inc., Florence, SC) was completely backed out as if set to deliver nitrogen at 0 psig. The oxygen supply regulator was set to 800 psig, which

was 100 psig higher than the highest expected test pressure in this study. Generally, the oxygen supply regulator should be at least 50-100 psig higher than expected test pressure..

After the High Pressure DA system was sealed, the nitrogen inlet valve (Model SS-41S2 Ball Valve, Swagelok, Inc. Solon, OH) was opened and the nitrogen regulator slowly adjusted to increase supply pressure just enough to provide flow in order to flush the system with nitrogen. During flushing, nitrogen flowed into the accumulation chamber, out through the isolation valve, into the oxygen rich chamber and out through the vent (Figure 3). At least 5-10 combined chamber volumes of gas were permitted to flow in order to completely flush the system. Once the system was flushed, a “low” oxygen calibration reading ($p_{O_2} = 0$) was made when Oxysense Analyzer calibration was necessary.

After flushing and calibrating, the vent valve was closed. The nitrogen regulator was slowly adjusted to increase nitrogen pressure to the desired test pressure. Once the desired test pressure was attained, the nitrogen inlet and chamber isolation valves were closed (Figure 3). Then the oxygen inlet valve was opened. Then the vent was then slowly opened to achieve purging flow of about 50-300 sccm. At least 5-10 Oxygen Enriched Chamber volumes were permitted to flow before commencing data collection for a test. We used a “purge-then-bleed” approach with oxygen, which involved a higher flowrate (~50-300 sccm) to purge the Oxygen Enriched Chamber with oxygen and then reducing flow to about 10 sccm for duration of the test.

When the Oxygen Enriched Chamber volume is sufficiently larger than the accumulation chamber (~5-10x), the vent valve may be closed for the duration of the test without incurring significant errors or modifying data reduction methods.

When tests were complete, the vent valve and gas inlet valves were closed. The Chamber Isolation Valve was opened and then the vent valve was

slowly opened to depressurize the system. Once depressurized, the chamber was opened in order to remove and replace samples for subsequent tests.

FABRICATION

We designed our system with cylindrical chambers with a 0.0508 m (2.00 inch) inner diameter and 0.0762m (3 inch) outer diameter, resulting in a gas transfer area of 0.002027m² and a sample mounting shelf 0.5 inches (0.0127m). The volume of the accumulation chamber was measured to be 12.7 cm³. The volume of the Oxygen Enriched Chamber was approximately 100 cm³.

All chamber materials were machined from 316 stainless steel except for a polycarbonate window through which the Oxysense Analyzer transmitted light to an OxyDot™ (Oxysense, Inc. Dallas, TX) mounted on the inside of the Accumulation Chamber. A picture of the actual prototype device is shown in Figure 4.



Figure 4--High Pressure OTR Prototype. Top of chamber shows (left to right) Nitrogen Inlet Valve, Oxysense Analyzer light pen, Chamber Isolation Valve.

TESTING

A moderate barrier test film was used to evaluate performance of the high pressure dynamic accumulation OTR measurement technique (Bemis Yellow Lidstock, Mat#W07-000711, Oshkosh, WI). Each test used a new sample cut with scissors from a master roll. Samples were approximately 10cm x 10 cm. OTR measurements were run at 200, 400 and 700 psig with 10 replicates at each test pressure. Commercial grade compressed nitrogen and oxygen were used for all tests. Accumulated oxygen measurements were made using an Oxysense 310 Optical Oxygen Analyzer coupled with Oxysense GenIII software running in Film Permeation mode (Oxysense, Inc., Dallas TX). For this study, raw accumulated oxygen data were exported to Excel (Microsoft, Redmond, WA) for manual analysis as described by Equation 3.

RESULTS AND DISCUSSION

Results are shown in Figures 5 and 6. Figure 5 shows average measured OTR values with error bars indicating plus and minus one standard deviation. Figure 5 shows that measured OTR values were not affected by test pressure.

Figure 6 shows average test times, in hours, (plus and minus one standard deviation) required to accumulate 5 mbar oxygen ($p_{O_2} = 5$ mbar) from an initially purged state ($p_{O_2} = 0$ mbar). Use of 5 mbar was chosen as an arbitrary, but practical end-point for the purpose of the test-time comparison. Figure 6 shows that increasing test pressure substantially reduced measurement time.

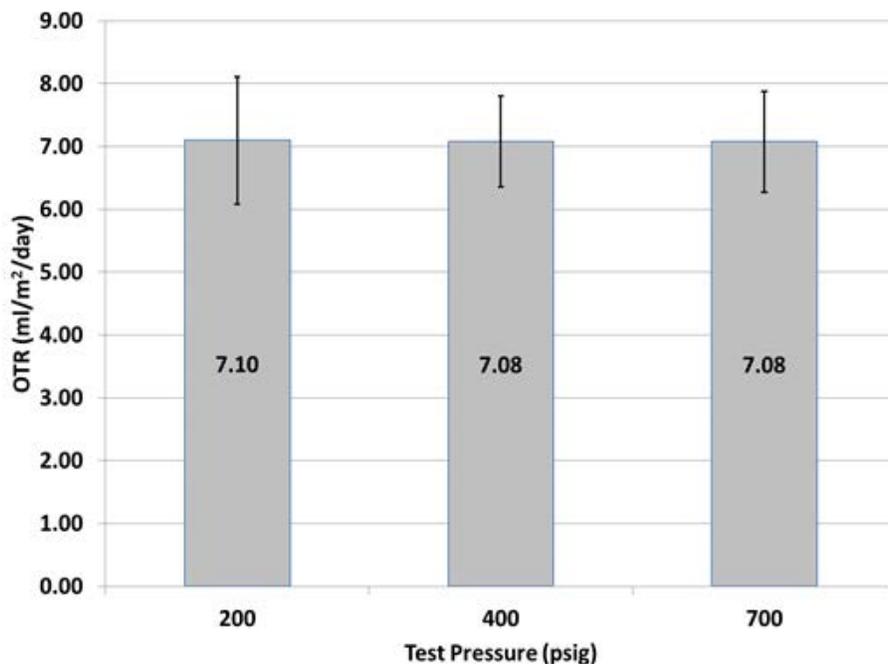


Figure 5--Average OTR values measured at different elevated pressures show that OTR result is independent of absolute test pressure.

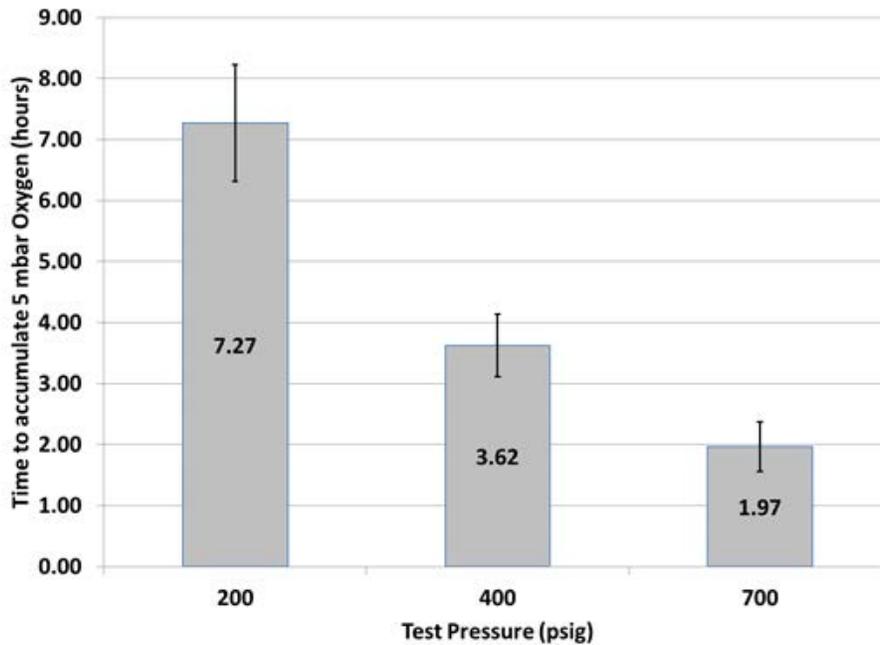


Figure 6--Average OTR test times at different absolute test pressures show that test times are reduced by increasing absolute test pressure.

CONCLUSIONS

This work showed that elevated absolute pressures can be exploited in order to drastically reduce gas transmission rate measurement times for the dynamic accumulation technique (ASTM F3136-15). A prototype was developed capable of performing measurements at pressures up to 1,000 psig. An operational protocol was developed to pressurize, test and depressurize without damaging samples.

While not demonstrated here, this work suggests that OTR measurements made using high pressure with the steady state method (ASTM D3985) would also benefit from enhanced signal-to-noise ratio, thereby permitting measurement of barrier materials greater than what is possible at atmospheric pressure. Therefore, exploitation of high pressure in gas transmission rate measurements

promises to extend the envelope of what is currently possible to measure. Intellectual property related to high pressure gas transmission rate testing is patent pending (Welt, 2013).

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