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**EFFECTS OF S/V ON SECONDARY PHASE
FORMATION OF WASTE GLASSES**

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EFFECTS OF S/V ON SECONDARY PHASE FORMATION ON WASTE GLASSES

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ABSTRACT

Simulated West Valley high-level nuclear waste glass, WV205, was leached with and without buffered media in both deuterated and ordinary water at glass surface area to solution volumes (S/V) of 200-6000 m⁻¹. Examination of the glass surface after testing for 14 days indicated that the S/V-induced pH change plays a dominant role in the development of the altered surface layer and the secondary phases formed. The changes due to S/V-induced pH determine the rate of surface layer formation, the element distribution in the surface layer, and possibly, the identities of the secondary phases. Changes due to S/V-induced elemental concentration also influence glass reaction rate in terms of the layer thickness and the elemental distribution in the surface layers.

INTRODUCTION

The ratio of glass surface area to solution volume (S/V) has long been recognized as an important parameter in glass corrosion tests [1-2]. Much of the recent literature on S/V effects involved studies on nuclear waste glasses for a number of reasons. First, the unsaturated hydrology of the host tuff rock at the possible location of the U.S. high-level nuclear waste repository at Yucca Mountain, Nevada [3], suggests that only water vapor and, perhaps, small volumes of migrating water will contact cracked waste glasses in breached canisters, which will result in a very high S/V (glass dominated). Alternatively, after breaching, a canister may fill with liquid water, giving rise to a low S/V (water dominated). Consequently, the durability of the waste glass over the entire range of possible S/V environments must be understood to predict waste glass performance under repository conditions. Nuclear waste glasses have been tested under very different S/V conditions in a variety of standard tests, such as MCC-1 [4], MCC-3 [4], and PCT [5]. A better understanding of the effect of S/V would be an important step toward a unified interpretation of the large body of data from such tests.

Second, the amount of leachant available per unit glass surface area determines the rate at which the solution reaches saturation in dissolved glass components, leading to the precipitation of secondary phases. Tests at high S/V are, therefore, often used to accelerate the attainment of solution saturation and the secondary phase formation [6-18]. There is an obvious appeal to such a reaction acceleration method since short-term test results could be easily extrapolated to longer periods of time to predict the performance of nuclear waste glass during the service life of the repository.

The effects of S/V on glass dissolution have been studied experimentally by numerous groups [6-18]. Our previous studies have shown that S/V changes resulted in systematic changes in leachate pH [17] and in the glass corrosion mechanisms [18]. The detailed effects of S/V on glass dissolution thus appear to be quite complex. In this paper we focus on the S/V effects on the formation of secondary phases (or surface layers) on reacted glass surfaces.

EXPERIMENTAL

The composition for the glass used in this study is that of the preliminary West Valley nuclear waste glass, WV205, which consists of 45.2% SiO₂, 11.8% Fe₂O₃, 11.0% Na₂O, 9.96% B₂O₃, 3.5% K₂O, 3.1% Li₂O, 3.3% Al₂O₃, 2.5% P₂O₅, 3.1% ZrO₂, and 6.5% others. The test procedure is a modified PCT [5] in which glass samples are leached in 304L stainless steel vessels (Whitey). The experiments used crushed glass powder in particle sizes of 74 to 149 μm (100 to 200 mesh). The requisite quantity of glass powder was immersed in a volume (usually 50-100 mL) of 0.1 M sodium borate buffer solutions in deionized water or in deuterated water (99.9 atom% D, Aldrich 15,188-2) in a precleaned vessel. The vessel was then placed in a convection oven pre-heated to 90°C. At each sampling interval, 4 mL of leachate was withdrawn from the vessel with a syringe inserted through a rubber septum fitted on the vessel. An equal amount of fresh leachant was then injected into the vessel to maintain a constant S/V. Each glass sample was tested in triplicate. The pH or operational pD of the leachate was measured immediately after the sample had been quenched to room temperature. The elemental concentrations were determined by DC plasma and atomic absorption spectrometry. The relative standard deviation is estimated to be less than 10% for all the major elements analyzed, as determined from the reproducibility of the triplicates.

Test Matrix

This study consists of two groups of experiments. The objective of the first group is to study the relationship between S/V and glass reaction mechanism that was reported previously [18]. The WV205 glass was leached at five S/V ratios (20, 100, 200, 2000, and 6000 m⁻¹) in both deionized water and in deuterated water (99.9 atom% D). The test duration was 1, 3, 7, 28, 56, and 120 days. The objective of the second group is to explore the effect of S/V on secondary phase formation by investigating WV205 glass at S/V = 200 and 2000 m⁻¹,

respectively, in ordinary water (H₂O) and heavy water (99.9 atom% D) buffered with 0.1 M sodium borate. The solution pHs were pH 8.5 and 10.0. The borate buffers in D₂O were prepared in such a way that the same amounts of solid boric acid and solid sodium hydroxide were added to the same volume of D₂O as in the corresponding H₂O solutions. As a result, the operational pDs [19] of the borate buffers in D₂O were 8.7 and 10.3, corresponding to the same acidity (pH 8.5 and 10.0) in the ordinary deionized water. The sampling periods for the second set of experiments were 1, 3, 9, and 14 days. Only the samples from the second group of tests were subjected to surface characterization.

Surface Analysis

The surface analyses include optical microscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and analytical electron microscopy (AEM). The thin sections for AEM analysis were prepared using an ultramicrotome equipped with a diamond knife, and procedures that allowed preparation of micrometer-sized thin sections [20]. Those electron transparent sections (500-800 Å thick) were examined with a JEOL 2000FXII transmission electron microscopy (TEM) using lattice-fringe imaging, selected area diffraction (SAD), microdiffraction, and quantitative thin-film X-ray analysis. The EDS compositions were calculated using the Cliff-Lorimer ratio method for quantitative analysis of thin films. The k-factors were experimentally determined using mineral standards. Only the samples reacted for 14 days were analyzed by SEM and TEM.

RESULTS AND DISCUSSION

Solution Analyses

The solution results from these leach tests were reported previously [17,18,21] and will be summarized here. The solution data from the first group of experiments indicated that increasing S/V increased solution pH. The leachate pHs were 9.6, 9.7, 9.9, 10.5, and 10.8 when the WV205 glass was tested in deionized water for 9 days at S/Vs of 20, 100, 200, 2000, and 6000 m⁻¹, respectively. The solution kinetics, the reaction rate change vs. time, and the isotope effects indicated that the controlling glass corrosion step changed from diffusion to matrix dissolution when the S/V changed from 200 to 2000 m⁻¹. The isotope effect is expressed in terms of the ratio of glass reaction rate in ordinary water over glass reaction rate in deuterated water. The results from the second group of experiments [21] showed that, in pH 8.5 buffers, the solution kinetics for corrosion of WV205 glass was always t^{0.5} at S/V of 200 and 2000 m⁻¹. On the other hand, in pH 10.0 buffers, the solution kinetics was always t¹ at S/V of 200 and 2000 m⁻¹. The isotope effects observed in experiments buffered at 8.5 were close to 1.1 for these two S/V, supporting diffusion-controlled corrosion. The isotope effects measured in pH 10.0 experiments were always much larger than 1.1 (as large as 3.6) at both S/Vs, indicating a matrix dissolution-controlled

process. Both the solution kinetics and isotope effects indicate that the S/V changes between 200 and 2000 m^{-1} in a constant pH environment did not alter the reaction mechanism, as was observed with unbuffered solution [18]. The solution pH clearly dominated the corrosion mechanism. That is, for WV205 glass reacted under PCT-type test condition, the controlling corrosion process was diffusion at pH 8.5 regardless of the S/V , while matrix dissolution dominated the corrosion process as long as the solution pH was \geq pH 10 regardless of S/V .

Thickness of Surface Alteration Layers

The surface examinations on the reacted samples reported below provided information on how the S/V affects the extent of glass reaction in terms of the thickness of the alteration layers, the element distribution, and the identities of the surface phases.

When in contact with an aqueous solution, waste glass is subject to progressive alteration. Constituent elements of the glass pass into the solution; elements initially in solution diffuse into, or are adsorbed onto, the solid (the unaltered and altered glass); and new phases appear. These processes form surface alteration layers on corroded glasses. The measurement of the thickness of the surface alteration layer with time also serves as an indication of glass durability.

Figure 1 shows the TEM cross sections of the samples reacted for 14 days in borate-containing D_2O solution. All the samples showed three regions: a crystalline secondary phase region, an *in situ* alteration region, and the unreacted glass region. The relative depths (or volume) of these regions varied substantially according to the test conditions. In particular, the solution pH appeared to dominate the glass reaction rate. That is, the reacted samples developed much thicker surface layers (including both the crystalline and alteration regions) at higher solution pH regardless of the S/V . For example, the samples reacted in pH 8.5 buffers had surface layers with thickness of about 0.2 μm (Fig. 1a) and 0.1 μm (Fig. 1b) at S/V of 200 and 2000 m^{-1} , respectively, while the surface layers were as thick as 2.1 μm (Fig. 1c) and 1.5 μm (Fig. 1d) when the glass was tested in pH 10.0 buffers at S/V of 200 and 2000 m^{-1} , respectively. These surface layer thicknesses indicate that the glass corrosion rate for tests at S/V of 200 m^{-1} accelerated 10 times when the solution pH increased from 8.5 to 10.0. Similarly, the tests at S/V of 2000 m^{-1} showed a glass reaction rate increase of 15 times for the same increase in solution pH.

As discussed in our previous reports [17, 18], increasing the S/V induced systematic pH increases [17] and elemental concentration increases [8]. Comparing the samples reacted at the same pH but different S/V generates information on how the S/V -induced elemental concentration affects glass reaction, since the S/V -induced pH effects are eliminated by the buffering. The surface layer thicknesses determined from Fig. 1 indicate that the reaction rate in

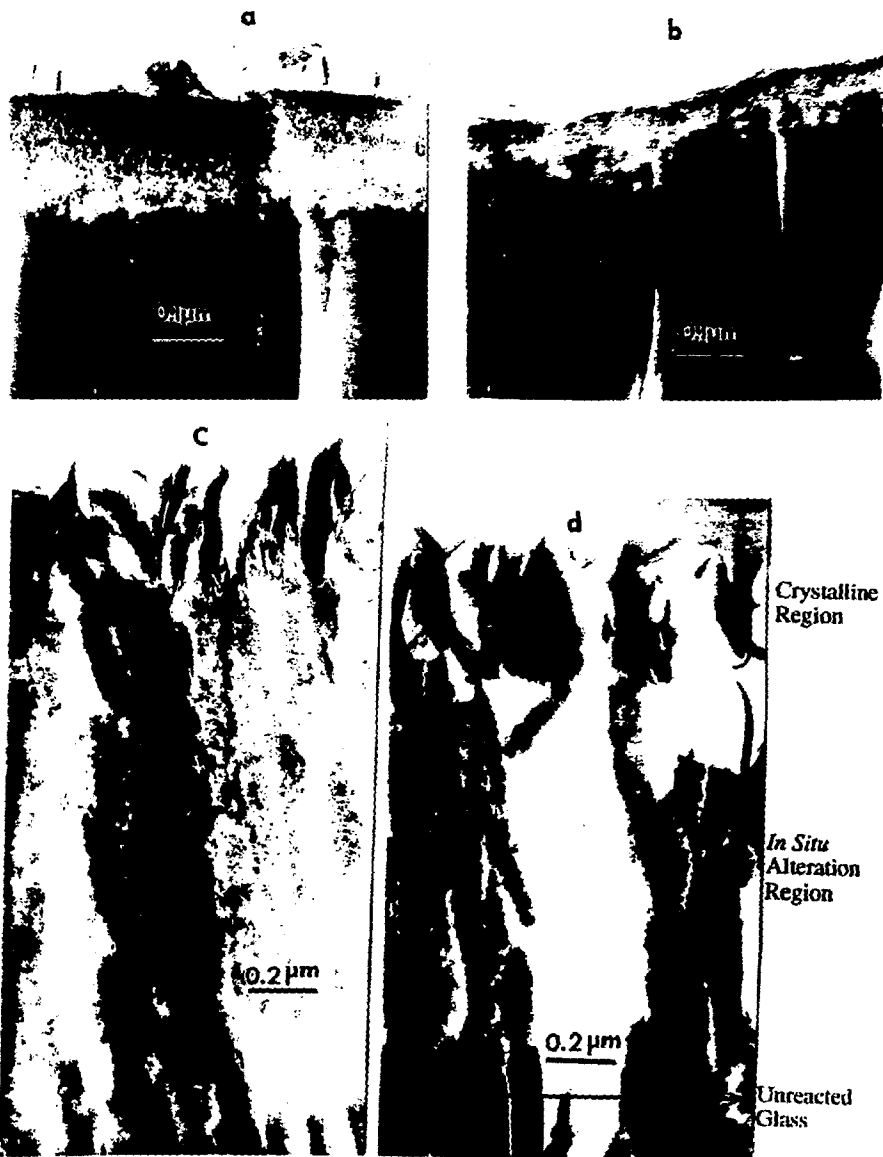


Fig. 1. TEM Cross Sections of WV205 Glass Reacted for 14 Days in D₂O Containing Sodium Borate Buffers: (a) pH 8.5 and 200 m⁻¹, (b) pH 8.5 and 2000 m⁻¹, (c) pH 10.0 and 200 m⁻¹, and (d) pH 10.0 and 2000 m⁻¹.

pH 8.5 buffers was reduced to half when the *S/V* was increased from 200 to 2000 m^{-1} , while the rate in pH 10.0 buffers was up to 40% lower for the same *S/V* increase.

The surface thicknesses determined by TEM on the samples reacted in borate-containing D₂O and H₂O is shown in Table I.

Table I. TEM Survey of Surface Layer Thickness of WV205 Reacted in 0.1 M Sodium Borate Buffers

Test ID	pH	<i>S/V</i> (m^{-1})	Solvent	Crystalline Region (nm)	<i>In Situ</i> Alteration Region (nm)
D85	8.5	200	D ₂ O	40-70	160-200
D852	8.5	2000	D ₂ O	20-50	50-100
H85	8.5	200	H ₂ O	50-100	200-300
H852	8.5	2000	H ₂ O	30-60	150-200
D10	10.0	200	D ₂ O	300-400	1600-2500
D102	10.0	2000	D ₂ O	300-400	800-1000
H10	10.0	200	H ₂ O	400-700	>4000
H102	10.0	2000	H ₂ O	400-700	>2000

The data indicate that the surface layer thicknesses of the samples reacted in ordinary water followed the same trend as that in D₂O. However, the surface layer developed in ordinary water was much thicker (about 2X) than that observed in D₂O. In fact, some glass particles reacted in H₂O were found to be completely altered, i.e., no unreacted glass was left in the sample. The lower glass alteration rate in D₂O than H₂O is consistent with the solution analysis results reported previously [18], probably due to the lower diffusion rate of D₂O for the test at pH 8.5 and the stronger D-O bonds than H-O bonds for the tests at 10.0 [18].

The above observations of the *S/V* effects on the layer thickness agree with our current understanding of glass corrosion. The glass tested at higher *S/V* attains high solution concentrations of glass components in the leachate much faster than the glass tested at lower *S/V*. The higher glass component concentrations reduce glass reaction affinity and, thus, reduce glass reaction rate. This is why the surface layers observed in samples of 2000 m^{-1} (Figs. 1b and 1d) were thinner than those of the corresponding samples of 200 m^{-1} (Figs. 1a and 1c). However, in the corrosion tests performed in deionized water or in weakly buffered groundwater, the *S/V* increase raised both the leachate pH and leachate elemental concentrations, and the glass corrosion rates measured in terms of the element release into solution may not be consistent with the rates based upon thickness of the surface layers. The glass corrosion rate in terms of element release into solution always increases with higher *S/V* since both the *S/V*-induced pH effects

and the S/V-induced concentration effects results in higher element concentration in leachates per unit time. On the other hand, the S/V-induced pH effect usually increases the thickness of the surface layer, while the S/V-induced concentration effect usually decreases this thickness. The overall S/V effects on surface layer thickness thus depend on both the pH effect and the concentration effect.

However, the long-term performance of waste glasses is usually measured by the element release into solution, and the layer thickness lacks direct relevance to the long-term performance. Therefore, the extent of glass reaction is better expressed by the element release than the thickness of the surface layers. Nonetheless, the thickness of the surface layer does significantly contribute to the understanding of glass corrosion and is, therefore, an important parameter of glass corrosion investigation.

The high S/V test is usually considered as a valid means to provide information about long-term glass behavior because it, in a relatively short time, provides data on both the long-term element release and the secondary phase formation. The secondary phases form more quickly in high S/V tests and control the long-term glass reaction rate [22].

Element Distributions in Surface Layers

Table II presents the TEM/EDS elemental profiles obtained for the glass reacted in D₂O solution containing sodium borate buffers. The EDS analyses of the unreacted glass in each sample shown in Table II indicate a relatively good consistency of the analyses between samples. Silicon was depleted in the crystalline layer compared to the unreacted glass, but the depletion decreased as the S/V increased and as the solution pH increased. Silicon was enriched in the *in situ* alteration layer except at low pH and low S/V (e.g., at pH 8.5 and S/V of 200 m⁻¹). Iron, manganese, and nickel were usually enriched in both crystalline and *in situ* alteration layers. This was also verified by the observation of precipitated iron, nickel, and manganese phases on the reacted glass surface observed under SEM. Titanium distribution in the crystalline phases seems affected only by solution pH, i.e., titanium was enriched in crystalline layer at pH 8.5 but depleted in the crystalline layer at pH 10.0 regardless of S/V. Titanium concentration in the *in situ* alteration layer was similar to that in the unreacted glass. Zirconium was usually enriched in the *in situ* alteration layer, depleted in crystalline phases at pH 10.0, and enriched in crystalline phases at pH 8.5. Magnesium was always enriched in the crystalline layers, regardless of solution pH and S/V. Alkalis such as potassium and sodium were depleted in both crystalline and *in situ* alteration layers (note that sodium borate buffer was used in the tests). The extent of potassium depletion from the *in situ* alteration layers was less than that from the crystalline layers. In fact, no depletion was found in the *in situ* alteration layers for 2000 m⁻¹. In general, the element distribution was affected much more by the solution pH than by the S/V-induced solution concentration.

The elemental distribution in samples reacted in ordinary water containing sodium borate buffers showed the same trends as those found in heavy water.

Table II. Estimated Composition of Selected Regions of WV205 Glass Leached with D₂O Solution Containing Borate Buffers (element wt% normalized to detectable elements)*

Element	pH = 8.5, 200 m ⁻¹			pH = 8.5, 2000 m ⁻¹		
	Crystal Layer	Alteration Layer	Glass	Crystal Layer	Alteration Layer	Glass
Si	29.7	32.8	45.5	34.8	51.7	47.3
Na	4.9	5.1	12.5	4.2	8.5	11.1
Mg	1.5	0.7	0.8	2.1	1.05	0.7
Al	3.9	4.9	5.2	2.6	5.5	5.4
K	0.4	0.9	4.7	0.6	3.9	4.3
Ti	3.2	3.2	1.8	3.5	1.7	2.1
Mn	7.0	5.5	2.9	5.5	3.4	3.2
Fe	38.7	35.9	20.3	33.9	19.8	20.1
Ni	3.5	2.4	1.6	7.6	1.0	1.5
Zr	7.3	8.8	4.4	5.2	3.5	4.0

Element	pH = 10.0, 200 m ⁻¹			pH = 10.0, 2000 m ⁻¹		
	Crystal Layer	Alteration Layer	Glass	Crystal Layer	Alteration Layer	Glass
Si	38.6	55.3	47.4	45.0	53.9	48.3
Na	1.3	5.2	14.5	0.6	5.2	11.9
Mg	6.7	0.4	1.1	5.5	0.0	0.2
Al	3.7	7.9	4.6	2.3	7.1	4.5
K	0.0	0.4	5.0	0.0	1.3	4.1
Ti	0.6	2.3	1.2	0.6	2.6	2.2
Mn	6.3	3.4	2.9	5.6	2.7	2.5
Fe	37.5	17.9	18.5	34.6	15.6	19.2
Ni	5.1	1.6	1.4	4.6	2.1	2.5
Zr	0.2	5.7	3.5	1.2	9.5	5.8

*Errors: ±5% for elements >20 wt%, and ±10-30% for elements <15 wt%.

Identities of Phases in Surface Layers

Figure 1 indicates that the surface layers were much better developed as the solution pH increased from 8.5 to 10.0, while the S/V changes did not contribute to much of the change in the characteristics of the surface layers. The crystalline phases were only beginning to form at pH 8.5. For pH 10, we observed a large number of randomly oriented crystals on the surface, indicating a large number of independent nucleation points. A large crystalline layer was formed growing in a single direction (upwards from the surface of the glass), as shown in Figs. 1c and 1d. This indicates that the crystalline layer nucleated from the altered sample surface and grew into the solution. The crystalline layers were probably formed by precipitation of elements from solution, not from the transformation of the

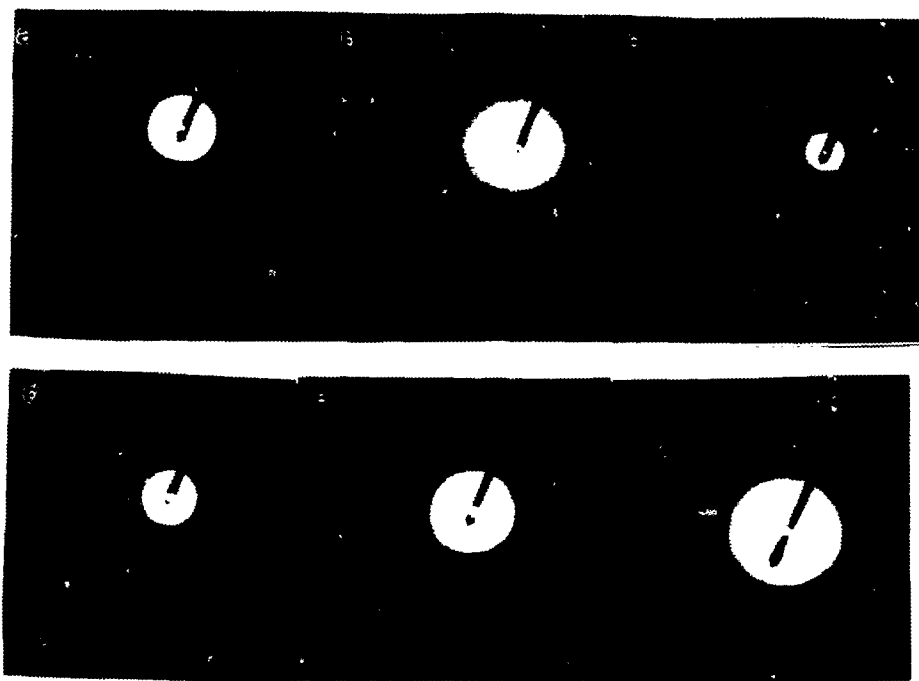


Fig. 2. Electron Diffraction Patterns of the Crystalline Regions of WV205 Glass Reacted for 14 Days: (a) D₂O at pH 10.0 and 2000 m⁻¹, (b) D₂O at pH 8.5 and 2000 m⁻¹, (c) H₂O at pH 10.0 and 2000 m⁻¹, (d) H₂O at pH 10.0 and 200 m⁻¹, (e) H₂O at pH 8.5 and 200 m⁻¹, and (f) H₂O at pH 8.5 and 2000 m⁻¹.

in situ alteration layers. Figure 2 shows the electron diffraction patterns of the crystalline layers formed in borate-containing heavy water and ordinary water. The c-axis lattice planes of the crystalline phases of the samples tested at pH 10.0 (Figs. 2a, 2c, and 2d) displayed a wavy character with many edge dislocations typical of a smectite clay. The c-axis lattice spacings were between 1.0 and 1.5 nm. In addition, the following spacings were also found from electron diffraction patterns: 0.45, 0.26, and 0.15 nm. These spacings match with *hk0* smectite spacings. The high iron content indicated in Table I would suggest nontronite as a likely phase. Only a few lattice fringes are present for the samples tested at pH 8.5 (Figs. 2b, 2e, and 2f) due to the poorly crystalline nature. However, the electron diffraction patterns from pH 8.5 samples were exactly the same as those from pH 10.0 samples. The diffraction patterns from the samples tested in D₂O at both pH 8.5 and 10.0 showed exactly the same trend as those in H₂O discussed above, except that the crystalline phases in D₂O were less developed.

The *in situ* alteration layers shown in Fig. 1 were similar in composition to the unreacted glass, except that alkalis were depleted and some less soluble species such as Si, Fe, Ti, Ni, Mn, and Zr were slightly enriched. They were probably formed *in situ* through ion exchange and network hydrolysis reactions.

The above data suggest that the composition of the crystalline phases of the surface layers were not influenced significantly by solution pH differences between 8.5 and 10.0. This may be only true for these samples reacted for 14 days. The identities of secondary phases on the reacted glass are known to be strongly influenced by solution pH and elemental concentrations. Very different secondary phases formed on the glasses with similar glass compositions but were exposed to different leachate pH after 364 days of glass reaction with groundwater under static test conditions [22]. Very similar identities of the secondary phases were reported on glass tested under the same conditions through 182 days [22]. The results presented here do not preclude the possibility of very different secondary phase formation among the pH 8.5 and 10.0 tests for longer test durations.

CONCLUSIONS

Our leach tests with WV205 glass indicate that S/V changes induce variations in leachate pH and elemental concentrations, and both the S/V-induced pH and S/V-induced elemental concentration affect the rate of surface layer formation and the elemental distribution in the surface layers formed in the surface layers. The leachant buffered at pH 10.0 was found to produce surface layers on the reacted glass with a thickness more than 10 times greater than that at pH 8.5 at the same S/V after 14 days of testing. The surface layer thickness was only decreased by a factor of two or less when the S/V of the test increased from 200 to 2000 m⁻¹, when the S/V-induced pH change was eliminated by buffering. Therefore, the S/V-induced pH effects dominate glass reaction rate in terms of surface layer formation. The element distributions in the surface layers were also strongly influenced by S/V-induced pH effects, and the distribution was only slightly affected by S/V-induced elemental concentration changes. No significant difference in the identities of the crystalline phases of the surface layers was observed between samples reacted for 14 days in pH 8.5 and 10.0 buffers. However, the identities of secondary phases on the reacted glass may be very different for the samples from longer test durations.

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