HYDROLYSIS OF R7T7 NUCLEAR WASTE GLASS IN DILUTE MEDIA: MECHANISMS AND RATE AS A FUNCTION OF pH

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ABSTRACT

R7T7 nuclear waste glass dissolution in highly dilute aqueous media under static conditions at 90°C occurs according to two different mechanisms depending on the solution acidity. In acid media (pH 4.8 and 5.5), preferential extraction of glass network modifiers results in the formation of an alkali metal-depleted surface region on which amorphous and crystallized (phosphate) compounds rich in transition elements precipitate. Steady-state dissolution conditions are not reached, as attested by variable normalized Si, B and Na mass losses. Glass dissolution is stoichiometric in basic media (pH 7 to 10): the strong bonds of the silicated network are broken at a rate that increases with the pH: the glass dissolution rate increases by a factor of 15 between pH 7 and 10. Under these conditions, alteration products at the glass/solution interface do not constitute a short-term kinetic barrier against the release of the major glass components.

INTRODUCTION

The development of predictive models for the geochemical interactions occurring within a geological repository for vitrified nuclear waste is one of the major goals for the next decade. A prior objective is laboratory-scale characterization of nuclear glass corrosion processes and kinetics to define the critical chemical parameters, the optimum radionuclide containment media, and the general physical and chemical laws.

The results of an experimental study in dilute media at 90°C demonstrate the important effect of the acidity of the aqueous solution on the nature of the alteration mechanism and on the corrosion rate of nuclear waste glass. Specific experimental protocols were required to identify this phenomenon, which has been widely observed and analyzed on natural silicates: dilute aqueous media subsaturated with regard to the reactant and to secondary alteration products, pH maintained constant at specified values, qualification of the reactant surface condition, coordinated analysis of the solution chemistry and reactant surface.

The experimental release rates for the principal glass matrix elements are interpreted from the standpoint of irreversible thermodynamic processes. The mathematical formalism developed by this theory is capable of describing pH-dependent variations in the corrosion rate.

EXPERIMENTAL PROTOCOLS

The experiments were conducted with "R7T7" borosilicate glass (refer to Pac ud et al.[1] for the detailed glass composition) in the form of thin rectangular prisms wet-polished w h No. 4000 silicon carbide. This glass is currently manufactured on an industrial basis. The specimens were then cleaned ultrasonically in ethanc' followed by distilled water to eliminate any particles adher ng to the polished surfaces. The 1000-cm³ "Savillex" test cells and the perforated baskets supporting tl glass slides were made of teflon. The glass surface area to solution volume (SA/V) ratio was 10 m⁻¹.

The initial pure water solutions were obtained using a Millipore MilliQ-plus system. Microquantities of a strong base (0.1M KOH) were added to obtain pH values of 7, 8, 9 and 10. Acid media were investigated with 0.25% and 0.05% KH_2PO_4 solutions to obtain pH values of 4.8 and 5.5, respectively. Control experiments were conducted using pure water, without maintaining a constant pH.

The test duration depended on the pH, ranging from a few hours in highly basic media to three weeks in neutral or slightly acid media. The objective was to maintain dilution conditions in which the glass corrosion rate was unaffected by saturation phenomena. Twelve 5 ml alteration solution samples
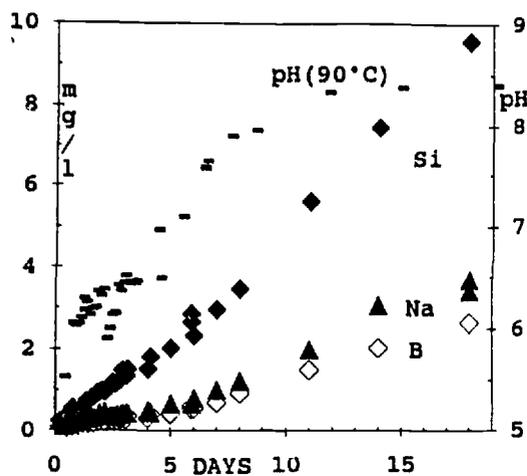
Figure 1a. Evolution of Si, B and Na
concentrations and pH during dissolution
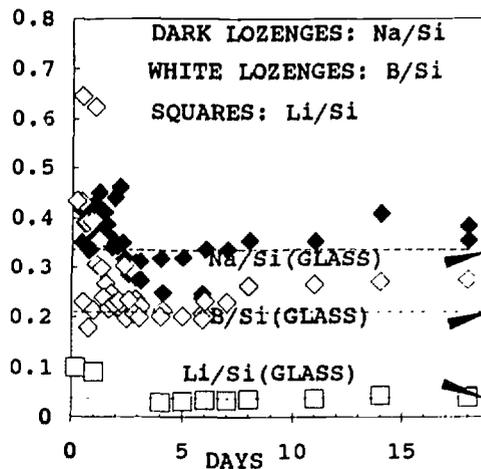of R7T7 glass in water at 90°C

Figure 1b. Evolution of Na, B and Li/Si
congruence ratios in solution at 90°C:
selective then stoichiometric dissolution

were averaged at regular intervals for each leaching cell. The resulting solution volume reduction did not exceed 7% of the initial cell volume at the end of each experiment.

Inductively coupled plasma (ICP) spectrometry was used to determine Si, B, Na, Li, Ca, Zn and Al. The solution pH was routinely measured at 90°C after each leachate sample was taken, and was adjusted if necessary to the initial value (the measurement error margin was on the order of 0.05 pH unit).

Ultramicrotome sections 500 Å thick[2] were prepared from the alteration layer for transmission electron microscope (TEM) observation (Philips EM 300 and EM 400). The resulting structural and textural data were completed by semiquantitative chemical microanalysis by energy-dispersive X-ray emission spectrometry (EDXS) on 100 nm^2 microregions or 10 nm dia spots using a Tracor 5420 device coupled with a JEOL 2000FX scanning transmission electron microscope (STEM).

RESULTS

Experiments in Initially Pure Water without Imposed pH Values

Three experiments were conducted simultaneously to monitor the glass-water system evolution over an 18-day period (Figure 1). The Si, B and Na concentrations in solution varied in a virtually linear manner, with a sharp change in slope after 6 days. The pH at 90°C rose from 5.5 initially to stabilize at 8.4 after 11 days (Figure 1a). During the first 3 days the Na/Si, B/Si and Li/Si congruence ratios in solution were higher than the corresponding ratios in the glass, indicating preferential extraction of the glass network modifiers Na, Li and Ca (not shown in the figure) and boron, although the latter is considered a network former (Figure 1b). During the next stage the ratios in solution tended to approach the ratios in the glass: dissolution was then stoichiometric. After 8 days, the B/Si and Na/Si congruence ratios rose again in solution above the glass values.

The glass corrosion rate (i.e. the normalized mass loss leach rate for an element relative to its concentration in the glass) between 3 and 6 days was 0.18 g·m^{-2}d^{-1} (±0.02). After 6 days the corrosion rate rose slightly to 0.3 g·m^{-2}d^{-1} (±0.02). TEM ob ervation of the alteration film on a glass mono ,th altered for 6 days (Plates 1a and 1b) revealed a granular texture in which the darker regions diffracted the electron beam (lines at 2.94 Å, 2.37 Å, 2.17 Å, 1.70 Å and 1.44 Å). The interface between the sound glass and the alteration film was clearly defined. The thickness of the film ranged from 0.08 to 0.15 μm, or only a third of the equivalent boron thickness (Plate 1a). Semiquantitative analysis (Table I) showed significant enrichment in phosphorus and metals: Fe, Zr, Al and Nd (the

Table I. Mean Values of 8 STEM Analyses of the Alteration Film after 6 Days in an Aqueous Medium without Imposed pH

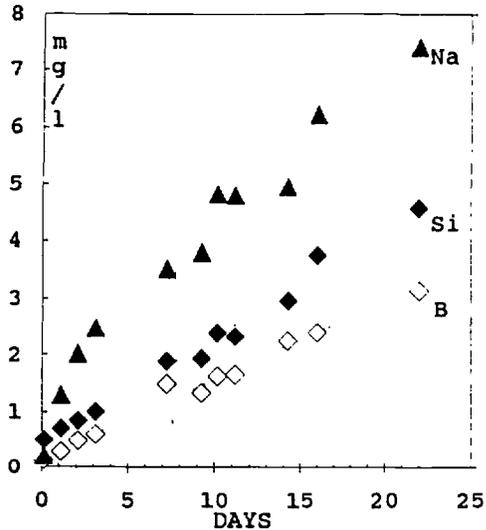| Ratios	Glass	Film	Std Dev
Fe/Si	0.10	2.09	0.98
Zr/Si	0.09	2.90	0.43
P/Si	0.08	1.59	0.26
Nd/Si	0.06	1.90	0.37
Al/Si	0.12	0.26	0.28
Oxide (wt%)		Film	std Dev
SiO$_2$		14.16	2.04
Fe$_2$O$_3$		18.99	7.13
ZrO$_2$		25.74	4.41
P$_2$O$_5$		23.68	2.52
Nd$_2$O$_3$		14.50	2.46
Al$_2$O$_3$		2.92	2.90
Total		100.00	

Figure 2a. Evolution of Si, B and Na
concentrations during corrosion of R7T7 glass
in water at 90°C at pH 4.8

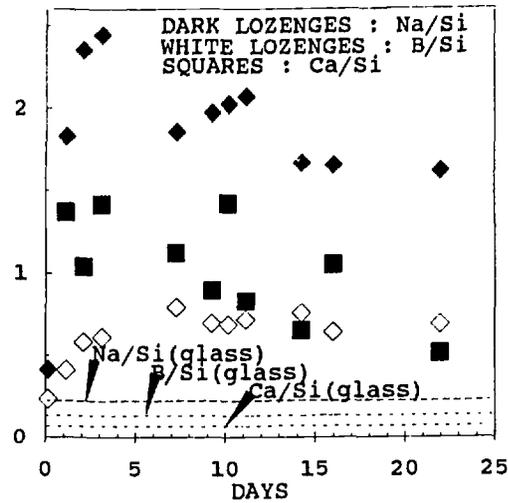

Figure 2b. Evolution of Na, B and Ca/Si
congruence ratios in solution at pH 4.8:
selective dissolution

latter including all the rare earths).The silica concentration did not exceed 14% of the oxide mass.

Experiments in Acid Media

In an acid medium at an imposed pH of 4.8, sodium was the dominant element in solution (Figure 2a). The initial evolution appeared to be parabolic, then linear. The silicon and boron concentration variations were linear virtually throughout the entire time period investigated. The congruence ratios were much higher than in the glass (Figure 2b), indicating preferential release of glass network modifiers and boron. Moreover, they appeared to approach constant values for the longer-duration experiments. The normalized mass losses were 0.08 $g \cdot m^{-2}d^{-1}$ (± 0.005) for silicon, 0.30 $g \cdot m^{-2}d^{-1}$ (± 0.02) for boron and 0.39 $g \cdot m^{-2}d^{-1}$ (± 0.02) for sodium.

Similar results were observed in a medium with an imposed pH of 5.5 over the same time period: the congruence ratios showed preferential extraction of the alkali metals and boron compared with silicon although the virtually steady-state ratios noted in solution were lower than for the experiment at pH 4.8: Na/Si = 0.8; B/Si = 0.45; Ca/Si = 0.35. The normalized mass losses at pH 5.5 were 0.17 $g \cdot m^{-2}d^{-1}$ (± 0.02) for silicon, 0.31 $g \cdot m^{-2}d^{-1}$ (± 0.03) for boron and 0.43 $g \cdot m^{-2}d^{-1}$ (± 0.03) for sodium.

SEM observation of the alteration film that developed on the surface of a glass specimen altered for 22 days at pH 4.8 (Plate 2a) showed a fibrous, highly contrasted outer layer 0.2 μm thick (Plate 2a position A) with scattered crystallized microregions (2.70 Å and 2.07 Å lines but not in sufficient quantities to identify the mineral) as well as a completely amorphous zone 0.6 μm thick with a relatively uniform texture (Plate 2a positions B, C and D). The interface with the glass splinters was clearly visible.

Chemical analyses were performed along a profile inward from the outer layer at an average of five points per level (Plate 2b). The outer layer (A) consisted essentially of phosphorus and metals (Al, Fe, Zn and Zr by order of decreasing abundance). The amorphous material (B, C and D) towards the interior differed from the outer layer primarily by a higher Zr content and extremely low Nd concentrations. (Note that the phosphorus concentrations re overestimated when zirconium is present: the zirconium lines are very close to the phosphorus K nes.) The silica content of the alteration film was low, about ·% of the oxide mass. The absence of a lica concentration gradient is worth noting: the alteration p duct was chemically relatively homogene s.

Analysis of the glass splinter showed that sodium and calcium were absent, and reveal the presence of 3 wt% of potassium: this element is not an R7T7 glass component, but was present n the 0.25% KH_2PO_4 solution. Potassium was observed throughout the thickness of the ultrathin section (1.2 μm). The silica content (about 70% compared with 45.48% in the sound glass) and the metal concentrations were appreciably higher than in the unaltered glass.

Experiments in Basic Media

Experiments under alkaline conditions were conducted at pH values ranging from 7 to 10. Figure 3a shows the evolution of the Si, B and Na concentrations over a 20-hour period at pH 10: the variations were linear throughout the experimental range. The congruence ratios showed stoichiometric
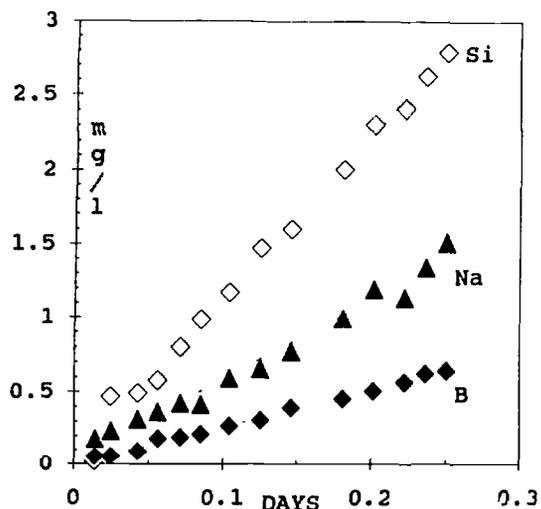
Figure 3a. Evolution of Si, B and Na
concentrations during dissolution of R7T7 glass
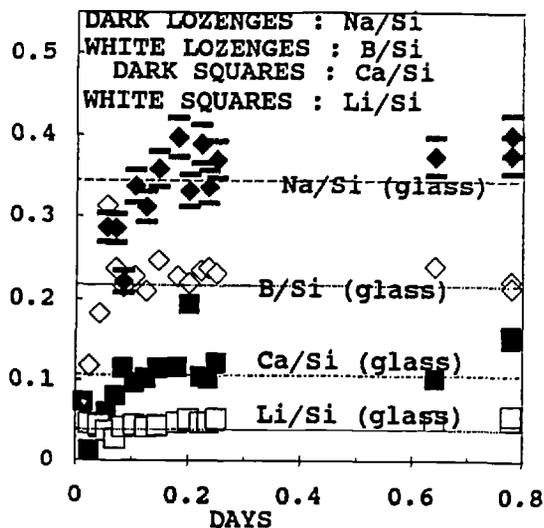in water at 90°C at pH 10

Figure 3b. Evolution of Na, B, Ca and Li/Si
congruence ratios in solution at pH 10:
stoichiometric dissolution

leaching of all the elements from the glass from the outset (Figure 3b). The normalized Si, B and Na mass loss values were all equal to 3.8 $g \cdot m^{-2} d^{-1}$. Observations at pH 7, 8 and 9 showed a similar evolution of the congruence ratios in solution: in all three cases, the Na/Si, B/Si, Ca/Si and Li/Si ratios were equal to the corresponding ratios in the glass from the outset. However, the glass corrosion rate systematically diminished as the pH dropped from 10 to 7: the normalized boron mass loss values (identical with the Na and Si mass losses) were 2.77 $g \cdot m^{-2} d^{-1}$ at pH 9, 0.78 $g \cdot m^{-2} d^{-1}$ at pH 8 and 0.36 $g \cdot m^{-2} d^{-1}$ at pH 7.

TEM examination of the alteration film that developed at pH 10 (Plate 3a) revealed an outer layer 0.1 to 0.15 μm thick (A) comprising filaments for which electron microdiffraction images were obtained at the 2.52 Å, 2.03 Å and 1.46 Å lines. The underlying totally amorphous layer (B) was relatively homogeneous throughout the cross section, and reached a thickness of 0.5 μm. No contact with the glass was visible in this section. The total observed thickness was 0.6 μm, compared with a dissolved glass thickness of 1.1 μm determined from the Si, B and Na release.

Chemical microanalysis indicated significant Ni, Fe and Mn enrichment of the crystallized fibers on the outer edge of the alteration layer (Plate 3b). Conversely, the amorphous material was considerably richer in ZrO_2 and Nd_2O_3 with an appreciably higher silica concentration. (The actual ZrO_2 concentration was probably higher than the stated value, and the P_2O_5 concentration accordingly lower.)

DISCUSSION

Nature of the Corrosion Mechanism

The experiments conducted in distilled water indicate a transition from selective dissolution to stoichiometric dissolution of the glass as the pH rises above 6.2. The progressive exchange of alkali metal ions (elements with the weakest bonds to the glass network) and boron ions from the glass with protons from the solution caused the pH to ris :, favoring the dissociation of strong Si-O-Si bonds. This hypothesis was confirmed by the experiments t imposed pH values.

In acid media, the congruence ratios in olution indicate the persistence of a selective dissolution mechanism over a 3-week period. Semiquan! ative STEM analysis of the glass showed an absence of sodium, a low calcium content and especially 1e presence of potassium from the solution to a depth of at least 1.2 μm in the glass (the length of the gl ss splinters analyzed: Plate 2). The equivalent dissolved glass thicknesses were 3.5 μm for Na and 2.8 μm for Ca, suggesting that the modified glass thickness is not only significant but variable for different elements. Potassium from the aqueous solution migrated into the glass, and proved to be an effective tracer of chemical modifications in the glass due to ion exchange; these modifications would probably have gone unnoticed otherwise, since nothing in the TEM image discriminates between modified glass and sound glass.

The mass ratios of various elements to silicon for the nominal R7T7 glass composition are compared in Table II with the mass ratios of the mean composition of the glass corroded in acid conditions as analyzed by STEM examination. The same trends may be observed: most of the "metal/silicon" mass ratios for glass corroded at pH 4.8 are comparable to the values for sound glass,

indicating the relative immobility of the glass network formers. In terms of the concentrations, for example expressed as an oxide weight percentage, glass modified by selective dissolution should be characterized in particular by an SiO_2 concentration higher than the sound glass (i.e. > 45.48 wt%); the same is true for insoluble elements such as the metals (Plate 2b).

Table II. Element Mass Ratios with Silicon for R7T7 Glass and Glass Altered in Acid Medium
(Average of 7 STEM Analyses)

	Fe/Si	Al/Si	K/Si	P/Si	Ca/Si	Nd/Si	Zn/Si	Zr/Si	Na/Si
R7T7 glass	0.096	0.13	0	0.004	0.136	0.064	0.094	0.092	0.304
Modified glass	0.080	0.131	0.066	0.045	0.007	0.064	0.011	0.080	0
Std Deviation	0.002	0.009	0.013	0.003	0.001	0.004	0.003	0.003	-

The nature of the corrosion mechanism changes in alkaline media: stoichiometric dissolution is observed from the outset. This reaction is augmented by the presence of OH^- ions[3] that favor the dissociation of strong bonds in the glass network. Under these conditions, all the elements are released in quantities proportional to the glass composition.

The rapid formation of a surface alteration layer consisting mainly of metallic elements reflects their low solubility limits. The crystallized structures and semiquantitative chemical compositions of the amorphous material indicate extensive glass structural modifications. Transmission electron microscope observations supplemented the solution analysis results: the amorphous surface layer that developed in an alkaline medium at pH 10 containing 10–20 wt% of silicon dioxide (Plate 3b) is not a modified glass in the sense the term was defined for an acid medium   . This phenomenon was generally observed in basic media, at pH 7, 8, 9 and 10. Although silica was present in all the alteration films formed under alkaline conditions, it did not appear to affect the glass corrosion kinetics: the concentrations of the major elements such as Si, B and Na increased linearly in time. In the short term, the alteration films do not constitute diffusion barriers.

The initial objective was therefore met under the experimental conditions: to interpret the evolution of the major elements in terms of the glass corrosion kinetics, excluding any secondary phenomena liable to interfere with the solution chemistry (silicate precipitations imposing steady-state silica conditions in solution, retarding the dissolution of species by diffusion in the alteration films).

It is important to note the similarity between the corrosion mechanisms of R7T7 glass and basaltic glass[4,5] and many silicated minerals[6,7,8]: dissolution is generally selective in acid media and stoichiometric in alkaline media. Nevertheless, diffusion exchange such as clearly revealed in acid media in these experiments is not necessarily absent in alkaline media; in the latter case, however, it is not a limiting mechanism, and does not affect the mass transfer balance.

Corrosion Kinetics: pH-Dependence of the Corrosion Rate

Figure 4 plots the variation of the glass corrosion rate versus the solution pH. These values were calculated by linear regression from the normalized Si, B and Na mass losses over the experimental time intervals, during which the element concentrations varied in a linear manner. The normalized mass loss is generally expressed in $g \cdot m^{-2} d^{-1}$, but was converted here to $mole \cdot cm^{-2} \cdot s^{-1}$ (molar weight of glass estimated at 69.39 $g \cdot mole^{-1}$), the reference unit reported by Aagard and Helgeson[7].

We attempted to interpret these experimental results in terms of transition state theory, a concept widely discussed during the last decade[8,9,10,11,12]. The proposed general rate equation postulates the existence of activated complexes at the surfa e of the reactant in contact with the aqueous phase: desorption of these complexes controls the r actant corrosion rate (Grambow[12] suggests a purely siliceous composition for the activated comp ex on borosilicate nuclear waste glasses). The rate equation is the following:

$$v_j = dc/dt = S \cdot _j \cdot (a_{H+})^{-n_{j,H+}} \cdot (1 - Q/K) \tag{1}$$

where v_j is the reaction rate of the limiting mechanism (j), k_j the rate constant, S the reactant surface area in contact with the alteration solution, a_{H+} the activity of the protons assigned the stoichiometric coefficient $-n_{j,H+}$. This coefficient allows for the dependence of the glass corrosion rate on the solution pH. In the highly dilute experimental media, the $(1-Q/K)$ term (corresponding to a drop in the corrosion rate v as the solution nears saturation with respect to the glass) is negligible. The preceding relation can therefore be rewritten as:

$$log(v_j) = log(S \cdot k_j) - (n_{j,H+} \cdot pH) \tag{2}$$

The $n_{j,H+}$ coefficient and k_j can then be determined graphically (Figure 4).
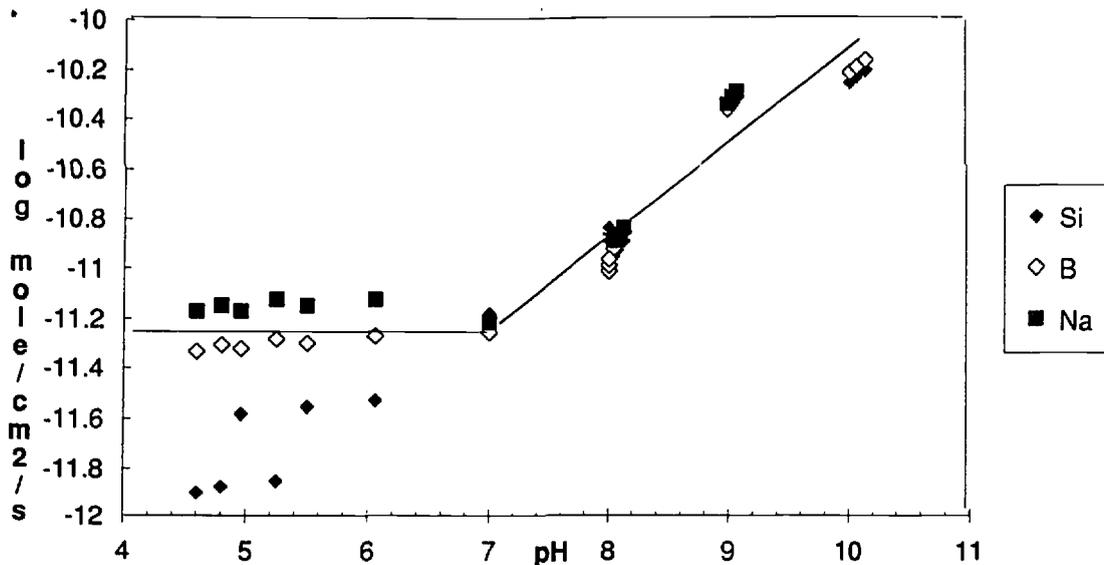
Figure 4. Dissolution rate (or Si, B, and Na normalized mass losses in mole·cm^{-2}s^{-1}) versus solution pH at 90°C

In acid media, alkali metal diffusion phenomena in the modified glass are also accompanied by partial dissolution of the glass from the exterior, since silica is present in solution. After a given time, the glass network modifiers and formers are released into solution at the same rate: the modified glass thickness through which the alkali metals diffuse is then constant. This description did not appear to be applicable to these experiments, however: there was a major discrepancy between the normalized Si mass loss and the normalized Na and B mass losses (Figure 4). Steady-state glass dissolution was not obtained, and the general rate equation (1) cannot be applied. Moreover, between pH 4.8 and 7 the Na and B mass losses were relatively independent of the pH, unlike the Si mass loss. The lower limit of the silicated network dissociation rate between pH 4.8 and 7 is therefore based on the normalized mass loss for Si: $\log(k_j)$ = -13.3 mole·cm^{-2}s^{-1} and n = 0.3. Experiments of longer duration (to identify steady-state dissolution conditions) and allowance for Na, Ca, Li and B diffusion from the glass into solution would be necessary to express the glass corrosion kinetics in acid media over a wider pH range and to develop suitable models. White showed with obsidian glasses that an approach of this type was feasible[13].

In alkaline media the glass dissolution rate increases linearly by a factor of 15 between pH 7 and 10: the slope of the line corresponding to the stoichiometric coefficient is 0.41 (±0.02) and the (logarithmic) kinetic constant is -14.0 mole·cm^{-2}s^{-1}.

CONCLUSION

The water-glass interaction in dilute media under conditions far from saturation with respect to the glass and at controlled pH revealed two corrosion mechanisms:

• In acid media, preferential extraction of the alkali metals assumes interdiffusion exchange with the protons in the leaching solution. The normalized mass losses for the major elements (Si, B and Na) are variable, and reflect the competition between slow dissolution of silicated network formers and leaching of network modifiers and boron. It is surprising that boron is extracted selectively in acid media although it is considered a glass network former: 's this behavior related to the actual boron environment in the glass network, or to the element r(iction mechanism involving aqueous species different from those that attack silica? The pH has little ifluence on the B and Na extraction rate in the acidity range investigated.

• No preferential extraction was observed in alkaline me(a (pH 7-10): glass dissolution was stoichiometric by dissociation of the strong glass network bond: . This mechanism caused the dissolution rate to increase with the pH. The mathematical formalism developed by Aagaard and Helgeson[7] is then applicable: the rate and the pH are related by a stoichiometric coefficient equal to 0.41 for R7T7 glass at 90°C.

Depending on the nature of the corrosion mechanism, two types of alteration film were revealed by TEM and STEM examination:

• A modified glass layer, characterized by the absence of Ca and Na, and by the same "transition element-to-silicon" mass ratios as unaltered R7T7 glass, developed in acid media. Its morphology and texture were the same as for sound glass.

• A compound with a texture fundamentally different from that of glass, rich in transition elements (with "transition element-to-silicon" mass ratios much higher than the unaltered glass) and exhibiting crystallized regions was observed in direct contact with the sound glass in alkaline media, and covering the modified glass in acid media. No silica concentration gradient could be identified in the layer, which was less than 1 μm thick.

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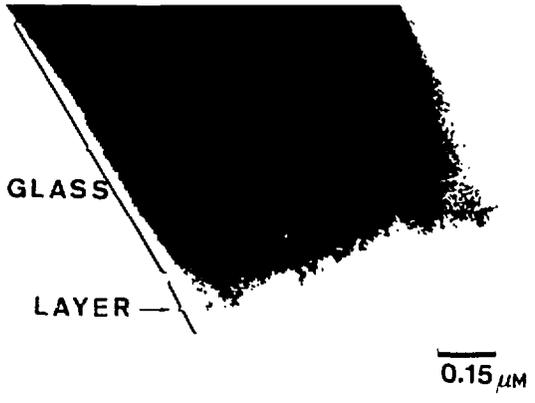
GLASS

LAYER →

0.15 μM

Plate 1.a. Ultrathin section of glass altered for 6 days in distilled water at 90°C at SA/V= 10m-1.

Plate 1.b. Electron diffraction pattern of dark granules (2.94A, 2.73A, 2.17A, 1.70A, 1.44A)

0.4 μM

SOLUTION

GLASS ▽

Plate 2.a : Ultrathin section of glass altered for 22 days in water at pH 4.8. Electron diffraction pattern obtained on external dark layer (2.70A, 2.07A)
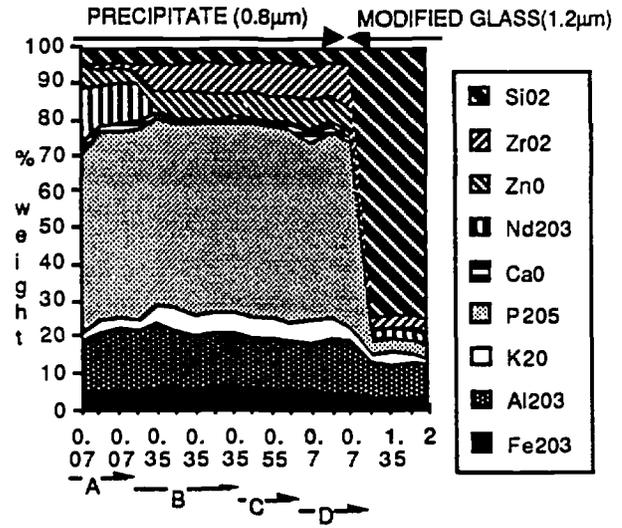

PRECIPITATE (0.8μm)   MODIFIED GLASS(1.2μm)

100
90
80
% 70
w 60
e 50
i 40
g
h 30
t 20
10
0

0. 0. 0. 0. 0. 0. 0. 0. 1. 2
07 07 35 35 35 55 7   7   35

A   B   C   D

■ SiO2
▨ ZrO2
▧ ZnO
▣ Nd2O3
▭ CaO
▨ P2O5
▭ K2O
▨ Al2O3
■ Fe2O3

Plate 2.b : Semiquantitative analysis of glass altered in acid medium for 22 days at pH4.8. " A"," B"," C" and "D" refer to analysis positions in μm (See Plate 2.a for spatial positions on ultrathin section).
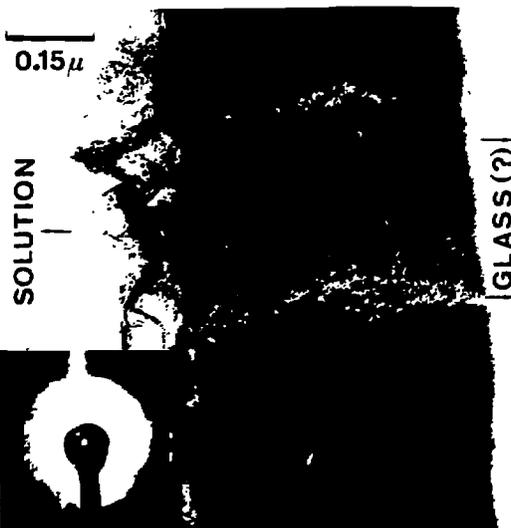

0.15 μ

SOLUTION →   GLASS (?)

Plate 3. a. Ultrathin section of externa l layer of glass altered for 8 hours at pH 10. Outermost fibrous zone is crystallized.

PRECIPITATE (0.65μm)   ← GLASS

100
90
w 80
e 70
i 60
g
h 50
t 40
% 30
20
10
0

0. 0. 0. 0. 0. 0. 0. 0.
02 1   1   26 26 4   65 65

A   B

▭ NiO
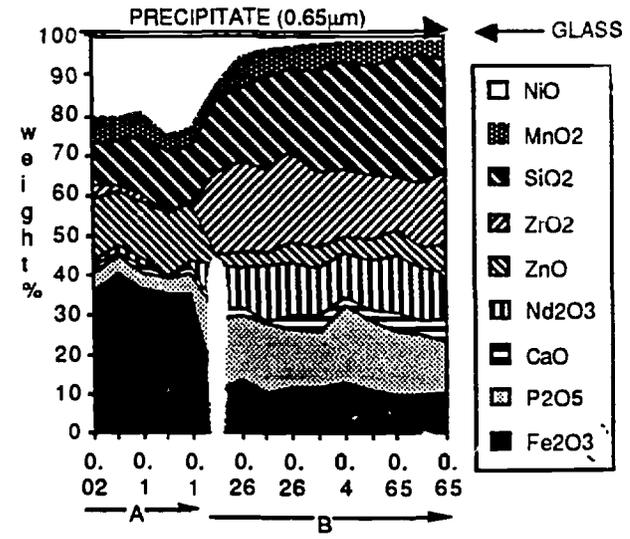▨ MnO2
◪ SiO2
▨ ZrO2
▧ ZnO
▥ Nd2O3
▭ CaO
▨ P2O5
■ Fe2O3

Plate 3.b : Semiquantitative analysis of altered layer (8 hours at pH 10). "A" refers to the crystalline external layer and "B" to the amorphous layer (See Plate 3.a).