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Effects of Aqueous Solutions on Slow Crack Growth of Soda-Lime-Silicate Glass

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Summary

The slow crack growth (SCG) parameters of soda-lime-silicate were measured in distilled and saltwater of various concentrations in order to determine if the presence of salt and the contaminate formation of a weak sodium film affects stress corrosion susceptibility. Past research indicates that solvents affect the rate of crack growth; however, the effects of salt have not been studied. The results indicate a small but statistically significant effect on the SCG parameters *A* and *n* at high concentrations; however, for typical engineering purposes, the effect can be ignored.

Introduction

The strength degradation of silicate glass when stressed in the presence of water is a well-known phenomenon. Less known are effects of common water-soluble environmental agents such as salt. A previous study indicates no effect of human body fluid simulant on slow crack growth (SCG) of alumina (Ref. 1). The effects of solvents on SCG rates of silicates were studied by Michalske and Freiman (Ref. 2) who demonstrated that in the presence of stress molecules having structures similar to water broke the silicate bond, whereas molecules lacking the shape and orbital configuration of water tended to have little or no effect. They concluded that the degradation mechanism is dissociative absorption of water, which causes the formation of silanol groups, effectively breaking the siloxane bonds (Fig. 1). This effect is of particular interest at damage sites in silicate glasses because the sites have residual stresses and cracks form or extend from these sites when external stresses are applied. If glass bonds dissociate or dissolve in water, any residual stresses and microcracks existing at the damage sites are relieved and blunted without significant damage to the aggregate material, resulting in higher strength.

Because salt forms an ionic solution in water, it might be expected to have little effect at low concentrations, whereas at high concentrations (such as in seawater), the charge of the dissolved ions may result in the formation of a weak film of sodium, motivated by the slightly polar siloxane bonds (Fig. 2). It follows that lower stress levels or stress rates would provide for further inhibition of the saltwater's effects by allowing increased ion infiltration at a crack site.

To study the effect of salt on the stress corrosion susceptibility of glass, soda-lime-silicate slide plates were tested in four-point flexure in both distilled water and seawater simulant at progressively greater stress rates. The SCG parameters were estimated in accordance with ASTM International C1368. This report compares parameters of SCG in distilled and saltwater.

*NASA Glenn Research Center, summer intern from Case Western Reserve University.

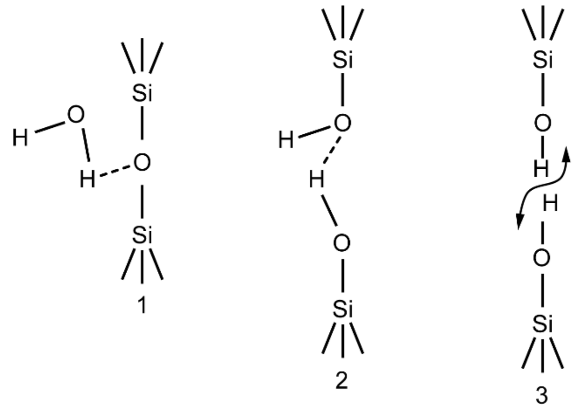


Figure 1.—Siloxane dissolution by water, as described by Michalske and Freiman in Reference 2.

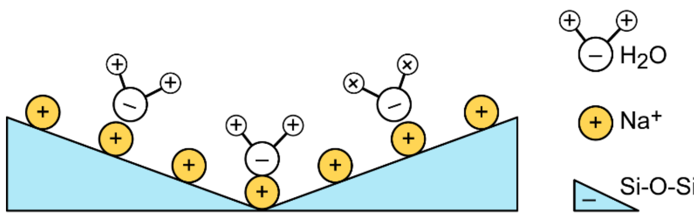


Figure 2.—Water interaction with positive sodium film attached to slightly susceptible siloxane bonds at glass flaw site.

Symbols

A	material/environmental slow crack growth parameter
B	parameter associated with A, n, fracture toughness, crack geometry, and loading configuration
D	parameter in Table I, $=10^{\beta}$
F_{α}	ratio of regression slope F statistics
K_I	Mode I stress intensity factor
K_{IC}	fracture toughness
ℓ	number of standard deviations corresponding to desired probability level
n	material/environmental slow crack growth parameter
Q	quantity in Equations (10), (12), and (14) defined in Equation (15) as $Q = \alpha - \beta \ln 10 + 1n\sigma_i$
SD	standard deviation
t_{α}	Student's t statistic
v	crack velocity
Y	geometry correction factor
α	slope of regression curve
β	intercept of regression curve
σ_f	fracture strength
σ_i	inert strength
$\dot{\sigma}$	applied stress rate
ϕ	degrees of freedom

Procedure

Fracture strength as a function of stress rate was measured at 20 °C by using four point flexure of annealed soda-lime-silicate slides (23- by 1.6-mm cross section loaded between 20 and 40 mm spans) at rates ranging from 10^{-3} to 10^{1} MPa/s in distilled water or simulant seawater.† In order to minimize variation, which was usually less than 3 percent of the mean at any stress rate, the specimens were precracked by using a Vickers indenter at 1 kg. In addition to running tests immediately after indentation, a set of specimens was subject to soaking in distilled water for at least 40 h. Usually 20 specimens were run per environmental condition. For the purposes of parameter analysis, the inert strength (i.e., the strength in the absence of a corrosive environment) was determined by testing 15 specimens per condition in silicone oil at a rate of ~25 MPa/s. This resulted in failure in 2 to 3 s.

Data Analysis

The data collected were fit to the power law formulation:

$$v = AK_I^n = A^*\left(\frac{K_I}{K_{IC}}\right)^n \tag{1}$$

where v is crack velocity. Constants A and n are the material and environment dependent SCG parameters, and K_I and K_{IC} are, respectively, the Mode I stress intensity factor and the critical stress intensity factor (or fracture toughness) of the material. For constant-stress-rate testing based on the power law formulation, the fracture strength, σ_f, is expressed as a function of stress rate as (Ref. 3)

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

where $\dot{\sigma}$ is the applied stress rate, σ_i is the inert strength, and B is a parameter associated with A, n, fracture toughness, crack geometry, and loading configuration (see Eq. (13)). The SCG parameter n can be determined from a plot of log σ_f as a function of log $\dot{\sigma}$ with Equation (2) written as

$$\log\sigma_f = \frac{1}{n+1}\log\dot{\sigma} + \log D \tag{3}$$

where

$$\log D = \frac{1}{n+1}\log\left[B(n+1)\sigma_i^{n-2}\right] \tag{4}$$

Once the slope α and intercept β are estimated by linear regression of Equation (3), the parameters n, D, B, and A, and their standard deviations SD, are estimated from (Refs. 4 and 5)

$$n = \frac{1}{\alpha} - 1 \tag{5}$$

†Instant Ocean Reef Crystals, Blacksburg, VA 24060; specific gravity ~1.021.

$$SD_n \approx \frac{SD_\alpha}{\alpha^2} \tag{6}$$

$$D = 10^\beta \tag{7}$$

$$SD_D \approx 2.3026\left(SD_\beta\right)\left(10^\beta\right) \tag{8}$$

$$B = \frac{\alpha\left(10^{\beta/\alpha}\right)}{\sigma_i^{\left(\frac{1}{\alpha}-3\right)}} \tag{9}$$

$$SD_{\ln B} \approx \frac{1}{\alpha}\sqrt{Q^2\frac{SD_\alpha^2}{\alpha^2} + (\ln 10)^2 SD_\beta^2 + (1-3\alpha)^2 SD_{\ln\sigma_i}^2 + 2Q\ln 10\frac{\mathrm{Cov}(\alpha,\beta)}{\alpha}} \tag{10}$$

$$A^* = \frac{2K_{IC}^2\ \sigma_i^{\left(\frac{1}{\alpha}-3\right)}}{10^{\beta/\alpha}(1-3\alpha)Y^2} = \frac{2K_{IC}^2}{B(n-2)Y^2} \tag{11}$$

$$SD_{\ln A^*} \approx \frac{1}{\alpha}\sqrt{\begin{aligned}&4\alpha^2\frac{SD_{K_{IC}}^2}{K_{IC}^2} + \left(Q-\frac{\alpha}{1-3\alpha}\right)^2\frac{SD_\alpha^2}{\alpha^2} + (\ln 10)^2 SD_\beta^2 \\ &+ (1-3\alpha)^2 SD_{\ln\sigma_i}^2 + 2\ln 10\left(Q-\frac{\alpha}{1-3\alpha}\right)\frac{\mathrm{Cov}(\alpha,\beta)}{\alpha}\end{aligned}} \tag{12}$$

$$A = \frac{2K_{IC}^{\left(3-\frac{1}{\alpha}\right)}\sigma_i^{\left(\frac{1}{\alpha}-3\right)}}{10^{\beta/\alpha}(1-3\alpha)Y^2} = \frac{2K_{IC}^{2-n}}{B(n-2)Y^2} \tag{13}$$

$$SD_{\ln A} \approx \frac{1}{\alpha}\sqrt{\begin{aligned}&(3\alpha-1)^2\frac{SD_{K_{IC}}^2}{K_{IC}^2} + \left(Q-\frac{\alpha}{1-3\alpha}-\ln K_{IC}\right)^2\frac{SD_\alpha^2}{\alpha^2} + (\ln 10)^2 SD_\beta^2 \\ &+ (1-3\alpha)^2 SD_{\ln\sigma_i}^2 + 2\ln 10\left(Q-\frac{\alpha}{1-3\alpha}-\ln K_{IC}\right)\frac{\mathrm{Cov}(\alpha,\beta)}{\alpha}\end{aligned}} \tag{14}$$

where

$$Q = \alpha - \beta\ln 10 + \ln\sigma_i \tag{15}$$

$$\mathrm{Cov}(\alpha,\beta) = -SD_\alpha^2\left(\overline{\log\dot{\sigma}}\right) \tag{16}$$

where $\overline{\log\dot{\sigma}}$ is the mean of the logs of the applied stressing rates, Y is the geometry correction factor for the stress intensity factor, and the standard deviation associated with the inert strength $SD_{\ln\sigma_i}$ is calculated in logarithmic space. Probability limits on the parameters B and A can be calculated from

$$B_{\substack{\text{Upper}\\\text{Lower}}} = \exp\left[\ln B \pm t\left(SD_{\ln B}\right)\right] \text{ and } A_{\substack{\text{Upper}\\\text{Lower}}} = \exp\left[\ln A \pm t\left(SD_{\ln A}\right)\right] \tag{17}$$

by using Student's *t* distribution for the degrees of freedom (DOF) and probability level desired. If the DOF is greater than ~40, then

$$B_{\substack{\text{Upper}\\\text{Lower}}} = \exp\left[\ln B \pm \ell\left(SD_{\ln B}\right)\right] \text{ and } A_{\substack{\text{Upper}\\\text{Lower}}} = \exp\left[\ln A \pm \ell\left(SD_{\ln A}\right)\right] \tag{18}$$

where ℓ is the number of standard deviations corresponding to the probability level desired. The DOF, ϕ, is given by

$$\begin{aligned}\frac{\left(SD_{\ln B}^2\right)^2}{\phi_{\ln B}} = {} & \frac{1}{\phi_{\ln \sigma_i}}\left[\frac{(1-3\alpha)^2}{\alpha^2} SD_{\ln \sigma_i}^2\right]^2 + \\ & \frac{1}{\phi_{\alpha\beta}}\left[Q^2 \frac{SD_\alpha^2}{\alpha^4} + (\ln 10)^2 \frac{SD_\beta^2}{\alpha^2} + 2Q\ln 10 \frac{\text{Cov}(\alpha,\beta)}{\alpha^3}\right]^2\end{aligned} \tag{19}$$

and

$$\begin{aligned}\frac{\left(SD_{\ln A}^2\right)^2}{\phi_{\ln A}} = {} & \frac{1}{\phi_{\ln K_{Ic}}}\left(4SD_{\ln K_{Ic}}^2\right)^2 + \frac{1}{\phi_{\ln \sigma_i}}\left[\frac{(1-3\alpha)^2}{\alpha^2} SD_{\ln \sigma_i}^2\right]^2 + \\ & \frac{1}{\phi_{\alpha\beta}}\left[\left(Q - \frac{\alpha}{1-3\alpha}\right)^2 \frac{SD_\alpha^2}{\alpha^4} + (\ln 10)^2 \frac{SD_\beta^2}{\alpha^2} + 2\ln 10\left(Q - \frac{\alpha}{1-3\alpha}\right)\frac{\text{Cov}(\alpha,\beta)}{\alpha^3}\right]^2\end{aligned} \tag{20}$$

where ϕ_{σ_i} is the DOF in inert strength (number of inert strength tests minus one) and $\phi_{\alpha\beta}$ is the DOF in regression (number of constant stress rate tests minus two).

Three approaches were used to estimate the slope and intercept of Equation (3): linear regression of (1) the individual data points; (2) the median values; and (3) the average values. Very little difference resulted between the approaches, and the parameter presented correspond to regression of the individual data points.

Inert and Time-Dependent Strength

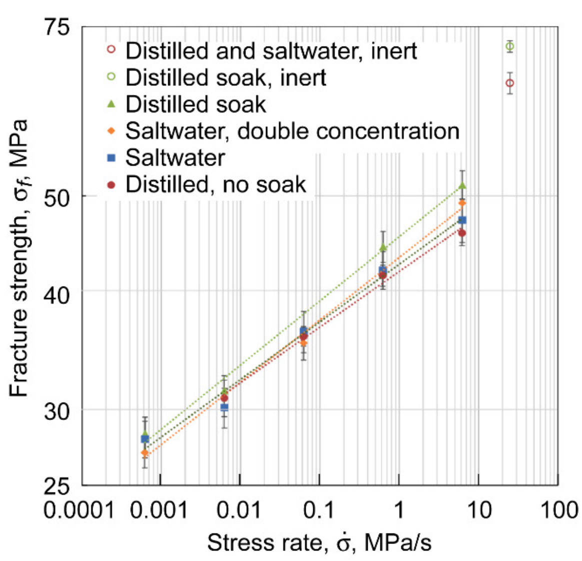
The fracture strength as a function of stress rate is plotted in Figure 3 for both median and mean values. Similar slopes are exhibited, with the distilled water (no soak) tests showing the least SCG and the 40-h soak distilled water tests showing the most SCG (greatest slope). The addition of salt increases the SCG rate compared to distilled water. Doubling the salt concentration increased the SCG further. Interestingly, the long-term strengths are similar, whereas the short-term strengths (10 MPa/s) are greatest for the soaked specimens and those tested in saltwater, implying blunting during soaking and a weak passivation for salt solutions. At slower stress rates, the effect of passivation is negligible, resulting in a steep slope and lower *n*. The strength increase with soaking is confirmed by the inert strength results shown in Figure 3, 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 h, were minimal.

To determine the significance of the slope differences of any two curves, the statistics F_α and t_α were calculated using (Ref. 6):

$$F_\alpha = \frac{SD_{\alpha 1}^2}{SD_{\alpha 2}^2} \text{ and } t_\alpha = \frac{\left|\alpha_1 - \alpha_2\right|}{\sqrt{SD_{\alpha 1}^2 + SD_{\alpha 2}^2}} \tag{21}$$

The value of *F* proved to be insignificant in all test cases implying similar variances, and the DOFs of the two slopes were pooled to equal N – 4. The combined DOF was used to determine if the slopes were significantly statistically different via Student's *t* test.

Saltwater and distilled water do not exhibit a statistically significant difference in SCG slope; however, doubling the salt concentration to twice that of seawater creates a small but significant difference at 94 percent confidence. Soaking indented test specimens creates a significant difference in SCG slope at 99 percent confidence. Despite the significances, the magnitudes of the differences are small, especially when the effect of changes in relative humidity is considered (Ref. 4).



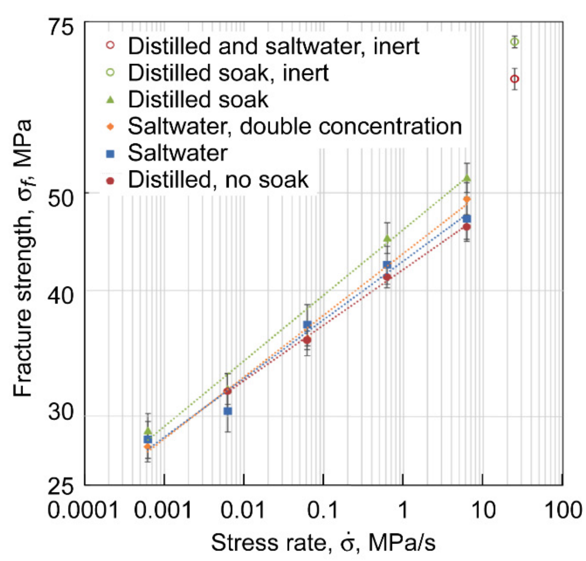


Figure 3.—Fracture stress as a function of stress rate for fits to mean and median values with 95 percent confidence interval.

It is noteworthy that the soaked specimens exhibited less scatter and higher average strength for inert strength tests than the freshly indented specimens (coefficient of variation (CV) = 2.5 vs. 4.6 percent), implying some stabilization of indentation cracks. 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. Because many components spend much of their lifetime at low loads in humid environments, presoaking test specimens might better reflect component crack growth behavior.

The SCG parameters estimated from Equations (5), (6), (8), and (13) are summarized in Table I, and the crack velocity as a function of stress intensity based on the estimated parameters is shown in Figure 4. The velocity curves reflect the ordering of the stress rate curves. For purposes of parameter estimation, the fracture toughness was taken as 0.80 $\text{MPa}\sqrt{\text{m}}$ (Ref. 4).

TABLE I.—REGRESSION STATISTICS AND SLOW CRACK GROWTH (SCG) PARAMETERS

Testing environment	Slope of regression curve,[a] α	Intercept of regression curve,[a] β	SCG parameter		
			n	A, m/s $\left(\text{MPa}\sqrt{\text{m}}\right)^{-n}$	B, $\text{MPa}^2{\cdot}\text{s}$
Distilled water (not soaked)	0.057±0.002	1.62±0.003	16.4±0.64	1.48×10^{-1}	6.15
Saltwater	0.061±0.003	1.63±0.005	15.5±0.76	5.93×10^{-2}	13.39
Double-concentration saltwater	0.064±0.002	1.64±0.005	14.7±0.59	2.63×10^{-2}	26.74
Distilled water (soaked 40 h)	0.067±0.002	1.66±0.004	13.9±0.47	1.95×10^{-2}	31.99

[a]From Equation (3) $\log\sigma_f = \frac{1}{n+1}\log\dot{\sigma} + \log D$, where σ_f is fracture strength, $\dot{\sigma}$ is applied stress rate, $n = \frac{1}{\alpha} - 1$, and $D = 10^{\beta}$.

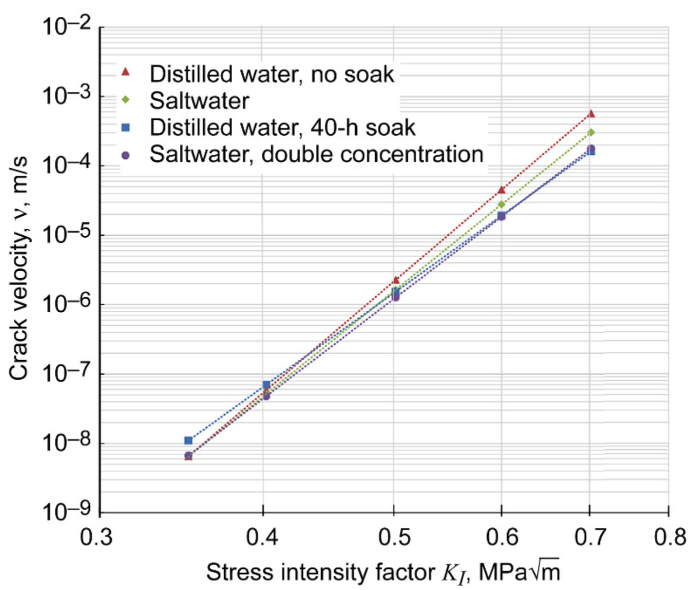


Figure 4.—Crack velocity as a function of stress intensity.

TABLE II.—COEFFICIENT OF VARIATION (CV) IN PERCENT FOR TEST SETS

Stress rate, MPa/s	Saltwater	Saltwater, double concentration	Distilled water, soak	Distilled water, no soak
6.2	4	3	2	2
0.62	4	--	3	2
0.06	4	3	--	2
0.006	4	--	3	3
0.0006	4	3	3	--
Inert (25)	5	5	2	5

Test Variance

The CV for each test set is listed in Table II. The CVs are relatively low in all cases (<10 percent), with the saltwater data exhibiting higher variances than the distilled water. This may be due to the weak film being relatively unstable. No trend with decreasing stress rate can be observed, and the soaked and no-soak data are similar. The most apparent trend is the decreased scatter for soaked specimens tested in an inert environment, as discussed in the previous section.

Conclusions

Based on the experimental data, the effects of saltwater at ocean levels of salinity and mineral content have little effect on the slow crack growth rate of glass. The small decrease in the slow crack growth (SCG) parameter *n* with increasing concentration at room temperature can be ignored for engineering purposes. Soaking of indented specimen does create a small but significant decrease in *n*, and improves inert strength and variance.

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