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ABSTRACT

Laboratory tests are being conducted using two radionuclide-doped Defense Waste Processing Facility (DWPF) glasses (referred to as SRL 131A and SRL 202A) to characterize the effects of the glass surface area/solution volume (S/V) ratio on the release and disposition of Tc and several actinide elements. Tests are being conducted at 90°C in a tuff ground water solution at S/V ratios of 10, 2000, and 20,000 m^{-1} and have been completed through 1822 days. The formation of certain alteration phases in tests at 2000 and 20,000 m^{-1} results in an increase in the dissolution rates of both glasses. The release of Tc parallels that of B and Na under most test conditions and its release increases when alteration phases form. However, in tests with SRL 202A glass at 20,000 m^{-1}, the Tc concentration in solution decreases coincidentally with an increase in the nitrite/nitrate ratio that indicates a decrease in the solution Eh. This may have occurred due to radiolysis, glass dissolution, the formation of alteration phases, or vessel interactions. Technetium that was reduced from Tc(VII) to Tc(IV) may have precipitated, though the amount of Tc was too low to detect any Tc-bearing phases. These results show the importance of conducting long-term tests with radioactive glasses to characterize the behavior of radionuclides, rather than relying on the observed behavior of nonradioactive surrogates.

INTRODUCTION

We are conducting static dissolution tests with two radionuclide-doped Defense Waste Processing Facility (DWPF) glasses (referred to as SRL 131A and SRL 202A) to study the effects of the glass surface area/solution volume (S/V) ratio on glass corrosion behavior. Of particular interest is the release and disposition of Tc and actinide elements. Such information is needed to calculate the long-term behavior of disposed high-level waste glasses. Tests conducted at high S/V ratios with these alkali borosilicate glasses have shown the glass dissolution rates to decrease initially, but then increase upon the formation of certain alteration phases [1,2]. Significant amounts of major glass components such as Si, Al, and Na become incorporated into alteration phases, while B is almost completely soluble. Tests with other glasses at lower S/V ratios have shown Tc to be highly soluble and to behave like B [3-7]. In this paper, we describe the behavior of Tc over long times for those tests that showed an increase in the glass dissolution rate coincident with the formation of certain alteration phases, and whether or not the release of B can be used to estimate the release behavior of Tc.

The formation of alteration phases as a glass corrodes is thermodynamically favorable. However, alteration phases characteristic of advanced stages of corrosion do not form in most dissolution tests because of insufficient reaction progress over the duration of the test. Instead, those tests yield alteration phases such as smectite clays and oxides of sparingly soluble glass components. The effects these phases have on glass corrosion and the disposition of radionuclides may be very different than the effects of phases formed at more advanced stages of corrosion. For alteration phases representing more advanced stages of corrosion to form within typical test durations, high S/V ratios and high temperatures are generally required. Tests conducted at high S/V ratios may be relevant to disposal conditions in which only small amounts of water contact a glass surface. For example, a 1-μm film of water on the glass surface produces an S/V ratio of 1×10^6 m^{-1}. Whether alteration phases that affect the glass corrosion rate and the disposition of radionuclides will form during the corrosion of disposed glasses within times of regulatory concern can only be determined by coupling a description of the disposal conditions with the glass corrosion behavior measured in laboratory tests.

EXPERIMENTAL

Glasses were prepared at Argonne National Laboratory by modifying SRL 131 and SRL 202 frits, which were provided by Savannah River Technology Center, to reflect waste loadings and doping with ^{99}Tc, ^{237}Np, ^{239}Pu, ^{241}Am, and natural U at levels of about 0.03, 0.01, 0.01, 0.0004, and 2 elemental mass %, respectively. The doped glasses are referred to here as SRL 131A and SRL 202A. Dopants were added in two steps to reduce the loss of Tc by volatilization. First, a solution containing Np, Pu, Am, and natural U was added to the frit and melted at 1150°C for 4 hours, quenched, and mixed by crushing. Second, this glass was remelted with an added NH_4TcO_4 solution for 1 hour, then poured into 95% platinum-5% gold molds and annealed in a separate oven at 500°C for 2 hours. The glasses were dissolved and analyzed with alpha spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) to measure the dopant concentrations. Analyses showed that about 90% of the added Tc had volatilized, and that the actual doped concentration was about 0.003 wt% ^{99}Tc in both glasses. The complete glass compositions have been given elsewhere [2].

Tests were conducted in a tuff ground water solution at an S/V ratio of 10 m^{-1} with monolithic glass samples following a modified MCC-1 procedure [8] and at S/V ratios of 2000 and 20,000 m^{-1} with crushed glass (-100 +200 mesh) following a modified PCT procedure [9]. The leachant solution, which is referred to as EJ-13 water, was prepared by reacting pulverized Topopah Spring tuff with water from well J-13 on the Nevada Test Site for 28 days at 90°C. The composition of the EJ-13 water is given elsewhere [2]. All tests were conducted in type 304L stainless steel vessels in a constant temperature oven at 90°C.

At the end of the test period, the leachate solutions were removed and filtered using a 450-nm filter. Some solutions were further filtered using a 50,000-molecular weight filter (which has a pore size assumed to be approximately 6 nm). The solutions were analyzed for pH with a combination electrode, for Tc and cations with ICP-MS, and for other anions with ion chromatography. The pH was measured at room temperature, and the reported values have not been adjusted to the test temperature or corrected for Na affects. After the reacted glass was removed from the vessel, the vessel was filled with a nitric acid solution (about 1 $\underline{M}$) and placed in a 90°C oven for about 24 hours to dissolve any material that had become fixed to the steel. Aliquots of this solution were analyzed with ICP-MS and alpha spectrometry.

RESULTS AND DISCUSSION

Technetium was found to be predominantly dissolved in the solution, and only trace amounts were associated with the vessel in most tests. The analytical results for SRL 131A and SRL 202A glasses in tests run for 364 days or longer are presented in Tables I and II, respectively, which summarize the measured amounts of Tc in the aqueous phase [Tc(aq)] and fixed to the vessel [Tc(ads)] in tests conducted for the longest durations at each S/V. The Tc concentrations in the 450-nm and 6-nm filtrate solutions were the same within analytical uncertainty, which indicates that Tc is not associated with colloids and that all the Tc in solution is dissolved, presumably as the pertechnetate ion, TcO_4^-.

Figure 1 shows the normalized mass losses based on B, Na, Si, and Tc for tests conducted with SRL 131A glass at S/V ratios of 10, 2000, and 20,000 m^{-1}. In tests at 10 m^{-1}, the release of B, Na, Si, and Tc is congruent, within the scatter of the data. In tests conducted at 2000 and 20,000 m^{-1}, the normalized mass losses based on Tc, B, and Na are similar, and all are greater than those based on Si. The release of B, Na, and Tc increases with the reaction time in all tests conducted at 2000 and 20,000 m^{-1} and these components do not approach steady-state concentrations. Note that the B and Na concentrations are about the same in tests conducted for 728 and 1100 days in tests at 20,000 m^{-1}. This occurs because almost all of the glass has reacted after about 728 days. The maximum NL(i) value for tests with -100 +200 mesh glass, which has a specific surface area of about 0.025 m^2/g, is 40 g/m^2.

Table I. Analytical Results for Tests with SRL 131A[a]

Reaction Time, d	10 m⁻¹			2000 m⁻¹			20,000 m⁻¹		
	pH	Tc(aq)	Tc(ads)	pH	Tc(aq)	Tc(ads)	pH	Tc(aq)	Tc(ads)
364							12.20	50	0.04
364							12.17	40	0.1
552							12.04	50	<0.002
560				11.49	4	<0.002			
728							12.02	80	0.2
728							12.05	b	0.02
1100							12.18	50	—b
980				11.74	3	0.006			
980				11.72	4	<0.002			
238	8.58	0.05	—b						
238	9.27	0.08	—b						
600	9.09	0.02	—b						
600	9.34	0.04	—b						
1400	8.96	0.01	—b						
1400	9.32	0.05	—b						
1820				12.14	10	0.08			
1820				12.11	9	0.009			

[a]Amount of Tc given in micrograms. Tc(aq) includes all dissolved and colloidal Tc and Tc(ads) is that associated with the stainless steel vessel.

[b]Not analyzed.

Table II. Analytical Results for Tests with SRL 202A[a]

Reaction Time, d	10 m⁻¹			2000 m⁻¹			20,000 m⁻¹		
	pH	Tc(aq)	Tc(ads)	pH	Tc(aq)	Tc(ads)	pH	Tc(aq)	Tc(ads)
364							12.03	1	0.009
364							12.02	7	0.005
504							11.86	0.4	0.02
560				10.42	0.4	0.002			
980				10.52	0.5	0.004			
980				10.65	0.5	<0.002			
728							11.96	0.07	0.23
728							11.97	0.1	0.02
1570							11.85	0.04	—b
600	8.57	<0.004	—b						
600	8.58	<0.004	—b						
1400	8.74	0.01	0.03						
1400	8.91	0.004	0.04						
1820				11.32	0.7	0.005			
1820				11.26	0.4	0.07			

[a]Amount of Tc given in micrograms. Tc(aq) includes all dissolved and colloidal Tc and Tc(ads) is that associated with the stainless steel vessel.
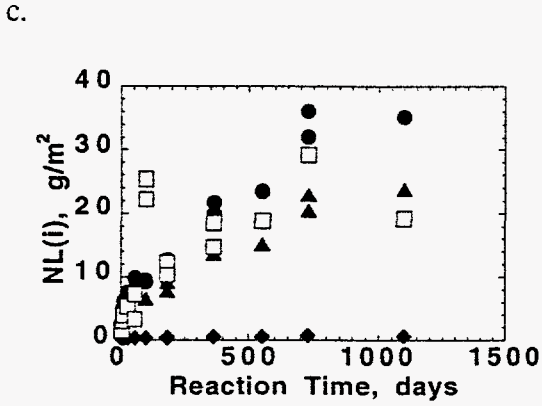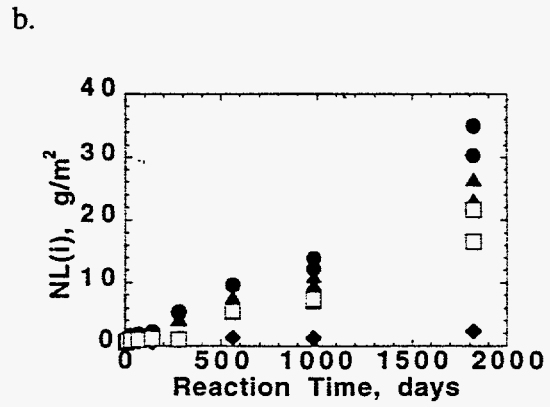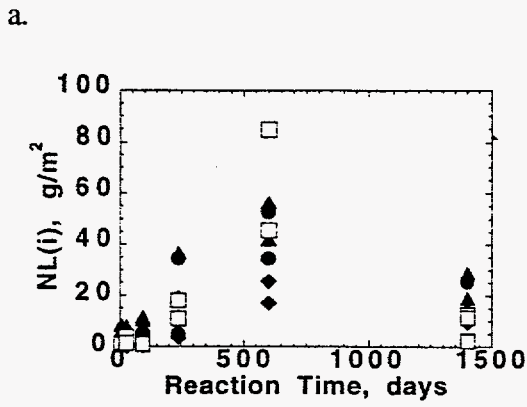
[b]Not analyzed.

a.

b.

c.

Figure 1. Normalized Mass Losses vs. Reaction Time for Tests with SRL 131A Glass at S/V Ratios of (a) 10 m^{-1}, (b) 2000 m^{-1} and (d) 20,000 m^{-1}. B ($\bullet$), Na ($\blacktriangle$), Si ($\blacklozenge$),Tc ($\square$).

a.

b.

c.
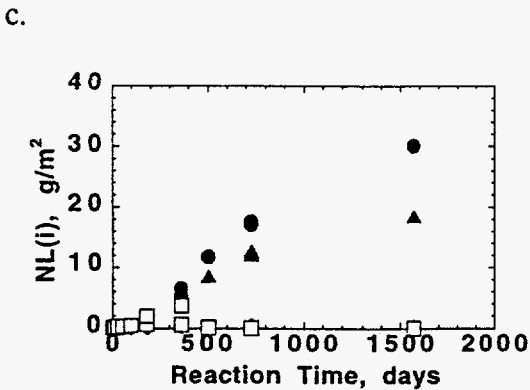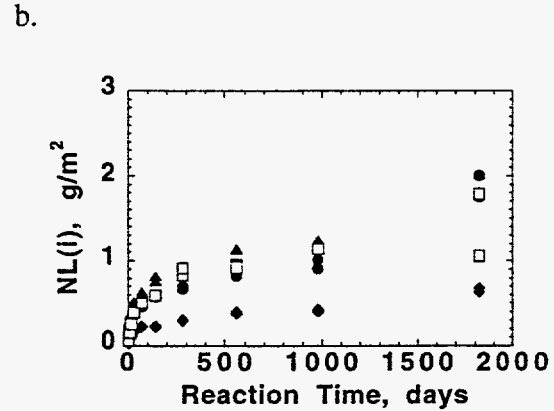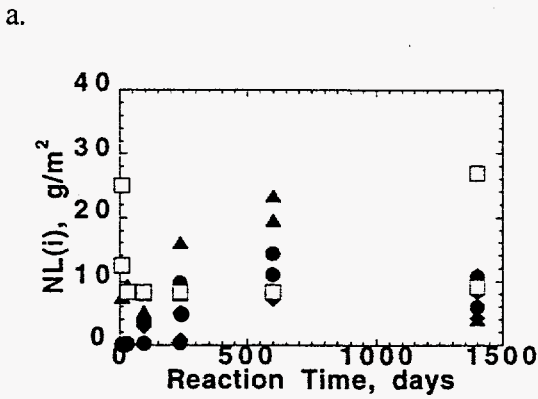

Figure 2. Normalized Mass Losses vs. Reaction Time for Tests with SRL 202A Glass at S/V Ratios of (a) 10 m^{-1}, (b) 2000 m^{-1} and (c) 20,000 m^{-1}. B ($\bullet$), Na ($\blacktriangle$), Si ($\blacklozenge$),Tc ($\square$).

Figure 2 shows the corresponding results for tests conducted with SRL 202A glass. In tests at 10 m^{-1}, the initial release of Na and Tc is much higher than that of B and Si, but the releases are similar at longer reaction times. Note that the Tc concentrations in tests at 28, 94, 238, and 600 days were below the detection limits, and the values plotted represent upper limits to NL(Tc). In tests conducted at 2000 m^{-1}, the normalized mass losses based on Tc, B, and Na are and all are greater than those based on Si. In tests conducted at 20,000 m^{-1}, the release of B, Na, and Tc increase congruently through about 364 days. However, the amount of Tc in solution decreases at longer times, while B and Na continue to be released into solution. The solution concentrations of Cl$^-$, SO$_4^{2-}$, HPO$_4^{2-}$, HCO$_3^-$, and C$_2$O$_4^{2-}$ also increase with the increased glass dissolution rates at reaction times greater than 182 [10]. The B release rate decreases between 728 and 1570 days due to the loss of surface area as the glass dissolves.

It is not yet known why the Tc concentration decreases after long reaction times in tests with SRL 202A at 20,000 m^{-1} but not in other tests. One important difference in the results of tests at 20,000 m^{-1} with SRL 131A and SRL 202A glasses is that the [NO$_2^-$]/[NO$_3^-$] ratio in tests with SRL 202A glass suddenly increases from less than 0.1 in tests run for 182 days or less to 14 and 18 in duplicate tests run for 364 days, although the ratio decreases to less than 0.5 at longer times. The [NO$_2^-$]/[NO$_3^-$] ratio in the EJ-13 water was 0.05. The increase in this ratio and the generation of HCO$_2^-$ and C$_2$O$_4^{2-}$ indicate that the Eh of the solution has decreased. It cannot be determined if the sudden decrease in the Eh after 364 days is an anomaly or a transient that occurred in all tests run for 364 days or longer.

The decrease in the Eh of the solution may have occurred due to radiolysis, glass corrosion, the formation of alteration phases, or vessel interactions. How each of these may have affected the solution Eh can be estimated by comparing the results of the tests conducted at 20,000 m^{-1} with SRL 202A glass with the results of other tests conducted in this program. The [NO$_2^-$]/[NO$_3^-$] ratio in tests with SRL 131A glass at 20,000 m^{-1} is less than 0.01 through 98 days and less than 1 at longer times. The ratios are less than 0.3 in all tests with both glasses at 2000 m^{-1}. Also, much less HCO$_2^-$ and C$_2$O$_4^{2-}$ is generated in tests with SRL 131A glass [10]. Although SRL 131A and SRL 202A contain the same amounts of radionuclides, the leachate solutions chemistries and the effects of radiolytic reactions on the solution Eh are very different.

The effects of glass dissolution on the Eh are expected to be similar in tests with SRL 202A and its nonradioactive analogue. All glasses contain both Fe(II) and Fe(III), and glass dissolution is expected to affect the solution Eh. However, tests conducted with a nonradioactive homologue of SRL 202A did not show any indications of a decrease in the solution Eh after long reaction times. That is, the [NO$_2^-$]/[NO$_3^-$] ratio and the concentrations of HCO$_2^-$ and C$_2$O$_4^{2-}$ remained very low. The effects of vessel interactions are expected to be similar in tests with SRL 131A and SRL 202A glasses. Therefore, the behavior observed in tests with SRL 202A at 20,000 m^{-1} is probably not due to the effects of radiolysis or the glass composition alone, rather it is likely a combination of the effects of radiolysis, glass corrosion, and perhaps the formation of alteration phases. While no Tc-bearing alteration phases were identified in these tests, formation of an unidentified K- and Tc-bearing alteration phase has been observed in other tests with SRL 202A glass [11]. The formation of such a phase could explain the drop in Tc concentration for SRL 202A glass at 20,000 m^{-1}. It is likely that any Tc that was precipitated in such a phase would have been reduced, since the measured solution concentrations of K and Tc show the solution to be well under-saturated with respect to KTcO$_4$ at 90°C (pK$_{sp}$(KTcO$_4$) = -0.6) in all tests.

The solubility of Tc is expected to decrease with a decrease in the Eh of the solution because the dominant solid phase under reducing conditions, TcO(OH)$_2$(am) [12], is much less soluble than the dominant solid phase under oxidizing conditions, probably NaTcO$_4$ or KTcO$_4$. Of these, KTcO$_4$ is less soluble, but, as noted above, is still too soluble to explain the observed decrease in the amount of dissolved Tc. Consideration of the Tc(IV)/Tc(VII) and Fe(II)/Fe(III) redox couples indicates that the presence of Fe(II) may reduce Tc under the pH conditions attained in these tests [13]. In addition, Tc has been observed to be scavenged by iron oxyhydroxides and ferrous-bearing minerals in both laboratory [13] and field analyses [14]. Unfortunately, the small amount of Tc present in the glasses complicates further determination of its disposition as the glass corrodes, and we have not yet identified the chemical or physical state of Tc that is not in solution.

CONCLUSIONS

Static dissolution tests conducted with radionuclide-doped glasses have shown the release of Tc to be similar to that of highly soluble cations, including B and Na, prior to the formation of alteration phases that increase the glass dissolution rate. These components are released into solution preferentially to Si under most test conditions. However, different release behaviors were observed in tests at an S/V ratio of 20,000 m^{-1} with the SRL 131A and SRL 202A glasses after alteration phases that increased the glass dissolution rate formed. Tests with SRL 131A glass showed that the release of Tc continued to be similar to that of B and Na, but the release of Tc into solution in tests with the SRL 202A glass suddenly decreased after about 364 days. Why the behavior of Tc changed in these tests is uncertain, although it coincided with a decrease in the solution Eh, as indicated by the formation of the radiolytic products formate and oxalate, and a transient increase in the $[NO_2^-]/[NO_3^-]$ ratio at 364 days. Reduction of the solution may have resulted from radiolysis, glass dissolution, the formation of alteration phases, or vessel interactions. Comparison with the results of other tests suggests that the behavior observed in tests with SRL 202A glasses at 20,000 m^{-1} results from a combination of these effects. The disposition of Tc released during glass corrosion in a disposal site will be strongly affected by the chemistry of Tc and the presence of corrosion products of other engineering and geological materials. It is, therefore, important that laboratory tests be conducted with actual radioactive waste forms rather than relying on the behavior of surrogates. Such tests will ensure that the sometimes subtle effects of chemistry and materials interactions are correctly taken into account when calculating the long-term behavior of radionuclides in a particular disposal site.

ACKNOWLEDGMENTS

REFERENCES

1.   W. L. Ebert, J. K. Bates, E. C. Buck, and C. R. Bradley, in *Scientific Basis for Nuclear Waste Management XVI*, edited by C. G. Interrante and R. T. Pabalan, (Materials Research Society, Pittsburgh, PA, 1993) pp. 569-576.

2.   W. L. Ebert and J. K. Bates, Nuclear Technol. **104**(3), 372-384 (1993).

3.   D. J. Bradley, C. O. Harvey, and R. P. Turcotte, *Leaching of Actinides and Technetium from Simulated High-Level Waste Glass*, Pacific Northwest Laboratory Report PNL-3152, 1979.

4.   S. Fillet, J. Nogues, E. Vernaz, and N. Jacquet-Francillon, in *Scientific Basis for Nuclear Waste Management IX*, edited by L. O. Werme (Materials Research Society, Pittsburgh, PA, 1985) pp. 211-218.

5.   F. Bazan, J. Rego, and R. D. Aines, in *Scientific Basis for Nuclear Waste Management X*, edited by J. K. Bates and W. B. Seefeldt (Materials Research Society, Pittsburgh, PA, 1987) pp. 447-458.

6.   N. E. Bibler and A. R. Jurgensen, in *Scientific Basis for Nuclear Waste Management XI*, edited by M. J. Apted and R. E. Westerman (Materials Research Society, Pittsburgh, PA, 1988) pp. 585-593.

7. E. Y. Vernaz and N. Godon, in Scientific Basis for *Nuclear Waste Management XV*, edited by C. G. Sombret (Materials Research Society, Pittsburgh, PA, New York, 1992) pp. 37-48.

8. *Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste* ASTM Standard C1220-92, American Society for Testing and Materials, Philadelphia, PA (1992).

9. *Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)* ASTM Standard C1285-94, American Society for Testing and Materials, Philadelphia, PA (1994).

10. W. L. Ebert, J. K. Bates, E. C. Buck, M. Gong, and S. F. Wolf, in Ceramic Transactions Vol. 45, Environmental and Waste Management Issues in the Ceramics Industry, pp. 231-241 (1994).

11. D. J. Wronkiewicz, L. M. Wang, J. K. Bates, and B. S. Tani, in *Scientific Basis for Nuclear Waste Management XVI*, edited by C. G. Interrante and R. T. Pabalan, (Materials Research Society, Pittsburgh, PA, 1993) pp. 183-206.

12. J. A. Rard, *Critical Review of the Chemistry and Thermodynamics of Technetium and Some of Its Inorganic Compounds and Aqueous Species*, Lawrence Livermore National Laboratory Report UCRL-53440 (1983).

13. T. T. Vandergraaf, K. V. Ticknor, and I. M. George, in *Geochemical Behavior of Disposed Radioactive Waste*, edited by G. S. Barney, J. D. Navratil, and W. W. Schulz, ACS Symposium Series 246, (American Chemical Society, Washington, D. C., 1984) pp. 25-43.

14. R. W. Buddemeier, R. C. Finkel, K. V. Marsh, M. R. Ruggieri, J. H. Rego, and R. J. Silva, Radiochimica Acta **52/53**, 275-282 (1991).