The Effects of Salt Water on the Slow Crack Growth of Soda Lime Silicate Glass

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Navy Ships at Sea

- Specialty window materials are being used on new navy vessels:

- Does the ocean environment change stress corrosion rates?
- Let’s measure the effects, starting with soda lime silicate.
Theory (Michalske et al.)

- Glass Bonds (Si-O-Si) have been shown to weaken in the presence of water due to Hydrogen-Oxygen interactions.
- Slow crack growth (SCG) is affected by this phenomenon, as the stressed surface area at crack/damage site is more susceptible.
Ionic Dissociation Model

Figure 1.—Siloxane dissolution by water, as described by Michalske and Freiman in Reference 2.
Theory (Cont’d)

• SCG in glasses and silica has also been investigated for environments other than water:

  - They demonstrated a shift in the SCG curve as function of environment, with little change in slope.

Theory (Cont’d)

• While SCG in glasses and silica has been exhaustively investigated, testing in a sodium solution (specifically sea water) has not been previously researched.

• It was hypothesized that the positive Sodium ions in sea water solution may inhibit water’s bond-breaking behavior.

• Sodium would congregate at Siloxane sites and act as a film upon the crack surface, repelling the water’s Hydrogen while attracting the Oxygen side.
Figure 2.—Water interaction with positive sodium film, attached to slightly susceptible siloxane bonds at glass flaw site.
Procedure

• Constant Stress-Rate Tests (ASTM C1368) (10 to 10\(^{-3}\) MPa/s stress rates)
• Annealed slide plates in 4-point flexure
• Distilled, deionized water or sea water simulant (PH 7 & 7.5)
• To minimize variation (CV = 3%), 1kg Vickers Indentation pre-cracks were used.
• ~5 tests at 4 stress rates.
• For inert strength testing, 15 tests were run in silicone oil at 25 MPa/s (~2s failure time).
Procedure

• Parameters SCG A and \( n \) were calculated using the curves generated from the SCG data, paired with the geometry of the samples and inert fracture strength data.
Slow Crack Growth Analysis

- Data was fit to the power law formulation:

\[ v = \frac{da}{dt} = AK_I^n = A^* \left( \frac{K_I}{K_{IC}} \right)^n \]

- \( V \) = velocity
- \( a \) = crack length
- \( t \) = time
- \( A, n \) = SCG parameters
- \( K_I \) = Mode I stress intensity factor
- \( K_{IC} \) = fracture toughness
**Slow Crack Growth Analysis**

- For constant stress rate testing, fracture stress is plotted as a function of stress rate:

\[
\sigma_f = \left[ B(n + 1)\sigma_i^{n-2} \dot{\sigma} \right]^{1/(n+1)}
\]

\[
B = \frac{2K_{lc}^{2-n}}{AY^2(n-2)} = \frac{2K_{lc}^2}{A^*Y^2(n-2)}
\]

- Parameter extraction via regression:

\[
\log_{10} \sigma_f = \frac{1}{n + 1} \log_{10} \dot{\sigma} + \log_{10} D
\]

\[
\log_{10} D = \frac{1}{n + 1} \log_{10} [B(n + 1)\sigma_i^{n-2}]
\]

(Slope \(\alpha\))  (Intercept \(\beta\))
Figure 3.—Fracture stress as a function of stress rate for fits to mean and median values with 95 percent confidence interval.

- The results are insensitive to the values fit
Results

• Regression Statistics and Slow Crack Growth Parameters:

\[ v = \frac{da}{dt} = A K_I^n = A^* \left( \frac{K_I}{K_{IC}} \right)^n \]

<table>
<thead>
<tr>
<th>Testing Environment</th>
<th>(a)</th>
<th>(\beta)</th>
<th>(n)</th>
<th>(A)  (m/s (MPa\sqrt{m})^{-n})</th>
<th>(B)  MPa²s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled (Not soaked)</td>
<td>0.057±0.002</td>
<td>1.62±0.003</td>
<td>16.4±0.64</td>
<td>1.48E-01</td>
<td>6.15</td>
</tr>
<tr>
<td>Saltwater</td>
<td>0.061±0.003</td>
<td>1.63±0.005</td>
<td>15.5±0.76</td>
<td>5.93E-02</td>
<td>13.39</td>
</tr>
<tr>
<td>Double concentration saltwater</td>
<td>0.064±0.002</td>
<td>1.64±0.005</td>
<td>14.7±0.59</td>
<td>2.63E-02</td>
<td>26.74</td>
</tr>
<tr>
<td>Distilled (Soaked 40 hours)</td>
<td>0.067±0.002</td>
<td>1.66±0.004</td>
<td>13.9±0.47</td>
<td>1.95E-02</td>
<td>31.99</td>
</tr>
</tbody>
</table>

• Nominal \(n\) is 15. Are the difference significant??
Statistical Significance

- To determine the significance of the slope differences of any two curves, the statistics $F$ and $t$ were calculated:

$$F_{\alpha} = \frac{SD_{\alpha_1}^2}{SD_{\alpha_2}^2}$$

$$t_{\alpha} = \frac{|\alpha_1 - \alpha_2|}{\sqrt{SD_{\alpha_1}^2 + SD_{\alpha_2}^2}}$$

- $SD$ = standard deviation of points used for slope calculation
- $\alpha$ = slope derived from regression
Results

• The value of $F$ proved to be insignificant in all but the pre-soak test cases, implying the slopes are directly comparable (similar variation).

• Salt and distilled water do not exhibit a statistically significant difference in SCG slope; however, doubling the concentration to twice that of sea water creates a small but significant difference at 94% confidence.

• Between pre-soaked and non pre-soaked data sets, the associated $F$ statistic shows the difference in variation to be significant, and indicates both a strength increase and scatter decrease for inert testing of glass in the case of pre-soaked specimens.
Results

- Long-term strengths are similar, whereas the short-term strengths (45~50 MPa) are greatest for the soaked specimens and those tested in saltwater, implying blunting during soaking and a weak passivation for salt solutions.
- The strength increase with soaking is confirmed by the inert strength results shown in the previous slide, and an improved variance is implied.
- This decreased variance was not observed at slower stress rates, implying that the effects of soaking during stress rate testing which lasted from ~5 s to ~10 hours were minimal.
Results

The results reflect the stress rate curves, with small but systematic differences.

Figure 4.—Crack velocity as a function of stress intensity.

- Distilled water, no soak
- Saltwater
- Distilled water, 40-h soak
- Saltwater, double concentration
Effect of Humidity on SCG of 8330 Borosilicate glass

- The effects of humidity are much greater than those of salt:
Conclusions

• Based on the experimental data, the effects of salt water at ocean levels of salinity and mineral content have little effect on the slow crack growth rate of glass.
  – From an application standpoint, this rules out concern for glass in constant contact submerged in seawater
  – However, surface glass may experience a buildup of salt (e.g. sea spray) in an environment of high relative humidity, which is where these findings should applied.

• The small decrease in \( n \) with increasing concentration at room temperature can be ignored for engineering purposes.
Conclusions

• Soaking of indented specimens does create a small but significant decrease in the SCG parameter $n$, and improves inert strength and variance.

• As many components spend much of the life time at low loads in humid environments, presoaking test specimens might better reflect component crack growth behavior.
Future Work

- Testing in varying ambient temperatures would be interesting, as it may affect the Sodium ion’s influence on the water-glass reaction.
- Static fatigue testing in circulated salt water or in a simulant sea spray environment would be beneficial to more accurately simulate SCG of glass in naval applications.
- Detailed study of the surface and Ph level to better understand the chemistry.
References


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