Chemical Behavior of Aluminum and Phosphorus during Dissolution of Glass Fibers in Physiological Saline Solutions

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The dissolution of textile glass fibers of four different compositions has been investigated at 37°C. In these glasses, which are isolation type, the P₂O₅ contents scatter between 0 and 2 wt% and Al₂O₃ from 0.12 to 3.4 wt%. Both static (30-mg fibers; 250-ml solution) and dynamic (50-mg fibers; 40 ml/day flow rate) conditions with or without bubbling of a gas mixture (95:5, N₂-CO₂) have been used. Two physiological solutions, one proposed by Kanapilly and the other by Scholze, were used. After each run (1, 3, 7, 14, and sometimes 30, 62 days) the solutions were analyzed for B and Si by inductively coupled plasma (ICP), the weight losses were determined, and the residual solid were observed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Static runs give a better agreement between measured and calculated weight losses from solution analyses than dynamic experiments. SEM examinations indicate diameter reduction and formation of a hydrated Si-rich layer. Sometimes hollow tubes, suggesting the detachment of these layers, are observed. XPS and energy dispersive X-ray (EDX) analysis indicate the formation of a veneer of calcium phosphate for the most rapidly dissolving glass. In other cases an Al increase is observed at the solid solution interface. Whatever experimental conditions are used, the relative dissolution rates of the four glasses are identical. The kinetics may be modeled with variable dissolution rates from initial high values to final low ones. The latter reflect the very low solubility of the residual product. — Environ Health Perspect 102(Suppl 5):77-81 (1994)

Key words: glass fibers, dissolution, aluminium, phosphorus, XPS, SEM, in vitro tests

Introduction

The idea that the risk of carcinogenesis related to fiber inhalation is decreased if these materials are rapidly dissolved in the lung is now widespread. For this reason, the in vitro dissolution rate of glass fibers in saline solutions has been measured by many authors (1–5). However, uncertainties remain about the chemical composition of the leached layer at the interface solid-solution specifically when glasses contain variable amounts of Al and P. These data, which can be supplied by surface analysis, are necessary to form a realistic picture of the dissolution of the fibers.

Among the parameters that can modify the dissolution rate, changes in the glass composition greatly affect the clearance of fiber. This study aimed to characterize modifications of the chemical durability of standard isolation fiber glass when the amount of Al is reduced and when extra components, such as P, have been added in very small amounts, and also to compare the dissolution processes of various glasses in physiological saline solution and to establish a general kinetic model.

Materials and Experimental Procedure

Materials

Glasses of four compositions were studied (Table 1). One is a commercially available isolation glass. The others are derivatives with lower percentages of Al₂O₃ and added percentages of P₂O₅. Fibers of uniform diameter (10 μm) were obtained by the textile process from a one-hole bushing in the Research Center of Saint-Gobain (Aubervilliers, France).

| Table 1. Ponderal composition of the four studied glasses. |
|-------------|
| CM3 | CM2 | CM19 | CM25 |
| SiO₂ | 65.01 | 68.28 | 65.90 | 65.41 |
| Al₂O₃ | 3.40 | 0.12 | 0.15 | 2.00 |
| CaO | 7.00 | 7.00 | 8.00 | 7.00 |
| Na₂O | 15.85 | 15.85 | 15.10 | 15.85 |
| MgO | 2.95 | 2.95 | 3.00 | 2.95 |
| B₂O₃ | 4.50 | 4.50 | 4.50 | 4.50 |
| P₂O₅ | — | — | 2.00 | 1.00 |
| F | — | — | 1.00 | — |

Two physiological saline solutions derived from the Gamble’s solution (6) were used. The first, referred to as solution L, was developed by Kanapilly (7) and used by Leineweber (8) and Feck (3). The second, solution W, which contains more calcium ions, was used by Scholze and Conradt (1). In both cases, 0.1% of formaldehyde was added to prevent microorganism proliferation. The chemical composition of solutions is shown in Table 2. The initial pH of both solutions ranged from 7.6 to 8.0.

| Table 2. Composition of the two solutions used.
|-------------|
| Solution L | Solution W |
| NaCl | 6.780 | 6.415 |
| NH₄Cl | 0.525 | — |
| CaCl₂-2H₂O | 0.029 | 0.255 |
| NaHCO₃ | 2.268 | 2.703 |
| NaH₂PO₄-2H₂O | 0.188 | — |
| Na₂HPO₄ | — | 0.148 |
| Glycine | 0.450 | 0.118 |
| Na₂Citrate-2H₂O | 0.059 | 0.153 |
| H₂SO₄ | 0.049 | — |
| Na₂SO₄ | — | 0.079 |
| MgCl₂-6H₂O | — | 0.212 |
| Na₂Tartrate-2H₂O | — | 0.180 |
| NaLactate | — | 0.175 |
| NaPyruvate | — | 0.172 |

* L solution used by Kanapilly; W, extracellular solution used by Scholze.

This paper was presented at the Workshop on Biopersistence of Respirable Synthetic Fibers and Minerals held 7–8 September 1992 in Lyon, France. This work was supported in part by Saint-Gobain Recherche, Aubervilliers, France.

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Experimental Procedures

The dissolution of glass fibers was studied under three experimental leaching conditions: static mode, unbuffered dynamic mode, and buffered dynamic mode.

In the first mode, fibers approximately 20 mm long were laid on a large teflon grid in a teflon waterproof vessel. The weight of fibers was 30 mg and the volume of solution was 250 ml, to reach only approximately 60% saturation with respect to amorphous silica, which in the case of complete dissolution of the fibers would be about 140 mg/l (9). The vessels thermostatted at 37°C ± 1°C and the runs lasted from 1 to 62 days. At the end of the experiment, fibers were removed from the solution, rinsed in deionized water, and air dried before weighing. The solution was filtered on a 0.22-μm pore diameter filter, and analyzed by inductively coupled plasma (ICP) or atomic absorption spectrometry (AAS).

In the second mode, 50 mg of fibers approximately 5 mm in length, were laid on a 0.22 μm pore diameter filter in a cell volume of 1.2 ml thermostatted at 37°C ± 1°C. The solution was delivered by a peristaltic pump at a flow rate of 40 ml/day. After each run, the fibers were removed from the filter for determination of weight loss and analysis. The fluid collected during the leaching was analyzed by ICP or AAS. The experimental conditions in the third mode were identical except that the pH in the supply container was buffered by bubbling through the solution a N2-CO2 gas mixture (95:5 by volume). pH measurements were made after each run, and for dynamic leaching the pH in the supply container was checked during the experiments. SEM analysis was made either directly on fibers or on polished sections of fibers embedded in epoxy resin. Fresh samples were used for each experiment.

Results and Discussion

Experiments in Static Mode

The weight loss with time of four fibers treated in the Kanapilly solution (L) is shown in Figure 1. As expected, the two more soluble fibers have the lowest alumina content (CM2 and CM19), while comparing CM19 with CM2, and CM25 with C3, it is evident that phosphate increases the dissolution rate. During leaching, the pH increased slightly due to ion exchange, but it remained at about 8.8. For the most rapidly dissolving glass (CM19) the weight losses at 14, 30, and 62 days were virtually the same. SEM observations showed a regular decrease in fiber diameter for CM19 and CM2 with the reaction time, reaching a diameter of about 2 μm, corresponding to 95% weight loss. At this stage (CM19, t = 14 days), irregular shapes were observed on polished sections of epoxy-resin-embedded fibers (Figure 2a). Some fibers were completely leached, and energy dispersive X-ray (EDX) analyses of such fibers indicate that the residual product is essentially siliceous, strongly enriched in aluminium. The Al/Si atomic ratio, which was 0.003 in the initial fiber, has risen to 0.13. In contrast, the C3 and CM25 fibers after 14 days' treatment, showed on polished sections, a fine hydrated layer surrounding an unaltered circular core (Figure 2b). The thickness of this layer is less for C3 glass (0.2 μm) than for CM25 (0.5 μm). Dissolved silicon and boron in the solutions were plotted against weight loss (Figures 3,4). The correlation between the fraction of dissolved silicon and the relative weight loss is good, indicating that the contribution of the leached layer is negligible compared with the fraction of dissolved glass when weight loss is less than 80%. At higher values, a slight discrepancy is observed indicating that

| Fibers | time (days) | Al/Si | Na/Si | Ca/Si |
|--------|------------|-------|-------|-------|
| C3     | 0          | 0.06  | 0.48  | 0.12  |
| CM2    | 0          | <0.01 | 0.45  | 0.11  |
| CM19   | 0          | <0.01 | 0.44  | 0.13  |
| CM25   | 0          | 0.04  | 0.47  | 0.11  |
| C3     | 14         | 0.25  | 0.17  |       |
| CM2    | 14         | 0.18  | 0.26  | 0.02  |
| CM19   | 28         | 0.19  | 0.17  | 0.03  |
| CM19   | 3          | 0.17  | 0.32  |       |
| CM19   | 7          | 0.16  | 0.28  | 0.03  |
| CM25   | 14         | 0.27  | 0.21  |       |
The correlation between dissolved boron and the weight loss is similar. Data of surface analysis by X-ray photoelectron spectroscopy (XPS) relative to a layer <10 nm thick, are given in Table 3; B, Ca, Mg, and P are rapidly leached from the surface veneer, but Na remains in the interface at about half of the initial Na/Si ratio in the glass. This is probably due to the high concentration of Na⁺ ions in the solution, rather than to precipitation of Na-salts. In contrast, Al is markedly enriched for all glasses and for each duration. The surface compositions of the residual products determined by XPS are not in complete concordance with those observed by EDX. The XPS approach suggests an "albite-like" gel composition with Al/Si and Na/Si atomic ratios at about 0.3 to 0.4. (The composition of crystallized albite is NaAlSi₃O₈.) The EDX data indicate lower Al/Si and Na/Si atomic ratios. Actually, there is probably a concentration gradient, with the interface being richer in aluminium and sodium.

**Experiments in Unbuffered Dynamic Mode**

The mean pH of the effluent solution is 8.8, similar to the pH observed in experiments in the static mode. The weight losses observed in solution L in both dynamic and static modes for three glasses are similar (Table 4). The kinetic curves, however, are more irregular in dynamic mode experiments, probably due to a more or less high degree of leaching of the fibers in the cell, related to the variation of the flow within the fiber mat. SEM observations reveal a variety of morphologies for the residual product of CM2 and CM19 fibers. For example, the CM19 glass that has been leached for 28 days shows tubular shapes, whose diameter is close to that of the original fiber. Apparently the dissolution of the fiber continues within this residual outer layer, possibly from the base of the cylinder. The chemical composition of these tubes is not well established, but EDX analysis indicates a high concentration of calcium, confirmed by XPS analysis which shows the presence of calcium phosphate. For runs of other durations, the surface composition of the fibers is lowered in Na, strongly reduced in B, P, Mg, and Ca: and enriched in aluminium as compared with the initial glass (Table 5). This is similar to the results obtained with the static mode.

**Experiments in Buffered Dynamic Mode**

Runs using the solution W richer in Ca⁺ ions, confirm the formation of surface calcium phosphate which reduces the dissolution rate of the most soluble glass (CM19). In this regard, Figure 5 clearly illustrates the role of the composition of the solution. XPS analysis indicates an apatite-like composition (P/Ca atomic ratio near 0.6) of the surface of such altered fibers.

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**Table 4.** Comparison between the weight losses for unbuffered dynamic mode (D40) and static mode (S250) in solution L.

| Fibers | time (days) | S250 | D40 |
|--------|-------------|------|-----|
| C3     | 7           | 93   | 88  |
| CM2    | 7           | 45.0 | 48.6|
| CM19   | 7           | 65.0 | 77.2|
| CM19   | 14          | 89.0 | 85.8|

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**Table 5.** Atomic ratios normalized to silicon determined by XPS on the surface of leached fibers for the unbuffered dynamic mode.

| Fibers | time (days) | A1/Si | Na/Si |
|--------|-------------|-------|-------|
| C3     | 7           | 0.24  | 0.29  |
| CM2    | 7           | 0.18  | 0.30  |
| CM2    | 14          | 0.21  | 0.34  |
| CM19   | 21          | 0.25  | 0.26  |
| CM19   | 7           | 0.27  | 0.26  |
| CM19   | 14          | 0.14  | 0.12  |

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**Table 6.** Atomic ratios normalized to silicon determined by XPS on the surface of leached fibers (14 days) for the buffered dynamic mode.

| Fibers | A1/Si | Na/Si | Ca/Si | P/Si | P/Ca |
|--------|-------|-------|-------|------|------|
| C3     | 0.29  | 0.30  | —     | —    | —    |
| C3     | 0.32  | 0.25  | —     | —    | —    |
| CM2    | 0.19  | 0.22  | —     | —    | —    |
| CM19   | 0.20  | 0.22  | —     | —    | —    |
| CM19   | 0.39  | 0.22  | 0.56  | 0.67 |
| CM25   | 0.30  | 0.28  | 0.61  | 0.41 |
| CM25   | 0.26  | 0.24  | —     | —    | —    |
(compared with 0.6 µm for CM25) and a residual core that is not completely circular, resulting, perhaps, from a local higher pH in stagnant zones between the fibers. From the mean diameter of these fibers, about 5 µm, a weight loss of 75% can be calculated, which is in good agreement with the figure of 71% obtained by weighing. EDX analysis indicates a higher concentration in Al in the leached layer for CM25 glass. This enrichment is less marked for CM2 glass probably because the leached layer is not so thick.

In altered CM19 fibers (Figure 7b), most have an outer residual layer with an unaltered core surrounded by a leached layer of variable thickness. EDX analyses indicate high phosphorus and calcium concentrations in the outer layer, and a leached layer that is essentially siliceous.

**Dissolution Rate Modeling**

Fibers are assumed to have a uniform initial diameter of 10 µm and the area of the extremities is neglected. The dissolution rate parameter \( k \) is supposed to vary from an initial rate value \( k_0 \), corresponding to the glass, to the dissolution rate constant of the residual product \( k_1 \). The shift from \( k_0 \) to \( k_1 \) can be described by an exponential expression as developed by Barkatt (10).

\[
k = k_0 e^{-at} + k_1 (1 - e^{-at}) \quad \text{in } \mu m/hr
\]

where \( \alpha \) is a constant in \( h^{-1} \)

Limit conditions are:

\[
t \to 0 \quad k \to k_0; \quad t \to \infty \quad k \to k_1
\]

The dissolution rate parameter \( k \) is expressed as the thickness dissolved per time using radial coordinates

\[
k = -\frac{dr}{dt}
\]

where \( r \) is the radius of the fiber in µm.

Combining equations 1 and 2 gives

\[
-dr = [k_0 e^{-at} + k_1 (1 - e^{-at})] dt
\]

The integration of the equation 3 gives the variation of the radius of the fiber with time

\[
r = R_0 \left[ 1 - \frac{k_0}{R_o} - \left( \frac{k_0 - k_1}{R_o} \right) \left( \frac{1 - e^{-at}}{a} \right) \right]
\]

where \( R_o \) is the initial radius of the fiber. This relation can also be expressed as weight loss

\[
\left( 1 - \frac{\Delta M}{M_0} \right)^{1/2} = 1 - \frac{k_0}{R_o} - \left( \frac{k_0 - k_1}{R_o} \right) \left( \frac{1 - e^{-at}}{\alpha} \right)
\]

where \( M_0 \) is the initial weight of the fiber and \( \Delta M \) the weight loss at time \( t \).

Where the dissolution rate parameter of the residual product \( k_1 \) is very low in respect to the initial dissolution rate \( k_0 \), equation 5 simplifies to

\[
\left( 1 - \frac{\Delta M}{M_0} \right)^{1/2} = 1 - \frac{k_0}{R_o} \left( \frac{1 - e^{-at}}{\alpha} \right)
\]

Equation 6 would describe the dissolution kinetics of a sparingly soluble glass at the early stage of dissolution. Equation 7 models the dissolution kinetics of rapidly dissolving glass that leaves an insoluble fraction. The higher the parameter \( \alpha \), the more rapid is the variation of the dissolution rate with time.

\[
M_1 = M_0 \left( 1 - \frac{k_0}{R_o} \right)^2
\]

The mass of the residual fraction, \( M_1 \), is given by:

\[
z = C - \frac{B}{AR_o} + \frac{Be^{-At}}{AR_o}
\]

with \( z = \left( 1 - \frac{\Delta M}{M_0} \right)^{1/2} \), \( A = \infty \), \( B = k_0 \)

and \( C = cte \ (c = 1) \)

The computed values for \( A, B, \) and \( C \) parameters in equation 9 for the four glasses are given in Table 7. The fit is good for all glasses (Figure 8), although with more experimental data the computations would be more accurate. The dissolution rate parameter \( k_1 \) is high compared with values

| Table 7. Computed parameters of equation 9 by using the nonlinear least squares method. |
|---------------------------------|----------|---------|-----|-------|-----------|
| Fibers | C | B | A | t_w | \( \nu_0 \) |
|--------|----------|---------|-----|-------|-----------|
| C3     | 5        | 0.0966  | 0.030 | 0.013 | 78        | 0.011    |
| CM2    | 6        | 1.001   | 0.218 | 0.053 | 8         | 0.140    |
| CM19   | 7        | 0.989   | 0.945 | 0.214 | 2         | 0.032    |
| CM25   | 6        | 1.011   | 0.108 | 0.048 | 22        | 0.038    |

\( n \): number of experiments
\( \nu_0 \): calculated time for a weight loss of 50%
\( \nu_0 \): calculated dissolution rate at time \( t_w \)

\( z = c(1) \): STATIC MODE

**Figure 7.** SEM image of CM2 fibers (a) and CM19 fibers (b) observed on polished sections showing unaltered cores (light gray regions), leached layers (gray regions), and, (only for b), residual external layers (brightest regions); buffered dynamic mode; \( t = 14 \) days; solution W.

**Figure 8.** Computed curves fitted to the measured points, weight losses in solution 1, for static experiments, by Equation 9 dissolution model with a dissolution rate varying from the initial dissolution rate of the glass \( k = k_0 \) to the very weak dissolution rate of the residual product \( k_1 \).
obtained by other authors (1,2). However, there is better agreement when the dissolution rate is calculated from equation 7, with values of Table 7, for weight loss of 50%. In these conditions, the dissolution rates of the four glasses C3, CM2, CM19, and CM25 as expressed in ng/(cm²-hr) (p = 2.5 g/cm³) are respectively 115, 1450, 6580, and 395. The value 115 ng/(cm²-hr) compares with k = 49 ng/(cm²-hr) found by Potter and Mattson (2) and with k = 36 ng/(cm²-hr) obtained by Scholze and Conradt (1) for glasses of similar composition. The higher value reported here may possibly result from the higher pH (>7.6) of solutions L and W, or from differences in the geometry of the reaction vessels.

Conclusion

From the data obtained from the residual fibers by XPS and SEM, we can postulate the dissolution mechanisms of the fibers in physiological saline solutions. Two types of solid-solution interactions may be considered. In the first, the unaltered core of the fiber is surrounded by a leached Si-gel layer and the diameter of the fiber decreases regularly with time. The dissolution process slows down greatly only when the diameter of the fiber becomes very small. In the second type, concentrations of dissolved calcium and phosphate, initially in the solution and resulting from glass dissolution, exceed the solubility product of an apatite-like calcium phosphate. This leads to the precipitation on, or the formation into, the Si-rich surface layer of a sparingly soluble calcium phosphate, which effectively reduces the measured weight loss. Moreover, the rate of dissolution of the inner glass probably would be lowered due to the protective effect of a calcium phosphate layer.

Only the interaction of the first type can be easily modeled because the geometric parameters of the leaching device are then not so important. If no precipitations of new phases occur during leaching, the dissolution rate of the fiber is, after an initial stage where ion exchange predominate, controlled by the solubilization of the hydrated silica-rich layer developed around the fiber. The composition of this amorphous layer does not remain constant because some cations, particularly Al ions, remain concentrated in the layer near the interface. In early stages, Al ions are only concentrated in the outer region of the hydrated layer. During leaching more and more Al ions are taken up by the leached layer and the thickness of the region of high concentration of Al increases with time. Finally, a residual product is formed, seen by XPS to be a sparingly soluble amorphous alumino-silicate gel with additional sodium. The gel at the interface has an albite-like composition (NaAlSi3O8) while the bulk is essentially siliceous with less aluminum than in albite. This result strongly suggests that there is a gradient of concentration of aluminium and sodium from the interface to the bulk of the residual product.

In conclusion, the roles of Al and P are well established in these experiments. During in vitro aqueous corrosion, aluminium remains in the residual Si-gel layer, probably creating new chemical bonds with silicon, when the dissolution-polymerization process occurs, resulting in a more stable Si-Al-gel. Phosphorus, which is important for the formation of the glass network, is easily leached in saline solution; this leads to the fragilization of the glass network during the dissolution process by increasing the hydrolysis of the silica. Under special conditions, when Ca and PO₄, ion concentrations are high, precipitation of calcium phosphate take place on the surface of the fibers. Although any correlation with in vivo experiments remains questionable (11), it is probably that the initial dissolution processes of Al and P would be similar to those observed in vitro. However, surface accumulation of Al in vivo may well be counteracted by Al complex formation by chelating organic molecules present in physiological media which could facilitate the total dissolution of the leached residue.

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