Glass Fiber Dissolution in Simulated Lung Fluid and Measures Needed to Improve Consistency and Correspondence to In Vivo Dissolution

Stephanie M. Mattson

Glass Research and Analytical Services, Owens-Corning Fiberglas, Granville, Ohio

The dissolution of a range of glass fibers including commercial glass and mineral wool has been studied using a modification of Gamble's solution in a flow system at pH 7.4 and 37°C. Dissolution has been followed by weight loss, effluent analysis, and morphology change of fibers and bulk glass. Flow per glass surface area can strongly affect both dissolution rate and morphology due to the effect of the dissolution process on the fluid. Effluent pH is shown to be a guide for choice of optimum flow/area conditions. These conditions provide measurable concentrations of dissolved glass in the effluent while maintaining their concentrations below the point at which they significantly affect the dissolution process. SiO₂ and Al₂O₃ vary widely in the extent to which they are involved in the leaching process, which removes alkalies, alkaline earths, and B₂O₃. This makes analysis of a single component in the effluent unsuitable as a means of comparing the dissolution rates of a wide range of compositions. — Environ Health Perspect 102(Suppl 5):87–90 (1994)

Key words: glass, fiber, dissolution, rate, mechanism, acellular, in vitro, improvement

Introduction

A number of workers have measured the dissolution rates of various glass fibers under in vitro conditions thought to simulate those of a fiber in the extracellular space of the lung (1–6). There is considerable variation both in the magnitude of the measured rates and in the relative ranking of the different compositions in terms of rate. These studies have used different modifications of Gamble's solution passing around the fibers at different flow rates and have used different analytical methods to measure the dissolution. This article addresses the effect of flow rate and analytical method on the measured dissolution rate. It shows that these can be significant sources of error in dissolution measurements and suggests means to eliminate such error by appropriate experimental design. In addition, it presents dissolution data on a number of previously unmeasured compositions and, from these data, expands our understanding of the compositional effects of dissolution rate and morphology.

In Vivo Extracellular Conditions

Gamble's solution generally is regarded as an acceptable though approximate model of lung fluid, but there has been no consensus on flow rate. Kanapilly's review (7) of the environment within the lung indicates that simple soluble ions in the lung fluid are exchanged rapidly with the blood stream. This may not be the case for complexes or species with limited solubilities. Kanapilly's data, together with the low fiber loading expected in the lung suggest that in vivo dissolution occurs without significant alteration of the fluid by the glass dissolution products. An accurate in vitro model of extracellular fiber dissolution should therefore have flow rate sufficient to eliminate such alteration.

The degree to which these conditions model the extracellular lung environment are best evaluated by comparison of dissolution rates and morphologies to in vivo results, guided by an awareness that multiple environments are present in animal lungs. Such comparisons are in progress. In vitro and in vivo dissolution rates are in good agreement for several compositions close to glasswool (6,8). In vivo studies of slag- and rockwools are in progress at Research and Consulting Company (RCC) in Geneva, Switzerland.

Experimental Methods

The compositions and select properties of the glass fibers used in this study are shown in Table 1. Glasses are differentiated by reference to the recognized compositional ranges of commercial products (9). Sample numbers with an "a" suffix are similar in composition but prepared differently. Samples tested as single fibers show the range of fiber diameter instead of the average diameter. To compare different glass types and to minimize the effects of different dissolution mechanisms, the dissolution rate constants, k, in Table 1 were calculated assuming leaching at a rate controlled by the surface area of the unaltered glass. Two dissolution constants are shown for the slagwool fibers, differentiating dissolution of glass components such as SiO₂ and Al₂O₃ that are part of the network from leaching of the modifiers such as CaO and MgO. Dissolution of the modifiers is indicated by the time to completely leach a 1 μm fiber and the apparent dissolution constant at this time. Samples of commercial slag- and rockwool fibers were provided by U.S. Gypsum who crushed, sieved and burned any oil off the raw products. Two samples derived from a slagwool (No. 2a) and a rockwool (No. 6a) were size-separated by Schuller to a fraction having an average diameter of about 1 μm. These samples are similar to those used in the RCC study in Geneva. Long, single fibers of sample 5a were pulled from an uncompressed and unchopped mat of slagwool. The remaining samples were produced as continuous fibers with much narrower diameter distributions (6). Samples 11 and 11a have compositions close to that reported by Bayer as ATF 3101 microfiber.
The compositions given in Table 1 are analyzed compositions or, for the continuous fibers, batched compositions modified by expected losses in boron and fluorine during melting.

The experimental techniques and analytical methods are based on the work described by Potter and Mattson (6). Solution flow rate to initial fiber surface area ratios were varied with glass composition. Chopped continuous fibers and the crushed and size-separated mineral wool samples were tested with the flow/area ratio varying from 0.06 to 145 ml/m²/min. The acceptability of a flow/area ratio for a given sample was tested by monitoring the effluent pH. The largest pH changes were observed within a few hours and were limited to no larger than 0.2 units (0.3 for the crushed mineral wool samples). The pH was limited to within 0.1 units of an empty cell after 24 hr. Arrays of approximately 3 cm long sections of fiber were run in the same flow-through system. The primary change in the dissolution fluid replaced sodium azide with 2000 ppm formaldehyde. Fe₂O₃, TiO₂, and MnO were included among analyzed solution components for the crushed mineral wool samples. Fe₂O₃ dissolves at the level of SiO₂ and Al₂O₃. TiO₂ was not detectable. Data collection times were adjusted to ensure coverage of dissolution before the fibers were completely leached. Dissolution constants in ng/cm²/hr were evaluated from weight loss or solution analysis for the fiber mats and from diameter changes for the single fiber arrays.

### Effect of Solution Flow Rate on Fiber Dissolution

In general, a dissolving glass can have two effects on the dissolution fluid if the flow rate is sufficiently low: First, dissolution of alkalies and alkaline earths in the glass consumes hydrogen ions in solution. If this exceeds the buffer capacity of the solution, it will raise the pH. Compositions near glass-wool dissolve faster when the solution is buffered to pH 8.5 versus 7.5 (6). Second, dissolution product concentrations in solution may approach saturation values, slowing the dissolution or changing its nature.

These influences lead to variable and unpredictable changes in dissolution rate and/or morphology with flow rate (10). The dissolution rate can increase or decrease by small amounts for most glass wool compositions and can decrease by large amounts for some rapidly dissolving glasses. Changes in dissolution mechanism have been observed with small changes in pH. Influences such as these can be large enough to change the relative ranking of a suite of glasses in terms of dissolution rate. Although most previous dissolution studies have guard against large changes in pH and a close approach to saturation, it has not been recognized previously how sensitive glass dissolution can be to small changes in these solution properties.

Figure 1 shows an example of the effect of flow per fiber surface area on the dissolution rate constant and on the maximum pH developed during the dissolution process. The data are for two glasses close to the Bauer glass which are among the most sensitive to solution conditions. With increasing flow/area the maximum pH decreases sharply. The dissolution rate increases sharply, approaching a limiting value near 30 ml/m²/hr, which is within experimental error the same as the value at near infinite dilution from the single-fiber tests. At the 30 ml/m²/hr point the pH change is about 0.2. The trends shown in Figure 1 represent many glasses with large sensitivity of the dissolution process to fluid characteristics. A pH change of 0.2 generally indicates the point at which the limiting value of the dissolution rate has been reached. This point represents the optimum conditions for experimental measurement of the dissolution rate. The dissolution products are in as high a concentration as possible (to allow measure-

---

**Table 1. Wt-% compositions and properties.**

| Component | Slagwool | Rockwool | Glasswool |
|-----------|----------|----------|-----------|
| SiO₂      | 4.15     | 4.15     | 62.15     |
| Al₂O₃     | 3.87     | 3.87     | 3.94      |
| P₂O₅      | 1.02     | 1.02     | 0.00      |
| CaO       | 0.59     | 0.59     | 3.51      |
| MgO       | 0.50     | 0.50     | 14.67     |
| Na₂O      | 0.73     | 0.73     | 0.17      |
| K₂O       | 0.02     | 0.02     | 0.00      |
| B₂O₃      | 0.61     | 0.61     | 0.00      |
| Fe₂O₃     | 0.00     | 0.00     | 0.00      |
| MnO       | 0.00     | 0.00     | 0.00      |
| TiO₂      | 0.11     | 0.11     | 0.15      |
| S         | 0.01     | 0.01     | 0.00      |
| SrO       | 0.00     | 0.00     | 0.00      |
| F₂        | 2.9±2.4  | 2.9±2.4  | 9.0±0.2   |
| Diameter, μm | 2.85   | 2.85     | 2.51      |
| Density, g/cm³ | 63±4²   | 8.25     | 116±2     |
| k, ng/cm²/hr | 260     | 20±25    | NA        |
| Modifier kₐ, ng/cm²/hr | 2.85 | 141±4²   | NA        |
| t, day     | 23       | NA       | NA        |

a Total iron. b Network species dissolution. c SO₄. d Not controlled by diffusion. NA, not applicable, congruent dissolution.
The dissolution rate of slag wool samples (1a and 5a) confirms that these predicted conditions do produce limiting dissolution rate constants. There are some limitations to this method for determining optimum dissolution conditions. As shown for glass wool and mineral wools, each general compositional system may have its own relationship between dissolution rate and optimum flow/area. Systems such as refractory ceramic fiber with little alkali or alkaline earth content, effluent pH may not be a useful indicator at all.

Other indicators of near infinite dissolution conditions include consistency of dissolution morphology within a sample and between samples tested under different conditions. For example, samples 9 and 10 were tested at near infinite dilution in single-fiber tests and as blocks of glass exposed to flow/area conditions appropriate for glasses with moderate dissolution rate constants. The glasses did not exhibit any leached material in the single-fiber tests, but thick leached layers partially topped by a Ca-rich material were evident on the blocks. Constancy of dissolution rate far from saturation may be the primary indication of near infinite dissolution conditions for some compositions.

**Analytical Methods**

Given the correct flow/area conditions, there remains some question of what analytical methods should be used to measure dissolution rate. Most commonly, weight loss, effluent analysis, and diameter measurements are used alone or in combination. Mattson (10) has shown that these three methods can yield equivalent values of the dissolution rate constant for a range of fiber compositions under conditions of near infinite dilution. It is clear that the three should be used together when possible since they provide complementary information as well as a check on accuracy.

Effluent analysis is a particularly useful measure since it identifies the behavior of individual components. But because these components can behave differently in different glasses, a single component, such as silica, cannot be used as a general measure of the dissolution rates of a variety of glasses. This point is illustrated in Figure 3, which shows for three glasses the effluent concentrations of selected oxides as a function of dissolution time. So that the data can be compared directly, the concentrations have been normalized to standard laboratory conditions (flow rate and initial surface area) and to their initial concentrations in the glasses. Silica participates to varying degrees in the leaching of the glass and the dissolution of the residual material. In compositions near glass wool, dissolution is close to congruent, and silica correlates to oxides traditionally identified as removed by leaching. In slag wool silica and alumina dissolve in a separate process from that of the alkaline earth oxides. In rock wool, dissolution is closest to congruent. The absence of leached layers on low alumina slag wools (not shown) indicates that they dissolve congruently.

**Dissolution Mechanism**

Traditional ideas of glass dissolution at near neutral pH involve leaching of alkali oxides governed by diffusion through the leached layer and much slower dissolution...
of the leached material. In the present and
previous work (6) dissolution characteristics differ significantly from this.
Compositions near glasswool have shown much more extensive dissolution of silica,
leaching rates dependent on the surface area of unaltered glass with no dependence
on leached layer thickness, and variable rates of dissolution of the leached layer
with cases approaching congruent dissolution. Slagwoods show the greatest deviation
from congruent dissolution. They also are characterized by the highest level of modi-
fier components (alkali and alkaline earths), which are known to reduce the
degree of polymerization of the silica network in the glass. A lower degree of poly-
merization may cause greater permeability of the glass to leaching of the modifier
cations. The congruency of the rockwool dissolution was noted previously (2) and is
consistent with data for other glasses with high alumina and a moderate level of modifier components.

Since slagwoods dissolve in a manner closest to that thought traditional for
glasses, the possibility of diffusion control in their dissolution was investigated for
three samples: two in single fiber tests, in which both leaching rate and dissolution
of the leached layer can be measured; one as a crushed sample, in which only the
leached layer thickness can be measured. The results for these experiments are
summarized in Figure 4. For diffusion control with no dissolution of the leached
layer, the leached layer thickness and the change in radius of the unaltered glass
should be identical and should show a linear dependence against square root of
time. Dissolution of the leached layer would cause the leached layer thickness to
be increasingly less than the change in radius of the unaltered glass and would
lead to some distortion from linearity for both curves. Dissolution data for sample
1a (Figure 4A) are consistent with diffusion control with some dissolution of the
leached layer. Sample 3 (Figure 4B) has intermediate behavior. Diffusion control
can be ruled out for sample 5a (Figure
4C), for which the leached layer shows an
approximately constant thickness with
time.

The data in Figure 4 suggest that alu-
mum has a stabilizing influence on the
leached layer. Aluminum content of the
slagwool samples in Figure 4 decreases
from top to bottom. Leached layer stabil-
ity clearly increases in the same order.
This effect is substantiated by the absence
of any leached material on the low alu-
mmina experimental slag compositions
(Table 1, samples 9 and 10).

**Dissolution Rate**

The rate data in Table 1 show that the basic character of the influence of each
glass component established previously (6) is the same over a wide compositional
range. Alumina and titanium oxide strongly decrease dissolution rate.
Modifiers such as the oxides of calcium, magnesium and sodium increase dissolution
rate by a roughly equal, moderate degree. Silica has a small negative effect.
The influence of iron depends on its oxida-
tion state and cannot be determined
from the available data. Slagwoods as a
group dissolve more quickly than rock-
woods. Commercial glasswoods dissolve at
rates varying from a factor of two greater
than rockwools to within the range of
slagwoods.

**REFERENCES**

1. Klingholz R, Steinkopf B. The reaction of MMMF in aphysiologi-
cal model fluid and in water. In: Biological Effects of Man-made
Mineral Fibers, Vol 2. Proceedings of a WHO/IARC conference
held 20–22 April 1982 in Copenhagen. Copenhagen:World Health
Organization, 1984:60–86.
2. Förster H. The behavior of mineral fibers in physiological solu-
tions. In: Biological Effects of Man-made Mineral Fibers, Vol 2.
Proceedings of a WHO/IARC Conference held 20–22 April 1982
in Copenhagen. Copenhagen:World Health Organization,
1984:27–59.
3. Furtak H, Tiesler H, Cohen I, Thelohan S. Fibres de verre suscep-
tibles de se décomposer en milieu physiologique. Eur Pat Appl
0412878A1 (1991).
4. Scholze H, Conradt R. An *in vitro* study of the chemical durability
of siliceous fibers. Ann Occup Hyg 31:685–692 (1987).
5. Bauer JF, Law BD, Roberts KA. A study of the solubility and dur-
ability of man-made mineral fibers in a synthetic physiological fluid.

Presented at the Environmental Chemistry Symposium, 30th
Rocky Mountain Conference, 1 August 1988, Denver, CO.
6. Potter RM, Mattson SM. Glass fiber dissolution in a physiological
saline solution. Glastech Ber 64:16–28 (1991).
7. Kanapilly GM. Alveolar microenvironment and its relationship
to the retention and transport into blood of aerosols deposited in the
alveoli. Health Phys 32:89–100 (1977).
8. Morgan A, Davis JA, Matson SM, Morris K. Effect of chemical
composition on the dissolution rate of glass fibers in *in vitro*
and *in vivo*. Seventh International Symposium on Inhaled Particles,
16–20 September, Oxford:Pergamon Press, 1992;in press.
9. Thermal Insulation Manufacturer's Association (TIMA). Man-
made Vitreous Fibers: Nomenclature, Chemical and Physical
Properties. Stamford, CT:TIMA Inc., 1991.
10. Matson SM. Glass fibers in simulated lung fluid: dissolution
behavior and analytical requirements. Ann Occup Hyg (in press).

90 Environmental Health Perspectives