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A LITERATURE REVIEW OF SURFACE ALTERATION LAYER EFFECTS ON WASTE GLASS BEHAVIOR

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A Literature Review of Surface Alteration Layer Effects on Waste Glass Behavior

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I. Introduction

When in contact with an aqueous solution, nuclear waste glass is subject to a chemical attack that results in progressive alteration. During this alteration, constituent elements of the glass pass into the solution; elements initially in solution diffuse into, or are adsorbed onto, the solid; and new phases appear. This results in the formation of surface layers on the reacted glass. The glass corrosion and radionuclide release can be better understood by investigating these surface layer effects.

In the past decade, there have been numerous studies regarding the effects of surface layers on glass reactions [1-12]. This paper presents a systematic analysis and summary of the past knowledge regarding the effects of surface layers on glass-water interaction. This paper describes the major formation mechanisms of surface layers; reviews the role of surface layers in controlling mass transport and glass reaction affinity (through crystalline phases, an amorphous silica, a gel layer, or all the components in the glass); and discusses how the surface layers contribute to the retention of radionuclides during glass dissolution.

II. Formation of Surface Layers during Glass Corrosion

Glasses undergo several reaction processes when exposed to aqueous and/or humid air environments that result in the formation of surface layers. Figure 1 shows the typical surface layers observed in corroded glass [13]: an outermost precipitation layer, an innermost diffusion layer, and a gel layer which is between the diffusion layer and the precipitation layer. These surface layers differ structurally and/or compositionally from the original glass and are usually formed by more than one reaction process. These processes are briefly discussed below.

1. Soluble Element Depletion and Water Diffusion

When waste glass is contacted with an aqueous system, water molecules diffuse into the glass matrix, and the glass undergoes ion exchange processes between the hydrogen in the water molecule and the alkali on the nonbridging oxygen sites in the glass [14]:

$$\equiv\text{Si-O-Na} + H_3O^+ = \equiv\text{Si-O-H} + Na^+ + H_2O \qquad (1)$$

The ion exchange process, together with diffusion of reactant (H_2O) and products (e.g., Na^+ and OH^-), increases the leachate pH and forms a surface region which is depleted in alkalis. This surface region is labeled as "diffusion layer" in Figure 1.

Water molecules must be present before ion exchange reactions take place. However, water diffusion without accompanying dealkalization has been reported for natural obsidian [15-18] and tektites [19]. A region of glass can, therefore, be hydrated but not alkali depleted.

2. Network Hydrolysis

Network hydrolysis reactions break down the glass network and lead to glass dissolution and restructuring of surface layers on the reacted glass. The major hydrolysis reactions for nuclear waste glasses can be expressed as follows:

$$\equiv\text{Si-O-Si}\equiv + OH^- \Leftrightarrow \equiv\text{Si-O}^- + \equiv\text{Si-O-H} \qquad (2a)$$
$$\equiv\text{Si-O-Si}\equiv + H_2O = 2\equiv\text{Si-O-H} \qquad (2b)$$

The above reactions involve silica, but they can also involve other network-forming elements, such as Al, B, and Zr.

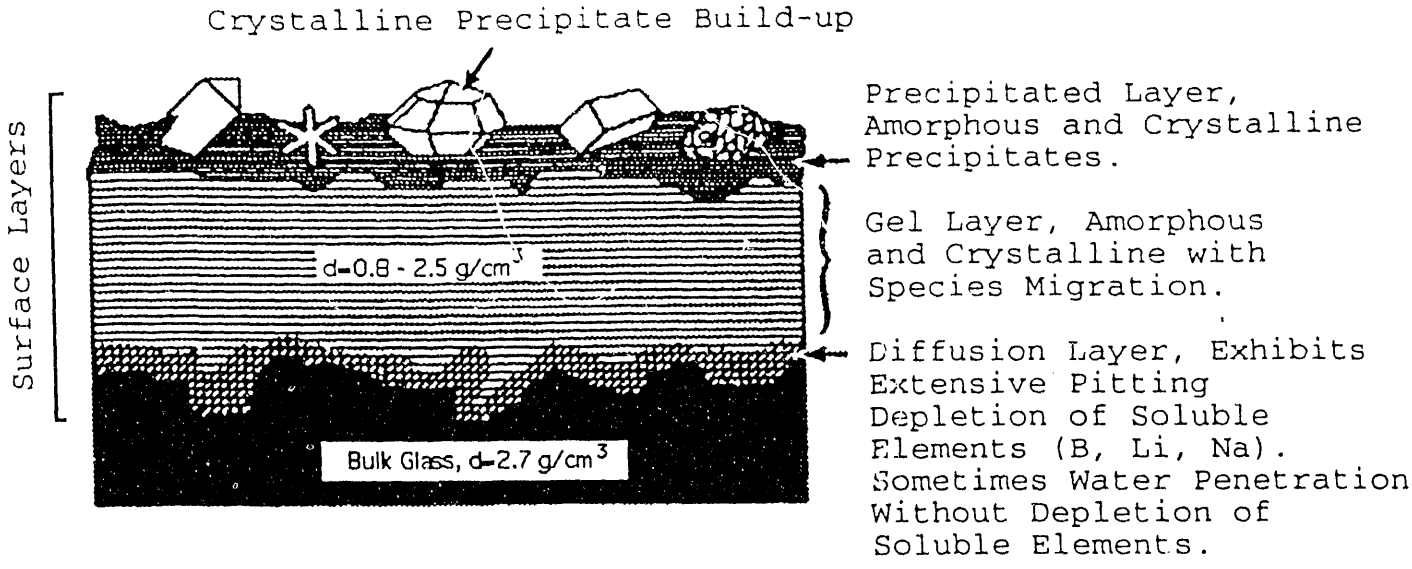

Figure 1. Schematic of Surface Layer on Leached Glass (after Ref. 13).

For most waste glasses, the initial reaction is diffusion-controlled ion exchange, which produces a diffusion layer. Hydroxide produced by ion-exchange reactions, together with hydroxide already in the leachant, promotes the hydrolysis reactions in the dealkalized layer and also couples the ion exchange and matrix dissolution processes. This transforms part of the diffusion layer into a gel layer (Figure 1) and limits the diffusion layer to less than 1 μm in thickness [13, 20]. The network hydrolysis and condensation reactions are also responsible for the restructuring and evolution of the gel layer [3, 8, 12, 21]. Another place where reaction (2) is important is the interface between the gel layer and the solution, where the main products are monosilicic acid or other molecular products of hydrolyzed network formers [22-24].

Network hydrolysis has also been proposed to have a strong correlation with diffusion-controlled ion exchange and water diffusion processes [11]. Both alkali exchange and matrix dissolution may be controlled by a similar process. Pederson [25] observed that the glass reaction rate in D_2O is 0.7 times lower than that in H_2O during both the initial alkali release stage and the later matrix dissolution stage. The isotope effect was explained by a proton transfer step in the alkali release and the matrix dissolution processes. Network hydrolysis and condensation reactions not only control gel layer formation but also water diffusion [11].

3. Precipitation/Adsorption

As glass reaction releases elements to solution, the leachate may become supersaturated with respect to some phases. This leads to precipitation from solution onto the glass surface and the walls of the test vessels, as well as formation of colloids in solution. This mass transfer from solution to the precipitated phases (Figure 1) in the surface layer is controlled by solubility and adsorption, which is mainly a function of solution composition and pH. Lee and Clark [26] studied the surface layers formed in chloride solutions containing Na, K, Mg, Ca, Zn, and Al. The compositions and properties of the surface layers formed on the reacted glass varied considerately as the solution composition changed. Knauss et al. [27] demonstrated that the surface layer composition varies as solution pH changes due to the pH-dependent solubility limit. The surface layers were devoid of Ca and Al when the glass was leached in pH 1-2 buffers because of the high solubility of these elements at this pH

range (the ion exchange is expected to be the main mechanism for the depletion of these elements). Between pH 3 and 6, the surface layers contained Al and a small amount of Ca due to decreased solubility. At pH 11.8, aggregates of a fine-grained secondary mineral were found coating the glass surface. Sometimes, precipitation can be caused by local variations in the pH without equilibrium with the bulk solutions [28, 29]. This local precipitation usually happens inside the gel layer.

The leached surface of the waste glass becomes electrically charged (usually negatively) as dissolution proceeds [30], because of the acid-base reactions between glass surface elements and water (H^+ or OH^-) [31]. The acid-base chemistry of a particular glass surface is characteristic of its composition and structure. Once charged, the surface of a glass attracts a swarm of oriented water molecules and counter ions. This promotes surface deposition of solution species, especially positively charged metal ions such as Ca^{2+} and Mg^{2+}, and hydrolysis products of metal oxides [such as $M(OH)^{x+}$ of Zn, Al, and Fe ions] or colloids from solution [30]. Therefore, precipitation and adsorption are important processes for the formation of altered glass surfaces [3, 8, 32-36].

Among the processes discussed above, dealkalization is considered to be a dominant corrosion process only during the initial glass-water interaction. In the longer term, the network hydrolysis is controlling [9, 37]. Grambow [39] has shown that network hydrolysis may follow a square-root-of-time dependence, if silica transport through the surface layer is rate-limiting. Recently reported studies on R7T7 glass in brines [39], on five Al-rich waste glasses in deionized water (DIW) [40], and on SM527 glass in DIW and in clay water [41] suggest that the long-term glass corrosion rate is diffusion controlled. Grambow et al.'s data [39] suggest that water diffusion is rate-controlling in the long term because the rate of the first-order dissolution reaction becomes so low, owing to silica saturation. Van Iseghem et al.'s data [40] suggest that ion exchange reactions between H_3O^+ and Na^+/Li^+, rather than diffusion of H_2O, is the long-term rate-controlling process. Grambow et al. [42] further pointed out that the rate-limiting step might change if the test conditions are changed. For example, it is possible another rate-controlling step could dominate glass dissolution when the surface reaction rate decreases with time. Such a situation might occur if secondary phase formation or sorption of silica on the surfaces of the glass leads to silica undersaturated conditions.

III. Effects of Surface Layers on Glass Corrosion

Surface layers may be "protective" or "unprotective" [5, 31, 43, 44]. Protective surface layers can slow down the glass corrosion rate. Unprotective layers have a porous structure of sparingly soluble solids and adsorbed species which do not significantly influence the reaction rate. Some systematic investigations have been conducted to clarify the role of surface layers on glass corrosion [2, 10, 32, 45-50]. This section will examine the effects of surface layers on the glass reaction, and the next section discusses the effects on radionuclide release.

The influence of surface layers on the glass corrosion rate is considered here in two parts: (1) how surface layers can act as physical mass transport barriers that influence the corrosion rates, and (2) how surface layers influence glass reaction affinity.

1. Surface Layers as Physical Mass Transport Barriers

Hench et al. [43, 45, 51] suggested that the leaching behavior of nuclear waste glass is largely a function of the surface composition, and Hench and Clark [51] have categorized glass surfaces into five types, based on the composition profile. Most discussions in the literature regarding the role of the alteration surface layers in glass reaction deal with whether the surface layers form physical mass transport (diffusion) barriers that inhibit further glass reactions by impeding the transport of reactants and products to or from the reaction zone [23, 52-62]. Observed decreases in leach rate with time can also be attributed to the approach to saturation limits of glass components in solution [32, 63-66]. The studies described below were designed to investigate the layer effects and to distinguish these from solution saturation effects.

Chick and Pederson [48] investigated whether the glass reaction rate is mainly controlled by diffusion through the surface layers or by solution saturation levels. Four simulated waste glasses,

each with very different compositions, were tested under MCC-1 conditions at 90°C. In the first experiment, samples were preleached for 56 days to build up a surface layer, and those samples were then placed in fresh water to leach for another 56 days. Comparison of leach behavior of the samples during the two 56-day leaching periods generated information on the role of the surface layers. Chick and Pederson found only a slight decrease in leach rate with the surface layers present. In the second experiment, a sample remained in the leachant for half of the allotted time. It was then removed and replaced by a new sample which leached for the remaining time. The results indicate the leach rate with no surface layers present, but with the solution already partially saturated, was almost identical with that from the samples that leached for the whole duration, suggesting that the rate of corrosion of the fresh glass inserted after the initial period was controlled by the leachate and not the glass surface condition. In sum, this study indicates that the surface layers provide some barrier to glass reaction, but solution saturation is the primary cause of leach-rate retardation.

High Solution pH Enhances Surface Layer Barrier Effect: Conradt et al. [49, 67] investigated the role of surface layers formed on SM 58 LW 11 nuclear waste glass in a salt brine (pH = 5.7 ± 0.3) under hydrothermal conditions at temperatures of 120 and 200°C. They found that surface layers formed in brine solution do not significantly contribute to mass transport between solution and the bulk glass. However, they found that in similar tests on the glass in 0.01M NaOH solution (pH = 12.0), the glass reaction rate is almost completely controlled by the surface layers, while the accumulation of reaction products in the solution has little effect. This result at pH 12.0 is significant because many leachates from testing nuclear waste glasses under static conditions have pH values around 12 [68, 69], where surface layers may play an important role in controlling glass reaction rate. This should provide some input to our efforts in modeling glass behavior in high alkaline solutions.

Solutions Containing Mg Foster Impervious Surface Layers: Malow [56] observed decreasing leach rates of C-31 3EC waste glass in salt solution of $MgCl_2$-$MgSO_4$-NaCl-KCl and found that Mg in the surface layers was enriched by a factor of 10 over the bulk glass composition. The dense and adherent surface layers found under these conditions were protective and impervious to both leachants and leachates. Grambow and Strachan [47] studied the protectiveness of the surface layers formed on PNL 76-68 and C31-3 nuclear waste glasses under MCC-1 test conditions in both DIW and 0.001M $MgCl_2$ solution. The leach behavior of samples with the surface layers removed after 57 days was compared with that of samples without layer removal for up to 158 days. Grambow and Strachan's data indicate that the surface layers formed in DIW have no effect on glass reaction, while the surface layers formed in 0.001M $MgCl_2$ solution yield a factor of three difference in leach rate. Hench and Clark [3] found that under both static and slow flow conditions, the leach rate of SRL 131-29.8% TDS waste glass in 1152 ppm $MgCl_2$ solution is much lower than in DIW, or solutions containing $AlCl_3$ (1028 ppm), $CaCl_2$ (1057 ppm), or $ZnCl_2$ (1025 ppm). Scanning Electron Microscopy (SEM) examination of the surface layers showed that the surface layers formed in $MgCl_2$ solution were the least porous and probably an efficient barrier. Barkatt et al. [70] found that the leach rates of waste glasses of PNL 76-68, SRL 165, and WV205, and microtektites in seawater were two orders of magnitude smaller than those in DIW. The systematic leachant composition studies and surface etching studies of Barkatt et al. indicate that the formation of an insoluble Mg-rich layer is the major cause for the retardation of glass leaching in seawater.

All these studies indicate that various Mg-ion-containing solutions foster the development of impervious surface layers. These types of surface layers hinder the transport of (1) reaction products from the reaction sites to solution and (2) reactants from solution to reaction sites, thereby slowing down the glass reaction.

Surface Barrier Effects Due to Silicic Acid Diffusion: The mass transport barrier effect on glass reaction was also attributed to the diffusion of silicic acid in the surface layers [42, 71-73] when silica is not saturated in the bulk solution. The gel layers on many waste glasses were considered to form a diffusion zone for the transport of H_4SiO_4 to the bulk solution. Because of the barrier effect, the H_4SiO_4 activity is higher in the layer than in the bulk solution, resulting in slower glass dissolution. Grambow [11, 42] proposed a criterion for assessing this diffusion barrier effect. Diffusion through the

layer is rate limiting when the term, $(D/L)K^*/k^+$ (where D = diffusion coefficient, L = thickness of the surface layer, K^* = "saturation concentration" of a silica polymorph, and k^+ = forward reaction constant), is smaller than unity [11, 42]. Silica transport may control the glass reaction rate only if matrix dissolution is the fastest process, whereas interdiffusion will be the dominant reaction if matrix dissolution is slower.

Surface Barrier's Contribution to Long-Term Glass Dissolution Rate: The recent work of Grambow et al. [39] on testing R7T7 glass in silica-saturated brines showed a square-root-of-time rate dependence for the long-term data (up to 800 days). Grambow et al. suggest that the long-term glass corrosion rate may be controlled by water diffusion through the growing surface layers when silica in the bulk solution is saturated. The work of Van Iseghem et al. [40] on borosilicate waste glasses [in deionized water at 90 and 150°C with a glass surface area to leachant volume ratio (S/V) of 100-10,000 m^{-1}] with test duration up to 600 days revealed that the long-term dissolution of soluble elements (B, Na, and Li) may be diffusion-controlled. These recent studies suggest that the barrier effect of surface layers may play an important role in the long-term glass dissolution.

In general, the experimental evidence suggests the following: surface layers can provide a barrier effect that slows down glass reaction, but the extent of this effect depends on glass composition, layer structure and composition, temperature, test conditions, and the silicic acid gradient in the surface layers. The effect is usually much less than the solution composition effect. However, the physical barrier effect of the surface layers may become important in a very alkaline solution, in leachants containing Mg ions, or in conditions where the matrix dissolution rate is very low. The latter suggests that the physical barrier effect may even control the long-term glass dissolution rate, where the matrix dissolution rate is usually low.

2. Surface Layer Effects on Glass Dissolution Affinity

Glass dissolution affinity is defined as (1 - Q/K) [74], where Q is the activity product of aqueous species involved in the dissolution reaction for the dissolving solid, and K is the equilibrium constant for that dissolving solid. When a glass reacts with water, the solution concentration increases gradually, and eventually it approaches the saturation level of one or several secondary phases. If the secondary phases do not nucleate or if the rate of crystal growth is slow, then the glass reaction is inhibited as the solution concentrations increase, i.e., Q increases and glass reaction affinity decreases. If precipitation does occur, the solution concentration is lowered, i.e., Q decreases and the glass reaction affinity increases.

Surface layers can act as an ion sink, which reduces the solution concentration and increases the affinity for glass dissolution. It has been suggested that the dissolution affinity may be influenced by the following: (1) precipitated crystalline phases [8, 75-77], (2) the amorphous silica phase(s) [12, 32, 33, 72, 78], (3) the gel layer [74], and (4) global components [79-81]. These are different considerations for the Q and K terms of the glass dissolution affinity: crystalline phases (Q is reduced when crystalline phases are formed); the amorphous silica (only Si concentration affects Q and K); the gel layer (only the components of the gel layer affect Q and K); and global components (all the components in the bulk glass affect Q and K).

Precipitated and Crystalline Phases: In hydration experiments on SRL 131 waste glass, the growth of surface layers initially followed a parabolic rate law [75]. Later in the experiment, layers suddenly grew at a much higher rate. Bates et al. [75] suggested a possible connection between accelerated glass reaction and the formation of tobermorite (a hydrated calcium silicate) on the glass surface, since this mineral was detected in the precipitated layer after testing times that corresponded to the onset of the accelerated layer growth. Ebert et al. [77] found that with WVCM44 and WVCM50 waste glass, reaction rates in steam at 200°C for the first 4-5 days are low, while the rates are as fast as 2.4 and 21 μm/day, respectively, beyond five days. This increased reaction rate is coincident with the formation of phases such as Li_3PO_4, hydroxyapatite, analcime, weeksite, orthoclase, and a potassium-containing zeolite. The initial low reaction rates were explained by the saturated solution

concentrations in the small volume of condensed water layer on the glass surfaces; this condition causes the reaction affinity to approach zero. The reaction acceleration after 5 days is attributed to reduction of the solution concentration and consequent increase in the dissolution affinity when crystals nucleated and grew on the reacting surface. In a comparison test on fully radioactive SRL 200R glass and simulated 200S glass at SA/V = 20,000 m^{-1} [82], a factor of 40 acceleration of the reaction rate was observed for SRL 200S at 364 days when mineral phases such as clinoptilolite were formed in the surface layers. No such phases were observed on the surface layers of SRL 200S before the reaction acceleration.

Van Iseghem and Grambow [83] noted increased glass reaction rates due to formation of analcime when SAN60 glass was tested at 90°C under hydrothermal conditions. Allen et al. [84] reported accelerated glass reaction coincident with the formation of analcime after testing SRL 131/TDS-3A glass for 2500 hours in the presence of basalt and the synthetic equivalent of groundwater at 150°C. The rate of increase in sodium concentration dropped sharply with time, probably because of analcime precipitation.

Amorphous Silica Phases: It has been suggested that the glass dissolution rate is controlled by the activity of H_4SiO_4 in solution [12, 32, 33, 72, 85]. Grambow and Strachan [72] used amorphous silica dissolution to successfully describe the leach behavior of JSS-A, PNL 76-68, and SRL 131 waste glasses tested at 90°C for up to 4 years. Different amorphous silica phases were proposed for these glasses. In addition, the leach data obtained with R7T7 glass at 100°C in water for test times up to one year was accounted for by amorphous silica affinity control with an accuracy of 10% [78]. The proposed metastable SiO_2(m) has never been observed in reacted-glass surface layers until recently, when Feng et al. [82] reported finding an almost pure amorphous Si phase in the surface layers of the SRL 200S glass after reacting at SA/V= 20,000 m^{-1} for 182 days. However, the rate-controlling effect of this reported amorphous phase was not established [82]. The corresponding saturation activity of H_4SiO_4 varies from glass to glass [72], as well as from test condition to test condition [86], although these variations are usually much less than an order of magnitude [72].

Petit et al. [81] investigated the leach behavior of R7T7 glass at 120°C in a static test system using a combination of glass powders and finely polished monolith samples. Their results indicate that even after silica had reached saturation, the release rate of soluble components of glass steadily decreased with time. Lutze et al. [87] also observed that the corrosion rate of R7T7 glass in brine solution at 110-190°C for periods up to 643 days did not cease after silica saturation, as evidenced by the continued increase of boron concentration in solution. A continuous leaching of sodium and boron from the waste glass tested in a silica-saturated solution (which was produced by boiling purified silica gel for one week) was also observed [88]. It appears that silica is not the only species that controls glass reaction affinity. Petit et al. [81] in their study of R7T7 glass dissolution suggested that major glass constituents, such as alkalis, should also be considered besides silica in evaluating the glass reaction affinity.

Gel Layer: Bourcier et al. [74] have suggested that dissolution of the gel layer is rate-determining in waste glass dissolution. The constituents of the gel layer determine the K term in the dissolution affinity. The deviation of the solution concentration from the saturation concentration of the gel layer controls the overall glass reaction affinity. Dissolution data for SRL and West Valley nuclear waste glass have been explained by the gel-layer affinity control [74, 89, 90]. Precipitation of various aluminosilicates, such as smectites or zeolites, observed in glass tests may maintain the solution largely undersaturated with respect to the gel layer; this condition may result in a high dissolution rate over the long term [12].

Global Components: Instead of considering only silica (as in the amorphous silica Phase approach), or several components (as in the gel layer approach), as the controlling elements for glass reaction affinity, the global components approach considers that all the components in the bulk glass contribute to glass reaction affinity. For example, the K term in (1-Q/K) should be derived from all the components of the bulk glass according to hydration energy model [79, 91], or according to the structural bond strength model [80, 92]. The Q term is determined from the ion activities of all the

glass components in the leachate.

Advocat et al. [78] calculated the ion activity product, Q, for all the dissolved species and compared these with K value determined from R7T7 glass based on hydration energy model. They found that saturation did not occur under the test conditions for R7T7 glass [78]. The calculated glass dissolution rate for R7T7 should remain at the initial rate for up to 2000 days, since the glass reaction affinity term, (1-Q/K), does not drop below 0.998. This is a considerable overestimation of the glass dissolution rate compared to experimental results [78].

IV. Effects of Surface Layers on Radionuclide Release

Before actinides enter solution in glass leaching tests, the glass network must be altered; as a result, the actinide release rate never exceeds the glass matrix alteration rate [13, 93]. The influence of surface layers on radionuclide release will be examined here by considering how radionuclides can be retained by the gel layer and incorporated in crystalline phases.

1. Gel Layer Retention

The retention of actinides increases as the gel layer thickness increases. Vernaz et al. [93] studied the actinide release from actinide-doped R7T7 glass. To quantify the retention relative to the extent of glass corrosion, the actinide retention factor was defined as RF = NL(B)/NL(act), where the numerator is the normalized release of boron, and the denominator is that of actinides. When R7T7 glass doped with ^{237}Np, ^{239}Pu, and ^{241}Am was leached at room temperature for 70 days with daily water renewal, a thin gel layer was observed on the reacted glass, and the RF value was also quite low (2 for Np and Pu, 4 for Am). In 28-day Soxhlet tests at 100°C with flowing water, the gel layers on the glass surface increased to a thickness of about 20 μm, and the RF values also increased (3.7 for Np, 412 for Pu, and 469 for Am). These data suggest a correlation between the increasing actinide retention and the increasing thickness of the gel layers. Vernaz and Dussossoy [20] conclude that the gel layer constitutes an actinide retention material.

The main mechanism for the retention is through (1) ion exchange with cations such as magnesium or calcium or with hydrogen in silanol groups, (2) hydroxide formation when the hydrolyzable silica concentration is low, or (3) the formation of hydrosilicates when the silica concentration is high in the gel layer or in the solution. Petit et al. [35] demonstrated (through comparison of the dissolution behavior of silicate glasses and silicate minerals implanted with increasing concentrations of lead ions, sorption experiments, and direct precipitation experiments) that gel layers readily retain heavy elements.

Adsorption also plays an important role in actinide retention. Barkatt et al. [23] reported that the leach rate of Th was much smaller than that of Si because of the adsorption of Th on the surface layers during the initial layer growing stage. The Th leach rate showed a progressive increase when the surface layer growth slowed. Barkatt et al. concluded that the low leach rates of actinides usually observed in testing nuclear waste glasses are transient, lasting only as long as substantial buildup of surface layers takes place. When the surface layers become saturated, the leach rates of actinides increase.

Different actinides were found to behave differently in the gel layers. Bates et al. [8] and Ebert et al. [94] reported that Am and Pu were retained mainly in the gel layers, whereas Np was mainly in solution (with a leach rate close to that of boron) for both ATM-10 and SRL 165 waste glasses. Vernaz [95] found the same preferential retention of Am and Pu over Np for R7T7 glass leached under Soxhlet and static test conditions. Hall et al. [96] found that the normalized release rates for MW (Magnox) glass tested at 70°C in deionized water decrease in the order:
Cs > Sr > Np > Tc > Eu > Am ~ Cm > Pu.

The retention of actinides in the gel layers is also expected to be related to the solubility of individual actinides under test conditions [97]. The less soluble the actinide is, the greater the expected retention of the actinide in the gel layer. Vernaz [95] found that the retention of Pu, Am, and Cm in the gel layer increased with temperature and was inversely proportional to the leachate renewal frequency. Under certain test conditions, the leach rates of some actinides are limited by

solubilities of actinide compounds. For example, Werme et al. [98] found that the soluble fraction of Pu ($\sim 10^{-9}$M) was independent of experimental conditions. Hall et al. [96] reported that the leach rates of Np and Am from MW glasses containing Magnox and THORP waste are probably limited by their solubilities. The measured concentrations of Np and Am in their leachates were close to the solubilities of those actinides under similar test conditions reported by Ewart et al. [99].

The solubilities of actinides are a strong function of pH [99], and the retention of actinides in the gel layer was also observed to vary (retention factor from 6 to 1300 for Pu, Am, and Cs) when the pH changed from 7 to 10 [95]. The retention of actinides in the gel layer is also strongly influenced by their oxidation states. Van Iseghem et al. [50] observed larger actinide release rates from SM527 glass in mixtures of clay with synthetic interstitial clay water under oxidizing conditions than under reducing conditions. This redox effect, however, is not obvious for SON68 glass reacted under similar test conditions.

The ability of the gel layer to retain actinides varies from glass to glass, as well as with testing conditions, packing materials, and complexing agents in the solutions. The final distribution of actinides among the gel layer, the solution, and the packing materials is determined by their relative tendencies to incorporate actinides [13, 50, 95, 100]. The gel layer will, however, eventually evolve into more stable crystalline phases, which will redistribute actinides. Numerous geological examples (e.g., palagonite) with structure similar to the gel layer of waste glasses have persisted over millions of years [101-104]. Actinide retention by the gel layers observed on waste glass may play a significant role in the long-term radionuclide behavior of nuclear waste glasses.

2. Crystalline Phase Incorporation

Crystalline phases in the surface layers have been found to incorporate actinides. Weeksite (a uranium mineral) is a reaction product in the surface layers of various waste glasses such as SRL 165 [13, 34, 105], SRL 131 [13, 34, 105], SRL 202U [106, 107], WVCM44 [106], and WVCM50 [77]. Other uranium silicate phases observed in the surface layers of the reacted waste glasses [90, 107] include uranophane, boltwoodite, and haiweeite. [108] Also found in the surface layers of a reacted waste glass is Am- and Pu-bearing brockite, which spalled off the glass and formed radionuclide-bearing colloids. Some important transuranic solids formed under repository-relevant conditions have also been studied by Nitsche [109]. Rother et al. [110] found crystalline lanthanoid phases, e.g., powellite solid solutions and cerianite-type materials formed on R7T7 glasses when treated in saturated salt solutions at 110°C, 150°C, and 190°C. These phases are host phases for actinide elements, such as americium and curium. Host phases such as $Na_{0.5}$, $Am_{0.5}$, MoO_4, a variant of powellite, can be synthesized and have a scheelite structure like powellite [110].

Clays that form in the surface layers are excellent sorbents for ^{137}Cs and ^{90}Sr because cations with relatively large ionic radii are preferentially retained by clays through ion exchange and adsorption [111]. Except for Mg, smaller cations are selectively leached [112, 113]; ^{137}Cs is taken up by montmorillonite-type clays [13, 71]. Abundant sheet silicates have been found to form in the surface layers of waste glasses [105]. Transuranic elements are chemically similar to rare earths; thus, the ability of phyllosilicates to accommodate rare earths in interlayer sites [114] can be expected to extend to transuranic elements. The various zeolites found in the surface layers of the reacted waste glasses have long been known to be able to incorporate radionuclides [115, 116]. In general, the radionuclide-containing phases identified in the surface layers of the reacted waste glasses are seldom mentioned in the literature, probably due to the difficulties in handling the radioactive samples under microscopy and due to the lack of instrumental techniques to detect the trace radionuclides in the solid sample.

V. Summary

Extensive research in the past decades has provided a good understanding of the formation mechanisms of the surface layers on nuclear waste glasses. The gel layer is the major component of the surface layers, which also include a diffusion layer and a precipitated layer. The nature and properties of the surface layers depend on glass composition, solution chemistry, test conditions, and reaction time. Surface layers are not only products of the initial reaction, but also potential reactants

in subsequent reactions. Furthermore, surface layers may provide a sink or reservoir for species in solution. The presence of the surface layers can influence the chemistry of the solution to such an extent that the dominance of a reaction process may be diminished and overcome by a parallel reaction mechanism, fundamentally altering the overall reaction. Surface layers influence glass reaction mainly by acting as physical barriers to the transport of reactants and corrosion products and influencing glass reaction affinity. The barrier effect is important in a very alkaline solution, in leachants containing Mg ions, or in conditions where the matrix dissolution rate is very low. The latter suggests that the physical barrier effect may even control the long-term glass dissolution rate, where matrix dissolution rate is usually low. The influences on reaction affinity by the surface layers occur through precipitate and crystalline phases, the amorphous silica, the gel layer, or all the components of the glass, reflecting different considerations in evaluating the Q and K terms of the glass dissolution affinity (1-Q/K). The surface layers influence radionuclide release mainly through crystalline phase incorporation and gel layer retention. The retention of radionuclides by gel layers depends on pH, redox conditions, and the ability of the gel layers to ion exchange, adsorb, complex, and interact with leachants and packing materials.

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