

INITIAL COMPARISON OF LEACH BEHAVIOR BETWEEN FULLY RADIOACTIVE AND SIMULATED NUCLEAR WASTE GLASS THROUGH LONG-TERM TESTING PART 2. REACTED LAYER ANALYSIS

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ABSTRACT

An initial comparison of glass behavior of simulated nuclear waste glasses has been made through long-term testing of general glass types SRL165, SRL131 and SRL200. The data demonstrate that up to 560 days at S/V of 2000/m, the reacted layers consist of one outer clay layer, which is undermined by discontinuous etch pits. The regions between the etch pits are alkali depleted. The surface layer becomes thicker as test duration progresses and the reacted layer after the same test time is thinner at higher S/V than at lower S/V. The relative glass durability measured by the thickness of the reacted layer is 165/42S > 131/11S > 200S, which is consistent with solution analyses. In general, the reacted layers on all glass compositions are poorly crystallized which makes the clay identification difficult. The diffraction spacings and EDS compositions for 131/11S and 200S, although not unique to, are consistent with Na (or Ca-) montmorillonite or nontronite. Both of these are dioctahedral smectites.

INTRODUCTION

Most testing to evaluate the performance of HLW glasses has been done using simulated nonradioactive analogs of the same general composition as the radioactive glass. To apply the knowledge gained in those studies to the assessment of the performance of the fully radioactive production glass, we have to demonstrate that the simulated experiments are an adequate representation of reaction that will occur with the actual production glasses. We have to assess: (1) do both glass types react through the same controlling mechanism, thereby producing the same secondary phases in the same sequences; (2) is there an effect due to the radioactivity that is not adequately simulated using the nonradioactive glass; (3) is there an effect of using glass that may not contain all the nonradioactive components that will be present in the sludge, supernate, and frit feeds to the actual production process since simulated glasses are generally produced using pure starting materials and the minor components are ignored, and (4) is there a difference in the durability of the two glass types.

The work reported addresses the above concerns by comparing the reactivity of these radioactive glasses with that of simulated non-radioactive glasses with closely matching compositions. The present study builds on the testing of radioactive glass that has been performed by WSRC (1-6) by extending the duration of tests to longer time periods, by using a range of glass surface area to solution volume (S/V) ratios, and by performing tests in silicate water. The test matrices allow for an evaluation of reactivity at selected time periods where solution compositions and the structure of the reacted glass layers can be compared. However, the tests are not intended to provide a complete elucidation of the reaction mechanism and, therefore, the number of sample periods are limited, especially at the early stage of the tests. A comparison between the leaching of radioactive and nonradioactive glasses has also been done as part of the joint Japanese, Swiss, Swedish (JSS) Program. Results from that program (7) indicate that after one year of testing there may be a factor of two difference in reactivity between the glass types. The JSS tests were done in an inert gas atmosphere and at a relatively low S/V. Both conditions would be representative of a saturated

storage environment and may mitigate reactivity differences. Another study on the fully radioactive and simulated MG (Magnox) glasses (8) found that the normalized leach rates of Tc, Np, Pu and Am from the fully active glass were higher than those of the simulated glass by factors of 2 to 8 except for Am where the factor was 75. However, those tests were done at 70°C and the low S/V of 100/m. Marples et. al. (9) also reported studies involving both fully radioactive and simulated glass in clay and granite but a comparison of the leaching behavior was not made because the radioactive samples were tested at 90°C while the simulated glasses were tested at room temperature. The present tests are designed to evaluate the reactivity under conditions that may be more representative of an unsaturated environment.

The available solution data from the current study (10) have demonstrated that for time periods through 280 days the differences in elemental release to solution range up to 400%. However, in general differences in glass reactivity as measured by the release of B, Li, and Na are less than a factor of 2. The differences in reactivity are not large enough to alter the order of glass durability for the different compositions nor to change the controlling glass dissolution mechanism. A radiation effect exists, mainly in terms of the influence on the leachate pH, which in turn affects glass reaction rate. The glass durability order based on the solution data is 165 > 131/11 > 200. In this paper the reactivity is examined by comparison of the altered surface layers. The analyses of the reacted layers have so far been performed only on the simulated glass samples. Comparison with the hot samples will be done in the future.

EXPERIMENTAL

The detailed experimental parameters for this study have been reported before (11). Only a brief description of the glasses and the tests is provided here.

Glasses

Three groups of glass compositions were used in this study. They are: (1) 165 based glass (165/42S is a simulated analog for glass frit 165 type plus sludge from tank 42), (2) 131 based glass (131/11S is a simulated analog for glass frit 131

type plus sludge from tank 11), and (3) 200 based glass (200S is a simulated analog for frit 200 type plus sludge from tank 8 and 12). These simulated glasses were made by closely matching the corresponding sludge based fully radioactive glass compositions produced at Westinghouse Savannah River Co. under similar conditions. They were produced by melting the components in a Pt crucible at 1150°C for 4 hours, followed by quenching the molten glass at room temperature. The fractured glass was remelted in a Pt crucible for 15 minutes and poured into molds to produce bars. The glass was then placed in a 500°C oven and the oven was turned off after two hours, allowing the glass to cool to room temperature.

Leach Tests

Each glass was tested using both monoliths at $S/V = 340/m$ and powders at $S/V = 2000/m$ and/or $20,000/m$ in J-13 well water equilibrated with tuff rock. The test vessel is a 22 mL 304L stainless steel bomb with copper gasket, and tests are done at 90°C usually in duplicate. Some of the tests have been in progress for more than 20 months. The solution analyses of all the terminated tests include leachate pH, cations, selected anions, total carbon, and actinides.

Reacted Layer Analysis

All the reacted glass samples were analyzed using analytical electron microscopy (AEM). The samples were prepared for analysis by mounting carefully selected and oriented individual powder particles in epoxy blocks. The blocks were then sectioned using ultramicrotomy which produced ~500 Å thick, electron transparent thin cross sections of the glass and reacted layer (12). This technique produces minimal damage to the layer and glass/layer interface regions. Only the results from surface layer analyses are presented here.

RESULTS AND DISCUSSION

Analyses of the reacted layers have so far been performed only on the simulated glass samples. Preparation for the analysis of the hot samples is underway. The results presented in this section are concerned only with simulated glasses at different S/V 's and times.

131-type Glasses

Transmission electron microscopy (TEM) images of 131/11S samples reacted for 30, 70, 140, and 280 days at $S/V = 2000 m^{-1}$ are shown in Fig. 1. Each sample displays an outer reaction layer made up of wisps of clay-like materials. In general this clay layer is continuous, but the fringes are observed only periodically due to orientation effect. This clay layer becomes thicker as the reaction duration progresses from 30 to 280 days with a thickness of the layer varying from 30 to about 160 nm as shown in Table I. Beneath the clay layer voids or etch pits are observed on all samples and typically attain 30 to 100 nm in diameter. As the etch pits form, sections of glassy appearing materials, or "stringers", remain as a bridge between the glass and the clay layer. Analysis of these stringers shows that they are composed primarily of Si, Al, and Fe. No sodium is observed even in the initial seconds of an acquisition. The lack of Na at the onset of an analysis is diagnostic of a lack of Na in the sample. However, Na is rapidly depleted by the electron beam, and it is difficult to use a fine probe to determine the exact Na content near the voids or in the other regions of the reacted layer. Lattice images of the outer clay layer show microcrystalline regions of only a few lattice planes (Fig. 1e). From this image, a basal spacing of 13-14 Å was measured. The electron diffraction patterns recorded at a set of standard conditions for samples reacted for different times show a progression. The samples reacted for the longer periods of time in general are better crystallized. All diffraction patterns are very weak, indicating that very little material has developed into a crystalline form. The spacings obtained

TABLE I

TEM Survey of Layer Thickness and Lattice Spacings

Glass	Duration	$S/V(m)$	Thickness	Spacings (Å)
131/11S	91d	340	50-200 nm	10, 3.4
131/11S	30d	2000	40-80 nm	14, 4.6, 2.7, 1.5
131/11S	70d	2000	50-100 nm	9, 4.4, 2.6
131/11S	140d	2000	80-150 nm	12, 10, 4.4, 2.6, 1.5
131/11S	280d	2000	120-170 nm	10, 4.6, 2.6, 1.5
165/42S	91d	340	100-125 nm	11
165/42S	30d	2000	0-40 nm	11
165/42S	70d	2000	0-45 nm	9
165/42S	140d	2000	15-45 nm	14
165/42S	280d	2000	40-80 nm	13
165/42S	560d	2000	50-90 nm	10
200S	56d	340	270-360 nm	11, 4.7, 2.6
200S	3d	2000	40-80 nm	9, 4.6, 2.6, 1.5
200S	14d	2000	65-145 nm	8, 4.7
200S	70d	2000	200-240 nm	11, 4.5, 3.4, 2.6, 1.5, 1.3
200S	15d	20000	50-80 nm	11, 4.6, 2.7
200S	56d	20000	125-180 nm	

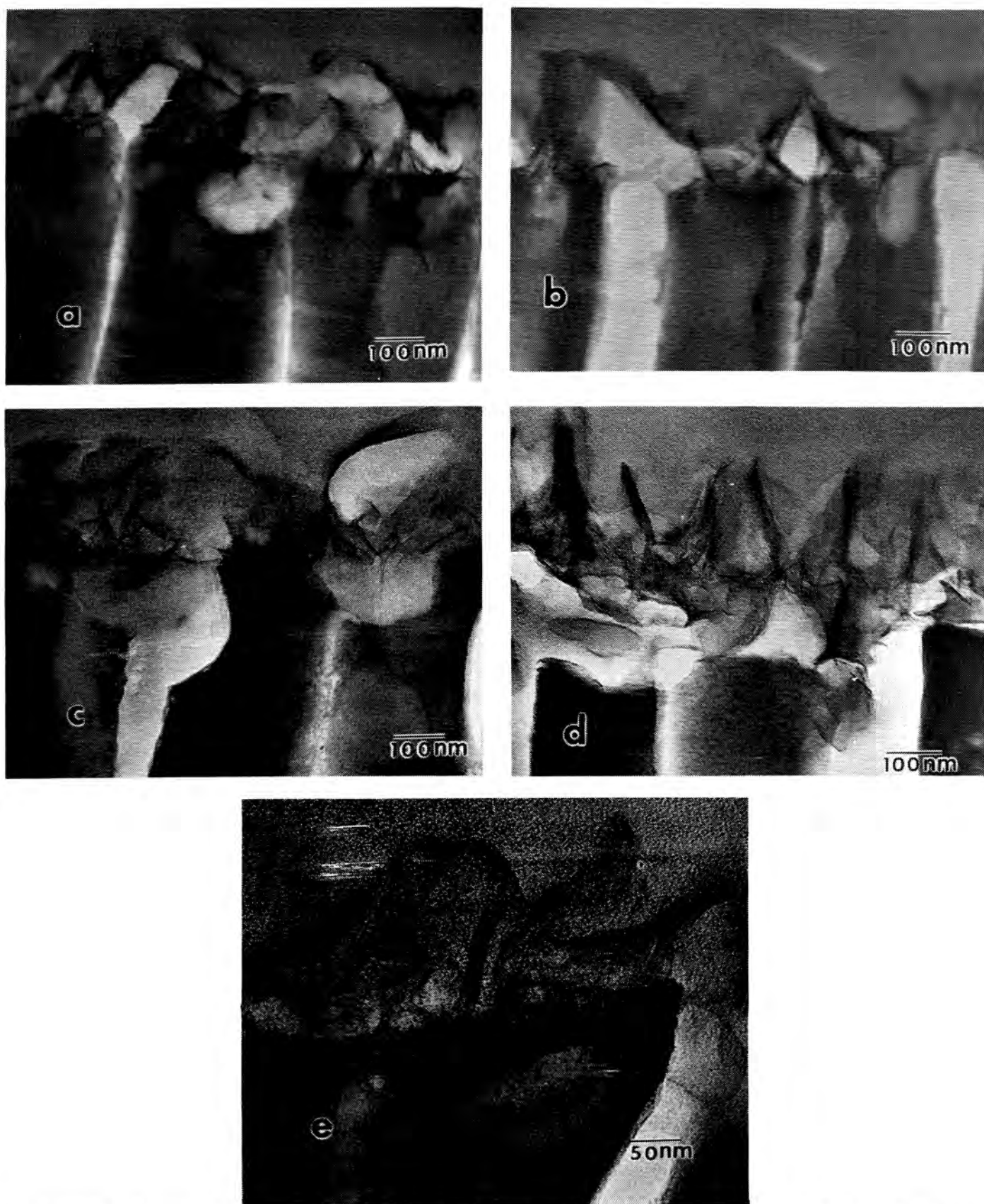


Fig. 1. 131/11S glass reacted at 2000/m for a) 30 days; b) 70 days; c) 140 days; d) 280 days; 3) the layer on the 30-day sample shown to highlight the developing clay layer that is seen as wisps of parallel fringes. A lattice spacing of 13-14 Å is observed.

from those diffraction patterns and lattice images are listed in Table I. The EDS composition analyses of the outer clay layers shows that they are composed of primarily Si, Na, Al, Fe, Mn, and Mg as shown in Table II. Each composition is the average of several acquisitions at various places in the clay layer. There is variability in the clay composition with trends being apparent for all elements except Si and Ca. These trends show a maturing as the clay develops. These composition and spacing data are consistent with Nontronite, or Na-Montmorillonite. The iron concentration observed is intermediate between these two. Brindly (13) points out that intermediate composition is quite common. There is also a Ca-montmorillonite with similar spacings. Both Na and Ca are taken up into clay structure in the spaces between silicate layers and readily substituted for each other and, therefore, a range of intermediate composition is possible. There is an unexpectedly high Cl content, which decreases with the extent of reaction. Chloride is a component in the leachant and also is presented in the glass to a minor extent. Whether the Cl content in the clay results from the reaction process or as a result of sample storage is being further examined.

The overall alteration layer structure can be considered as a single layer with etched areas. This simple layer structure is in sharp contrast to the complicated six band layer structure observed on SRL131 glass at S/V of 10 m^{-1} reacted in deionized water (14). We attribute this difference mainly to the difference in glass compositions and to the low S/V of 10 m^{-1} of the previous study. The 131/11S glass has much higher Al (9.2 vs. 3.4%) and Si content (45.8 vs. 42.7%) and 131/11S is a more durable glass.

200-type Glasses

The reaction progress is shown clearly in Fig. 2a for 200S glass tested at S/V = 2000/m for 3, 14 and 70 days respectively.

The reacted layers grow thicker with time and the precipitated crystalline layers were better developed with time. The layers were still in contact with glass shards at 3 days and gradually separated from the glass as reaction progressed for longer times. The development of reacted layers of 200S glass at S/V = 20000/m is also the same as shown in Fig. 3, where the layer became thicker from 15 to 182 days and the layers were more crystalline at longer times. The separation between layers and glass is also evident at 56 days or longer. The observed layer is similar to that described for 131/11S glass in that a simple clay structure forms and is undermined by etch pits. The identification of the clay is not conclusive due to the poor crystallinity of the layer. The lattice spacings obtained from both high magnification photographs - lattice fringes and from diffraction for 200S glass are listed in Table I and the EDS composition analyses of the layers are listed in Table II. The diffraction spacings are not unique to but are consistent with Na (or Ca-) montmorillonite or nontronite. Both are dioctahedral smectites.

165-type Glasses

Compared with 131/11S and 200S glasses this glass type is much more durable as shown in Fig. 4, where the reacted layers can be seen to be very thin for those 165/42S glass samples reacted at S/V = 2000/m for 30 and 70 days. The reacted layers did become thicker as shown in Fig. 4 as reaction time increased to 140 and 560 days. Etch pits were also observed under the layers for the longer time samples. The crystallinity of the alteration layers is very poor and no spacing can be obtained from the diffraction patterns. Only occasionally is a region found where lattice fringes are visible as shown in Table I. Spacings obtained from these images are between 9 and 14 angstroms and are difficult to measure accurately. The clay can be identified only when longer duration samples

TABLE II

EDS Compositions of Reacted Layers

	Si	Na	Mg	Al	Cl	Ca	Ti	Mn	Fe	Ni
131/11S at 2000/m										
30d	46.5	17.7	2.9	8.7	5.4	2.1	1.7	4.0	8.9	1.7
70d	45.5	10.2	3.1	8.9	7.8	2.0	3.0	5.6	11.3	2.2
140d	40.2	15.2	4.5	9.8	2.3	1.5	4.0	5.6	14.3	2.2
280	43.9	4.5	5.5	11.2	0.4	2.2	4.6	7.0	17.3	3.0
165/42S at S/V = 2000/m										
30d	55.8	3.6	0.0	2.0	4.9	0.0	0.2	7.1	19.0	7.2
70d	69.1	7.5	1.2	6.8	4.1	0.8	0.1	2.1	6.9	1.3
140d	55.2	8.6	1.4	9.0	6.9	0.4	0.0	4.1	12.0	2.0
280d	45.0	7.6	1.4	10.5	4.1	1.2	0.3	6.1	20.5	2.9
560d	49.3	4.6	2.6	10.4	1.0	2.1	0.4	7.2	18.5	3.3
200S at S/V = 2000/m										
3d	37.9	12.6	3.1	5.1	3.1	1.2	0.3	6.9	25.1	4.2
14d	37.8	13.7	5.9	6.3	2.4	1.0	0.0	6.4	21.6	4.5
70d	51.8	2.5	5.0	8.6	0.3	0.5	0.0	6.1	21.6	3.2

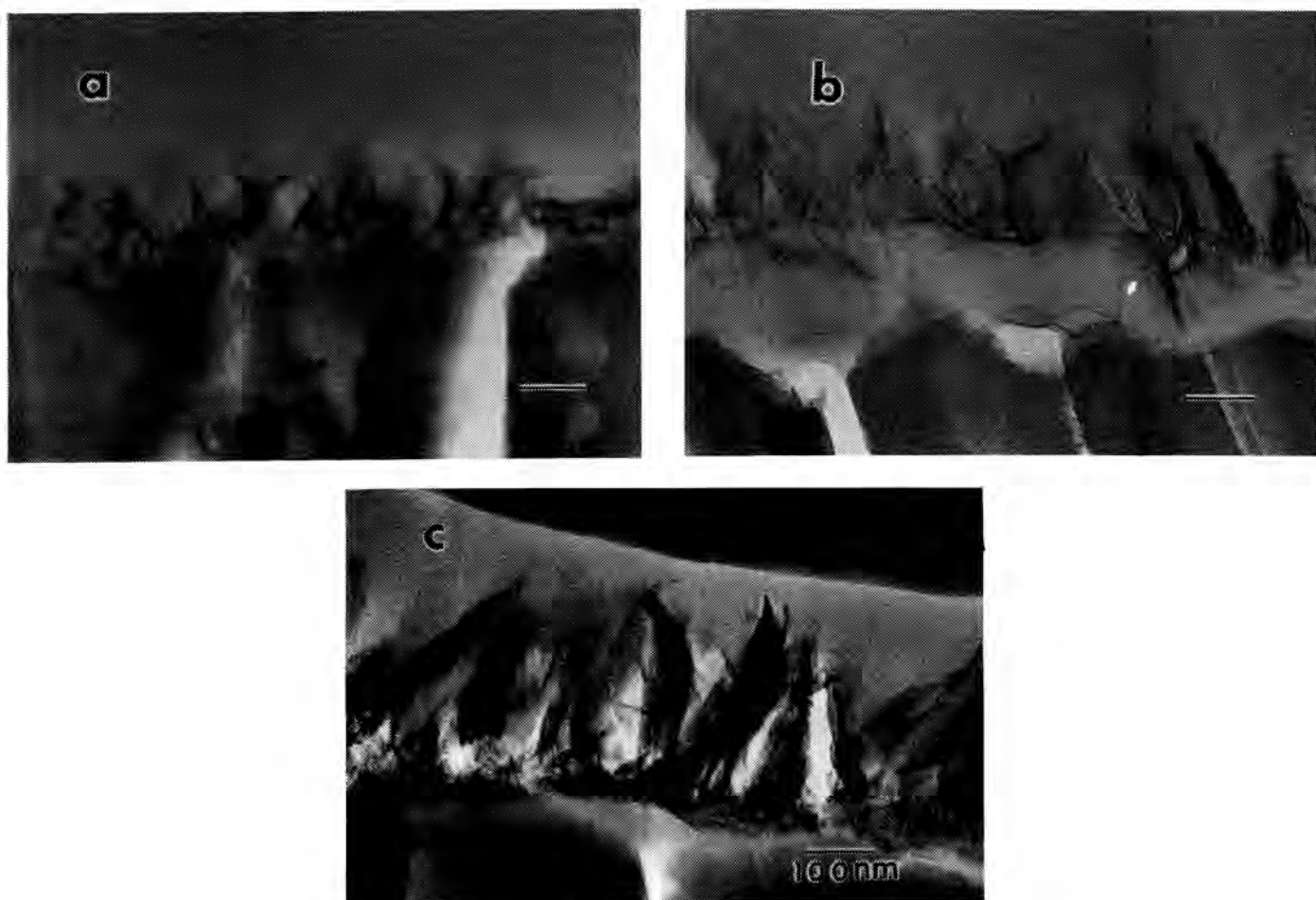


Fig. 2. 200S glass reacted at 2000/m for a) 3 days; b) 14 days; c) 70 days.

are available. The EDS composition results for the reacted layers are also shown in Table II.

Composition and S/V Dependence of the Reacted Layers

The results in Table I indicate that the reacted layer thickness ranged from a few nms for monolith SRL165/42S glass to about 360 nm for 200S glass. The thickness of the reacted layers at the same S/V and reaction time is different with different compositions. The 200-type glass exhibits the largest thickness and the 165-type shows the least reaction and the thinnest reacted layers when compared at the same S/V and reaction time. The durability measured by reacted layer thickness is SRL165/42S > SRL131/11S > 200S, which agrees with the durability order derived from solution analysis (10).

Tests at high S/V usually generate concentrated leachate solution after shorter reaction times and the reaction affinity is reduced more than in similar tests at lower S/V. The reacted layers of the tests at higher S/V is, therefore, usually thinner than those tests at lower S/V for the same length of time. It was observed for 200S glass that the reacted layer thickness decreased when the S/V's of the tests increased from 340/m to 20,000/m as shown in Table I. Similar observations are also true for 131/11S and 165/42S compositions as indicated by Table I.

The ongoing static tests will be continued. The detailed analyses of the reacted layers for radioactive samples are

underway. Data will be generated to compare the identities and sequences of secondary phases of radioactive glasses and the simulated analogs. The solution data combined with surface analysis results will be utilized to compare further the reactivity of the radioactive and nonradioactive glasses and to provide a data base for validation of glass performance models.

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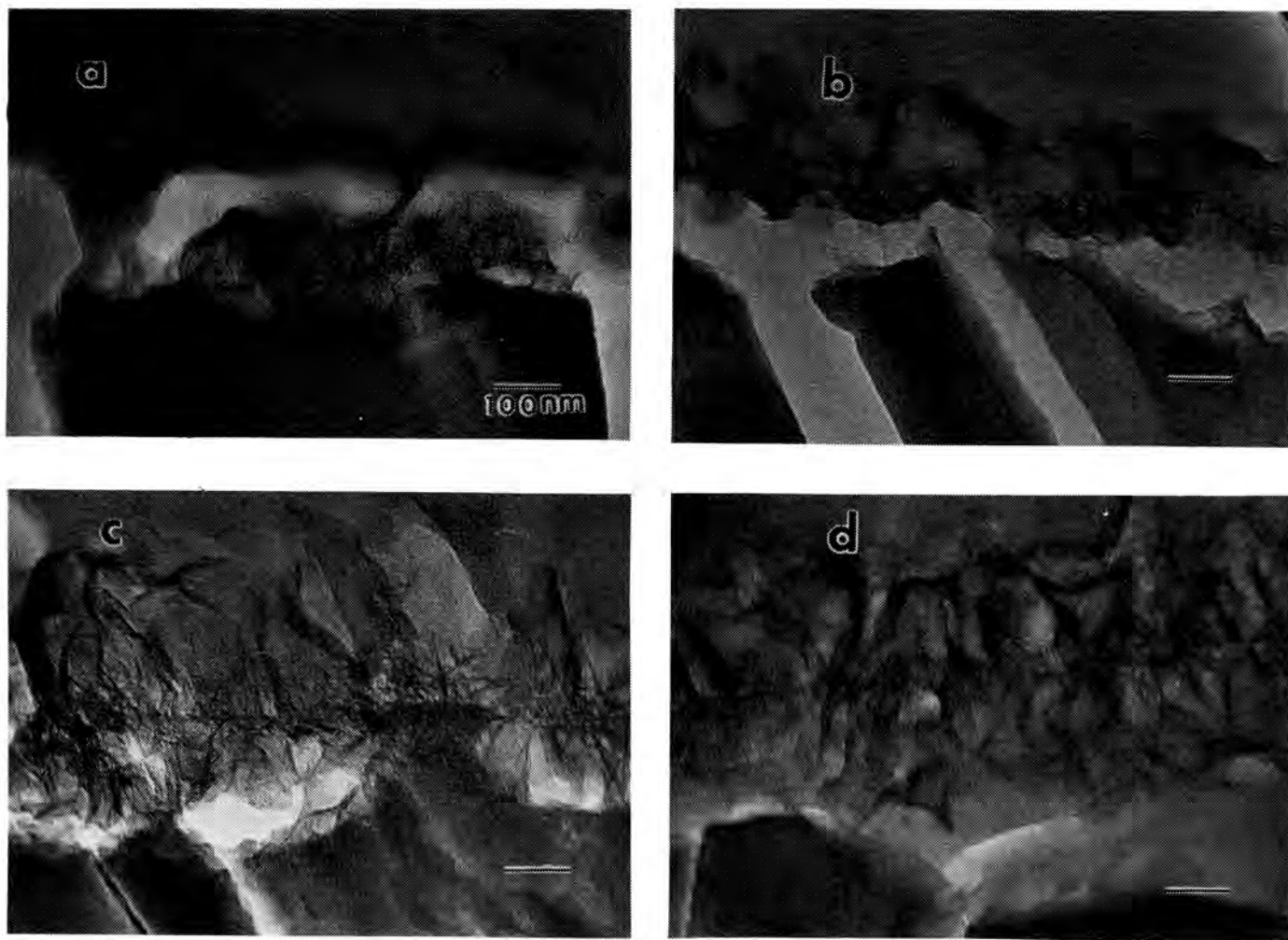


Fig. 3. 200S glass reacted at 20,000/m for a) 15 days; b) 56 days; c) 98 days; d) 182 days.

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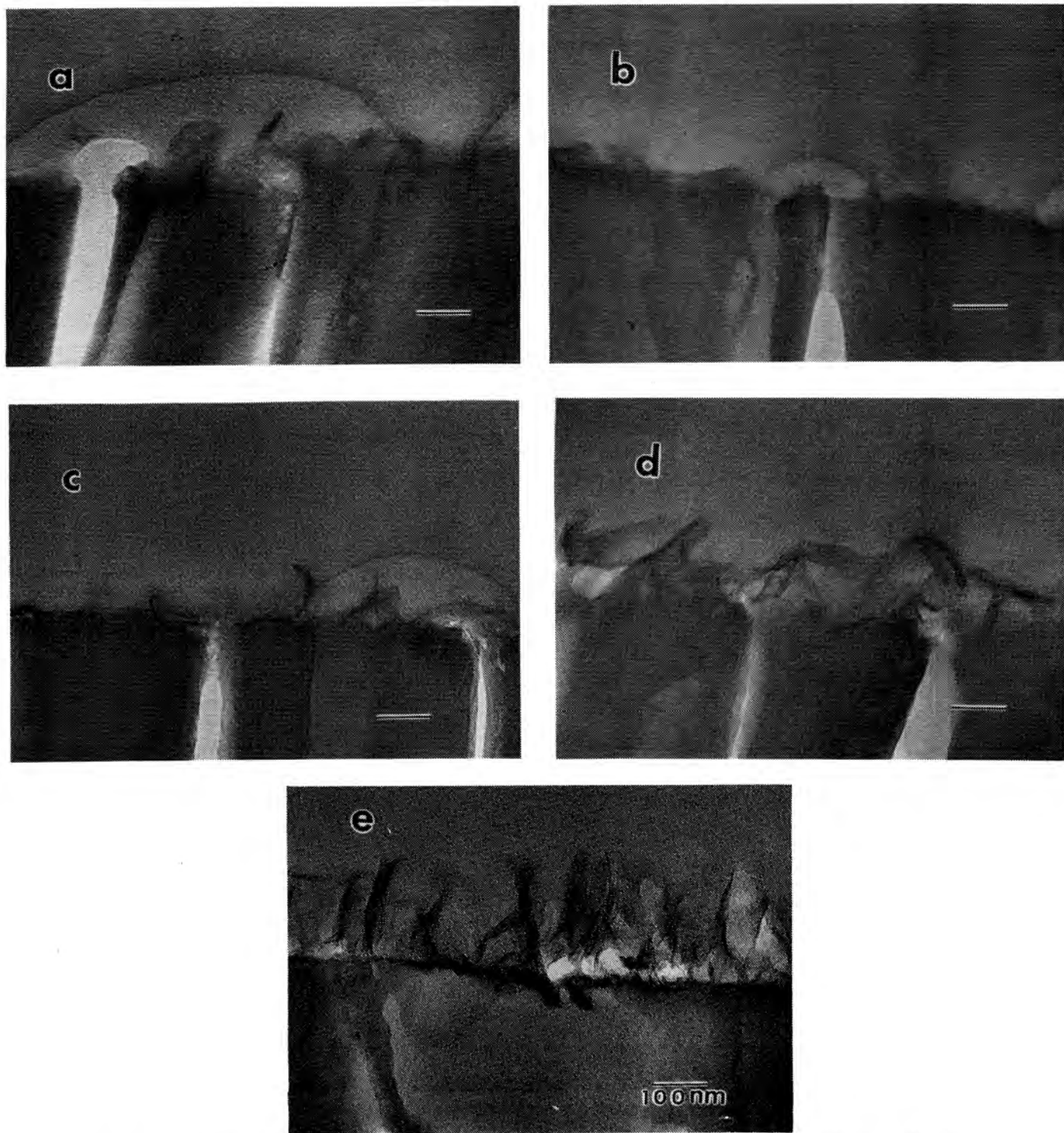


Fig. 4. 165/42S glass reacted at 2000/m for a) 30 days; b) 70 days; c) 140 days; d) 280 days; e) 560 days.