In Vitro Assessment of the Biopersistence of Vitreous Fibers: State of the Art from the Physical–Chemical Point of View

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Biopersistence is a function of different parameters: low solubility of the vitreous phase in physiological media, good mechanical properties of altered fibers, limited ability of phagocytosis to digest residual fragments. This article emphasizes solubility problems. From studies related to nuclear waste storage and other industrial problems, the mechanisms (formation of a leached layer of variable thickness and structure) and the kinetic laws describing the dissolution of vitreous fibers are now fairly well known. Appropriate methods depend only on the composition of the vitreous fibers that have to be chosen to determine intrinsic dissolution rates. All other parameters influencing the dissolution rate have to be fixed (radius of the fibers, composition of the saline solution) or within a convenient range (flow-rate, \( V_s \).) Additionally, physicochemical parameters may be derived from a known relation (Arrhenius plot for \( T \), kinetic equation for \( pH \), geometrical equation for \( S \). In spite of their widespread use, flow-through systems, in our opinion, give less precise kinetic results than large-volume closed systems with small \( V_s \) ratios (less than 0.5 cm\(^3\)). In closed and open systems, we suggest the use of two parameters for describing the dissolution rates at 37\(^\circ\)C: the initial rate constant, \( v_0 \), and the time constant, \( k \), for a rate decreasing at variable \( S \). — Environ Health Perspect 102(Suppl 5):25-30 (1994)

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Introduction

Natural and man-made mineral fibers have been implicated in mesothelioma, lung cancer, and other diseases (1). To reduce the toxic effects of these industrial materials, the surface properties of durable fibers may be modified, or fibers that are biodegradable may be used. The first approach has been developed, for example, in Canada with surface treatment of asbestos (2) forming the so-called “chrysophosphate” whose surface properties are different from those of chrysotile (3). Because of the widespread use of glass fibers and rockwool, and because it is possible to increase the solubility of those fibers by moderate modifications of composition, the second approach is more generally applied. With the exception of glasses whose composition includes toxic elements (e.g., lead-rich glasses) or some wools derived from slag, which is a byproduct of the base-metal smelting processes, the in vivo dissolution of vitreous fibers liberates harmless products. Since it is reasonable to postulate that health hazards are more or less proportional to the time that respirable fibers remain within the lungs, a limited biopersistence will a priori result in limited biological effects even if durability is not the prime factor contributing to the biological potential of fibers.

Biopersistence is a function of different parameters: low solubility of the vitreous phase in physiological media; good mechanical properties of altered fibers to prevent their “crumbling”; limited digestion of residual fragments by phagocytosis.

Emphasis will be given here to solubility problems. After a brief overview of the dissolution processes of glass in saline solutions, dissolution tests will be discussed from the point of view of experimental conditions and kinetic modeling. Finally, the use of experimental data for predicting the biopersistence of respirable fibers will be considered.

Mechanisms and Kinetics of the Dissolution of Glass in Aqueous Solutions

Introduction to Glass Corrosion

Corrosion of glass may occur in several ways: reaction with the corrosive solution to form new compounds on the surface; preferential dissolution leaving a leached layer; total dissolution continuously exposing fresh glass (4). However, fresh glass exposition is more likely to occur as a special case of the second method, after detachment of a nonadhering surface leached layer. The solubilization of glass fibers and rockwool, generally used for industrial purposes, involves all three ways. The process of preferential dissolution occurs at solid-solutions interfaces through nucleation and growth of new phases; the other two processes are, respectively, characteristic of selective and nonselective dissolution (5). The type of glass corrosion by water results intrinsically from the nature and proportions of “network formers” (Si\(^{4+}\), B\(^{3+}\), P\(^{5+}\)) and “network modifiers” (Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) etc.) (6).

The solubility of simple soda–lime–silica glasses in acid solutions results from anion exchange reactions followed by total dissolution of the siliceous hydrated layer. The first step appears to be controlled by diffusion through the leached layer (7) so that ion exchange proceeds at a decreasing rate over time until it reaches a stationary state with, in theory, a reverse flow at a constant rate from a leached layer of constant thickness (4).

Leached layers are more rapidly attacked in alkaline solutions than in neutral or acid ones because the alkali supplies hydroxyl ions for reaction with the silica network.

Dissolution of vitreous materials of more complex compositions will involve several of the following processes: preferential dissolution of “network modifiers” and of boron, a “network former” with formation of a residual Si-Al rich amorphous
hydrated layer which may accommodate other elements sometimes as precipitated microphases; congruent or preferential dissolution of the residual layer; precipitation of insoluble amorphous or crystalline phases, nucleated at the solid–liquid interface or within micropores of the residual layer itself; later restructuring or transformations both of residual layers and of early precipitates by reaction with elements, either present in the solution or liberated from the glass at the hydration front.

Several of these processes make up a complex "alteration microprofile," whose structure has been deciphered by transmission electron microscopy of ultrathin sections that show the hydration of glassy slags, which can be described as a CaO–dominated, SiO₂, Al₂O₃, MgO system, producing complex surface layers (8). Between the glass and the solutions there are three zones: A complex inner zone sticks to unaltered glass (Figure 1). Its lower part is a dense residual layer, enriched in Si, Al, and Mg, while its upper part is a high porosity lamellar layer, which apparently results from a restructuration of the lower part. The total thickness of this inner zone increases with time and may exceed 2 μm after 6 months. An intermediate zone made of hydroxalcite-type compounds is formed after only 2 days and remains of nearly constant thickness (0.3 μm) with time. The third zone is an external mixture of amorphous solids with rare crystalline phases that have precipitated at the solid liquid interface. This poorly adhering veneer may exceed 10 μm in thickness after 6 months.

Other complex "alterations microprofiles" have been described after attack of basaltic glasses by sea water (9,10). Other detailed investigations concern, for example, the so-called "R7T7 glass" used as a model for nuclear waste disposal (11–13).

Reactions Involved in Glass Hydrolysis

In acid aqueous solutions, selective dissolution involves an ion exchange reaction between protons and "network modifiers" (14). The exact nature of the diffusing H⁺-bearing species has been studied by chemical profiling, using secondary ions mass spectrometry (SIMS) or nuclear magnetic resonance (NMR) and suggesting an association of H₂O⁺ and/or H⁺ with free molecular water (15). The following reactions are supposed to occur:

\[
(Si-O-Na)_{glass} + H^+ = (Si-OH)_{glass} + Na^+ \]  
\[
(Si-O-Na)_{glass} + H_2O^+ = (Si-OH)_{glass} + Na^+ + H_2O \]  
\[
(Si-O-Na)_{glass} + H_2O = (Si-OH)_{glass} + Na^+ + OH^- \]

This letter is immediately followed by the neutralization of OH⁻ by siloxane groups:

\[
(Si-O-Si)_{glass} + OH^- = (Si-OH)_{glass} + (SiO^2-)_{glass} \]  
\[
(Si-O-Si)_{glass} + OH^- = (Si-OH)_{solution} + (SiO^2-)_{glass} \]

In acid media, reactions 1 or 2 and 3 occur. In neutral solutions, reaction 3 is dominant while in basic media, reaction 5 liberates silica in the solution.

The selective dissolution of boron, a "network former" element, is well known. The reactions involved (16,17) with H₂O⁺ entailing as a first step, a modification of the coordination number of boron from IV to III (tetrahedral to triangular).

The subsequent liberation of the borate ion results from an acid attack:

\[
(BO_3)_{4-}^{glass} + 3H_2O^+ = (H_3BO_3)_{solution} + 3H_2O \]  
\[
2(Si-OH) = (Si-O-Si) + H_2O \]

Dissolution Kinetics

The dissolution of glass involves transport processes both hydrodynamic and diffusive in the solution and diffusive in the leached layer, as well as chemical processes. The slowest is rate determining and dissolution is either transport- or reaction-controlled. In the dissolution kinetics of basaltic glasses, at different temperatures (100–300°C) and pH (2–10), chemical surface reaction is usually the rate determining step. However, at extreme pH values (<2,>10), and for elevated temperatures, the dissolution is diffusion controlled (19).

For the corrosion of simple soda–lime–silica glasses, the rate is diffusion-controlled through the leached layer, following a parabolic law for the variations of the conductivity (7) and sodium content (20) of the corrosive solution.

The modeling of glass dissolution kinetics must take into account the following processes: ion-exchange at the hydration front, at the bottom of the leached layer; dissolution of the leached layer through surface reactions; transport in the solution; and transport by diffusion through the leached layer.

In the classical approach (21,22), the model of glass corrosion is under diffu-
sional control. It has to include the following processes: rate of movement of the hydration front in contact with the fresh glass; the interdiffusion of “modifiers” with protons or H₂O within the leached layer; and the rate of movement of the initial interface in contact with the solution.

Unfortunately any quantitative approach may depend on a number of hypotheses and on mathematical simplifications. The only feasible theoretical treatment deals with the third process, and concerns the modeling of the energetics of the surface reaction using the transition state theory (23). In this approach, the reaction between solution and the surface involves formation of an activated complex, which has a strong tendency to dissociate through a loose vibrational mode (24). This decomposition to reaction products is supposed to be the rate-limiting step.

It is possible to derive a general kinetic law, with different forms applicable to pH-dependent dissolution of crystalline silicates (25) and of basaltic glasses (19). The pH dependence of silicate hydrolysis may be modeled from a simplified expression proposed by Aagard and Helgeson (24), far from equilibrium (33).

\[ v = S \cdot K \cdot a_{H^+}^{-n} \]  

where 
\[ v \] = effective reacting surface area
\[ K \] = rate constant
\[ a_{H^+} \] = activity of hydrogen ion
\[ n \] = stoichiometric coefficient

A general rate equation for nuclear waste glass corrosion has been derived by Grambow (26) with application for nearly neutral to slightly acid constant pH and constant temperature. It is based on the hypothesis that silica is the main component of the activated complex. The following equation may be written:

\[ v = v_o (1 - [H_2SiO_4] / [H_4SiO_4]^*) \]  

where \( v_o \) = kinetic constant initial rate value: [H₂SiO₄] = silica concentration, and [H₄SiO₄] = “saturation” concentration with respect to glass.

The surface composition of the leached layer, as determined by X-ray photoelectron spectroscopy (XPS), may give more exact information about the composition of the activated complex. For different glasses, surface composition after corrosion by physiological saline solutions may be approximated (27) by the formula

\[ NaAlSiO₄(nH₂O) \] (“hydrated albite gel”) corresponding possibly to the activated complex that has been proposed for the dissolution of crystallized albite (28).

Experimental Studies

Most experimental work in this field has been focused on the determination of the “initial” rate of dissolution of glass fibers, i.e., the kinetic constant of the “Grambow law.” This rate is dependent on the composition of the glass; hence the possible influence of other parameters on the dissolution kinetics has to be determined. Among these parameters are, first, the ratio of the surface of the solid to the volume of the solution (the \( \gamma \) ratio), second, the pH and the composition of the saline solutions, and finally, the temperature, and the mean diameter of the fibers. In addition, the effect of experimental procedures (static and dynamic runs) has to be considered.

Influence of the \( \gamma \) Ratio

It is unlikely that dissolution—precipitation mechanisms would remain the same at different \( \gamma \) ratios. With this in mind, Advocat (13) determined the pH of Volvic water (initial conductivity 162 μS) reacting with the R7T7 glass, after runs of different durations (1 week—1 year). For a given \( \gamma \) value, irregular scattering of pH between runs was observed, varying from ±0.3 pH unit (for \( \gamma = 4 \) cm⁻¹) to ±0.1 pH-unit (for \( \gamma = 200 \) cm⁻¹). These variations indicate that a steady state is more rapidly attained in more confined systems, suggesting that different reaction mechanisms may operate at the lowest \( \gamma \) ratios from those operating at the highest \( \gamma \) ratios. Some of the \( \gamma \) ratios used by Advocat in closed system were high, which imply significant pH increases.

For a range of values of \( \gamma \) in which the mechanism remains the same, only variations of \( S \) have to be considered, whatever the initial value of \( \gamma \).

Dissolution rates may be considered with respect to either the solution or the solid. With respect to the solution, the rate is \( dx/dt \), where \( x \) is usually SiO₂ or B.

Assuming a first order kinetic law with respect to the \( \gamma \) ratio (5).

\[ dx/dt = K S I V \]  

where \( K \) is a factor including the kinetic constant and the effect of chemical parameters.

During time \( dt \), the relative mass loss \( q \) of the fibers is then

\[ dq = (V/w)dx = (KS/w) \cdot dt \]  

where \( w \) = weight fraction of \( x \) within the glass.

Thus, if \( S \) remains constant during \( dt \), the dissolution rate expressed as

\[ k = dq/dt \]  

is also constant. Accordingly, if transport in the solution is not a limiting factor and if the surface reaction rate remains constant, \( dq/dt \) is constant, whatever \( V \) and the initial value of \( S \). The effect of decreasing \( S \) during dissolution may be accounted for by using a “geometrical” kinetic equation.

The simplest geometrical model is based on a constant rate, \( v \), of backward movement of the fiber-solution interface \( (v = -dR/dt \) where \( R \) is radius of the fiber). With respect to the relative mass loss \( q \) and \( R_o \), the initial radius of the fibers, one has

\[ z = (1 - q) = 1 - v_o \cdot t/R_o \]  

where \( v_o \) = initial dissolution rate of the glass, \( v \) = dissolution rate of the leached remnant, and \( t \) is a constant. As \( v \) is certainly very much smaller than \( v_o \),

\[ v = v_o e^{-kt} \]  

and hence

\[ z = 1 - [v_o/(R_o \cdot k)] (1 - e^{-kt}) \]  

This model (27) describes the experimental results with respect to two parameters only: the initial rate constant, \( v_o \), and the time constant for rate decrease, \( k \).

Alternatively, the fiber may be considered as consisting of two fractions, one dissolving rapidly, the other, slowly (29).

The foregoing equations apply to textile fibers of constant diameter. Other equations may take into account the fact that the initial diameter of the fibers is not constant but fits a Gaussian distribution (29).

Applying these equations, within a relatively large window of geometrical and hydrodynamical experimental conditions (including size and shape of the reactors, flow rates, degree of mechanical stirring in closed systems), the dissolution rate of glass fibers may be determined using a variety of static and dynamic conditions. In other
words, for a given glass and a given saline solution, static and dynamic tests should give similar (q) versus time curves (27).

Closed System Experiments

Glass dissolution in deionized water and in various saline solutions (e.g., sea water) has been studied for different glass compositions using unchanged solutions (closed systems). Except for low \( \rho \) ratios (e.g., 0.2 cm\(^{-1} \)), dissolution rates are dependent on two factors: a pH increase through time, reflecting the fixation of protons by ion exchange and leading to an enhancement of the dissolved silica when the pH reaches the pK value of H\(_2\)SiO\(_4\), i.e., 9.8 at 25°C (18); and an increase of dissolved silica decreasing the decomposition rate of the silica-rich activated complex.

Physiological saline solutions have a "buffering reserve" due to their composition in contrast with a sodium chloride (NaCl) solution of comparable ionic strength. Longer runs in NaCl solution show a continuous increase of the pH, leading to a high concentration of soluble silica.

In addition, a practical advantage of the static experiment is the possibility of using a pH-stat device or a system of CO\(_2\)-bubbling to analyze the effect of pH on dissolution rates.

Dynamic Experiments

Most recent research devoted to determination of dissolution rates of vitreous fibers used flow-through techniques (30,31). They were assumed to be carried out under conditions of constant rate, i.e., without significant back-reaction limiting the decomposition of the silica-rich activated complex.

For their glass no. 18a, Potter and Mattson (29) demonstrated that in the range 0.08 to 1.00 ml/min, the initial dissolution rate was independent of the flow rate, which was sufficiently high to eliminate the effects of dissolved components. In this respect, the situation is similar to the "large volume" static experiments (\(\Gamma = 0.2 \text{ cm}^{-1}\)).

As explained above, the dissolution rate calculated from the relative mass loss and standardized to actual S is independent of the initial \( \rho \) ratio, provided that the surface reaction rate remains constant. Accordingly within this constant range, the volume of the reaction cell and the mass of fibers are not rate controlling factors. However, experimental discrepancies found during dynamic experiments suggest that the basic hypotheses are not exactly fulfilled. A possible reason is the variability of the dissolution process, where some fibers may be totally attacked, while others remain partially intact, for example at the contact point of two fibers. For this reason, it is essential to ensure that the texture of the aggregates of fibers is correctly reproduced from run to run.

In addition, the pH of the solution should be controlled before flowing through the fibers, by bubbling a N\(_2\)-CO\(_2\) mixture through the solution tank (27,29,31). However this is less accurate than the pH regulation obtained in "large volume" reactors.

The development of dynamic runs initially was based on a rough simulation of the biological processes occurring in the lungs. However, for accurate kinetic studies, static runs at low \( \rho \) values (e.g., 0.2 cm\(^{-1} \)) give more reproducible results. Moreover, they permit the mechanical stirring of the solutions as well as an accurate pH control.

Influence of Physical–Chemical Parameters on the Kinetics of Glass Dissolution

In vitro tests are targeted to model the behavior of glass fibers in simulated biological media. For this reason, temperature, pH, and solution composition are fixed in a limited range. However, a better compilation of rate constants may derive from determinations of activation energies. Extrapolations to body temperature of rate data from the published literature are probably correct if the rate controlling factors remain constant. For such extrapolations, an Arrhenius equation may be used provided \( E_a \), the activation energy, is known. For example, \( E_a \) has been determined for the dissolution of basaltic glass in deionized water and sea water at different pH. In the range pH = 4 to pH = 10, \( E_a \) is about 60 kJ/mole (9), a value characteristic of a reaction-controlled dissolution process. Very acid or basic conditions (19) lead to smaller values around 10 kJ/mole, indicating transport-controlled kinetics.

Potter and Mattson (29) found a value of 64 kJ/mole for their glass 18b. Apparently, as a first approximation, an activation energy of 60 to 65 kJ/mole may be used to correct dissolution rates for the effect of temperature.

Predictions of Glass Fibers Durability

In vitro tests are performed to estimate the biopersistence of glass fibers. Independent theoretical predictions may be combined with experimental data to establish predictive models.

Thermodynamics of Hydration

Although glasses and solutions can hardly be at equilibrium because of the irreversible character of glass dissolution, one may calculate from thermodynamic tables a theoretical pH-dependent free energy of hydration using the following relation (32).

\[
\Delta G_{\text{hyd}} = \sum x_i \Delta G_{\text{hyd}} \cdot i
\]

From the simple calculation of \( \Delta G_{\text{hyd}} \), a classification of glasses by "increasing solubilities" at constant pH in deionized water may be theoretically established. For a set of eight compositions, a fair positive correlation is observed with dissolution rates of the glasses (13). This correlation results from the evident fact that sparingly soluble solids dissolve at a lower rate than highly soluble ones. However, such a correlation is only approximate. This approach may be useful for approximating initial dissolution rates at very different pH; but applications to biopersistence problems appears to be limited, as illustrated by calculations using glass compositions and initial dissolution rates given by Potter and Mattson (29).

Kinetics of Glass Dissolution

Introduction. One must emphasize a practical difference between studies devoted to the durability of glasses not submitted to mechanical perturbations and studies of the biopersistence of glass fibers. In the first case, surface reactions leading to the dissolution of the leached layer are supposed to be the rate determining step (13,19). In the second case, the rate of degradation may be higher than the dissolution rate because degradation may involve peeling and crumbling of the leached layer. Fibers recovered from animals show a reduction in diameter with no evidence of a leached layer. As underlined by Potter and Mattson (29), "mechanical weakness [of this layer] may lead to physical removal while in the animal or during the extraction process." If this hypothesis of mixed chemical and mechanical degradation of the fibers is true, then the rate limiting step will be the "peeling process," at present difficult to model. Alternatively, a purely chemical degradation could be favored, in which the dissolution of the leached layer then will be the rate-determining step, since it is the slowest process until a steady state is attained.

Empirical and Theoretical Kinetic Equations: the Role of pH. A number of studies have been performed recently on...
the role of pH. For example, the rate of quartz hydrolysis has been determined as a function of pH at 70°C (33). Kinetic data indicate a change in mechanism at a pH significantly lower than the pH at which the quartz solubility rises sharply. In acid media, below pH 6, the dissolution rate is pH-independent, while above about pH 6 dissolution follows the "Aagard and Helgeson law" (see above, [24] with $n_{pi}^+ = 0.5$).

A similar $n_{pi}^+$ value, in the range 0.5 to 0.6, may be derived from the data published by Potter and Matson (29) for their "glass no. 13."

Clearly, more experimental data are required to determine $n_{pi}^+$ and the transition pH from pH-dependent to pH-independent rates and to relate these values to glass compositions and solubilities. In this respect, one may quote the values obtained for the rate of hydrolysis of a basaltic glass at 50°C (19, 34): in the alkaline region, $n_{pi}^+ = 0.7$. The pH-independent zone ranges between pH 4 and pH 8, and is dominated by H₂O adsorption on the glass surface.

**Empirical and Theoretical Kinetic Equations: the Role of [H₄SiO₄]* Concentration.** At constant pH, adapting the kinetic law established by Grambow (26) for complex multicompontent glasses one may write, with respect to the relative mass loss:

$$rate = K \cdot S \cdot w \cdot (1 - [H_4SiO_4]/[H_4SiO_4]^*)$$

where $w =$ weight percent of component $X$ in the glass.

$[H_4SiO_4]^*$ is supposed to be an intrinsic "saturation value" for each glass, and its determination from long-range studies (e.g., 1 year run) enables the rate decrease in closed systems to be determined. However, aging of the amorphous-silica rich layer clearly will influence the determination of $[H_4SiO_4]^*$. The development of a dense, poorly soluble silica veneer may explain the nonzero dissolution rate of the "RT77" nuclear glass even after very long runs with elevated $\delta^T$ ratios. The condensation of this layer prevents the silica concentration from reaching the "saturation value" (i.e., $[H_4SiO_4]^*$) with respect to glass (13, 26).

Most rate determinations used during in vitro testing of glass fibers aim to determine the "initial rate" of dissolution. Accordingly, in closed systems, the effect of the back reaction may be discarded, by checking the linear dependence of silica concentration with respect to time. In flow-through systems, identical steady state concentrations have to be found for variable flow-rates.

**Conclusion**

From studies of nuclear waste storage, glassware durability, research for new fertilizers, and other industrial problems, the mechanisms and the kinetic laws describing the dissolutions of vitreous silicate materials are now fairly well known. As a specific case, the in vitro simulation of the biopersistence of vitreous fibers received considerable attention several years ago (30, 31).

Uncertainties remain about the ability of the insoluble layered leachers, which form on vitreous fibers, to be detached, then "crumbled," and finally submitted to phagocytosis within the human body. Two limiting cases, therefore, have to be considered: the sticking protective leached layer and the "peelable" leached layer.

A choice must be made to obtain the best experimental device to determine intrinsic dissolution rates, depending only on the composition of the vitreous fibers. All other parameters influencing the dissolution rate have to be kept constant (initial diameter of the fibers, composition of the saline solution) or within a convenient range (flow-rate, $\delta^T$ ratio). Alternatively, they may be accounted for by applying a known equation (Arrhenius equation for $T$, kinetic equation for pH, geometrical equation for $S$). In spite of their widespread present use, flow-through systems, in our opinion, give less precise kinetic results than large-volume closed systems with small $\delta^T$ ratios (less than 0.5 cm²/s).

In closed and open systems, we suggest the use of two parameters for describing the dissolution rates of fairly soluble glasses at 37°C: the initial rate constant, $\nu_0$, and the time constant for decreasing rates, $k$.

For sparingly soluble glass- and rock-wool fibers, only the initial rate constant may be determined, and we suggest "high temperature" (i.e., 90°C) long-range runs, and use of the Arrhenius equation to approximate the constant, $k$.

New tests to determine the mechanical strength of residual fibers must be found. This parameter is of paramount importance in determining the biopersistence of sparingly soluble vitreous materials, which have a sticking leached layer. The practical problem is whether such residues would break into fragments small enough to be phagocytosed.

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