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The effect of HCl permeation through PFA on expected component life

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ABSTRACT

Metal and ceramic parts in components used in high purity liquid delivery systems are susceptible to attack by concentrated acids. If these parts are exposed to the acids they can be corroded and may result in premature failure of the part or contamination of the acid. An example of parts that are susceptible to acid attack are the magnets in the impellers in magnetically-levitated centrifugal pumps manufactured by Levitronix. In order to prevent attack, the magnets are encapsulated with a perfluoroalkoxy (PFA) coating to protect them from attack. However, if acid gases permeate through the coating they can still attack the magnet in the impeller thereby causing premature failure of the pump and contamination of the acid. This study was undertaken to measure the permeation rate of HCl through the PFA used to encapsulate the magnets in Levitronix pump impellers as a function of the temperature and the concentration of hydrochloric acid to which the impeller is exposed.

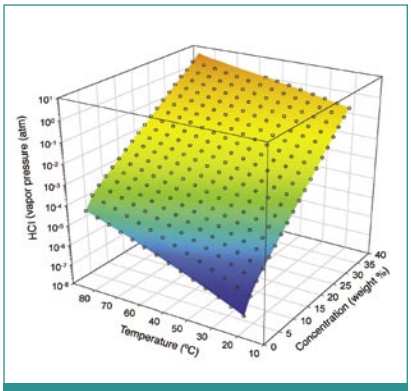

Figure 1. The effect of concentration and temperature on HCl vapour pressure.

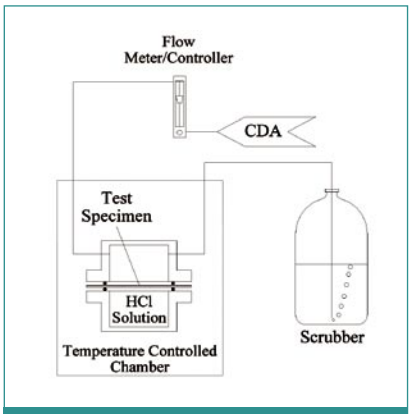

Figure 2. Test system schematic for measuring acid gas permeation.

Experience has shown that hydrochloric acid and hydrofluoric acid are the acids most likely to cause corrosion. These acids, aqueous solutions of hydrogen chloride (HCl) or hydrogen fluoride (HF), are widely used in semiconductor microchip manufacturing. The permeation rates of HCl through the PFA coating in the Levitronix pumps were measured and used to develop a model that predicts pump relative lifetime as a function of operating conditions assuming that pump lifetime is inversely proportional to permeation rate. Pump lifetime under conditions that lead to a high permeation rate is being measured in a separate study. Once this life test is complete, the model developed in this study can be used to predict pump lifetime under a variety of operating conditions.

Although this study was specific for developing a model to predict the lifetime of the specific materials and components tested, the approach is generic and can be used to develop models for other components subject to degradation by acid gas-induced corrosion.

Background

Under most conditions, the permeation rate (mass flow rate) of a gas through a solid material can be calculated using equation 1. Equation 1 indicates that the permeation rate increases linearly with exposed area and gas vapour pressure and decreases with material thickness.

$$M = \frac{P P_V A}{T} \quad (1)$$

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

Note that the permeation rate is proportional to the gas vapour pressure and not to the concentration of HCl in the liquid. If HCl behaved as an ideal gas, the vapour pressure would be proportional to the concentration in the liquid. However, HCl does not behave ideally as it reacts strongly with water and partially dissociates into H+ and Cl- ions. The extent of dissociation is nearly complete at low concentrations and decreases with increasing concentration. Hence, the vapour pressure increases more rapidly with increasing concentration than it would if HCl behaved like an ideal gas.

The vapour pressure of HCl over hydrochloric acid solutions as a function of concentration and temperature is shown in Figure 1 [1]. Selected conditions are also included in Table 1. Vapour pressure is seen to be highly dependent on both concentration and temperature. The vapour pressure over a 37% solution at 60°C is more than 2 million times that of a 5% solution at 20°C. The vapour pressure over the solution in the on-going pump life test (32% HCl at 75°C) is approximately 3000 times that over a typical SC2 cleaning solution (6.3% HCl at 75°C).

The permeability coefficient, P, shown in Equation 1 is expected to be dependent upon temperature and independent of HCl concentration. If this is true, and the temperature dependence of P for HCl through PFA is known, then the permeation rate of HCl through a PFA coating of known thickness can be predicted if the temperature and concentration are known.

The reaction rate between HCl and materials subject to corrosion by HCl is believed to be very rapid as long as water is present. Water vapour permeates through PFA fairly quickly [2]. Therefore, the rate of permeation through PFA is expected to be an accurate predictor of component failure rate due to acid attack.

Testing was performed to determine the dependence of P on temperature, to confirm that P is independent of HCl concentration and PFA thickness, and to confirm that the permeation rate is proportional to the vapour pressure of HCl over hydrochloric acid solutions.

Experimental

Permeation rate measurements were made using the test system shown in Figure 2. In this system, the PFA test

sample was housed in a permeation cell that was then placed in a temperature-controlled enclosure. The cell contained two chambers with the PFA sample between them. The exposed surface area of the sample was 20cm^2. The bottom chamber was filled with acid, while the upper chamber was purged with compressed dry air (CDA) that swept any acid that permeated through the PFA sample into a scrubber where it was absorbed into water. The purge rate was high enough to remove HCl from the test cell shortly after it permeated through the sample and slow enough to achieve essentially complete removal in the scrubber. The HCl concentration in the scrubber water was measured using a chloride-specific ion electrode to determine the acid gas permeation rate.

Tests were performed using the conditions shown in Table 2. HCl concentrations were varied from 14.0 to 36.2% by weight. Temperatures ranged from 30 to 74°C. Under these conditions, the HCl vapour pressure varied from 0.0014 to 0.67 atm. All measurements were made after the permeation rate had achieved steady-state. Steady-state was achieved in 1–14 days depending upon the test HCl concentration and temperature. Three samples were tested under each set of conditions.

TABLE 1: VAPOUR PRESSURE OF HCl OVER SELECTED HYDROCHLORIC ACID SOLUTIONS

HCl concentration % by weight	Temperature °C	Vapour pressure atm
5	20	5.5×10^{-7}
6.3	75	2.1×10^{-4}
37	20	0.17
37	40	0.55
32	75	0.66
37	60	1.51

TABLE 2: EXPERIMENTAL TEST MATRIX

HCl concentration % by weight	Temperature °C	Vapour pressure atm	Thickness mm
14.0	74	0.0018	1.5
20.2	39	0.0014	1.5
20.2	48.5	0.0029	1.5
20.2	62	0.0071	1.5
20.2	74	0.015	1.5
26.7	30	0.0083	1.5
26.7	48.5	0.028	1.5
26.7	63.5	0.067	1.5
26.7	73	0.113	1.5
36.2	30	0.25	1.5
36.2	40	0.43	1.5
36.2	48.5	0.67	1.5
36.2	39	0.38	1.0
36.2	39	0.38	2.0

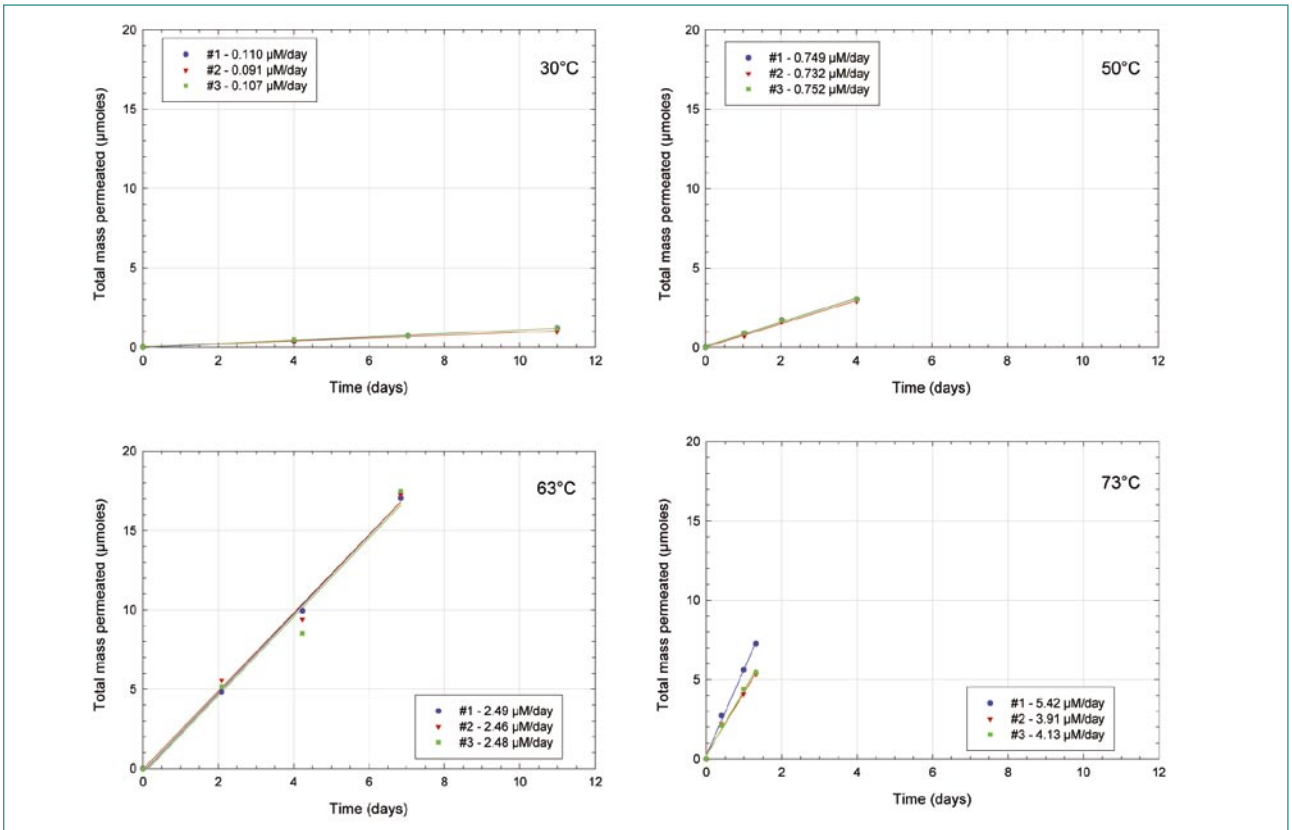

Figure 3. Examples of permeation data using 1.5mm samples with 26.7% HCl.

Results and discussion

Figure 3 shows examples of data obtained during typical experiments. Four graphs are shown depicting HCl permeation through 1.5mm-thick samples exposed to the vapour over 26.7% HCl at different temperatures. The graphs present the total mass of acid collected in the scrubber over time. Each graph contains 3 sets of experimental points; one for each of three samples tested. Linear regressions of each data set are also shown. The slopes of the linear regressions indicate the permeation rates. The rates determined from the regressions are included in the graph legends.

Figure 3 indicates that:

- The total mass collected over time was quite linear in all cases indicating that steady-state had been achieved
- The three samples tested showed similar permeation rates in all of the tests
- Permeation rate increased substantially with increasing temperature.

Figure 4 presents the measured HCl permeation rate through 1.5mm-thick samples as a function of temperature and HCl concentration. Four data sets are shown; one each for the 4 concentrations of HCl tested. The permeation rates shown are normalized for surface area. Error bars are included in the figure and represent ±1 geometric standard deviation. In general, the error bars were larger at lower permeation rates where the permeation rate is more difficult to measure due to the low chloride ion concentrations in the scrubber. The figure also includes log-log regressions at each acid concentration.

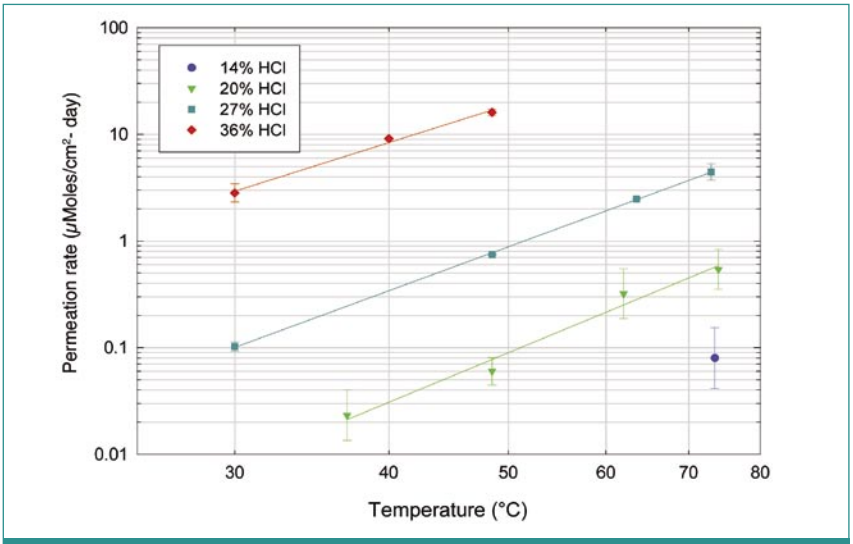

Figure 4. The effect of temperature and HCl concentration on HCl permeation through 1.5mm-thick samples.

Figure 4 indicates that the permeation rate increased substantially with both increasing temperature and increasing concentration. A 25°C increase in temperature increased the permeation rate approximately tenfold. Decreasing the concentration from 36% to 20% decreased the permeation rate by a factor of more than 100.

Figure 5 shows the permeability coefficient, P, for the 1.5mm samples tested. P was calculated by normalizing the data shown in Figure 4 for the HCl vapour pressure (Table 2) and multiplying by the test sample thickness. Figure 5 includes a log-log regression of all the data in the figure.

Figure 5 indicates that the permeability coefficient increased with temperature and was independent of HCl concentration as expected. The permeability coefficient increased approximately fourfold between 25 and 75°C.

Figure 6 shows the effect of thickness on the permeability coefficient. It compares measurements made with 1.0mm- and 2.0mm-thick samples with the measurements made with 1.5mm-thick samples shown in Figure 5. The permeability coefficients measured with the thin and thick samples were indistinguishable from the 1.5mm samples indicating that the permeability coefficient is essentially independent of thickness as expected.

Lifetime prediction model

The regression line shown in Figure 6 can be used to determine the permeability coefficient of HCl through the PFA tested at temperatures between 20 and 80°C. Also, the data shown in Figure 1 can be used to determine the HCl vapour pressure in equilibrium with hydrochloric acid solutions over this temperature range. Therefore, since

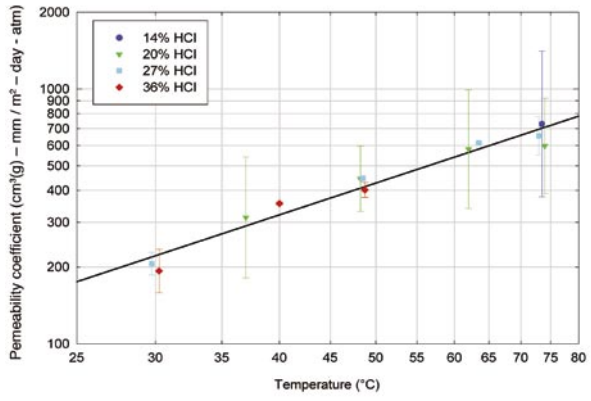

Figure 5. The effect of temperature and concentration on the HCl permeation coefficient.

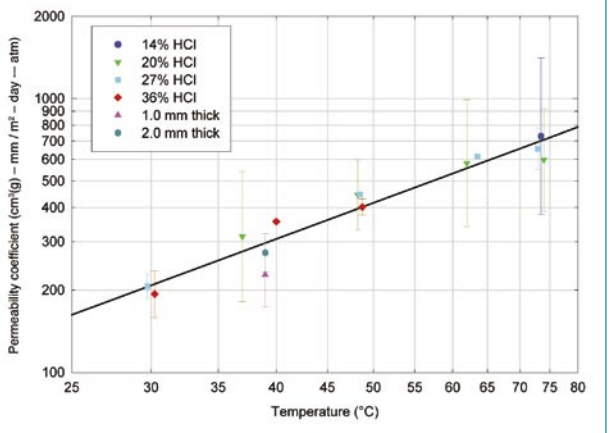

Figure 6. The effect of thickness on the permeability coefficient.

TABLE 3: PREDICTED RELATIVE IMPELLER LIFETIMES AT SELECTED CONDITIONS

HCl concentration % by weight	Temperature °C	Predicted relative lifetime
5	20	7,000,000
6.3	75	3,100
37	20	22
37	40	2.7
32	75	1
37	60	0.6

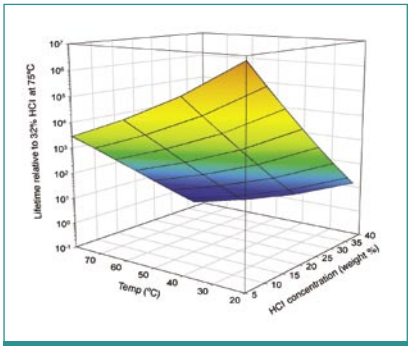

Figure 7. Predicted relative impeller life based on HCl permeation rate.

the permeability coefficient has been shown to be independent of thickness and HCl vapour pressure, Equation 1 can be used to predict the rate at which HCl permeates the PFA if the material thickness, temperature and acid concentration are known. Hence, with the assumption that failure rate is proportional to HCl exposure, the failure rate of a PFA encapsulated component due to HCl permeation can be predicted as a function of temperature and acid concentration.

Figure 7 shows predicted relative lifetime of pump impellers coated with 1.5mm-thick PFA as a function of temperature and acid concentration. Lifetimes relative to the conditions under which pumps are being tested (32% HCl at 75°C) are shown. Relative lifetimes at selected conditions are also shown in Table 3. Figure 7 and Table 3 indicate that pump impeller failures due to permeation are expected to be considerably less frequent than in the on-going life test except under extreme conditions. For example, the impeller is predicted to last 3,100 times as long in SC2 (6.3% HCl at 75°C).

Impeller life tests

Tests to determine impeller life are in process. Three sizes of Levitronix pumps (BPS1, BPS3, and BPS4) with impellers that have PFA encapsulated magnets are circulating 30-32% HCl at 75°C. Pumping performance and metal extraction are being monitored. Once these tests are complete, the model can be used to predict impeller life under different operating conditions. In addition, a single pump is circulating 37% HCl at room temperature. This test, in which the permeation rate is predicted to be 1/22 of that in the other life test, is being run to verify the longer lifetimes predicted by the model.

The high and low temperature tests have been running for 9 months and 5 years respectively, with no pump failures to date. A lifetime of > 9 months in the high temperature test under these test conditions, combined with the data in Table 3, indicates that impeller life based on corrosion-induced failure due to HCl permeation in 37% HCl at room temperature would be > 16 years; in SC2 (6.3% HCl at 75°C) it would be > 2,000 years. The predicted > 16 years in 37% HCl at room temperature has been verified to > 5 years in the room temperature test. Obviously, it is improbable that the impeller will really last 2000 years in SC2. What these model predictions do indicate is that impeller failure due to permeation is unlikely during the expected lifetime of the pump.

Summary

Testing was performed to determine the effects of exposure conditions on the permeation rate of HCl through the PFA used to encapsulate the magnets in Levitronix pump impellers. The permeation rate was found to be proportional to the vapour pressure of HCl over hydrochloric acid solutions rather than the concentration in the acid. The permeability coefficient of HCl through the PFA was found to be independent of the HCl vapour pressure, independent of PFA thickness, and to increase with increasing temperature.

A model was developed to predict the failure rate of impellers in Levitronix pumps due to HCl permeation. The relative failure rate can be predicted based solely on the acid concentration and temperature. The model predicts that impeller lifetime is substantially influenced by concentration and temperature, more in the case of the former than the latter. For example, lifetime based on failure due to HCl permeation in 5% HCl at 20°C is predicted to be 7,000,000 times that in 32% HCl at 75°C. The model will be used to predict actual failure rates once an on-going life test is completed.

REFERENCES

[1] Perry, J.H. 1963, *Chemical Engineers' Handbook*, 4th Edition, p. 3-61.

[2] Massey, L. 2003, *Permeability Properties of Plastics and Elastomers, A Guide to Packaging and Barrier Materials*, 2nd Edition, p. 94.

ABOUT THE AUTHORS

Don Grant is the founder and CTO of CT Associates, Inc., a contract research, development and testing services company for contamination control, particle measurement and control, filtration, permeation and chemical engineering. He is inventor or co-inventor of 7 patents and has 4 patent applications pending, and has authored or co-authored over 140 papers. He has an M.S. in mechanical engineering from the University of Minnesota and a B.S. in chemical engineering from Case Western Reserve University.

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