

Formation of Technetium Salts in Hanford Low-Activity Waste Glass

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The distribution and physical form of technetium in a Hanford low-activity waste (LAW) glass was examined with scanning electron microscopy (SEM) and X-ray diffraction (XRD). A simulated Hanford LAW glass was spiked with varying amounts of potassium pertechnetate and melted at 1000°C. The glass was melted in a sealed quartz ampoule with the air pumped out, so that volatile material could leave the glass but would not be lost from the system. Previous studies have shown that technetium remains in the glass up to about 2000 ppm, but rises to the top of the melt as a separate salt phase above this concentration. Examination by SEM shows that crystals of technetium compounds appear to grow out of the hot glass, which implies that the hot glass was supersaturated in technetium salts. Some of the technetium compound crystals had apparently melted, but other crystals had obviously not melted and must have formed after the glass had partially cooled. The technetium compounds in the salt layer are KTcO_4 and NaTcO_4 , according to SEM and XRD. No TcO_2 was found in the salt phase, even though Tc(IV) has been previously reported in the glass.

Keywords: nuclear waste; radioactive waste; volatilization

I. Introduction

OLD War production of plutonium at Hanford generated a large volume of radioactive waste which still resides in underground storage tanks, awaiting final disposition. The waste came from chemically processing irradiated uranium reactor fuel to recover plutonium and uranium. Almost all of the plutonium and uranium were removed during the process, leaving most of the fission products in the waste stream. The chemical processes added a huge volume of nonradioactive chemicals used in the early plutonium separation processes. Practically all the mass of the tank waste consists of stable elements, but the small amount of fission product makes the waste quite radioactive. The composition of the waste varies widely from tank to tank. A typical raw tank waste consists of crystalline salts and wet, gelatinous, dark brown material, with not much free liquid. Chemically, the tank waste is largely sodium nitrate, nitrite, carbonate, and hydroxide, with a large amount of aluminum.^{1,2} It may have up to several percent iron, chromium, and zirconium and may have up to percent levels of phosphate, sulfate, fluoride, and chloride. The short-lived fission products have decayed off, but the fission products with half-lives greater than about

5 years are still present (other than the fission gases xenon and krypton). The long-lived fission product ^{99}Tc is present at a few parts per million. This waste will be vitrified to place it in a safe configuration for permanent disposal.

The current plan is to separate the raw tank waste into a small volume of high-level waste, highly radioactive from ^{90}Sr and ^{137}Cs , and a much larger volume of low-activity waste (LAW), which has most of the ^{99}Tc and ^{129}I .³ The high level and low-activity waste streams will be vitrified separately. Technetium will be found in the LAW stream. These waste streams will be mixed with glass formers and vitrified. Technetium is well-known to evaporate out of the glass during the melting process.^{4–7} One of the objectives of this work was to measure the maximum loading of technetium in the glass. The glass will retain technetium up to some maximum concentration, and anything beyond that will tend to migrate to the melt surface and form a salt layer or volatilize into a gaseous form. The maximum technetium loading in a typical Hanford LAW glass is ~2000–2800 parts per million by mass, depending on the redox conditions in the glass.⁸ Reducing conditions can slightly increase the technetium loading to the high end of this range. The high nitrate and nitrite concentration in the tank waste will cause highly oxidizing conditions early in the vitrification process, hence, the lower loading level is likely the more relevant. Since the raw tank waste has only a few ppm technetium, this data show that the glass could hold the Hanford inventory of technetium.

The chemical form of technetium in the glass is not accurately known. According to X-ray absorption near edge spectroscopy (XANES), both Tc(VII) and Tc(IV) are found in the glass.^{8–10} Technetium may be present as isolated TcO_4 tetrahedra, but some may be present as inclusions of compounds such as TcO_2 or a solid pertechnetate salt. It may be more accurate to refer to this as “maximum technetium loading” rather than “technetium solubility limit,” since some of the technetium may not be truly dissolved in the glass.

The mechanism through which technetium evaporates and leaves the melt is not well-known. Technetium may evaporate out of the melt even though its concentration is below the measured maximum loading. The data reported here is part of a larger effort to determine the chemical and physical form of technetium in the glass, and the mechanism by which technetium leaves the glass.

In this paper, we present the results of physical characterization of the glass with scanning electron microscopy (SEM) and X-ray diffraction (XRD), particularly the form and location of technetium in both the glass and in the salts above the glass.

II. Experimental Procedure

A nonradioactive glass simulant was formulated to resemble a Hanford LAW glass. This glass was used in all experiments

C. Jantzen—contributing editor

Manuscript No. 38370. Received March 23, 2016; approved July 13, 2016.

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discussed in this paper. The preparation of this glass has been described previously.⁸ The target weight percent of each glass component and the results of chemical analysis by inductively coupled plasma optical emission spectroscopy have been previously reported.⁸ Table I shows the results of energy dispersive spectroscopy (EDS) analysis of this glass (the same instrument used to measure elemental composition of glass later in this paper). The expected weight percent of each element was calculated from the target concentration. The expected composition was renormalized using only the elements observable by EDS (i.e., not including boron). Table I shows that the analytical precision of EDS in this glass is $\pm 20\%$ to $\pm 30\%$. Because this simulant glass was not batched from nitrates, it did not have the strongly oxidizing conditions expected in the melter. A stock of solid, crystalline KTcO_4 was prepared for this series of experiments to spike the glass simulant. This stock of KTcO_4 was analyzed for ^{99}Tc by liquid scintillation and found to be stoichiometric KTcO_4 , within analytical uncertainty. Its preparation was described previously.⁸

For each glassmelt, 20 g of pulverized glass was accurately weighed, then spiked with an accurately weighed amount of solid KTcO_4 . Glass melts were made with 1000, 2000, 3000, 4000, and 6000 ppm technetium (measured by mass as the element). The spiked, pulverized glass was mixed for several minutes in a ball mill to uniformly distribute the KTcO_4 . The 1000, 2000, 3000, and 4000 ppm spikes were mixed in an alumina ball mill. The 6000 ppm spike was mixed in a tungsten carbide ball mill, which causes slightly reducing conditions from a few milligrams of tungsten carbide shed from the ball mill into the glass sample. The tungsten carbide contamination slightly increases the technetium retention in the glass, as described previously.⁸

Certain components in the waste glass, particularly pertechnetate salts, are volatile at the temperature of the glassmelt, and would be lost if the glass were melted in an open vessel. To measure the maximum loading of technetium in the glass without losing the technetium, the melts were performed in a sealed quartz vessel. Volatile components can escape to the headspace above the glass, but cannot leave the system. Salts present at a concentration above their maximum loading (above their solubility in the glassmelt) migrate to the surface of the melted glass and form a salt layer. Some compounds evaporate out of the melt and condense on the quartz above the melt. Technetium distributes among these phases.

The spiked glass simulant was loaded into the quartz ampoule as described previously.⁸ The fused quartz ampoule with the spiked glass sample was pumped down to about 10^{-3} Torr to remove air (so that the ampoule would not

pressurize at temperature), then sealed shut with an oxygen-propane torch. The ampoule was placed in the furnace at 750°C . The temperature was raised to 1000°C at 5°C per minute and held there for two hours, and then the ampoule was withdrawn from the furnace and allowed to cool to room temperature.

As the ampoule cools, the quartz extensively cracks from the difference in thermal expansion between the sample and the quartz, though in all cases, the glass ingot stayed contained inside the fractured ampoule. During the melting process, some of the salts in the sample may rise to the top of the melted glass and form a separate phase. As the glassmelt cools, it cracks extensively, and the melted salt layer gets drawn into the cracks. As the temperature continues to drop, the salts freeze, but the glass continues to crack, so that some cracks in the glass are free of salts, while others are coated in salts.

The cooled samples were subsequently dissected for analysis. The glass was analyzed for ^{99}Tc by ICP-MS, technetium speciation by XANES and EXAFS, Raman spectroscopy, and Fe(II)/Fe(III) for indication of the redox conditions in the glass. The data has been previously reported^{8,11} and is not repeated here.

Samples of glass were taken from various places in the melt analyzed by SEM and XRD. Specimens of the technetium-bearing glasses were then deposited on a sticky carbon tape, coated with conductive carbon and analyzed with an FEI (Hillsboro, OR) Quanta250 field-emission gun scanning electron microscope equipped with an EDAX (EDAX Inc., Mahwah, NJ) compositional analysis system. Images were obtained under secondary electron imaging (SEI) at low energy to provide detailed morphological micrographs and at higher energy with backscattered electron (BSE) imaging conditions to provide compositional information. Both energy dispersive X-ray spectra (EDS) and chemical maps were collected from specific areas of interest. The beam intensity and counting time had a strong effect on the sodium value and easily caused depletion of the signal. To establish the most accurate sodium value for the glass, an EDS analysis was performed for a short duration at low intensity. This was repeated several times to obtain reasonable counting statistics.

The glasses and salt layers were also analyzed by XRD. The glass samples were weighed, then combined with 5 wt% CaF_2 as an internal standard. The mixtures were ground in an alumina ball mill, then mounted on a slide for XRD. The mixture was held down on the slide with clear Krylon paint diluted with amyl acetate. The mounted samples were analyzed on a Rigaku Ultima IV diffractometer (Rigaku Corporation, Tokyo, Japan). The instrument scanned 5° – 80° 2θ at a rate of 0.02° 2θ per min. Spectra were quantitatively analyzed using whole pattern fitting Rietveld refinement. The XRD analysis used the FIZ/NIST Inorganic Crystal Structure Database.

Table I. Composition of Low-Activity Waste Glass Measured by EDS

Element	Expected weight percent	Observed by EDS (spot size 4.0 μm) 1000 ppm glass
Al	6.37	6.53
Ca	2.84	3.26
Cr	0.03	0.04
Fe	7.08	7.13
K	0.81	0.92
Mg	1.56	1.37
Na	29.54	22.47
Si	40.83	46.28
S	0.19	0.17
Ti	1.59	1.71
Zn	5.35	5.34
Zr	3.82	4.25

Note that boron is not shown since it is not detectable by EDS. Technetium is not detectable at 1000 ppm by EDS in this glass.

EDS, energy dispersive spectroscopy.

III. Results

At high technetium loadings, SEM imaging of the glassmelt showed that two types of technetium compounds crystallized on the surface of the glass — blocky crystals that appear to have been melted, and needlelike crystals that obviously had not melted. Sodium and potassium in various proportions always accompany technetium in these crystals. At decreasing technetium loadings, the technetium was present as increasingly smaller isolated particles that were less than 1 μm in diameter. At these lower waste loadings, it was not possible to resolve the crystalline forms of the technetium or be confident about their composition.

Figure 1 shows the glass with 1000 ppm technetium loading. Figure 1(a) is a low magnification image of the glass showing the shattered surface, with some gas bubbles. The glass appeared uniform. Figure 2(b) shows a small group of bright particles that were enriched in technetium. The main

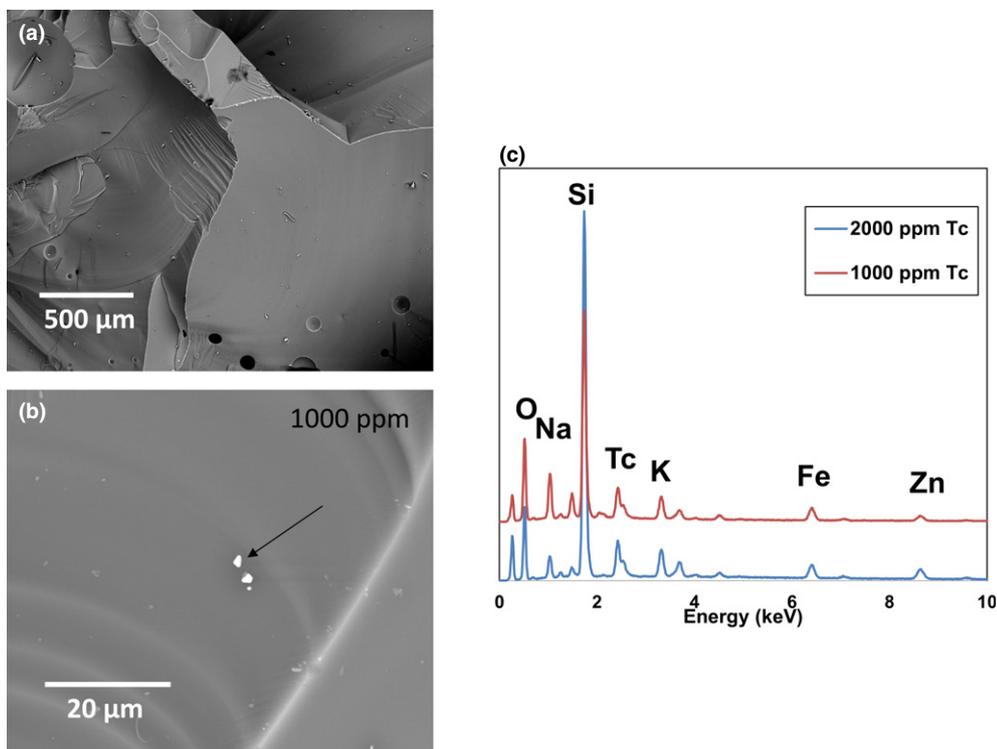


Fig. 1. Low (a) and high (b) magnification of the 1000 ppm sample, and the analysis of a technetium salt crystal (c) from the 1000 and 2000 ppm glasses. The energy dispersive spectroscopy (EDS) analysis of the spot (marked with an arrow) shows the presence of Tc, O, and a small amount of Na and K. Some of the EDS peaks, such as the Si, Fe, and Zn, may be from the underlying glass.

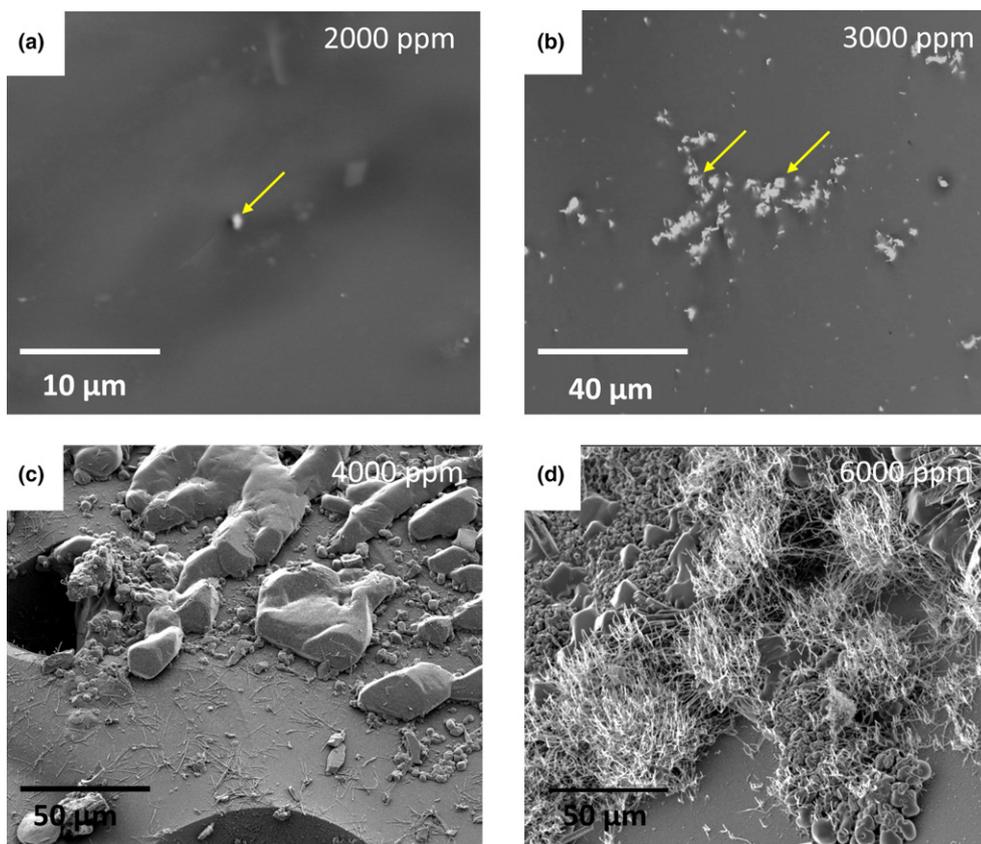


Fig. 2. Scanning electron microscopy images of the steady progression of the quantity of technetium on the surface of the glass, going from 2000 to 6000 ppm technetium (a–d). Specks of technetium are marked with arrows on the lower concentration glasses.

evidence that these are discrete particles comes from the SEM-BSE image. The EDS spot analysis spectra [Fig. 1(c)] show the spectra from isolated particles on the glass surface

from the 1000 ppm sample and 2000 ppm sample. The isolated particle may have fallen onto the broken glass surface from elsewhere in the melt (such as the salt layer), but even

so, it still represents technetium that did not incorporate into the glass at that spike concentration. (The amount of technetium not incorporated in the 1000 and 2000 ppm glasses is a very small fraction of the total technetium added to the glass. Above the measured maximum technetium loading, the amount of technetium-containing salt increases sharply). Because of the small size of these particles in both these specimens, the beam would have penetrated through the particle and caused excitation of the underlying glass. This makes it impossible to determine if the particle contained Na or K. To determine both the composition of the glass and the composition of these individual particles, a higher resolution technique would be required, such as transmission electron microscopy analysis of the isolated particles and the cross-sectioned glass.¹²⁻¹⁵

In Fig. 2, the backscattered image shows bright particles on the surface of the 2000 and 3000 ppm glass. There is also evidence elsewhere in the sample for brighter contrast regions

that could correspond to technetium-enriched regions below the surface of the glass. However, without obtaining a cross section through the glass, this cannot be confirmed. Analysis of this feature indicated the presence of technetium. Analysis of the surrounding glass revealed the expected glass composition. The subsequent images shown in Fig. 2 show the surface of the glass at increasing technetium loading. Above 3000 ppm technetium, the amount of salts at the surface of the glass increases sharply. At the higher loading, the technetium crystals initially form blocklike forms on the surface and at the highest loading, the technetium is also present as fine wispy structures. Figure 3 shows a higher magnification image of technetium crystals on the 6000 ppm glass. Several shapes of technetium can be seen — blocky crystals, filaments, lichenlike deposits, and hairlike wisps. The blocky crystals appear to have been melted.

The elemental maps and analysis of the 4000 ppm sample (Fig. 4) show the existence of at least two types of

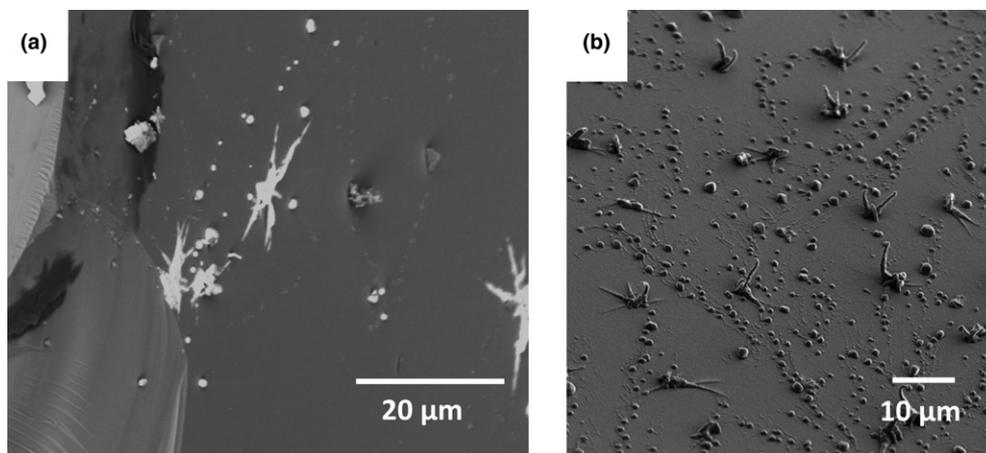


Fig. 3. (a) Backscattered electron image of the glass showing fine technetium-rich filament-like phase on the 6000 ppm glass sample and (b) SE image of similar feature showing that these salts have grown up from the glass surface.

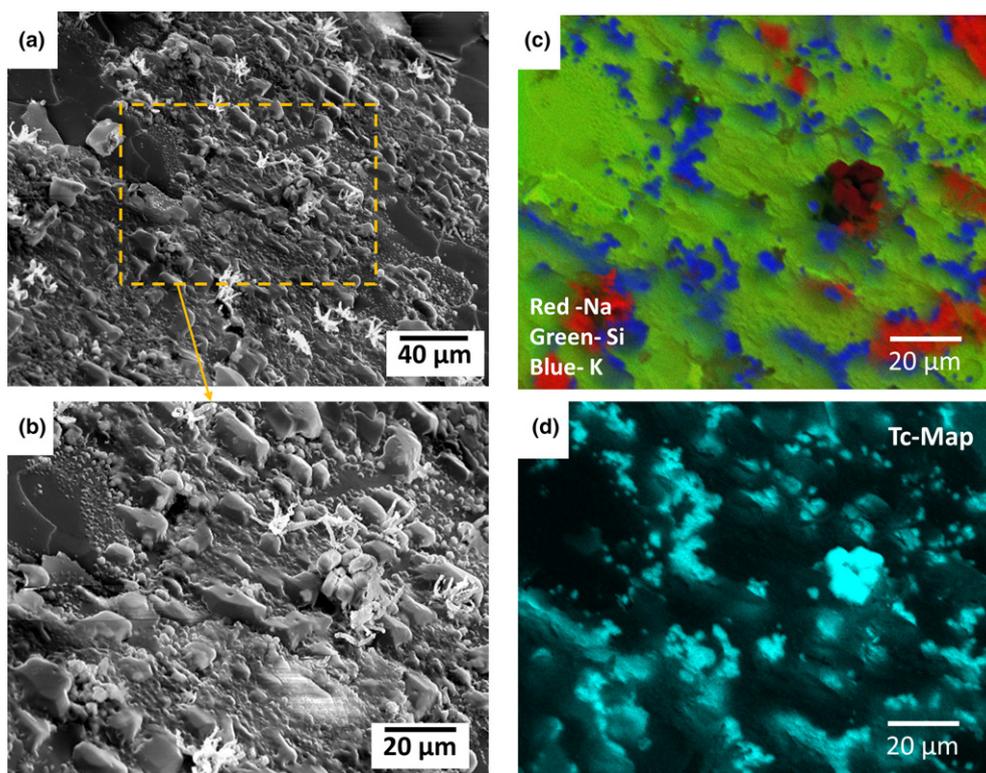


Fig. 4. Two types of technetium phase on the glass surface of the 4000 ppm Tc sample. SE image (a) shows a medium magnification view of the glass surface. (b) shows an enlargement of (a). Pictures (c) and (d) show elemental maps of a nearby surface of the same glass.

technetium phases. Some of the technetium appears in the form of blocky (melted) crystals, and some appear as filaments (not melted). The spiny crystals contain potassium and technetium but the blocky phases on the surface contain primarily sodium and technetium. Oxygen is present in these phases as well, but the oxygen X-ray signal could be coming mostly from the underlying glass.

Figure 5 shows an elemental analysis of a mass of technetium-bearing phase on the surface of the 6000 ppm glass. Both the sodium and oxygen peaks are barely visible owing to the severe attenuation of the characteristic X-rays by the heavy element technetium; however, the absence of any glass elements, such as silicon or aluminum, shows that oxygen and sodium are present in the technetium phase. The samples had been coated with carbon which accounts for carbon peak. The lower energy beam was used to improve the electron cross-section for sodium and technetium.

The SEM pictures suggest that technetium compounds crystallize out of the glass rather than being deposited by gas-phase evaporation and condensation.

Two of the bulk glasses (spiked to 3000 and 4000 ppm Tc) were analyzed by XRD (Fig. 6). These showed essentially no peaks other than Al_2O_3 (from the ball mill) and CaF_2 (the internal standard), in addition to the expected broad humped background of the Si–O tetrahedral structure at low angles. The 4000 ppm glass did suggest 0.1 wt% KTcO_4 , though the low fraction of this phase makes its identification uncertain.

Figure 7 shows the XRD patterns from the salt layer above the 4000 and 6000 ppm glass melts. The XRD

measurement shows sodium and potassium sulfates, KTcO_4 , and in the 6000 ppm sample what appears from the database to be NaTcO_4 . No powder pattern for the latter is available, but the pattern was refineable from isostructural KTcO_4 or NaIO_4 , since all are known to have the scheelite structure (space group $I4_1/a$).^{11,16} The sodium–technetium phase was confirmed in the SEM analysis in the high technetium-containing glasses (see Fig. 4). The technetium spike was added to the glasses as the potassium salt, but the glass has much more sodium than potassium, and it is reasonable to believe that the KTcO_4 could have partially converted to NaTcO_4 by metathesis during the melt. The salt consists of a larger fraction of technetium-containing phases (~40 wt%) for the 6000 ppm sample than for the 4000 ppm sample (~20%), with the balance being sulfur-containing phases. SEM-EDS shown in Figs. 8 and 9 confirm the presence of Na–Tc–O, K–Tc–O, and Na–S–O phases in the 6000 ppm sample.

IV. Discussion

The measured waste loading of technetium in a simulated Hanford low-activity waste glass is between 2000 and 3000 ppm, but the chemical and physical form of the technetium in the glass is poorly known. The technetium may be truly dissolved as one or more species, and part could be dispersed throughout the glass as tiny particles. Abundant technetium salts appeared in the salt layer above the 4000 and 6000 ppm melts, but occasional crystals of technetium

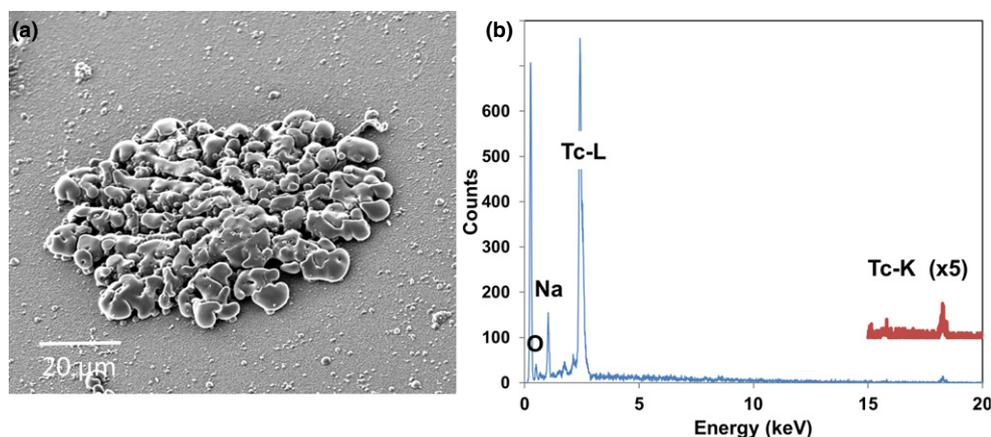


Fig. 5. (a) SE image showing clump of sodium–technetium–oxygen phase on the 6000 ppm glass surface. (b) The X-ray spectrum of this mass.

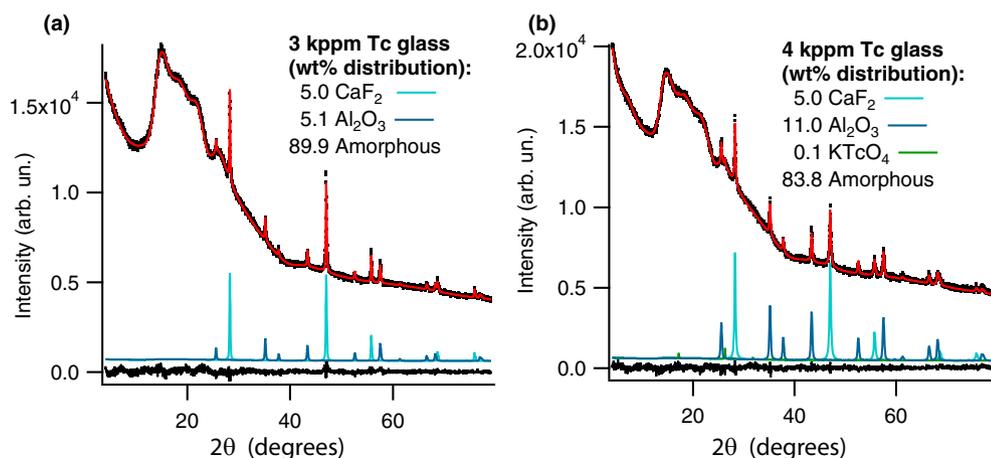


Fig. 6. X-ray diffraction patterns from the (a) 3000 and (b) 4000 ppm glasses. Spectra were taken with an internal standard of 5.0 wt% CaF_2 . Shown are the experimental (black points), fitted (red line), and difference pattern (gray) of the fit, along with the peaks for the crystalline phases (these have been offset from the main pattern for clarity). Inset shows the wt% distribution of phases.

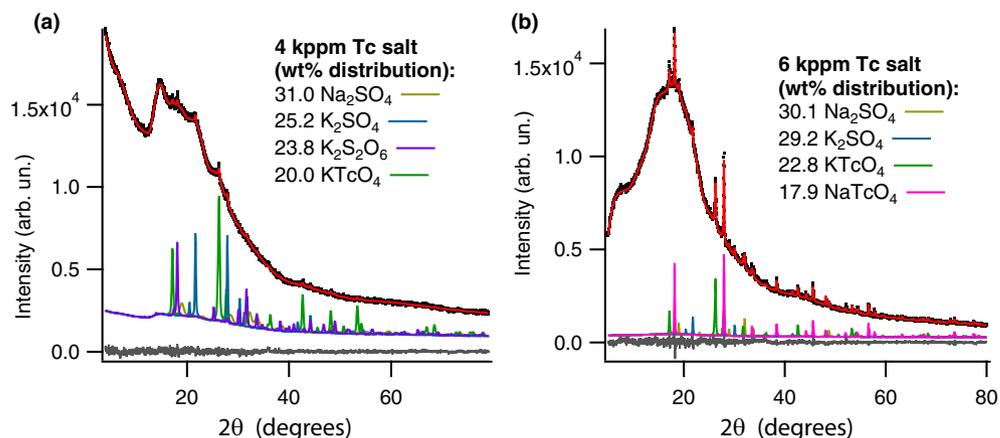


Fig. 7. X-ray diffraction patterns from the (a) 4000 and (b) 6000 ppm salt. Samples had no internal standard, so distribution of phases is for crystalline phases only. Shown are the experimental (black points), fitted (red line), and difference pattern (gray) of the fit, along with the peaks for the crystalline phases (these have been offset from the main pattern for clarity). Inset shows the wt% distribution of phases.

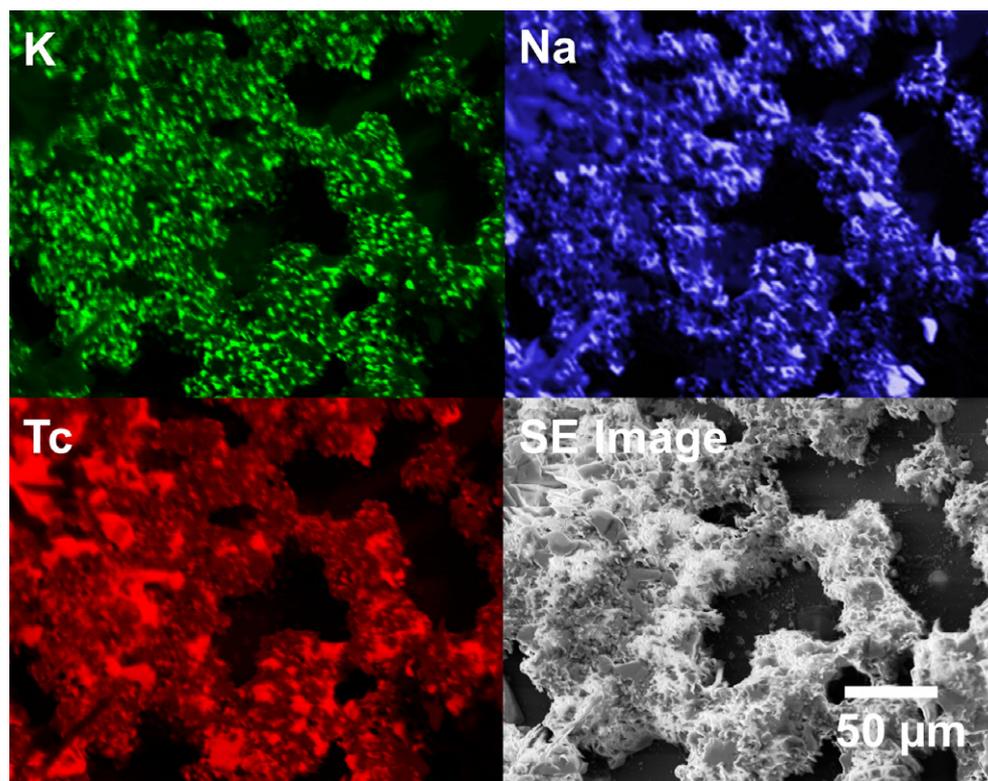


Fig. 8. Scanning electron microscopy analysis of salt phase on the surface of the Tc-loaded glass (6000 ppm added Tc) showing the occurrence of K–Tc–O and Na–Tc–O.

compounds appeared in all glasses, including the 1000 ppm melt, which is below the maximum measured technetium loading. At only half the maximum technetium loading, occasional crystals of a technetium compound still appear on the fractured surface of the glass. The occasional particles of a technetium compound apparently constitute only a small fraction of the technetium inventory in the 1000 and 2000 ppm glass, since the amount of salt layer increases sharply between 3000 and 4000 ppm, but the increase in KTcO_4 that was added to the glass is only about 30%. The KTcO_4 spike in the glass must have dissolved in the glass at temperature, since it converted by metathesis to NaTcO_4 . If the solid KTcO_4 spike had moved to the salt layer by some mechanical means, then it would have appeared there as KTcO_4 , not NaTcO_4 .

If the glass has any technetium, even a small amount, then at the temperature of the melt, some nonzero fraction of it

will partition into the gas phase above the melt (sodium and potassium pertechnetates are fairly volatile at 1000°C^{17}). As the melt cools, this technetium can be expected to condense into crystals. The condensed pertechnetate will form primarily on the quartz ampoule above the glassmelt, since it cools faster than the bulk glass below. Particles of this condensed pertechnetate may contaminate the glass below when samples are taken for analysis. However, this mechanism alone does not explain all of the observations. The glass was spiked with KTcO_4 , and had no oxidizing agents or reducing agents. After the glass was fused, part of the technetium in the glass was found to be Tc(IV) according to XANES analysis. However, the salts above the glass always show technetium in conjunction with sodium or potassium, which hardly fits Tc(IV). The technetium appears to be undergoing chemical reactions in the glass, and not merely diffusing through the hot glass and then evaporating at its surface.

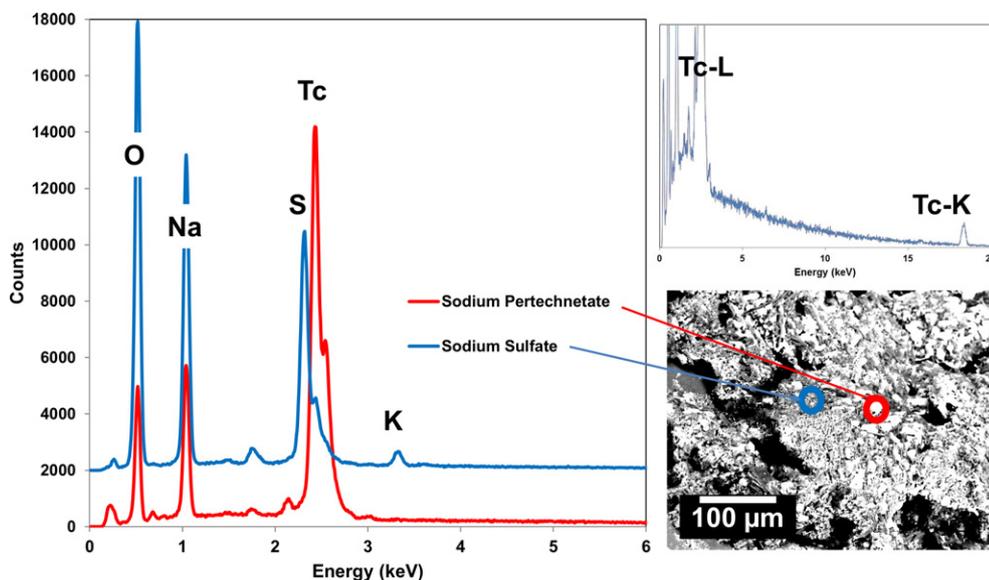


Fig. 9. Elemental analysis of salt layer from the 6000 ppm Tc-loaded glass showing Na–Tc–O and Na–S–O phases (presumably NaTcO_4 and Na_2SO_4).

Long, needlelike crystals of technetium compounds pointing up out of the surface of the glass strongly imply that technetium compounds crystallize out of the glass, and do not merely evaporate from the surface of the hot glass. If the technetium had simply evaporated from the hot glass, then it would crystallize elsewhere in the salt layer, but not at the surface of the hot glass. The technetium compounds had to somehow reach supersaturation in the hot glass, or crystals could not grow. If the technetium never reached supersaturation, then solid crystals of KTcO_4 (from the original spike) or NaTcO_4 would have to somehow rise to the surface through the highly viscous melt. It is not clear what process could make the technetium compounds (presumably pertechnetates) supersaturated in the hot glass. The needle crystals had obviously not melted, but other crystals look like they did melt. The unmelted crystals appear to be KTcO_4 (mp 530°C), and the melted crystals appear to be NaTcO_4 (mp 790°C ¹⁷). If the compounds on the glass really are NaTcO_4 and KTcO_4 , then the higher melting compound formed and melted first, and the lower melting compound formed later when the glass had cooled, and never did melt. This is hard to explain except through chemical processes occurring in the glass.

The composition of the layer of salts above the glass varied with the amount of KTcO_4 spike, even though the only difference between the various spiked glasses was the quantity of KTcO_4 added to each glass. The amount of salt layer increased sharply above 3000 ppm (as expected), but the chemical composition of the salts was not pure KTcO_4 and NaTcO_4 . The sodium in the salt layer is not surprising, since the glass has much more sodium than potassium, but the salt layer also had sulfate (see Figs. 7 and 9). Apparently, when a pertechnetate salt migrates to the surface, it carries other ionic compounds with it, compounds which would not leave the glass on their own. Migration of such salts to the surface of the glass during the melt has been previously reported.^{18–21} Molten sulfate-containing salts form at much lower values of SO_3 (0.16 wt% of unspiked glass) than typical sulfur solubility (1.6 wt% but depends greatly on alkali concentration²²) when in the presence of other anions. This has been shown for various anions in the same low-sulfate LAW composition discussed here. In technetium-containing glasses, sulfate is observed in the salts for glasses with ≥ 3000 ppm target Tc⁸ in rhenium-containing glasses at ≥ 6400 ppm target Re,²⁰ and in iodine-containing glasses at $\geq 12\,000$ ppm target I.²³ This synergistic effect on solubility is expected to be similar for other anions such as halides, molybdate, chromate, and

phosphate. In the case of pertechnetate and sulfate ions in the salt melt, as in the current samples, alkali sulfates should always crystallize first on cooling since melting points of the alkali sulfates are much higher than alkali perhenates or alkali pertechnetates.^{5,21}

V. Summary and Conclusions

Potassium pertechnetate will dissolve and disperse in a low-activity waste glassmelt up to about 2000 ppm, and the excess beyond that will migrate to the top of the melt and form a clearly visible salt layer. The salts consist of largely sodium salts, not the potassium salt used, to spike the glass. The salts also tend to carry other anions such as sulfate out of the glass, which is not at a high enough concentration in the glass to separate on its own. We have shown for the first time the SEM and XRD evidence of these alkali technetium oxide phases in glass and in the salt phase. The technetium oxides form crystals with varying morphologies which range from blocky euhedral crystals to wispy filaments. Needlelike technetium compounds appear to grow out of the hot glass.

Acknowledgments

The authors are grateful for the financial support provided by the Federal Project Director William F. Hamel, Jr. of the Department of Energy's Hanford Tank Waste Treatment and Immobilization Plant. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. DOE under contract DE-AC05-76RL01830. The authors thank Peggy Smoot, Jarrod Crum, and Jose Marcial for assistance with XRD measurement and phase fitting.

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