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TEMPERATURE EFFECTS ON WASTE
GLASS PERFORMANCE

by

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ABSTRACT

The temperature dependence of glass durability, particularly that of nuclear waste glasses, is assessed by reviewing past studies. The reaction mechanism for glass dissolution in water is complex and involves multiple simultaneous reaction processes, including molecular water diffusion, ion exchange, surface reaction, and precipitation. These processes can change in relative importance or dominance with time or changes in temperature. The temperature dependence of each reaction process has been shown to follow an Arrhenius relationship in studies where the reaction process has been isolated, but the overall temperature dependence for nuclear waste glass reaction mechanisms is less well understood. Nuclear waste glass studies have often neglected to identify and characterize the reaction mechanism because of difficulties in performing microanalyses; thus, it is unclear if such results can be extrapolated to other temperatures or reaction times. Recent developments in analytical capabilities suggest that investigations of nuclear waste glass reactions with water can lead to better understandings of their reaction mechanisms and their temperature dependences. Until a better understanding of glass reaction mechanisms is available, caution should be exercised in using temperature as an accelerating parameter.

EXECUTIVE SUMMARY

This report presents results from a literature review to assess whether temperature can be used as an accelerating parameter in the durability testing of glasses, particularly nuclear waste glasses. Temperature is an important parameter to consider because it affects glass reaction mechanisms and rates in laboratory glass durability tests as well as within the nuclear waste repository. A review of the chemical reaction processes that constitute nuclear waste glass/water interactions indicates that the overall glass/water reaction is a cumulative result of the constituent reactions: molecular water diffusion, ion exchange, silicate network dissolution, and secondary mineral precipitation. These reaction processes often operate simultaneously, and the nature of their interactions is poorly understood at present.

The temperature dependence of each individual reaction has been examined, although the reactions usually cannot be isolated in glass/water systems. The constituent reaction steps of glass reactions often have a temperature dependence that can be quantitatively expressed using the Arrhenius equation, which is derived from empirical observations. The temperature dependence is often described by an activation energy, the threshold energy, above which a chemical reaction is likely to occur. The basis for Arrhenius-type formulations can be related to basic physical chemistry principles, although the connection has not been rigorously defined. The Arrhenius equation has been used to describe the temperature dependence of glass dissolution based on several kinetic measurements, including the rate of cation release to solution

and the rate of growth of alteration layers and secondary minerals. Volcanic glass, or obsidian, hydrated in water vapor provides an opportunity to study a single reaction mechanism, namely, molecular water diffusion, as a function of temperature in a glass/water system. Such studies have concluded that use of the Arrhenius equation is acceptable for describing the effect of temperature in accelerating obsidian hydration. Furthermore, studies of secondary mineral precipitation have also found that the Arrhenius equation successfully describes the temperature dependence of these reactions over the temperature ranges examined. A general conclusion is that temperature can be used as an accelerating parameter for chemical reactions when the chemical reaction is identified and understood.

Often, experimental results indicate that the rate-controlling steps vary as a function of temperature. Because glass reaction is the result of a complex interaction of several reaction processes, changes in experimental temperatures frequently result in a change in a dominance or control of a particular reaction step on the overall reaction. Consequently, the effect of temperature as an accelerating parameter on the overall glass/water reaction is poorly understood.

Based on the results of this report, it can be concluded that several key aspects of glass/water reactions must be investigated in order to understand the reaction at any temperature. These include changes in solution concentrations over time and the alteration phases formed. After the key aspects of glass/water reactions are known, the final step is to develop a kinetic model of the glass/water reaction process. This step will synthesize the understanding of the overall reaction into a description that can be used to accelerate glass/water reactions in a meaningful way.

The rate-controlling reaction step cannot be identified by investigating a single monitor of experimental reaction progress, such as the change in solution concentrations, changes in reaction layer thicknesses, or composition of the alteration phase assemblage. Several studies have demonstrated that the task of identifying the rate-controlling reaction would be facilitated through use of analytical techniques. In reviewing past work, it is clear that the most effective way to study alteration phases includes the use of analytical electron microscopy (AEM), a powerful tool that allows high-resolution investigations of alteration phases and provides mechanistic insight. This type of information, considered in conjunction with more routinely collected measurements such as solution concentration, can allow researchers to elucidate reaction mechanisms more easily.

The lack of a comprehensive data set from studies of the temperature dependence of glass/water interactions (including information on the reaction processes participating in the overall reaction and their respective temperature dependences) suggests that caution should be exercised in using temperature as an accelerating parameter, at present.

1.0 INTRODUCTION

The goal of this review is to assess the effect of temperature on the reaction between nuclear waste glass and water. Temperature is an important parameter to consider because it affects glass reaction mechanisms and rates in glass durability tests in the laboratory as well as within the nuclear repository waste itself. This report describes and reviews work on the effects of temperature in accelerating glass/water reactions. However, while the focus temperature for waste glass testing is 90°C and accelerated tests are performed at higher temperatures, the long-term temperature in a repository will be less than 90°C. Therefore, this report also discusses the results of testing performed at lower, repository-relevant temperatures. While the emphasis is on nuclear waste glasses, considerable work has been performed with natural glasses and is also presented.

Temperature is one of several test parameters used to accelerate waste glass durability experiments. Accelerating conditions are necessary to evaluate glass performance so that a sufficient, measurable amount of reaction will occur within a laboratory time frame. The goal of such testing is to evaluate the chemical durability of nuclear waste glasses, principally by distinguishing differences in leaching behavior. Ultimately, the results of durability experiments will also be used in validating the results of long-term repository predictive modeling. In using a test-acceleration experimental approach, it is necessary to demonstrate that the reaction mechanism is invariant between the experimental temperatures and the temperature range of interest. If there is any change in mechanism, then it must be identified and understood so that it can be accounted for in predictive modeling. The results of several investigations of glass/water interactions indicate that the rate-controlling reaction mechanisms can change as a function of temperature below 300°C [e.g., ZAGAR; CAUREL; VERNAZ; MENDEL]. If this occurs, the experimental results can not be used to derive the temperature dependence of the reaction studied. Thus, a convincing demonstration that an overall reaction has not changed requires an understanding of how temperature affects the constituent reaction mechanisms of glass dissolution, including the kinetic effects on the reaction mechanisms, the solution chemistry, and secondary phase formation.

Another reason to understand temperature effects on glass/water interactions is that the temperature within the repository is expected to vary during the first 300 post-closure years between ambient conditions and 240°C. The precise values of temperature and time will be determined by the final placement geometries selected for the waste packages. The heat will be generated by decay of the radionuclides; thus, the maximum temperatures attained will be within the waste packages themselves. After the repository cools below the local boiling temperature of water (96°C for the proposed Yucca Mountain site), the waste package will be exposed to varying amounts of water vapor and relatively small amounts of liquid water. The local variances in temperature and the availability of water require that glass/water interactions be understood for a range of conditions. Several studies have been performed investigating the effects of temperature on the dissolution of waste glasses. In addition, results from other disciplines are presented here to supplement the effects of temperature on chemical processes known to occur during water glass interactions.

This report is organized to establish a basis for evaluating temperature effects on glass/water interactions by reviewing (1) the important reaction steps known to occur and (2) the Arrhenius equation. The primary issue to be addressed is whether temperature can be used as an accelerating parameter in glass durability testing. The following section reviews the Arrhenius equation, an expression used to describe the temperature dependence of many chemical reactions. Section 3.0 reviews and describes the important glass/water reaction processes that have been identified, including dissolution processes (Section 3.1 and 3.2) and secondary mineral formation (Section 3.3). Within this context, the effects of temperature on waste glass/water reactions for several different glass types are then critically reviewed and evaluated in Section 4.0.

2.0 ARRHENIUS RATE LAW

The temperature dependence of chemical reactions can be described using the Arrhenius equation,

$$k = A \exp(-E_a/RT) \quad (1)$$

where k is the reaction rate constant, A is a pre-exponential term and a function of composition, E_a is the overall energy of activation of the reaction, T is temperature in K, and R is the gas constant. The activation energy of the overall reaction, E_a , may have a weak dependence on temperature that is difficult to determine experimentally [LASAGA]. This relationship has been observed to hold for numerous chemical processes, including glass/water reactions dominated by rate-controlling reaction mechanisms such as molecular water diffusion [TOMOZAWA-2], ion exchange [WESTIK-1, -2], and network dissolution [HENCH]. The Arrhenius relationship has also served as the basis for using increased temperatures to accelerate reaction progress in experimental studies. The characteristic values that describe the temperature dependence, the activation energy, and the pre-exponential term are commonly determined empirically by rearranging Eq. 1 to

$$\ln k = \ln A - E_a/RT \quad (2)$$

and plotting the logarithm of the experimentally determined rate constant against reciprocal absolute temperature. When experimental data can be described by a linear relationship, the activation energy (derived from the slope of the line and, therefore, temperature independent) and the reaction mechanism are constant [LASAGA]. Such a linear relationship allows a reaction rate to be interpolated for any temperature within the studied temperature range. A common experimental strategy is to perform experiments at higher temperatures than the temperature of interest and thereby obtain measurable results in a reasonable period of time. It is then assumed that the reaction mechanism (and, therefore, the activation energy) is constant outside of the experimental range, so that lower temperature rates may be estimated by extrapolation.

Although the Arrhenius equation is derived from empirical observations, detailed molecular theories [e.g., MOORE] typically contain temperature-dependent pre-exponential terms. The existence of a temperature dependence on chemical reactions similar to the Arrhenius equation is expected. Since chemical reactions are the result of the crossing of potential barriers, such as breaking bonds or molecular collisions, the exponential term in Eq. 1 arises from applications of Boltzmann's distribution. The probability of a chemical species having sufficient energy, E^* , to overcome a potential barrier is proportional to the term $\exp(-E^*/RT)$. Integrating this probability from the minimum energy required to overcome the potential barrier, $E^* = E_a$, to $E^* = \text{infinity}$ results in a term proportional to $\exp(-E_a/RT)$ (cf. Eq. 1).

Application of the Arrhenius equation to specific chemical reactions requires an understanding of its associated assumptions. As noted earlier, the pre-exponential term has a weak dependence on temperature, but this dependence is generally unable to be resolved in experimental studies. With respect to waste glass durability experiments, this dependence can be disregarded. A second factor to be considered, as discussed above, is that the Arrhenius equation describes the *overall* reaction kinetics for a system. This equation will be most useful in waste glass/water interaction studies when it can be shown that a single reaction mechanism is rate controlling over the entire temperature range investigated. When this condition is satisfied, then temperature can be successfully used to accelerate glass/water reactions.

In cases where the Arrhenius equation can be used to accelerate chemical reactions, the magnitude of empirically measured energies of activation can provide information regarding the rate-limiting step of

reaction [ATKINS; LASAGA]. Activation energies of 70 to 320 kJ/mol are characteristic of surface reaction processes, such as etching or bond breaking, while solution transport-limiting mechanisms, such as diffusion in an aqueous media, have activation energies of less than 50 kJ/mol. As described in Section 3.2, activation energies for nuclear waste glass/water reactions are often in the 40 to 80 kJ/mol range and probably reflect the interaction of two or more reaction steps. Understanding the temperature dependence of the reaction can often help elucidate the rate-determining process and help estimate the effects of temperature.

It is difficult to ascertain if using temperature as an accelerating parameter in laboratory experiments will produce results with rate-determining steps which are representative of those expected in the repository. The Arrhenius relationship provides a basis for empirically determining the temperature dependence of a reaction and assists in assessing whether one or more reaction mechanisms are rate controlling for a particular process. The ability of the Arrhenius relationship to describe the temperature dependence of both dissolution and precipitation reactions makes it particularly useful in studying nuclear waste glass/water reactions, as evidenced by the large number of investigations where it has been utilized.

3.0 MECHANISMS OF GLASS/WATER REACTIONS

Glass/water interactions are generally believed to be the result of several reaction processes occurring simultaneously [e.g., CLARK-1, -2; ABRAJANO-1; BOURCIER; BUNKER-1; DRAN; PETIT-1, -2]. While it is beyond the scope of this document to mechanistically describe these interactions in detail, a brief review is necessary in order to evaluate temperature effects.

Glass/water processes can be separated into two general classes according to the type of reaction they produce: dissolution reactions and secondary mineral formation reactions. Dissolution reactions include those between the initial glass and the reacting solution. Secondary mineral formation reactions include those which occur in the reacting solution or within alteration layers resulting from dissolution reactions. Although secondary mineral formation may seem somewhat removed from the process of glass and water interactions, the two processes are intimately linked through the solution chemistry [BOURCIER] (see Section 3.1). Therefore, a complete discussion of the effect of temperature on glass/water reactions will include secondary mineral formation processes.

3.1 Dissolution Mechanisms

The dissolution mechanisms for water/glass reactions have been characterized by a number of studies. Each of the following processes is known to occur in glass/water interactions, often simultaneously: molecular water diffusion, dealcalization, network hydrolysis, and network dissolution. It is generally agreed that these processes are affected by such parameters as temperature, glass composition, solution composition, and the ratio of experimental glass surface area to solution volume (SA/V). Unfortunately, these parameters are seldom identical from one investigation to the next, which can lead to difficulties in isolating the effect of temperature on glass reaction when different studies are compared. Therefore, it is useful to understand the possible reaction processes to assess temperature dependences.

One process is called molecular water diffusion and involves the diffusion of molecular water into the silicate glass framework [e.g., LEE]. The growth of these hydration layers has been observed to be proportional with the square root of time, a functionality characteristic of diffusional processes.

A second reaction, dealcalization, is based on a simple ion exchange of cations and a hydrogen species [e.g., ISARD]. The kinetics of this process are also proportional to the square root of time. The rate-determining factors of this process are the diffusivities of the exchanging species.

A third reaction, network hydrolysis, involves the base-catalyzed breaking of the bridging oxygen bonds in the silica lattice framework [BUNKER-2]. The controlling parameters of this reaction include the availability of hydroxide and the ability of released species to be removed from the alteration layer.

A fourth reaction, network dissolution, is an extension of the network hydrolysis reaction, where the last bridging Si-O bond is hydrolyzed, resulting in the formation and release of a solvated species [ABRAJANO-1]. This reaction occurs primarily at the solid/solution interface.

Each of these reactions has been described for experiments performed in hydrothermal and vapor phase environments. The relative dominance of a particular reaction mechanism may vary in constant temperature experiments performed under hydrothermal or vapor environments (low SA/V or high SA/V) [BATES-3; ABRAJANO-1]. The interactions of these processes are poorly understood, at best. Until a comprehensive model of glass dissolution is developed, understanding these interactions may benefit from a combined theoretical/empirical approach.

One model that has been used to try to understand the complex kinetics that take place during glass/water reactions is based on the dissolution affinity of the dissolving phase in the reacting solution [BOURCIER]. This model assumes that the overall glass dissolution rate is controlled by the dissolution rate of an alkali-depleted surface (gel) layer for borosilicate glasses. The Bourcier model is similar to Grambow's model [GRAMBOW], where silica saturation is thought to be the parameter that controls the glass dissolution rate. However, Bourcier's model predicts that all components concentrated in the surface layer affect glass dissolution rates. The good agreement between the Bourcier model and the experimental data suggests that the long-term rate of glass dissolution will be dependent primarily on the solution ion concentrations. This implies that secondary phase formation, strongly dependent on solution ion concentrations, can have an important effect on nuclear waste glass/water reactions. Modeling glass/water reactions in terms of the affinities can initially help simplify our understanding of this complicated process. This model also provides an initial basis for understanding how dissolution and precipitation reactions are related with respect to glass/water interactions. This, in turn, can allow an assessment of the temperature dependence of glass/water interactions.

It is difficult to assess the effects of each dissolution step because they occur simultaneously. Consequently, the results of the overall reaction (e.g., changes in cation concentration and alteration layer characteristics) are complicated and often cannot be easily assigned to a particular mechanism. Investigations of this nature are discussed in Section 4.0. The discussion below focuses on an instance where a single dissolution step can be isolated.

3.2 Example of Isolated Mechanism: Molecular Water Diffusion

Molecular water diffusion is one process that can be isolated and that has been studied in detail in natural silica-rich glasses (obsidian). Molecular water diffusion in obsidian results in the formation of a strained water-rich layer, easily observable as a birefringent layer when viewed using light microscopy. When the obsidian hydration dating technique was initially developed [FRIEDMAN-1], the reaction was described as the inward diffusion of molecular water into the silicate structure of obsidian (glass). This reaction has been used as the basis for an absolute dating technique to assign ages to geologic features, such as obsidian outcrops [FRIEDMAN-2], and archaeologic artifacts, such as obsidian tools or weapons [FRIEDMAN-1, -3; MICHELS; MEIGHAN]. Measurements of the birefringent alteration layer are assigned ages based on estimates of the rate of molecular water diffusion at the effective reaction temperature. In developing the method, Friedman and Long [FRIEDMAN-3] described the use of high temperature experiments to obtain lower, ambient-temperature rates using the Arrhenius relationship. These lower temperature rates are in reasonably good agreement with associated artifacts dated by other means, such as ^{14}C [MICHELS; MEIGHAN].

Subsequent studies of natural obsidian samples using resonant nuclear reaction analyses (RNRA) have confirmed that the inward diffusion of molecular water into obsidian is the dominant reaction mechanism for these types of samples [LEE]. This assertion has been subsequently disputed based on an experiment where obsidian was hydrothermally leached. It was concluded that ion exchange was the dominant reaction mechanism for these reaction conditions [LANFORD; SHIRAKI]. Recently presented RNRA results show that under hydrothermal reaction conditions both ion exchange and molecular water diffusion are important, detectable reaction steps for sodium silicate glasses, including obsidians [DRAN; PETIT-2; MAGONTHIER; YANG]. Additional studies based on characterizations of the hydrated layers have found that different overall reactions occur, depending on whether obsidian is exposed to a water vapor environment or a hydrothermal leaching environment [BATES-3]. These studies imply that when glass (obsidian) is exposed to water vapor, the relatively small volume of water can approach saturation with respect to secondary phases relatively quickly, as suggested in Bourcier's model [BOURCIER].

When this happens, the etching and ion exchange processes are impeded due to a decreased chemical affinity for the glass surface to react; however, molecular water diffusion continues to occur.

The energy of activation for molecular water diffusion in rhyolitic glasses at low temperatures (<200°C) has been reported to range from 75 to 95 kJ/mol. Recent studies in our laboratory have determined similar activation energies and have also found that the activation energy is dependent on the intrinsic water content of the unreacted obsidian, which ranges between 0.02 and 1.3 wt % H₂O [MAZER-3]. These activation energy values are in good agreement with the results reported by Pfeffer and Ohring [PFEFFER], 70 kJ/mol for molecular water diffusion in SiO₂ films. Tomozawa and Tomozawa [TOMOZAWA-2] report an energy of activation of 52 kJ/mol for the diffusion of water into a commercial borosilicate glass (SiO₂ = 71 wt %). This value was obtained by measuring the infrared transmission spectra for water species in the reacted glasses and then calculating the inward migration of molecular water. The discrepancy between these results and other diffusion-based activation energies may be the result of different experimental methods having been used to determine water diffusion rates; however, they may also indicate that different processes have taken place in borosilicate glasses and in obsidians reacted under similar conditions. Activation energies of ~50 kJ/mol are below the range of bulk diffusion processes, typically 80 to 330 kJ/mol, and may reflect the dominance of other reaction mechanisms, such as dissolution of the silica framework [LASAGA].

Some obsidian hydration dating studies have convincingly demonstrated that the temperature dependence of molecular water diffusion follows an Arrhenius-type relationship between 100 and 180°C. Correlations of extrapolated rates with other independent dating methods, such as ¹⁴C, are in agreement, suggesting that the temperature dependence extends as low as 20°C. The large temperature range where molecular water diffusion occurs provides a basis for using temperature to accelerate the molecular water diffusion mechanism in silica-rich glasses, such as obsidian. The findings of Tomozawa and Tomozawa [TOMOZAWA-2] may indicate that temperature-accelerated reactions for borosilicate glasses occur via a different reaction path than obsidians.

Experiments have been conducted where the effects of relative humidity, glass composition, and temperature on obsidian hydration were evaluated. These experiments were performed in water vapor environments to isolate the molecular water diffusion reaction in silicate glass systems. This study allowed a better understanding of obsidian hydration over a temperature range of 110 to 175°C to be developed [MAZER-1].

In each experiment, the growth rate of the birefringent hydration layer was proportional to the square root of time. Such a dependence is consistent with previous observations [e.g., FRIEDMAN-1, -3; MICHELS; BATES-2] and is characteristic of diffusional rate-controlling mechanisms. Using the results of experiments performed over a range of temperatures and the Arrhenius equation, the temperature dependence of the process was examined. The activation energy of hydration for this process ranged from approximately 70 to 95 ± 5 kJ/mol for each of the obsidians hydrated. The dependence of the activation energy was examined as a function of the obsidian composition. A number of compositional parameters were considered, and the strongest correlation discovered was with the intrinsic water content of obsidian.

Natural obsidian contains a small amount of structurally bound water, referred to as intrinsic water, that is present at the time of its formation. The observation that the hydration of obsidian is a function of its intrinsic water content is consistent with our understanding of obsidian hydration processes. Since molecular water diffusion is the rate-determining reaction, then the reaction can be expressed as the chemical potential difference between water in the reacting solution, $\mu_{(\text{solution})}$, and the intrinsic water present in the glass, $\mu_{(\text{glass})}$, so that

$$\text{Force} = -(d\mu/dx) = \frac{\mu_{(\text{solution})} - \mu_{(\text{glass})}}{\Delta x} \quad (3)$$

where x refers to the length of diffusion. This approach predicts that a change in the chemical potential of water in solution will affect the driving force and be reflected in the measured hydration rate constants. The increase in hydration rates with increasing intrinsic water content is unexpected from Eq. 3. However, Eq. 3 is based on the assumption that diffusion is occurring in an unchanging medium. Intrinsic water is thought to depolymerize the silica tetrahedra network which makes up the obsidian, forming sites more energetically favorable for the inward diffusion of water and effectively changing the diffusive characteristics of the glass. A more phenomenological expression for the rate of diffusion processes is given by Fick's first law

$$J_x = -D (\delta c / \delta s) \quad (4)$$

where J_x is the flux of matter (quantity time⁻¹ area⁻¹), D is the diffusion coefficient (area time⁻¹), c refers to concentration, and x refers to distance. Differences in the diffusive characteristics of the medium are manifested in values of D . Apparently, the increase in hydration rates due to the effect of depolymerization is much greater than the decreases in hydration rates due to changes in the chemical potential of intrinsic water, $\mu_{(\text{glass})}$.

The above results indicate that temperature can be used to accelerate obsidian hydration in vapor environments over a temperature range of 110 to 175 °C. The Arrhenius equation can be used to describe the temperature dependence, suggesting that the reaction mechanism remains constant over the range of experimental conditions examined. The activation energy values for each obsidian can be related compositionally to the intrinsic water content, an observation which is consistent with the current understanding of the reaction mechanisms of obsidian hydration. This understanding of molecular water diffusion in obsidian may prove useful in later investigations of the waste glass/water reaction mechanism.

3.3 Secondary Mineral Crystallization

After dissolution mechanisms, the other important set of reactions involved in nuclear waste glass/water reactions is crystallization mechanisms of secondary phases, which include precipitation and transformation. Precipitation is defined as the formation of solids from solution, while transformation is used to refer to the *in-situ* crystallization that occurs within hydrolyzed gels. Both types of mineral formation are believed to consist of two processes, nucleation and crystal growth. This section will review the mechanisms of secondary mineral crystallization with respect to glass/water interactions.

When glass/water reactions are initiated, species are released from the glass to the solution at some initial rate. As the concentrations of these released species accumulate, they approach the saturation values of secondary phases. The decrease in the chemical affinity between the reacting glass and the solution then inhibits the further release of species from the glass, without changing the individual reactions that make up the overall glass reaction. When secondary phases start to precipitate, the chemical affinity of the reacting solution increases, and glass reaction is less impeded by saturation effects. Note that the reaction paths of glass reaction are not affected by saturation but the extent of reaction is impeded to some degree by the dissolution affinity.

The kinetics of crystallization as they pertain to silicate/water systems have been reviewed [BERNER]. Nucleation can be thought of as the series of steps leading to the formation of a seed crystal, which serves as a site for subsequent crystal growth. As a body (crystal embryo) precipitates from a supersaturated solution, its growth is impeded by a free energy barrier forming at the interface between

the crystal and the solution. This interfacial free energy is initially greater than the decrease in free energy of the overall system that results from the decrease in supersaturation of the solution during nucleation. As the crystal embryo grows, the net free energy increases become progressively smaller until the interfacial and bulk terms balance each other. Once the interfacial free energy is overcome, the body is considered to be a critical nucleus and can increase in size and then undergo a decrease in free energy. The precipitated body is now considered a true crystal, and further increases in size are considered crystal growth.

The degree of supersaturation of the solution will affect the path of nucleation and precipitation. For instance, a greatly supersaturated solution has a lower free-energy barrier to overcome and is able to produce more nuclei. These additional nuclei then have less excess solute available for solution growth, and the net result is a fine-grained precipitate. Similarly, increased temperatures also lower the energy barrier to nucleation and allow more nuclei to form within a solution, which ultimately results in a finer-grained precipitate than would otherwise form at lower temperatures. The interplay between temperature and seed crystal nucleation may play an important role in glass/water systems, where the source of ions for crystal growth can be either from a solution (precipitation) or a gel (transformation). The gels formed as a result of glass/water interactions are thought to be a highly cross-linked network, composed primarily of hydrolyzed silicon and aluminum. Such a medium may act as a highly supersaturated solution and affect the nucleation kinetics of secondary minerals.

Considerable research has been performed to determine the effects of temperature on mineral precipitation, particularly by material scientists and chemical engineers (cf., BARRER; DECARREAU-1, -2). These studies find that, in general, an increase in temperature increases both the rates of nucleation and the subsequent rate of crystal growth as a result of increased concentration of species within the reacting solution (see Section 3.3). Supporting qualitative evidence [MAZER-3] indicates that the smectite clay phase which forms on hydrothermally altered basalt glass increases from poorly crystalline to more crystalline between 90 and 187 °C. Similar observations have been made for the crystallization of zeolites formed from either gels or minerals in alkaline solutions at temperatures under 300 °C [BURRIESCI; YOSHIDA; KOMARNENI-2; HU].

The temperature dependence of nucleation kinetics can be described using the Arrhenius equation to examine rates of crystal nucleus formation. This type of analysis has been used to determine an "apparent energy of activation" for the formation of the naturally occurring zeolite phillipsite (56.5 to 59.8 kJ/mol) and of the synthetic zeolite ZSM-5 (38.1 kJ/mol) [HAYHURST]. The precise meaning of this empirically derived term is unresolved, and it is unclear if these values are comparable with apparent energies of activation of crystal growth. The ability of these investigations to use the Arrhenius relationship to describe the temperature dependence of nucleation kinetics suggests that it is a very useful tool for this type of research. The range of values for the apparent energy of activation could be helpful in elucidating the rate-controlling step and in determining the temperature dependence in glass/water reactions.

The temperature dependence of crystal growth has been described for clay minerals [e.g., DECCAREAU-1, -2] and zeolites [e.g., KOMARNENI-1; BARRER]. Energies of activation ranging from 29 to 50 kJ/mol have been reported for the precipitation of smectites as a function of composition. A similar compositional dependence has been described for a synthetic zeolite [KACIREK], where the energy of activation increased from 49.4 to 65.3 kJ/mol as the Si/Al ratio in the crystals increased. The energies of activation for zeolite precipitation range from 29 to 80 kJ/mol. These values are thought to be characteristic of a surface growth reaction process, rather than diffusion of dissolved species in solution, and are typically 12 to 16 kJ/mol. The energies of activation of layer growth in glass/water reactions that have been reported include some for nuclear waste glasses hydrated in steam [BATES-1]. Their value of

33 kJ/mol is in good agreement with the values others have found for clay or zeolite crystallization. Based on the similarities of the activation energies observed, it is possible, in this case, that the rate-controlling mechanism is the formation of secondary phases on the glass surfaces.

The observation has been made that secondary mineral precipitation is often not a final step in the crystallization process. This may be important for nuclear waste glass/water reactions if a mineral phase that sequesters radionuclides later transforms to a phase unable to accommodate these species. The Ostwald rule of successive transformations indicates that the first mineral phase or precipitate formed tends to be a thermodynamically less stable polymorph. Similar reaction schemes that reduce the free energy have also been reported for zeolite precipitation, where a hypothetical reaction mixture able to form two different secondary minerals will precipitate the metastable phase first [BRECK]. The mineral formation continues until a thermodynamically stable assemblage exists between solids and solution. Each phase subsequently formed tends to be more stable under local synthesis conditions. The material from which these later-forming phases are derived can often come from phases initially precipitated under experimental conditions and elevated temperatures, ~160 to 200 °C [BRECK], and natural conditions where the temperature may have been as low as 10 °C [KEITH]. Experimental studies of zeolite stability as a function of temperature have also shown Ostwald-type successions of secondary mineral formation. Other studies have shown that clays can be transformed to zeolites when subjected to hydrothermal conditions and elevated temperatures [KOMARNENI-1; HAWKINS; BURRIESCI; BRECK]. Furthermore, these studies also demonstrated that the composition of zeolite can be controlled by supersaturating the reacting solution with various cations. The similarity between the observations of Ostwald-type progressions at both high and low temperatures suggests that this phenomenon occurs over a relatively large temperature range. The rate at which these transformations occur should be related to the degree of supersaturation of the reacting solution and, therefore, the reaction temperature (see Section 3.3).

The Ostwald rule can be used to evaluate the reaction progress of a system by evaluating the relative maturity of the secondary phases present. The precise mineral phases and time of succession are a function of the reaction temperature and initial glass composition. It has been reported [BRECK] that with increasing temperature, denser and less hydrous zeolites, such as laumontite and analcime, become more stable as compared to more hydrous and less dense types, such as chabazite and stilbite.

While generic examples [BRECK] have been used to describe concepts such as the Ostwald rule, a specific example of an Ostwald-type succession has been described for a naturally altered basalt [KEITH]. At this site, clays and minerals that had formed on a basalt outcrop had been exposed since the Eocene, approximately 40 million years ago. A correlation was discovered between particular zeolites and the corresponding age. The paragenetic sequence has been used to assign deposition ages for the various basalt outcrops. While the paragenetic sequence observed by Keith and Staples [KEITH] is uniquely associated with a particular parent glass, it is useful for studies projecting the long-term durability of nuclear waste glasses. A paragenetic sequence unique to nuclear waste glasses could also be determined. It would define the relative maturity of the waste glass/water reaction and provide a quantitative measure of how well a reaction has been accelerated.

One consequence of increasing temperatures to accelerate reactions is that the secondary phases which form are often poorly crystalline or microcrystalline, for reasons discussed above. Since these alteration mineral assemblages occur on a very fine scale, they are difficult to detect using conventional analytical techniques, such as light microscopy or scanning electron microscopy (SEM). Recent advances in sample preparation techniques [ABRAJANO-2] have demonstrated that AEM analyses of hydrated nuclear waste glasses are routinely possible. The resolution reported indicates that observations of poorly crystalline and microcrystalline phases that are otherwise undetectable may result in more complete

descriptions of the alteration phases produced in glass/water reactions. The ability to detect nanometer-sized phases is also greatly enhanced using these techniques. It is often unclear which process is rate-controlling with respect to secondary phase formation on hydrated glasses because the crystallization rate is low and detecting microcrystalline phases is difficult using standard analytical techniques. This powerful analytical tool has not yet been fully utilized, and the possibilities it offers scientists investigating glass/water reactions are exciting.

The secondary phases that form on glasses with low SiO_2 contents, such as basalt glasses and borosilicate nuclear waste glasses, generally include smectite clay, calcium silicates, and zeolites such as analcime and phillipsite. Byers et al. [BYERS] described the experimental hydration of a synthetic basalt glass in steam over temperatures from 122 to 240°C. The alteration products formed in these experiments were similar to those found in naturally altered samples. This suggests that increased temperatures had not altered the reaction mechanisms of interest, although it could not be determined what effect reaction time played in the process. Subsequent analyses of Byers's samples [MAZER-1] indicate that the alteration layer growth could be described by the Arrhenius equation. Similar results have been described for basalt glasses that have been hydrothermally leached [SEYFRIED; FURNES; MALOW]. However, steam-reacted samples appear to be more effectively accelerated than hydrothermally hydrated samples, based on the sequence of secondary phases formed.

4.0 TEMPERATURE EFFECTS ON NUCLEAR WASTE GLASS/WATER REACTIONS

A number of studies that have examined the effects of temperature on the experimental alteration of complex glasses are summarized in Table 1. In many of these studies, the identity of the dominant alteration mechanisms was not definitively established. Consequently, the temperature dependences reported often reflect the interaction of two or more mechanisms. These studies are still useful because

Table 1. Description of Experimental Studies Investigating Temperature Effects on Glass/Water Reactions^a

Glass Studied	Temp. Range, °C	Test Conditions	Reference
SRL 131	90, 150	hydrothermal	ALLEN
SRL 131	40, 90	vapor,	WICKS; BIWER
		hydrothermal	
SRL 131	40, 90	hydrothermal	STRACHAN-3
SRL 131	23-120	hydrothermal	BARKATT-1
SRL 131	120-240	vapor	BATES-1
SRL 131	75-240	vapor,	ABRAJANO-1
		hydrothermal	
SRL 165	100-250	hydrothermal	BOURCIER
SRL 211	120-240	vapor	BATES-1
R7T7 (SON68)	90, 100	hydrothermal	NOGUES
R7T7 (SON68)	150-250	hydrothermal	CAUREL
R7T7 (SON68)	25-250	hydrothermal	VERNAZ
SAN60	40-190	hydrothermal	VAN ISEGHEM
SAN60	90, 120	hydrothermal	PATYN
SM58	40-190	hydrothermal	VAN ISEGHEM
SM58	90, 120	hydrothermal	PATYN
UK209	40-190	hydrothermal	VAN ISEGHEM
SON58	40-190	hydrothermal	VAN ISEGHEM
SON64	40-190	hydrothermal	VAN ISEGHEM
PNL 76-68	25-350	hydrothermal	WESTIK-2
PNL 76-68	6-90	hydrothermal	BARKATT-2
PNL 76-68	40-250	hydrothermal	STRACHAN-1, -2
PNL 76-68	120-240	vapor	BATES-4
²³⁸ Pu-doped waste glass	25, 90	hydrothermal	BANBA
Obsidian	25-90	vapor	FRIEDMAN-2
Obsidian	150-200	hydrothermal	MICHEL
Obsidian	110-175	vapor	MAZER-1
Obsidian	60-200	hydrothermal	PETIT-2
Basalt glass	122-240	hydrothermal,	BYERS
		vapor	
Basalt glass	50-300	hydrothermal	GUY
Simple glasses	40-85	hydrothermal	MAZER-2
Simple glass	50-100	hydrothermal	ZAGAR
Simple glass	60-100	hydrothermal	RANA

^aThe temperature dependence of natural glasses and simple glasses has also been examined by a number of studies not included here. The studies listed here are believed to be representative of those germane to the subject at hand.

they can indicate whether the overall reaction changes with temperature. Reaction progress in hydrothermal studies was frequently monitored by measuring the change in solution concentration with time, while the glasses and their reaction products were not characterized. Consequently, the dissolution rates reported and any conclusions regarding the temperature dependences apply only to the overall reaction.

4.1 SRL 131 Glass

A study of the hydrothermal leaching of SRL 131, a nonradioactive borosilicate glass, was carried out at temperatures of 90 and 150°C for up to one year [ALLEN]. The glass was crushed to increase the effective surface area and accelerate the reaction. Abrupt increases in the rate of change of the solution concentrations of Na and B after 2500 h of reaction at 150°C, not observed after a similar period of time at 90°C, led the authors to conclude that the alteration mechanism had changed from ion exchange to network dissolution. An iron-rich smectite clay was found on the surface in both sets of experiments, but crystals of calcium silicate and the zeolites analcime and clinoptilolite were found only on the glass reacted at 150°C. The energy of activation for the reaction was not reported.

The conclusions reached by Allen et al. [ALLEN] regarding a change in reaction mechanism were based on the observation that the alteration assemblage and the release rate for cations to solution had changed, not on a firm understanding of the detailed reactions which make up the overall reaction. Although abrupt increases in the rate of change of the solution concentrations of Na and B were observed, they were probably the result of the onset of precipitation of secondary minerals (calc-silicates and zeolites). As these phases form and remove elements (e.g., Si and Ca) from solution, their dissolution affinities increase, favoring the addition of more elements, including Na and B, to solution. This is precisely the behavior that would be predicted with an affinity model for glass dissolution [BOURCIER]. In this case, it appears that increasing experimental temperatures affected the kinetics of secondary mineral precipitation and, thus, the overall reaction with respect to solution concentration changes. It would be inappropriate to use Allen's results to quantify the effect of temperature on the reaction because of the limited number of temperatures examined and the incomplete understanding of the overall reaction.

Similar studies of the hydrothermal reaction of SRL 131 glasses at 40 and 90°C for up to four years were performed [WICKS and BATES-2]. Biwer et al. [BIWER] reported additional analyses of these samples; they focused on the alteration layers and performed detailed characterizations using AEM. Samples reacted at 90°C contained secondary mineral phases, including bimesite, a hydrated Mn-oxide, a Mg-rich montmorillonite, a U-Ti bearing phase, and an Fe-rich layer that traced the original glass surface. Samples reacted at 40°C did not have a multilayer structure; instead, they had a single, thin noncrystalline layer with some U and Ti. The appearance of this layer (at 40°C after 4 years) showed no correlation with those formed at 90°C between 3 days and 3-1/2 years. The presence of a nonrestructured layer and the absence of secondary phases at the lower experimental temperature may indicate that at 40°C the reaction kinetics were not rapid enough to form a more structured phase assemblage, as found on samples reacted at 90°C. Interestingly, the layer formed at 40°C on SRL 131 glass did have an appearance similar to layers formed on SRL 165 glass reacted at 90°C for periods of less than 56 days.

Hydrothermal leaching experiments with SRL 131 glass at 40 and 90°C in deionized water for periods of up to two years have also been reported [STRACHAN-3]. Monitoring changes in solution concentration was the primary means of studying the overall reaction, complemented by SEM and X-ray diffraction (XRD) analyses. The alteration layers formed at 40°C were characterized as thin (<5 µm) and amorphous after 728 days of reaction, while the solution analyses indicated that normalized mass loss of B was greater than that of Si. At 90°C, the normalized mass loss of B was also greater than that of Si after 728 days, while the alteration layer formed was much more complex. Evidence for the formation of

a crystalline phase rich in Mn-Fe-Si was observed using SEM, but it was not detectable with XRD analysis. This suggests that there were either minute quantities of the material or that it was poorly crystalline. In addition, a thin, U-bearing band of crystallites within the alteration layer was found [STRACHAN-3]. A comparison of the normalized release of Si and B, the two elements studied in detail, indicated that at 40 and 90°C each element reached a steady state of release after approximately 100 days of reaction.

This study [STRACHAN-3] did not focus on the effect of temperature on glass/water reactions and did not address this issue in its conclusions. It did conclude that glass/water reactions involved a complex sequence of events that is influenced by such factors as the concentrations of species in solution and the formation of secondary alteration phases. When these results are compared with those for SRL 131 reacted in deionized water at 40 and 90°C [BATES-2; BIWER; WICKS], it is obvious that the descriptions of the alteration phases observed in each study are similar. The superior resolution of AEM techniques relative to SEM makes the recent results [BATES-2; BIWER; WICKS] more informative than earlier ones [STRACHAN-3] in that the characterization of alteration phases is more complete. These better data can aid in identification of the rate-controlling processes. However, the results of each set of experiments are complementary.

Leaching experiments of SRL TDS/131 glass between 23 and 120°C were performed utilizing a flow test apparatus and carried out for up to 28 days [BARKATT-1]. Deionized water and a simulated basaltic groundwater were used as leachants. Since no post-test surface characterization was performed, it is unknown whether any precipitation occurred during the tests. The authors found that their test data agreed with an activation energy of 100 ± 13 kJ/mol when the flow rate was approximately 250 m/yr. Leaching was proposed as the rate-controlling mechanism in these tests, based on the authors' interpretation of the trend of the release of species to solution.

The reported activation energy of ~100 kJ/mol is somewhat higher than those typically reported for the dissolution of nuclear waste glasses. Careful examination of the data used to derive this value suggests that the dissolution may not be typical of an Arrhenius-type temperature dependence. Barkatt et al. did not report estimates of their experimental error, but there may be two separate regimes that are described by Arrhenius behavior. Between 75 and 125°C, a case can be made for Arrhenius behavior with an activation energy of approximately 70 kJ/mol within the range typically reported for the dissolution of nuclear waste glasses. Below 75°C, it is unclear what temperature dependence, if any, exists since the experimental data exhibit large amounts of scatter. It is not immediately obvious if these results are directly comparable to static leach tests. This study would be more useful if the authors' contention that a leaching process is rate-determining could be confirmed. Characterization of the reacted glass using micro-analytical techniques would be one way to check this.

The reaction of water with SRL 131 glass has also been studied in vapor environments, that is, under conditions with a relatively high SA/V ratio [BATES-1, -2]. Over a temperature range of 120 to 240°C, SRL 131 and SRL 211 glasses were hydrated at 100% relative humidity for up to 92 days. The reacted glasses, including cross sections, were characterized by XRD and detailed SEM with an energy-dispersive X-ray detector (SEM/EDS), and the kinetics of the overall reaction were studied by monitoring the growth rate of the alteration layer. A number of secondary phases were found on the altered SRL 131 and SRL 211 glass surfaces, including analcime and tobermorite, a hydrated calc-silicate, on the outermost surface and a smectite clay (possibly stevensite) making up the inner layer. Also, two additional unidentified phases were detected on the surface of SRL 211 glass. Elemental line profiles of all of the hydrated layers clearly show that the two alteration layers are compositionally distinct, and that the reaction temperature does not appear to have had a profound effect on the resultant assemblage.

Complex alteration layer growth kinetics were also reported [BATES-1]. The rate of growth was initially proportional to the square root of time at each temperature. After 144 h at 202 °C and 24 h at 240 °C, the growth rate of the alteration layers on SRL 131 glass increased significantly. A similar change in the growth rate of the alteration layers on SRL 211 glass was also reported. This change was later correlated with the appearance of tobermorite [ABRAJANO-1]. An activation energy for SRL 131 glass, based on the initial growth rate of the alteration layer, was reported as 75 kJ/mol.

The results reported by Bates et al. [BATES-1] and Abrajano et al. [ABRAJANO-1] suggest that the same reaction processes are occurring in hydrothermal and vapor environments. However, the overall reaction, with respect to the nature of the alteration layer, is quite different. Differences in the SA/V ratios drastically affect the rate-determining step(s) and the extent of reaction. Since the reaction in vapor environments takes place in the small amount of water sorbed onto the glass surface, the affinities of the reacting species start to decrease in a much shorter period of time relative to reactions in hydrothermal environments. This results in the formation of secondary phases much earlier than is observed in hydrothermal tests, presumably since the kinetics of precipitation are favored by more saturated solutions. The episode of increased layer growth after tobermorite is initially observed supports Bourcier's model [BOURCIER]. The increased rates of layer growth reported in vapor tests [BATES-1] are apparently analogous to observations of increased rates of release of cations to solution in hydrothermal testing [ALLEN]. These observations highlight the importance of understanding the reactions that make up the overall reaction and the effects of factors such as temperature and SA/V ratio.

4.2 SRL 165 Glass

Bourcier et al. [BOURCIER] reported the results of the experimental dissolution of uranium-doped SRL 165 glass under hydrothermal conditions between 100 and 250 °C. These experiments were performed to provide results for evaluating a kinetic model of glass dissolution based on the dissolution affinity of a surface alteration layer. It was observed that at 100, 150, and 200 °C, the normalized rate of release of cations to solution followed a trend where $Li > B > Si > Al > U$. At 250 °C this sequence had changed so that $B > Li > Si > U > Al$. Because the normalized rates of release were not equivalent at any of the temperatures examined, the authors concluded that the glass was not dissolving stoichiometrically. Although detailed characterization of the altered glasses was not performed, they referred to the secondary ion mass spectroscopy (SIMS) results for an identical glass composition reacted in a similar experimental setup at 90 °C [ABRAJANO-1; BATES-1]. The SIMS results indicate that Fe, Al, Si, Ca, and Mg were enriched in the alteration gel layer. The activation energy of the dissolution process was not subjected to an Arrhenius-type analysis, and a complete assessment of the temperature effect on the reaction of this glass has yet to be completed. Modeling of these experiments suggests that during glass dissolution a surface alteration layer quickly forms on the glass surface, and its dissolution affinity controls the subsequent overall glass dissolution rate.

As Bourcier et al. concluded, their modeling efforts could be improved by incorporating better thermodynamic data for the alteration layer, by accounting for all of the observed secondary phases formed during experiments, and by better characterizing the nature of the alteration layer using techniques with nanometer-scale resolution. They recognized that the need for detailed characterization of the alteration layer formed during the hydrothermal alteration of SRL 165 glass is rooted in their modeling efforts, which attempted to understand glass dissolution by elucidating the rate-controlling step(s) of the overall reaction. Their observation that the normalized rates of release of B and Li reversed between 200 and 250 °C was not investigated, so it is unclear whether this resulted from a change in the alteration assemblage or from a change in the relative dominance of one reaction at the expense of another. Work is ongoing to better characterize the alteration phases on these samples. These additional data will allow a

more complete understanding of the temperature effects, including the rate-controlling processes, on the reaction of SRL 165 glass with water.

4.3 R7T7 Glass

Vernaz et al. [VERNAZ] reported that between 25 and 250°C the activation energies determined from the release of Si and B from R7T7 glass in leach experiments varied from 24 to 58 kJ/mol. They suggested that activation energies in this range were associated with an unidentified hydration reaction process operating independently of the solution concentration. Thus, overall reactions with activation energies near 25 kJ/mol were believed to indicate that saturation of the reacting solution had occurred, and that this unidentified hydration reaction process had become rate controlling. At 250°C the alteration mineral assemblage changed, with the formation of pollucite, a Cs-rich phase, also indicating that the change in temperature had affected the reaction. When the reaction was performed at 300°C, the apparent activation energy of reaction increased to 143 kJ/mol. X-ray EDS line profiles of cross sections from glasses reacted at temperatures up to 250°C indicated that the alteration layer consisted of two parts, an altered layer rich in Zn and Fe on the outer surface and an inner gel layer rich in Zr and rare earth elements (REE). Those observations are similar to those reported for glass reacted similarly at 90°C [NOGUES] and at 100°C [THOMASSIN]. The activation energy of the initial corrosion period, 60 kJ/mol, was noted as being similar to previous overall activation energy determinations for nuclear waste glasses. It was suggested that at 300°C the controlling process was no longer glass corrosion but a glass transformation whereby water, temperature, and pressure synergistically transformed the glass into a secondary mineral [VERNAZ].

Whether the changes in the reaction rate or secondary mineral assemblage were the result of different reaction mechanisms or simply accelerated reaction progress due to increased temperatures was not examined; therefore, it is difficult to evaluate the author's claims that at 300°C the reaction process changed into one of glass transformation. The large increase in the activation energies determined from the normalized release of cations to solution is analogous to observations made by Bates et al. for SRL 131 glass [BATES-1, -2] and may result from the formation of secondary mineral phases. The observation that the overall secondary mineral assemblage varied with temperature probably reflects the effects of precipitation kinetics on nucleation rate of various secondary phases.

Vernaz et al. [VERNAZ] concluded that, while temperature may be useful to accelerate some processes that are difficult to study at lower temperatures, a direct extrapolation of the overall reaction does not seem possible. The authors correctly recognized the need to identify each reaction process (in their case, hydration, diffusion, dissolution, and phase formation) and then develop an understanding of each mechanism's temperature dependence.

The characterization of R7T7 glass, hydrothermally leached in double-distilled water at 150 and 250°C for up to one year, was reported [CAUREL]. Leachates and secondary products were characterized by a number of analytical techniques, including inductively coupled plasma (ICP), transmission electron microscopy (TEM), SEM/EDS, XRD, and cathodoluminescence. At 150°C the solution concentrations reached an apparent steady state after 30 days. At 250°C the rate of increase in solution concentrations of Si, Na, and B decreased for the initial 21 days of reaction, at which point the release rates of Na and B suddenly experienced a significant increase and finally reached apparent steady-state values after 190 days. A layer of smectite was formed at 150°C with an amorphous silica-enriched phase. Equivalent layers were also formed at 250°C, along with zeolites (analcime, natrolite, thomsonite, and gmelinite), calcium silicates (tobermorite or gyrolite), and an undefined boron-rich species. Qualitatively, these results are similar to those reported by Allen et al. [ALLEN], in that an apparent change in leaching behavior, as seen by changes in release of species to solution, is accompanied by a

change in the alteration phase assemblage. In each case, experiments performed at the higher temperature tend to form a greater number of more crystalline secondary mineral phases. As with other leaching studies, the usefulness of this work is limited in that the temperature dependence of the overall reaction between 150 and 250°C was examined. It is unclear how high or how low in temperature these results can be extrapolated. A more detailed study which identified the reaction mechanism operating in the tests might have allowed such extrapolations to be made.

Detailed characterizations of the alteration layers formed from the dissolution of R7T7, a French borosilicate glass (also referred to as SON68) hydrothermally leached in double-distilled water at 90 and 100°C for up to 91 days, were obtained by Nogues et al. [NOGUES]. Qualitatively, these studies indicate that alteration layers formed at 90 and 100°C are similar to those formed at higher temperatures [VERNAZ]. A combination of SEM/EDS, wavelength dispersive spectroscopy (WDS) with an electron microprobe, and TEM analyses was performed on the altered glasses [NOGUES]. A complex alteration assemblage was described, which included an outer layer consisting of Fe- and Zn-rich phyllosilicates (clays) and an amorphous, gel-like inner layer. In addition, two very thin layers, $>0.1\ \mu\text{m}$, one lying between the inner and outer layers (described as having a very fine granulated texture) and one between the inner layer and the unreacted glass (described as enriched in rare earth elements), also formed. Because the experiments were only performed at two temperatures, no attempts were made to quantify the temperature dependence using the Arrhenius relation.

The detailed analyses performed by Nogues et al. [NOGUES] provide useful information that helps provide a basis for starting to understand how water reacts with glass. The authors were unable to reach any conclusions regarding the effect of temperature on glass/water reactions, but such careful characterizations can aid in deciphering the complex interactions of multiple reaction processes. Additional samples reacted over a reasonable range of temperatures, with similar detailed analyses of the alteration assemblage, are needed to assess the temperature dependence of the reaction.

In summary, the authors of each of these three studies [VERNAZ; CAUREL; NOGUES] all had similar results with respect to solution analyses and characterization of alteration layers. This suggests similar conclusions regarding the temperature effect on the reaction of R7T7 waste glass with water. Vernaz et al. [VERNAZ] found that the influence of temperature was complex, as evidenced by the fact that the activation energies determined did not correspond to any known values of glass dissolution or to the solubility of any known mineral. Caurel et al. [CAUREL] concluded that the results of experiments performed at 150 and 250°C were not comparable because the reaction processes at each temperature were different. Based on the present state of understanding of the reaction processes, temperature could not be used to accelerate the reaction of R7T7 glass with water in a predictable manner. To gain such an understanding, one must identify rate-controlling processes at each temperature of interest and develop a model demonstrating that the experimental observations, including alteration phase formation, changes in concentration of species in solution, and measured activation energies, could all be accounted for. The major research need before such a model can be developed is a description of the rate-controlling processes.

4.4 PNL 76-68 Glass

Westik et al. [WESTIK-1] reported on the temperature dependence of the leaching behavior of PNL 76-68 glass in deionized water between 25 and 350°C for up to 341 days. After monitoring the release of Na, B, Si, and Mo in hydrothermal tests, they concluded that the leaching behavior was not constant over this temperature range, and that three distinct reaction regimes could be recognized on an Arrhenius plot: between 25 and 150°C, between 150 and 250°C, and between 250 and 350°C. The activation energy for the overall reaction, based on the release of Na, B, Si, and Mo to solution between

25 and 150°C, was reported as 54 kJ/mol. Strachan et al. [STRACHAN-1] also reported on the leaching behavior of PNL 76-68 glass between 90 and 250°C. Although the temperature dependence was not quantified, they reported that between 150 and 250°C the leaching behavior showed significant changes. Unfortunately, the nature of these changes was not described. These results were based solely on analyses of the species concentration in solution and, while instructive, do not provide enough information to allow an assessment of the effect of temperature. It is unclear from these results whether the process controlling the dissolution of the glass has changed as a function of temperature.

A more detailed report of the leaching of PNL 76-68 glass at 40, 70, and 90°C in deionized water, silicate water, and several brine solutions was presented [STRACHAN-2]. This study made no attempt to quantify the temperature dependence of the reaction. Strachan noted that the release rate of Si and Cs to solution was lower at 40°C than at 90°C, but that of Sr to solution at 40°C was approximately ten times greater than at 90°C. Qualitative conclusions regarding the effect of temperature on the reaction were that experiments need to be run for periods of time greater than a year to achieve measurable reaction at all temperatures. Post-test alteration layer characterizations were performed using SEM/EDS and secondary ion mass spectroscopy (SIMS). These analyses indicated that a gel layer, enriched in Ti, Zr, Nd, Ce, Zn, and Fe formed on the surface of the glass reacted at 40°C. Small particles rich in Nd and Zr or P were also found on the surface. Samples reacted at 90°C were found to have produced two distinct layers. An outer layer, formed by precipitation on the glass surface, consisted predominantly of Zn and Si, with trace amounts of Cs, Ca, and Ti. An inner gel layer rich in Fe, Nd, La, and Ti formed as soluble material was leached from the glass matrix. The inner layer reportedly grew at a rate roughly proportional to the square root of time. Interestingly, similar observations were made for SRL 131 glass [BIWER], namely, that the alteration layers formed at 40 and 90°C, while grossly similar in composition and appearance, do not have the same layer structure and are not equivalent.

Leaching experiments with crushed PNL 76-68 glass have been performed over the range of 4 to 90°C in distilled water for up to 21 days [BARKATT-2]. Reaction progress was monitored by measuring the release of Si, Na, Cs, Sr, Fe, and Zn to solution. An apparent activation energy of 50 kJ/mol was calculated for the reaction, based on the release of Si to solution. The releases of Na, Cs, and Fe resulted in activation energies of approximately 67 kJ/mol, while the release of Zn did not exhibit Arrhenius behavior. (The release at 70°C was less than at 20°C.) In their interpretation of these results, the authors recognized that their apparent activation energies were derived from a diffusion-related term and a matrix-dissolution term of the overall reaction. They postulated that ion exchange was the rate-determining step in their reactions, but no surface characterizations were performed on the reacted glasses. It is, therefore, difficult to confirm their assertions.

Without an identification of the rate-controlling process(es), it is unclear what overall reaction is taking place. Interestingly, a range of activation energies can be determined from these experimental results. Furthermore, the non-Arrhenius release of Zn to solution clearly indicates that complex dissolution behavior, possibly retrograde solubilities, is involved. This would seem to indicate that (1) multiple processes are involved in the overall reaction mechanism, and/or (2) using the release of species to solution as the only measure of reaction progress may not be suitable for studying multiple process reaction mechanisms.

Overall, these studies of the temperature dependence of PNL 76-68 glass leach behavior are consistent in that the leach behavior observed is similar in each study, although the lack of any supporting detail by Strachan et al. [STRACHAN-1] makes those results difficult to review critically. The results reported by Strachan [STRACHAN-2] cannot be critically assessed because no effort was made to investigate the temperature dependence of the overall reaction. The results of Westik et al. [WESTIK-1] would have benefited from some post-test solids characterization. A description of the secondary mineral

assemblage formed at each temperature could have assisted in understanding the processes involved in each test and may have been analogous to results found in studies of SRL 131 glass [ALLEN; BIWER]. The qualitative characterizations of the layers formed at 40 and 90 °C [STRACHAN-2] indicate that temperature might be affecting the secondary phase assemblage, a conclusion noted by Strachan, who suggested that the overall reaction is at least partially controlled by decreases in dissolution affinity of the reacting phases. It is unclear whether the observed differences are the result of an actual change in the overall reaction or whether at 90 °C the increased temperature increases the kinetics of precipitation to such an extent that a second, precipitated layer forms. As Strachan implied in his conclusions, additional experiments are needed to better define the rate-controlling processes of the overall reaction.

4.5 European Waste Glasses

The long-term corrosion of two Belgian high-level waste glasses (SAN60 and SM58) was investigated at 90 and 120 °C in distilled water for durations up to one year [PATYN]. The solids were powdered to increase the reactive surface area and, consequently, were not characterized after the experiments were terminated. The solution concentrations at 90 °C show a steady increase with time; however, at 120 °C there is a sudden, significant increase in the release rate of all elements to solution between 50 and 90 days. Subsequent attempts to model this behavior using the geochemical modeling codes PHREEQE and GLASSOL were unable to successfully describe these episodes of enhanced release. Since these computer codes assume that H_4SiO_4 activity in solution is the rate-controlling parameter, their failure to predict the long-term dissolution behavior of these glasses implies that the affinities of other solution species should also be considered, as in Bourcier's model [BOURCIER]. The use of powdered glass also appears to have limited the amount of post-test alteration-phase characterization, which would have been beneficial information in analyzing the geochemical modeling. Analogous testing with monolithic glass samples could have alleviated this shortcoming.

Van Iseghem et al. [VAN ISEGHEM] describe the corrosion behavior of five European high-level waste glasses, including SON58, SON64, UK209, SM58, and SAN60, in distilled water between 40 and 190 °C for periods up to eight months. The solution concentrations of Si and Al after 28 days were reported as being at their "saturation values" for experiments above 150 °C. Van Iseghem et al. observed that at 150 and 190 °C, a significant amount of secondary minerals formed on the glass surface, including analcime, another unidentified Na-rich zeolite, the Li-rich aluminosilicate eucryptite, and an unidentified calc-silicate. The authors speculate that similar observations of mineral formation could be made for experiments performed at 90 or 120 °C with reaction periods greater than eight months. Their observations and speculations are consistent with what is known regarding nucleation kinetics (see Section 3.3), that is, higher temperature experiments permit earlier nucleation of secondary phases.

In summary, Van Iseghem et al. [VAN ISEGHEM] did not evaluate the effect of temperature on the reaction of waste glasses with water. They did find that corrosion, or dissolution, of the glasses was enhanced at temperatures greater than 150 °C because of a decrease in the solution concentration caused by extensive precipitation. These results are incomplete with respect to understanding the temperature dependence of the reaction because it is unclear what the rate-controlling processes are at each temperature. Additional work is required to better characterize the rate-controlling processes of the overall reaction and further identify the alteration phases that form. Patyn et al. [PATYN] correctly concluded that additional experimental work was required to understand their experimental results and, consequently, allow them to develop better geochemical models of their systems.

4.6 Japanese Waste Glass

The dissolution behavior of a ^{238}Pu -doped glass was reported by Banba et al. [BANBA]. Based on the normalized elemental mass loss measured in ISO leach tests, they found that between 23 and 70 °C the release of Si, Na, Sr, and Cs has an Arrhenius temperature dependence with an energy of activation of 80 ± 9 kJ/mol, suggesting that each of these cations is being released from the glass via the same unidentified reaction process. The Pu release also displayed an Arrhenius temperature dependence, but the corresponding energy of activation obtained was 22 ± 10 kJ/mol. The relatively low activation energy derived from the Pu release data was subsequently attributed to the formation of hydrous plutonium dioxide. The activation energies of secondary phase formation described in Section 3.3 is consistent with Banba's interpretation that the E_a associated with Pu release to solution is due to the formation of hydrous plutonium dioxide. The formation of this secondary phase was not confirmed and apparently did not inhibit the release of the other elements monitored.

In this work, Banba et al. [BANBA] found two distinct activation energies, which described the release of elements to solution. The ability to do so is good evidence that the unidentified reaction mechanism(s) has not changed with temperature. It is uncertain whether the release of the other reported elements is also controlled by secondary phase formation. The Pu release activation energy is similar in magnitude to those reported for other secondary phases (see Section 3.3). This study demonstrates that over the temperature range examined, the release of Si, Na, Cs, Sr, and Pu to solution behaves in a predictable manner. The identity of the precise reaction mechanism(s) is, however, unclear.

Banba et al. did not assess the temperature effect in their conclusions, so additional research is necessary. Specifically, formation of a hydrous plutonium dioxide phase, as well as any other alteration phases, must be confirmed before the rate-controlling processes of the overall reaction can be identified. The observation of Arrhenius behavior of the species in solution is intriguing, but it would be much more informative if this behavior were correlated with information about alteration phases. As a result, without a firm understanding of the rate-controlling mechanism(s) and its temperature dependences, the range of temperatures to which these data can be extrapolated is unknown.

4.7 Synthetic Basalt Glass

The dissolution behavior of basalt glass with respect to solution concentrations under hydrothermal and vapor hydration conditions was studied at 90 to 240 °C for durations up to one year [BYERS]. The normalized release rates of the major elements (Si, Al, Mg, Ca, and Na) were proportional to the square root of time for periods up to one year and were near zero after one year of reaction in hydrothermal leach tests. The alteration assemblage produced in the hydrothermal tests consisted entirely of a smectite clay composition phase that was amorphous to poorly crystalline. The phases that formed on basalt glass closely matched the alteration phases formed on SRL 165, a waste glass reacted under similar conditions, suggesting that basalt glass is a suitable natural analogue. Byers et al. [BYERS] described the alteration phases produced in the vapor environments, which indicate that the crystallinity of the clay-like surface layer increased with temperature. In addition, detectable occurrences of secondary minerals, primarily zeolites and calcium silicates, were found on samples reacted in vapor above 187 °C.

Mazer and Bates [MAZER-3] subsequently characterized the altered glass monoliths from the study by Byers et al. [BYERS] in detail using SEM/EDS techniques to measure the alteration layer growth with time. They found that, over the temperature range examined, the Arrhenius equation could be used to describe the temperature dependence with an activation energy of 43 kJ/mol, a value similar to those found for the nucleation of smectites. These studies report that the composition of the clay layer which formed on the glass surface varied slightly as a function of the reaction temperature. Clays formed

at higher temperatures were richer in Al, Mg, Ca, and water, relative to silicon. The conclusion of both sets of authors was that vapor hydration experiments resulted in alteration assemblages on basalt glass that are more similar to natural basalt glasses which have been reacting at lower temperatures for periods up to tens of thousands of years.

5.0 CONCLUSIONS

In general, the Arrhenius equation can be used to describe the temperature dependence of glass/water reactions, at least over small temperature ranges. These dependences can be described for several measures of glass reaction, including solution concentration changes and alteration layer thicknesses. Leach tests have reported an Arrhenius temperature dependence on the rate of release of cations to solution for borosilicate waste glasses [e.g., STRACHAN-1; GRAMBOW] and simple glasses (e.g., RANA; MAZER-2; KNAUSS). These studies have examined the overall reaction of each system, and the Arrhenius behavior suggests that the rate-controlling process, while not always identified, does not change over the temperature range considered. In several investigations, particularly where secondary phases are abundant, the energy of activation measured has a value similar to that found for nucleation kinetics of secondary phases, including clays and zeolites [e.g., VERNAZ; WESTIK-1; MAZER-1, -3]. Control of an overall glass/water reaction by the nucleation and formation of secondary phases is consistent with models where solution concentrations can impede the reaction by decreasing the chemical affinity of the dissolving phase(s). Studies where secondary phases have formed on the glass are particularly noteworthy because they were performed for extended periods of time and are thought to be more representative of long-term reaction within a repository.

Most studies have only considered the changes in concentration of species in solution for glass/water interactions. Such information may reflect the overall reaction, but it does not allow definitive identification of the rate-controlling process(es). Studies that included solids characterization have been much more informative, particularly studies utilizing AEM.

To use temperature as an accelerating parameter in nuclear waste glass/water studies, one must identify the rate-controlling reaction steps at the experimental temperatures and the temperature of interest (repository). After this identification is made and characterized as a function of temperature, and it is found that the rate-controlling reaction step does not change, then temperature can be used to accelerate glass/water reactions in a meaningful way.

One example where this approach has been employed successfully is described by Knauss et al. [KNAUSS]. Isothermal flow-through dissolution experiments were performed on a simple five-component borosilicate glass from pH=1 to 13. Experiments were performed at 25, 50, and 70°C, and dilute buffer solutions maintained constant pH during the experiments. Post-test analyses included solution analyses and solids characterization. The flow-through experimental setup allowed the authors to examine the kinetics of glass dissolution yet avoid the complications caused by dissolution affinities. Although the mechanism of glass dissolution was not fully described, this study provided information on the early kinetic steps in the process and may help eventually elucidate the reaction mechanism for this glass. This type of experimental approach will ultimately be the most useful in eventually deciphering glass/water interactions.

Identification of the rate-controlling reaction step cannot be made by investigating a single monitor of experimental reaction progress, such as the change in solution concentrations, changes in reaction layer thicknesses, or composition of the alteration phase assemblage. Several studies have demonstrated that the task of investigating the identity of the rate-controlling reaction would be facilitated through use of analytical techniques such as AEM, which can allow detailed examination and identification of alteration phases. This type of information, considered in conjunction with more routinely collected measurements, such as solution concentration, can allow researchers to elucidate reaction mechanisms more easily.

The results of studies examining the temperature dependence of waste glass/water reactions provide tantalizing data suggesting that temperature can be used as an accelerating parameter.

Unfortunately, the lack of a complete data set (including all of the reaction processes participating in the overall reaction and their respective temperature dependences) suggests that one should be cautious when temperature is used as an accelerating parameter.

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