Technetium Chemistry in the Fuel Cycle: Combining Basic and Applied Studies

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ABSTRACT: Technetium is intimately linked with nuclear reactions. The ultraminute natural levels in the environment are due to the spontaneous fission of uranium isotopes. The discovery of technetium was born from accelerator reactions, and its use and presence in the modern world are directly due to nuclear reactors. While occupying a central location in the periodic table, the chemistry of technetium is poorly explored, especially when compared to its neighboring elements, i.e., molybdenum, ruthenium, and rhenium. This state of affairs, which is tied to the small number of laboratories equipped to work with the long-lived ^{99}Tc isotope, provides a remarkable opportunity to combine basic studies with applications for the nuclear fuel cycle. An example is given through examination of the technetium halide compounds. Binary metal halides represent some of the most fundamental of inorganic compounds. The synthesis of new technetium halides demonstrates trends with structure, coordination number, and speciation that can be utilized in the nuclear fuel cycle. Examples are provided for technetium—zirconium alloys as waste forms and the formation of reduced technetium species in separations.
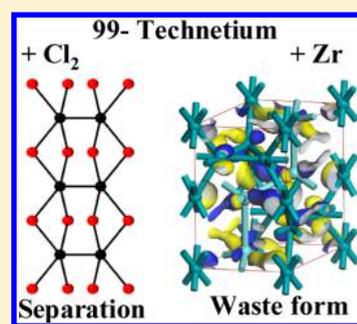
INTRODUCTION

Technetium is the lightest radioelement. Its formation is associated with nuclear processes. In the environment, microscopic levels of technetium are present because of the spontaneous fission of uranium isotopes. The discovery and identification of technetium can be traced to nuclear reactions from early cyclotron experiments.[1] The specific nuclear reaction was deuterium on molybdenum, a byproduct of experiments conducted by Ernest O. Lawrence at University of California—Berkeley. After months of irradiation, Lawrence presented the irradiated molybdenum foil to Emilio Segrè. At the Royal University in Palermo, Italy, Carlo Perrier and Segrè isolated two metastable technetium isotopes, ^{95m}Tc ($t_{1/2}$ = 61 days) and ^{97m}Tc ($t_{1/2}$ = 91 days). These separated isotopes were shown to be chemically distinct from the known elements between zirconium and ruthenium and similar to rhenium.

The fission of actinides provides the current route to technetium isotopes. The chemical investigations of technetium are strongly coupled to radiopharmaceuticals and the nuclear fuel cycle. For radiopharmaceuticals, ^{99m}Tc is the acknowledged workhorse of diagnostic nuclear medicine. The isotope ^{99m}Tc, with a half-life of 6.01 h, is obtained from ^{99}Mo. ^{99}Mo is a primary fission product of ^{235}U. The β decay of ^{99}Mo ($t_{1/2}$ = 66 h) principally populates the nuclear excited state of technetium, yielding ^{99m}Tc. Radiopharmaceutical generators of ^{99m}Tc exploit the chemical differences between molybdenum and technetium. The generator columns retain molybdenum as molybdate, $[^{99}MoO_4]^{2-}$, while ^{99m}Tc produced through β decay elutes, in a saline solution, as pertechnetate, $[^{99m}TcO_4]^-$. Once in solution the oxidation state of ^{99m}Tc is manipulated in the presence of ligands and chemical reducing agents to form a desired complex, typically the 5+ or 1+ oxidation states.

The most readily available technetium isotope for chemistry studies is ^{99}Tc ($t_{1/2}$ = 2.12 × 10^5 years). This isotope has a fission yield (via ^{99}Mo from ^{235}U) of nearly 6%, which is sufficiently high to produce weighable quantities. In a typical light water nuclear reactor, ^{99}Tc production is around 2 g/day for every 100 MW of thermal energy. This high production rate and long half-life make technetium an element of concern in the nuclear fuel cycle, particularly in separations and waste forms. Because of its high fission production rate, the amount of technetium on Earth may ultimately exceed that of rhenium, its heavier congener. Despite its important role in radiopharmaceuticals and the nuclear fuel cycle, the fundamental chemistry of technetium is not as well developed as that of the neighboring transition metals. Chemical investigations of technetium provide a unique opportunity to expand both basic scientific knowledge and useful data for applications.

The isotope ^{99}Tc is sufficiently persistent to use in milligram quantities in the laboratory. It is available commercially in the form of ammonium pertechnetate, NH$_4$[TcO$_4$], which is the

starting material for all other technetium compounds, including the metal. The latter has a high melting point at 2413 K, similar to molybdenum and ruthenium. Technetium has a range of oxidation states, from 7+ to 1−, and its chemistry has considerable similarities to rhenium; e.g., it has extensive pentavalent chemistry. Both technetium and rhenium form metal−metal multiple bonds, a characteristic that is absent with manganese. All elements in group 7 form $M^{VII}O_4^-$ anions in aqueous solution. The oxidizing power of these species and the standard reduction potential of the MO_4^-/MO_2 and MO_4^-/M couples follow the order Mn ≫ Tc > Re. However, the reduction potential of the TcO_2/Tc couple is higher than the one reported for manganese and rhenium.[2] Currently, two oxides of technetium have been unambiguously identified, TcO_2 and Tc_2O_7. Technetium dioxide sublimes in vacuum at 1300 K and disproportionates to technetium metal and Tc_2O_7 above 1400 K.[3,4] In contrast, the *melting point* of Tc_2O_7 is a mere 392.5 K.[5] The influence of the technetium oxidation state on the volatility behavior manifests itself in both chemical synthesis and the nuclear fuel cycle.

The basic chemistry of technetium described above has important implications in the nuclear fuel cycle. The PUREX process, the main route for chemically treating used nuclear fuel worldwide, begins with dissolution of the uranium oxide fuel in nitric acid. Technetium is present as an insoluble metal phase together with molybdenum, ruthenium, rhodium, and palladium, as well as a solution pertechnetate species. The organic phase of the PUREX process contains ∼30% by weight of tributylphosphate (TBP), $(n\text{-}BuO)_3P{=}O$, in dodecane. Technetium can be extracted into the organic phase as the tributyphosphate adduct of $HTcO_4$ or as $UO_2(NO_3)(TcO_4)$-$(TBP)_2$.[6] The pertechnetic acid maximum extraction is reached at 0.6 M HNO_3. The extraction of technetium with uranium under modified PUREX conditions decreased the nitrate concentration, and the presence of acetohydroxamic acid (AHA) in the aqueous phase was examined as a potential new used nuclear fuel treatment route.[7] In this route, the extracted uranium and technetium are separated from the spent nuclear fuel and then backextracted into 0.01 M HNO_3. The pertechnetate is then separated from uranyl by anion exchange.[8]

In the fuel cycle, technetium volatility is a significant problem, one that necessitates methods to capture and treat off-gas species. At high nitric acid concentrations, volatile technetium species include Tc_2O_7 and $HTcO_4$. In glass waste formation, the volatility of technetium is also an issue, and the Tc^{VII} oxidation state has a much higher volatility than Tc^{IV}.[9] Understanding the technetium redox chemistry and speciation during the glass formation process can have profound impacts on the waste treatment process and is a current topic of investigation.[10] In uranium enrichment via gaseous diffusion of UF_6, any technetium present forms volatile TcF_6. TcF_6 tends to follow the light [235]U isotope during the enrichment process.

It is clear that technetium is intimately connected with nuclear processes and the nuclear fuel cycle. The location of technetium in the periodic table and the dearth of detailed studies on the element provide opportunities to advance basic scientific knowledge while addressing specific applications. It is apparent that the various redox chemistries and volatile nature of technetium species drive a number of fuel cycle concerns. The ability to understand and exploit fundamental technetium behavior can be used to improve the fuel cycle. This will be discussed by connecting molecular and solid-state technetium

chemistry. Gaps in fundamental knowledge will be demonstrated by examining technetium halide complexes. For solid phases, information on technetium alloys will also be presented. Solution-phase chemistry will be examined through separations, examining methods to utilize and exploit technetium redox chemistry. The discussion will demonstrate the rich chemistry of technetium that can be explored for utilization in the nuclear fuel cycle.

■ TECHNETIUM HALIDE CHEMISTRY

For many transition-metal elements, binary compounds help to define and demonstrate their fundamental properties. The formation of binary halide species is particularly instructive and permits intercomparisons of elemental properties. Technetium was notably lacking in these compounds, with only three species, TcF_6, TcF_5, and $TcCl_4$, identified prior to 2008. Since then, several new technetium binary chlorides and bromides have been prepared. These compounds, prepared in sealed tubes through the reactions of elements or by the flow of HX gas (X = Cl, Br) over preformed technetium starting compounds, can be divided into three distinct categories: those with molybdenum and ruthenium analogues, those with only rhenium analogues, and those with no neighboring element analogues.

Technetium tri- and tetrabromide have been prepared through stoichiometric reactions of the elements in sealed tubes heated to 400 °C.[11] The $TcBr_4$ and $TcBr_3$ products were analyzed by single-crystal X-ray diffraction (SC-XRD; Figure 1).
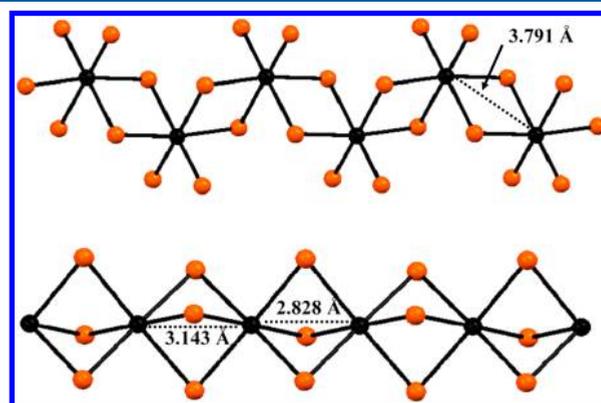

Figure 1. Infinite chains of $TcBr_3$ (bottom) and $TcBr_4$ (top) with Tc−Tc separations. Technetium and bromine atoms are in black and orange, respectively.

Technetium tetrabromide consists of infinite-ordered zigzag chains of edge-sharing $TcBr_6$ octahedra with Br⋯Br contact distances of 3.6913(4)−3.7767(4) Å. This distance is only slightly less than the sum of the van der Waals radii, i.e., 3.8 Å.[12] The Tc−Tc separation of 3.791 Å indicates the absence of metal−metal bonding. This compound is isomorphous with $TcCl_4$.[13] Unlike $TcBr_4$, $TcBr_3$ has similarities with its molybdenum and ruthenium analogues. In $TcBr_3$, the $TcBr_6$ octahedra are face-sharing and parallel to the *c* axis. A regular alternation of short [2.8283(4) Å] and long [3.1434(4) Å] Tc−Tc distances is observed, which is common for TiI_3-type structures.[14] This behavior is also observed for $MoBr_3$ and $RuBr_3$. For $TcBr_3$, the three bromine anions between the face-sharing $TcBr_6$ octahedra are pushed out from the center of the chain compared to the three bromine atoms along the long Tc⋯Tc distance.
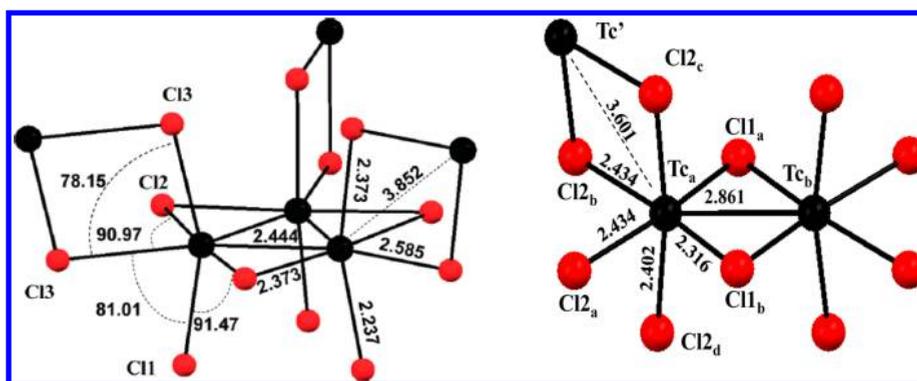
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Figure 2. Two polymorphs of technetium trichloride: α-TcCl$_3$ (left); β-TcCl$_3$ (right). Bond distances are in angstroms and angles in degrees. Technetium and chlorine atoms are in black and red, respectively.

The technetium chloride system also shows a variation of behavior compared to the neighboring second-row elements. The reaction routes for the synthesis of the tri- and dichloride technetium species include sealed tube reactions between the elements[15,16] and acid−base reactions involving HCl gas flowing over a quadruple metal−metal-bonded dimer.[17] Technetium trichloride exists in two forms. α-TcCl$_3$ (Figure 2) is formed from the reaction of Tc$_2$(O$_2$CCH$_3$)$_4$Cl$_2$ with HCl(g) at 300 °C.[17] The initial product is amorphous but sublimes in vacuo to give hexagonal-shaped crystals. Analysis of a hexagonal crystal by SC-XRD indicates α-TcCl$_3$ to be isostructural with Re$_3$Cl$_9$. The structure of α-TcCl$_3$ consists of triangular Tc$_3$Cl$_9$ units with C_{3v} symmetry, with each technetium atom connected to two technetium neighboring atoms and five chloride ligands. The Tc−Tc bond distance is 2.444(1) Å, indicative of a double bond, and is 0.045 Å shorter than the Re−Re distance in Re$_3$Cl$_9$. A second polymorph of technetium trichloride, β-TcCl$_3$, was produced from the reaction of the elements at 450 °C and characterized by SC-XRD.[15] β-TcCl$_3$ crystallizes with a distorted AlCl$_3$ structure type and is isostructural with α-MoCl$_3$.[18] The structure of β-TcCl$_3$ consists of infinite-ordered layers of edge-sharing TcCl$_6$ octahedra. The observed short Tc−Tc distance, 2.861(3) Å, is somewhat larger than the bond distance in α-TcCl$_3$ but still indicative of a strong metal−metal interaction. First-principles calculations show that both α-TcCl$_3$ and β-TcCl$_3$ exhibit a Tc=Tc double bond with σ and π character. Technetium dichloride is synthesized from a stoichiometric reaction of the elements in a sealed tube at 450 °C.

The composition and stoichiometry of TcCl$_2$ were initially determined by energy-dispersive X-ray (EDX) spectroscopy, and the divalent character of the technetium atom was confirmed by X-ray absorption near-edge structure spectroscopy.[19] Large TcCl$_2$ needles were produced by vapor-phase transport using AlCl$_3$ and examined by SC-XRD. Technetium dichloride exhibits a new structure type that consists of infinite chains of eclipsed Tc$_2$Cl$_8$ units oriented along the c axis (Figure 3). The eight chlorine atoms form a rectangular prism comprised of two square and four rectangular faces, with the Tc−Tc vector parallel to the square faces. Within each Tc$_2$Cl$_8$ unit, the Tc−Tc bond distance is 2.127(2) Å, indicative of multiple metal−metal bonding between the metal centers. First-principles calculations are consistent with the presence of a Tc≡Tc triple bond. The Tc−Tc vectors of adjacent units are parallel, and the distances between technetium atoms of the adjacent units [3.417(2) Å] preclude any metal−metal bonding between these units.
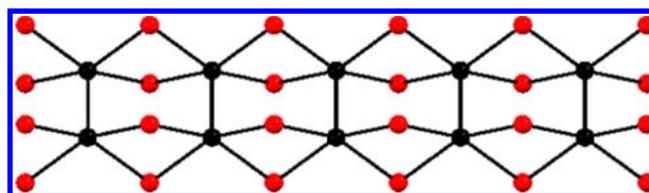

Figure 3. View of a TcCl$_2$ chain along the c axis. Technetium and chlorine atoms are in black and red, respectively.

An obvious trend in the binary technetium halides is a decrease in the Tc−Tc bond length with lower metal valence. In the technetium halides examined, the metal electronic configurations change from d^3 to d^5 as the oxidation state decreases from 4+ to 2+. In the d^3 technetium tetrahalides, the large Tc−Tc bond distances indicate no appreciable metal−metal interactions. For the d^4 technetium trihalides, a metal−metal interaction is observed. The metal−metal bond distance varies from 2.44 to 3.14 Å, depending on the halide and specific technetium−technetium interaction. The technetium−technetium double-bond interactions in the trihalides are supplanted by a triple Tc≡Tc bond in TcCl$_2$, with a bond distance of 2.127(2) Å. The latter is comparable to what we have found in a number of technetium(II) dimers.[20,21] This increase in technetium−technetium interaction can be utilized in fuel cycle chemistry, and the lower technetium oxidation states may have a role in improved separations and waste forms. Furthermore, the novel chemistry of technetium demonstrated with the halides can be used to develop compounds that provide advantages in fuel cycle chemistry.

■ WASTE FORMS

Durable waste forms for the fission products resulting from the processing of used nuclear fuel are needed for any advanced nuclear fuel cycle. An engineered metallic host phase for some fission products is potentially attractive because the efficient immobilization and disposal of fuel cladding or other metals remaining after electrochemical separation operations can easily be incorporated into a metal ingot. Undissolved solids, such as the epsilon phase (containing mainly metallic molybdenum, technetium, ruthenium, rhodium, and palladium), and cladding shards can remain in metallic form after fuel dissolution; these and other candidates for incorporation into a suitable metallic phase also include technetium. Because of volatilization of Tc^{VII} species, disproportionation of Tc^{IV} during glass formation, low mass loading of technetium in borosilicate glass types, and a high leaching rate of pertechnetate from these glass formers, a
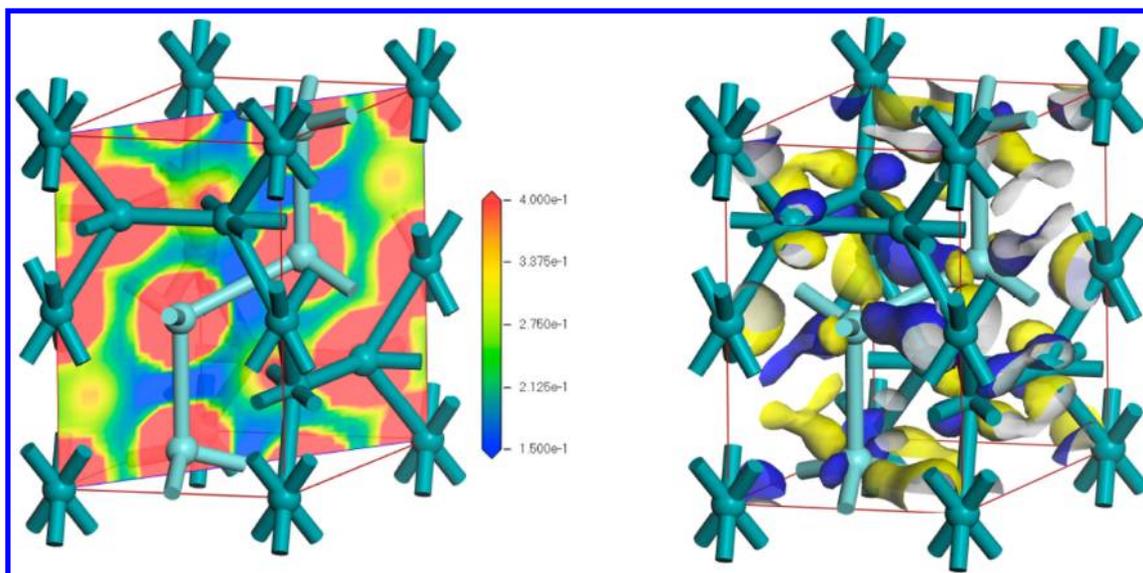
Figure 4. Tc_2Zr charge density (left) and highest occupied molecular orbital (right) calculations.

metallic phase to incorporate this pseudonoble metal may also be advantageous. For this reason, metallic forms of technetium have been investigated as potential waste forms.[22] These low-valent species should incorporate metal−metal interactions as exhibited in the technetium halide system, enhancing the stability of the product.

Zirconium is the main constituent of the cladding of the spent nuclear fuel from light water reactors. The development of technetium−zirconium alloys would enable the combination of two waste streams of the spent fuel reprocessing into a single waste form. The systematic evaluation of technetium−zirconium alloys provides a route to examine the influence of the relative technetium concentration on the material. Technetium−zirconium alloys of 6:1 and 2:1 atomic ratios were prepared and characterized by X-ray diffraction, microscopy, and first-principles calculations.[23] Two different intermetallic phases were found: Tc_6Zr and Tc_2Zr (Figure 4). The Tc_6Zr phase has variable compositions, with technetium-to-zirconium stoichiometries varying from 4.80 to 6.25, with an increase in the lattice parameter along the a axis with a decrease in technetium. The observed structural parameters were successfully modeled by first-principles calculations. The calculations indicate that valence and conduction bands near the Fermi level are composed primarily of 4d orbitals. For the Tc_2Zr species, the highest-lying valence band molecular orbitals are d−d σ bonds. These bonds connect the zirconium and technetium networks and stabilize the technetium framework. At higher technetium stoichiometries, only the technetium 4d orbitals meaningfully contribute to the valence band.

In the high technetium material Tc_6Zr, selective oxidation of zirconium was observed. Other studies on a 1:1 technetium-to-zirconium ratio presented similar results.[24] The 1:1 technetium-to-zirconium sample was found to contain both TcZr and Tc_2Zr phases. The oxidation stability was investigated by treating the material at 1500 °C for 60 h under an Ar/O_2 atmosphere. X-ray diffraction revealed ZrO_2 and technetium metal as the resultant species, with phase separation due to oxidation. The general trend observed in these studies is that higher levels of technetium tend to stabilize alloys. This behavior agrees with the observations on technetium interactions at lower valence, as shown by the halides. For

technetium, these results indicate that the metal itself, encased in a suitable storage container, may be an extremely stable waste form.

■ SEPARATIONS

In proposed fuel cycle separation schemes involving technetium, conversion to a number of different species is proposed. For a metal waste form, this may include evaporation to dryness, precipitation of an insoluble pertechnetate salt, and reduction to the metal by thermal treatment under reducing atmospheres. Advantages due to step minimization can be achieved by exploiting the fundamental properties of technetium. An obvious benefit would be to reduce the technetium solution species to the lowest oxidation state during separations. In this context, the aqueous reduction of pertechnetate by borohydride in the presence of acetic acid has been considered[25,26] with the formation of an uncharacterized precipitate.[27] The precipitate was examined in other work by microscopy, EDX, and extended X-ray absorption fine structure (EXAFS) spectroscopy.[28] Results were consistent with the presence of trivalent and tetravalent technetium within the compound.

Technetium can be reduced in solution for separations. For example, ammonium pertechnetate in solution is reduced with a mixture of 4 mol equiv of sodium borohydride and sodium hydroxide. The solution remains translucent but slowly develops a pink hue indicative of a reduction to Tc^V or Tc^{VI} species. Upon the addition of acetic acid, gas evolution occurs along with precipitation of a dark solid, which was collected and characterized. UV−visible spectroscopy of the supernate indicates the formation of a Tc^{IV} polymer from the reaction with borohydride. The EXAFS measurements of the dark precipitate are consistent with the presence of the $[Tc(\mu\text{-}O)_2Tc]^{3+}$ fragment within the compound. Other studies on technetium under fuel cycle conditions show the reduction of pertechnetate by acetohydroxamic acid (AHA).[29] The overall proposed route for this reaction is the formation of an octahedral Tc^{VII} complex that interacts with AHA and eventually results in a Tc^V complex that is reductively nitrosylated by the coordinated AHA ligand to Tc^{II}. The compound has been analyzed by EXAFS spectroscopy, and

results are consistent with the stochiometry of $[Tc^{II}(NO)(AHA)_2(H_2O)]^+$ (Figure 5). This Tc^{II} complex is highly soluble
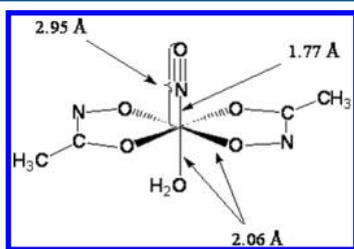
Figure 5. Structure of $[Tc^{II}(NO)(AHA)_2(H_2O)]^+$ determined by EXAFS spectroscopy.

in water, extremely hydrophilic, and not extracted by TBP in dodecane. Following the discovery of $[Tc^{II}(NO)(AHA)_2(H_2O)]^+$, a process for the separation of uranium from technetium using AHA was developed.[30]

The technetium reduction studies described above do not result in the formation of the metallic state, a phase with obvious advantages for alloy waste forms. However, the ability to reduce technetium in solution can eliminate some processing steps and provide a more manageable process stream. The concurrent reduction of technetium during separation can reduce or eliminate the presence of Tc^{VII} species. For nuclear waste processing, this can diminish technetium volatility, simplifying separations. Control of the technetium solution oxidation state can also provide a means to concentrate this fission product in targeted solution streams. The varied oxidation states of technetium, and the methods to achieve selected states in solution, can be used to selectively isolate this element during separations. Finally, the formation of reduced species can provide more suitable precursors for the final reduction to metal and increase options for waste form synthesis. Control of the oxidation state can also be used to directly achieve the formation of technetium metal; e.g., electrochemical reduction of technetium to the metal has been demonstrated in acidic environments using gold foil cathodes.[31] This work demonstrates the exploitation of technetium chemistry for a recovery process that results in the direct formation of technetium metal. The use of technetium's rich redox chemistry is currently underutilized in separations. Exploiting this property may be a key to easing fuel cycle management concerns while exploiting and utilizing the fundamental chemical properties of technetium.

CONCLUSION

Understanding and manipulating the chemistry of technetium in the fuel cycle has obvious advantages. Because of its high fission yield and long half-life, ^{99}Tc is an isotope of concern that requires treatment. The range of technetium oxidation states can make the chemistry difficult to predict and control. High-oxidation-state species can form volatile compounds that are particularly difficult in aspects of the nuclear fuel cycle.

Utilizing coordination chemistry and speciation provides valuable insight into technetium chemistry, which, in turn, has benefits in the nuclear fuel cycle. The study of simple halide compounds demonstrates the varied, interesting, and some-times unanticipated nature of technetium. The overall trends clearly demonstrate increasing technetium–technetium inter-actions with decreasing oxidation state. This property can be exploited in the fuel cycle for both waste forms and in

separations. In certain waste forms, the technetium metal is shown to be resistant to oxidation. In particular, the formation of metallic waste forms with high concentrations of technetium should improve corrosion resistance and therefore is a robust material for disposal. In separations, controlling technetium reduction can be exploited. The formation of tri- and tetravalent species can lead to precipitation; a property that may be problematic or utilized as an advantage if controlled. Examining and understanding the reduction mechanisms will ultimately lead to preferred routes for the formation of targeted species, including technetium metal. The synthesis of these technetium compounds opens up new possibilities for the nuclear fuel cycle.

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Notes
The authors declare no competing financial interest.

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