

Chapter 2

Theoretical Part

The corrosion mechanisms of glass by air humidity and by water are the same in principle. It is a complicated process described by many different concepts and scientific theories.

The following short overview on concepts of the reaction between glass and water shows a general theory of glass corrosion.

H^+ and H_3O^+ play a very important role in the reaction. Therefore, the fundamental concept of hydrogen ions is discussed with high priority.

H^+ , the Nonconformist Ion (Ernsberger, 1983)

The hydrogen ion is formed when the hydrogen atom loses the only electron it has. When this happens, it becomes a bare proton. This is the only ion of chemical significance that has no electron. It is this unique characteristic that underlines the extraordinary nature of the hydrogen ion.

When protons are accompanied with oxygen ions, we have to keep in mind that bare protons do not exist in aqueous solutions. Rather, the protons enter the electron clouds of the large O^{2-} ions. This is because there is no electron cloud on the proton to be repelled by the electrons of the oxygen ion. In other words, the proton is swallowed by the oxygen ion, thus forming the sequence

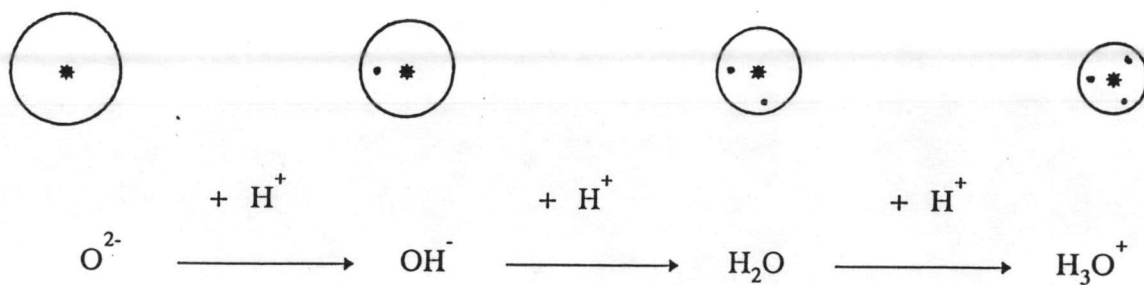


Fig. 2.1 Sequence of the absorption of protons by the oxygen ion.

With ever decreasing molecular diameter, the above dissociation reaction of the water molecule can be understood as the minor shift of a H^+ from one electron cloud to a neighboring one.

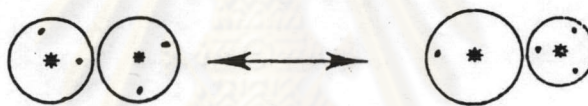


Fig. 2.2. Ionization of water.

The mechanism is stated in a book by Caldin and Gold (1975). Proton transfer can occur only through the initial formation of the hydrogen-bonded complex. The physical reason for the rule is obvious; it permits the transfer of the proton to occur entirely within the region of contact between the electron clouds of two oxygen ion (see figure 2.2).

Basic Reactions

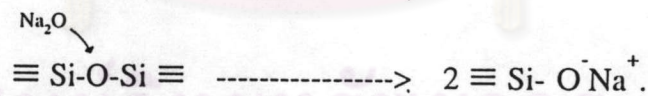
The alkali contained in the glass is very mobile and tends to react with water. The reaction is usually interpreted as a result of a combination of two independent processes:

1. leaching process which is the extraction of alkali ions out of the glass matrix
2. the dissolution of the glass matrix itself.

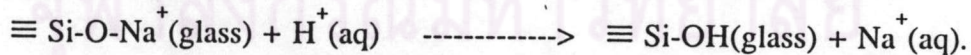
Leaching

Leaching is an ion exchange process where alkali ions (which are the network modifiers) are replaced by protons with a certain amount of water simultaneously entering the glass. In soda lime glass, it is described as the ion exchange between Na^+/H^+ and $\text{Na}^+/\text{H}_3\text{O}^+$.

In the melting process, Na_2O is introduced like



During primary ion exchange, the following reaction is observed:



The quantitative analysis of this ion exchange by many authors has led to the conclusion that the alkali contents going into solution during the primary ion exchange are proportional to the square root of time. The investigation of the concentration of Na in the leached glass surface, by Scholze, Helmreich, and

Bakardjiev (1975) are shown in figure 2.3. This curve has also been found by other authors. The extent of the Na leaching is independent or only slightly dependent on the pH value in the pH region from 1 to 7

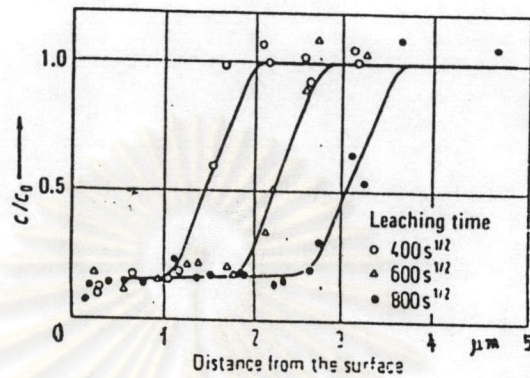
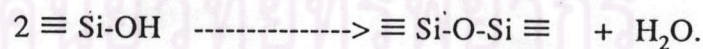


Fig. 2.3. Na_2O concentration profiles (in relative Na_2O concentrations c/c_0) of a Na_2O - CaO - SiO_2 glass (20-6-74 mol %) after leaching in 0.1 N HCl at 60 °C.

After the ion exchange step, a silica and water rich layer is thus formed at the glass/solution interface. This layer is called a “gel layer” which is different from the original glass. It contains molecular water condensed from silanol groups. The condensation reaction follows the ion exchange process instantaneously



There is experimental evidence for the occurrence of this condensation by near IR spectroscopy and most lately by Si-MAS-NMR (Bohm et. al, 1995). These condensation reactions start quickly after the glass is placed into the corrosion solution. Approximately 80 % of the silanol groups condense to $\equiv \text{Si-O-Si} \equiv$. This value dose not change significantly with increasing corrosion times.

In most cases, the number of silanol groups is lower than the number of $\text{SiO}^- \text{R}^+$ sites in the bulk. This means, that not only an exchange between alkali ions and protons, but also a consumption of protons takes place by formation and condensation of silanol groups. A remarkable fact is the high mobility of molecular water in the gel layer, proved by the rapid exchange between D_2O from a gel layer prepared in $\text{DCl-D}_2\text{O}$ solution and the humidity of the air (Baer and Pederson, 1984). This may be called a secondary exchange. Figure 2.4 is a sketch illustrating the leaching mechanism.

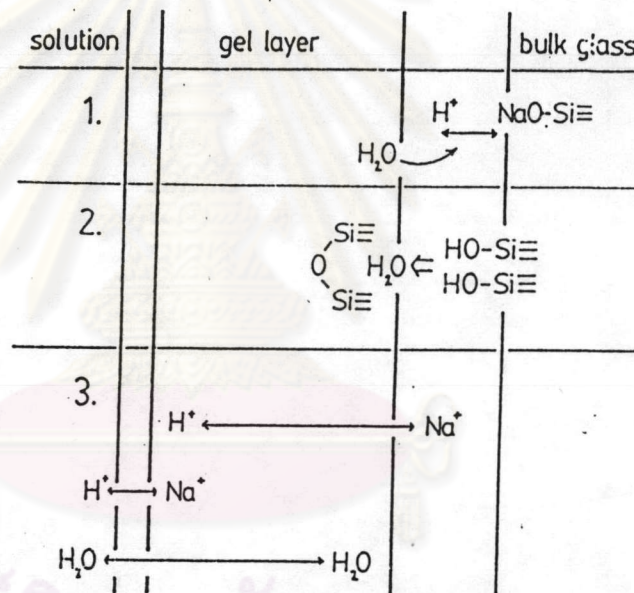


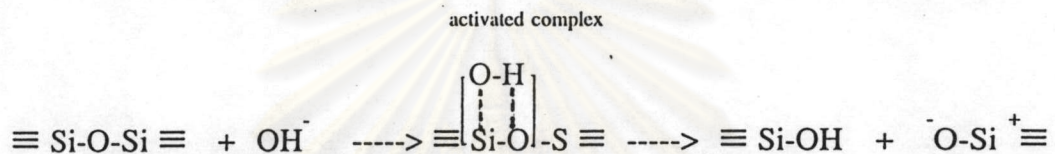
Fig. 2.4. Illustration of leaching mechanism (Conradt, 1996).

Three zones, the outermost surface zone, the gel layer, and the bulk glass can be distinguished by their different dissolution behavior.

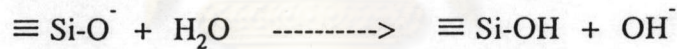
Network Dissolution

In the interaction of glass with aqueous solution, the dissolution of the silica network is an essential process which effects, for example, the overall ion exchange between the two phases.

After the gel layer is formed, the secondary exchange leads to the increasing of alkalinity. In the alkali solution, silicate glasses dissolve more easily, hence, the Si-O network is split, which can be represented schematically as followings;



the latter group, in the presence of H₂O, can react further according to the equation;



which shows that the OH⁻ ions can act as a catalyst. The probability of the reaction is $\exp(-E_A/RT)$ (E_A = activation energy \sim 70-80 kJ/mol)

Solubility of silica

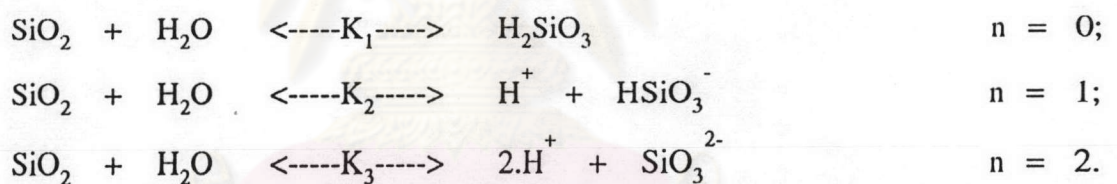
To understand the network dissolution mechanism more clearly, it is necessary to know about the solubility of silica. Solubility is governed by the general equation;



where A_{aq} represents the entire set of species originating from the dissolved A. For example, with $A_{solid} = Na_2CO_3$, $A_{aq} = 2*Na^+(aq) + CO_3^{2-}$. The factor n may be positive or negative depending on the acidic or basic character of the reaction. The molar Gibbs free energy of dissolution is given by

$$G^{diss} = G(A_{aq}) - G(A_{solid}) - m*G(H_2O).$$

Among the dense monolithic materials, the ones with the most negative G (A_{solid}) yield the lowest solubility. So, vitreous silica is more soluble than any crystalline form. And low-T quartz as the most stable among the latter materials is the least soluble form of silica. In detail, silica solubility occurs via a three-step equilibrium presented by Paul, 1982 which is



With $K_i = \exp(-G_i^{diss}/RT)$, solubility can be readily calculated from the law of mass action. The values for $\log K_i$, $i = 1, 2, 3$, are -5.20, -15.20, -27.2, for low-T quartz, and -3.43, -13.43, -25.43 for an amorphous silica powder with 250 m²/g specific surface.

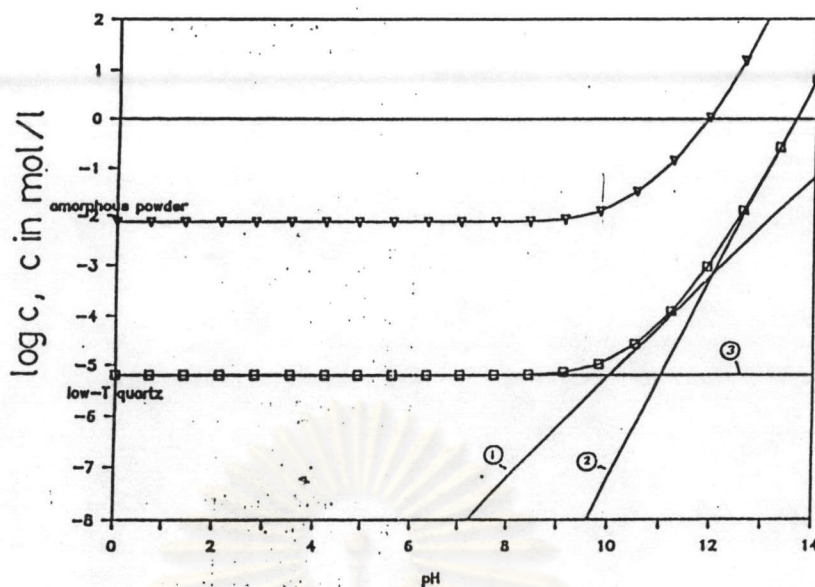


Fig. 2.5. Solubility (or stability) diagram of silica in various pH, Pimkhaokham et al, 1992.

The figure above shows three distinct pH zones based on the predominance of one particular silicate species. For example, in the first zone ($\text{pH} < 10$), the minimum solubility is presented by the undissociated but soluble portion of H_2SiO_3 . This species predominates up to $\text{pH} = 10$. In the second zone ($\text{pH} = 10$ to 12), most of the silicate which passes into the solution is due to the formation of HSiO_3^- species. In the third zone ($\text{pH} > 12$), SiO_3^{2-} predominates. From the figure, it is also evident that the quantity of silica extracted from both quartz and vitreous silica follows the same pattern but the solubility of silica from the glassy form is higher than that from quartz. This is because the Gibbs free energy of quartz is more negative than that of vitreous silica, or in other words, quartz is thermodynamically more stable than vitreous silica.

The relative solubility of silica in water is one of the main factors in the corrosion of glass. In the glass, it is well known that pH is a factor which can effect the durability of glass and also the reaction of oxides in water. The Gibbs free energy (ΔG^0) of hydration can be found when standard value G^0 of each species is

known. This leads to a plot between log activity and pH from 0 to 14 called “stability diagram”. From this diagram, it can be predicted which species will predominate in the selected pH range. The stability diagram of silica is a good example.

Most of all stability diagrams can be described in three pH ranges (Geasee, 1993) The first range is an acid unstable range. The second range is a stable range with completely hydrated species. The third range is a basic unstable range. Deprotonated species are predominated. The slopes of the unstable ranges are dependent on the amounts of proton excess or deficiency The location relative to the pH scale is a function of the specific oxide. For example, within the range $0 < \text{pH} < 14$, SiO_2 exhibits the stable and the basic unstable ranges only, while alkali oxides show nothing else but the acid unstable range

Another way of presentation of speciation diagram is created by plotting the relative amount in the percentage of aqueous species versus pH as shown in the following figure.

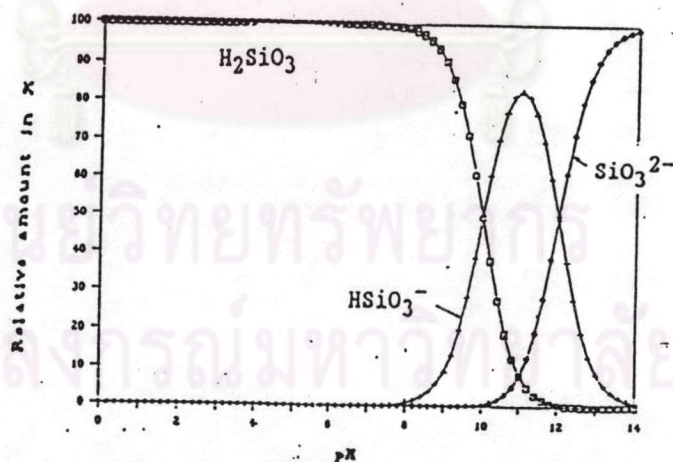


Fig. 2.6. Speciation diagram of silica.

Boksay et al. (1979) measured the total dissolved silica about $2 \cdot 10^{-6} \text{ mol/cm}^2$ is a linear function of time irrespective of the pH of the solution as shown in figure 2.7.

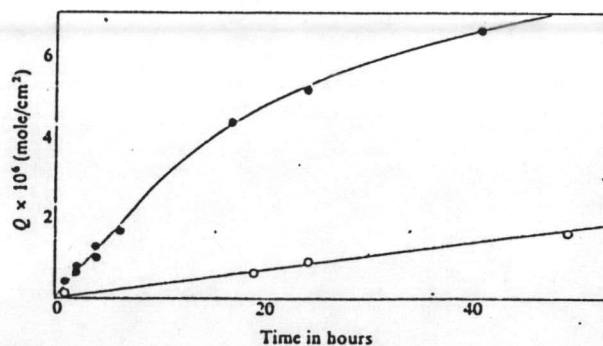


Fig. 2.7. Total silica dissolved from McInnes-Dole glass samples at 75 °C as a function of leaching time

● pH 11-23 solution ○ pH 3-6.5 solution

The dissolution rate plotted against pH is shown in figure 2.8 where every point represents the mean value of three or more independent measurements. The curve shows a broad minimum in the pH range between 3-5 and the graph indicates that the variation in the rate exceeds two orders of magnitude.

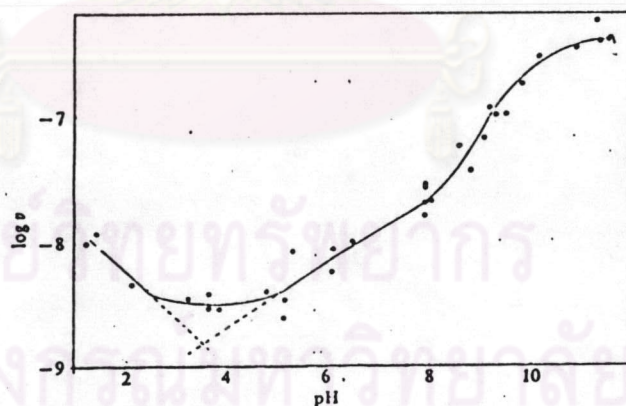


Fig. 2.8. Dissolution rate of McInnes-Dole samples as a function of the pH, Boksay et al, 1980.

Up to now we have considered the relationships in the system glass/water. As mentioned before, the mechanism between glass and water or air containing water

vapor are the same. The system glass/humidity with normal air as carrier gas leads to the weathering phenomenon.

Weathering

When glass is stored in air, it is not only prone to getting wet, but also weathered by acidic gases in the air such as CO_2 or SO_2 . "Soda bloom" is the result occurring from this phenomenon.

In the air one finds water vapor, which is eventually adsorbed by the glass surface. The H_2O molecules that are then found on the surface have fundamentally the same reaction possibilities as in the system glass/liquid water, except that the water skin found on the glass is normally only a few molecule layers thick and observed reactions occur. The situation becomes different, however, if the humidity of the air lies near the dewpoint or if small quantities condense on the glass. Then the reactions described above can appear more distinctly. CO_2 and SO_2 gases in the atmosphere dissolve in water on the glass surface, and form crystallites which may precipitate upon the surface, i.e. NaOH , CaCO_3 , CaSO_4 , CSH (calcium silicate hydrate phases = "cement"). If external conditions change in the direction of lower humidity, for example, through a rise in temperature, then water evaporates from the surface leaving the crystallites behind. The alkalinity rapidly increases and a strong attack occurs at the surface. When the glass surface is wet again, the weathering cycle will continue on a day to day basis. The surface can then become iridescent or matte. Figure 2.9 illustrates the cycle of weathering.

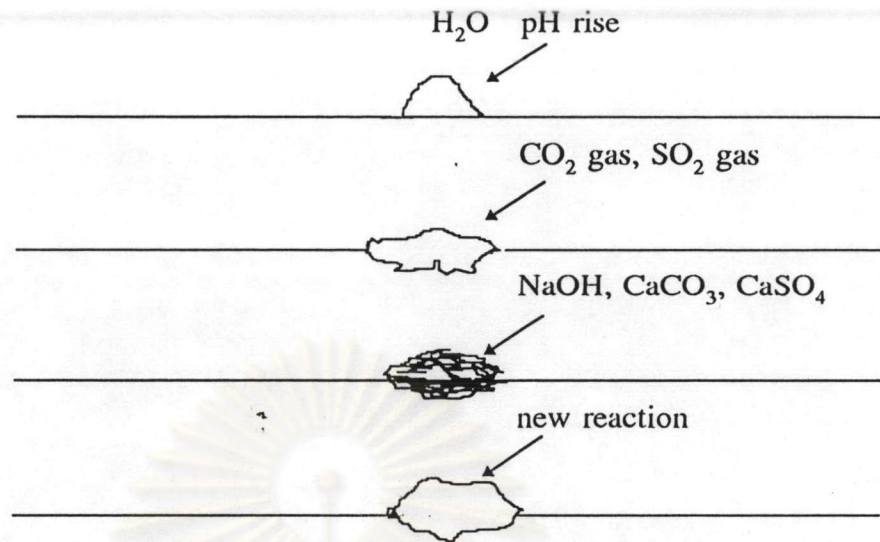


Fig. 2.9. Weathering process on glass surface.

The weathering depends on several factors, including the chemical composition of the glass, the length, humidity and temperature of the storage, and the nature of the glass surface.

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