

EFFECT OF ALTERATION PHASE FORMATION ON THE GLASS DISSOLUTION RATE

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1 - INTRODUCTION

The dissolution rates of many glasses have been observed to increase upon the formation of certain alteration phases. It is important to understand the mechanism by which alteration phases affect glass corrosion behavior and the glass dissolution rate to reliably predict whether or not similar effects will occur in a disposal environment and the impact of phase formation on the long-term performance of waste glass. While solid state transformation of a glass to thermodynamically more stable phases is kinetically prohibitive, contact by water provides an energetically favorable pathway for this transformation to occur by a dissolution-precipitation mechanism. The kinetics of the transformation depends on the dissolution kinetics of the glass and the precipitation kinetics of the alteration phases. The rates of these two processes are linked primarily through the solution activity of orthosilicic acid (and perhaps also that of an aluminum-bearing species). The effect of phase formation on the glass behavior can be discussed in terms of the rate expression for glass dissolution [1]:

$$\text{rate} = k_0 \cdot 10^{b \cdot \text{pH}} \cdot e^{-E_a/RT} \cdot (1 - (Q/K)^\sigma) \quad (1)$$

where the terms on the right hand side give the dependence of the rate on the glass composition, solution pH, temperature, and solution composition, respectively. The term quantifying the solution composition effect, $(1 - (Q/K)^\sigma)$, is usually referred to as the affinity term. The value of the affinity term is one when the solution does not contain solutes that affect the dissolution reaction and decreases as glass components accumulate in the solution. Phase formation may affect the pH and affinity terms by removing solute and disrupting the quasi-equilibration between the glass and the solution. Since the glass dissolution rate is most strongly affected by silicon and perhaps aluminum in solution, phases that incorporate these elements have the greatest effect on the glass dissolution rate.

The formation of some phases has only a minor effect on the glass dissolution rate. For example, clays form during the corrosion of most high-level waste glasses, but the effect of their formation on the dissolution rate is immeasurably small. This may be because clays form by transformation of leached glass rather than precipitation from a saturated solution [2], or because the clay and the glass have similar solubilities. The formation of other phases may result in a significant increase in the dissolution rate. For some glasses, the dissolution rate may become equal to the forward rate [3]. The effect of phase formation is usually intermediate between these two extremes. While simulations based on the Eq. 1 have predicted the accelerating effect of formation of certain phases [4],

the phases predicted to form in computer simulations are usually different than those observed to form in experiments [5]. This is because kinetically favored phases form first in experiments, while simulations predict the thermodynamically favored phases. Therefore, the identity of the phases and the resulting glass dissolution rate must be measured experimentally.

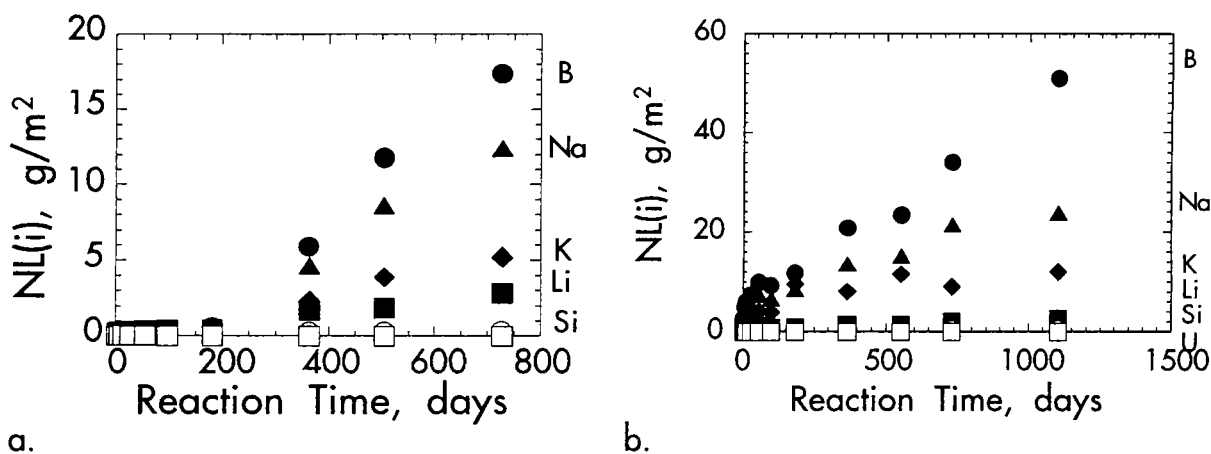
Test results

Static dissolution tests with crushed glass have been used to measure the glass dissolution rate after alteration phases form. The results of tests conducted with several glasses are shown in Fig. 1. The normalized mass loss (NL) values based on various glass components are plotted. The value of NL based on glass component i is calculated as

$$NL(i) = m(i) / (S \cdot f_i) \quad (2)$$

where $m(i)$ is the mass of i in solution, S is the surface area of the glass, and f_i is the mass fraction of i in the glass. Note that the values of $NL(B)$ (which are represented by circles on all plots) are consistently higher than other $NL(i)$ after phases form because B is not incorporated into alteration phases. Tests conducted for different durations show the temporal trend in $NL(B)$ and can be used to calculate the glass dissolution rate, although differences in the time required for alteration phases to nucleate in each test will add uncertainty to the calculated rate. For most high-level waste glasses, the difference in when nucleation occurs in different tests appears to be small, as evidenced by the fact that the data for glasses in Figs. 1a-e follow a smooth trend. In contrast, the time at which phases form is significantly different in tests with the low-level glass LD6-5412. For example, LD6-5412 in the 195-day test was completely altered to zeolite phases, while alteration phases had just recently formed in the 202-day test with that glass. The difference between the behaviors of high- and low-level waste glasses may be due to the fact that clays, which may be nucleating sites in tests with high-level waste glasses, do not form during corrosion of LD6-5412 glass.

The reaction time necessary for an alteration phase to precipitate is related to the rate at which the solution becomes saturated with respect to that phase, which depends on the dissolution rate of the glass. An alteration phase is likely to form after a shorter reaction



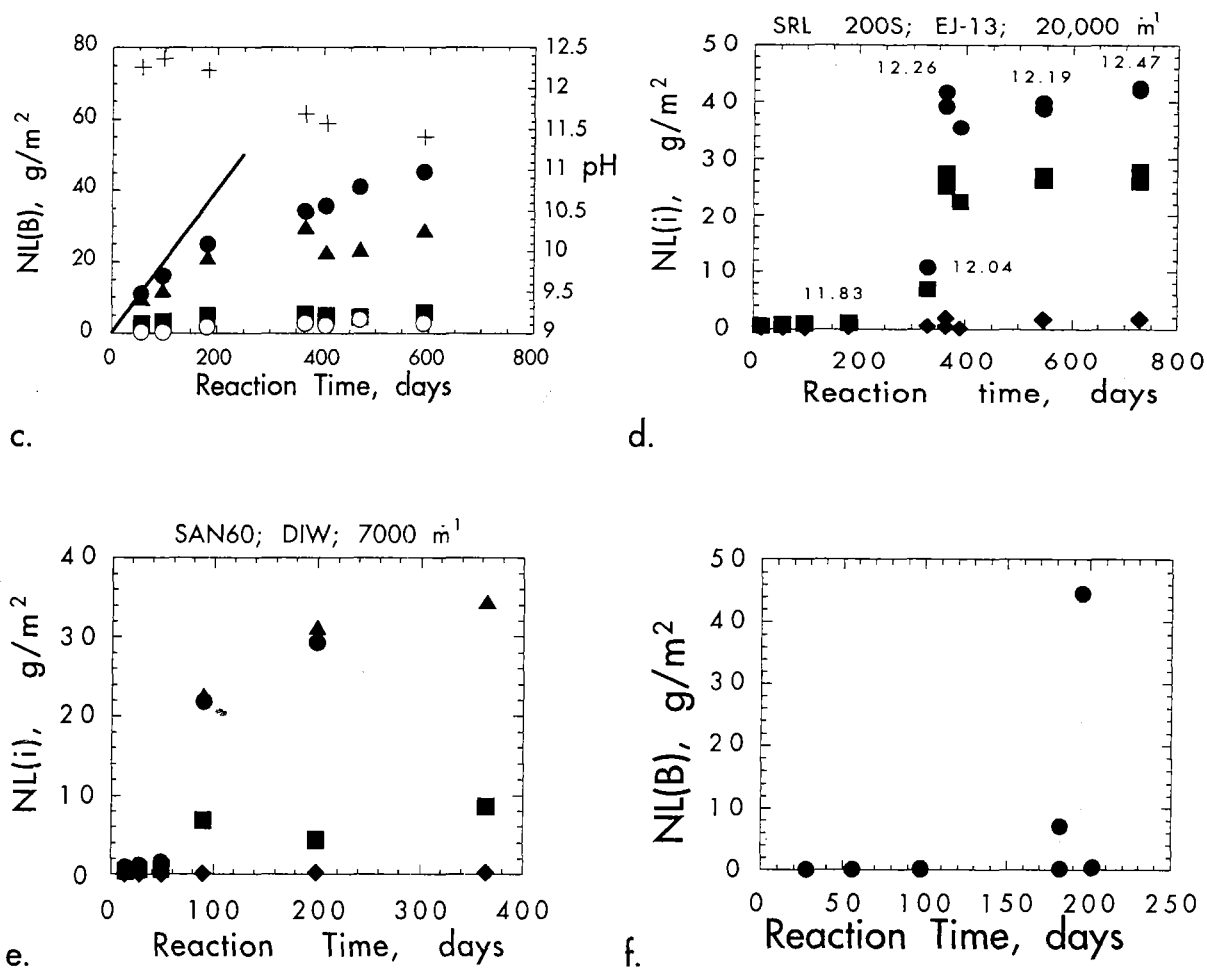


Figure 1: Results of PCTs conducted at 90°C and 20,000 m⁻¹ for extended durations with various glasses: (a) SRL 202A [6], (b) SRL 131A [6], (c) SRL EA [7], (d) SRL 200S [8], (e) SAN60 (7000 m⁻¹) [9], and (f) LD6-5412 [3]. pH values are given for some tests. Dissolution rates increase simultaneously with the formation of zeolite alteration phases.

time in tests with a more reactive glass. Of course, the solution chemistries will differ in tests with glasses having different compositions. For example, the reaction times necessary for zeolites to form increases in the order SRL EA, SRL 131A, SRL 202A, SRL 200S. The reactivities of these glasses, as measured by the values of NL(B) in 7-day Product Consistency Tests (PCTs), decrease in the same order. While the time required for phases to form may be related to the intrinsic glass reactivity, the dissolution rate after phases have formed is not. This is seen by comparing the results of tests with SRL 202A and SRL 200S in Figs. 1a and 1d. The SRL 200S glass is almost completely altered soon after alteration phases form, while the SRL 202A glass dissolves much more slowly than the SRL 200S glass. The difference may be due to the fact that a phase similar to clinoptilolite $\{(Na,K)_6(Al_6Si_{30}O_{72}) \cdot 20H_2O\}$ had formed in tests with SRL 200S glass, while analcime $\{Na_{16}(Al_{16}Si_{32}O_{96}) \cdot 16H_2O\}$ was the predominant phase in tests with SRL 202A. It may be that the formation of clinoptilolite leads to faster glass dissolution than does the formation of analcime because clinoptilolite requires less Al per mole Si consumed than does analcime. The formation of zeolites has been seen to be limited by the availability of Al in the solution (see below).

Accounting for loss of surface area

Because glass dissolution rates are calculated on a per area basis, an important effect in tests conducted with crushed glass is the decrease in the surface area of glass that is available for reaction as the glass dissolves. In fact, the glass in many tests in Fig. 1 has been almost completely altered. (The maximum possible value of $NL(B)$ is 50 g/m^2 for the $-100 +200$ mesh glass when calculated with the initial surface area.) The NL values calculated with the initial surface area and the rates calculated from these data will be too low. The loss of surface area must be taken into account when calculating the dissolution rate.

The decrease in glass surface area leads to a "roll over" in the $NL(B)$ values. This is seen most clearly in the tests with SRL EA glass shown in Fig. 1c. The line shows the average dissolution rate between 0 and 56 days extrapolated to longer times. The $NL(B)$ values fall below this line at long test durations because the surface area is continually decreasing during the test. We have adjusted the results of tests with several glasses to determine if the decrease can be attributed solely to the loss of surface area [10]. The $NL(B)$ values were corrected for the decrease in surface area by calculating the surface area remaining after each test duration from the measured boron concentration and modeling the particles as shrinking spheres. We then normalized the adjusted rate for each glass to the dissolution rate immediately after the rate-affecting phases formed and the reaction time needed for the phases to form. The resulting normalized plot is shown in Fig. 2. The symbols give the adjusted experimental values of $NL(B)$ and the curve gives the theoretical value of $NL(B)$ if the glass continued to dissolve at the rate measured immediately after the phases form. The curve shows the net effect of an increasing numerator, $m(B)$, and a decreasing denominator, S , in the calculation of $NL(B)$ in Eq. 2. While the data agree with the curve soon after rate-affecting phases form, they clearly deviate negatively as more glass dissolves. This indicates that the glass dissolution rate is decreasing with time due to the effect of some process besides the loss of reactive surface area, which may be the precipitation of the alteration phases, mass transfer of material through the building surface layers on the glass particles, or some other process.

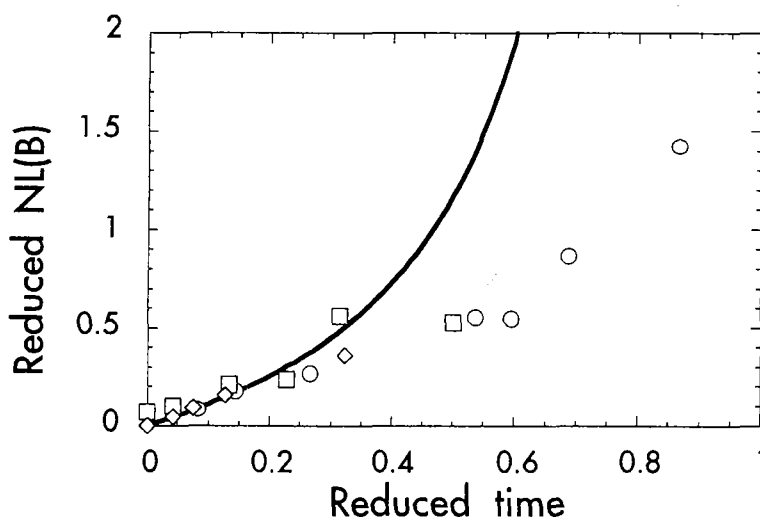


Figure 2: Comparison of Measured and Predicted Long-Term $NL(B)$, Taking into Decrease in Surface Area. Data from PCT at 90°C and $20,000 \text{ m}^{-1}$ with SRL EA (circles), SRL 202A (diamonds), and SRL 131A (squares) glasses. from [10]

Tests with the SRL EA glass have also been conducted with two particle sizes: -100 +200 mesh and -200 +325 mesh. The dissolution rates measured with the two particle sizes are the same, within experimental uncertainty. In all cases, the particle sizes are significantly larger than those for which the dissolution rate increases due to geometry, except when the glass is almost completely dissolved.

Effect of Composition

The phases that form and their effect on the dissolution rate are probably related to the glass composition. While resumption of a high dissolution rate has been observed to occur for many glasses, it has not been observed to occur in tests with all glasses. This may be because either the alteration phases responsible for the increased rate have not formed in those tests or the effect of their formation on glass dissolution is too small to measure. In most systems, the leachate chemistry is dominated by dissolved glass components. Therefore, the alteration phases that may form depend on the glass composition. The impact of phase formation on the glass dissolution rate also varies according to the solubility products of the alteration phases and how the orthosilicic acid activity (and, perhaps, the activity of other solutes) is affected.

Vapor hydration tests (VHTs) have been used to promote of the formation of alteration phases and qualitatively assess their effects on the glass dissolution rate. These tests are conducted at high temperatures, and phases form after much shorter reaction times than in hydrothermal tests. The VHTs have shown that the propensity of a glass to form rate-affecting alteration phases is not related to its reactivity in such short-term tests as MCC-1, PCT, Soxhlet, etc. For example, the glass PNL 76-68 is more reactive than most waste glasses as measured in MCC-1 and PCTs, but alteration phases do not form in VHTs with PNL 76-68 glass except when conducted at 240°C [11]. Likewise, the dissolution behavior of R7T7 is similar to other glasses in most tests, but alteration phases formed only in VHTs conducted at 200°C for long reaction times, and the dissolution rate of R7T7 did not increase significantly after formation of alteration phases. While the effect of glass composition on the tendency to form rate-affecting alteration phases is not fully understood, the amount of Al in a glass appears to affect phase formation and the propensity for accelerated dissolution. The PNL 76-68 glass has an Al concentration of only 0.6 mass %, which severely limits the amount of zeolite that can form. The Ca content of a glass has shown a similar effect. In VHTs conducted at 150°C with a series of glasses, alteration phases formed in tests with glass that contained Ca (all had 4 mass % CaO or more) and the glasses were completely corroded in about 28 days. However, glass without Ca did not corrode to a significant extent over the 28-day period [12]. The role a particular glass component plays in alteration phase formation should be considered when formulating waste glasses.

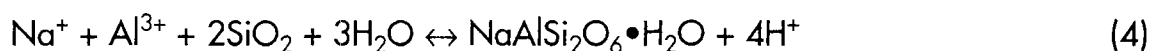
The mechanism by which phase formation affects the glass dissolution rate remains uncertain. However, the effect has been successfully modeled by determining if formation of the alteration phases consumes the surrogate for the glass based on phase

stability fields [13]. It may be possible to determine the extent to which an alteration phase affects the glass dissolution rate by comparing the relative thermodynamic stability of the assemblage of alteration phases and the glass surrogate. Obviously, the choice of a surrogate for the glass will be important in such an analysis.

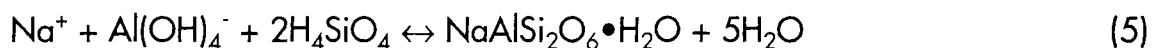
A simplified example of this approach is outlined below. Dissolution of the glass is usually modeled by the reaction



The formation of analcime (a common alteration product in tests with waste glasses) can be written as



or



The dissolution of the glass and the formation of analcime are linked by the solution activity of orthosilicic acid in the dissolution-precipitation mechanism. Dissolution of the glass to provide Na^+ and Al(OH)_4^- will also affect the formation of analcime. Formation of analcime depends on the activities of Na^+ , Al(OH)_4^- , and H_4SiO_4 and the solution pH. How much glass must dissolve before analcime forms will depend on the glass composition. Of course, actual systems are further complicated by the formation of other phases, possible nonstoichiometric dissolution due to ion exchange, etc.

Accelerated Dissolution Test

Insight into the relationship between the glass dissolution rate, solution chemistry, and alteration phase formation is provided by the results of accelerated dissolution tests (ADTs) [3]. These tests were conducted by sealing in a vessel (1) a fresh monolithic sample, (2) a sample that had been vapor-hydrated to generate alteration phases, and (3) the leachate from a PCT that was conducted at $20,000 \text{ m}^{-1}$ for 21 days at 90°C . These were reacted at 90°C . The vessel was opened periodically to measure the mass of the fresh monolith and take an aliquot of the solution for analysis. Solution results are plotted in Fig. 3. The dotted lines mark the concentrations in the leachant. The concentrations of B, Na, and Si increase with the reaction time, while the Al concentrations in all but one test are significantly less than the starting concentrations. The growth of the zeolite alteration phases in these tests may be limited by the availability of aluminum. This, in turn, limits the consumption of silica by the phases and the effect on the glass dissolution rate. The importance of aluminum with regard to glass dissolution in solutions with high silicon contents has recently been demonstrated in flow-through experiments [14]. These results indicate that the affinity term in Eq. 1 may require modification to include an Al species.

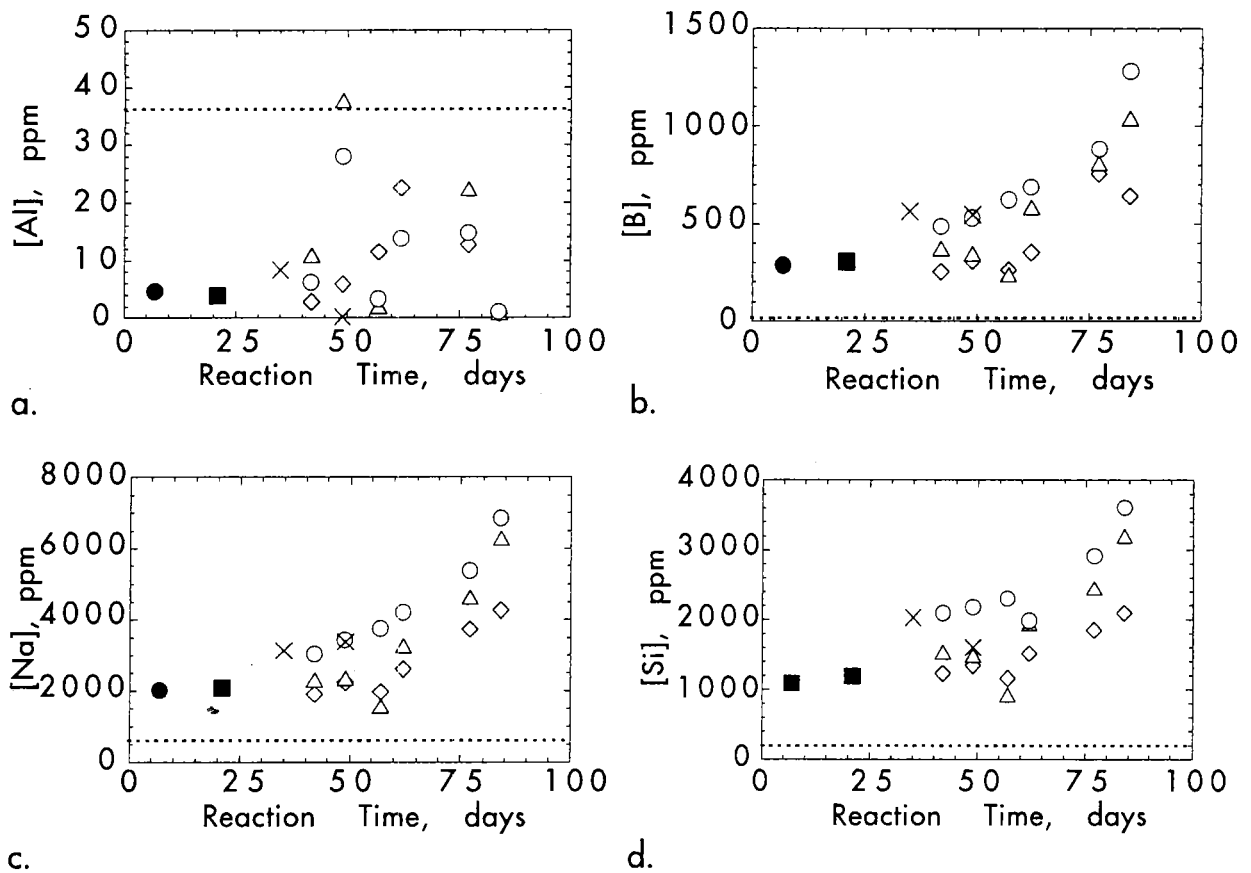


Figure 3: Measured Concentrations in ADTs vs. Reaction Time for (a) Aluminum, (b) Boron, (c) Sodium, and (d) Silicon. Tests 6 (●), 7 (■), 8 (x), 9 (q), and 10 (o). Crosses (X) give concentrations measured in leachant + vapor-hydrated disk control tests.

Figure 4 shows the mass loss in blank tests conducted with the fresh monolith sample and the PCT solution (Fig. 4a) and three replicate ADTs (Fig. 4b). The mass losses in the blank tests are negligible. The rates of mass loss in the three ADTs are very similar after an incubation period. The phenomenon responsible for the incubation period is not fully understood but may be related to interactions between the alteration phases and the solution that occur preferentially to dissolution of the glass. The observation that test 10 had the longest incubation period but generated the most concentrated solutions indicates that the vapor-hydrated sample dissolved to a greater extent in that test than in the other tests. The glass dissolution rate is measured to be $1.4 \pm 0.4 \text{ g}/(\text{m}^2 \cdot \text{d})$, based

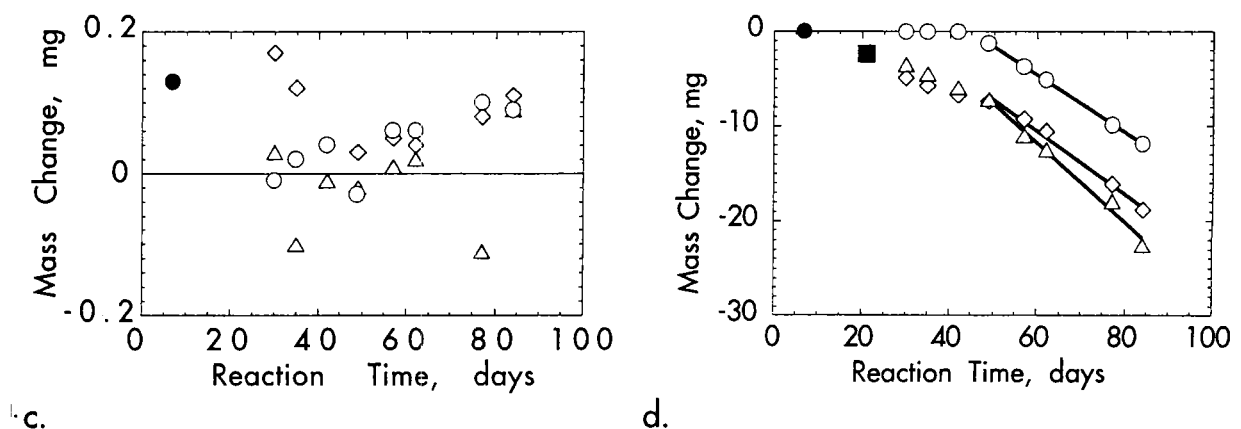


Figure 4: Measured Mass Change of Monolithic Glass Samples vs. Reaction Time for (a) control tests with leachant + glass, [Tests 1 (●), 2 (■), 3 (x), 4 (q), and 5 (o)], and (b) ADTs, [Tests 6 (●), 7 (■), 8 (◊), 9 (q), and 10 (o)]. Regression lines in (b) are shown for 49-84 day intervals.

on the mass loss after the incubation period. The solution pH was about 12 in all tests. The forward rate at the same pH is calculated to be about 2 g/(m²•d) from flow tests [1].

Effect on Actinide Release

Probably the most important consequence of an increased glass dissolution rate is the possible increase in the release of radionuclides. In the few tests that have been conducted with actinide-bearing glasses, most of the actinides released from the glass were contained in solid alteration products, as pseudo-colloids that have settled out of solution, or fixed onto the steel test vessel. For example, Table 1 summarizes the actinide retention factors (RFs) for tests conducted with actinide-containing SRL 202A glass [15]. (The retention factor of an actinide is calculated as $RF(An) = NL(B)/NL(An)$, where An is an actinide.) In these calculations, actinides fixed to the steel test vessel were counted as being released. The retention factors for Np, Pu, and Am increase slowly prior to the formation of rate-affecting phases but increase rapidly after those phases form. The increase in the retention factors is due to the formation of thick clay layers at the glass surface that are depleted of boron and other soluble elements, but not depleted of actinides. The low solubilities of the actinides limit their release into solution both before and after alteration phases form. The solubilities of actinides may be affected by the formation of different solubility-controlling phases. For example, weeksite, which forms during the corrosion of many glasses, may replace a uranium carbonate as the solubility controlling phase at advance stages of corrosion. While the actinide content in the layers is similar to that in the glass, these layers are fragile and may act as a source of colloids under conditions that may occur during disposal, such as contact by dripping water, wet/dry cycles, etc. Rapid glass dissolution results in the formation of fine-grained clay crystallites that may be more susceptible to spallation.

Table 1. Actinide Retention Factors for Tests with SRL 202A Glass at 20,000 m⁻¹.

Time, days	NL(B)	RF(Np)	RF(Pu)	RF(Am)
before rate-affecting phases formed				
14	0.20	0.12	1.9	3.6
28	0.24	0.70	3.8	5.3
56	0.31	1.2	13	14
98	0.38	1.7	14	17
182	0.53	2.3	18	19
after rate-affecting phases formed				
364	5.2	9.0	120	160
504	12	28	400	360
728	18	54	180	210

Summary- The formation of certain alteration phases has been observed to increase the dissolution rates of some glasses. Very aggressive test conditions of temperature and/or glass surface to volume ratio are usually required to promote phase formation

within an experimentally accessible time frame. The glass behavior under such conditions in laboratory tests remains to be linked with glass behavior in a disposal site to reliably predict if an acceleration of the dissolution rate can occur under disposal conditions. The highly concentrated solutions usually present when alteration phases form complicate the determination of the mechanism by which phase formation affects the glass dissolution rate and the glass dissolution and precipitation kinetics. In addition, variations in the nucleation of alteration phases from test to test and the loss of surface area as the glass dissolves add to the uncertainty when measuring the dissolution rate.

The solubility limits of many sparingly soluble elements are reached before alteration phases form. Rapid dissolution of the glass after rate-affecting phases form results in most other elements attaining solubility limits. The formation of alteration phases may affect the solubilities of some elements, including radionuclides, due to changes in the pH or the formation of new solubility-controlling phases.

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