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THE INCORPORATION OF TECHNETIUM INTO A REPRESENTATIVE LOW-ACTIVITY WASTE GLASS

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DISCLAIMER

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ABSTRACT

A glass that has been tested to understand the corrosion behavior of waste glasses with high soda contents for immobilizing Hanford incidental wastes has been made by melting crushed glass with either TcO_2 or $NaTcO_4$ at 1100-1300°C. Incorporation of technetium in the glass was affected by solubility or kinetic effects. Metallic technetium inclusions formed in all the TcO_2-doped glasses. Inclusions also formed in glasses with added $NaTcO_4$ that were melted at 1100°C, but a glass melted at 1200°C did not contain detectable inclusions. The presence of Tc-bearing inclusions complicates the interpretation of results from dissolution tests because of the simultaneous release of technetium from more than one phase, the unknown surface areas of each phase, and the possible incorporation of technetium that is released from one phase into another phase. A glass containing about 0.15 mass % Tc dissolved in the glass is being used in dissolution tests to study the release behavior of technetium.

INTRODUCTION

Incidental wastes recovered during remediation of Hanford tanks will be vitrified for final disposal. The resulting waste forms will have low levels of radioactivity, referred to here as "low-activity waste" (LAW), and will be disposed in a near-surface disposal site. However, before LAW can be disposed, it must be demonstrated that the disposal system will adequately contain radionuclides and prevent them from contaminating the surrounding environment. Assessments conducted to provide guidance to the Storage and Disposal Project for Hanford LAW have identified Tc-99 to be the major dose contributor (about 70% of the peak dose) during the first 30,000 years after disposal [1]. The next highest contribution to this peak is from Se-79 (about 20%). Doses at times beyond 30,000 years are due primarily to uranium isotopes and Np-237. Under the oxidizing conditions of anticipated disposal sites, the Tc released from the glass will dissolve as the pertechnetate ion, TcO_4^-, which is highly soluble. This species is stable under anticipated disposal conditions. Reduced forms are stable only under strongly reducing conditions. Since the transport of pertechnetate away from the disposal site will likely not be restricted by interactions with minerals in the surrounding geology, the glass waste form will provide the primary containment for technetium.

The work described in this paper is part of a program that is underway at Argonne National Laboratory to study the release behavior and disposition of technetium and other radionuclides from low-activity waste glasses. Two main issues related to the management of Tc-bearing wastes are (1) how technetium is incorporated into a LAW glass and (2) the process by which technetium is released from the glass. We are addressing these issues by studying the incorporation of technetium into and the release of technetium from LD6-5412 glass, which is a glass that has been studied extensively in recent tests [2-4]. The LD6-5412 glass was developed in a program to study the relationship between composition and various properties of glasses for immobilizing low-activity waste streams that will be generated during the treatment of Hanford tank wastes [5].

Two aspects of the corrosion behavior of LD6-5412 glass are expected to impact the release and disposition of radionuclides. The first is that ion exchange to release sodium from the glass continues for very long time periods at the low temperatures relevant to LAW disposal systems; dissolution tests being conducted at 20°C have shown sodium to be released from the glass preferentially to B and Si through two years [2]. This behavior differs from the transient nature of ion exchange observed in tests with other glasses conducted at higher temperatures. This may mean that components that are weakly bound in the glass structure, possibly including technetium, may be leached from the glass much faster than the glass matrix dissolves. The second is that relative release rates of Na, B, and Si are different in tests that maintain dilute solutions than in tests in which dissolved glass components accumulate. Boron is released congruently with sodium and faster than silicon in very dilute solutions, but is released congruently with silicon and slower than sodium in more concentrated solutions. Therefore, we are conducting tests to determine if the release of either Na or Si can be used to approximate the release of technetium.

Several researchers have investigated the dissolution of Tc into silicate glasses, and thorough reviews have been published by Vida [6] and by Darab and Smith [7]. In fact, Darab and Smith themselves doped LD6-5412 glass with technetium. The vitrification of technetium is strongly affected by the high volatilities of most Tc-bearing species. Technetium has been added to glasses as Tc(VII) in a pertechnetate salt (e.g., $NaTcO_4$ or NH_4TcO_4), and it has also been reduced to Tc(IV) and added as the oxide $TcO_2 \cdot 2H_2O$. Several studies have shown that a greater percentage of technetium is retained in glasses made with TcO_2 than with pertechnetate salts [7]. However, $TcO_2(s)$ is known to sublime at temperatures above 900°C and disproportionate at temperatures above about 1100°C to generate metallic Tc and gaseous Tc_2O_7 [6].

In this paper, we discuss the production of Tc-doped glasses by remelting a dry mixture of crushed LD6-5412 glass with either TcO_2 or $NaTcO_4$. While the primary purpose of this work was to produce a glass for use in laboratory dissolution tests, the results are also relevant to the vitrification of actual waste streams. Because of their high volatilities, large amounts of Tc-bearing species will need to be recovered from off-gas systems during vitrification. Separation of technetium from the waste stream into the off-gas will provide an opportunity for developing a treatment to increase the amount retained in the waste during recycle. The present study may also provide insight into whether or not reduction to Tc(IV) will increase the retention of technetium in either low-level or high-level silicate waste glasses.

EXPERIMENTAL

Several glasses were prepared by remelting crushed LD6-5412 glass with various amounts of TcO_2 or $NaTcO_4$. Other glasses were prepared in preliminary tests from crushed LD6-5412 (without added technetium) to study the effect of the melting temperature on the glass. The composition of the LD6-5412 glass used in these experiments was measured at ANL and is given in Table I. The original LD6-5412 glass was obtained from Pacific Northwest National Laboratory. The glass had been prepared by melting oxide components at about 1400°C [5]. We desired to remelt the Tc-doped glasses at as low a temperature as possible to decrease the amount of technetium lost to volatilization. Therefore, tests were conducted by melting small amounts of the LD6-5412 glass at temperatures of about 900, 1000, 1100, 1200, and 1300°C for about 1 hour then quenching the samples in air to (1) determine the temperature at which the glass could be remelted and (2) determine if insoluble phases were exolved during remelting. The resulting glasses were examined with a scanning electron microscope (SEM) to determine if the glass had completely vitrified and to detect and identify any exolved phases.

Table I. Measured Composition of LD6-5412 Glass

Oxide	mass %	Oxide	mass %	Oxide	mass %
Al_2O_3	12	F	0.31	Na_2O	20
B_2O	5	Fe_2O_3	0.005	NiO	<0.03[a]
CaO	4	I	0.14	P_2O_5	0.19
Cl	0.36	K_2O	1.51	SO_3	0.22
Cr_2O_3	0.04	MgO	0.003	SiO_2	55.65
CsO	0.15	MnO	0.002	SrO	0.12
CuO	<0.03[a]	MoO_3	0.16		

[a]Below detection limit.

Aliquots of crushed LD6-5412 glass were then doped with small amounts of TcO_2 or $NaTcO_4$. The TcO_2 was prepared by first dissolving 0.8 g of NH_4TcO_4 in 30 g H_2O plus a few drops of concentrated NaOH. The TcO_4^- was then reduced by adding 5 mL of a 5% aqueous hydrazine solution. A finely divided, black precipitate formed, probably $TcO_2 \cdot 2H_2O$. The precipitate was removed from suspension by filtration through a bed of crushed (-200 +325 mesh) LD6-5412 glass. A bed of crushed glass was used because filtration of the precipitate alone had clogged 0.4 mm filters. The bed was washed with additional hydrazine solution then removed from the filter. The resulting mixture of $TcO_2 \cdot 2H_2O$ and crushed glass was allowed to air dry at room temperature. The amount of $TcO_2 \cdot 2H_2O$ recovered was calculated from the mass of the LD6-5412 bed before and after filtration. The $TcO_2 \cdot 2H_2O$ /glass mixture was transferred into a glovebox, and an aliquot was mixed with more crushed LD6-5412 glass in a platinum crucible to achieve the desired loading of technetium. The amount of technetium added to the glass was calculated by assuming homogeneous distribution of technetium both in the filter bed and in the mixture with the added glass.

The $NaTcO_4$ was prepared by first acidifying NH_4TcO_4 with HNO_3 and taking the resulting solution to dryness. The white crystalline residue was then dissolved in about 10 mL water, to which 0.2 mL conc. NaOH was then added to precipitate

$NaTcO_4$. This was filtered through a bed of crushed LD6-5412 glass, mixed with crushed glass, and melted following the same procedure described above.

The crucibles for all glasses were covered with a loose-fitting lid to prevent splattering of the molten glass. The lid did not restrict the movement of air into or out of the crucible. The crucible was placed into a furnace that had been preheated to the desired temperature and left undisturbed for the scheduled melting time. A bottom loading furnace was used to melt the glass. After the desired melting time, glass was poured from the crucible into platinum loaf pans that had been preheated to about 500°C. The glass in the loaf pans was then annealed at about 500°C. After about 2 hours, the annealing oven was turned off and allowed to cool to room temperature with the loaves of glass still in the oven. The glass was then broken out of the loaf pans and small chips were removed for analysis.

Before analysis, the small pieces of glass were polished to a 600-grit final surface finish with carborundum paper and water lubrication. These samples were examined with an SEM to determine if inclusion phases had formed in the glasses. Chips of some glasses were also examined with analytical electron microscopy (AEM), which is a transmission electron microscope with associated energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS).

Small amounts of these glass were crushed and dissolved for analysis. The glass was dissolved overnight in HCl and HF at 200°C in a sealed Teflon vessel. Insoluble material remained after dissolution of one of the glasses. This material was dissolved after the further addition of HNO_3. The technetium concentrations were measured with inductively coupled plasma-mass spectrometry (ICP-MS).

The specific procedures followed for making the various glasses with TcO_2 or $NaTcO_4$ are described with the results of the examinations summarized below.

RESULTS

Undoped LD6-5412: Glasses made by remelting crushed LD6-5412 glass at temperatures of 1200°C and below were all opaque. Examination of these glasses with SEM revealed the presence of various small (<0.5 mm) inclusions that contained Cu, Ni, Fe, and/or Cr. As given in Table I, the original glass contained small amounts of Cr and Fe, but Cu and Ni were not detected. Small Cr-bearing inclusions had been detected in LD6-5412 glass previously. Included phases were not detected in the glass melted at 1300°C. It was transparent and lime green, and appeared identical to the original glass that had been crushed. Analysis of the glasses with EDS indicated that the compositions of the glasses remelted at 1200°C and below were the same as that of the original glass. Remelting at 1300°C led to a very small decrease in the amount of sodium--from 15.0 ± 0.5 mass % Na in the original glass to about 14.3 ± 0.2 mass % Na in the remelted glass.

Glasses Made with $TcO_2 \cdot 2H_2O$

Glass 1: A mixture of 0.108 g $TcO_2 \cdot 2H_2O$ was mixed with 7.0 g glass (total of glass in filter bed and glass added to mix) then melted for 60 minutes at about 1300°C. The molten glass was poured into loaf pans and annealed at 500°C for 2 hours, then slowly cooled to room temperature. The glass was visibly dark and opaque. A small amount of this glass was dissolved for chemical analysis; it was found to contain 0.20 mass % Tc; this includes technetium present in inclusions and dissolved in the glass. The as-mixed fraction of technetium was about 1.5 mass %, so about 87% of

the added technetium was volatilized. Examination of polished cross sections with SEM revealed the presence of small (1-5 mm) particles distributed in the glass. Analysis with EDS in the SEM indicated that the particles contained technetium, but the amount of technetium in the glass was below the detection limit. An SEM image of one large and two small Tc-bearing inclusions in a polished cross-section is shown in Figure 1.

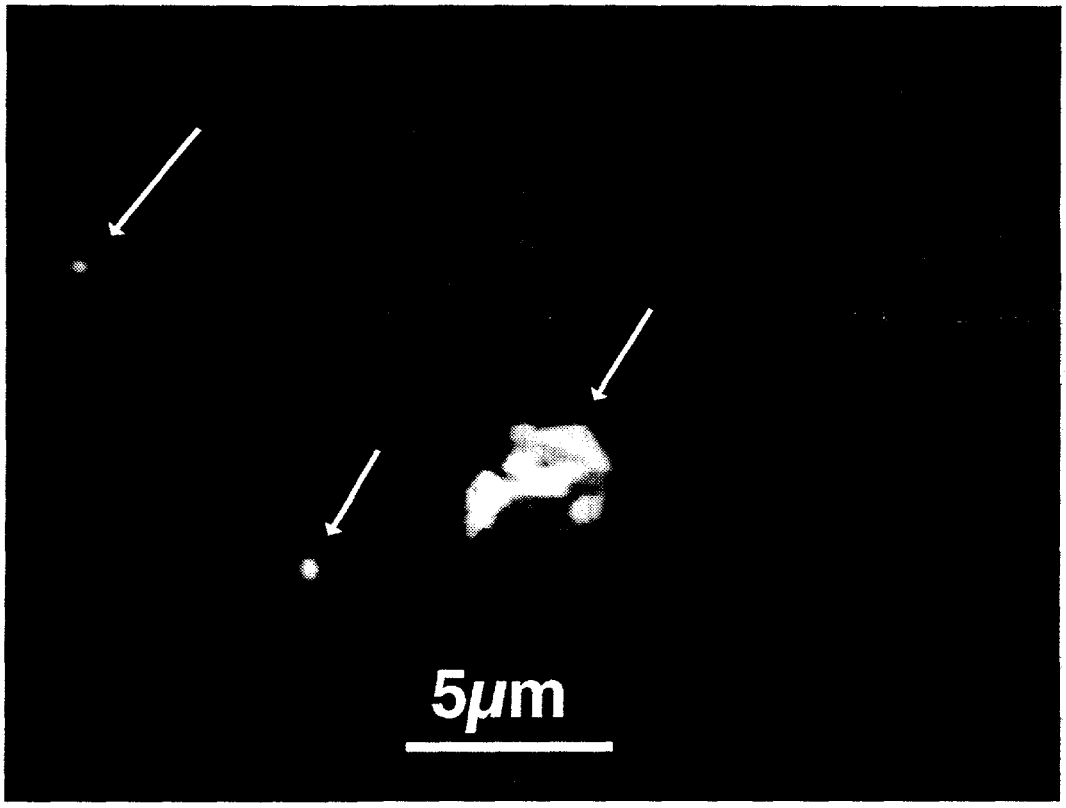

Figure 1. Polished Cross-Section Showing Tc-Bearing Inclusions in Tc-Doped LD6-5412 Glass

Glass 2: About 40 g of glass 1 was crushed and mixed with about 70 g of LD6-5412 glass to dilute glass 1. The mixture is calculated to contain 0.07 mass % Tc. This glass was melted at 1300°C for one hour, then heated to 1400°C for another hour. The molten glass was poured into loaf pans and annealed at about 500°C for about 2 hours. Examination of the resulting glass with SEM/EDS revealed the presence of small (about 1 mm) Tc-bearing inclusions similar to those found in glass 1, except they were smaller and less abundant. Dissolution and ICP-MS analysis of glass 2 indicated that the glass contained about 0.01 mass % Tc total in inclusions and dissolved in the glass. Similar to glass 1, about 15% of the technetium was retained after remelting. Given the size and abundance of the inclusions, it is likely that most of the technetium retained in glasses 1 and 2 is present in the inclusions.

The inclusions were examined with AEM to determine if they were undissolved TcO_2 or metallic technetium. Several samples were prepared for AEM examination from small chips of glass 2 that contained inclusions visible in an optical microscope. Sections containing the included phase were prepared with an ultramicrotome. The chemical compositions of the inclusion and the adjacent glass were analyzed with an ultra-thin window detector. The spectrum for the inclusion is shown in Fig. 2a. The spectrum is dominated by the peak at about 2.4 keV, which is due to the Tc $\beta_1(L_{II}M_{IV})$ and $\alpha_1(L_{III}M_V)$ transitions at 2.54 and 2.42 keV, respectively. A strong peak was also observed at about 18.4 keV, which is due to the Tc $\alpha_2(KL_{II})$ and $\alpha_1(KL_{III})$ transitions (not shown in Fig. 2a). Essentially no oxygen was detected in the analysis, which indicates that the technetium in the inclusion is metallic. This is consistent with the deformation and curling of the inclusion that were observed during sectioning. We have found these attributes to be characteristic of sectioned metallic samples. Technetium was not detected during analysis of the glass next to the inclusion, as shown by the absence of a peak near 2.4 keV in Fig. 2b. Evaluation of other sections revealed that some inclusions contained technetium plus small amounts of nickel; inclusions containing nickel, chromium, and iron had been detected after remelting the stock LD6-5412 glass.

These results suggest that disproportionation of Tc(IV) leading the the generation of Tc_2O_7 and metallic technetium has occurred during melting. The metallic inclusions probably formed from small clusters of TcO_2 that were not well mixed in the glass. If the TcO_2 had been better mixed, the inclusions may have been too small to be detected.

Glasses Made with $NaTcO_4$

Glasses 3 and 4: These glasses were made by mixing 0.09 g $NaTcO_4$ with 6.82 g LD6-5412 glass (1.4 mass % Tc as-mixed) and by mixing 0.009 g $NaTcO_4$ with 7.18 g LD6-5412 glass (0.13 mass % Tc as-mixed), respectively. These glasses were heated in quartz crucibles for about 1 hour at 1100°C. The molten glasses were not annealed, rather they were quenched in air. Examination of the resulting glasses with SEM revealed the presence of small Tc-bearing inclusions. Examination of the inclusions with AEM has not yet been completed. They are probably undissolved $NaTcO_4$, since Tc(VII) cannot not disproportionate. Chemical analysis of glasses 3 and 4 showed that they contained a total of about 0.15 and 0.05 mass % Tc, respectively. This includes both dissolved and precipitated technetium.

Glasses 5 and 6: These glasses were made with mixtures of LD6–5412 glass and $NaTcO_4$ that were the same as those used for glasses 3 and 4. Glasses 5 and 6 were melted in platinum crucibles for 1 hour at 1200°C, whereas glasses 3 and 4 were melted at 1100°C. No inclusions were found during examination of glasses 5 and 6 with SEM. Chemical analyses of these glasses show that they contained 0.18 and 0.06 mass % Tc, respectively.

Glass 7: A large batch of glass was made under the same conditions used to make glasses 5 and 6. About 120 g of a mixture of $NaTcO_4$ and crushed LD6-5412 glass was melted in a platinum crucible at 1200°C for about 1 hour. The mixture contained about 1 mass % Tc. The molten glass was poured into platinum loaf pans and annealed at 500°C for about 2 hours, then slowly cooled. Examination of a chip of the resulting glass showed it to contain inclusions. Therefore, the glass was crushed

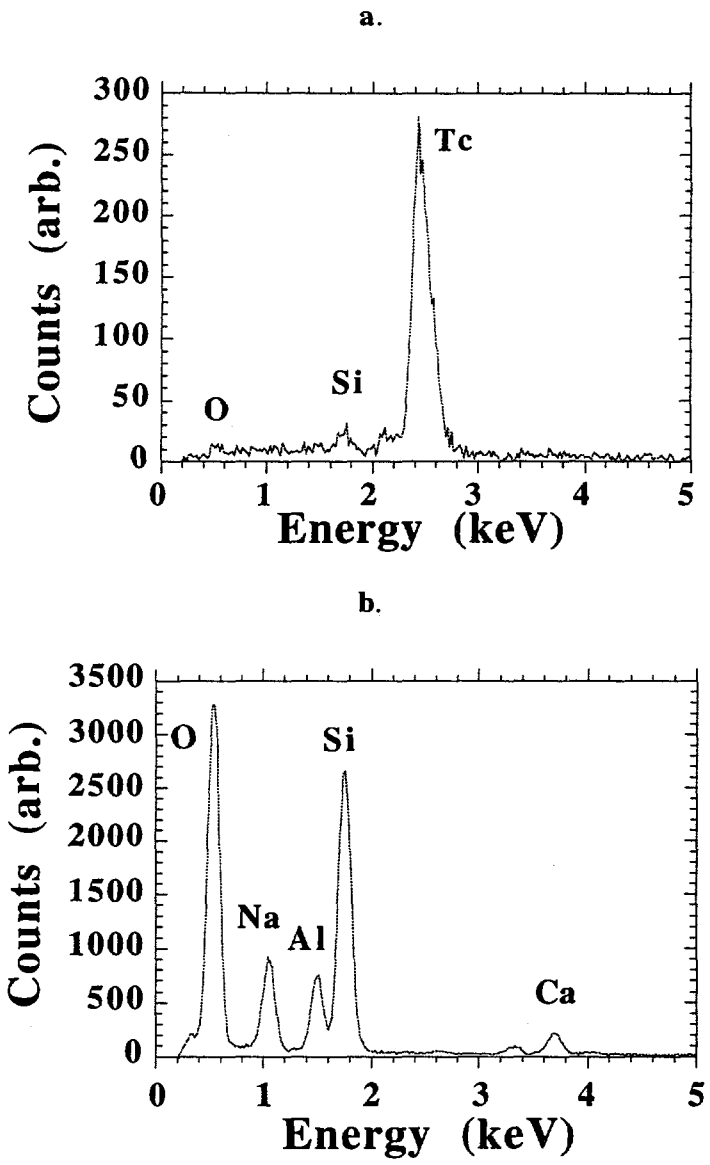

Figure 2. Compositional Analysis of (a) Inclusion and (b) Adjacent Glass

and remelted at 1300°C for 1 hour, annealed, then allowed to cool to room temperature. No Tc-bearing inclusion phases were observed in this glass. Some of the glass was dissolved in HF and HCl and analyzed with ICP-MS. The glass was found to contain 0.15 mass % Tc. This matches the target concentration in the "final base glass" for simulated double-shell slurry feed (DSSF) reported by Darab and Smith [7]. Samples of glass 7 have been prepared for use in corrosion tests.

DISCUSSION

These results indicate that, while the retention of Tc(IV) that is added to waste glasses may be greater than the retention of Tc(VII), disproportionation of the Tc(IV) results in the formation of metallic inclusions. Reduction of technetium prior to recycling would lead to several disadvantages in vitrification. The formation of metallic inclusions in glass melts is detrimental to Joule-heated melters, and phase separation in the final waste form complicates its qualification. From the stoichiometry of the disproportionation reaction, only one-third of the added Tc(IV) is reduced to the metal. The rest is lost as the highly volatile heptoxide. Analysis of the glasses made with TcO_2 indicates that less than 20% of the added technetium is retained. The behavior of the metallic inclusions during glass corrosion remains to be determined.

Technetium added as $NaTcO_4$ did dissolve in the glass that was melted at 1200°C, but did not fully dissolve in glasses melted at lower temperatures for one hour. It is not clear whether the inclusions in glasses melted at temperatures below 1200°C remained because of solubility or kinetic limitations. However, the amount of technetium that was fully dissolved in glass 7 is less than that reported by Darab and Smith [7] for glasses made with NH_4TcO_4. They did not report if the glasses were analyzed to verify that the technetium was completely dissolved in the glass and not present as undissolved inclusions.

The presence of technetium in the glass and in inclusions complicates the characterization of the release of technetium with laboratory tests. This is because technetium released as the glass dissolves may sorb onto the included phase and not be detected by solution analysis. Alternatively, the simultaneous dissolution of the glass and inclusion phases will prevent measurement of the rate at which technetium is released from the glass. That is why it was important to verify that included phases were not retained in the glass to be used in the corrosion tests.

CONCLUSION

Small amount of TcO_2 or $NaTcO_4$ were mixed with a representative low-level waste glass for Hanford incidental wastes and melted to produce glasses doped with technetium. Examination with SEM and AEM of the TcO_2-doped glasses melted at 1300°C revealed the formation of small inclusions of metallic technetium. This is probably a results of the disproportionation reaction in which Tc_2O_7 and metallic technetium form. The size of the inclusions is probably related to the size of the agglomerates of TcO_2 that were added to make the glass. The amounts of technetium dissolved in the glasses doped with TcO_2 were below the detection limit of EDS, so most of the technetium that was retained in these glasses is present in the inclusions. Therefore, treatment to reduce pertechnetates in the waste stream or collected as off-gas does not facilitate the dissolution of technetium into this glass, although the total amount incorporated in the glass, including metallic inclusions, may increase.

Small Tc-bearing inclusion phases were also observed in glasses doped with $NaTcO_4$ that were melted at temperatures of about 1200°C and below; we assume the inclusions are undissolved $NaTcO_4$. No inclusions were observed in glasses melted at about 1300°C. A glass having the target technetium content for Hanford DSSF wastes (about 0.15 mass%) can be produced that contains no detectable inclusions. The release behavior of technetium from that glass is being studied.

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