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DISCUSSION OF GLASS - WATER INTERACTIONS
Physical and Chemical Processes

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Advanced Technology Development Section
Research and Development Department
Chemical Processing Division

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DISCUSSION OF GLASS - WATER INTERACTIONS

Physical and Chemical Processes

F. E. Diebold

SUMMARY

Leaching data for the alkali and alkaline earth silicate glasses are reviewed with the objective of generating a plausible mechanism for describing glass-water interactions. The mechanism is based on the concept of the structure of alkali and alkaline earth silicate glasses being dominated by SiO_4 tetrahedra forming a random network by sharing their corners (bridging oxygens). The oxygens introduced by the alkali and alkaline earth metal oxides are primarily nonbridging oxygens which have a pronounced effect on the glass properties by weakening the siloxane bonds. The dealkalization of the glass is considered to be initiated by the proton adsorption on to the glass surface. The proton then migrates through the glass lattice to sites where it electrophilically attacks the nonbridging oxygen releasing the alkali or alkaline earth metal ions. The metal ions are then free to migrate through the glass lattice with high diffusion coefficients due to the absence of trapping oxygens in the lattice. In addition, the adsorption of the proton and its migration through the lattice results in the increase of the solution pH, thereby causing an increase in the lattice attack, i.e., nucleophilic attack by the OH^- on the silicon. The intermediate to long term interaction is considered to be characterized by a steady state between the dealkalization and lattice attack such that the leached zone maintains a constant thickness. This mechanism is used to successfully explain leaching data existing in the literature.

INTRODUCTION

Upon reviewing the voluminous literature and observing the seemingly varied data on interactions between various glasses and aqueous solutions one becomes easily convinced that the chemistry is quite complex and is unique for each experimental leaching procedure. But if meaningful and reliable predictions of leaching data are to be proposed an attempt must be made to devise a general mechanism which can be used to describe these seemingly diverse leaching data existing in the literature. Much of the mechanism contained herein has, in part, been proposed in the literature and what will appear here is the result of an attempt to collect these partial mechanisms into a unified theory to explain much of the existing leaching data. The discussion of the chemical and physical interactions of glasses with aqueous solutions will be limited to the alkali- and alkaline earth silicate glasses. But it is suggested that the mechanism is of sufficient utility that with only slight alterations and additions it can be applied to all silicate glasses. The format will be to present a general mechanism describing diffusion, ion exchange, and chemical lattice attack. This mechanism will then be exemplified by its application to a number of experimental phenomena noted in the literature.

GENERAL MECHANISM

DISCUSSION

Any discussion of a mechanism describing the interaction between glasses and aqueous solutions must be closely correlated with a concept concerning the structure of glass. A review of the literature indicates that the state of understanding the structure of glassy oxides is presently well behind that of crystalline solids. Bell and Dean⁽¹⁾ note a consensus of opinion that the basic structural unit in all silicate glasses is the SiO_4 tetrahedron. These tetrahedrons are linked at their vertices by bridging oxygens to form a connected three-dimensional network. Of the

number of theories regarding the geometry of this network of connected tetrahedrons, Bell and Dean state that the random network theory of Zachariasen is the most widely accepted today. These authors calculated a configurational entropy based upon the number of ways a tetrahedon may be added to an existing structure which agreed with that calculated from the random network models. In addition, based upon such entropy considerations and upon experimental infrared spectroscopy, the authors conclude that broken Si-O-Si bonds occur to a very small extent in unirradiated vitreous silica. This same conclusion is made by Smyth,⁽²⁾ Weyle and Marboe,⁽³⁾ and Huggins and Huggins.⁽⁴⁾ Thus the ideal structure of vitreous silica consists of a random network, i.e., no long range order, of silica tetrahedons. Huggins and Huggins (1970) have considered the defect structure of vitreous silica to consist of small equilibrium concentrations of oxygen atoms having either one (a nonbridging oxygen) or three close silicon neighbors and defect electrons and holes. The small equilibrium concentrations of these defects are sensitive to the concentration of added constituents, e.g., O_2 and alkali metal oxide. These authors have calculated the relative concentrations of these defects in pure vitreous silica and an alkali silicate glass as a function of partial pressure of O_2 gas. For pure vitreous silica at a $P_{O_2} = 1$ atm, the predominate defects are the equal amounts of oxygens having one and three close silicon neighbors. For the silicate glass of low alkali concentrations and $P_{O_2} = 1$ atm, the predominate defect is the nonbridging oxygen and this is equal to the alkali ion concentration.

This effect of alkali on the structure of glass is also noted by Smyth.⁽²⁾ He comments that when the alkali concentration is low the nonbridging oxygens may be attached to only one alkali ion at the most. But as the alkali concentration is increased the cations become coordinated with a larger number of nonbridging oxygens.

Weyle and Marboe⁽³⁾ cite the effect of various alkali metal oxides upon the melting temperature of vitreous SiO_2 as evidence for their effect on the structure. These authors report that the greater decrease in the

melting temperature with addition of oxides containing alkali metals of increasing atomic weight can be explained by the consequent increasing polarizability of the additional nonbridging oxygens coordinated to a silicon and an alkali metal ion. The increased polarizability of the oxygen weakens the bond to the other bridging oxygens, thereby causing a greater decrease in the melting temperature. Thus the concept of the structure of an alkali and alkaline earth oxide-silicate glass is that of the SiO_4 tetrahedrons forming a random network through the bridging oxygens. The alkali and alkaline earth oxides are incorporated into the structure as metal ions coordinated with various numbers of bridging and nonbridging oxygens. The nonbridging oxygens have in effect been introduced by the metal oxide and serve to decrease the siloxane bonds (Figure 1).

FIGURE 1. Schematic Representation of Sodium Silicate Glass Structure

The mechanism of glass-water interaction will be based upon this concept of the glass structure and will involve the physical processes of adsorption, ion exchange and diffusion and the chemical processes of lattice attack and ionic reaction in the aqueous phase.

The net process of release of an alkali ion to the aqueous phase by diffusion can be considered as two separate steps; one involves the process by which the alkali ion bonded to the nonbridging oxygen is released and the other involves the migration of this "free" cation through the lattice. It is suggested that both steps always take place, but that the actual mechanism of each depends upon the experimental conditions. One example of a specific experimental condition is when the self-diffusion of alkali ions in silicate glasses is investigated by electrical conductivity measurements. The release mechanism in this case is that the bonded metal ion must attain sufficient energy in the vibration mode which, when oriented along the bond direction, can break the metal ion - nonbridging oxygen bond. Since there is an energy distribution for the alkali ions at any specific temperature there will be a certain number of the metal ions available for migration through the glass lattice. In addition, since these alkali ions are coordinated with various numbers of bridging and nonbridging oxygens, there should exist a range of binding energies for the alkali ions. Thus it is reasonable to consider some alkali ions as most easily released and others not so easily released. This concept has a direct relation to the terms "easily and not so easily leached." The free metal ion then migrates predominately in the direction of its largest "mean free path." This direction is toward the surface since the reverse direction has a greater number of sites occupied by bonded or free metal ions. The mean free path toward the surface, although relatively long compared with that toward the glass interior, is quite short, since the migration path contains nonbridging oxygens with an unsatisfied negative charge (trapping oxygens). Cooper⁽⁵⁾ expresses this diffusion mechanism in terms of an atomistic approach in which the diffusion coefficient is related to the mean free path, λ , which is the distance of successive jumps of the diffusing ion from one nonbridging

oxygen to another. The time interval between successive jumps is related to the frequency of atomic vibrations and the probability that a vibration is of sufficient energy to allow a jump to take place. At room temperature the number of alkali ions possessing sufficient energy to break the bonds to the nonbridging oxygens is quite small. Therefore at these temperatures the experimental diffusion coefficient would be quite low. In contrast, the diffusion coefficients measured when the glass is in contact with an aqueous solution is several orders of magnitude larger.

The other example, then, of a specific experimental condition is the investigation of alkali ion diffusion in silicate glasses immersed in an aqueous solution. In this case diffusion will also be considered as the sum of the two separate steps of release and migration of the alkali ion. The distinction between this case and that noted above is that the mechanisms of the two steps are different and that there are a series of processes occurring at the glass surface which are prerequisites for diffusion in the glass to proceed. Once the glass has been immersed in the aqueous phase the surface metal ions become hydrated and, as a consequence, are removed from the surface sites where they were bonded to lattice nonbridging oxygens. These nonbridging oxygens then become protonated, if the hydrogen ion concentration of the solution is sufficient. This protonation, or chemical adsorption of hydrogen ions, is the first step leading toward their diffusion into the glass lattice. Since the ionic potential of the proton is sufficiently large compared to the alkali metal ions, the H-OSi bond will form at the expense of the Na-OSi bond. This ion exchange takes place primarily near the surface during the early stages of the glass-water interaction, but will progress further into the lattice as the diffusion of the hydrogen ions proceeds with increasing time. In the case of the alkaline earth metal ions the energy required by the hydrogen ions for ion exchange is sufficiently large that these metal ions may be removed from the glass only when the SiO_2 lattice has been chemically attacked. The alkali ion is now "free" to migrate within the glass lattice. Since the diffusion of hydrogen ions is from the glass surface, the nonbridging

oxygens in that direction will have their negative charge satisfied by a hydrogen ion. Thus the "mean free path" for the migrating metal ions will be toward the surface and should be relatively long compared to that in the glass of the electrical conductivity experiments. The diffusion of the protons from the surface may be considered as a dynamic process involving hydrogen ions exchanging for alkali metal ions and other hydrogen ions bonded to the lattice nonbridging oxygens. These hydrogen-bonded oxygens represent sites over which not only released metal ions, but also other hydrogen ions can migrate relatively "freely." It is quite probable that a hydrogen ion may migrate past a site containing a bonded alkali ion without ion-exchange taking place. Thus ion-exchange may very well be taking place deep within the lattice, but due to the larger number of hydrogen ions nearer the glass surface, it is here that the greatest amount of ion-exchange will take place. This relative rapid diffusion of hydrogen ions into the lattice, the phenomenon of ion exchange releasing the alkali ions, and the hydrogen-bonded nonbridging oxygen sites available for "free" migration of metal ions accounts for the relatively large leaching diffusion coefficients as compared to those determined by electrical conductivity measurements.

It is obvious that the rate of migration of species through the glass lattice is quite sensitive to the concentration gradient of that species in the glass. Thus any change in the nature of the glass surface, e.g., changes in the nature of the surface potential determining ion, would have an effect on the migration rate. An example of pH effects on the rate of dealcalization of glasses will be described later. The explanation of this effect involves a change in the nature of the potential determining ion, i.e., the pH sensitive adsorption of the alkali ion on and the desorption of the hydrogen ion from the glass surface. The adsorption of the alkali ion served to increase the rate of back migration of the ion. The result was a decrease in the concentration gradient of the alkali ion migrating toward the surface, thereby causing a decrease in the rate of dealcalization. The point here is that the rate of migration of various species through the glass lattice can be quite sensitive to such surface processes as adsorption and desorption.

Another process that must be included in the general mechanism depicting glass-water interactions is the chemical attack of the silicate lattice. This process is occurring simultaneously with the above described processes of adsorption and desorption, ion exchange, and ion migration. The interdependence of these processes is exemplified by an indirect effect of the adsorption of hydrogen ions and their migration into the glass lattice upon the chemical attack of the lattice. This adsorption and migration of protons results in a diminished hydrogen ion concentration in the aqueous phase. There is a subsequent increase of hydroxide ion concentration through ionization of water in order to satisfy its ionization constant. The effect of this increase of hydroxide ion concentration is an increase in the rate of chemical attack on the silicate lattice, i.e., increased rate of nucleophilic attack of the hydroxide ion on the silicon ion. The result is that the siloxane bond (Si-O-Si) is converted to a (Si-O-H) bond and a $(\text{Si-O})^-$ site. This $(\text{Si-O})^-$ site then undergoes electrophilic attack either by a hydrogen ion or by a water molecule. The latter releases an hydroxyl which can be used for further Si-O-Si attack. Experimental data will be described later that will verify this indirect effect of dealcalization and proton diffusion upon the rate of chemical attack of the lattice. In addition to the nucleophilic attack of the hydroxide ion on the silicon ion, Budd⁽⁶⁾ reports that the bridging oxygens are subject to electrophilic attack but that the "hydrogen ions are not sufficiently powerful to cause disruption of the O-Si bond." The author points out that this electrophilic attack of the hydrogen ion on the bridged oxygen would become possible, if accompanied by simultaneous nucleophilic attack by a reagent on the associated silicon ion. It can be further suggested that the nature of the alkali or alkaline earth cation effects the polarizability of the nonbridging oxygens and this will have an effect on the Si-O-Si bond strength. Thus the activation energy required for the hydrogen ion electrophilic attack on the bridged oxygens will be altered. The probability of the hydrogen ion attacking the siloxane bond will be discussed in more detail later in relation to the experimental data in the literature. In either case, i.e., OH^- nucleophilic

attack on the Si^{+4} or H^+ electrophilic attack on the bridging oxygens, the end result is the increase in concentration of orthosilicate molecules in the aqueous phase.

It is quite probable that not only orthosilicate acid but also various polymers of ortho- and metasilicic acid are initially released to the aqueous phase. Elgawhary and Lindsay,⁽⁷⁾ on the basis of reported equilibrium constants, have calculated that the orthosilicic acid is for all practical purposes the only aqueous SiO_2 species at $\text{pH} < 8$, at $8 \leq \text{pH} \leq 13$ the second and third ionized forms of diorthosilicic acid (a polymer of orthosilicic acid) become predominate, and at $\text{pH} > 13$ a form of orthosilicic acid with the silicon in 5-fold coordination, $\text{HSiO}_4(\text{OH})^{-4}$, becomes predominate. These authors did not consider either metasilicic acid or any of its polymers to be of sufficient concentration or the effect of alkali and alkaline earth ions on the upper pH limit of monomer H_4SiO_4 stability. Hauser⁽⁸⁾ describes the effect on Si^{+4} on the surrounding $(\text{ONa})^-$ groups in comparison to OH^- groups. Since the oxygen is more strongly polarized by the proton the strong potential field of the Si^{+4} is not sufficiently screened. Thus $\text{Si}(\text{OH})_4$ would be expected to polymerize into units in which the Si^{+4} is surrounded by six OH^- ions. An added complication, noted by Iler,⁽⁹⁾ is that neutral salts induce polymerization ($\text{Li} > \text{K} > \text{Na}$). These polymers are aggregates of alkali-metal silicate molecules by coordination through the metal ions, rather than a polymerization of silicate ions through siloxane bonds. The rate law for the alkali ion induced polymerization was given as follows $R = k (\text{metal ion})^4 (\text{silicate ion})^{1/2}$. At the low aqueous SiO_2 concentration observed in most leaching solutions, it can be concluded that alkali induced polymerization can be neglected and the upper pH limit for monomeric $\text{Si}(\text{OH})_4$ stability be considerably extended above $\text{pH} \approx 8$. The question as to whether the monomer meta- or orthosilicic acid will persist in the solution is considered by Wang and Tooley.⁽¹⁰⁾ They concluded that the products of the reaction between glass (12% CaO , 14% Na_2O , 74% SiO_2) and water were sodium metasilicate, calcium metasilicate, and metasilicic acid. This was based on the indirect evidence

that simulated extracts made from these constituents paralleled most closely the rate curves obtained with the actual extracts. Even though this is a conclusion which is certainly open to question, it will be considered here that either or both the dehydrated or hydrated monomeric silicic acid, i.e., H_3SiO_3 or H_4SiO_4 , are the forms existing in the aqueous leaching solution. This conclusion also implies that the groups of SiO_4 tetrahedra, which are linked at their corners, undergo either electrophilic attack by H_3O^+ or nucleophilic attack by OH^- in the solution phase and are quickly converted into monomeric silicic acid. Thus the rate determining step in the chemical attack of the silicate lattice is the release of monomers or polymers of silicic acid to the solution phase.

DESCRIPTION OF PROCESSES

Surface Processes

Upon immersion of the glass into pure H_2O adsorption of H^+ and/or H_2O and desorption of alkali and alkaline earth metal ions takes place. The subscripts s and i represent surface and interior entities, respectively. S represents a site which can accommodate a metal ion, hydrogen ion, water molecule, etc., C represents a metal element. In this case it will represent an alkali metal. If C is to represent an alkaline earth metal, then the appropriate stoichiometric coefficients must be used in the reaction in order to maintain the electrical neutrality of the glass.

1. Adsorption of H^+ (or H_3O^+) and/or H_2O onto the glass surface.

or

2. Surface ion exchange

- (a) Electrophilic attack of H^+ (or H_3O^+) on nonbridging oxygen bonded to metal ion.

- (b) Nucleophilic attack of H_2O on bonded metal ion either followed by or simultaneous with electrophilic attack of H^+ (or H_3O^+) and/or H_2O on the nonbridging oxygen.

and

and/or

Migration of Hydrogen Ion

The migration of H^+ (or H_3O^+) into the glass lattice can be considered to be initiated by its adsorption onto the glass surface. Although the adsorbed H^+ is strongly bound to the surface oxygens it should be considered in dynamic interchange with the aqueous H^+ ions which are constantly impinging upon the surface. There is a certain probability that these hydrogen ions will become located in a surface site such that, due to their random thermal motion, they will move into the lattice. The probability of hydrogen ions, upon impinging onto the surface, migrating into the lattice

instead of being trapped by the surface oxygens can be considered to be comparatively small until these surface sites have become saturated with respect to hydrogen ions. Thus as noted above the surface processes of adsorption and ion exchange are essential initial steps for the diffusion of the hydrogen ions and, therefore, for the dealkalization of the glass.

Migration of hydrogen ion from the solution to the glass interior.

Ion Exchange Within the Lattice

The same ion exchange process that took place on the glass surface can now take place within the lattice. If the lattice site, to which the hydrogen ion has migrated, is surrounded by bridging oxygens, then the H^+ is relatively free to randomly migrate to another interior site. But if the site contains an alkali or alkaline earth ion bonded to a nonbridging oxygen, there is a certain probability that ion exchange will take place. This ion exchange is the release mechanism that frees the metal ion for migration through the lattice. It should be pointed out that the hydrogen ion could continue to migrate deeper into the glass before undergoing ion exchange. But since the mean free path for these free metal ions is relatively short in all directions, this ion exchange deep within the lattice contributes very little to dealkalization of the glass. Therefore, ion exchange within the diffusion front will be that considered to contribute significantly to metal ion migration.

Ion exchange of a hydrogen ion for a cation within the lattice.

Migration of Metal Ions Within the Lattice

These metal ions are now free to randomly migrate to other interior sites. As noted earlier, the net migration will be toward the surface since this is the direction of the longest mean free path. Once on or near the surface, these metal ions are quickly hydrated and removed from the surface and diffuse into the aqueous phase.

Migration of metal ion from an interior to a surface site.

Hydration and desorption of metal ion from the surface.

Chemical Attack of the Lattice

As noted earlier this process occurs simultaneously and is directly related to the physical processes of adsorption, ion exchange, and migration. There are two plausible processes for lattice chemical attack, both of which have the same result, i.e., an increasing concentration of monomeric silicic acid in the aqueous phase.

1. Nucleophilic attack of OH^- on Si^{+4}

or

Then each Si-O-Si bond is successively attacked until monomeric silicic acid exists in the solution phase. Again, monomeric units may not be directly released to the solution thus the final conversion of the polymers will take place in the aqueous phase.

2. Electrophilic attack of H^+ on bridging oxygens

It should be pointed out that, due to the lack of sufficient energy of the H^+ , this process may not be significant unless simultaneous nucleophilic attack by some species, e.g., F^- , on the Si^{+4} is taking place. Also, since the alkali ions of low ionic potential allow the nonbridging oxygens to be polarized to a large extent by the Si^{+4} , the silicon bonds to the bridging oxygens are weakened. Thus this H^+ electrophilic attack on the bridging oxygens may very well be significant during the early stages of leaching of a Cs or Rb glass. Regardless of which process is predominate, each Si-O-Si bond is successively attacked until monomeric silicic acid exists in the solution phase. Again, since monomeric units may not be directly released to the solution, the final conversion of the polymers to monomers will take place in the aqueous phase.

APPLICATIONS

BERGER'S STATEMENT AND DATA

The following statement was made by Berger:⁽¹¹⁾ "As not only the silicate ions have been proved to retard the attack (chemical attack), we must assume that a reduction generally will be caused by the presence of the components dissolved out of the glass." This statement concerning the role of silicate ions is based on an experiment in which alkali glasses, covered by rubber except for a small portion, were placed in 300 cm³ of a leaching solution. In one case the leaching solution was 0.5 N NaOH and in the second it was a 0.5 N NaOH solution into which 2 gm K₂SiO₃ had been added. The degree of attack in the solution containing only the NaOH was 40 times greater than that in the solution containing not only the NaOH but the K₂SiO₃.

Berger's statement is at first glance somewhat confusing in relation to the proposed mechanism, in that the presence of K₂SiO₃ would tend to raise the pH. Thus the K₂SiO₃ should increase the rate of chemical attack and not result in a retarding effect. The explanation here is that the indirect effect is not due to an increased pH, which certainly would be minimal in a 0.5 N NaOH solution, but is due to the initially high SiO₃⁻² concentration. This is sufficiently high such that with the initially high rate of dissolution, i.e., production of still more SiO₃⁻², the solubility limit is exceeded for amorphous SiO₂. Leaching of the glass of its alkali metals would certainly have accompanied the dissolution and the leached-glass lattice being essentially SiO₂ would serve as a site for precipitation of amorphous SiO₂. This layer of amorphous SiO₂ would certainly act as an inhibitor, i.e., retarder, to further chemical attack.

Experiments were performed by Berger⁽¹¹⁾ to illustrate the effect of the frequency of changing the leaching solution. A series of leaching tests were performed in which an alkali glass was leached at 93°C in 100 cm³ of a 0.5 N aqueous solution. In one case 90 cm³ of the initially 0.5 N NaOH leaching solution were replaced with 90 cm³ of fresh 0.5 N NaOH

every 30 minutes and in the other only 10 cm^3 were replaced every 20 minutes. In the third case, the solution was not renewed. The higher rate of dissolution of the first case can be seen in Figure 2.

FIGURE 2. Effect of Changing Leaching Solutions upon Rate of Lattice Attack, Berger⁽¹¹⁾

This data would certainly seem to validate that part of the general mechanism which involves the role of the OH^- in attacking the lattice. It would appear that the replenishment of OH^- in the first case was sufficient to maintain an essentially constant OH^- concentration and, therefore, a constant rate of reaction. Whereas in the second case the replenishment was not sufficient and the OH^- concentration diminished with time, thereby resulting in a decreased rate of reaction. The third case also illustrates this same effect of diminishing OH^- concentration in the aqueous phase.

BERGER, DOUGLAS, AND EL-SHAMY

Tests were performed by Geffcken and reported by Berger⁽¹¹⁾ (Figure 3) on the effect of composition of the solution upon the initial leach

FIGURE 3. Initial Velocity in μ/hr of the Decomposed Glass at 100°C in Relation to Concentration, Berger⁽¹¹⁾

rate. An additional study of the net rate of lattice attack for $0 < \text{pH} < 12$ is illustrated by the data of Douglas and El-Shamy⁽¹²⁾ (Figure 4).

FIGURE 4. Effect of pH on Rate of Silica Extraction from Fused Silica Powder at 80°C , Douglas and El-Shamy⁽¹²⁾

These results serve to illustrate the effect of pH on the rate of chemical attack of the lattice and validate that portion of the general mechanism involving the role of OH^- . Any process, such as H^+ exchange for the diffusing cations of the glass, would have a significant effect on the rate of the dissolution process, i.e., chemical attack of the lattice. Berger makes the point that these data illustrate "that there are at least three kinds of attack which are distinctly typical, the water attack which in particular releases the monovalent oxides, the acid attack which includes the di-valent oxides and essentially leaves only the silicic acid on the surface, and the alkali attack which dissolves all the components." At pH = 7 and near room temperature there are insufficient number of protons having enough energy to displace any cation from its charge-unsatisfied oxygen in the glass other than those of relatively low ionic potential, i.e., the monovalent alkali cations. But in an acidic solution there are sufficient protons with the appropriate energy to displace even the di-valent cations which, due to their relatively high ionic potential, are held more firmly to the charge-unsatisfied oxygens. In both the neutral and acidic solutions the lattice attack, i.e., disruption of the siloxane bonds, is much slower due to the very low concentration of hydroxide ions. The increase in rate with increase of H^+ concentration at pH below zero must be due to the increased number of H^+ having sufficient energy to protonate the Si-O-Si bonds.

DOUGLAS AND EL-SHAMY

Douglas and El-Shamy⁽¹²⁾ made the point that "unlike alkali, silica extracted from the glass at any temperature decreases as its percentage in the glass increases." This is based in part on the results of a series of leaching experiments with $\text{K}_2\text{O-SiO}_2$ glasses illustrated below in Figure 5. The explanation of these results must be based on the effect of the cations in the glass. One of these effects pertains to the indirect increase of OH^- concentration in the solution due to the ion exchange of the $\text{H}_{(\text{aq})}^+$ for the diffusing cations. This increase of OH^- has the effect of increasing the rate of chemical attack of the lattice.

FIGURE 5. Time Dependence of Silica Extraction by Water for Potassium Oxide-Silica Glasses, Douglas and El-Shamy⁽¹²⁾

Another effect due to the cations is that of weakening the structure by their diffusion and the consequent protonation of the charge-deficient oxygens. Thus a higher concentration of cations in the glass lattice results in a greater OH⁻ concentration increase in the solution and a decrease in the number of Si-O-Si bonds that must be attacked within the lattice. A third possible effect that the cations exert is that of a potential structural transformation of the leached zone. If the size of the cation, e.g., Na⁺, is not sufficiently large, a proton instead of the larger hydronium ion may be the predominate exchanging species. Due to the large difference in size of the proton and the diffusing alkali or alkaline earth cation, the structure of the leached zone may be deformed. This deformation could result in an increase in the ease of access of components from the aqueous phase, H⁺, OH⁻, and H₂O, into the lattice. This ease of access of the protons to the diffusion front would accelerate the diffusion process, which in turn would have an acceleration effect on the

lattice attack due to the increased rate of OH^- production in the aqueous phase. In addition, as Douglas and El-Shamy point out, the lattice attack would be accelerated due to the increase of the leached layer-liquid interfacial area "owing either to the reaction proceeding more and more throughout the layer or to some form of channeling."

This effect of alkali removal from the glass upon the chemical attack of the lattice is further emphasized by the data of Douglas and El-Shamy presented in Figure 6. These leaching results illustrate a strong interdependence between alkali removal and lattice attack. The explanation of these data involves, again, the role of the aqueous H^+ or H_3O^+ exchange for the alkali ion of the glass. This produces an increase of OH^- in the solution phase and this OH^- is an essential reactant in the chemical attack of the lattice. This is especially well illustrated in this experiment since the leaching solution was water in which the initial OH^- concentration was insufficient to sustain a measurable rate of chemical attack of the lattice.

Douglas and El-Shamy designed an additional series of experiments to illustrate the effect of removal of alkali from the leaching solution, not the glass, on the extraction of silica. These experiments do not illustrate the intended effect but actually that noted above, i.e., the effect of alkali removal from the glass upon the chemical attack of the lattice. The experiments were conducted in the following manner. "Some soda-silica glass powder was agitated for some time in a beaker containing water and the glass was then transferred to similar beakers at regular intervals; in a similar experiment, alkali ions passing into solution were partially removed by placing a suitable amount of a cation exchange resin (Zeo-Karb 225 in the hydrogen form) in each beaker before each experiment was started." The results are presented in Figure 7. The explanation of these data does not involve the effect of the alkali ion in the solution phase but the effect of H^+ exchange for the Na^+ in the glass, the subsequent increase of OH^- in the solution phase, and the consequent increase of the rate of chemical attack of the lattice. Since the resin was

FIGURE 6. Extraction of Alkali and Silica in Long-Term Water-Leaching Runs on 15 K_2O -85 SiO_2 Glass at 61.3°C Douglas and El-Shamy (12)

FIGURE 7. Effect of Removal of Alkali from Attacking Solution on Silica Extraction, Douglas and El-Shamy (12)

initially in the acid form, adsorption of Na^+ from the aqueous phase by the resin resulted in an increase of H^+ concentration in the solution. This H^+ neutralized the aqueous OH^- , which was produced by the H^+ exchange for the glass alkali. Thus, in the case of the water plus resin, the rate of the lattice attack is diminished due to the lower OH^- in the solution phase and is not directly related to the lowered Na^+ concentration in the solution.

Since the pH of a leaching solution would be expected to change with time of contact with a glass, a series of experiments were performed to illustrate the extraction of various glass components as a function of the pH of the solution. The effect of pH on SiO_2 extraction from a glass, as reported by Douglas and El-Shamy, was noted above. The effect of pH on the extraction of alkali for all the glasses studied by Douglas and El-Shamy⁽¹²⁾ is illustrated in Figure 8.

FIGURE 8. The pH Dependence of Alkali Extraction at 35°C from $\text{K}_2\text{O} - \text{SiO}_2$ Glasses, Douglas and El-Shamy⁽¹²⁾

The explanation of these data is based on the effect of the surface properties of the glass and the consequent effect the adsorbed constituents have on the diffusion of alkali ions from the glass interior. It has been frequently illustrated that the freshly broken glass has a surface

which expresses a negative surface potential in an aqueous solution. As a consequence positive ions are attracted to the glass surface with the development of an electrical double layer marking the interface between the solution and the glass. The nature of the positive species adsorbed at the glass surface is a function of ionic potential and concentration of the positive species in the solution phase. At low pH it is supposed that the H^+ is the predominate adsorbed species. Under these conditions, i.e., high concentration of H^+ on and near the glass surface, the rate of ion exchange for the alkali within the glass is enhanced. But with an increase in pH, the H^+ on the surface is replaced by Na^+ from the solution phase. These aqueous Na^+ ions have resulted from diffusion from the glass. The presence of a high concentration of Na^+ on and near the glass surface serves to decrease the Na^+ concentration gradient within the glass via back diffusion of Na^+ and thus the Na^+ diffusion from the glass is retarded. A simultaneous effect due to the reduction of H^+ on and near the glass surface is the decrease of H^+ diffusion into the glass. Since the mobility of the alkali ion bonded to the charge-deficient oxygens within the glass is enhanced by the H^+ interacting with these nonbridging oxygens, the decrease in alkali extraction is also the result of a decrease of H^+ available for migration into the glass.

It should be noted that at these high pH's at which alkali extraction is retarded, there should be a consequent decrease in chemical attack of the lattice. But the decrease in the rate of production of OH^- due to the decreased ion exchange is insignificant at these high pH's. Thus one would probably not be able to measure any consequent change in the rate of chemical attack.

An additional series of experiments are suggested in order to further validate this proposed mechanism. Since the order of adsorptability of cations is a function of their ionic potential, Ca^{+2} , which is similar in size than the Na^+ , should be preferentially adsorbed at the glass surface. The increased concentration of Ca^{+2} on and near the surface would have the effect of keeping the Na^+ concentration gradient within the glass from decreasing. Thus the result should be to increase

the sharp break in slope to regions of higher pH with increasing concentrations of Ca^{+2} in the solution phase.

EL-SHAMY, LEWINS, AND DOUGLAS

The same effect of pH on the dealkalization of silicate glasses was noted by El-Shamy, et. al.⁽¹³⁾ The explanation of this effect by Lewins⁽¹⁴⁾ paralleled that given above, i.e., dissociation of surface SiOH groups produced a negative surface which attracts alkali ions from the solution. The statement was made by Clark-Monks and Ellis⁽¹⁵⁾ that this implied that the diffusion of alkali and H^+ through the electrical double layer was rate controlling as the pH exceeds nine. El-Shamy⁽¹⁶⁾ conducted an experimental verification that the rate controlling step in dealkalization in solutions of pH 9 is diffusion not through the electrical double layer but through the leached layer of attacked glass. The main point of interest here is that, since the diffusion in the leached glass is rate controlling, any effect on the concentration gradient of alkali ions or H^+ in the glass will have a marked effect on the rate of dealkalization. As noted above, this change in the concentration gradient within the glass is brought about at $\text{pH} > 9$ by desorption of H^+ and adsorption of alkali ions on the glass surface. This also emphasizes the associated processes of alkali and hydrogen ion diffusion, i.e., $-\text{SiO}-\text{Na}^+_{(\text{glass})} + \text{H}^+_{(\text{aq})} \rightarrow -\text{SiOH}_{(\text{glass})} + \text{Na}^+_{(\text{aq})}$, which El-Shamy⁽¹⁶⁾ notes "has been repeatedly suggested in the literature."

BUDD AND FRACKIEWICZ

Budd and Frackiewicz⁽¹⁷⁾ performed a series of experiments concerning the establishment of an "equilibrium pH" of a leaching solution as a function of the initial composition of the leaching solution and particle size of the glass, varying from silica, soda-silica, and soda-alumina-silica. The "equilibrium pH" was experimentally determined by repeatedly exposing fresh glass surface to the same leaching solution until there occurred no more immediate pH change. It is interesting to note that the glass in solutions of initial pH = 11 exhibited the greatest rate in obtaining the "equilibrium pH." The glasses with the greatest surface area also more rapidly

attained the "equilibrium pH." Since these changes in pH were observed only minutes after exposing fresh glass surfaces to the solutions, it is most probable that the involved processes occurred on the glass surface. These surface processes are identical to those that are proposed to occur at depth in the glass, i.e., electrophilic attack of hydrogen ions on the nonbridging oxygens and nucleophilic attack of the hydroxide ions on silicons associated with bridging oxygens. The only distinction between these processes occurring on the surface and at depth in the glass is that the rates at the surface sites are not controlled by diffusion within the glass lattice. In a separate series of experiments the authors illustrated that varying concentrations of Na^+ , K^+ and Li^+ in the solution had an insignificant effect on the "equilibrium pH." The only effect was that the time necessary to reach the "equilibrium pH" was significantly increased with increasing concentration of metal ions in the aqueous phase. Budd and Frackiewicz did not venture an explanation of this effect. But it would appear that increasing concentration of metal ion in solution would result in competition of the metal ions for the surface sites that would be occupied by the H^+ . This would have the effect of increasing the time to reach steady state between the two surface reactions noted above. This explanation could be partially verified by conduction of a series of experiments to indicate whether Li^+ , due to its ionic potential being higher than K^+ , would have a greater effect of extending the time interval than would K^+ . In an explanation of the relationship between glass composition and "equilibrium pH," Budd and Frackiewicz derived the following function: $[\text{OH}^-]_{(\text{aq})} = K[\text{-}\overset{\cdot}{\text{SiO}}^-]_{(\text{glass})}$. This would indicate that the activity of nonbridging oxygens in the glass controls the hydroxide ion activity in the aqueous phase. This function is derived on the assumption that the two surface processes, which utilize the hydrogen and hydroxide ions, actually reach equilibrium. In a second paper Budd and Frackiewicz⁽¹⁸⁾ made an attempt to illustrate that there was a specific $\text{Na}_2\text{O}/\text{CaO}$ ratio for $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ glasses which exhibited a minimum in "equilibrium pH." This was explained in terms of a minimum activity of the oxide ions within the glass when each nonbridging oxygen ion was

coordinated with both a Ca^{+2} and a Na^{+} . But still the activity of the oxygen was related to the aqueous OH^{-} activity via an equilibrium assumption. This equilibrium assumption does not seem reasonable since the pH was measured within the first 2 minutes after exposing the glass surface to the aqueous phase. It certainly seems more reasonable that the most that can be expected is that at a specific pH the relative rates attained by these two processes are such that the decrease of OH^{-} and H^{+} are equal. Any effect on the rate of either of these two processes would produce an effect on the pH of the solution in which these two processes have reached steady state. As noted by Weyl and Marboe⁽³⁾ the addition of an alkali or alkaline earth oxide to SiO_2 glass introduces nonbridging oxygens which are coordinated to the introduced cation and the silicons. Weyl and Marboe reported that the Si-O internuclear distance for nonbridging oxygens is approximately 10% less than for the bridging oxygens. These nonbridging oxygens in an alkali glass can be considered as centers of asymmetry. Since the polarizability of these oxygens are dependent upon the nature of the alkali or alkaline earth cation with respect to which they are coordinated, the degree of asymmetry would vary with the cation. The same number of nonbridging oxygens introduced by Li_2O would be expected to have a smaller effect, since the oxide ions counterpolarized by Li^{+} ions have a lower polarizability than those counterpolarized by Cs^{+} ions. Thus the introduction of nonbridged oxygens of predictable polarizability could be correlated with the activity of the oxygens noted by Budd and Frackiewicz. The difference in degree of hydration of the alkali and alkaline earth metal ions coordinated to the nonbridged oxygens on or near the glass surface certainly must have an effect on their rate of removal and the subsequent protonation of the nonbridged oxygens. This change in the rate of the ion exchange process of hydrogen ions in the solution phase for the alkali or alkaline earth ion in the glass structure would have the effect of changing the "equilibrium pH." Thus the activity of the nonbridged oxygens do have an effect on the "equilibrium pH" but not through the equilibrium control of $[\text{OH}^{-}]_{\text{aq}}$. This hypothesis could be partially verified by experimentally noting the shift of "equilibrium pH" with that predicted on the bases of the polarizability of the

alkali or alkaline earth cation. In addition, since the ion exchange and the chemical attack of the lattice are occurring at and near the glass surface without the influence of diffusion within the glass lattice, the relative rate of these two processes could be experimentally determined for different alkali and alkaline earth oxide glasses. These data would be especially valuable aids in the attempt to decipher the leaching data of various glasses in terms of the proposed steps in the general mechanism.

LYLE

Lyle⁽¹⁹⁾ investigated short- and long-term dealcalization data for glass bottles at high and low temperature, respectively. He derived the following diffusion equation by assuming that the concentration gradient of Na^+ in the glass could be represented as a linear function of distance from the surface:

$$\frac{dN}{dt} = \frac{k \sum A (W_0 - W_s)^2}{2N}$$

where $N \equiv$ moles of Na^+ in the aqueous phase at time t

$A \equiv$ glass surface area

$W_0 \equiv$ moles of Na^+ in cm^3 of glass

$W_s \equiv$ moles of Na^+ / cm^3 of glass at glass-water interface

Assuming that W_0 , W_s , k , and A remain constant with time, the function is integrated to give $N = Kt^{1/2}$ or $\log N = \log K + 1/2 \log t$. The author then attempts to correct for the assumption concerning the concentration gradient and changes the coefficient of t from $1/2$ to the variable 'a.' This function is applied to the short- and long-term dealcalization data of two lots of bottles, differing in chemical composition as noted in Figure 9. Lyle has made no attempt to consider the effect of chemical attack in the derivation of his function. But when he finds it necessary to change the coefficient of t from $1/2$ to the variable 'a,' it is quite probable that is due to the effect of chemical attack of the lattice. In other words, it is quite probable that for certain glasses the relative

FIGURE 9. Time-Attack for Two Lots of Bottles (1 and 2), Lyle¹⁹

activation energies of the diffusion, ion exchange, and chemical attack processes may be such that a steady-state situation is developed progressively earlier with higher leaching temperatures. A log-log plot of the dealcalization data would be a straight line and thus be expressed as an identical function, i.e., $\log N = A \log t + \log K$. It should be noted that at lower temperatures there is progressively longer leaching time data that is plotted as a straight line. These curves for the same glass exhibit the same slope, i.e., same coefficient of t of approximately 5.5 mg/l hr. The point here is that the interpretation by Lyle that diffusion is the controlling process with a $t^{5.5}$ term at these long leaching time intervals is doubtful.

BEATTIE

Beattie⁽²⁰⁾ described the mechanism of leaching for short periods as the following:

a) Glass surface reactions

b) Glass interior reaction

These processes are very similar to those proposed in the general mechanism by the present author. The only distinction is that the third and fourth processes are considered as consisting of three individual processes: diffusion of H^+ into the glass, ion exchange of H^+ for Na^+ , and diffusion of Na^+ out of the glass. Beattie makes the point that, since the experimental rate law is not zero order, the diffusion of either Na^+ or H^+ in the glass must be the rate controlling step. The author uses Fick's first law to derive the diffusion function noted below:

$$Q = 2AC(Dt/\pi)^{1/2}$$

where $C \equiv$ original concentration of sodium in the glass

$A \equiv$ surface area of powder

$D \equiv$ diffusion coefficient

$Q \equiv$ quantity of ion diffusing through a unit area of surface

The assumptions made are that for short-time leaching the diffusion can be considered as occurring in a semi-infinite solid bounded by planes an infinite distance apart and that the equilibrium concentration of diffusing species are immediately established at the glass-water interface. This assumption of equilibrium at the surface by Beattie involves only ion exchange of H^+ for Na^+ , whereas Budd and Frackiewicz (1961) considered it to also involve chemical attack of the lattice. In addition, Beattie assumes "that at equilibrium all the sodium ions are replaced by hydrogen ions." This does not seem compatible with his earlier statement unless the equilibrium constant for exchange of H^+ for Na^+ is a very large number. Also, since the glass surface is constantly exposed to fresh solution, it

does not seem reasonable that equilibrium was attained. It seems much more reasonable that the removal of Na^+ from the surface to the aqueous phase is a very rapid process in comparison to Na^+ diffusion from the glass interior to the surface. This would mean that the $[\text{Na}^+]$ on the glass surface would be diminished very quickly upon exposure of fresh glass-surface to the aqueous phase and would be kept at this low value throughout the early leaching period. Therefore, an identical function could be derived, but without the necessity of making the seemingly erroneous surface equilibrium assumption. Beattie did successfully apply this function to early leaching data of glasses of varying SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , and CaO concentrations, i.e., conductivity of the leaching solution was a linear function of $t^{1/2}$. In addition, Beattie not only observed that the introduction of CaO in the glass caused a decrease in Na^+ diffusion, but that the removal of Ca^{+2} was at the same rate as that of silicon. The latter observation would indicate that an insufficient number of hydrogen ions are energetic enough to displace the Ca^{+2} from the unbridged oxygens and the diffusion of Ca^{+2} in the glass is slow. This slow Ca^{+2} diffusion is even more pronounced because the "freed" Ca^{+2} would have a marked tendency to displace a hydrogen bonded to unbridged oxygen in a nearby site. The Ca^{+2} , if freed by a energetic hydrogen ion, would then become trapped before migrating very far from its original site. Thus the rate of Ca^{+2} diffusion would be slow relative to chemical attack of the lattice, which would determine its rate of removal. Also, the high positive force field of the "trapped" Ca^{+2} ions would tend to retard the movement of the Na^+ ions through the lattice. Beattie interpreted this as "partial blocking by the calcium of holes and channels for migration."

RANA AND DOUGLAS

Rana and Douglas^(21,22) experimentally investigated the reaction between water and two series of glasses:

Series 1: 15% Na_2O , 0 - 15% CaO , 85 - 70% SiO_2

Series 2: 15% K_2O , 0 - 15% CaO , 85 - 70% SiO_2

Two separate leaching tests were performed, one for long-term interaction (0 to 5000 hr) and the second for short-term interaction (0 to 15 hr). Both tests were conducted so that the glass particles were in contact with fresh leaching solutions for essentially continuous periods. The short-term test resulted in data of Na_2O and SiO_2 concentrations which were linear functions of the half power of time (first mechanism) and at longer time intervals the concentrations of Na_2O and SiO_2 were linear functions of the first power of time (second mechanism). Contrary to what one would expect from the relative larger size of the K^+ compared to the Na^+ , the K_2O glasses were less durable, i.e., more K_2O was leached than Na_2O for glasses of the same CaO content. The durability of both types of glasses, as exhibited by the short-term interaction test, was decreased to an essentially constant value after addition of only 5 mole % CaO . The long-term interaction data exhibited a maximum in durability at approximately 5% CaO . The ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ during the first mechanism increased with percent CaO and temperature. For all cases, except for the highest temperature for the 15% CaO glasses, the ratios were well below that in the original glass. This is what one would expect, if the Ca^{+2} is actually blocking the diffusion of the Na^+ in the glass. The same trend was noted in the second mechanism for both Na_2O and K_2O glasses, the latter of which exhibited leaching data that had a $\text{SiO}_2/\text{K}_2\text{O}$ ratio which was slightly higher than that for the Na_2O glasses.

Since the first mechanism yields concentration data which is a linear function of the half power of time, it is tempting to make the assumption that the early leaching time is represented by simple diffusion. Rana and Douglas determined diffusion coefficients for Na^+ and K^+ in these glasses by electrical conductivity measurements. The values for the diffusion constants from these measurements (D_C) were orders of magnitude (10^2 to 10^3) smaller than those obtained from the early leaching data (D_R). Additionally they calculated the activation energies from the conductivity and the leaching data and found that in both the Na_2O and the K_2O glasses the activation energies increased with CaO content. Although the leaching activation energy values for the K_2O glasses were below those from the conductivity

measurements, contrary to prediction those for the Na_2O glasses were above those for the conductivity method. Rana and Douglas seem somewhat discouraged by this lack of agreement between the early leaching data and that from the conductivity measurements. They made the statement that "in view of the very large values of the ratios D_R/D_C it is only with extreme caution that one may attempt to interpret these (leaching) activation energies as diffusion activation energies." To add further to the suspicion that the two methods indicate different mechanisms one can site the trend of resistivity as a function of CaO and compare this with the trend of $Q/t^{1/2}$ as a function of 5% CaO . The point is that the resistivity measurements do represent diffusion and that the resistivity versus percent CaO curve is not matched by the early leaching data (Figures 10 and 11).

FIGURE 10. Resistivity (ρ) Versus Composition for Sodium Glasses, Rana and Douglas(22)

FIGURE 11. Leaching Durability Versus Composition for Sodium Glasses, Rana and Douglas(21)

As indicated in the general mechanism proposed herein, one can conclude that the diffusion coefficients must exhibit different values since the diffusion mechanism in the two experimental methods is different. In the conductivity method the temperature of the glass must be such a measurable number of Na^+ or K^+ ions have sufficient energy of vibration to momentarily break the bond to the nonbridging oxygens. Before the ions

have migrated very far in the lattice they will lose a portion of their energy by collisions and become captured by another nonbridging oxygen. Thus the process of acquiring sufficient energy of vibration oriented along the bond direction must begin anew. This mechanism is in two fold contrast to that occurring in the early leaching period.

1. The displacement of the Na^+ and the K^+ from the nonbridging oxygens is facilitated by an electrophilic attack on these oxygens by hydrogen ions which have diffused into the glass from the aqueous solution.
2. The nonbridging oxygens within the leached layer of the glass are coordinated with a hydrogen ion. Thus the Na^+ and the K^+ ions migrate relatively freely and have little tendency to displace the hydrogen ions.

Therefore, since a large number of hydrogen ions have sufficient energy to displace a large number of Na^+ and K^+ and these ions can migrate relatively freely within the glass lattice, one would certainly expect that D_R would be greater than D_C .

This same argument applies to the observation that the D_R for K^+ is greater than that for Na^+ . Since the ionic potential of K^+ is less than that for Na^+ , the K-O-Si bond strength should be less than that for Na-O-Si bond. One would, then, expect that a greater number of hydrogens will possess sufficient energy to displace the K^+ than will be able to displace the Na^+ . Therefore, the D_R for K^+ should be greater than for Na^+ in those glasses in which the size of the interstices are large enough for essentially uninhibited migration of the larger cation, i.e., the K^+ ion.

DAS AND DOUGLAS

This same concern about the early leaching data being represented as simple diffusion of the alkali ion through the glass lattice was voiced by Das and Douglas.⁽²³⁾ These authors experimentally determined

leaching data for a number of glasses varying in composition with respect to the following metallic elements, Na, K, Ca, Al, Zn, Cd, Mg, Sr, Ba, Pb, Cu, Ti, and Zr. They observed that the diffusion coefficients measured from electrical conductivity were smaller than those measured from leaching experiments. In response to this dilemma, the authors stated that "the diffusion process (during leaching) is thus not simply one of alkali ions diffusing through the glass itself but, presumably through the siliceous layer on the glass surface." The reason that the diffusion of the alkali ions is faster in the leaching zone is that the trapping centers, i.e., unbridged oxygen without bonded hydrogens, are at a minimum. Therefore, one certainly would expect a higher diffusion coefficient obtained from a leaching experiment.

In addition, Das and Douglas, as did Rana and Douglas,⁽²¹⁾ observed the early leaching data to be a linear function of $t^{1/2}$ and the later data to be a linear function of t . They interpreted the later leaching data as representing a situation of steady state, i.e., where the rates of removal of alkali and silica are equal. This then means that the thickness of the silica layer will be constant, and the rate of removal of alkali becomes directly proportional to the time. This concept of steady state can be related to an indirect verification of the general mechanism presented here. Since the rate of the chemical attack of the glass lattice is increased and the rate of removal of Na^+ is decreased by an increase of pH, the approach to steady state should be observed to occur earlier in the leaching test with an increase of pH.

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