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Hydrofluoric Permeation through polymeric materials.

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Objective: The magnets in Levitronix's pump impellers are susceptible to attack by concentrated acids. They are currently encapsulated with a perfluoroalkoxy (PFA) coating to protect them from attack. Permeation of an acid gas through the coating however, can cause premature failure. The lower the permeation rate of an acid gas through the coating, the longer the impeller life.

The objective of this project was to measure the permeation rate of concentrated hydrofluoric acid (HF) through several polymeric materials. The materials selected for this study were PFA 440HP, ECTFE 901, PVDF, ETFE, and PP. They represent potential encapsulation materials for the impellers within Levitronix pumps.

Experimental: Permeation measurements were made using the test system shown in Figure 1. In this system, the material to be tested was placed in a permeation cell. The cell was placed in a temperature-controlled enclosure. The cell contained 2 chambers with the test sample between them. The bottom chamber was filled with 49% HF. The upper chamber was purged with air that swept any acid gas that permeated through the test sample into a scrubber.

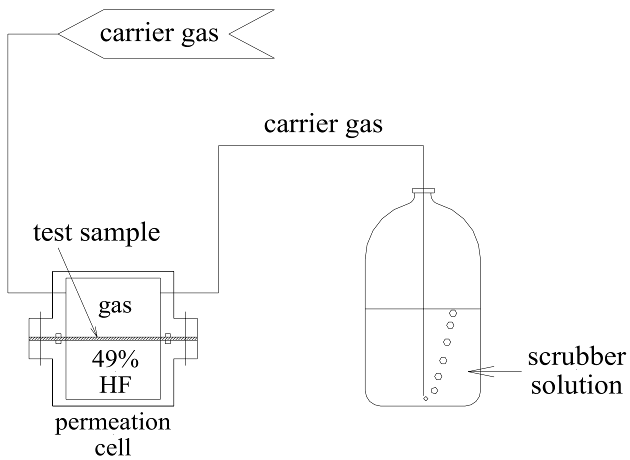
The amount of HF permeating through the test sample was determined by measuring the concentration of fluoride in the scrubbers over time. Concentration was measured using a specific ion electrode. Tests were conducted at a temperature of 33°C. The sample thickness was 1.5mm. All materials were tested in triplicate. Only 8 cells were available for use at one time; hence, the experiment was conducted twice at identical conditions to complete the test matrix. Background fluoride concentrations were measured prior to introducing HF to the cells the first experiment. Two negative blanks were included in both experiments. Table I displays the experimental test matrix.

Table I: Experimental Test Matrix

	Set 1							
Cell #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Material	PP	PP	PTFE	PTFE	ECTFE	PVDF	PFA440HP	PFA440HP

	Set 2							
Cell #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Material	PP	PTFE	ECTFE	ECTFE	PVDF	PVDF	PFA440HP	N/A

Figure 1: Test system schematic for measuring acid gas permeation



Results and discussion: Figure 2 shows the background data obtained prior to filling the first set of cells with 49% HF. The amount of fluoride collected over time was very low ($< 2 \times 10^{-3}$ µmoles/day).

Figures 3 and 4 show data obtained during each test. The graphs present the total mass of acid collected in the scrubber over time. The graphs include linear regressions of the data after steady state was achieved. The slopes represent the permeation rate and are included in the legend for each curve.

The acid mass collection rates from the PFA, PVDF, ECTFE, and PTFE samples quickly reached steady state conditions in both tests relative to the PP samples. The PP samples were slow to reach steady state in both tests with no measurable amount of permeation until after the 12^{th} day. However, once the PP samples reached steady state, the permeation rate through the PP samples was higher than all other materials with the exception of PVDF. The permeation rate of HF through a polymer is proportional to the product of the diffusion coefficient and the solubility of HF in that polymer. The slow approach to steady state combined with the high permeation rate, suggest that the solubility of HF in PP is high and the diffusion coefficient is low compared to other materials.

Figure 2: Background permeation data collected prior to experiment 1

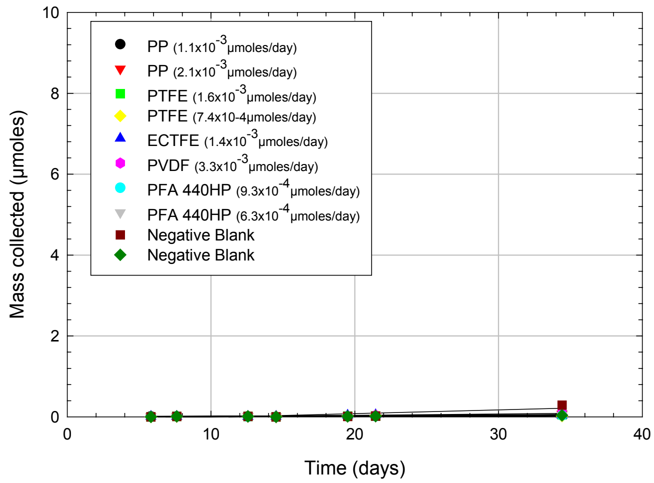


Figure 3: Permeation data in 49% HF at 33°C – experiment 1

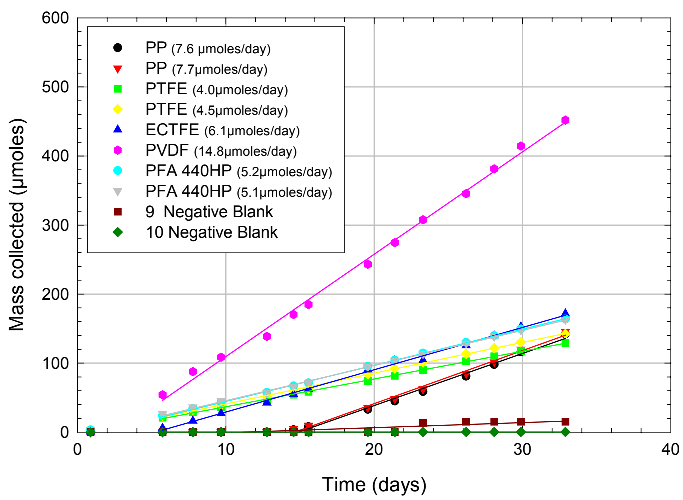
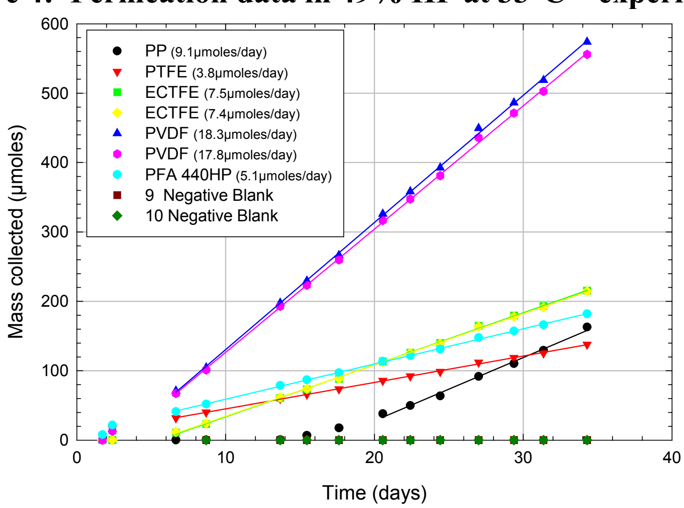


Figure 4: Permeation data in 49% HF at 33°C – experiment 2



The permeation coefficient for each material was calculated using equation 1. The mass flow rate used to calculate the permeation coefficient of the material with equation 1 is simply the slope of the mass collected versus time curve determined once steady state had been achieved. These values are shown in the graph legends in Figures 3 and 4. The vapor pressure of HF over 49% HF at 33°C is approximately 33 mmHg. The area available for diffusion in the test cell was 15 cm^2.

$$M = \frac{\mathrm{P} P_V A}{T} \tag{1}$$

Where M = Mass flow rate
P = Permeation coefficient
P_V = Gas vapor pressure
A = surface area available for diffusion
T = material thickness

The HF permeation coefficients for each material calculated using equation 1 are shown in Table II and displayed graphically in Figure 5. The permeation coefficients are expressed in units of Barrer. A Barrer is equivalent to 1 cm^3 (STP)-cm/cm^2-sec-cm Hg x 10^{-10}.

Table III displays the relative permeation coefficient for each material compared to PFA. PFA is currently used for the protective coating on the Levitronix impeller. The permeation coefficient of HF in PVDF is more than 3 times that of HF in PFA. PTFE is the only material that had a lower permeation coefficient than PFA.

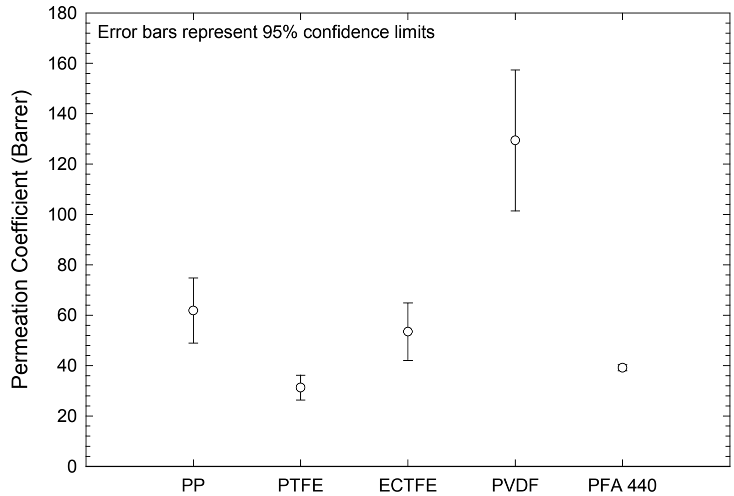
Table II: HF Permeation coefficients in several polymeric materials.

Replicate	**Permeation coefficient (Barrer)**				
	PP	**PTFE**	**ECTFE**	**PVDF**	**PFA 440HP**
1	59	32	48	117	41
2	60	35	59	144	40
3	72	30	58	140	40
Average	64	32	55	133	40
Std. Dev.	6.8	2.6	6.0	15	0.6

Table III: Relative HF Permeation coefficient in polymeric materials to PFA.

	PP	**PTFE**	**ECTFE**	**PVDF**	**PFA 440HP**
P Relative to PFA	1.6	0.8	1.4	3.3	1.0

Figure 5: HF Permeation Coefficients in Polymeric Materials



The larger the HF permeation coefficient, the greater the mass-flux of HF through the material. Therefore, when selecting a material for a protective coating a low permeation coefficient is desired. In general, the permeation coefficients of HF in the polymers tested were similar to each other and within a factor of 2 with the exception of PVDF, which was 3.3 times that of PFA.

Previously studies have been completed to determine the permeation coefficient of HCl in PFA at varying temperatures. The permeation coefficient of HCl in PFA at 33°C is 3.6 Barrer. This is 1/10 the permeation coefficient of HF in PFA at the same conditions. It would at first appear that the HF would be more problematic than HCl. However, because the vapor pressure of 37% HCl is more than 8 times that of 49% HF, the mass permeation rates of the 2 gases are similar when exposed to these solutions.

Table IV compares the permeation rates of HF and HCl through PFA at varying concentrations at 33°C. While the permeation rates with 37% HCl and 49% HF are similar, permeation rates of HF are much higher than HCl at low concentrations. The ratios of the vapor pressures of 37% HCl and 49% HF to their vapor pressure at 6.3% are 10^5 and 180 respectively. This is because HF is a weak acid and doesn't dissociate as readily as HCl, a strong acid. This explains why the permeation rate of HF is higher than HCl at low concentration but similar at high concentrations.

Table IV: Comparison of HF and HCl permeation rates through 15 cm^2 of PFA at 33°C

	Permeation Rate in µmoles/day at 33°C (Vapor pressure in mmHg)	
Concentration in wt%	**HCl**	**HF**
49%	-	5.0 (33)
37%	4.0 (290)	1.3 (8.3)
6.3%	0.000042 (0.003)	0.027 (0.18)
0.5%	-*	0.0030 (0.02)

*Model for HCl vapor pressure not well defined at very low concentrations.

Summary: The permeation coefficients of HF through PFA440 HP, PP, PTFE, ECTFE, and PVDF were measured using 49% HF at 33°C. The materials were found to have the following permeation coefficients.

Material	Permeation Coefficient (Barrer)
PVDF	133 ± 15
PP	64 ± 7
ECTFE	55 ± 6
PFA 440HP	40 ± 1
PTFE	32 ± 3