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GLASS SURFACES - 1982

L.L. Hench

Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, U.S.A.

Résumé

Une nouvelle catégorie de surface des verres est décrite. Les surfaces du type IIIB sont constituées par des couches multiples d'oxydes, hydroxydes et des silicates hydratés, provenant des réactions de précipitation entre la surface du verre et la solution de lixiviation. Les très faibles vitesses de lixiviation ainsi que les faibles épaisseurs d'érosion pour certaines compositions des verres complexes de déchets nucléaires sont principalement dues a une surface du type IIIB. Les limites de solubilité qui établissent l'équilibre des concentrations ioniques pour les eaux d'immersion, établissent aussi les muliples barrières de couches du type IIIB qui protègent les verres de déchets nucléaires en contact avec ces eaux d'immersion.

Abstract

A new category of glass surface is described. Type IIIB surfaces are composed of multiple layers of oxides, hydroxides, and hydrated silicates resulting from a sequence of solution-precipitation reactions between the glass surface and leaching solutions. Very low leach rates and then ion depletion depths of certain compositions of complex nuclear waste glasses are due to Type IIIB surfaces. The solubility limits that establish the equilibrium ionic concentrations for burial ground waters also establish the multiple barrier Type IIIB films, to protect nuclear waste glasses in contact with those ground waters.

Introduction

Understanding and controlling the surface reactions of glass is a subject of major technical importance. It has long been recognized that glass performance, such as the durability of glass containers, the useful life of windows and optical glasses, pH electrode lifetime, and static fatigue is related to glass surface - environment interactions. During the last five years there has been a growing awareness that the reliability of glasses developed for immobilization of high level radioactive wastes is also dependent on glass surface chemistry. We now know that the mechanisms of nuclear waste glass leaching comprise an important new category of glass surface behavior.

Understanding the kinetics and mechanisms of the new type of glass-environment interaction characteristic of nuclear waste glasses is important for several reasons. First, the quantity of nuclear waste glass required for immobilization of defense and commercial radioactive waste is millions of kilograms and the estimated cost is billions of dollars. Secondly, there must be reasonable assurance that the glass surface will be stable in contact with

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ground waters during geologic burial for thousands to hundreds of thousands of years. Thirdly, the mechanisms responsible for stabilization of nuclear waste glasses might be applied in the design of glasses for redox-sensing (Eh) electrodes or glasses with unique gradients in optical properties. Lastly, our ability to generalize glass-environment interactions is expanded with this new category of surface behavior.

Thus the primary objectives of this paper are to review the evidence for a new class of glass surface behavior, compare this behavior with other categories of glass surfaces, and relate the significance of the surface structure and reaction kinetics of these glasses to the geologic performance of nuclear waste glasses.

Background

Previous efforts to generalize the surface behavior of silicate glasses proposed five types of glass surfaces to represent a broad range of glass-environment interactions, Figure 1.[1,2] It was suggested that any silicate glass could be described in terms of one of the five surface types at any particular instant in its processing and environmental history. Recent studies indicate however that another type of surface, IIIB, must be added to this scheme. Figure 1 incorporates this change.

The ordinate in Figure 1 represents the relative concentration of SiO_2 (or other oxides in Type III surfaces) in the glass and the abscissa corresponds to the depth into the glass surface. If species are selectively dissolved from the glass surface the relative SiO_2 concentration will increase producing a SiO_2-rich surface layer. If all species in the glass are dissolved simultaneously (congruent dissolution) the relative concentration of

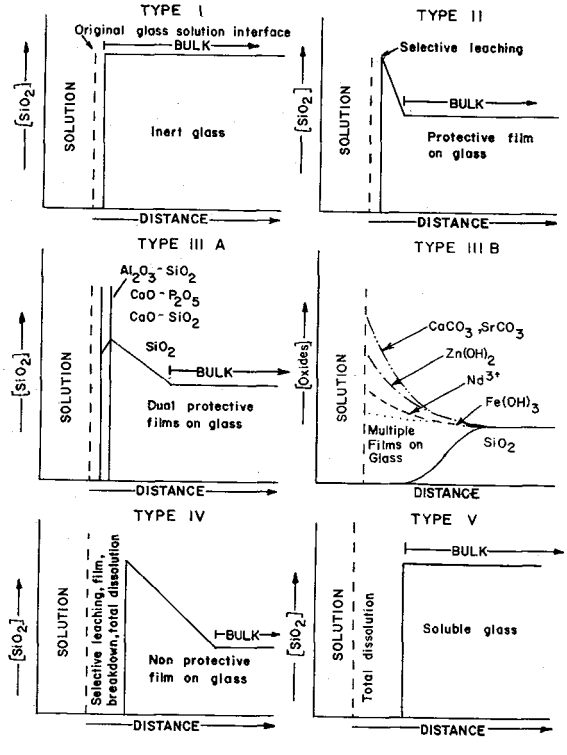


Fig. 1. Five types of glass surfaces and six surface conditions resulting from glass-environment interactions.

SiO_2 will remain the same as in the original glass. When combinations of selective dissolution, congruent dissolution and precipitation from solution occur then any one of the 6 surface conditions shown in Figure 1 is possible.

Type I glasses have undergone a surface reaction that is only a monolayer thick and no compositional profile is measureable. High purity vitreous silica exposed to neutral solutions is an example of a Type I surface. Exchange of alkali and alkaline earth ions with hydrogen and/or hydronium ions (i.e., selective dissolution) results in Type II glass surfaces if there is sufficient concentration of network formers in the surface film to stabilize it. Type III surfaces will be described later. If network formers are not sufficient, or if the environment is rich in OH^- or other species which can break Si-O-Si network bonds, the surface layer is unstable and a Type IV surface is produced. A glass that is undergoing total network attack (also referred to as congruent dissolution) is described as having a Type V surface. Often from the perspective of average surface compostion there is little distinction between Type I and Type V surfaces. However, large quantities of ions are being lost from a Type V surface during corrosion and consequently extensive surface pitting can result due to localized heterogeneous attack. Additionally, large dimensional changes often accompany corrosion of glasses wtih Type V surfaces.

Surface Reaction Kinetics

Studies of the kinetics of the above processes show that Type II surfaces are present when

$$C_1 = k_1 t^{1/2} \qquad (1)$$

where C_1 is the concentration of species in solution, t is reaction time and k_1 is the rate constant for the diffusion controlled process. Type V surfaces correspond to a regime of kinetics where

$$C_2 = k_2 t^1 \qquad (2)$$

where C_2 and t have the same meaning as in Equation 1 and k_2 is the rate constant for the interface controlled network dissolution process. Type IV surfaces result when both processes occur together; e.g.

$$C_3 = k_1 t^{1/2} + k_2 t \qquad (3)$$

$$C_4 = k_1 t^{1/2} + k_2 t - k_3 t^x \qquad (4)$$

Continued exposure of a glass to many chemical environments leads to progressive changes in both compositon and thickness of the surface films. Figure 2 describes such a change under static corrosion or various flow rates where the ions from the glass are permitted to build up in solution and increase the pH. Selective leaching (dissolution) behavior results in formation of a silica-rich surface film and a Type II surface . With increasing time in static conditions or slow flow rates, dissolution of the surface film network occurs due to buildup of OH^- in the solution leading to a Type IV surface. Eventually at high pH's the surface film network is totally destroyed and the glass is corroding congruently (i.e., Type V behavior). Congruent dissolution proceeds until complete dissolution of the glass occurs or until the solution in contact with the glass becomes saturated with respect to the individual species. Fast flow rates prevent a pH excursion and limit the onset of congruent dissolution.

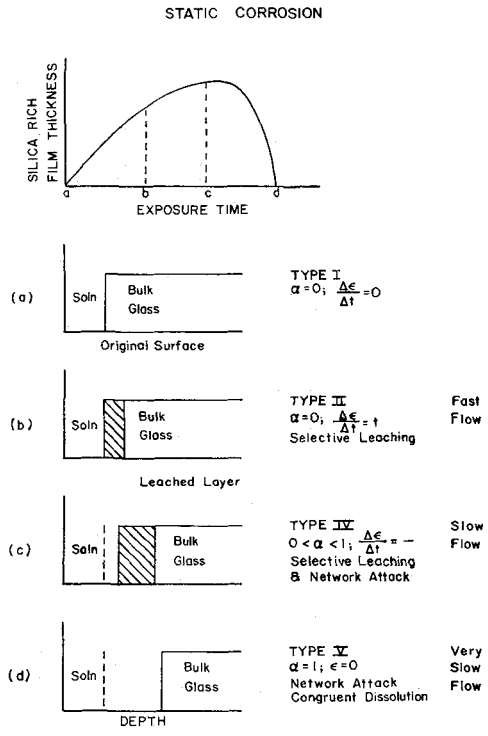


Fig. 2. Time dependent changes of glass surfaces with static leaching or flow.

A glass dissolution parameter (α) and a film formation parameter (ε) can be calculated to describe these processes.[3,4] The relation of these parameters to glass surface type and reaction sequence is shown in Figure 2.

$$\alpha = \frac{\text{moles } SiO_2 \text{ in solution}}{\text{moles alkali in solution}} \Big/ \frac{\text{moles } SiO_2 \text{ in glass}}{\text{moles alkali in glass}} \qquad (5)$$

when $\alpha \to 0$, incongruent dissolution and film formation;
$\alpha \to 1$, film destruction;
$\alpha = 1$, congruent dissolution;

$$\varepsilon = \text{ppm } SiO_2 (\text{in solution}) \quad \frac{1-\alpha}{\alpha} \qquad (6)$$

when $\frac{\Delta\varepsilon}{\Delta t} = +$, film deformation

when $\frac{\Delta\varepsilon}{\Delta t} = -$, film destruction

when $\varepsilon = 0$, congruent dissolution

The film formation parameter, ε, is related to the quantity of excess silica available for formation of a surface film. However, the density of the silica-rich film can vary considerably. Consequently, there may be a considerable quantity of excess silica on the glass surface of a thickness of 10-100 μm, but because of porosity and low density the film is not a barrier to diffusion (Type IV). In contrast, a thin (<1μm) film of dense SiO_2 remaining after selective ion exchange can serve as a highly protective surface (Type II).

A number of studies of glasses of various compositions have shown depth compositional profiles for Type II, IV, and V surfaces. The techniques used include Auger electron spectroscopy (AES)[5-8], secondary ion mass spectroscopy (SIMS)[9], resonant nuclear reactions (RNR)[10], electron spectroscopy for chemical analysis (ESCA)[11,12], secondary ion photoemission spectroscopy (SIPS)[13,14], infrared reflection spectroscopy (IRRS)[15-17]. Film depths in the range of 0.01-1.0 μm are generally observed for Type II glasses. Type IV glasses typically exhibit films of 1.0-100 μm depth. Adding network modifiers of high electric field strength to the glass changes Type IV surfaces to Type II, greatly decreases the thickness of the silica-rich films and increases the film density.

Type III Glass Surfaces

Previous surface studies of biologically active invert silicate glasses containing CaO and P_2O_5 (bioglasses)[18,19] and certain compositional ranges of Li_2O-Al_2O_3-SiO_2 glasses[20] showed that dual films developed on the glass. The secondary films were either hydrated CaO-P_2O_5 or Al_2O_3-SiO_2 layers. Chemical depth profiles using AES showed that the dual films formed on top of a silica rich film which resulted from rapid ion exchange of alkali for protons (or hydronium ions). Other work showed that such a dual film could be formed by addition of either phosphate[19] or aluminum ions in solution[21] as well as through release of phosphate or aluminum ions from the glass.

Analysis of anion concentrations of the dual apatite film formed on bioglasses showed some exchange of CO_3^{2-} ions for OH^- ions similar to that found for bone.[22] This study also showed that incorporation of CaF_2 in the glass results in a fluorapatite film[22] forming on the glass. Previous dental implant studies suggested a favorable tissue response to the fluoride containing glasses[23] and recent results show excellent biocompatibility of the fluoride anion doped surface layers.[24]

Studies also show that the effectiveness of a number of alkaline corrosion inhibitors[25], such as soluble calcium or beryllium salts, are due to formation of dual films composed of insoluble alkaline earth-silicate compounds[26,27].

This type of glass surface is designated type III A, dual protective film, in Fig. 1. The thickness of the secondary films can vary considerably, from as little or 0.01 μm for Al_2O_3-SiO_2 rich layers or as much as 30 μm for CaO-P_2O_5 rich layers.

Studies in a number of laboratories have shown that alkali borosilicate glasses designed to immobilize high level raadioactive wastes have an even more complex surface behavior than Type III A glasses. There is considerable evidence that such glasses develop multiple layers of oxides or hydroxides on their surface when exposed to water. This behavior is designated Type III B in Figure 1.

The theoretical basis for Type III B glasses is the recent investigation of B. Grambow which predicts the formation of a series of insoluble reaction products on glass surfaces.[28] He shows that the strong pH dependence of nuclear waste glass leaching can be explained in terms of the pH dependent solubility limits of simple reaction compounds of many constituents in the glass. In low and high pH leachants glass dissolution is controlled by congruent dissolution (eq. 2) but at intermediate pH values solubility of reaction species such as $Fe(OH)_3$, $Zn(OH)_2$, $Nd(OH)_3$ $SrCO_3$, $CaCO_3$, or $CaSiO_3$ control the surface reactions. Thus k_3 in eq. 4 involves a summation of the solution-precipitation reactions of all of the above constituents.

A mathematical model has been recently developed which attempts to describe some of the above processes.[29] It is based on the empirical observation that the concentration ratios of various elements in four different waste glass systems were independent of time in static leach tests after 3 days; however, the elemental ratios in solution differed from the corresponding ratios in the glasses throughout the 28 day static leach period. Thus, the model assumes that the glass corrodes congruently and the rate of corrosion is controlled by the rate of reaction of amorphous silica with water as well as the rate of diffusion of soluble silicates through an insoluble layer between the glass and bulk solution. This leads to the stable incongruency in the leachants. The thickness of the insoluble layer is proportional to the amount of glass that has dissolved from the start of the experiment with a silicate concentration gradient in the layer equal to the difference in silicate concentration at the glass layer interface and that in the leachrate divided by layer thickness.

Wicks and Wallace conclude,[29] "The model predicts that the slope of log concentration vs. log time plot should be initially 1 then shift to 0.5 at a later time and finally approach 0 as the leachate becomes saturated with silicates. The point at which the transition from a slope of 1 (matrix dissolution controlled) to 0.5 (diffusion controlled) occurs depends primarily on the ratio of the reaction rate constant to the diffusion coefficient. The point at which saturation becomes important depends primarily on the ratio of surface area of glass to volume of leachant. For large values of this ratio, saturation may become important before the shift from matrix dissolution to diffusion controlled kinetics occurs. In open systems where the products of leaching are not allowed to accumulate (but surface layers are formed) the slopes should shift from 1 to 0.5 but not drop below that value. A simple matrix dissolution model (involving no protective surface layers) predicts a slope of 1 which remains near that value until saturation becomes important when it then drops toward zero.

Experimental values of the slopes in four sets of static tests varied between 0.5 and 0.25. The estimated fractional saturation of silicates in these tests was sufficient to account for slopes from 0.48 to 0.41 for the surface layer model." Even lower values approaching 0.05 are observed in long term tests.[30,31]

Glass / Oxide (%)	M 1	M 2	M 3	M 4	M 5	M 6	M 7
SiO_2	47.6	42.7	51.13	45.6	50.0	48.4	46.1
Al_2O_3	-	8.6	4.05	4.9	3	2.0	5.0
Na_2O	12.4	14.2	13.19	8.8	12.5	11.28	12.5
B_2O_3	18.6	17.8	13.56	22.0	14.41	18.47	14.2
Fe_2O_3	6.4	4.0	1.601	2.8	2.96	2.96	2.96
CaO	-	-	4.10	-	2	3.76	4.1
MgO	-	-	0.348	-	-	-	-
MoO_3	2.47	2.09	1.592	2.62	1.7	1.7	1.7
Li_2O	-	-	-	-	2.0	-	2.0
* S.W.P.	15	12.7	10.9	15.9	12.22	12.22	12.22

Table 1. Nuclear Waste Compositions (Weight %).

* Simulated Waste Products

The solubility limited-multiple layer models imply that certain compositional ranges may exist where glasses can form a sequence of stable and continuous films capable of greatly inhibiting diffusion of other species through them or dissolution of the matrix underneath them. Results of several nuclear waste glass compositional studies show that there is a critical range of glass composition where leaching in minimal.[32-35] For example, one of the studies [33] comparing seven glasses (Table 1) for solidification of French nuclear wastes showed that glass surface attack and leach rates were strongly dependent on the concentration of network formers in the glass, Fig. 3. On the ordinate of Fig. 3 is plotted the number of days required for a glass surface to be attacked sufficiently for its IRRS spectrum at 950 cm^{-1} (Si-O-alkali region) to be decreased by 15%. The abscissa is the sum of various combinations of glass network formers. The graph shows that a critical concentration of $SiO_2 + Al_2O_3 + Fe_2O_3$ > approximately 55% (by weight) or $SiO_2 + Al_2O_3$ > 53% must be present in the glass for the surface to be resistant to leaching. Comparison of pH changes and ion solution concentrations after 28 days, 90°C yield the same conclusion.

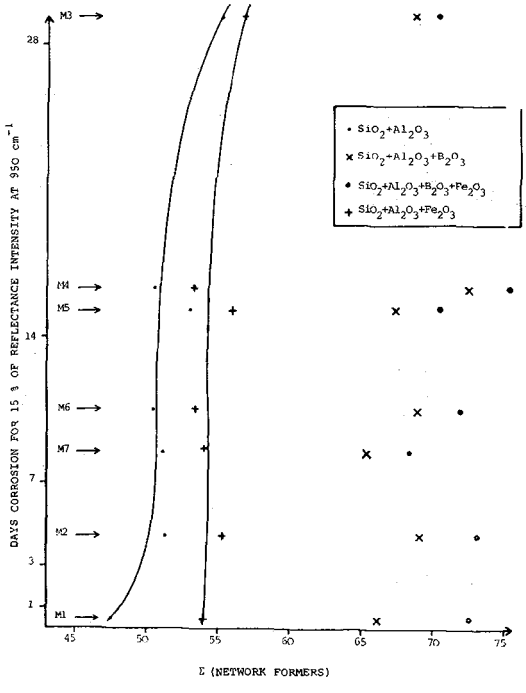


Fig. 3. Time required for IRRS spectra of nuclear waste glasses to degrade 15% during static 90°C leaching.

Another study investigated the relative importance of ZnO and Fe_2O_3 in stabilizing the surface film on alkali-zinc-borosilicate glasses[34]. For the composition studied, replacement of half of the 6% ZnO with Fe_2O_3 degraded the leach resistance by 3X. Both glasses appeared to be protected by dual films, one rich in SiO_2 and a second very thin film rich in multivalent species. The second film containing the mixture of ZnO and Fe_2O_3 was less stable than ZnO alone, suggesting critical concentrations of film formers are necessary to produce a film sufficiently dense and continuous to serve as an effective diffusion barrier.

McVay and Buckwalter have shown that the role of Fe in leaching can be especially complicated when iron silicate colloids form in the leachant.[36] Formation of iron silicate precipitates effectively removes many elements from

solution and therefore eliminates many of the effects of ground water chemistry. Since the precipitates retard the saturation effects by removing species from solution, higher sustained glass leach rates and greater total elemental removal from the glass is observed. Leaching in the presence of solid pieces of ductile iron give rise to this effect and excessive concentrations of Fe in the glass may also, since high waste glasses containing large ionic Fe concentrations leaches more than 10x faster than a high Al waste.[37]

In order to generalize composition effects of Type III B glasses a computerized comparison of the compositional dependence of 27 nuclear waste glasses studied worldwide has been conducted.[35] Figure 4 illustrates the findings. All 27 glasses were leached in DI water using MCC-1 static leach procedures at 90°C for 28 days. The glass compositions were divided into 3 groups; the weight percentage of oxides of Si, B, and Na are located at the top and right corners of the ternary plot. The oxides of Al, Fe and all other constituents, labeled as WP ("waste products") are added together and comprise and 3rd axis. All of the glasses in the data file were enclosed within the compositional space labelled 45.0 in Fig. 4. Thus all nuclear waste glasses stored have a leach rate for Si at 28 days of less than 45 $g/m^2/day$. A narrower field of compositions, but still extensive, possess leach rates of 0.1 to 0.2 $g/m^2/day$. However, only a few compositions exhibit the very low range of 0.02 $g/m^2/day$ and these all contain nearly equivalent 51-53 w/o SiO_2 and ±2% of the other constituents.

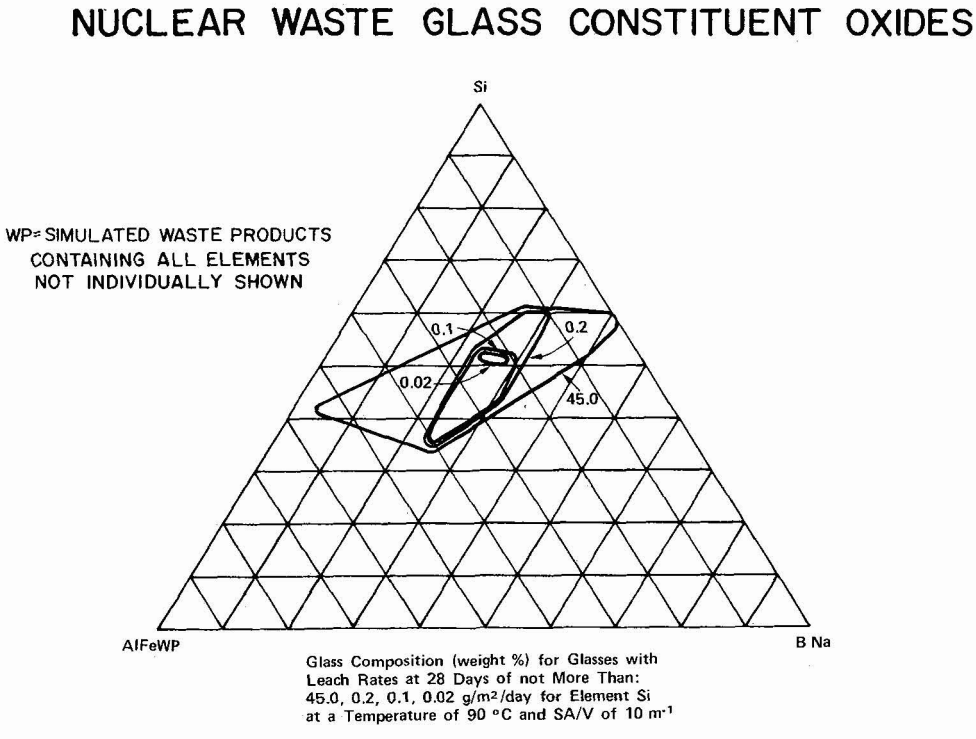


Fig. 4. Compositional dependence of nuclear waste glass leaching.

The results of Figure 4 for Si in solution are similar to the general findings of this study; i.e., there is a narrow compositional range where nuclear waste glasses achieve leach rates as low as 0.02 g/m^2/day in a static MCC-1, 90°C leach test. However, a much broader range of glass compositions will yield leach rates of 0.1 g/m^2/day. The best compositional range tends to be approximately 51-53% (SiO_2), 24-28% (Na_2O + B_2O_3), and 21-25% (Al_2O_3 + Fe_2O_3 + WP). Analysis of the time dependent changes of the compositional space for lowest leach rates leads to the conclusion that a critical concentration of Al_2O_3, Fe_2O_3, and waste product constituents are needed to produce low leach rates. This is consistent with surface analyses that show many of these species being incorporated in surface films which serve as diffusion barriers[31,36-40] slowing down long term release rates.

It has also been shown that the thickness of the Type IIIB films decreases with increasing percentage of waste constituents and multiple valence oxides.[29] Leach rates for all elements are much lower for the glasses with thinner films which indicates not only that the films formed quickly but that they were sufficiently continuous and dense to prevent congruent attack of the glass. It is especially important that burial studies of nuclear waste glasses in deep Swedish granite with 90°C centerline heaters have shown that Type IIIB surfaces form under conditions expected in long term geologic repositories.[41,42] The presence of metallic overpack interfaces such as Pb, Ti, or Cu, accelerate formation of the multiple layers apparently due to high surface area to solution volume ratios which lead to rapid precipitation of insoluble metallic compounds.[42]

Summary

Type IIIB, multiple barrier surfaces constitute an important new class of glass surface reactions. A number of alkali borosilicate nuclear waste glasses that exhibit Type IIIB surface behavior have elemental leach rates as low as 0.02 to 0.2 g/m^2/day with a time dependence of static leaching of $t^{0.5}$ to $t^{0.2}$ or less after 28 days at 90°C. A discussion of the variables controlling formation of Type IIIB surfaces follows.

Although a short (several days) period of alkali-hydrogen ion exchange may occur for IIIB glasses, the dominant, long term mechanisms controlling corrosion is a combination of matrix dissolution followed by incongruent dissolution and solution/precipitation reactions. The extent of matrix dissolution and onset of surface precipitation will depend on the time required for various species in the glass to reach saturation in solution. Saturation of species (i) will be a function of the initial solution pH, amount of alkali in the glass and rate of alkali release, temperature, initial concentration of species (i) in the solution, SA/V which influences solution concentration, or flow rate which also affects solution concentration. Until saturation of some species in solution is reached, the glass dissolves congruently at a rate proportional to kt^1.

When solution saturation of species (i) is reached there is no longer any driving force for that species to leave the glass surface. Consequently species (i) will accumulate at the glass-solution interface as the matrix dissolves, leaving species (i) behind in the glass. If the matrix dissolution releases alkali ions, as will be the case for most glasses, there will be a concomitant rise in pH proportional to the flow rate or SA/V of the system. An increase in pH can have several simultaneous effects on the glass, the solution, and the glass-solution interface. At the new pH, a second species (j) may reach solution saturation and subsequently be retained in the glass surface along with species (i) The extent of incongruent dissolution of the glass is thereby increased. In addition, the pH can have either one of

three effects on species (i), previously in saturation; 1) it remains saturated but at a higher concentration; 2) it becomes supersaturated and precipitates either on the glass or other surface or as a colloid; or 3) it becomes undersaturated and species (i) in the glass surface once again begins to be released. The sequence of events that occurs is predictable based upon the solubility limits of each species at a given pH, as shown by Grambow[28] Figure 5, based upon Grambow's work, shows that the $Fe(OH)_3$ solubility limit should be exeeded over a broad range of pH and therefore nuclear waste glasses containing Fe oxides should concentrate Fe within surface layers. Zinc, Nd, Sr, and Ca should be concentrated as well in nearly neutral or slightly alkaline solutions with Na and B depleted. Figures 6 and 7 obtained by electron microprobe analysis and AES profiling of corroded nuclear waste glasses,[29,38] shows the concentration of Fe (Fig. 6) and other heavy metal species (Fig. 7) in the glass surface. Many other studies confirm the prediction of solubility limited surface layers.[11,29-31,36-42]

A consequence of the formation of the multiple barrier, IIIB films is low overall leachability of many nuclear waste glasses over a pH range from 4.5 to 9.5. Figure 5 superimposes a plot of Si leachability from a Savannah River Lab composite waste glass immersed in a 5 day static 23°C solution buffered to various pH values from 3.5 to 10.7. Wicks[43] data shows that over the pH range expected for repository ground waters,[43] shown by arrows, glass leachability is lowest. Thus, we can conclude that the solubility limits that establish the equilibrium ionic concentrations for the ground waters should also establish the multiple barrier films to protect nuclear waste glasses in contact with those ground waters.

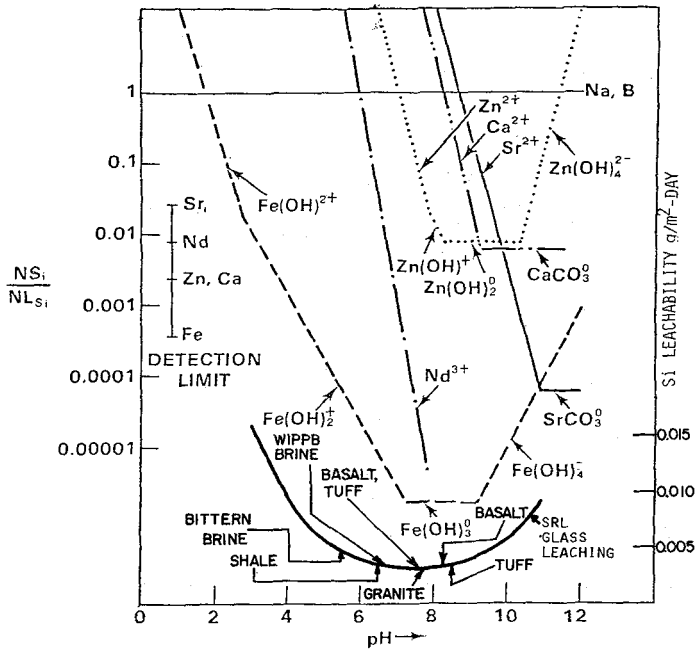
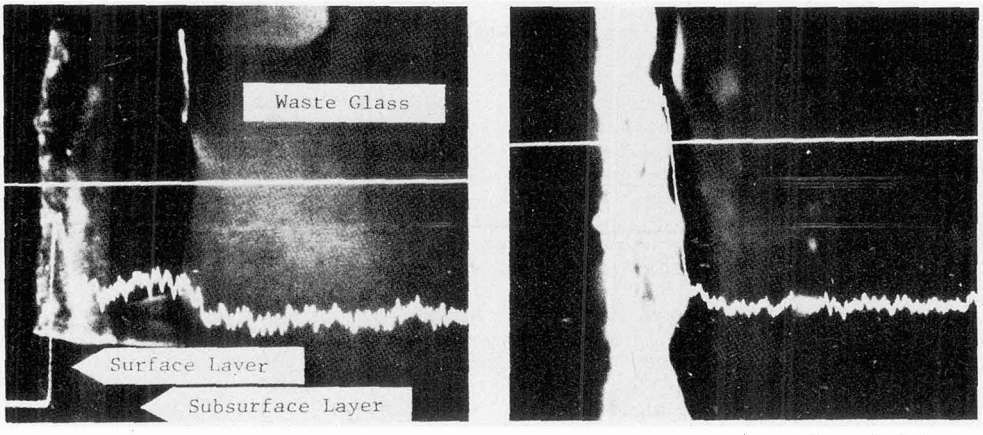


Fig. 5. Correlation between solubility limits of nuclear waste glass surface reaction products and 23°C glass leach rates in different pH solutions.



20 wt% Waste 5 μm

L (mass loss) = 1.19 g/(m^2-day)

30 wt% Waste 2 μm

L (mass loss) = 0.51 g/(m^2-day)

Cross sections of leached layers for 20% and 30% waste loaded glasses with x-ray line profiles of waste constituent Fe.

Fig. 6. Fe concentration in leached nuclear waste glass surface layers.

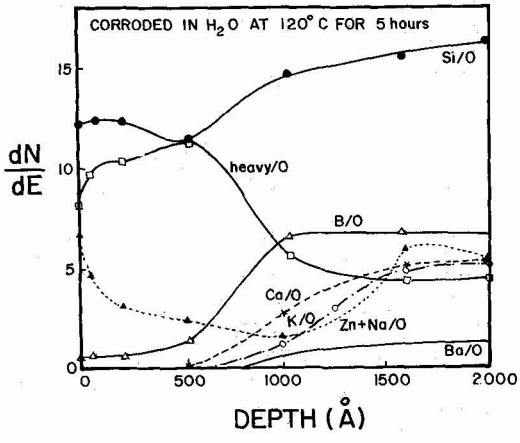


Fig. 7. Surface chemical composition profiles of a leached nuclear waste glass.

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