

Ionic effects on silica optical fiber strength and models for fatigue

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ABSTRACT

The strength and fatigue behavior of bulk fused silica is well understood in terms of the growth of microcracks under the combined influence of stress and environmental attack. The behavior of high strength, flaw free silica optical fiber shows significant differences from the bulk material for poorly understood reasons making long term predictions unreliable. It is known that silica fiber strength and fatigue are sensitive to such environmental parameters as temperature, humidity and pH. However, this paper presents results which also show a sensitivity to ionic species in the environment. These results are interpreted in terms of possible models for the fiber behavior.

1. INTRODUCTION

In most ceramic materials and, in particular, in oxide glasses, failure can occur after prolonged application of a constant stress which is significantly lower than the stress required to cause catastrophic failure on a short time scale. This phenomenon, called fatigue or delayed failure, can determine the long term reliability of ceramic components. A complete understanding of the mechanisms that produce delayed failure would allow one to make reliable lifetime predictions for components (in our case, optical fiber) under operating conditions.

The mechanism that causes fatigue in most ceramic materials consists of slow growth of pre-existing cracks up to the critical size for fast crack growth. The slow growth is due to stress-enhanced environmental attack of the strained bonds at the crack tip. The empirical relationship between the rate of growth of a macroscopic crack, dc/dt , and the applied stress intensity factor, K_I , may be described by a power law:¹

$$\dot{c} = A K_I^n \quad (1)$$

where n is the stress corrosion susceptibility parameter. By combining it with the Griffith relation,

$$K_I = \sigma Y c^{1/2} \quad (2)$$

and integrating, two equations can be obtained:

$$t_f = 2\sigma_a^{-n} \frac{1}{AY^2(n-2)} \left(\frac{\sigma_{IC}}{K_{IC}} \right)^{n-2} \quad (3)$$

relates the time to failure, t_f , to a constant applied stress, σ_a , (static fatigue) while

$$\sigma^{n+1} = 2\dot{\sigma} \frac{(n+1)}{(n-2)} \left(\frac{\sigma_{IC}}{K_{IC}} \right)^{n-2} \frac{1}{AY^2} \quad (4)$$

relates the strength, σ , to the loading rate, $d\sigma/dt$ (dynamic fatigue). It is noted that dynamic fatigue experiments can be used to determine the unknown parameters in Eq. (3) and hence predict time to failure under static conditions.

The slow crack growth model provides a good explanation of fatigue behavior for crack containing bulk glass. By considering the published data for high strength silica fiber, however, some discrepancies are noted. The value of n derived from Eq. (3) and (4) for weak, bulk silica is around 40, in good agreement with crack velocity measurements made

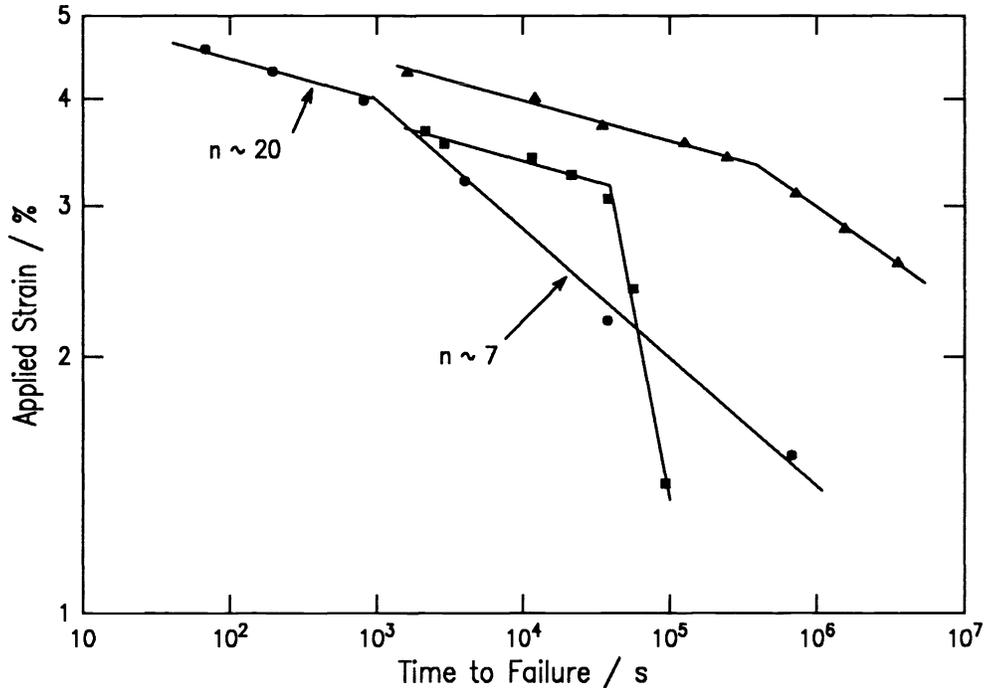


Fig. 1. Static fatigue results for fiber tested in tension. Key: • bare fiber in 90°C water³, ■ coated fiber in 90°C water⁴ and ▲ coated fiber in 40°C water.⁴

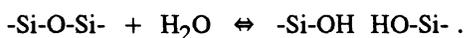
on silica containing macroscopic cracks. In contrast, the values reported for high strength silica fiber are typically around 20.² Furthermore, as seen in Fig. 1, results from long term fiber static fatigue indicate that, at least in a liquid water environment, the power law behavior of Eq. 1 does not hold at low applied stresses/long times to failure, and n falls to around 7 for as yet unknown reasons.

The crack growth theory does not provide an adequate explanation of the fatigue behavior of silica optical fiber. Kurkjian, Krause and Paek⁵ found that the liquid nitrogen strength of fiber is close to the theoretical ultimate strength of silica and that the distribution of strength is narrow and practically single valued. Therefore, they suggested that the fibers are essentially flaw-free (pristine) and do not contain sharp, well defined cracks. This implies that the fatigue mechanism involves surface crack initiation as the rate controlling step. Two initiation processes have been proposed in literature.

Kurkjian *et al.*⁵ suggested that the fiber fatigue is controlled by the formation and subsequent growth of surface "pits" that arise from differential corrosion rates caused both by fluctuations in the glass structure and by differences in local stress as the pit develops. The surface pits so formed are regions of stress concentration and stress assisted etching takes place. The stress profile in these regions produces a corresponding variation of the etching rate. The differential etching rates around the pit cause it, in contrast to the crack growth model, to change shape as well as depth.⁶

Dabbs and Lawn⁷ proposed a crack initiation stage caused by the presence of residual stresses around defects. For a more extensive discussion of this model see the article by Lin and Matthewson in this volume.⁸

On a molecular level, Michalske and Freiman⁹ proposed a mechanism for crack growth in fused silica in which water molecules (H₂O or D₂O) attack the strained bonds at the crack tip to produce two silanol groups, according to the reaction scheme



White, Freiman, Wiederhorn and Coyle¹⁰ suggested a second mechanism by which the silicon is attacked by a hydroxide ion. This mechanism explains the faster crack growth and strength degradation for high silica glasses at high pH.

Silica fiber fatigue is sensitive to the same parameters as bulk crack-containing silica. Strength or time to failure decrease with increasing temperature and humidity (e.g. Duncan, France and Craig¹¹) and increasing pH (e.g. Matthewson and Kurkjian¹²) reflecting the link with increasing water and hydroxyl activity and availability.

The influence of different ionic species in the environment (other than hydroxide) has been largely ignored, although some recent work does show a strength dependence on various ionic species.^{13,14} This paper presents results for strength and fatigue measurements in various aqueous hydroxides. It is found that at high pH the nature of the cations significantly influences the strength.

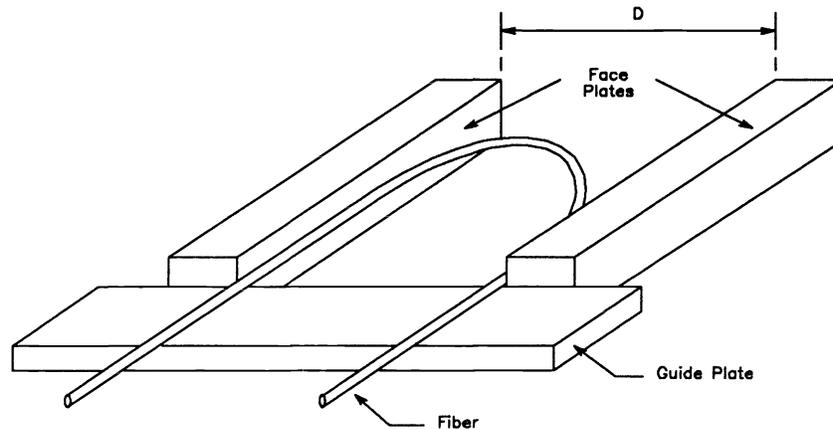


Fig. 2. Schematic of the two point bend apparatus for determining fiber strength.

2. EXPERIMENTAL

The two point bend apparatus that has been used to measure the strength of the fiber is shown schematically in Fig. 2. The fiber is held between two polished face plates that are brought together by a computer controlled stepper motor until the fiber breaks. An acoustic transducer and amplifier detect the break and halt the stepper motor. Polished face plates are used because their flat surface allow to test unprotected bare fiber to be tested without damaging the fiber surface.¹⁵ A different version of the apparatus, in which the fiber is held between grooved plates, is used for testing coated fiber.¹⁶ The two point bend technique is particularly useful for this kind of experiment because it is simple to use and the face plates with the fiber can easily be immersed in an environment. Short term dynamic fatigue experiments can be complimented by long term static fatigue in two point bending using precision bore glass tubes.¹⁷

The maximum strain on the fiber, ϵ_f , is calculated from the face plate separation at failure, D , using

$$\epsilon_f = 2.396 \frac{r}{D-d} \quad (5)$$

where r is the fiber radius and d is the overall fiber diameter including any coating. The polymer protective coating was stripped from the section of fiber to be tested by dipping into hot concentrated sulfuric acid. Therefore, in Eq. 5 $2r = d = 125\mu\text{m}$. Since this work is concerned with the interaction of the silica with the environment and since the time scale of the dynamic fatigue experiments is short compared to the diffusion times through the coating, no effects would be detected by using coated fiber. On the other hand, the results for bare fiber under accelerated testing conditions are thought to be a good model for polymer coated fiber under long term service conditions, when corrosion of the silica surface rather than diffusion through the coating is the rate controlling step for fatigue.¹² Immediately after stripping, the fiber was loaded in the two point bend apparatus at a face plate separation of 12mm (1.3% strain) and immersed into the test solution.

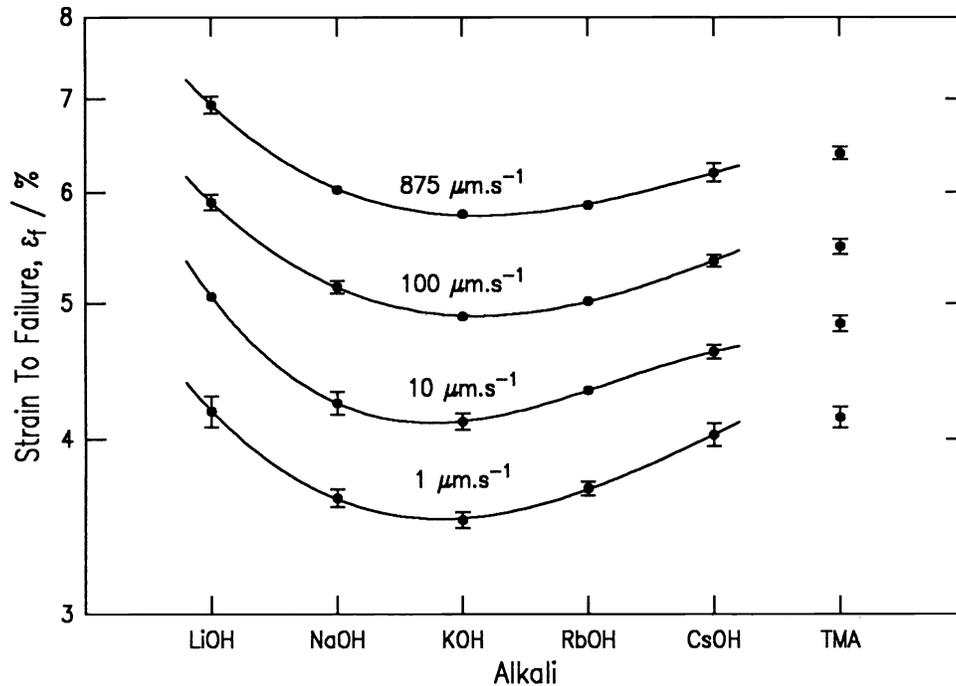


Fig. 3. Strain to failure as a function of 1N alkali solutions for four different face plate velocities.

Solutions of LiOH, NaOH, KOH, RbOH, CsOH and $(\text{CH}_3)_4\text{NOH}$ (tetramethylammonium hydroxide or TMA) in concentrations of 1N, 10^{-2}N and 10^{-4}N were made up in deionized water. All materials were kept in tightly stoppered bottles to minimize adsorption of atmospheric moisture and carbon dioxide. All the tests were performed at ambient laboratory temperature. The temperature of the test solution was measured for each specimen. The temperature dependence of strength was determined and all results have been corrected in order to take into account the small temperature variations.

3. RESULTS

Fig. 3 shows the results for strength measurement of the bare fiber in 1N alkali solutions. Each point represents an average of ten specimens and the error bars represent a 95% confidence interval. A pronounced cation effect is observed for the alkali metal hydroxides with a minimum strength for potassium.

Fig. 4 presents results for strength measurements of bare fiber as a function of alkali for three different ionic strengths. The cation effect observed in 1N solution is still apparent though less pronounced in 10^{-2}N (nominal pH 12) solution, but no effect is detectable at 10^{-4}N (nominal pH 10). The cation effect is therefore only important in the most basic solutions and this observation probably explains why ionic effects are rarely reported in the literature. However, ionic effects can have practical relevance as well as academic, since fiber cables can experience a highly basic environment, for example if accidentally immersed in alkaline cleaners.

Fig. 5 shows the data of Fig. 3 replotted as strain to failure versus face plate velocity on logarithmic axes. The data fit a power law dependence closely. Apart from the LiOH, the lines appear to converge at a face plate velocity of the order of $0.1\text{m}\cdot\text{s}^{-1}$ corresponding to a time scale of a few microseconds. This means that the interaction of the cations with the silica surface takes place on an extremely short time scale. The stress corrosion parameter, n , may be determined from the slopes of these lines and the results are shown in Fig. 6. There is a systematic trend with cation, again with a minimum around sodium or potassium. This shows that the strength differences observed in Fig. 3 are a result of differing values for n . The measured values of n are somewhat lower than the generally accepted value of around 20 measured under more neutral conditions (pH ~ 7). However, the results are consistent with static fatigue measurements at 90°C on stripped silica fiber by Krause and Shute¹⁸ who observed n fall from 21 at pH 7 to 13 at pH 14.

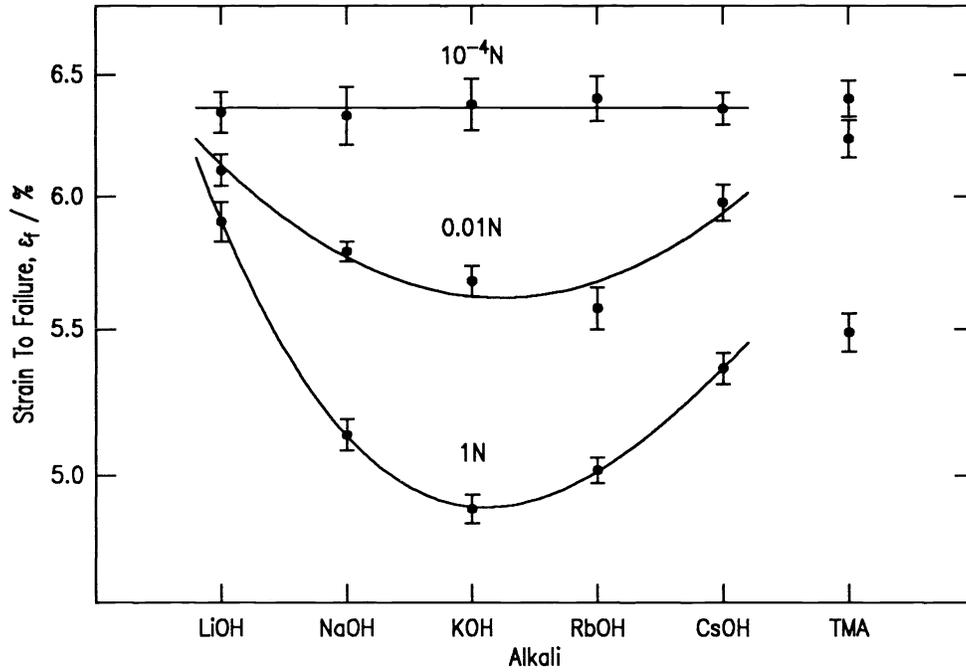


Fig. 4. Strength as a function of hydroxide for three different concentrations and a face plate velocity of $100\mu\text{m}\cdot\text{s}^{-1}$.

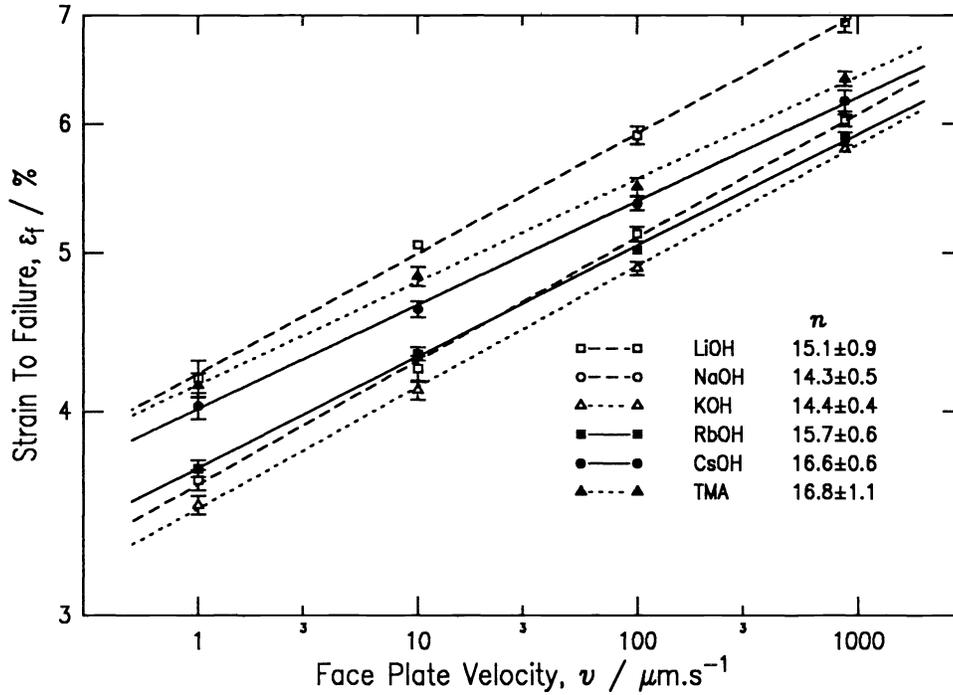


Fig. 5. Data of Fig. 3 replotted as dynamic fatigue curves.

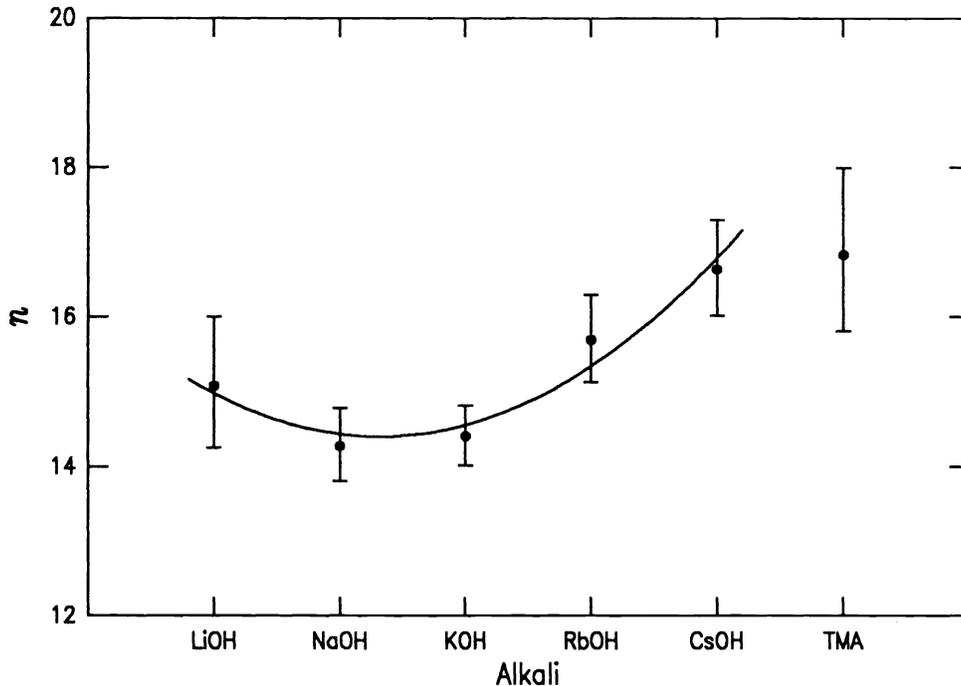


Fig. 6. Stress corrosion parameter, n , as a function of alkali for dynamic fatigue in 1N solution.

4. DISCUSSION

The data reported here indicate that the cation effect is actually due to the presence of different cationic species and is not (except perhaps partially for lithium) due to different effective hydroxide concentrations, even though the cation dependence of the strength degradation is evident only at high pH values. The alkali metal ions, therefore, have different catalytic powers on the strength degradation mechanism.

Ionic effects are well known in sol-gel chemistry; in particular, the dissolution rate of silica is known to be cation dependent. In Fig. 7 is shown the dissolution rate of silica gel in 3N alkali metal hydroxides examined by using ^{29}Si -NMR.¹⁹ There is a remarkable correlation with the strength results shown in Fig. 3; the cations giving the highest strength exhibit the lowest dissolution rates. The strong correlation between strength and dissolution rate suggests that the strength degrading mechanism involves dissolution. It does not constitute proof, though, since many aspects of silica chemistry are cation dependent. However, such a correlation would be expected from the "pit" model of Kurkjian *et al.*⁵ A further implication of our results is that the early controlling stages of high strength fiber fatigue is an essentially surface or near-surface process and does not involve diffusion of reactants into and products out of the body of silica.

Published data for macroscopic crack growth velocities in bulk silica glass are similar in 1N NaOH, KOH and CsOH.¹⁰ Apart from the anomalous behavior of lithium which reduces the effective pH by associating with hydroxide ions, these data show no cation dependence for crack growth, in marked contrast to the results presented here. Therefore, our results can not be explained in terms of crack growth kinetics.

The reasons for the observed cation effect are not clear, however one can postulate mechanisms. At high pH the fatigue is clearly dominated by hydroxyl attack, rather than by molecular water attack, since strength generally falls with increasing pH. Silica, above the isoelectric point around pH 3, has an increasingly negative surface charge in aqueous environments that saturates at a maximum value above pH 11. This surface charge will repel the negatively charged hydroxide ions. Charge neutrality requires that a layer of cations be near silica surface and therefore we propose that the cations act as intermediaries that overcome the electrostatic repulsion between the surface and the hydroxyls. They perform this task by

associating with the hydroxyls and screening their negative charge with the hydration layer. The efficacy of this mechanism depends not only on the extent of the hydration layer but also on how tightly the cation binds to the water and anions. Lithium has a large hydration shell but the bare cation radius is small enabling tight binding to the hydroxide ion which can not then easily be released. On the other hand, cesium has a weakly bound hydration layer but it is too thin to significantly screen the charge on the hydroxide ion. In contrast, potassium has a hydration shell that is both thick enough and loosely bound enough to effectively transfer the hydroxyls to the silica surface, resulting in the highest rate of attack and hence fastest strength degradation. This mechanism, therefore, views the cation effect as being due to the different catalytic powers of the different ionic species.

There is currently no analytic model for high strength fiber fatigue that considers these complicated processes. Therefore, any lifetime predictions must be considered merely empirical extrapolations. Predictions for behavior under different environments and stress conditions not fully explored by appropriate experiments must be treated with conservatism.

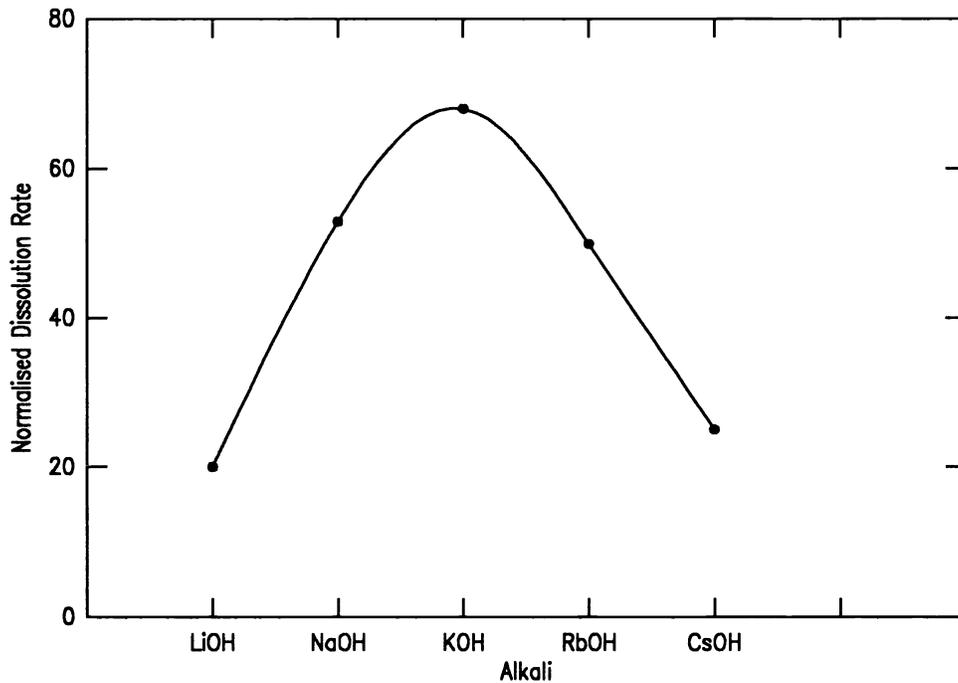


Fig. 7. Rate of dissolution of silica in various 3N alkalis (from Wijnen *et al.*¹⁹).

5. CONCLUSIONS

Strength and dynamic fatigue experiments have been performed using the two point bend technique on bare pristine silica fiber immersed in different alkali hydroxide solutions. The results for 1N concentration indicate a strong cation dependence of the fiber strength. The effect diminishes in more dilute solutions and is not apparent at 10^{-4} N. The stress corrosion susceptibility parameter, n , shows the same cation dependence.

These results correlate closely with published solubility data. The maximum degradation in strength corresponds to the maximum rate of dissolution (KOH). A direct implication of these results is that the rate controlling mechanism of fiber fatigue is a surface process not involving diffusion through the body of the silica. This correlation provides evidence for the pit model for silica fiber strength proposed by Kurkjian *et al.*⁵ Stress activated dissolution at surface pits causing sharpening of the pits is considered the mechanism of initiation of well defined cracks in the surface of the silica.

The experiments, performed under accelerated conditions on a short time scale on bare fiber, are an effective model for studies on long term reliability of optical fiber. The protective coating acts, on a short time scale, as a diffusion barrier to reactants and reaction products. On a long time scale, however, diffusion is less significant and the strength degradation is controlled by the interaction between the silica and the environment.¹² Therefore, in order to investigate the degradation mechanisms that affect the long term in-service behavior of the fiber, it is necessary either to perform fatigue tests on coated fiber for long times or to test, as in our case, bare fiber under accelerated conditions.

6. ACKNOWLEDGEMENTS

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