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Procedures to Assess Material Degradation in Membrane Diffusers

A dissertation submitted in partial satisfaction of the
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by

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ABSTRACT OF THE THESIS

Procedures to Assess Material Degradation in Membrane Diffusers

by

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Master of Science in Civil Engineering
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With so many types and brands of membrane diffusers that are available in the market today, buyers often have difficulty choosing one. Many times buyers have to base their decisions solely on the product catalogs, which may not be very objective. This thesis describes laboratory experiments that simulate stresses that membrane diffusers undergo during operation, and describes techniques to quantify material degradation in membrane diffusers. Four different brands of ethylene-propylene-diene (EPDM) membrane diffusers were subjected to stress and soaked in degrading chemicals for six weeks. Through out the experiment, the Young's modulus, hardness, and orifice creep of the membranes were monitored. The findings showed that different brands of EPDM diffusers behaved differently, and measuring orifice creep is a better way to quantify

membrane diffusers degradation in comparison to hardness and Young's modules measurements.

INTRODUCTION

After the energy crisis of the 1970's, more and more municipal wastewater treatment plants that utilized the activated-sludge process have switched to fine pore aeration systems. Various types of materials have been used to manufacture fine pore diffusers. These include ceramics, filament-wound tubes, sintered plastics, and punched plastics or polymers, generally called membranes. Two types in common use today are porous ceramic discs or domes and punched, polymeric membranes in the shape of discs, tubes or sheets.

Ceramic stones, in the form of domes, were developed in England in the 1960's. These domes were imported to the United States but used at only a few treatment plants. The Los Angeles Glendale Water Reclamation Plant was one of the first plants to use ceramic dome diffusers on the West Coast. A single 9 m wide by 90 m long tank was equipped with dome diffusers in the 1970's for evaluation. A flat ceramic disc diffuser was also available in the 1970s (Aberly *et al.*, 1974) but was not installed in many locations.

Ceramic plates were used extensively in the United States. These plates were generally more porous than currently available ceramic diffusers [Warriner and Rooney, 1992]. Ceramic tubes have also been used. Ceramic diffusers are in common use today and most installations use a ceramic disc. The discs use a locking ring, which is a preferred feature over other types of hold-down techniques.

A problem with all fine pore diffusers is scaling and fouling [Houke *et al,* 1981; Boyle *et al,* 1983;] that build up on its surface. Ceramic diffusers developed a reputation for fouling, with resultant increase in pressure drop and reduction in transfer efficiency. It is now known that all fine pore diffusers require periodic cleaning. Ceramic diffusers may be cleaned in a variety of ways, but most methods require that the aeration tank be emptied to allow access for physical cleaning [Boyle and Hung, 2001]

Flexible membrane diffusers were developed to overcome some of the disadvantages of ceramic diffusers. It is believed that a flexible membrane is more resistant to fouling, and can be bent to dislodge fouling or scaling material. Also membrane diffusers are punched, so that the orifice size and number can be engineered to optimize performance [Ashley *et al,* 1991; Redmond, 1994]. Ceramic diffusers have a range of pore sizes and diameters. Fouled ceramic diffusers often show high air flux in small areas, which creates bubbles with large diameters, and destroys aeration efficiency.

A problem with membrane diffusers is a deleterious interaction of the membrane and wastewater. The flexible material may harden, reducing airflow and change efficiency [Stenstrom and Iranpour, 2001]. In other cases, the membrane may soften and expand. The reasons for problems are not universally known and are usually attributed to site-specific conditions, such as wastewater characteristics, and may depend on the membrane material.

There is no consensus as to which diffuser material is better. Treatment plant owners may prefer one material to another for arbitrary reasons, or may have had good or bad experience with a particular material. Owners and consultants often prefer membrane diffusers for biological nutrient removal plants, because the airflow may need to be reduced to very low rates. Reduced airflow is generally implicated in ceramic diffuser fouling. Membrane diffusers are believed to tolerate low or zero airflow.

There have been many investigations on ceramic diffusers, but there are only a few on membrane diffusers. Many of the issues relating to ceramic diffusers apply to membrane diffusers, such as mass transfer characteristics, orifice size and bubble formation, and perhaps fouling mechanisms. However, there are issues unique to membrane diffusers. One issue is the problem of material degradation.

The objective of this thesis is to investigate degradation of membrane diffusers, specifically material deformation of ethylene-propylene-diene (EPDM) membrane diffusers and its effects on performance, as part of overall operational. Membrane diffusers performance was assessed by examining orifice characteristics in membrane sections exposed to varying conditions. Oxygen transfer efficiency (OTE), which is strongly affected by orifice size, can be predicted or correlated to changes in orifice characteristics.

The thesis includes a background chapter, which consists of two main topics: polymer degradation and fouling mechanisms. The next sections are devoted to tests and devices that were used in the experiments described in this thesis, followed by a section that explains the procedures of this experiment and description of materials/ specimens used. The last section discusses the results of the experiments and conclusions.

Although the experiments described in this thesis are about mechanical degradations in polymer materials, the thesis discusses material degradation only briefly. The reason is because this thesis was written by, and was to be read primarily by environmental engineers. This thesis also dedicates some amount of discussion on fouling mechanisms, because failure in operation of membrane diffuser is caused by both material degradation and fouling. Hence, not mentioning fouling mechanisms would be an incomplete overview of overall operational failure.

BACKGROUND

In general, failure in porous media occurs as a result of material clogging. Both organic and inorganic material can accumulate in the porous media or on its surface and can partially or completely cover media pores. Membrane diffusers are also prone to material degradation types of failure, i.e.: hardening, softening of material, or any changes in the properties of material. Any material changes are usually harmful to transfer efficiency, since the manufacturer has optimized the diffuser characteristics for the new or unaltered membrane properties. Both material degradation processes and clogging of organic and inorganic material over membrane surfaces are covered in background of this thesis.

Types of Polymer Degradation

EPDM, or ethylene-propylene-diene is the fastest growing all-purpose elastomer[*] on the market today. EPDMs have several advantages that make them desirable materials: excellent resistance to ozone and oxidation without the use of anti degradants, low temperature flexibility, color stability, and the ability to accommodate large quantities of filler and oil without creating unnecessary instability [Gamlin, 2003], and wide range of operational temperature. About 40% of the diffuser membranes in the market today are made of EPDM.

EPDM, like any other polymer material is susceptible to degradation. It is important to study degradation process in polymers in order to understand membrane diffuser failures, because degradation processes change material properties of membrane diffusers.

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[*] Elastomers are a subpart of polymers; however since the discussion of this thesis is limited only to EPDM, which is an elastomer, the term ‘elastomer’ and ‘polymer’ are used interchangeably.

All polymers, and more importantly elastomers, are sensitive to elevated temperatures, mechanical stresses, harmful fluids, and radiation [Kelen, 1983; Gent, 1992]. Each of these factors will be discussed in more detail below.

Heat degradation is not relevant for membrane diffuser application in common activated sludge processes. Heat becomes a significant factor only when the polymer is used in an environment where temperature is 40% or more of the melting temperature of the polymer. However, elevated temperatures are often used in experiments to accelerate degradation processes [Kelen, 1983], where long experiment time is undesirable.

At highly elevated temperature all rubbery/ elastomer materials will undergo degradation reactions, which may lead to loss of physical properties. At moderately elevated temperature rubbery material will undergo additional cross-linking, which causes hardening [Gent, 1992]. Different types of materials have different sensitivity to temperature. EPDM's highest service temperature is about 125^o C, and it varies in accordance to substances added to EPDMs to alter their properties. Radiation has a similar effect on polymer degradation as temperature, has little relevancy to activated sludge processes.

Mechanical degradation includes every kind of mechanically induced breakdown of material, such as: irreversible deformation, cracking, fracture, and fatigue of polymeric bodies under both static and dynamic loading [Kelen, 1983]. While the types of mechanical degradation are numerous, only a few are applicable to membrane diffuser usages. Creep and fatigue are important degradation mechanisms. Creep results from applying static load to material, usually under elevated temperatures. Static load can cause a progressive increase in deformation as a function of time. There are two types of creep in a rubbery material, physical creep, due to molecular chain slippage, and chemical creep, due to molecular chain breaking [Gent, 1992].

The other type of mechanical degradations is fatigue, which results from applying cyclic loading-unloading to a material. Depending on how membrane diffusers are used, they can experience creep or fatigue. Turning on a blower for a long period of time resembles creep, and turning on and off blower in short period interval resembles fatigue.

Membrane diffusers are always operated in fluid environment. Elastomers in general are not completely resistant to fluids. Elastomer materials tend to absorb liquid and become weak. Different types of liquids affect elastomers differently. Organic liquids generally weaken elastomers by physicals means only, while acidic and alkali attack them chemically [Gent, 1992]. A softening/ weakening of elastomers in general indicates absorbency of solvent. If the solvent evaporates, the elastomer may resume its original hardness [US EPA Office of Research and Development, 1989].

Liquid uptake by elastomer is a two steps process: absorption that occurs on surface of elastomer, and diffusion that penetrates further. These processes depend on temperature, type of fluid, and material properties [Crank, 1975; Cussler, 1984].

Fouling Characterization and Mechanism

Fouling in fine pore aeration systems is a concern because fouled membranes cause operational problems such as increases in Dynamic Wet Pressure (DWP), or decreases in oxygen transfer efficiency (OTE), and increase in bubble release vacuum (BRV) [US EPA Office of Research and Development 1989]. Increases in DWP or BRV result in increased system pressure and power costs. A decrease in OTE requires greater airflow rates, which also increases power cost.

Different authors characterized fouling differently. [Boyle *et al,* 1983] in his studies on ceramic diffuser fouling classified fouling into three types: A, B, and C. Type A is characterized by accumulation of inorganic foulants such as particles and participates, which were not removed in primary clarifiers. Type B fouling is caused by biofilm formation composed of bacterial cells and polysaccharides produced by microbial metabolism. Type C fouling is caused by inorganic particles trapped within the bacterial matrix. In general the term fouling refers to organic material clogging, and the term scaling refers to inorganic material. However, since fouling and scaling process rarely occur independently in activated sludge, the terms are often used interchangeably.

Other fouling classifications are documented in US EPA Design Manual [US EPA Office of Research and Development, 1989]. It characterized fouling into two types. Type I is similar to type A fouling, and type II is similar to type B fouling described in the preceding paragraph.

Epstein [1983] proposed a 5 x 5 matrix to describe fouling. Although Epstein's classification was based scaling in boilers and heat exchangers, Epstein's proposal can be applied to membrane diffuser fouling. Others have adapted Epstein's fouling matrix to other systems. Sheikholeslami [1999] used Epstein's 5 x 5 matrix for reverse osmosis (RO) membrane fouling.

Epstein's five major components of fouling are crystallization/ precipitation, particulate (deposition), biological (fouling), corrosion, and chemical reaction fouling, although corrosion and chemical reaction fouling are unlikely to occur in common activated sludge processes. Chemical reaction fouling can involve both inorganic and organic materials, however, it seems that Sheikholeslami [1999] only refers to chemical reaction fouling of organic material, which occurs frequently in petroleum refining. In addition, inorganic chemical reaction fouling overlaps with fouling from precipitation reactions. Therefore to avoid confusion, chemical reaction fouling is limited to organic material.

Both particulate and crystallization fouling are caused by inorganic salts such as silica. Silica (SiO_2) may precipitate as monosilic acid, $Si(OH)_4$ or more in a complex geometry as colloidal silica, gypsum ($CaSO_4 \bullet 2H_2O$), calcium carbonate ($CaCO_3$), or other unknown precipitates. Precipitation of inorganic salts usually does not occur until a high concentration, or saturation value, is exceeded. The saturation values of inorganic salts are not constant, and depend on the nature of inorganic aquatic chemistry in the surrounding system. If the concentration in solution is high enough, it is possible that precipitants will grow as large crystals as opposed to settling as single particles. Particulate matter such as wastewater suspended solids (TSS) or bioflocs (e.g., mixed-liquor suspended solids, MLSS) may worsen or inhibit precipitation rates, depending on the type of particulates in suspension. TSS may have a scouring affect and inhibit fouling, or may provide more surface area for nucleation and promote crystallization [Sheikholeslami, 1999].

Particulate deposition and crystallization usually occur in a symphony. In a case where solid materials promote crystallization, particulate deposition usually occurs first as it provides surface area for nucleation/ crystallization [Sheikholeslami and Tan, 1999; Sheikholeslami, 1999]. Once crystallization occurs, the deposition rate increases, and more surface area for nucleation is available. The reactions then become a cycle and both nucleation and precipitation occur at progressively increasing rates, until equilibrium of inorganic material in dissolved and solid forms is achieved.

In order for scaling from inorganic salts to occur, salts must attach to membrane surfaces. More than one transport mechanisms may be responsible for transporting foulants to the membranes surface: settling flux of the particles, flux due to diffusion, and impingement. An upward flux of particles due to bubble rise with entrapped particles may decrease particle flux to diffuser surfaces. After arriving on membrane surfaces, particles must attach to the surface to become a foulant. Van der Walls, electric double layer and Born energies of particles are responsible for attachment [Sheikholeslami, 1999].

The attachment process for inorganic particulates is greatly influenced by, the characteristic of membranes surfaces, hydrodynamics of the flow, and water quality parameters, such as pH, hardness and CO_2 concentration. While there is not much that can be done to improve water quality and hydrodynamics, engineers may make changes on membrane surfaces characteristic to help control fouling or scaling. A membrane that has rougher surfaces tends to be more susceptible to particulate fouling, since the concave surfaces provide shelter to prevent particle re-suspension, and convex surfaces provide more surface area for nucleation.

Choosing hydrophilic or hydrophobic membranes can also help in reducing fouling. Hydrophilic or hydrophobic properties of the membrane affect the attractiveness of bacteria to membrane surfaces [Marshal, 1976]. For example, if the bulk water has a high concentration of negatively charged colloids, a negatively charged membrane can reduce fouling [Mulder, 1996].

The next item in the matrix is biological fouling. Biological fouling occurs in a water body that has microorganisms and nutrients, which make an activated sludge basin an ideal place for biological fouling to occur. In order for bacteria to grow, they need surfaces for attachment (i.e.: membrane diffuser surface), and organic materials as a source of nutrients. Therefore both bacteria and organic material must come in contact with membrane surfaces. The arrival process of organic material on membranes surfaces is similar to those of inorganic salts transport mechanisms.

For microorganisms, their transport to the surface in a turbulent environment may be governed by frictional drag [Characklis, 1981], and turbulence down sweep [Lister, 1981]. However, when the diffusers are not operating and liquid is quiescent, other mechanisms such as simple deposition and Brownian motion [Marshal, 1976] may govern the transport process.

Once microorganisms and nutrients arrived on the membrane surface microorganisms attach themselves and multiply, in a processed called 'colonization'. Different authors proposed slightly different models of bacterial growth on surfaces in environmental/ chemical engineering processes [Caldwell, 1983; Gilbert, 1983; Caldwell and Lawrence, 1986], but in general the colonization processes consists of the following steps. First bacteria grow and multiple until monolayer is formed. If growth continues, the layer becomes thicker and the attachment becomes irreversible. At this point these bacteria have embedded themselves in a network of extra cellular polymeric substance, commonly called a biofilm. During the colonization process other particulate like inorganic salts may deposit in biofilm, and worsen the fouling.

Some bacteria may also produce acid that degrades the membrane even more. Bacteria that are embedded in the very fist layer of the biofilm, as their environment become oxygen deficient, may switch to anaerobic metabolism which produces acid products. This is similar to the processes that cause human tooth decay.

Regardless types of fouling that occur on diffuser membrane surfaces, all fouling mechanisms have two things in common: transport of fouling materials to the membrane surfaces, and attachment. While altering membranes properties will not affect transport processes, doing so may influence attachment processes. Therefore, creating a diffuser membrane that is resists degradation and repels fouling material is the goal of research.

Figure 1--A fouled membrane diffusers is being tested. The fouling in the middle and left sections of the membrane diffuser are worse than the right section. The right section of the membrane diffuser produces more uniformed and smaller droplets.

TESTS & MEASURING DEVICES

In the experiment described by this thesis, three tests were used to assess degradation: Young's modulus, hardness (Durometer), and a specialized creep test conducted in heated graduated cylinders containing different fluids These tests were chosen based on practicality, repeatability and appropriateness.

Young's Modulus

An instrument for measuring Young's modulus was used in this thesis that was similar to instruments described by ASTM D412 (in this thesis this instrument will be called small load cell apparatus), except that the shaft that controls elongation of the specimen was driven manually instead of by a motor, see Figure 2 for small load cell apparatus. According to the ASTM D412 procedure, uneven rate of shaft turning may cause reduced precision. A different rate of elongation allows elastomer bonds to adjust and rearrange themselves over different periods, which means an uneven rate of elongation may result in measuring a biased Young's modulus.

Measurements of specimen stresses were taken every 2 mm, or about 0.35% of elongation, until 3.51% elongation was reached (see Figure 3 for specimen dimensions). Young's modulu was determined by calculating a slope of stress-strain curves. A least square method was used to calculate slopes.

The small load cell apparatus does not measure the stress directly. A load cell responds to the force experienced by the specimen, and the output is expressed in volts. A conversion from volts to N (Newton) must be made experimentally, and functions as a calibration curve (see Appendix II for the calibration procedure). Once forces in Newton units were obtained, a stress can be calculated by dividing forces with the cross sectional area of the specimen. The cross sectional area is the membrane thickness times the width of narrow section, or W in Figure 3.

To address the issue of reduced precision in measuring Young's modulus due to uneven rate of elongation, several repetitive tests were conducted on a single rubber band. It was believed that the Young's modulus of the rubber would not change with repetitive stretching, and that the test-to-test precision of the small load frame could be evaluated. Table 1 shows the results of five repetitive tests, conducted at one-minute intervals. The modulus did not change with repetitive testing and the test-to-test variation was small and did not show a trend. The coefficient of variance was found to be very small, 0.74%, and it was concluded that the small load apparatus gives a consistent result and very close to the true value.

Durometer, Type A

A Durometer is an instrument used to measure hardness of non-metallic material. Hardness according to ASTM is defined as the resistance to indentation as measured at a specific condition. The test is described in the American Society for Testing and Material specification as ASTM D2240. There are four types of Durometer: A, B, C, and D. Type A is the most appropriate for rubbery material, and type D is used for plastic or ebonite material. Care should be taken when using a Durometer, the dimensions of the test piece or specimen must be large enough to permit measurement at least 12 mm from any edges, and attain a minimum thickness of 6 mm. However, given the dimensions of the specimen used in this experiment, it was impossible to comply with these guidelines. Failure to follow these guidelines may yield in an "apparent" hardness value. In a test where real value of hardness is not necessary, an “apparent” value is acceptable since an “apparent” value still can be useful for comparison purpose [Gent, 1992]. The primary value of hardness for diffuser testing is to show changes or trends.

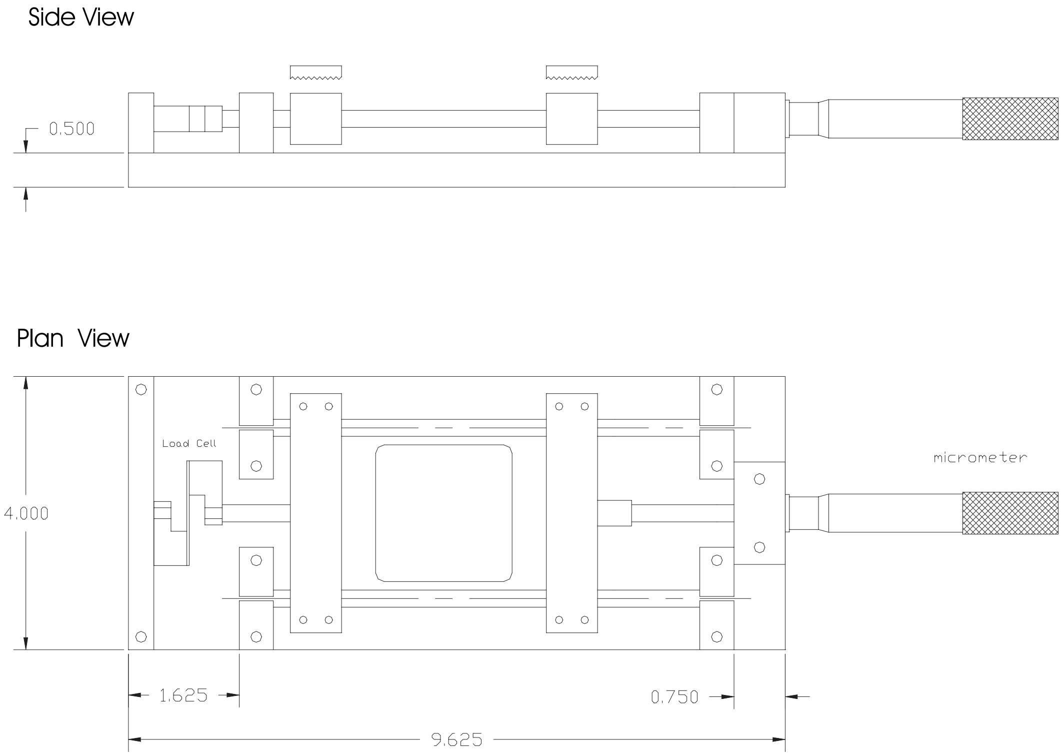
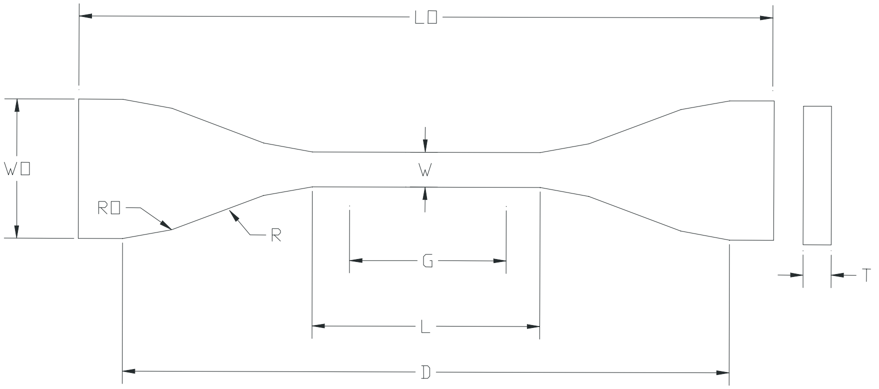


Figure 2--Micro load cell.



Dimensions (mm)

W Width of narrow section: 12.9
L Length of narrow section: 57.0
W□ Width overall: 25.5
G Gage length: n/a
D Distance between grip: 80.0
R Radius of fillet: n/a
R□ Outer radius: n/a
T Thickness: see: Table 1
L□ Length overall: 101.5

Figure 3--Specimen dimensions (adapted from ASTM D638).

For the experiment described in this thesis, measurements were taken five times, and average value was recorded. Table 2 provides various hardness values for different brands of membrane diffuser that are available in the market.

Orifices Creep

The formal mathematical definition of creep is:

$$\text{Creep } \% = \frac{\Delta l}{l_o} \bullet 100 \tag{1}$$

where Δl is elongation after removal of stress, and l_o is the initial length of a specimen. The specimen dimensions used in this study are shown in Figure 3, and the dimension L represents l_o in equation 1.

For membrane diffusers, the critical property is not the membrane length, but the orifice opening. The goal was to determine how much the orifice opening dilated, after the specimens were subjected to static load for defined periods of time. Orifice opening is of critical importance because it controls bubble size and transfer efficiency.

Orifice opening was determined by microscopic observation. Specimens were placed under a low power (6 to 100x) stereoscopic microscope and the widest distance between two the two sides was measured. To measure orifice opening at operating pressure, the membranes were placed under stress equivalent to membrane backpressure of 4.48, 8.97, and 13.4 kPa (18, 36, and 54 inches of H_2O pressure condition, and 18 inches of H_2O is the typical DWP of an EPDM membrane diffuser in operation). The stress used in the load frame was calculated as follows:

$$\Delta l = Y \bullet \Delta p \qquad (2)$$

where Y is Young's modulus and Δp is the Hoop's stress or, S_1 (see Appendix 1), caused by DWP acting on internal membrane wall. The membrane was placed in the load frame and stretched the appropriate distance. Orifice opening was measured using the microscope and a calibrated scale.

Micrometer

A micrometer is an extremely precise instrument used to measure specimen's thickness. A Mitutoyo model no. 227-101 was used. This micrometer is designed to be used with flexible materials. It has a pressure sensor so that each measurement can be made at the same compression of the specimen.

Tests	Young's Modulus (N/m2)
1	6.63E+05
2	6.73E+05
3	6.75E+05
4	6.66E+05
5	6.71E+05
Ave	6.70E+05
Std. Dev.	5.19E+03
Coefficient of varriance	0.77%

Table 1--Rubber band Young's modulus over 5 tests and its statistical values.

Material	Thickness (mm)	Durometer
Amber high den. (new)	0.65	84.95
Amber low den. (new)	0.67	84.68
Berlin (new)	1.68	56.10
Berlin (old)	1.82	56.30
EPDM 05-I, PU / EPDM 06-T, PU (new)	1.81	53.00
EPDM 480 N3-L PU / EPDM N4-T PU (new)	1.65	49.50
EDI Polyurethane Black (new)	0.68	88.93

Table 2: Hardness and thickness of several membrane diffusers.

EXPERIMENT METHODS AND MATERIAL

Experiment Methods

Four different types of membranes diffuser were cut into dog bone shapes. Cut membranes are termed specimen(s). Dimension of the dog bone-shaped/ specimen is in accordance with ASTM D638 (see Figure 3). There were 20 specimens from four different brands of membranes subjected to five different solutions.

Each of these specimens was placed in graduated cylinders containing various degrading solutions. Each specimen was loaded by hanging a lead anchor, weighing approximately 197 grams (7 ounces) to the specimen, which is approximately equivalent to a pressure of 18 inches of water (details on this calculation can be found in appendix A). Then cylinders were placed in a hot water bath to elevate the temperature to 80 degree Celsius. Four other specimens were not subjected to load but were put in DI water, also at elevated temperature. These four specimens served as controls.

Every two weeks all specimens were relieved from loads and taken out from the degrading solutions to dry at room temperature. The next day, after drying the specimens for about 24 hour at room temperature, all twenty specimens were tested for their young's modulus, hardness, and orifices creeps.

Materials

All diffusers membranes used in this experiment were made of EPDM. Four different manufacturers produced these membranes, and they were punched differently. The thickness and the orifice width of each membrane are listed in Table 3. Each specimen was labeled with figures and letters**.** Figures in labeling indicate brands of membranes, and letters indicate type of solutions. See Table 4 for detailed information about specimens

Brands	Thickness (mm) *	Orifice Width (mm)
1	1.94	1.20
2	1.77	2.40
3	1.65	3.00
4	1.74	1.80

Table 3: Various information on the four different membrane diffusers.

*: Average values of 20 measurements.

Label	Solution	Subjected to wt
1	DI water	No
1A	DI water	Yes
1B	5% glacial acid	Yes
1C	5% Hexane	Yes
1D	Missing specimen	-
2	DI water	No
2A	DI water	Yes
2B	5% glacial acid	Yes
2C	5% Hexane	Yes
2D	5% Isopropyl Alcohol	Yes
3	DI water	No
3A	DI water	Yes
3B	5% glacial acid	Yes
3C	5% Hexane	Yes
3D	5% Isopropyl Alcohol	Yes
4	DI water	no
4A	DI water	yes
4B	5% glacial acid	yes
4C	5% Hexane	yes
4D	5% Isopropyl Alcohol	yes

Table 4: LIST OF SPECIMENS SOAKING SOLUTIONS

RESULTS AND DISSCUSSION

After six weeks of soaking there were no obvious trends in changes in Young's modulus and hardness. Figure 4 shows Young's modulus and hardness for each membrane as a function of time and solution. Both hardness and Young's modulus fluctuated over time. By the end of the sixth week most specimens showed slightly increased Young's modulus.

Hardness results were also mixed. Membranes soaked in acetic acid (HAC) generally softened as shown in Figure 4 for membrane types EPDM 1, 2 and 4. Membrane types EPDM 1 and 2 showed no change in hardness for the other chemicals. Membrane types EPDM 3 and 4 showed small increase in hardness for the other chemicals.

A dramatic swelling was observed in EPDM 4 that was soaked in acetic acid (see Figure 7). The specimen elongated and its thickness nearly doubled. Figure 7c and figure 7f shows the orifice opening before and after soaking when subjected to stress equivalent to a membrane backpressure of 4.48 kPa.

Orifice opening creep showed a consistent trend. All orifices opening dilated over time for all chemicals, except those at sixth week. Orifice opening is inversely proportional to Young's modulus. Since Young's modulus increased, it is expected that orifice opening would decrease. Orifice opening results are presented in Figure 5 for EPDM 1 and EPDM 2, and Figure 6 for EPDM 3 and EPDM 4.

To relate orifice opening and bubble size, the following empirical formula can be used:

$$a = \left(\frac{3}{2} \frac{R\sigma}{\Delta\rho g} \right)^{1/3} {}^{*} \qquad (3)$$

where a = bubble radius, cm

R = orifice radius/ opening, cm.

σ = surface tension, dynes/ cm.

g = gravitational constant, cm/sec^2

$\Delta\rho$ = difference density between the bubble and the liquid, gr/cm^3.

According to formula above (3), bubble diameter is proportional to the cube root of the orifice size. It means that the change in orifice opening would not affect bubble size greatly. Bubble sizes calculated from the orifice opening of specimens subjected to equivalent DWP of 4.48 kPa for all six weeks measurements ranges from 0.9 to 1.9 mm, which corresponds to orifice opening of 0.1 to 0.6 mm.

Even though all materials were made of EPDM, they behaved differently. These differences are most likely due to different EPDM formulations. EPDMs are formulated with different ethylene and propylene ratios, as well as the different amounts and type of diene used, and may be a unique characteristic of each brands; furthermore, the formulation maybe a trade secret of the manufacturer.

Another question that must be answered is the similarity of this experiment to the real operational. The use of extreme conditions (i.e., elevated temperature, high concentrations) to accelerate degradation processes that occur too slowly for observation during routine application may not be representative of to real conditions.

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[*] Stenstrom, M. “C&EE255B: Biological Processes for Water and Wastewater Treatment” Spring 2003, University of California at Los Angeles.

Scientists have tried to develop models to extrapolate experiment results. Models ranges from empirical [Dolezel, 1965; Koikov *et al;* 1969; and Zherdev *et al,* 1978], non-empirical, to semi empirical prediction/ extrapolation [Vinogradov, *et al* 1976; Karphukin *et al,* 1978; Botshitzkii, 1978; and Urzhumtzev, 1976], although their reliability is very limited and extrapolation to extreme times is not suggested [Buchachenko, 1978]. Despites all these difficulties in predicting material service life, accelerated experiment conditions are routinely used in many different fields. A methodology suitable for diffusers would be extremely useful for their evaluation in treatment plants. While the experiment described in this thesis may not be able to predict service life of membrane diffusers, it represents a procedure, which if perfected, could result in considerable savings or cost avoidance for treatment plant owners.

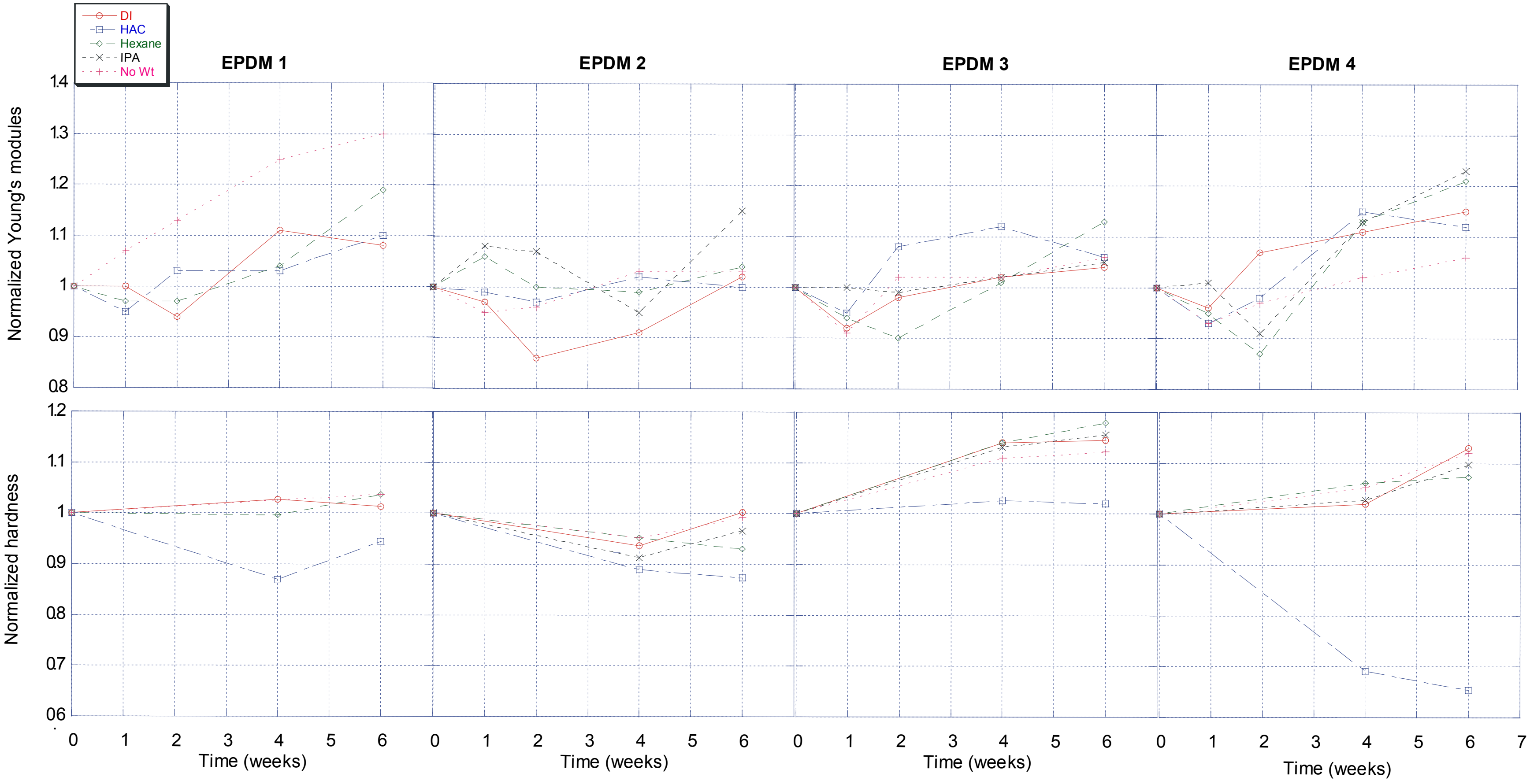

Figure 4 --Change in Young's modules and hardness, normalized value.

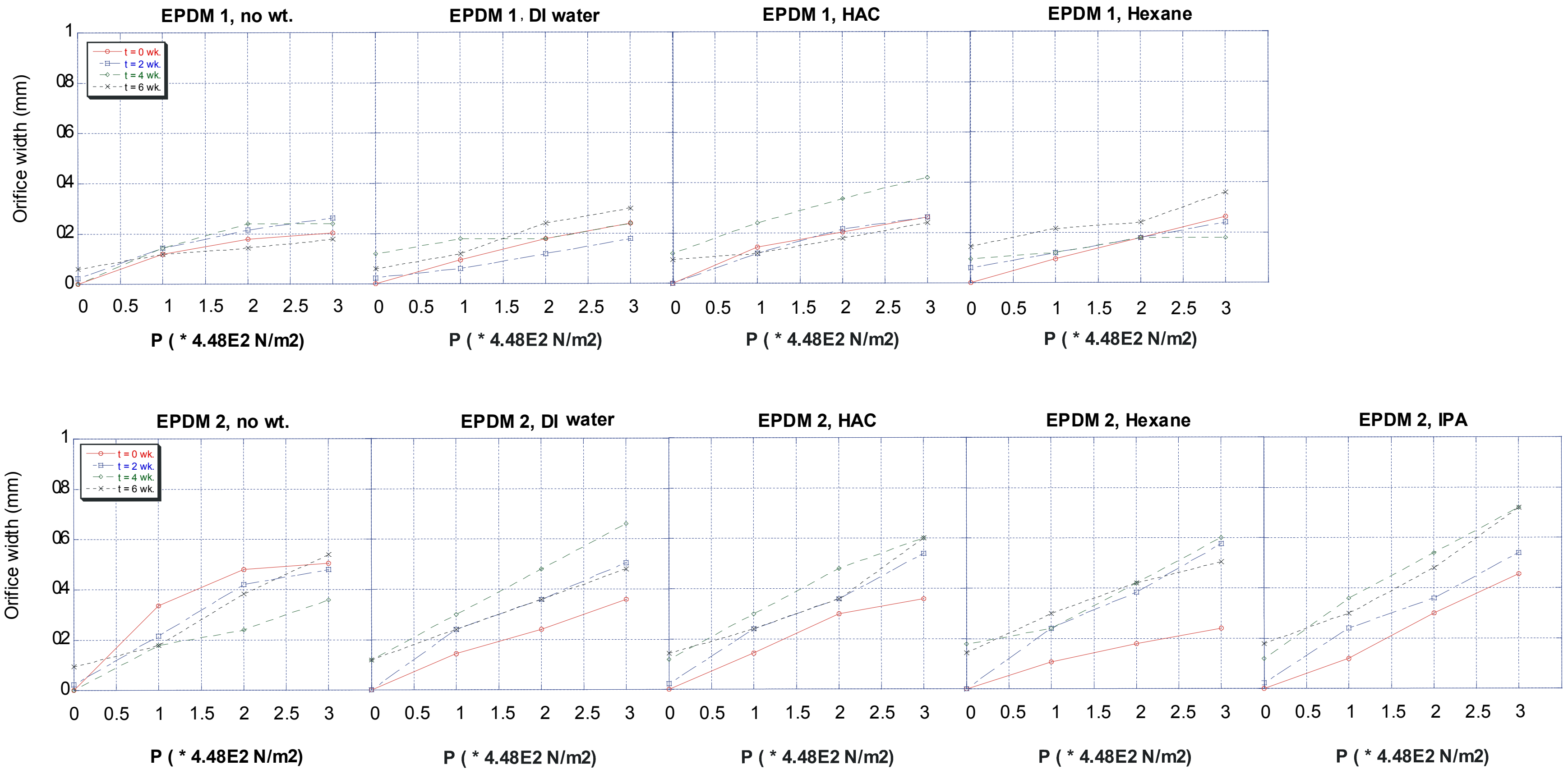

Figure 5 --Orifice opening for EPDM 1 and EPDM 2 for various pressures.

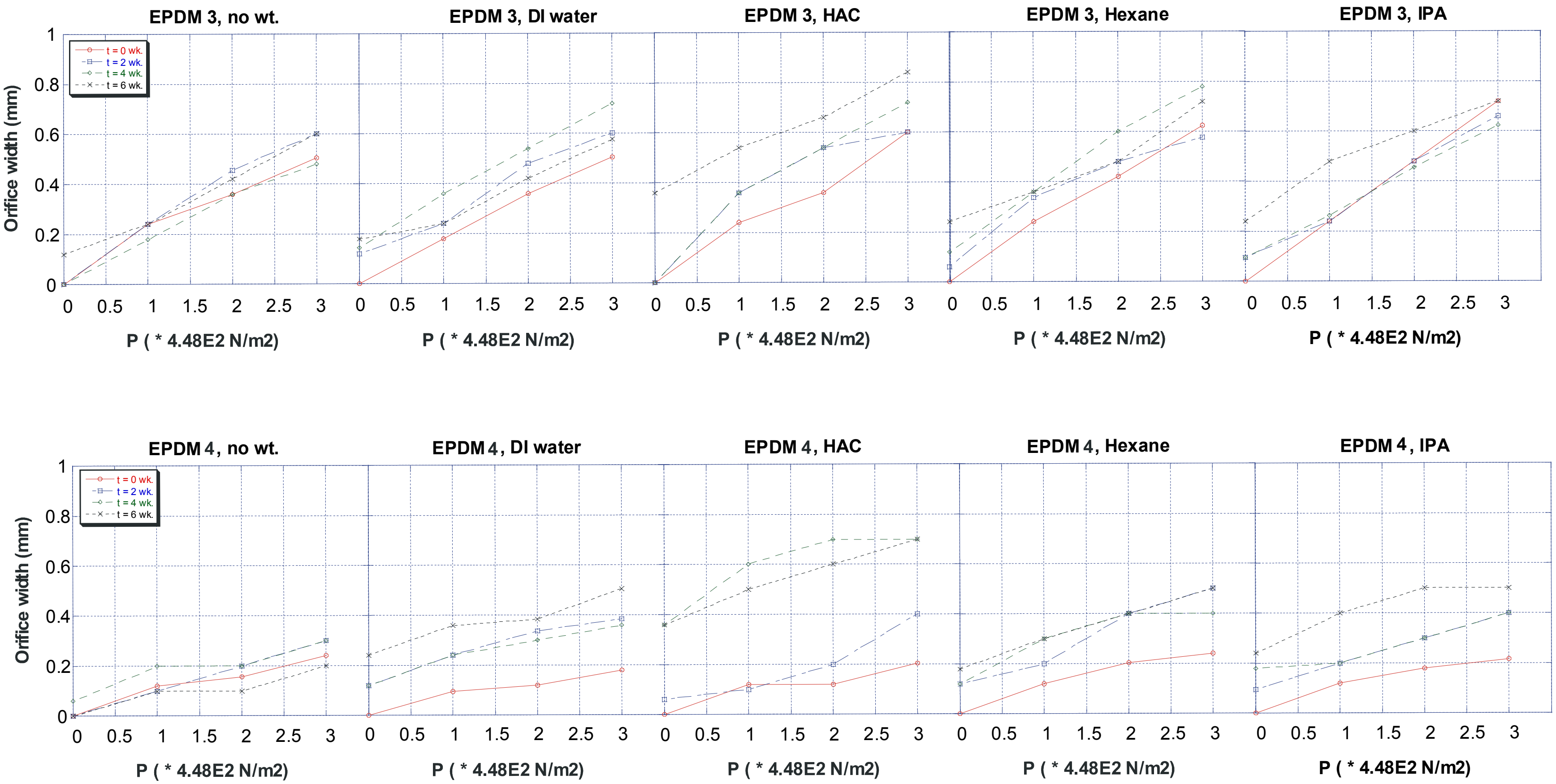

Figure 6--Orifice opening for EPDM 3 and EPDM 4 for various pressures.

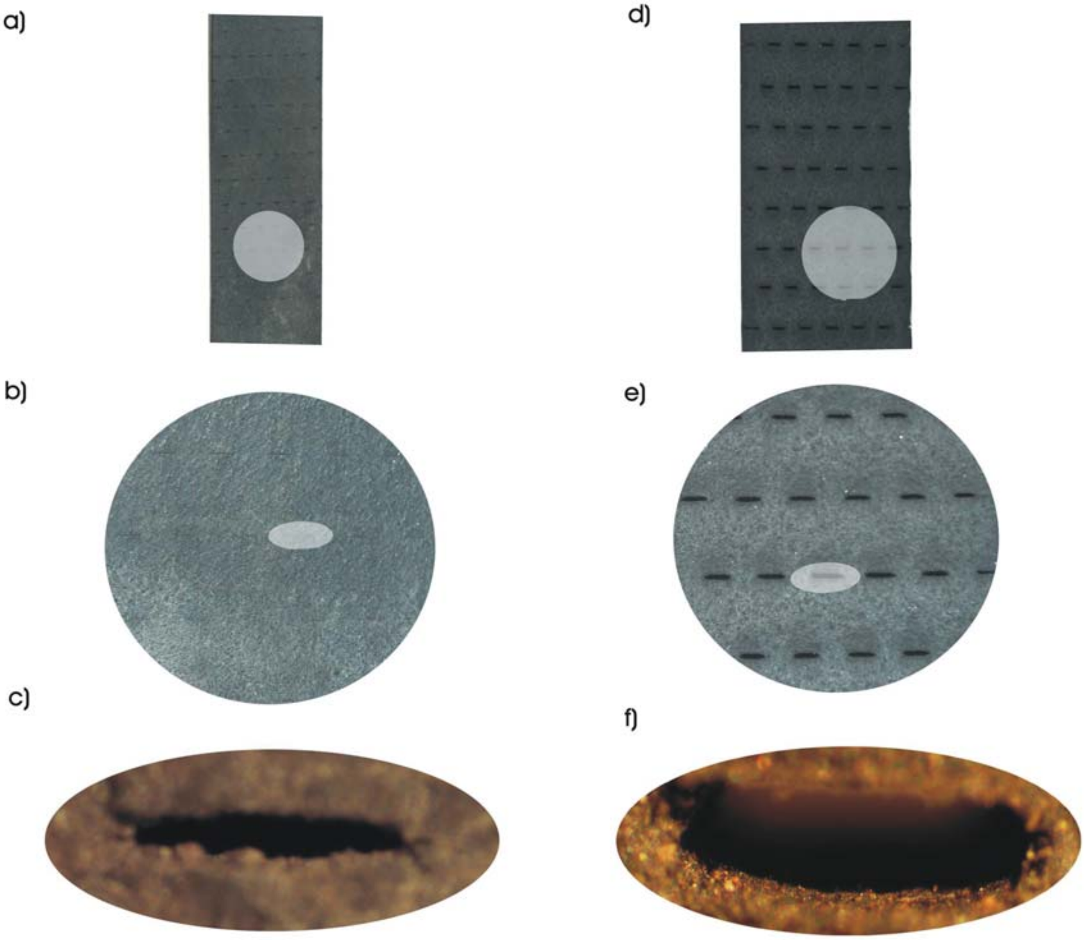

Figure 7--Specimen 4B before (a,b, and c)and after (d,e, and f) soaking. Figures a,b,d and e were captured without magnification; figures c and f were captured with 40x magnification.

CONCLUSIONS

This thesis describes laboratory experiment that simulates stresses that membrane diffusers undergo in their operation, and proposes ways to quantify material degradation in membrane diffusers. The experiment showed that EPDM (ethylene-propylene-diene) diffusers undergo significant changes during soaking with various degrading solvents at elevated temperatures. The following conclusions are made:

- Young's modulus and hardness (Durometer Type A) of all specimens fluctuated thorough out the six weeks of the experiment.
- By the end of the sixth week, Young's modulus of all specimens slightly increased.
- Hardness tests showed mixed results, although it decreased for specimens soaked in acid solutions.
- Both Young's modulus and hardness may be too imprecise to document changes in material properties over the life and degradation observed in the six weeks of experiments.
- The orifices of all specimens dilated, and orifices creep occurred. Measuring orifice opening was a more sensitive way of documenting material changes.
- Different brands of membranes behaved differently, although they were all made of EPDM. EPDM from different manufacturers which may be formulated differently, and should be treated as different materials with different membrane life expectations.

APENDIX A: LOAD/ WEIGHT CALCULATION

The objective of the following derivation is to calculate amount of load must be put on each specimen to simulate real pressure that exert on diffuser membrane in its operation.

Refers to figure A1:

$$F_1 = \int_0^{\pi} Plr.d\theta.\sin\theta$$

$$F_1 = Plr\int_0^{\pi} \sin\theta.d\theta$$

$$F_1 = 2Plr = Pld \qquad (1)$$

Where P is pressure exert on inside wall of membrane diffuser, in this case P is the dynamic wet pressure; l is length of diffuser membrane; d is diameter of membrane diffuser.

Force F_1, must be opposed by an equal and opposite force at the other end of the half cylinder, which create a Hoop Stress, S_1, which equal to F_1 divided by area of which stress is distributed, $2 \cdot T \cdot l$, where *T* is the thickness of the membrane diffuser.

$$S_1 = F_1 / 2 \cdot T \cdot l$$

$$S_1 = (Pld)/(2 \cdot T \cdot l)$$

$$S_1 = Pd / 2T \qquad (2)$$

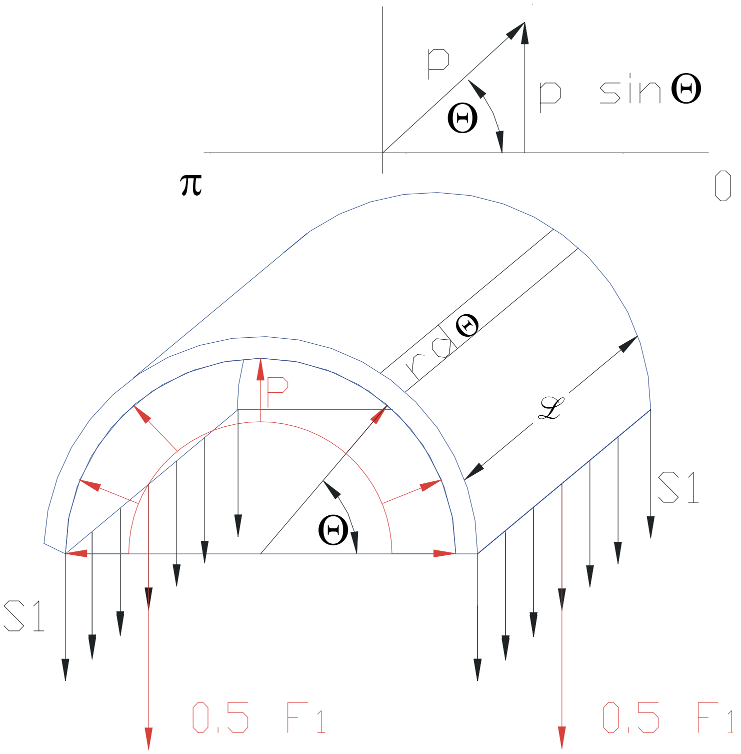

Figure 8 --Hoop Stress

To calculate force (F) that acts on a specimen, multiply S_1 by cross sectional area of narrow section of specimen, which is Wt .

$$F = S_1 \bullet (WT)$$

$$F = \frac{Pd}{2T} \bullet (WT)$$

$$F = PdW / 2 \tag{3}$$

Now the force must be converted into mass (m).

$$m = F / g \tag{4}$$

g is acceleration due to gravity.

Once the mass is known, the volume of the load can be calculated (in this experiment lead is used as loading object):

$$V_{lead} = m / \rho_{lead} \tag{5}$$

However since the leads are submerged, effective density must be used instead of density: For simplicity, it is assumed that all solutions have densities of water's.

$$V_{lead} = m / (\rho_{lead} - \rho_{water}) \tag{6}$$

Substituting (3) to (4), and (4) to (6), the following was obtained:

$$V_{lead} = \frac{PdW}{2g.(\rho_{lead} - \rho_{water})} \tag{7}$$

Last step is to convert volume of lead into mass of lead by multiplying with density of lead, since it is easier to specify mass then volume when purchasing weighs.

$$m_{lead} = \frac{PdW}{2g.(\rho_{lead} - \rho_{water})} \bullet \rho_{lead} \tag{8}$$

The following values are used:

$$P[N/m^2] = 4.48E3$$
$$d[m] = 0.06$$
$$W[m] = 1.32E-2$$
$$\rho_{lead}[kg/m^3] = 11340$$
$$\rho_{water}[kg/m^3] = 997.046$$
$$g[m/\sec^2] = 9.8$$

(m_{lead} = 0.197 kg, or 7.0 ounces)

APENDIX B: VOLTS TO UNIT MASS CONVERSION FACTOR

The small load cell apparatus measures force in volt unit. To get this measurement useful, a conversion to stress must be made. Stress is define by

$$P = \frac{F}{A}, \tag{1}$$

where P is pressure (N/m^2), F is force (N), and A is cross sectional area (m^2). Equation (4) is used to calculate force, given mass. Since the small load cell apparatus measure mass in unit of volts, a conversion factor must be determined. This was done by subjecting small load cell apparatus with various known weights and registering each correspondent value in unit of volt. The slope of mass [gr] versus volt is the conversion factor from volt to gram, and was found to be 44.26 gr/volt.

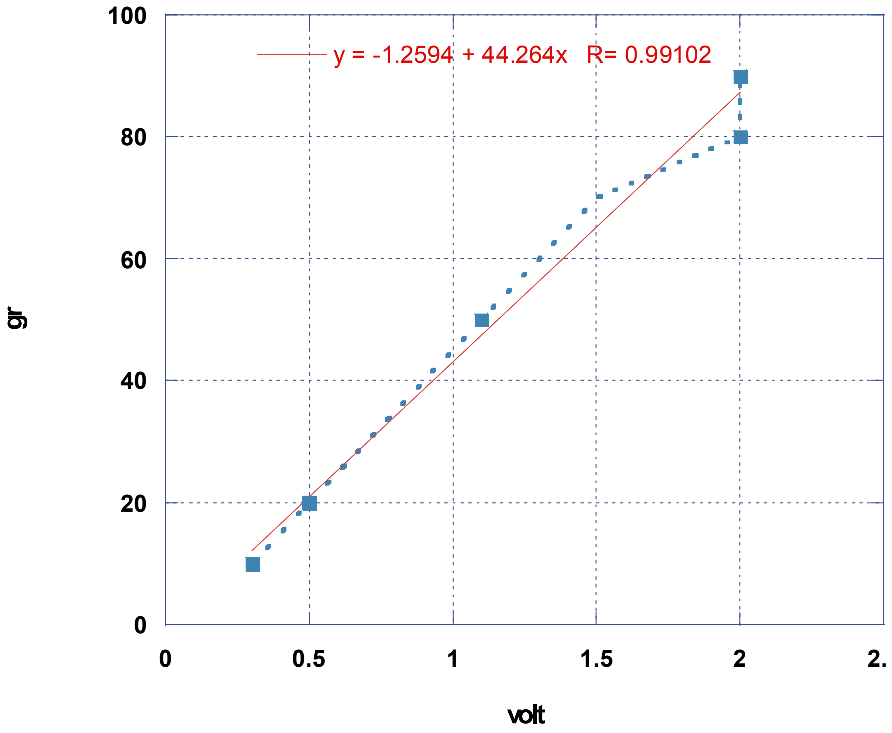

Figure 9 -- Conversion curve from volt to gram.

APPENDIX C: DATA

WEEK 0 (April 4, 2003)

			Orrifice width [mm] and stretching (dy)						
Specimen	Hardness	Y [N/m^2}	0 " H2O	dy (mm)	16" H2O	dy (mm)	32" H2O	dy (mm)	48" H2O
1A	52.2	1.20E+06	-	3.28	0.80	6.57	1.50	9.85	2.00
1B	52.2	1.18E+06	-	3.34	1.20	6.67	1.70	10.01	2.20
1C	52.2	1.23E+06	-	3.21	0.80	6.42	1.50	9.63	2.20
I	52.2	1.07E+06	-	3.68	1.00	7.35	1.50	11.03	1.70
2A	50.6	1.07E+06	-	3.63	1.20	7.26	2.00	10.89	3.00
2B	50.6	1.09E+06	-	3.72	1.20	7.43	2.50	11.15	3.00
2C	50.6	1.06E+06	-	3.92	0.90	7.85	1.50	11.77	2.00
2D	50.6	1.01E+06	-	4.27	1.00	8.54	2.50	12.81	3.80
II	50.6	9.25E+05	-	3.67	2.80	7.34	4.00	11.00	4.20
3A	45.6	1.08E+06	-	3.52	1.50	7.05	3.00	10.57	4.20
3B	45.6	1.12E+06	-	3.67	2.00	7.33	3.00	11.00	5.00
3C	45.6	1.08E+06	-	3.57	2.00	7.13	3.50	10.70	5.20
3D	45.6	1.11E+06	-	3.57	2.00	7.13	4.00	10.70	6.00
III	45.6	1.11E+06	-	3.43	2.00	6.86	3.00	10.28	4.20
4A	49.2	1.15E+06	-	2.71	0.80	5.41	1.00	8.12	1.50
4B	49.2	1.46E+06	-	2.68	1.00	5.37	1.00	8.05	1.70
4C	49.2	1.47E+06	-	2.74	1.00	5.48	1.70	8.22	2.00
4D	49.2	1.44E+06	-	2.70	1.00	5.40	1.50	8.10	1.80
IV	49.2	1.46E+06	-	2.63	1.00	5.26	1.30	7.90	2.00

WEEK 2 (April 28, 2003)

			Orrifice width [mm] and stretching (dy)						
Specimen	Hardness	Y [N/m^2}	0 " H2O	dy (mm)	16" H2O	dy (mm)	32" H2O	dy (mm)	48" H2O
1A		1.13E+06	0.20	3.48	0.50	6.97	1.00	10.45	1.50
1B		1.22E+06	-	3.24	1.00	6.48	1.80	9.72	2.20
1C		1.20E+06	0.50	3.30	1.00	6.61	1.50	9.91	2.00
I		1.22E+06	0.20	3.25	1.20	6.50	1.80	9.75	2.20
2A		1.22E+06	-	4.22	2.00	8.44	3.00	12.66	4.20
2B		9.36E+05	0.20	3.83	2.00	7.66	3.00	11.49	4.50
2C		1.03E+06	-	3.93	2.00	7.86	3.20	11.79	4.80
2D		1.00E+06	0.20	3.99	2.00	7.97	3.00	11.96	4.50
II		9.91E+05	0.20	3.82	1.80	7.63	3.50	11.45	4.00
3A		1.04E+06	1.00	3.60	2.00	7.20	4.00	10.80	5.00
3B		1.10E+06	-	3.40	3.00	6.80	4.50	10.20	5.00
3C		1.16E+06	0.50	3.94	2.80	7.89	4.00	11.83	4.80
3D		1.00E+06	0.80	3.61	2.00	7.21	4.00	10.82	5.50
III		1.10E+06	-	3.36	2.00	6.72	3.80	10.08	5.00
4A		1.18E+06	1.00	2.80	2.00	5.61	2.80	8.41	3.20
4B		1.41E+06	0.50	2.96	0.80	5.92	2.00	8.88	3.00
4C		1.34E+06	1.00	3.16	2.00	6.32	3.00	9.47	4.00
4D		1.25E+06	0.80	2.76	2.00	5.52	2.50	8.28	3.00
IV		1.43E+06	-	2.46	1.20	4.93	1.80	7.39	2.20

WEEK 4 (May 15, 2003)

			Orrifice width [mm] and stretching (dy)						
Specimen	Hardness	Y [N/m^2}	0 " H2O	dy (mm)	16" H2O	dy (mm)	32" H2O	dy (mm)	48" H2O
1A	53.6	1.33E+06	1.00	2.96	1.50	5.92	1.50	8.88	2.00
1B	45.4	1.22E+06	1.00	3.25	2.00	6.50	2.80	9.75	3.50
1C	52.0	1.28E+06	0.80	3.09	1.00	6.18	1.50	9.27	1.50
I		1.35E+06	-	2.93	1.20	5.86	2.00	8.79	2.00
2A	47.4	1.35E+06	1.00	4.00	2.50	8.00	4.00	11.99	5.50
2B	45.0	9.88E+05	1.00	3.64	2.50	7.28	4.00	10.92	5.00
2C	48.2	1.09E+06	1.50	3.95	2.00	7.90	3.50	11.85	5.00
2D	46.2	1.00E+06	1.00	4.51	3.00	9.02	4.50	13.54	6.00
II	48.2	8.76E+05	-	3.56	1.50	7.12	2.00	10.68	3.00
3A	52.0	1.11E+06	1.20	3.47	3.00	6.94	4.50	10.40	6.00
3B	46.8	1.14E+06	-	3.28	3.00	6.56	4.50	9.84	6.00
3C	52.0	1.20E+06	1.00	3.54	3.00	7.08	5.00	10.62	6.50
3D	51.6	1.12E+06	0.80	3.51	2.20	7.02	3.80	10.53	5.20
III	50.6	1.13E+06	-	3.36	1.50	6.73	3.00	10.09	4.00
4A	50.2	1.17E+06	1.00	2.66	2.00	5.32	2.50	7.98	3.00
4B	34.0	1.49E+06	3.00	2.37	5.00	4.74	5.50	7.11	6.00
4C	52.2	1.67E+06	1.00	2.43	2.50	4.87	3.00	7.30	3.50
4D	50.6	1.62E+06	1.50	2.35	2.00	4.69	2.50	7.04	3.00
IV	51.8	1.68E+06	0.50	2.37	1.50	4.74	2.00	7.11	2.50

WEEK 6 (June 11, 2003)

				Orrifice width [mm] and stretching (dy)					
Specimen	Hardness	Y [N/m^2}	0 " H2O	dy (mm)	16" H2O	dy (mm)	32" H2O	dy (mm)	48" H2O
1A	52.9	1.30E+06	0.50	3.05	1.00	6.09	2.00	9.14	2.50
1B	49.3	1.30E+06	0.80	3.04	1.00	6.08	1.50	9.12	2.00
1C	54.1	1.47E+06	1.20	2.69	1.80	5.38	2.00	8.08	3.00
I	54.1	1.39E+06	0.50	2.83	1.00	5.66	1.20	8.50	1.50
2A	50.7	1.39E+06	1.00	3.54	2.00	7.09	3.00	10.63	4.00
2B	44.2	1.11E+06	1.20	3.70	2.00	7.40	3.00	11.11	5.00
2C	47.1	1.07E+06	1.20	3.76	2.50	7.52	3.50	11.28	4.20
2D	48.9	1.05E+06	1.50	3.72	2.50	7.44	4.00	11.15	6.00
II	50.2	1.06E+06	0.80	3.55	1.50	7.10	3.20	10.65	4.50
3A	52.2	1.11E+06	1.50	3.40	2.00	6.80	3.50	10.20	4.80
3B	46.5	1.16E+06	3.00	3.46	4.50	6.92	5.50	10.38	7.00
3C	53.8	1.14E+06	2.00	3.17	3.00	6.33	4.00	9.50	6.00
3D	52.7	1.25E+06	2.00	3.40	4.00	6.80	5.00	10.19	6.00
III	51.2	1.16E+06	1.00	3.23	2.00	6.45	3.50	9.68	5.00
4A	55.6	1.22E+06	2.00	2.55	3.00	5.10	3.20	7.65	4.20
4B	31.6	1.55E+06	3.00	2.19	4.00	4.37	5.00	6.56	6.00
4C	53.2	1.81E+06	1.50	2.27	2.50	4.54	3.50	6.81	4.00
4D	54	1.74E+06	2.00	2.41	3.00	4.81	4.00	7.22	4.50
IV	55.1	1.64E+06	-	2.30	1.20	4.59	1.20	6.89	2.00

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