Modeling of component lifetime based on accelerated acid gas permeation measurements

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February 11, 2009
Introduction

• Metallic parts in chemical handling systems are subject to corrosion by acid gases like hydrogen chloride (HCl) and hydrogen fluoride (HF).
  – Examples include springs in valves and magnets in mag drive and maglev pumps
• Polymers, like perfluoroalcoxy (PFA), are often used to isolate these parts from acid gas containing liquids to prevent corrosion.
• Acid gases in these liquids can permeate through polymers and corrode the parts.
• One objective of this study was to determine the rates at which HCl and HF permeate through various polymers that could be used to encapsulate Levitronix pump impellers as a function of coating thickness, acid concentration and temperature.
• The second objective was to determine pump impeller lifetime under controlled conditions.
• The third objective was to combine the results of the first 2 objectives to develop a model to predict the lifetime of pump impellers coated with different polymers under different operating conditions.
Outline

• Diffusion theory
• Permeation rate measurement experimental procedures
• The effect of operating conditions on permeation rate thru PFA
  – Concentration
  – Temperature
  – PFA thickness
• Permeation rates of HCl and HF thru various polymers
• Life test status
• Predicted relative lifetimes under different operating conditions
• Summary
Steady-state permeation

\[ M = \frac{PP_VA}{T} \]

Where
\[ M = \text{Mass flow rate} \]
\[ P = \text{Permeability coefficient} \]
\[ P_V = \text{Gas vapor pressure} \]
\[ A = \text{surface area available for diffusion} \]
\[ T = \text{material thickness} \]

Note: The mass flow rate is proportional to the gas vapor pressure; not the acid concentration.
Partial pressure of HF over hydrofluoric acid solutions

Comparison between vapor pressures of HF and HCl over hydrofluoric and hydrochloric acids


Comparison of HCl and HF vapor pressures

Vapor pressure of HCl over selected hydrochloric acid solutions

<table>
<thead>
<tr>
<th>HCl concentration (% by weight)</th>
<th>Temperature (°C)</th>
<th>Vapor pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20</td>
<td>5.5 x 10^{-7}</td>
</tr>
<tr>
<td>6.3</td>
<td>75</td>
<td>2.1 x 10^{-4}</td>
</tr>
<tr>
<td>37</td>
<td>20</td>
<td>0.17</td>
</tr>
<tr>
<td>37</td>
<td>40</td>
<td>0.55</td>
</tr>
<tr>
<td>32</td>
<td>75</td>
<td>0.66</td>
</tr>
<tr>
<td>37</td>
<td>60</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Vapor pressure of HF over selected hydrofluoric acid solutions

<table>
<thead>
<tr>
<th>HF concentration (% by weight)</th>
<th>Temperature (°C)</th>
<th>Vapor pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>20</td>
<td>1.2 x 10^{-5}</td>
</tr>
<tr>
<td>5.0</td>
<td>20</td>
<td>7.5 x 10^{-5}</td>
</tr>
<tr>
<td>49</td>
<td>20</td>
<td>0.018</td>
</tr>
<tr>
<td>49</td>
<td>60</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Experimental approach – permeation measurements

- Determine the effects of vapor pressure, temperature and coating thickness on permeation rates of HF and HCl through PFA.
- Measure the permeation rate of HCl through various polymers as a function of temperature.
  - Polyethylene (PE)
  - Polypropylene (PP)
  - Polyvinylidene difluoride (PVDF)
  - Ethylene-chlorotrifluoroethylene (ECTFE)
  - Perfluoroalkoxy (PFA) - 3 types
  - Polytetrafluoroethylene (PTFE)
- Measure the permeation rate of HF through various polymers at room temperature.
  - Polypropylene (PP)
  - Polyvinylidene difluoride (PVDF)
  - Ethylene-chlorotrifluoroethylene (ECTFE)
  - Perfluoroalkoxy (PFA)
  - Polytetrafluoroethylene (PTFE)
Test System Schematic

Flow
Meter/Controller

CDA

Test Specimen

HCl Solution

Temperature Controlled Chamber

Scrubber

Test conditions

- Effect of concentration, temperature, and thickness on permeation rate:
  - HCl
    - Concentrations: 14-36% by weight
    - Temperatures: 30-75°C
    - 3 thicknesses (1.0, 1.5 and 2.0 mm)
  - HF
    - Concentrations: 5-49% by weight
    - Temperatures: 33-60°C
- Comparison of polymer permeation rates
  - HCl
    - 35% by weight
    - Temperatures: 30-55°C
  - HF
    - 49% by weight
    - 33°C
- All tests run in triplicate
Example of permeation data – 49% HF at 3 temperatures
The effect of vapor pressure, temperature, and thickness on the permeation rates of HCl and HF through PFA
The effect of temperature and hydrochloric acid concentration on HCl permeation rate through 1.5mm thick samples

Temperature (°C)

Permeation rate (µMoles/cm² day)

- 14% HCl
- 20% HCl
- 27% HCl
- 36% HCl

Permeability coefficient

\[ M = \frac{PP_v A}{T} \]

Where \( M \) = Mass flow rate
\( P \) = Permeability coefficient
\( P_v \) = Gas vapor pressure
\( A \) = surface area available for diffusion
\( T \) = material thickness

Permeability coefficient units

Gas volume – thickness

----------------------------------------
Area in contact with gas– Time - Vapor pressure

\( \text{cm}^3 \ (g) – \text{mm} \)

-------------
\( \text{m}^2 – \text{day} - \text{atm} \)
The effect of temperature on the permeability coefficient of HCl through PFA
The effect of thickness on the permeability coefficient of HCl through PFA
The effect of temperature on the permeability coefficient of HF through PFA
Permeation of HF and HCl through PFA

- Permeation rate
  - Is proportional to the acid gas vapor pressure
  - Increases with temperature
  - Is inversely proportional to the coating thickness
- The HCl permeation coefficient increases more rapidly with temperature than the HF permeation coefficient.
  - HCl permeability increased 2.5X between 30 and 60°C
  - HF permeability increased 2.1X between 30 and 60°C
- The HF permeation coefficient is larger than the HCl permeation coefficient at typical use temperatures:
  - 15X at 30°C
  - 12X at 60°C
Polymer permeability comparison
Permeation coefficient of HCl through different polymers

![Graph showing permeation coefficient of HCl through different polymers.](image-url)
Permeation coefficient of HCl through different polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Prop Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>0</td>
</tr>
<tr>
<td>PP</td>
<td>200</td>
</tr>
<tr>
<td>PVDF</td>
<td>400</td>
</tr>
<tr>
<td>ECTFE</td>
<td>600</td>
</tr>
<tr>
<td>PFA</td>
<td>800</td>
</tr>
<tr>
<td>PTFE</td>
<td>33°C</td>
</tr>
</tbody>
</table>
Permeation coefficient of HF through different polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeation Coefficient (cm³(g)·mm/M²·day·atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>4000</td>
</tr>
<tr>
<td>PVDF</td>
<td>8400</td>
</tr>
<tr>
<td>ECTFE</td>
<td>6000</td>
</tr>
<tr>
<td>PFA</td>
<td>2000</td>
</tr>
<tr>
<td>PTFE</td>
<td>10000</td>
</tr>
<tr>
<td>Prop Coating</td>
<td>10000</td>
</tr>
</tbody>
</table>

Comparison between HCl and HF permeation coefficients

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeation coefficient, cm³(g)-mm/M²-day-atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td>PE</td>
<td>430</td>
</tr>
<tr>
<td>PP</td>
<td>600</td>
</tr>
<tr>
<td>PVDF</td>
<td>75</td>
</tr>
<tr>
<td>ECTFE</td>
<td>45</td>
</tr>
<tr>
<td>PFA</td>
<td>300</td>
</tr>
<tr>
<td>PTFE</td>
<td>250</td>
</tr>
<tr>
<td>Proprietary Coating</td>
<td>8</td>
</tr>
</tbody>
</table>

@ 33°C
Comparison between HCl and HF permeation rates with “as-received” acid

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Relative permeability</th>
<th>Vapor pressure, atm</th>
<th>Relative permeation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
<td>HF</td>
<td>37% HCl</td>
</tr>
<tr>
<td>PE</td>
<td>9.6</td>
<td>-</td>
<td>0.44</td>
</tr>
<tr>
<td>PP</td>
<td>13.3</td>
<td>93</td>
<td>0.44</td>
</tr>
<tr>
<td>PVDF</td>
<td>1.7</td>
<td>196</td>
<td>0.44</td>
</tr>
<tr>
<td>ECTFE</td>
<td>1.0</td>
<td>80</td>
<td>0.44</td>
</tr>
<tr>
<td>PFA</td>
<td>6.7</td>
<td>58</td>
<td>0.44</td>
</tr>
<tr>
<td>PTFE</td>
<td>5.6</td>
<td>60</td>
<td>0.44</td>
</tr>
<tr>
<td>Coated PFA</td>
<td>1.4</td>
<td>58</td>
<td>0.44</td>
</tr>
</tbody>
</table>

@ 33°C
Component lifetime predictions

Assumption: Component lifetime is inversely proportional to the rate at which the acid gas reaches the component.
Predicted PFA coated component life based on HCl permeation rate
(assumes that failure rate is proportional to permeation rate)
Predicted relative lifetimes of PFA coated components under expected use conditions

<table>
<thead>
<tr>
<th>Acid</th>
<th>Concentration (weight %)</th>
<th>Temperature (°C)</th>
<th>Relative lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>6.3</td>
<td>75</td>
<td>3,100</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>40</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>75</td>
<td>1.0</td>
</tr>
<tr>
<td>HF</td>
<td>0.5</td>
<td>20</td>
<td>8,400</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>1,350</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>20</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Impeller life tests

- Three studies on-going
- BPS3 pump circulating 35-37% HCl at room temperature
  - PVDF housing
  - ECTFE impeller magnet encapsulation
- BPS1, BPS3 and BPS4 pumps are circulating 30-32% HCl at 75°C.
  - Pump body
    - BPS3 – PFA
    - BPS1 and BPS4 - PTFE
  - PFA impeller magnet encapsulation
- Static soak of PFA impellers with two encapsulation thicknesses (1.4 mm and 0.7 mm) in 30-32% HCl at 70°C.
- No contamination related failures have been observed in any of the tests.
Levitronix design approach for contamination prevention

- Pumps are designed to sense and respond to changes in impeller size.
- The response provides an early indication of impeller swelling due to magnet corrosion.
- These accelerated life tests are designed to determine:
  - when the impeller size changes enough for the pump to sense and respond to impeller swelling (useful service life) and
  - if or when metal ions are released from the impeller (safe life)
- Goal is to have a safe life well beyond the useful service life of the impeller.
Predicted lifetimes based on pumps and impellers currently under test

<table>
<thead>
<tr>
<th>Pump Model</th>
<th>Run Time (Days)</th>
<th>Average Temp (°C)</th>
<th>Average HCl Assay (wt%)</th>
<th>Service Life @ 37%/20°C (Years)</th>
<th>Safe Life @ 37%/20°C (Years)</th>
<th>Service Life @ 6.3%/75°C (Years)</th>
<th>Safe Life @ 6.3%/75°C (Years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPS 3</td>
<td>2150</td>
<td>RT</td>
<td>35-37</td>
<td>&gt; 5.9</td>
<td>&gt; 5.9</td>
<td>&gt; 830</td>
<td>&gt; 830</td>
</tr>
<tr>
<td>BPS 1</td>
<td>546</td>
<td>70.0</td>
<td>28.7</td>
<td>10.5</td>
<td>&gt; 12.0</td>
<td>1,500</td>
<td>&gt; 1,700</td>
</tr>
<tr>
<td>BPS 3</td>
<td>590</td>
<td>74.4</td>
<td>29.9</td>
<td>15.5</td>
<td>&gt; 19.9</td>
<td>2,200</td>
<td>&gt; 2,800</td>
</tr>
<tr>
<td>BPS 4</td>
<td>590</td>
<td>74.3</td>
<td>30.2</td>
<td>&gt; 20.7</td>
<td>&gt; 20.7</td>
<td>&gt; 2,900</td>
<td>&gt; 2,900</td>
</tr>
<tr>
<td>BPS 3 Impellers</td>
<td>115</td>
<td>69.9</td>
<td>30.6</td>
<td>&gt; 3.2</td>
<td>&gt; 3.2</td>
<td>&gt; 450</td>
<td>&gt; 450</td>
</tr>
</tbody>
</table>
Summary

- The permeation rate of HCl and HF through PFA was shown to:
  - Be proportional to the HCl or HF vapor pressure
  - Be inversely proportional to the coating thickness
  - Increase with temperature
- The permeation rates of HCl and HF through different polymers indicated that comparisons between HCl permeation rates through different polymers are not a good indicator for HF permeation rates through the same polymers (and vice versa).
- A model was developed to predict component failure rate resulting from acid gas (HCl or HF) permeation.
- The model, combined with on-going life test data, predicts pump lifetimes with PFA-coated impellers > 10 years under challenging use conditions.
- All observed failures have been pump efficiency related. No failures resulting in chemical contamination have been observed in any of the tests.