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INVESTIGATION OF CHEMICAL DURABILITY
MECHANISM IN FLUORIDE GLASSES

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ABSTRACT

In our previous research, leaching data on two families of fluoride glasses were collected in aqueous media and in solutions buffered at various pH values. The corrosion process was analyzed, leading to the development of a model for dissolution. In this 2nd year of research, we have broken down the dissolution model into component mechanisms and have analyzed each component separately. While many processes take part in the aqueous corrosion of fluoride glasses, we have been able to identify the results of these processes and have developed a quantitative description of each part and of what role it plays in the dissolution of zirconium-fluoride based glasses. A paper, presently under review by the American Ceramic Society, was written to present these results. We are currently applying this analysis method to thorium-fluoride glasses and are preparing a publication on those results.

The comparison between the leach rates of different classes of fluoride glasses (ZrF_4, ThF_4 and UF_4) has been of great value in understanding the effect of composition variations on the leaching processes. Monitoring the pH variations and conducting tests in pH buffered solutions have led us to understand the effects which enhance the corrosion rate of these glasses, and makes them far less durable than silicates. Several publications will result from these studies. The first one, to be published in Materials Research Summaries, is included here.

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by

Catherine J. Simmons and Joseph H. Simmons

Annual Report #2

Introduction

Our research, prior to the past year, has consisted primari-
ly of conducting measurements of the aqueous corrosion behavior
of zirconium-fluoride glasses and thorium-fluoride glasses. We
found that, despite their relative ease of dissolution, when com-
pared to oxide glasses (silicates), the processes which control
the dissolution are extremely complex. The tests usually con-
ducted for these measurements proved inadequate, and as you will
see in the enclosed paper (submitted to the Journal of the
American Ceramic Society), many of the results obtained can be
deceiving during the interpretation or the identification of con-
trolling processes. At the end of the past year, we had achieved
a sufficient understanding of the processes to develop a rudimen-
tary form of a comprehensive leaching model for these glasses.

This year, beginning from that level, we have broken down
the dissolution model into component mechanisms and have analyzed
each component separately. This analysis has led to a publica-
tion (Paper #1, included here), describing the leaching process

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in zirconium-fluoride glasses. The comprehensive model described in this paper is the first published description of the aqueous corrosion of zirconium fluoride glasses which discusses the solution and glass reaction processes. While the paper specifically addresses zirconium fluoride glasses, the model encompasses all halide glass systems. In the next year, we will be adding to this publication with a paper on the corrosion behavior of thorium-fluoride based glasses, a paper on the dependence of the corrosion process on the solution pH, and a paper on the corrosion of other heavy metal fluoride glass compositions.

During the year, we have concentrated our experimental efforts on measurements of leaching effects in uranium fluoride glasses, on the leaching of glasses in pH buffered solutions, and on the deposition and growth of crystals on the corroded surface of fluoride glasses. The results of leaching tests on uranium fluoride glasses and the pH dependence of the leaching process will be reported in several publications. The first one (Paper #2) is included here. At least two more will follow in the next year. The measurements on the formation of crystal deposits on fluoride glass surfaces during leaching are still on-going and will be completed in the next year. Some of the results have been included in Paper #1, but at least one separate publication will result.

Additional experimental efforts are presently underway on doped fluoride glasses to develop improvements in leaching be-

havior. We also have interest in the behavior of glasses in low solution volumes corresponding to the behavior of coated materials. Research in this area was begun recently and preliminary results indicate excellent agreement with our published corrosion model.

Results

The results are best described by a summary, followed by the two papers submitted for publication in this past year. Paper #1, "Chemical Durability of Fluoride Glasses -- I. Reaction of Fluorozirconate Glasses with Water," reviews data gathered by us and supporting data obtained by other laboratories to develop a comprehensive model for the corrosion behavior of fluorozirconates. The static leaching process of fluoride glasses differs markedly from that of silicate glasses; therefore, new concepts had to be developed. While the chemical imbalance in solution resulting from the leaching of silicate glasses drifts toward high pH values, that of fluorides goes rapidly toward low pH values. Depending on the degree of pH drift from neutral values, this behavior can cause a significant acceleration of the leaching process. In the following paper, and in our proposal, we have suggested that, as we demonstrated in our development of highly durable silicates for nuclear waste vitrification, improvements in the corrosion behavior of fluorides come from control of the solution pH.

The model which we present in Paper #1 shows that the static leaching of flurozirconate glasses is a complex process involving component solubility, matrix dissolution, ion exchange, hydration, species saturation and reprecipitation. This model is based on measurements conducted in our laboratories which show that, as fluorozirconates leach rapidly in water, their solution pH becomes acidic quickly, a thick hydrated surface layer forms which absorbs a large amount of water, and crystal precipitates grow on the hydrated layer surface. These results come from measurements of solution composition by plasma emission spectroscopy, of degree of hydration by infrared absorption, of layer thickness and structure by scanning electron microscopy, and of crystal precipitate compositions by x-ray diffraction and electron microprobe analysis which were conducted on a series of fluorozirconate samples under this research grant.

The corrosion mechanism which emerges from these conclusions can be summarized as follows:

1. The zirconium-based fluoride glasses corrode primarily by matrix dissolution. However, unlike silicates which go into solution as hydroxides, the components of these glasses go into solution as fluorides without a prior hydroxylation step.

2. LiF, NaF, AlF_3 and, in some cases, BaF_2 dissolve at faster rates than either ZrF_4 or LaF_3. This difference in extraction rates leads to the formation of a porous, hydrated corrosion layer at the glass surface.

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3. With time, the leach rates of LiF, NaF, and AlF_3 remain high, while that of BaF_2 decreases significantly as a possible result of:

   (i)   an increase in $[F^-]$ ion concentration, which can interfere with BaF_2 solubility, and

   (ii) the depletion of BaF_2 from the glass surface.

4. LaF_3 is highly insoluble in aqueous solutions, and, therefore, remains in the surface layer.

5. Zirconium fluoride dissolves in a solution as ZrF_4. Evidence of the dissolution of ZrF_4 is supported by its appearance as a precipitated surface crystal. A partitioning in solution favors $[ZrF_3]^+$ over $[ZrF_4]$ at low $[F^-]$ concentrations; the two species are equal at about 3 ppm of $[F^-]$ and the $[ZrF_3]^+$ concentration drops to only 20% when 10 ppm $[F^-]$ is present in solution. Since the fluoride ion concentration rapidly increases to > 3 ppm during corrosion, it appears that, while the $[ZrF_3]^+$ radical dominates in the early stages, it makes up a relatively small percentage of the leachate after several hours, when the fluoride ion concentration increases above 10 ppm.

6. A decrease in solution pH with time is observed which results from successive hydrolysis of the zirconium fluoride species. Measurements of the equivalent hydroxyl concentration exchanged, as described in the titration tests, indicate that two hydroxyls are exchanged per Zr in solution.

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7. Under static conditions, the outer layer of the corroded glass is porous and hydrated and is covered by reprecipitated crystals of two distinct types. These are long, needle-like crystals identified by x-ray diffraction as ZrF_4 and spherical assemblages of thin plate-like crystals tentatively identified as $ZrBaF_6$. These crystals form by reprecipitation due to saturation at the glass-solution interface. The two crystal types appear to form simultaneously, since they are seen to grow around one another.

   Under dilute, well stirred conditions, however, no reprecipitated crystals are formed, even after leaching for ten days.

8. The thick, porous layer plays a minor role in protecting the unreacted bulk glass and acts as an ireffective diffusion barrier to reduce the leach rate. The porosity of the layer reflects the molar volume of highly soluble species (NaF, LiF, AlF_3, PbF_2) in the glass composition and can be related to the comparative leach rates of different glasses. For example, the less durable glasses have a thick and highly porous layer.

9. The pH drift of the solution into an acidic region during the leaching raises the solubility of zirconium fluoride, which accelerates the glass dissolution by several orders of magnitude, causing it to be comparable in durability to the poorer silicates. The addition of any buffer to the solution can have a profound effect on the leach rate if it eliminates or retards the pH drift.

In Paper #2, "Leaching Behavior of Heavy-Metal Fluoride Glasses," presented at the 3rd International Symposium on Fluoride Glasses, Rennes, France, June 1985, we discuss the effect that solution pH drift during leaching has on the leach rates of ZrF_4, ThF_4, and UF_4 glasses. The data show that, while fluorozirconate glasses exhibit the highest leach rates in aqueous, unbuffered solutions (Fig. 1), their leach rates dip to the lowest minimum of all glasses studied if their solution pH is buffered at pH 8. This result promises a clue for future research directions for the improvement of the leaching behavior of fluoride glasses.

Summary of Activities

Presentations:

"Characterization of Uranium IV and Transition Metal Fluoride Glasses," 87th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May, 1985.

"Leaching Behavior of Heavy Metal Fluoride Glasses," 3rd International Symposium on Halide Glasses, Rennes, France, June, 1985.

"Corrosion of Fluoride Glasses," Invited Lecture, Gordon Conference on Glass, New Hampton, New Hampshire, August, 1985.

Publications:

"Chemical Durability of Fluoride Glasses - I. Reaction of Fluorozirconate Glasses with Water," Submitted to the Journal of the American Ceramic Society.

Leaching Behavior of Heavy Metal Fluoride Glasses," to be published in Materials Research Summaries.

Honors and Awards:

None.

Participants:

Joseph H. Simmons - Professor

Catherine J. Simmons - Engineer

Din Guo Chen - Graduate Student, M.S. Level

Michael S. Randall - Graduate Student, M.S. Level

Joelle Guery - Visiting Postdoctoral Associate

There were no degrees granted to students during this period.

Other Sponsored Research:

(1) "Slow Crack Growth in Solids - A Molecular Dynamics Study," sponsored by NSF, $85,056.

(2) "Investigation of Non-Linear Optical Behavior of Semi-conductors for Optical Switching," sponsored by AFOSR, $221,500.

PAPER #1

Chemical Durability of Fluoride Glasses --
I.   Reaction of Fluorozirconate Glasses with Water

by

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ABSTRACT

The chemical durability of five fluorozirconate glass compositions was studied. Measurements of leachant composition and solution chemistry by plasma emission spectroscopy, pH, and fluoride analysis are reported. Changes in surface structure were monitored by scanning electron microscopy, electron-probe x-ray analysis, and x-ray diffraction. The modifier additives with high aqueous solubility (AlF_3, NaF, LiF, PbF_2) exhibited the highest leach rates with ZrF_4, BaF_2, and LaF_3 exhibiting lower rates. The leaching order of $Zr > Ba > La$ was maintained for all samples.

The leaching process consists of the dissolution of the glass matrix, leaving a thick and porous layer containing Zr, Ba, La, and molecular water. Hydroxylation of the Zr species to form a hydroxy-fluoride complex in solution dominated a decrease in pH to moderately acidic values. The resulting increase in component solubility (particularly zirconium fluoride) in the acidic solutions accelerated the glass dissolution rate and demonstrated that, if no buffer is present to avert the pH drift, the chemical durability of these glasses in aqueous environments is extremely poor, being roughly equivalent to that of $Na_2O \cdot 2SiO_2$.

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Introduction

Fluorozirconate glasses are under study for a variety of IR transmitting applications; therefore, their optical properties and phase stability behavior have received intense scrutiny. We have found these glasses of great interest in studies of chemical corrosion behavior due to the large contrast in behavior with silicate glasses. Our initial studies of the chemical behavior of a Zr-Ba-La-Al-Li fluoride glass in water[1] suggested far different processes from the known typical silicate leaching processes which are characterized by alkali-ion exchange for protons in solution followed by matrix dissolution as the solution pH drifts into the basic range.[2]

In this paper, we examine the leaching behavior of a series of fluorozirconate glasses whose added components are well known for producing changes in the leaching behavior of silicates. The behaviors of these glasses are compared to one another and compared to established silicate glass leaching mechanisms. A sample containing PbF_2 was selected because it represents a composition of current interest for fiber optics applications.[3] The chemical durability behavior of fluoride glasses not containing zirconium will be reported in later publications.

Experiment

Fluorozirconate glasses melted at various laboratories were obtained for the chemical durability study. Table 1 shows the

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glass compositions selected, the commonly used mnemonics for them, and the sources of the glasses. These glasses were melted under a variety of conditions varying from the use of oxide raw materials with added ammonium-bifluoride[4] to the direct use of anhydrous fluoride raw materials, melted under an Ar or CCl_4 atmosphere.[6,7] In the case of ZBLA, samples melted by both techniques were studied. In all cases the glasses showed low water and low oxide content, as determined spectroscopically.

Corrosion tests were conducted with deionized, pH 5.6, water at room temperature. The tests, except where noted, were conducted on solid samples polished under Halocarbon oil, which is oxygen and water-free, in order to remove the aged surface layer and obtain a reproducible surface finish without aqueous contact. Samples were rinsed in toluene to remove the oil. Solution analysis was conducted by removing the soaking solution and analyzing duplicate samples using a DC Plasma Spectrometer, a fluoride selective electrode and an Ion Chromatograph. Static tests were conducted in PMP containers with the samples supported by pre-washed Teflon baskets, following the test procedures recommended by MCC.[8] The solution volume to sample surface area was maintained at a constant ratio of 100:1 for all tests in order to minimize saturation effects.

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Results

Leach rates in solution for the fluorozirconate glasses are plotted as a function of time in Figs. 1 and 2. These rates are normalized by the concentrations of ions in the glass for easy comparison between different elements, as well as different compositions. As shown in Fig. 1A, zirconium leaches at the fastest rate in the ZBL glass, followed by barium, with lanthanum appearing at a much slower rate. This Zr/Ba/La order appears for all the compositions studied. The addition of Al to the glass (ZBLA) (Fig. 1B) induces little change in the leach rates of Zr and La, but reduces the Ba leach rate by a factor of approximately three, while the Al additive exhibits the highest normalized leach rate. The addition of Al and Li to the glass (ZBLAL) (Fig. 2A) appears to cause little change in the leach rate of the ZBL components with both Li and Al exhibiting the higher normalized leach rates. The addition of Na and Al to form the ZBLAN glass (Fig. 2C) increases the corrosion rate of all of the components with again Na and Al providing the higher leach rates. The highest leach rate observed for zirconium, however, is found in the fiber optics glass containing the base ZBL composition with additives of Al, Li, and Pb (Fig. 2B). Initially, lead enters the solution at the same rate as Al and Li, decreasing only slightly at longer times. The major difference between this glass and its predecessors is that it does not exhibit the marked decrease with time in component leach rate observed for the other compositions. After five

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days of soaking, the Li and Al leach rates are five to six times higher in the ZBLALPb glass than in the ZBLAL glass. In general, the tests were stopped after five days because of the thick surface corrosion layer (>150 μm), which developed in that time.

Discussion

A composite curve of the average weighted leach rates of all five glasses (Fig. 3) shows the curious result that, within a factor of 10 in leach rates, all the glasses behave in a similar manner with equivalent rates, closely following the behavior of ZBL and relatively unaffected by either the addition of modifiers or by varying the preparation conditions. This result contradicts that reported recently by Barkatt and Boehm,[9] who claim to see a large melting history effect due to the presence of residual ammonium bifluoride in the glass. However, Moynihan et al.[10,14] have shown that there is little, if any, effect on durability in samples melted with and without ammonium bifluoride. In general, therefore, it appears that in deionized water the leach rate of fluorozirconate glasses is controlled by both the behavior of the zirconium and barium components, as shown here, and by the pH drift of the soaking solution during the test, as described in detail below and elsewhere.[11,12] Additives of matrix modifiers such as the fluorides of Al, Pb, Li, and Na, have only a limited effect on the leach rate of fluorozirconate glasses. In contrast, the oxides of these elements normally have
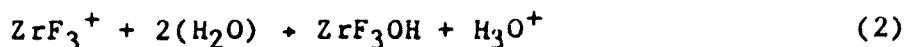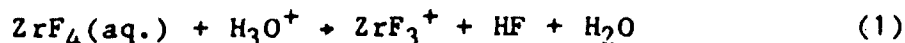
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a profound effect on the balance between ion exchange and matrix dissolution of silicate glasses. For example, the addition of 10-20% alkali to a silicate glass produces a decrease in durability of several orders of magnitude. The lower leach rate of La appears to come from the lower solubility of LaF_3. In subsequent papers, we will show that composition dependent differences do appear in the aqueous leach rates of glasses containing the thorium,[11] rare-earth, and uranium fluorides,[12] but that these differences arise from the pH dependence of the respective solubilities.

1. pH Drift Behavior

A clue to the major difference between fluorozirconate and silicate glasses lies in the measurement of solution pH during the leaching process. Silicates containing alkali oxides exhibit a solution pH drift to basic values generally above 10. This results from a dominating ion exchange process between alkali ions in the glass with protons (H^+) or hydronium ions (H_3O^+) in solution. Figure 4 shows the temporal variation of solution pH for the five fluoride glasses. All show a marked decrease in pH to between 3.6 and 4.5 within the first few hours. A test was conducted to determine the equilibrium solution pH of ZBLAL glass by soaking an excess of fine powder in deionized water at a pH of 5.6 while stirring in a rotating cylindrical bottle. After an initial rapid drop in pH, the solution maintained a constant value of 2.46 over several days. This decrease in pH could

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result from either an ion exchange of OH⁻ in the solution for F⁻ in the glass corroded layer, or from the OH⁻/F⁻ exchange of dissolved species in solution.

In order to determine the effect of the individual glass components on pH, we conducted a test where the crystalline form of each component fluoride (ZrF_4, BaF_2, AlF_3, PbF_2, NaF, and LiF) was dissolved separately in de-ionized water. The results showed that as little as 12 ppm of ZrF_4 produced a significant decrease in the solution pH from 5.45 to a value of 3.95. Subsequent additions of ZrF_4 to solution, above 30 ppm, caused an increasingly smaller drop in pH, indicating that the dissociation of fluoride and subsequent hydrolysis of zirconium decrease with increasing concentrations of fluoride ions in solution. None of the other components affected a significant decrease in pH when dissolved individually. It appears, therefore, that it is the hydrolysis of zirconium fluoride which is responsible for the majority of the pH drop during leaching of fluorozirconate glasses. The species formed appears to be $[ZrF_x(OH)_y]^{+4-x-y} [H_2O]_n$. The reaction may be written as:

$$ZrF_4(aq.) + H_3O^+ \rightarrow ZrF_3^+ + HF + H_2O \qquad (1)$$

$$ZrF_3^+ + 2(H_2O) \rightarrow ZrF_3OH + H_3O^+ \qquad (2)$$

$$ZrF_3OH + H_3O^+ \rightarrow ZrF_2OH^+ + HF + H_2O \qquad (3)$$

$$ZrF_2OH^+ + 2(H_2O) \rightarrow ZrF_2(OH)_2 + H_3O^+ \qquad (4)$$

A chemical analysis of the supernatant solutions for metal and fluoride ion concentration indicated that, on the average, each Zr and Ba ion retains a fluoride ion despite the addition of

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a strong complexing agent. One of every six atoms of Al at low concentrations and one of every three Al atoms at higher concentrations also retain a fluoride ion. This indicates that, in the pH ranges covered by the test, and particularly for Zr, the metal does not release all its fluoride ions. These results also explain the lower than anticipated values obtained in fluoride ion concentration measurements of the leachate solutions using electrode analysis.

Since the major pH drift occurs during the first hour, a titration experiment was performed to determine the rate and degree of hydrolysis occurring during that time in a solution of constant pH. A freshly powdered sample of ZBLAL was placed in water whose pH was adjusted to 5.0 using dilute HCl. The solution was stirred constantly and the pH was monitored throughout the test. A dilute NaOH (10^{-3} M) solution was added by means of a burette in order to maintain the solution at pH 5.0. The amount of additional OH$^-$ necessary to maintain the pH was monitored as a function of time and is shown in Fig. 5. After a brief induction period, the hydrolysis reaction is seen to follow $t^{1/2}$ behavior. The induction period may be due to a short delay in ZrF_4 dissolution and hydrolysis following the preferential leaching of Li and Al. Table 2 summarizes the data obtained through solution analysis. It is clear from the results of individual component dissolution, above, that none of the dissolving species, except ZrF_4, undergoes hydrolysis to any significant

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degree. By comparing the concentration of Zr in solution (27.6 μmoles) to the titrated hydroxyl concentration (58.2 μmoles), we obtain the result that the dominant zirconium hydroxy-fluoride complex discussed above contains two hydroxyl ions (i.e. y = 2).

A calculation of the dependence of the relative concentrations of the various dissociated $[ZrF_x]^{+4-x}$ species was conducted based on published values of association constants.[13] The results are plotted in Fig. 6 and show that, over the range of solution fluoride concentrations encountered in these tests, the dominant species are $[ZrF_2]^{+2}$, $[ZrF_3]^+$, and $[ZrF_4]$. Most of the test results obtained after one hour of corrosion were at concentrations between 1 and 10 ppm F^-, showing a dominance of $[ZrF_4]$ with between 50% and 20% of $[ZrF_3]^+$. The more highly dissociated species is only expected in appreciable relative concentrations in the very early stages of corrosion.

In conclusion, the pH behavior of the solution and the zirconium fluoride species formed are strongly dependent on the concentration of dissociated F^- and the availability of hydroxyls; therefore, the most probable zirconium species in solution are the hydrated forms of $[ZrF(OH)_2]^+$ and $[ZrF_2(OH)_2]$, with the neutral species favored at higher fluoride concentrations (>10 ppm).

2. Surface Water Content

Infrared absorption measurements showed, for all glasses, the same OH stretching (2.9 μ) and HOH bending (6.1 μ) vibrations

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seen in our previous studies,[1] with increasing absorption for longer corrosion times. This obviously indicates that the formation of a hydration layer occurs by a complementary mechanism to the leaching process. Loehr et al.[14] have measured the intensity of both vibrations in short term leach tests for the first four glasses reported here; the time dependence closely follows our leaching behavior. Their measurement also shows the same relative differences and ordering of the hydration rates between the various glasses that we report in Fig. 3. The time dependence of the growth of the water and hydroxyl bands appears to follow a t^1 power law for times up to 20-30 min. and then a $t^{1/2}$ law for longer times. These authors were not able to separate, in the hydroxyl vibration, the contributions due to molecular water from that due to metal hydroxides. However, by comparing the rate of growth of the two peaks and calculating a constant ratio, they concluded that only molecular water is present in the glass's hydrated layer. Based on these results and some solution analysis, Doremus et al.[15] have suggested that only matrix dissolution occurs in these glasses and that leaching occurs congruently. Since only one composition was studied, the consistent difference in leach rates between the glass components reported here was not observed. This difference becomes important in determining the mechanism of formation of the porous leach layer. Furthermore, Loehr and Moynihan deduced a lack of OH formation in this leached layer from a comparison of the time dependence of the ratio of

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absorption peak heights of the water bending to OH stretching motions. The peaks, however, broaden considerably, particularly for the OH stretching motion, and our preliminary results indicate that if one calculates the integrated peak area instead, the OH vibration peak grows slightly faster than the HOH bending peak. This would indicate the formation of some hydroxides in the layer and would be more consistent with the development of an oxide peak during drying as seen in Ref. 1.

The series of glasses studied in Ref. 14 exhibits an order of hydration rate with respect to composition (ZBLAN > ZBLAL > ZBL > ZBLA) which is the same as that observed in our leach tests based on solution analysis. The combination of these results suggests that the layer forms as a result of the selective leaching of the more soluble glass species (NaF, LiF, AlF$_3$, PbF$_2$) and that the leach rate is controlled both by solubility and by the diffusion of molecular water through the layer to the unreacted glass surface and the counter diffusion of dissolved species into the solution. Thickening of the layer with time is expected to lead to an increase in diffusion time and a decrease in leach rate. Since the steepest decrease in leach rate is observed in the ZBLA glass, and this glass has the thinnest layer, the porosity of the layer must play a major role in the diffusion process. The more durable glasses evidently develop the less porous and thinner layers, while the less durable glasses, such as ZBLALPb, develop a thick layer with a sufficiently high porosity

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to maintain a nearly constant leach rate with time. In the case of ZBLALPb, the rapidly dissolved species (LiF, AlF_3, PbF_2) constitute 28 molar % of the glass composition, while ZBLA contains only 4% AlF_3.

3. Effects of Atmospheric Moisture

Most non-durable silicates are highly susceptible to corrosion in humid environments, frequently exhibiting visible surface damage within hours of exposure Tests were conducted on ZBLAL glass samples exposed to an environment of 100% relative humidity at 80°C for up to seven days. Care was taken to avoid temperature cycling and moisture condensation on the sample surface during the tests. The samples showed no visible evidence of corrosion. Figure 7 shows the infrared transmittance spectra of the as polished sample as compared with a four and seven day exposure period. A 2-3% increase in absorbance at 2.85 μm is evident after four days, increasing slightly at seven days. This may be due to the formation of an extremely thin reaction layer or to the presence of a small amount of atmospheric water adhering to the surface. This result demonstrates that, in spite of their poor durability in aqueous environments, Zr-based fluoride glasses are relatively unreactive in the presence of atmospheric moisture. Similar results were reported by Robinson, et al.,[16] who noted that no corrosion was observed up to 200°C for a variety of fluoride glasses containing ThF_4.

4. Microscopic Appearance of Surface

Scanning electron microscopic observations of the corroded surface gave essentially the same results as our previous study of ZBLAL.[1] All glasses exhibited precipitated crystal deposits over the entire surface with a highly porous, thick hydrated layer of material beneath the crystals and above the uncorroded glass surface. Figure 8 shows the corroded surface of a ZBLA glass after two days in solution. Figure 9 shows various aspects of the corroded surface of the same glass after five days in solution, with Fig. 9B showing the surface with crystals removed and Fig. 9C showing a cross-section of the crust of ZBL glass. The results of EDS analysis of the surface pictured in Fig. 8 are shown in Figs. 10A-D. The most significant change observed, when comparing the spectrum of the uncorroded glass (A) with that of the leach layer, or crust (B), is the appearance of a measurable amount of La concentrated in the layer. This is in good agreement with our solution analysis, showing a much lower leach rate for La. The crystals consist of two distinct structures: long parallelopipeds shown by EDS analysis to contain a high concentration of Zr (Fig. 10D) and spherical shapes made up from a multitude of thin platelets containing Zr and Ba (Fig. 10C). The long crystals were identified by x-ray diffraction to be ZrF_4. They comprise the majority of the surface deposits seen. Doremus[17] has also reported that the needle-like crystals are ZrF_4, while Pantano[18] has recently suggested that they are a

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hydrate form $[ZrF_4 (OH_2)_x]$. X-ray diffraction measurements also tentatively identify the thin Ba-rich platelet crystals making up the spherulites of Figs. 8, 9A, and 9D as $ZrBaF_6$. In several tests where the Ba concentration in solution was observed to become independent of corrosion time due to solution saturation, the spherical crystals became more abundant with no appearance of new crystal types, indicating that those crystals resulted from reprecipitation from solution near the surface of the sample undergoing corrosion. Since the ZrF_4 crystals were mixed with the Zr-Ba crystals, occasionally becoming surrounded by them (for example, see Fig. 9D), it is clear that they also form by continuous reprecipitation from solution. Nearly all tests reported here, and in Refs. 17 and 18, were conducted under static conditions. These results strongly suggest the formation of a rapidly saturated static diffusion layer in the solution surrounding the glass. This conclusion is supported by results of our studies comparing the leach rates of stirred powders with those of static solids,[19] which show an increase in leach rate in stirred solutions, and by the results of Houser and Pantano,[20] who stirred the solution around solid samples and observed an increase in the hydration depth. Our SEM comparison of the corroded surfaces of bulk samples leached under static and stirred conditions showed a complete absence of crystal deposits in the latter. These results, therefore, lead to the conclusion that a major step in the static leaching of these glasses is the dis-

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solution and subsequent saturation and precipitation of fluorides at the glass/solution interface.

The formation of a static diffusion layer in the solution surrounding the glass apparently leads to the saturation of ZrF_4 and Ba containing fluoride compounds in solution, which is then followed by precipitation of the crystals. It is, therefore, the combination of the inter-diffusion of water and the dissolving species through the porous layer and the rate of crystal precipitation which controls the temporal evolution of the leach rate of the glass. This could explain the $t^{1/2}$ time law observed without the requirement of involving an F^- diffusion process through the glass or the hydrated crystalline layer, which is seen beneath the precipitated crystals. The hydrated corrosion layer attained a thickness of >150 μm within five days (Fig. 9C) and, under microscopic examination, appeared severely cracked due to dehydration in vacuum. Where pieces of the layer had peeled off, further chemical attack and mild cracking was observed extending into the glass (Ref. 1, Fig. 3B).

5. Corrosion Mechanism

These results, when combined with the work of others, begin to form a composite understanding of the leaching process in fluorozirconate glasses. This model is best examined in the context of and in comparison with known leaching processes in silicate glasses.

Briefly described, silicate glasses leach by the competing mechanisms of ion exchange and matrix dissolution. While both

processes are always occurring, their rates can be drastically affected by the composition of the glass and by the events occurring during leaching, such as the formation of a protective, de-alkalized layer. Generally, it is the porosity and the chemical composition of the de-alkalized layer which controls the temporal evolution of the leach rate characteristic of a silicate glass. The de-alkalization process involves the exchange of alkali metal cations for either protons or hydronium ions. The behavior of the de-alkalized layer and its effectiveness in protecting the glass matrix from further de-alkalization and matrix dissolution are dependent upon alkali diffusion through the layer, layer porosity, layer thickness, precipitated or adsorbed species, and the pH of the solution before and during corrosion. Under static conditions the rapid de-alkalization process drives the pH to basic values whose limit is determined either by the other glass components, such as the dissociation of boric and silicic acids, or by buffers in the soaking solution. Since the solubility of silica is greatly increased in basic solutions, the increase in pH accelerates the matrix dissolution rate. In well mixed or flowing solutions, the concentration of silica from durable silicate glasses generally increases, first with a $t^{1/2}$ law, due to the rate controlling interdiffusion of alkali metal ions and H^+ or H_3O^+ ions, and then as t^1, due to matrix dissolution through a steady-state de-alkalized layer. With time, the silica concentration in solution reaches a saturation level for the ambient

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pH. This can drastically lower the leach rate, but often complexes are formed with silica which precipitate in the form of crystals or colloids. Frequently, other effects may complicate the observed behavior, such as inadequate solution exchange or stirring, the appearance of other buffers, the reprecipitation into the layer of selected components from the glass (such as the alkaline earths and the transition metals), and possible mechanical damage to the layer. But, in silicate glasses, the underlying principles are clear.

Our data suggest that fluorozirconate glasses undergo little, if any, ion-exchange and that the corrosion process occurs primarily by selective extraction followed by matrix dissolution. The high leach rates of the alkali fluorides and AlF_3 also suggest that they have a high solubility and, as demonstrated by our results, they precede ZrF_4 dissolution. Only the Ba and La components are removed from the layer at a lower rate than Zr. The drop in pH, which results from the dissolution and hydrolysis of ZrF_4 increases the solubility of all of the fluoride components and accelerates dissolution, thus leading to a severe attack on the glass in a manner similar to that exhibited by silicates at high pH (nucleophilic attack).

There are numerous additional complications in the corrosion process which must be carefully analyzed. For example, the presence of a liquid diffusion layer allows saturation of the Zr, La, and Ba components and is responsible for the presence of pre-

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cipitated crystals on the surface of samples corroded in static solutions. The formation of the non-protective, yet very thick, hydrated layer results from the selective leaching process and its porosity influences the temporal behavior of the leach rate. Therefore, studies of the thickness or water content of the layer, while reflecting the surface hydration which occurs during the leaching process, do not investigate the controlling corrosion mechanisms, which appear to be matrix dissolution with a subsequent formation of zirconium hydroxy-fluoride complexes. The latter process, because it leads to a reduction in solution pH and an increase in the leaching process, is most responsible for the comparatively poor durability of fluorozirconate glasses in water.

6. Coatings

In order to take full advantage of the unique optical properties of these fluoride glasses, it is imperative that hermetic coatings be developed to shield them from severe attack in aqueous environments. In some cases, particularly for use with lenses and laser windows, these coatings must also be transparent in the IR. One promising coating material currently under study is diamond-like carbon.[21] Results of infrared transmissions spectroscopy for short term (4 hour) aqueous corrosion tests on identical ZBLA samples,[22] coated (A) and uncoated (B), are plotted in Fig. 11. The differences in degree of corrosion are evident from a comparison of the before and after spectra of the

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two samples. Whereas very little change is seen to have occurred in the coated sample, fairly extensive surface hydration is observed in the uncoated ZBLA. This observation was confirmed by SEM; the surface of the uncoated sample was covered with the typical dehydration cracking discussed above, while the coated surface showed only isolated pit corrosion and no cracking or spalling of the surface was observed. The pit corrosion is thought to have resulted from pin holes in the experimental coating and it is believed that with improved deposition techniques this problem can be overcome.

Conclusions

The static leaching of fluorozirconate glasses appears to be a complex process involving component solubility, matrix dissolution, ion exchange, hydration, species saturation, and reprecipitation. For this reason, weight loss measurements cannot be relied upon to determine either the controlling mechanisms or the comparative resistance of various fluoride glasses to leaching.

As shown in this study, fluorozirconates leach rapidly in water, their solution pH becomes acidic quickly, a thick hydrated layer forms which absorbs a large amount of water, and crystal precipitates grow on the hydrated layer surface. Measurements of solution composition by plasma emission spectroscopy, of degree of hydration by infrared absorption, of layer thickness and structure by scanning electron microscopy, and of crystal precip-

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itate compositions by x-ray diffraction and electron microprobe analysis were conducted on a series of fluorozirconate samples. These measurements have now led to the evolution of a comprehensive model of the corrosion process.

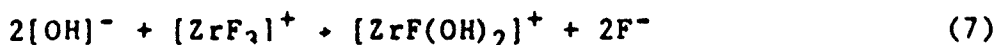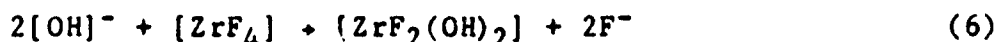The corrosion mechanism which emerges from these conclusions can be recapitulated as follows:

1. The zirconium-based fluoride glasses corrode primarily by matrix dissolution. However, unlike silicates which go into solution as hydroxides, the components of these glasses go into solution as fluorides without a prior hydroxylation step.

2. LiF, NaF, AlF_3 and, in some cases, BaF_2 dissolve at faster rates than either ZrF_4 or LaF_3. This difference in extraction rates leads to the formation of a porous, hydrated corrosion layer at the glass surface.

3. With time, the leach rates of LiF, NaF, and AlF_3 remain high, while that of BaF_2 decreases significantly as a possible result of:

    (i)   an increase in [F^-] ion concentration, which can interfere with BaF_2 solubility, and

    (ii) the depletion of BaF_2 from the glass surface.

4. LaF_3 is highly insoluble in aqueous solutions, and, therefore, remains in the surface layer.

5. Zirconium fluoride dissolves into solution as ZrF_4. Evidence of the dissolution of ZrF_4 is supported by its appearance as

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a precipitated surface crystal. In addition, there is a partitioning as shown below:

$$xH_3O^+ + yZrF_4 \rightarrow yZrF_3^+ + (y-x)F^- + xHF + xH_2O. \qquad (5)$$
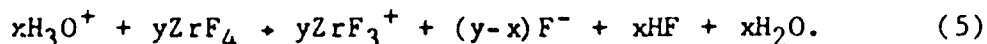
This partitioning favors $[ZrF_3]^+$ over $[ZrF_4]$ at low $[F^-]$ concentrations; the two species are equal at about 3 ppm of $[F^-]$ and the $[ZrF_3]^+$ concentration drops to only 20% when 10 ppm $[F^-]$ is present in solution. Since the fluoride ion concentration rapidly increases to > 3 ppm during corrosion, it appears that, while the $[ZrF_3]^+$ radical dominates in the early stages, it makes up a relatively small percentage of the leachate after several hours, when the fluoride ion concentration increases above 10 ppm.

6. A decrease in solution pH with time is observed which results from successive hydrolysis of the zirconium fluoride species [eqs. (1)-(4)]. Measurements of the equivalent hydroxyl concentrations exchanged, as described in the titration tests, indicate that two hydroxyls are exchanged per Zr in solution:

$$2[OH]^- + [ZrF_4] \rightarrow [ZrF_2(OH)_2] + 2F^- \qquad (6)$$

$$2[OH]^- + [ZrF_3]^+ \rightarrow [ZrF(OH)_2]^+ + 2F^- \qquad (7)$$

7. Under static conditions, the outer layer of the corroded glass is porous and hydrated and is covered by reprecipitated crystals of two distinct types. These are long, needle-like crystals identified by x-ray diffraction as ZrF_4 and spherical assemblages of thin plate-like crystals tentatively

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identified as ZrBaF$_6$. These crystals form by reprecipitation due to saturation at the glass-solution interface. The two crystal types appear to form simultaneously, since they are seen to grow around one another.

Under dilute, well stirred conditions, the corrosion layer appears to be similar in character; however, no reprecipitated crystals are formed, even after leaching for ten days.[18]

8. The thick, porous layer plays a minor role in protecting the unreacted bulk glass, and acts as an ineffective diffusion barrier to reduce the leach rate. The porosity of the layer reflects the molar volume of highly soluble species (NaF, LiF, AlF$_3$, PbF$_2$) in the glass composition and can be related to the comparative leach rates of different glasses. For example, the less durable glasses have a thick and highly porous layer.

9. The pH drift of the solution into an acidic region during leaching raises the solubility of zirconium fluoride, which accelerates the glass dissolution by several orders of magnitude, causing it to be comparable in durability to the poorer silicates (Fig. 12). The addition of any buffer to the solution can have a profound effect on the leach rate if it eliminates or retards the pH drift. The results of varying the pH of the solution on the leach rate of fluorozirconate glasses will be presented in a subsequent publication.

Figure Captions

Figure 1: Normalized leach rates vs. time from leachate analysis for individual elements of glasses: (A) ZBL; (B) ZBLA.

Figure 2: Normalized leach rates vs. time from leachate analysis for individual elements of glasses: (A) ZBLAL; (B) ZBLALPb; (C) ZBLAN.

Figure 3: Compositionally weighted average leach rates for all five glasses (La neglected).

Figure 4: Temporal variation of solution pH for all five glasses.

Figure 5: Moles of titrated hydroxyls plotted vs. $time^{1/2}$ (•solid circles) and $(t-t_0)^{1/2}$ (△open triangles), showing the rate of hydrolysis of $(ZrF_x)^{+4-x}$ from ZBLAL glass in a solution maintained at constant pH.

Figure 6: Relative $[ZrF_x]^{+4-x}$ species concentrations as calculated from association constants.

Figure 7: IR transmission spectra of ZBLAL glass exposed to 100% relative humidity for four and seven days at 80°C.

Figure 8: Typical crystal deposits on the surface of ZBLA glass following two days in stagnant, deionized water. Letters correspond to EDS analysis in Fig. 10.

Figure 9: SEM micrographs of: (A) surface crystal deposits; (B) corrosion layer with crystals removed; (C) cross-section of corrosion layer; (D) magnified crystal deposits.

Figure 10: EDS analysis of a ZBLA sample from Fig. 8 showing: (A) uncorroded, as-polished surface; (B) dehydrated corrosion layer (crust); (C) spherical crystal deposits; (D) blade-shaped crystal deposits.

Figure 11: IR transmission spectra of ZBLA samples before and after corrosion: (A) surface coated with diamond-like carbon; (B) without coating.

Figure 12: Comparison of the collective leaching behavior of fluorozirconate glasses with three well studied silicate glasses ($Na_2O \cdot 2SiO_2$, $Li_2O \cdot 2SiO_2$),[23] (Pyrex).[24]

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TABLE I

Composition (mole %)

MNEMONIC	ZrF$_4$	BaF$_2$	LaF$_3$	AlF$_3$	LiF	NaF	PbF$_2$	Source
ZBL	62.0	33.0	5.0	--	--	--	--	RPI[4]
ZBLA	57.5	34.5	4.0	4.0	--	--	--	RPI,[4] RADC[4]
ZBLAL	51.8	20.0	5.3	3.3	19.6	--	--	NRL[3]
ZBLAN	54.0	15.0	6.0	4.0	--	21.0	--	RPI[5]
ZBLALPb	50.4	15.5	4.9	3.1	20.2	--	4.9	NRL[3]

NRL = D. C. Tran, Naval Research Laboratory, Washington, DC.

RPI = C. T. Moynihan, A. J. Bruce, and K. H. Chung, Rensselaer Polytechnic Institute, Troy, NY.

RADC = M. G. Drexhage and O. H. El-Bayoumi, Rome Air Development Center, Hanscom Air Force Base, MA.

TABLE 2

Equivalent F⁻ Calculated from DCP Cation Analysis

Cation	Analyzed [M^+] (10^{-6} moles)	Equivalent F⁻ (10^{-6} moles)	% of Total F⁻	Normalized Leach Rate (g cm^{-2} d^{-1})
Zr^{+4}	27.6	110.4	72%	3.57 x 10^{-2}
Ba^{+2}	10.0	20.0	13%	3.36 x 10^{-2}
La^{+3}	0.08	0.24	0.1%	1.03 x 10^{-3}
Al^{+3}	3.2	9.7	6%	6.56 x 10^{-2}
Li^+	14.0	14.0	9%	4.80 x 10^{-2}
Equivalent Moles F⁻ (10^{-6})		154.34	100%	
Titrated Moles OH⁻ (10^{-6})		58.20	38%	

Fig. 1

NORMALIZED LEACH RATE ($g\ cm^{-2}d^{-1}$)

(A) ZBLAL — Li, Al, Zr, F, Ba, La

(B) ZBLALPb — Li, Al, F, Zr, Pb, Ba, La

(C) ZBLAN — Al, Na, F, Zr, Ba, La

TIME (days)

Fig. 2.

Fig. 3

Figure: Solution pH versus Time (hr) for glass compositions (1) △ ZBL, (2) ● ZBLA, (3) ■ ZBLAL, (4) ▼ ZBLAN, (5) × ZBLALPb. Curves labeled 4,5 and 3 and 1,2.

Fig. 5

PPM F$^-$

0.010.1 1.0 10 100

$\log\ [ZrF_x]^{+4-x}$

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}

$[ZrF_4]$

$[ZrF_3]^+$

$[ZrF_2]^{+2}$

$[ZrF]^{+3}$

$[Zr]^{+4}$

10^{-6} 10^{-4} 10^{-2}

$\log\ [\,F^-\,]$ (mole/liter)

Fig. 7

MICRONS

2.5 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10

AS POLISHED

4 DAYS

7 DAYS

ZBLAL in 100 % RH – 80 C

TRANSMITTANCE

WAVENUMBER (CM⁻¹)

4000 3500 3000 2500 2000 1800 1600 1400 1200 1000
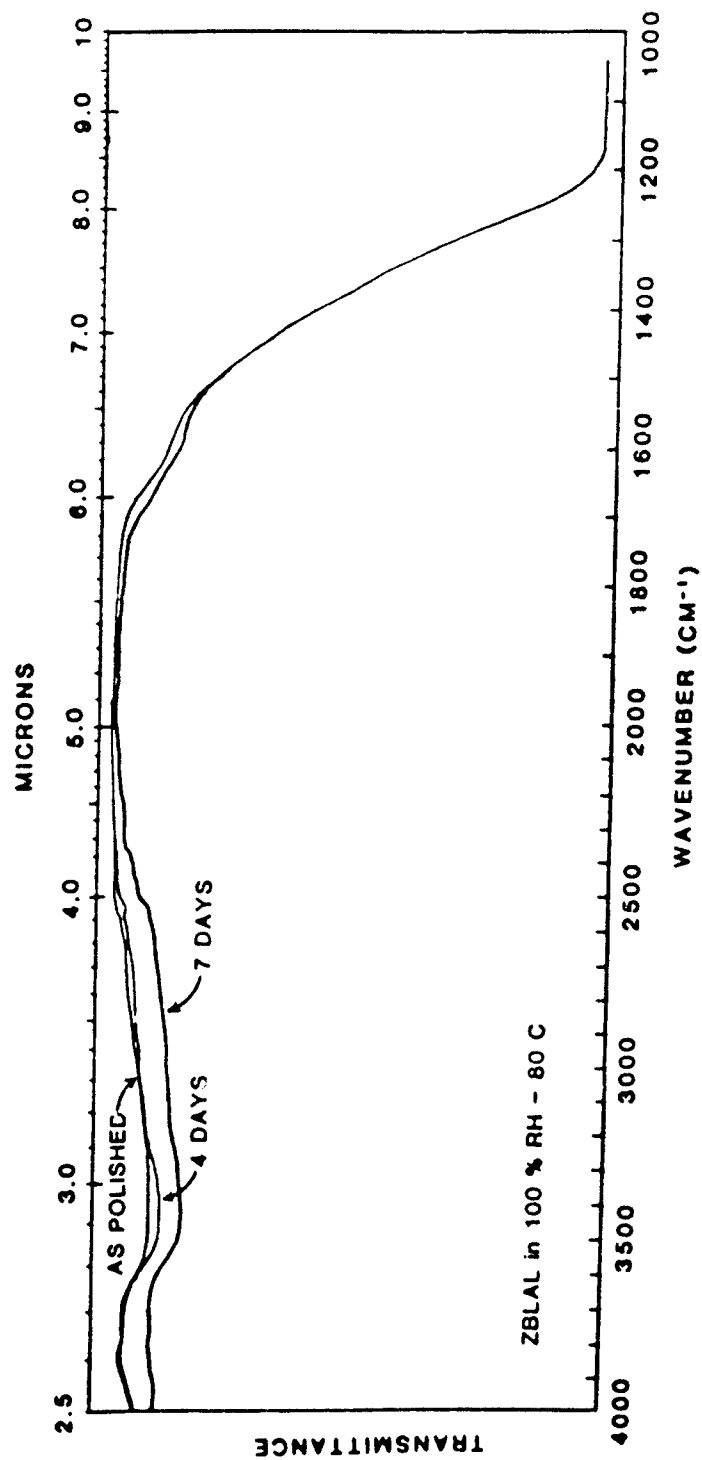
SURFACE STRUCTURE AFTER LEACHING
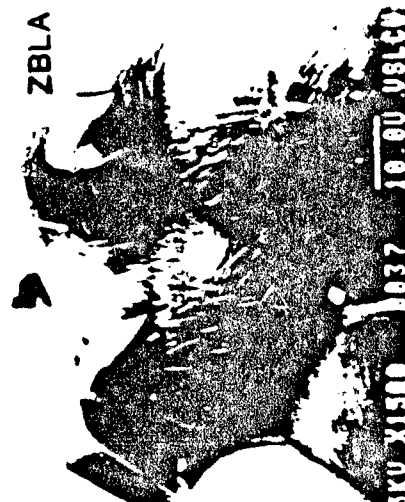
5 DAYS AT 25 C

(A) Precipitated Crystal Deposits

(B) Dehydrated Surface Layer

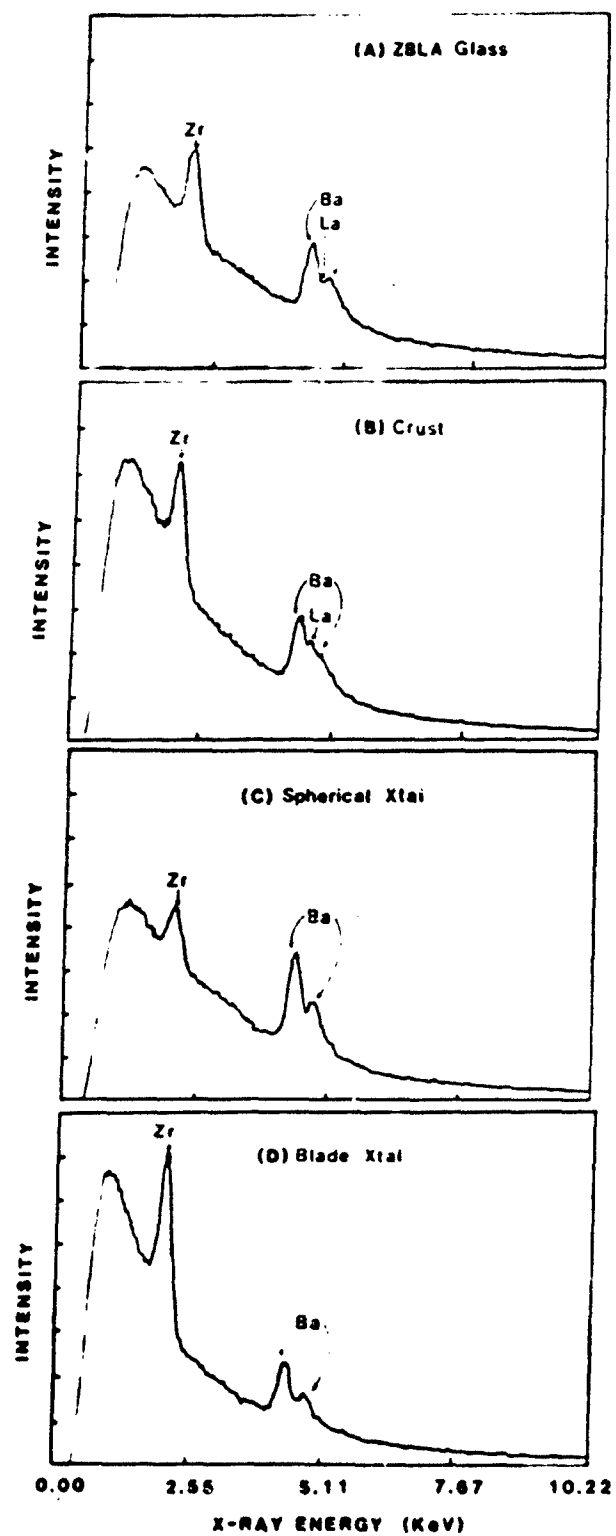(C) Cross-Section of Surface Layer

ZBL

ZBLA

(D) Two Types of Crystals

(A) ZBLA Glass

(B) Crust

(C) Spherical Xtal

(D) Blade Xtal

X-RAY ENERGY (KeV)

Fig. 10

MICRONS

Graph (A): ZBLA w/ DLC COATING — Transmittance vs Wavenumber (CM⁻¹), showing "AS POLISHED" and "4 HR. in H₂O" curves.

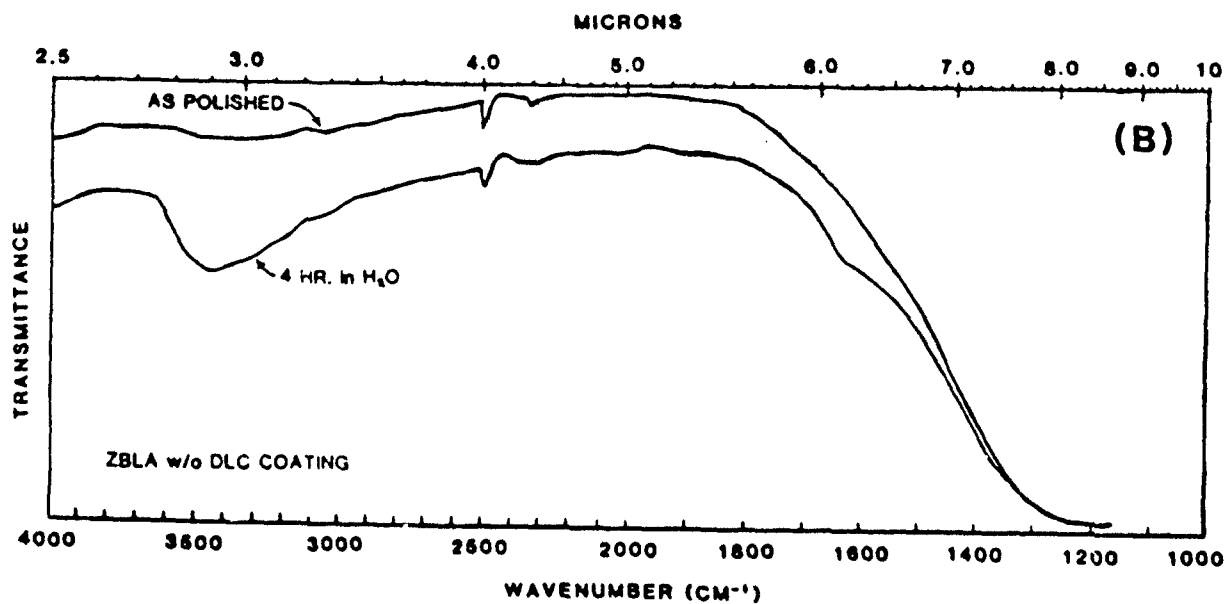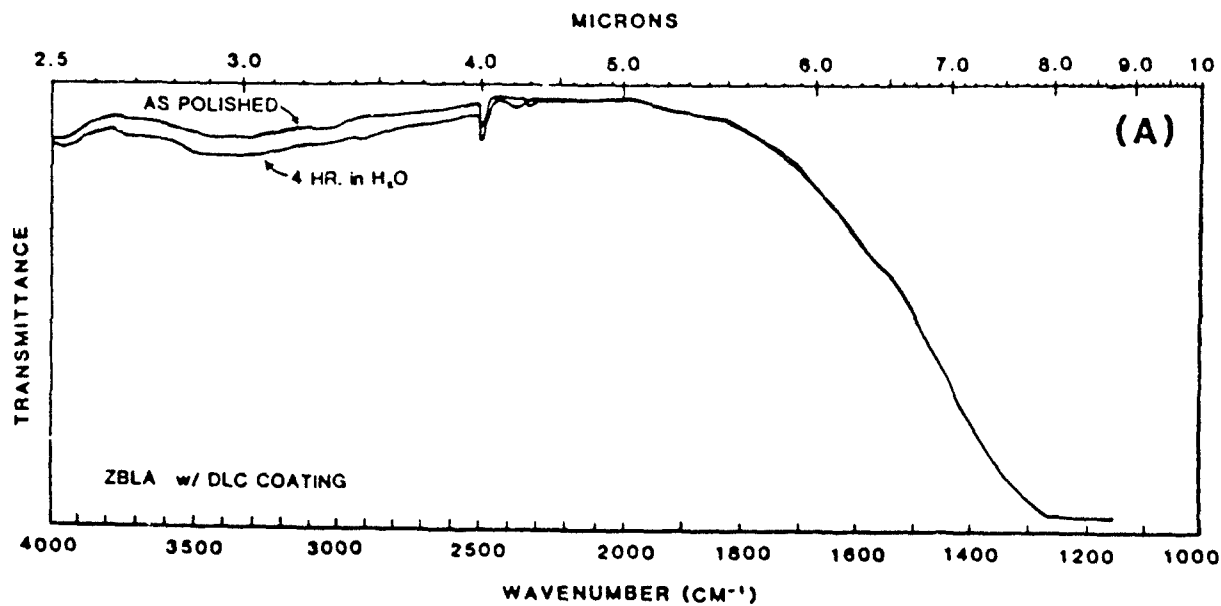Graph (B): ZBLA w/o DLC COATING — Transmittance vs Wavenumber (CM⁻¹), showing "AS POLISHED" and "4 HR. in H₂O" curves.

Fig. 11

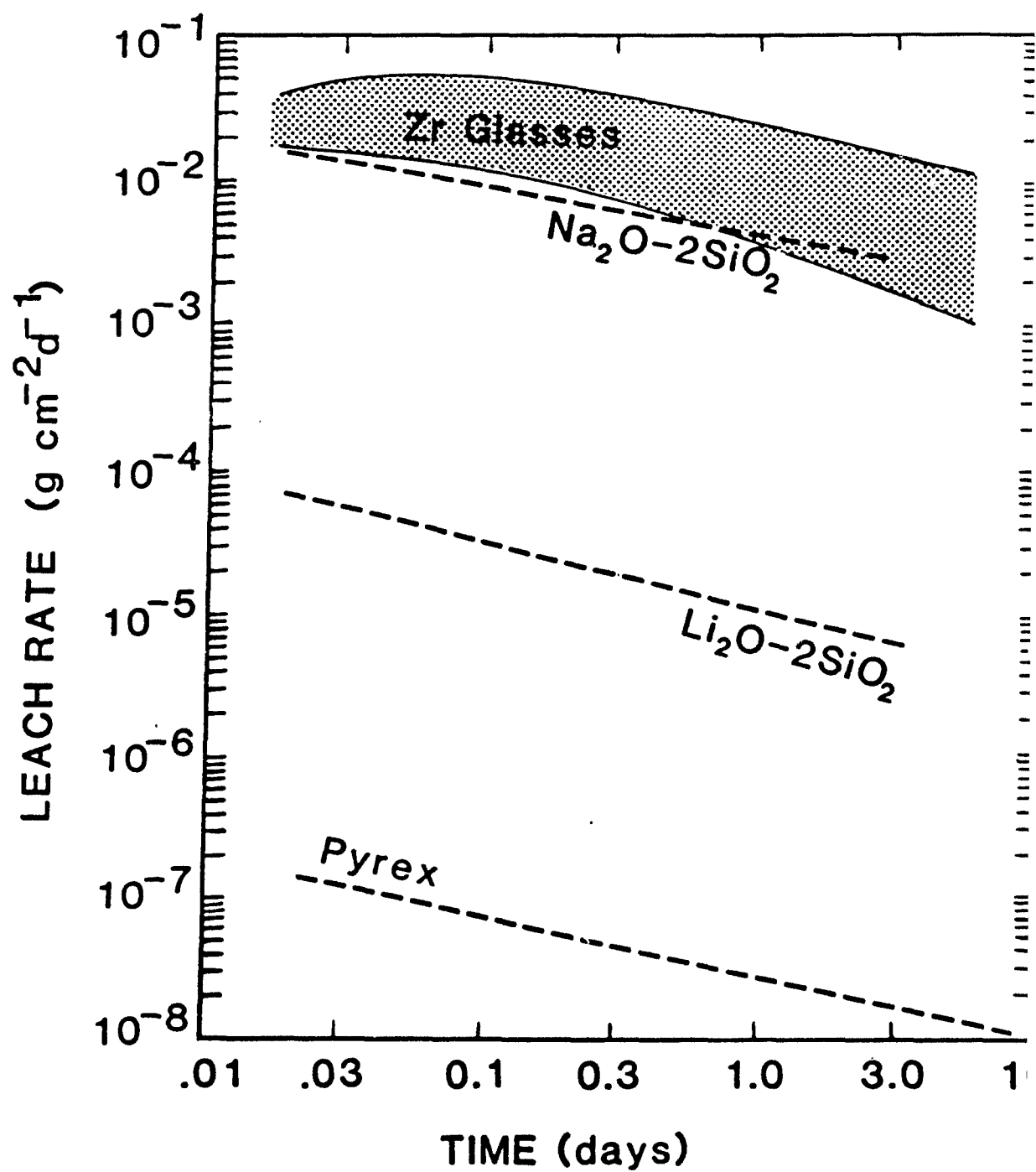Fig. 12

PAPER #2

LEACHING BEHAVIOR OF HEAVY METAL FLUORIDE GLASSES*

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Introduction

The aqueous corrosion of fluoride glasses has received increasing atten-
tion since the onset of studies of these non-oxide glasses. In 1982 the first
results of aqueous leach tests on a fluorozirconate glass (generally denoted
a ZBLAL) were reported.[1] The corrosion rate reported, obtained by solution
analysis, showed that the major components of the glass, including Zr, Ba, Al,
L , and F, were leached at comparable rates (differing by less than a factor
of 5), while the rare-earth, La, was leached at a rate 2 orders of magnitude
lower (see Fig. 1, Ref. 1). Scanning electron microscope studies showed that
the surface was covered by crystalline deposits (Fig. 3A, Ref. 1) and that a
thick (> 100 µm/5 days) hydrated, transformed layer lay beneath the crystals
(Fig. 3B, Ref. 1). This layer was cracked due to dehydration during drying in
vacuum. IR absorption measurements of the leached glass showed high absorp-
tion due to the stretching OH and bending HOH vibrations, which increased with
time and layer thickness. These absorption bands remained, even after drying
in vacuum, indicating that a large water content was present in the hydrated
layer. It was also noted that the pH of the solution drifted rapidly from 5.8
to 3.4 within 18 hours.

Leach rate studies of thorium-based glasses (Zn-Ba-Y-Th, Zn-Ba-Yb-Th, Zn-Ba-Yb-Th-Na) were later reported[2] and showed that these glasses were 50-100 times more resistant to corrosion by deionized water than the zirconium-based series. Leach rates for individual elements in the non-alkali composition were observed to be similar for all except Yb, which followed the same behavior as La in the Zr glasses. In the alkali-containing glass, the Na release rate was much higher at short times, presumably due to bulk diffusion, and was seen to decrease with time as the Na was depleted from the surface. Little, if any, drift of solution pH was observed during these tests.

Reports by Guery et al.[3] indicated that some uranium fluoride glasses could be even more resistant to corrosion than Zr- or Th-based glasses. Soak tests conducted at pH of 1 and 10 for 100 hours showed no visible evidence of the formation of crystals or a hydrated surface layer.

It has been reported[2,4] that the leach rate of ZrF_4-based glasses increases dramatically with decreasing solution pH, yielding a vital clue to understanding the controlling mechanisms of aqueous corrosion in fluoride glasses. This data led to the proposal that, unlike silcates, whose leaching behavior is dominated by alkali-proton ion exchange at acidic pH, the major factor in determining the leach rate of zirconium-based fluorides in water is the dissolution of ZrF_4.[5]

In this paper, we report a comparison between the aqueous corrosion processes in Zr-, Th- and U-based fluoride glasses. This comparison is not based solely on their leach rates in deionized water. Instead, it combines this data with leaching data obtained in buffered solutions at a variety of pH values to study the mechanisms dominating aqueous corrosion in these glasses and the reasons for their apparent differences in resistance to aqueous attack.

Results

Measurements of aqueous leach rates were conducted on zirconium-, thorium-, and uranium-based fluoride glasses (Table 1) as a function of time in deionized water. The curves of Fig. 1 show the relative leach rates of the three types of glass. From this data, it is clear that the ZrF_4-based glass appears to be far less durable than the others. However, it has been noted previously that the solution pH drift is far more severe in the case of the Zr glasses due to the dissolution of ZrF_4.[5] From an initial pH of 5.8, the

solutions drifted to 4.5, at short times, and 3.2 at longer times for ZrF_4 glasses, 5.6 for ThF_4 glasses, and 4.0 for UF_4 glasses.

In order to determine how the degree of pH drift and the resulting change in solubility of ZrF_4, ThF_4, and UF_4 contribute to these differences, measurements were conducted in buffered aqueous solutions at pH values from 2 to 10. The results are shown in Fig. 2.

While all glasses tested exhibit similar behavior, with a minimum near neutral pH, there are several interesting differences worth noting. First, we find that, at low pH, the ZrF_4 glass has the highest leach rate. Second, we find that, at basic pH, all the glasses show an increase in leaching, with the ZrF_4 glass showing the smallest rise. Finally, and most surprising, we find that, at neutral pH, the ZrF_4 glass exhibits a lower minimum than either the ThF_4 or UF_4 glasses.

Clearly, the combination of pH drift and the acid leaching behavior of these glasses explains the differences in durability observed in earlier tests in unbuffered deionized water. Comparing the leach rate at short times in Fig. 1 with the measured leach rates in Fig. 2, it can be seen that the ZrF_4 glass, leaching at 3×10^{-2} g cm^{-2} d^{-1}, should be in a solution at pH = 4.7, in good agreement with the value of 4.5 measured in the leaching solution; while the ThF_4 glass leaches at a rate of 2×10^{-4} g cm^{-2} d^{-1} at a pH of 5.6, and the UF_4 glass leaches at a rate of 2.1×10^{-3} g cm^{-2} d^{-1} at pH = 4.0.

In basic solutions, hydroxides are formed and the glass leach rates are controlled by the dissolution rates of these species.[2] These results support our earlier conclusions[2,5] that matrix dissolution is the major factor controlling the corrosion behavior of these glasses.

References

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TABLE 1

COMPOSITION
(mole %)

Group I

	ZrF$_4$	BaF$_2$	LaF$_3$	AlF$_3$	LiF
ZBLAL	51.8	20.0	5.3	3.3	19.6

Group II

	BaF$_2$	ZnF$_2$	YbF$_3$	ThF$_4$	NaF
BZYbT	19.0	27.0	27.0	27.0	---
BZYbTN	10.0	27.0	27.0	27.0	9.0

Group III

	BaF$_2$	LiF$_4$	AlF$_3$	YF$_3$	ZnF$_2$	MnF$_2$	FeF$_3$
BUYAZ	30.4	30.4	2.0	4.8	32.4	---	---
BUYAM	30.4	30.4	2.0	4.8	---	32.4	---
BUYFe	20.0	40.0	---	20.0	---	---	20.0

Normalized Leach Rate (g cm⁻²d⁻¹)

pH

ZBLAL

BUYF
BZYbT
BZYbTN

Normalized Leach Rate (g cm⁻²d⁻¹)

Time (days)

Zr Glasses

Na₂O–2SiO₂

U Glasses

R.E. Glasses

Li₂O–2SiO₂

Pyrex