PARAMETRIC EFFECTS OF GLASS REACTION UNDER UNSATURATED CONDITIONS

JOHN K. BATES, THOMAS J. GERDING, AND ALAN B. WOODLAND, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

CONF-891119--3

DE90 002275

ABSTRACT

Eventual liquid water contact of high-level waste glass stored under the unsaturated conditions anticipated at the Yucca Mountain site will be by slow intrusion of water into a breached container/canister assembly. The water flow patterns under these unsaturated conditions will vary, and the Unsaturated Test method has been developed by the YMP to study glass reaction. The results from seven different sets of tests done to investigate the effect of systematically varying parameters such as glass composition, composition and degree of sensitization of 304L stainless steel, water input volume, and the interval of water contact are discussed. Glass reaction has been monitored over a period of five years, and the parametric effects can result in up to a ten-fold variance in the degree of glass reaction.

INTRODUCTION

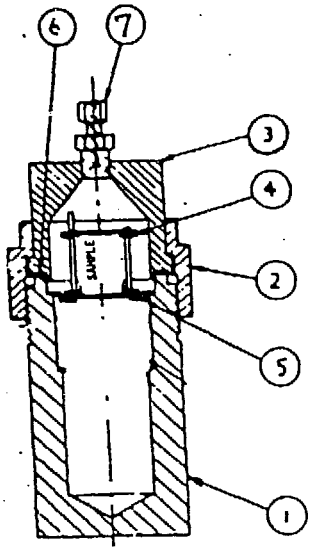
The Unsaturated Test method has been developed [1,2] as a procedure to monitor the reaction of high-level nuclear waste with water under conditions that are relevant to the proposed repository site at Yucca Mountain, Nevada. The repository horizon is located in welded tuff, and the anticipated hydrology is unsaturated. This unsaturated environment adds a new dimension to waste form testing in that the amount of water expected to contact the waste is minimal, and the sequence of water/waste interaction will be from humid air to small volumes of dripping water. The emphasis of the Unsaturated Test is to investigate interactive effects between waste package components, to identify processes that are accentuated due to the small water contact volume, and to provide a measurement of waste form reaction as a function of time. Data obtained from the Unsaturated Test may be used to validate models of glass reaction [3], that have been developed independently from site-specific considerations.

BACKGROUND

The Unsaturated Test method has been applied rigorously to study the behavior of glass waste. Three types of interactions that affect the reaction of glass are anticipated to occur under unsaturated conditions. These include (1) contact between the glass and moist air, followed by periodic rinsing of the glass surface with flowing water; (2) contact between the glass and standing water; and (3) contact between the glass and standing water in close contact with partially sensitized 304L stainless steel. The Unsaturated Test provides for the possibility that these interactions will occur, and specifies analyses be performed to judge the importance of each one.

A schematic diagram of the test apparatus is shown in Fig. 1. The components are the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package assemblage (WPA), which consists of the waste form and presensitized metallic components representing the canister; and a solution feed system to inject test water.

The WPA is contacted very 3.5 days by 0.075 mL (drops) of repository water that has been preequilibrated with tuff at 90°C. The test is conducted at 90°C and the nature and degree of reaction are determined by



1. Body
2. Nut
3. Cap
4. Retainer Top
5. Retainer Bottom
6. Ethylene Propylene Gasket
7. Swagelok Fitting

Fig. 1. Schematic Drawing of the Unsaturated Test Apparatus

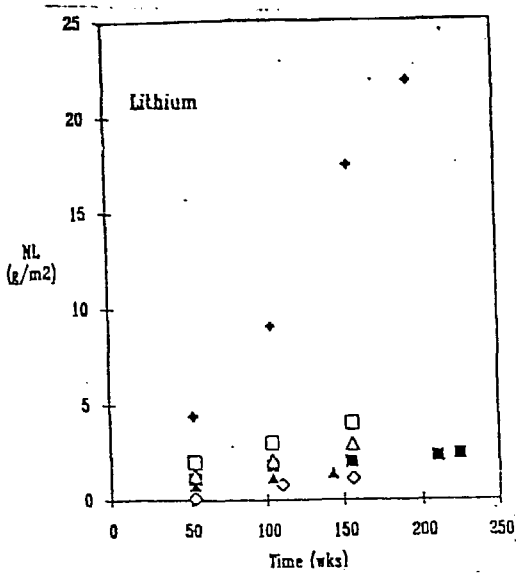
analysis of the water that has contacted the WPA and by surface analysis of the WPA components. The test schedule incorporates batch and continuous testing. In the batch mode, tests are terminated at 13-week intervals through 52 weeks. In the batch mode, the test apparatus is disassembled and analyses of both the solution and components are performed. In the continuous mode, the WPA (including liquid associated with the WPA) is transferred to a new test vessel, and the test is continued. Generally, both batch and continuous tests are replicated. In addition, investigation of the test components is possible at the termination point, and yet the test can continue for an unspecified number of test periods or until information most useful to repository evaluation is obtained.

Savannah River Laboratory black frit based 165 glass (see [4] for composition) has been tested over an ongoing period 208 weeks using the above-described standard procedure. The normalized releases of B, Li, and U in the standard set of experiments is shown in Fig. 2. Boron and lithium are commonly used to monitor glass reaction because they are released most rapidly from the glass and do not readily form secondary phases or interact with metal components of the test. Uranium is a long-lived actinide present in both glasses. The results of experiments from this standard set form a basis for comparison with subsequent test sets where the test conditions are varied to study parametric effects.

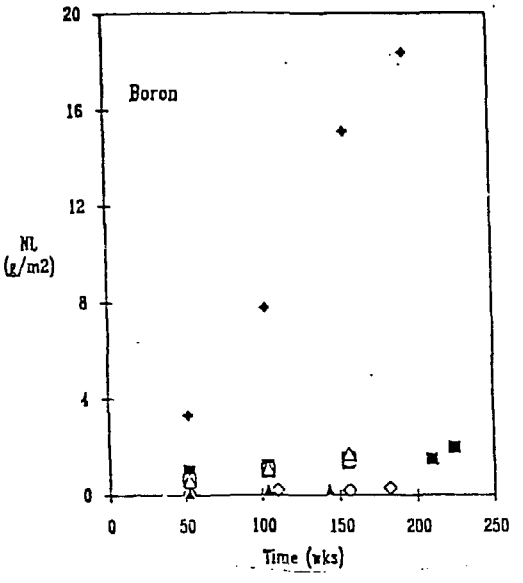
One key to the applicability of the data generated using the Unsaturated Test is the relationship between the standard conditions used in the test and the eventual conditions encountered in the repository. Since it is likely that conditions will vary between individual waste packages, a series of parametric experiments have been initiated to determine to what degree various factors affect glass reaction. The parametric experiments in progress are listed in Table I. Details of these experiments are presented in [5]. In this report, a descriptive presentation of the highlights of the parametric experiments is made.

RESULTS AND DISCUSSION

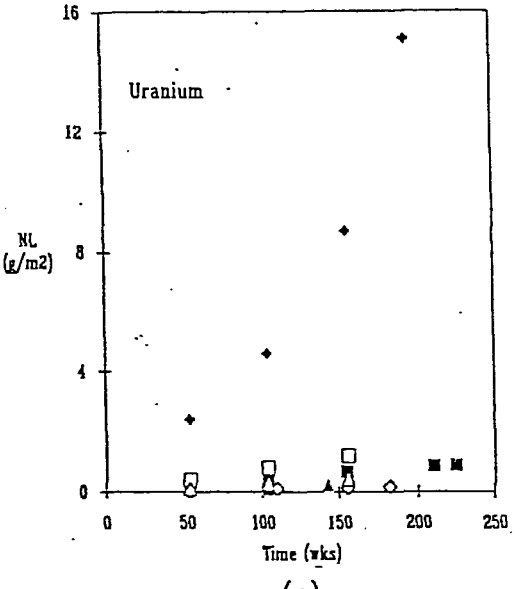
Both the test solutions and the test components (glass and metal) have been examined to describe the reaction process. In Fig. 2, the normalized releases of B, Li, and U are shown for the parametric experiments. The results for each set of experiments are discussed below.



(a)



(b)



(c)

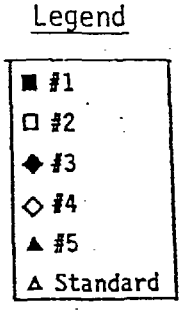


Fig. 2. Normalized Release of (a) Li, (b) B, and (c) U from the Parametric Experiments and the Standard Test

TABLE I
Experimental Conditions Used in Parametric Unsaturated Test Series

Experiment #	Experimental Parameter(s)
Standard	Glass surface area of 13.5 cm^2, drop volume of 0.075 mL, drop interval every 3.5 days, glass in contact with sensitized 304L stainless steel.
1	Exclusion of metal contact with glass, standard conditions.
2	65% reduction in cast glass surface area, standard conditions.
3	65% reduction in cast glass surface area, 50% reduction in drip volume.
4	Drop interval rate increased from 3.5 days to 14 days.
5	Varying degrees of metal sensitization, standard conditions.

Experiments #1 and #4

Experiments #1 (no metal retainer) and #4 (14-day drip interval) had the smallest elemental release of all experiments (Fig. 2). Specific elemental release trends for experiment #1 are shown in Fig. 3 as total nanograms released. These experiments were performed in Teflon™ vessels using Teflon™ stands, and all elemental release can be attributed to the glass. Lithium, boron, and uranium are released at slowly declining rates through 200 weeks, at which point there was a marked increase. This increase corresponded to an in-line design change which reduced water loss from the Teflon™ vessels and facilitated the rinsing of salts from the glass surface. The release of Na was erratic (not shown), eventually showing a net depletion from solution after four years. Silicon, magnesium, and calcium showed steady depletion from solution.

For both test sets, the release of all elements showed evidence of evaporation of water from the glass, in that for some periods there was no U detected in the leachate. This was taken as evidence that no water had dripped from the glass. In other periods there was a large release pulse indicating that some dripping had occurred. Thus, release trends were taken in context of the four-year period, with less attention paid to individual sampling periods.

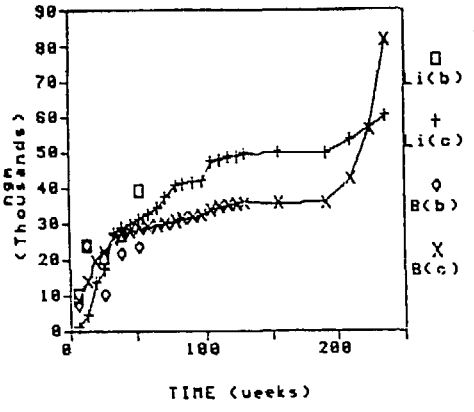
During sampling, it was noted that the top glass sections were either dry or only slightly damp, and that a white crusty material, which became more pervasive with time, formed almost immediately. The batch samples for both experiments #1 and #4 gained weight. The precipitate coverage and weight gain were greatest for experiment #1, and typical precipitate coverage is shown in Fig. 4a. The major precipitates as identified by x-ray diffraction, are calcite and gypsum. However, the glass surface itself has also undergone considerable alteration, resulting in the rough, irregular appearance shown in Fig. 4b. The surface layer is comprised mainly of a Si-rich mat, and its formation obscures most of the original as-cut surface.

The bottom surface, which was always damp with varying amounts of standing water present, had less coverage of the Ca-rich phases, and had small clusters of the smooth appearing phase shown in Fig. 4b. Based on EDS analysis, this phase was composed of Na. It degraded rapidly in the electron beam, and while unidentified, is a source for nonsolubilized Na, as exemplified by the erratic Na release trend. The major temporal changes in surface appearance were the increased volume of reaction products, and in the 52-week batch experiment, a small section of the bottom reacted layer had separated from the glass.

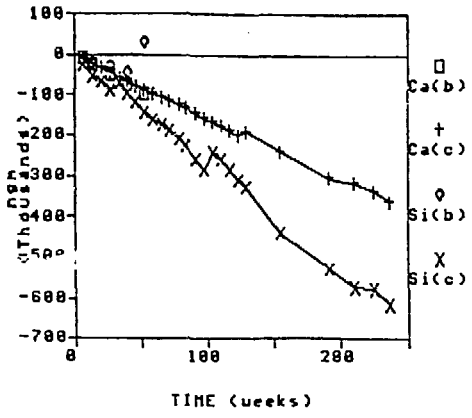
The glass reaction in both of these experiments, as measured by the release of B and Li, is about 50% that noted using standard test conditions. However, both the extension in the drip rate and the lack of a metal retainer results in evaporative processes significantly affecting the formation of phases and the release of elements from the glass. Such evaporative processes are expected to be enhanced under actual repository conditions due to self heating of the waste.

Experiments #2 and #3

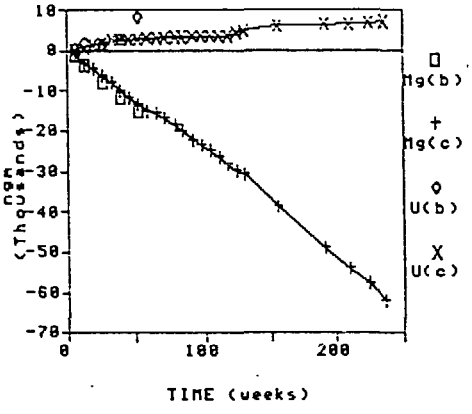
Experiment #2 (reduced surface area, standard conditions) and experiment #3 (reduced surface area, 50% reduction in drip volume) had the largest reaction of all the experiments (see Fig. 2). The cumulative release from experiment #3 is shown in Fig. 5. The batch and continuous experiments showed consistency in the amount of reaction, and the rate of elemental release from the continuous experiments was fairly constant over the first 104 weeks, showing a slight increase between 104 and 156 weeks. The elemental release results from experiment #2 are more erratic than



(a)



(b)



(c)

Fig. 3. Cumulative Release of (a) Li, B; (b) Ca, Si; and (c) Mg, U in Parametric Experiment #1 (No Metal Retainer). Cumulative releases were calculated by subtracting from the total release, that fraction attributed to the EJ-13 water.

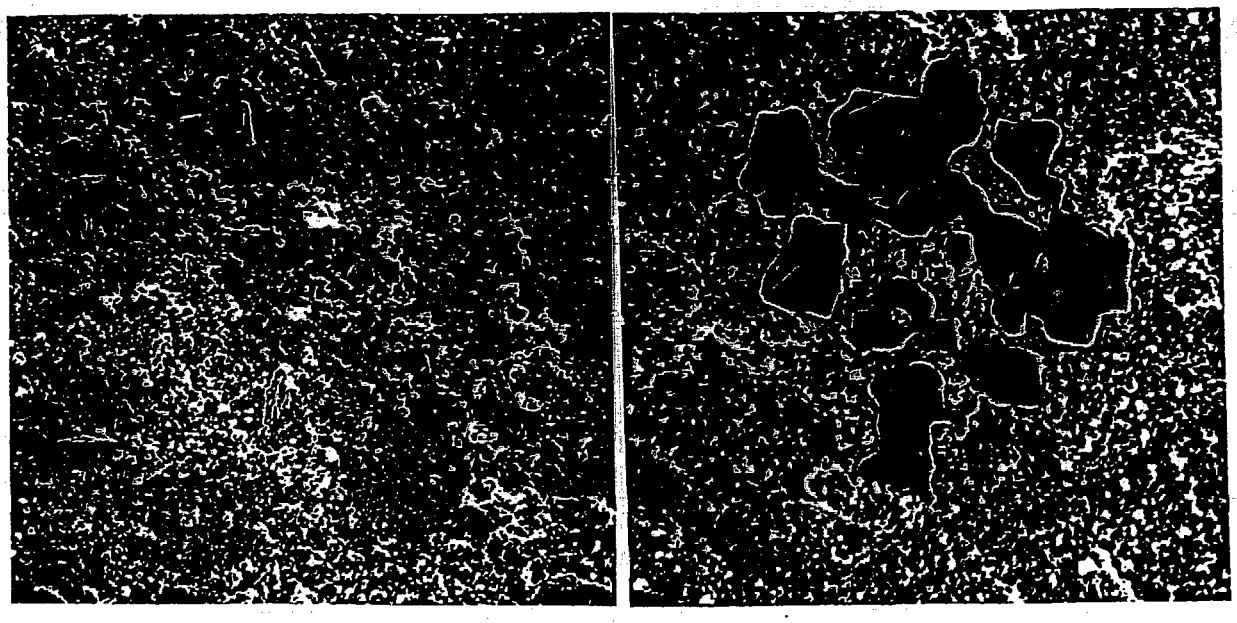
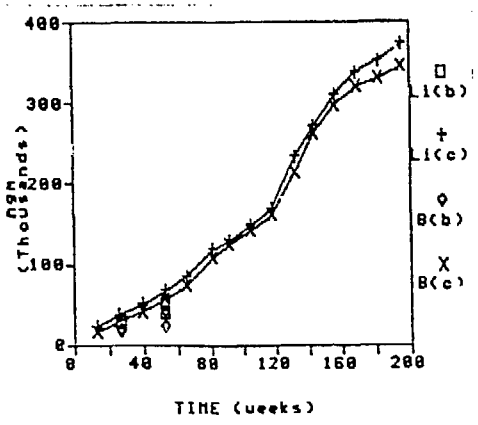
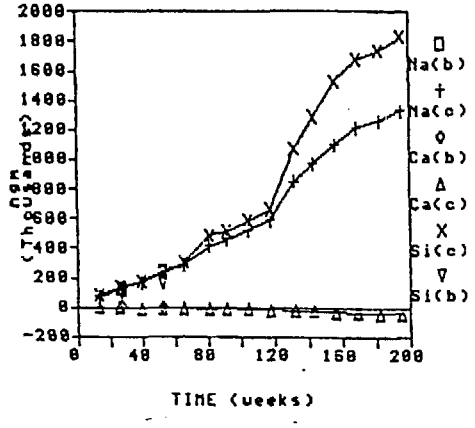


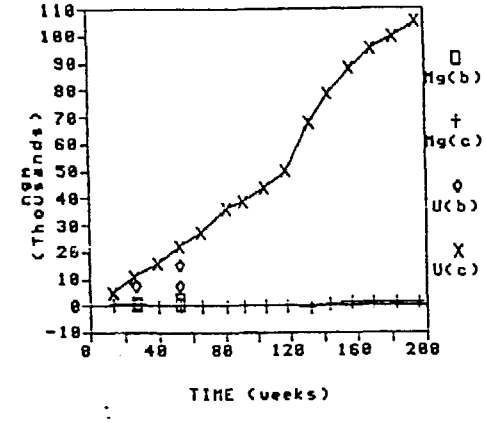
Fig. 4. SEM Photomicrographs of the Reacted Surfaces from Set #1. (a) General surface at 100X magnification showing precipitated Ca phases. (b) Na-rich precipitate on the bottom surface, magnification = 1900X.



(a)



(b)



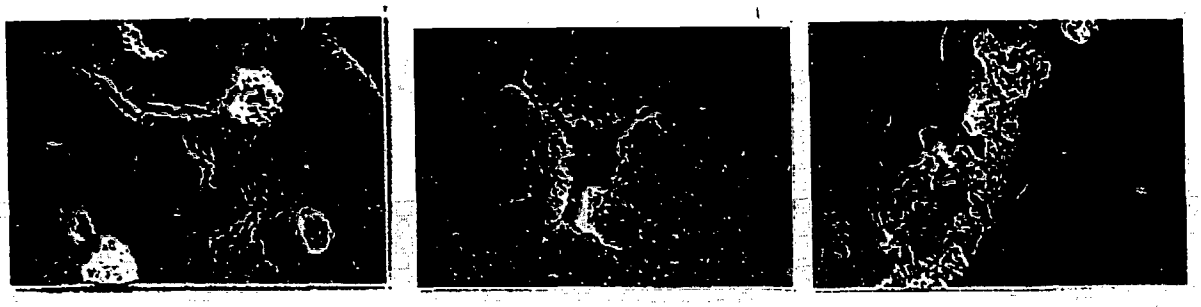
(c)

Fig. 5. Cumulative Release of (a) Li, B; (b) Na, Ca, Si; and (c) Mg, U in Parametric Experiment #4 (50% Reduction in Drop Volume)

for #3 with the batch results nearly equivalent in the two experiments. However, the release from the #2 set of continuous experiments, while about two times greater than the standard results, are about five times less than observed for experiment #3. Note that except for Ca, all elements show a positive release to solution.

Analysis of the metal and glass provides some indication as to the cause for the erratic nature of the results, and the up to ten-fold increase in release for set #3 compared to the standard conditions. After 26 weeks the top and bottom glass surfaces for all samples showed some indication of exfoliation of the reacted layer. Evidence of exfoliation is shown in Fig. 6, which depicts a sequence of surface appearances, from the initiation of exfoliation, to the exposure of fresh glass surface, to reprecipitation of a secondary phase back onto the newly exposed surface. The larger the extent of exfoliation observed on the reacted surfaces, the larger the elemental release. Note that the separated surface layer is not filtered from the test solution, but is dissolved during an acid soak step and is treated as material available for transport from the waste package. Small pieces of exfoliated layer are sometimes observed in the test solution during sampling.

While the exfoliation quantitatively relates the erratic and large amount of release to process that occurs during these two sets of experiments, the cause of the exfoliation is still being investigated. It was observed that in both of these experimental sets, the top and bottom surfaces remained wet with standing water. Usually set #3, with the smaller drip volume, had the largest amount of water remaining in contact with the glass. It is possible that the surface layers are unstable in all



(a) (b) (c)

Fig. 6. SEM Photomicrographs of Reacted Surfaces from Set #4.
(a) Initiation of spallation, magnification = 6000X;
(b) spallation, magnification = 240X; and
(c) reprecipitation, magnification = 6000X.

the experiments, but only when the surfaces remain wet, and are contacted by intermittent flow, can the exfoliated material be effectively transported from the glass.

Experiment #5

Experiment #5 was performed to study the effect of metal sensitization on glass reaction. The standard test conditions utilize partially sensitized metal in contact with the glass. The sensitization process degrades the protective properties of the stainless steel, and Fe from the metal and Si from the glass react to form iron silicate and iron oxyhydroxide reaction products that are clearly visible on the test components. To further study the sensitization affect, a low carbon 304L steel was used (0.014 wt % C, compared to 0.028 wt % in the standard test). The steel was treated at 550°C for 24 hours and cooled slowly to room temperature. These conditions were used to induce sensitization in the standard test (Fig. 2).

In set #5, two key observations were made. First, in the 52-week batch experiment was there evidence of strong metal/glass reaction. This was indicated by the formation of visible amounts of reddish brown rust-like reaction products, and by an elemental release equivalent to that observed in the standard test set. The other experiments in the set, which showed no evidence of strong reaction, had small elemental releases similar to those observed in sets 1 and 4. Secondly, the top glass surfaces were dry and the bottom surfaces damp during sampling. This observation correlates with lack of exfoliation noted in examination of the reacted surfaces, and reinforces the role of water contact in promoting exfoliation.

CONCLUSIONS

The Unsaturated Test method has been used to study the effect of parameters on glass reaction. Under conditions where evaporative processes dominate, e.g., no metal retainer or extended drop interval, release from

the glass is minimized and Ca-rich secondary phases are the dominate reaction products. When varying degrees of sensitization are imparted to the metal retaining sections, an increase in release of up to twofold is observed compare to tests performed with non-sensitized metal, and the dominant reaction products are iron silicates and oxyhydroxide phases. However, when the top and bottom glass section remain wet, the elemental release from the WPA is increased up to a factor of ten. This increase results from the exfoliation of reacted glass layers, followed by transport of these released layers from the glass by intermittent water contact. While some exfoliation release is present under all conditions, it is particularly dominant when enough water is present for transport from the glass.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, under Contract Number W-31-109-Eng-38.

REFERENCES

1. J. K. Bates and T. J. Gerding, "NNWSI Phase II Materials Interaction Test Procedure and Preliminary Results," Argonne National Laboratory report ANL-84-81 (1985).
2. J. K. Bates and T. J. Gerding, "One-Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application," Argonne National Laboratory report ANL-85-41 (1986).
3. W. L. Bourcier, "Geochemical Modeling of Radioactive Waste Glass," Lawrence Livermore National Laboratory report UCRL-57012, in press.
4. J. K. Bates and T. J. Gerding, "Application of the NNWSI Unsaturated Test Method to Actinide Doped SRL 165 Type Glass," Argonne National Laboratory report ANL-89/24 (in press).
5. J. K. Bates, Argonne National Laboratory, unpublished results (1989).