# Technetium Management for Hanford Tank Waste Processing and Disposition – 16399

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## ABSTRACT

Technetium-99 (Tc) generated from the fission of $^{235}$U and $^{239}$Pu in high yields is one of the most difficult contaminants to be addressed at the U.S. Department of Energy (DOE) Hanford Site. Among radioactive constituents in the tank waste, Tc presents a unique challenge in that it is radiotoxic ($\beta$ = 292 keV), has a long half-life ($T_{1/2}$ = 2.11×10$^5$ y), and exists predominantly in the liquid fraction of the alkaline tank waste, generally in the anionic form of pertechnetate $TcO_4^-$, which is highly volatile at low-activity waste vitrification melter temperatures and mobile in the subsurface environment. This makes immobilization of Tc into high-durability waste forms a critical technical challenge for nuclear waste management. The complex behavior of Tc under storage, treatment, and immobilization conditions significantly affects its management options. The overall objective of the Technetium Management program is to provide the DOE Office of Environmental Management with practical solutions to Tc needs encountered in the processing of Hanford tank waste.

To reduce the technical uncertainty associated with the long-term environmental impact of Tc, a systems-based approach is needed to address Tc management needs by evaluating and developing science and engineering options for treatment, immobilization, and disposition of Tc contained in Hanford tank wastes. This paper describes major elements of Technetium Management program, including:

- Identifying the chemical forms of Tc in tank waste through analytical speciation of low-valent Tc(I) species in alkaline solutions.
- Performing proof-of-concept demonstration for detection of low-valent Tc(I) by fluorescence spectroscopy.
- Identifying alternative non-glass Tc immobilization methods.

## INTRODUCTION

In the Hanford Tank Waste Treatment and Immobilization Plant (WTP) baseline, the majority of the Tc is fed to the low-activity waste (LAW) melter (Fig 1). The current WTP Tc management strategy centers around the capture of Tc in LAW glass and the recycle of Tc present in the submerged bed scrubber (SBS) condensate streams requiring a second LAW vitrification facility. Only about 2% of the total Tc will be immobilized in high-level waste (HLW) glass. In the melter, only a fraction of the Tc fed is incorporated into the LAW glass product (ca. 50%), while the balance is vented to the system off-gas and captured by the SBS and the wet electrostatic precipitator (WESP). The Tc captured by these two processes is supposed to be recycled to the WTP pretreatment facility, where it is incorporated into future LAW batches. Through

this recycle process, it is anticipated that approximately 97% of the Tc can be incorporated into LAW glass.

Besides challenging the capacity of the WTP LAW facility, this Tc recycle process encompasses several inherent challenges and uncertainties. The first of these is the requirement for the pretreatment facility to handle Tc recycled from the LAW facility. However, if the pretreatment facility is unavailable, an alternative path would be required for dispositioning the Tc captured from the LAW off-gas.
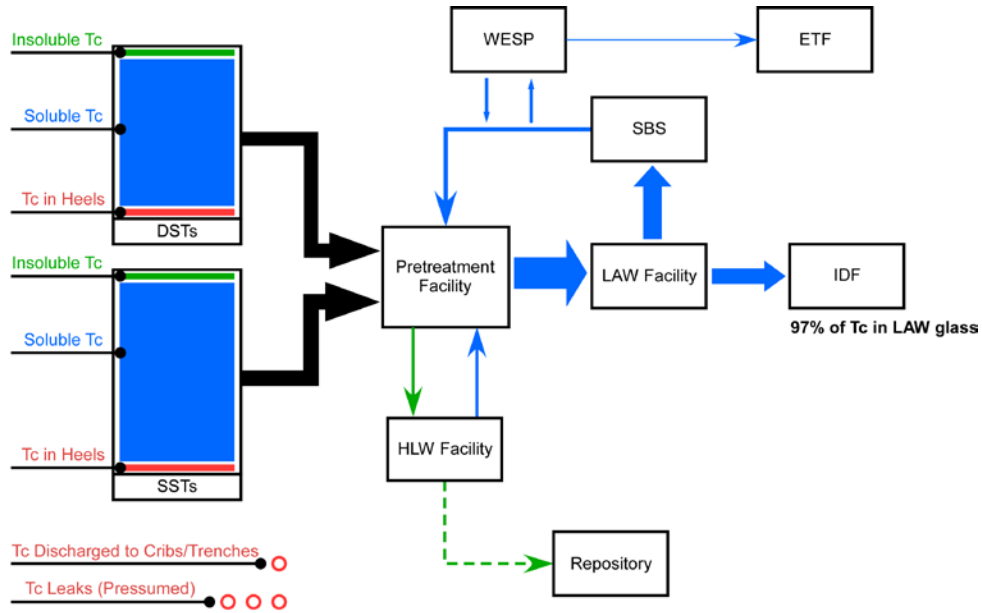


Fig. 1. Technetium Flowsheet: Baseline Case.

The second uncertainty is the impact of Tc on any proposed low-temperature supplemental treatment. The impact of Tc on the performance of any low-temperature waste form would need to be assessed. In addition, a Tc removal step might be required to enable acceptable use of a low-temperature waste form.

Finally, the impact of the recycled material on LAW melter performance needs to be understood. The potential to improve LAW melter performance by routing the overheads for alternative disposition may provide a significant benefit to the WTP. There remain several significant gaps in the understanding and modeling the fate of Tc. The first such gap is associated with the uncertainties of Tc speciation in waste tanks. A significant fraction of the Tc is present in tank waste as a non-pertechnetate species that has not been identified and to date cannot be effectively separated from the wastes. It remains uncertain if alkaline tank conditions support the formation of proposed low-valent Tc species, i.e. Tc(I) carbonyl compounds. The presence of this species affects both the ability to separate Tc from LAW and the performance of any alternative low-temperature waste forms.

A second gap is associated with effective removal of Tc from various process streams. While there has been significant work on the removal of the pertechnetate ion from solution, there has been limited work in the removal of the non-pertechnetate species. Only limited information exists regarding separation of Tc from off-gas streams.

A third gap is associated with Tc incorporation into various waste forms. For example, the retention of Tc in glass varies significantly due to a broad range of waste compositions. It has been shown that the Tc retention can be significantly improved with some additives, such as Fe(II) oxalate, $ZrO_2$, or sugar [1]. In addition, Tc retention in low-temperature waste forms needs to be assessed.

A fourth gap is associated with the repository performance of any Tc dispositioned in a near-surface environment. The current WTP baseline calls for disposition of Tc on the Hanford Site in a near-surface repository. The impact of this disposition on the total Hanford Tc hazard should be assessed.

## APPROACH

### Technetium Distribution and Speciation

The successful management of Tc requires understanding of the Tc speciation in each waste stream, the development of effective separation techniques to remove Tc species from the respective waste streams, and the development of approved waste forms for immobilizing Tc for permanent disposal. Technetium is present in some underground waste tanks with a variety of waste constituents. Although the pertechnetate anion, $TcO_4^-$, is expected to be the predominant species in the supernatant phases of most waste mixtures, a significant quantity of soluble non-pertechnetate Tc exists in tank waste. There is also evidence of soluble, reduced-technetium species that have been identified as neutral Tc(IV)gluconate and Tc(IV)glyoxylate and the cationic Tc(I)carbonyl complex.

A basic understanding of Tc thermodynamics and solution speciation is necessary to develop of enhanced technologies to separate Tc from complex waste streams and to predict the migration of Tc in the subsurface. While a great deal is known about the solution phase species of Tc(VII), much less is known about the speciation of reduced forms of Tc, including thermodynamic properties under variable ionic strengths and/or in complexing media as found in chemically extreme environments, such as in the presence of high salt or base, and where radiolytic processes dominate. Additionally, little is known about the impact of chelating agents or complexation reactions for reduced Tc species or the mechanisms that trigger and stabilize the formation of reduced Tc aggregates and colloidal species. The formation of reduced Tc species is complicated by Tc's multivalent nature, which makes understanding details of its redox behavior critical for predictive models. This is especially important under the range of chemical conditions that typify tank waste or separations processing. Therefore, a major research challenge is to determine the aqueous speciation of Tc under extreme conditions such as in high-level nuclear waste tanks. Research into Tc speciation will provide the scientific basis for advanced separations chemistry and developing appropriate waste forms.

The Tc speciation component of the Technetium Management program at Pacific Northwest National Laboratory (PNNL) consists of several elements designed to close the knowledge gap regarding Tc thermodynamics, redox, and chemical behavior. Most of the Tc at the Hanford Site is soluble Tc in the supernatant fraction of both single- and double-shell tanks. In strongly alkaline environments, Tc exists as $TcO_4^-$ (Fig. 2a) (oxidation state +7) and in the reduced forms (oxidation state < +7) collectively known as non-$TcO_4^-$ species. A significant (2% to 25%) fraction of the Tc in tank waste may be present as a non-$TcO_4^-$ species that has not been identified and, based on experimentation to date, cannot be effectively separated from the wastes. It remains uncertain whether alkaline tank conditions even support the formation of proposed low-valent Tc species, i.e., Tc(I) carbonyl compounds (Fig. 2b). There is no definitive information on the origin of the non-$TcO_4^-$ species, nor is there a comprehensive description of their composition and behavior. The objective of this work is to investigate aspects of the nature and chemistry of the non-$TcO_4^-$ species derived from the $Tc(CO)_3^+$ coordination center, specifically under the conditions typical for the alkaline liquid fraction of the tank waste, and to gain better understanding and control over their redox behavior. This includes exploratory tests on Tc behavior in tank-like environments, where conditions for $TcO_4^-$ reduction seem favorable and elucidation of the mechanistic pathways for the formation of non-$TcO_4^-$ species.
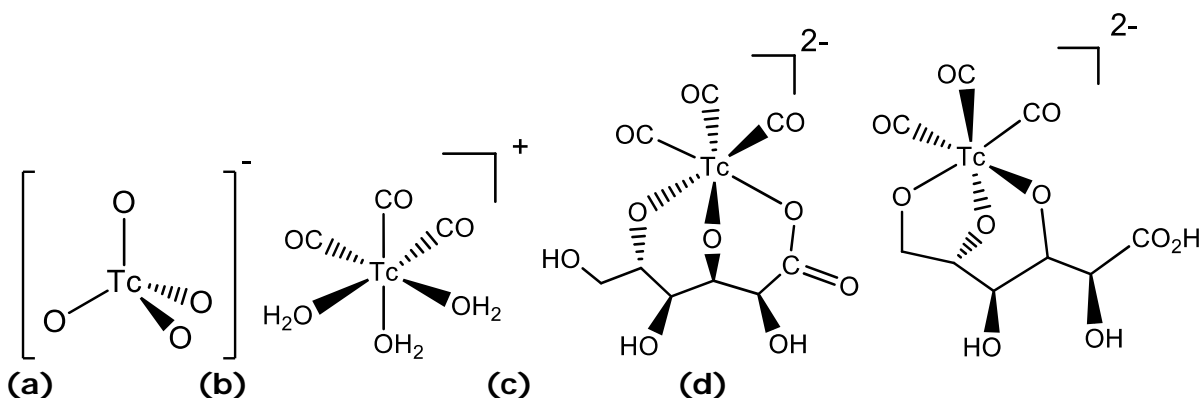


Fig 2. Examples of Tc Species in Soluble Fraction of Tank Waste, including Structures of (a) Pertechnetate Anion; (b) Tri-carbonyl-tris-aqua-technetium(I) Cation; (c) Tri-carbonyl-gluconate-technetium(I) Anion, Structure Proposed by Lukens et al. [2]; (d) Tri-carbonyl-gluconate-technetium(I) Anion, Alternative Structure.

The main objectives of this task are 1) characterization of the composition, chemical properties, and stability of the proposed non-pertechnetate species in greater detail; 2) gaining a better understanding and control over their redox behavior (changes between species of differing Tc oxidation states); and 3) evaluation of feasibility of separation of total Tc from LAW by either designing methods for direct removal of non-pertechnetate Tc or oxidizing it to Tc(VII) and subsequent removal as pertechnetate by the established methods.

The first step toward understanding non-pertechnetate Tc behavior and design of treatment strategies is to gain knowledge regarding its redox speciation and identification of boundary conditions that enable the formation of non-pertechnetate Tc species (those in the low oxidation states). The spectroscopic library for the identification of non-pertechnetate Tc in actual tank wastes needs to be developed. Another goal of this work is to investigate inter-conversion among soluble $TcO_4^-$ and non-$TcO_4^-$ species as well as among insoluble and soluble Tc species, including exploratory tests on technetium behavior in tank-like environments, where conditions for pertechnetate reduction seem favorable, and to elucidate the mechanistic pathways for the formation of non-$TcO_4^-$ species. Once the identities of the non-$TcO_4^-$ species and mechanisms of their generation are understood, new separation methods for their removal by either direct separation or oxidation to $TcO_4^-$ can be designed. Understanding how the oxidation state of Tc may change as waste streams differ during processing is important in developing effective separation and immobilization technologies for Tc.

The results obtained to date are briefly summarized below [3-5].

A synthetic procedure for preparation of Tc(I) $[Tc(CO)_3]^+$ species was optimized. The preparation of $[Et_4N]_2[(CO)_3TcCl_3]$, an insoluble solid that in mildly acidic solution forms the target starting compound $[(CO)_3Tc(H_2O)_3]^+$ in an overall 75% yield, was achieved based on two-step reduction of ammonium pertechnetate. The reaction product was characterized by several techniques, including Tc-99 nuclear magnetic resonance (NMR), infrared and ultraviolet-visible spectroscopies, and electrospray ionization mass spectrometry.

Oxidative stability and hydrolytic speciation of $[Tc(CO)_3(H_2O)_3]^+$ in a pseudo-Hanford tank supernatant simulant solution at variable nitrate and hydroxide concentrations was investigated. The method used for these studies was primarily Tc-99 NMR spectroscopy. It was demonstrated that in the solutions with the high hydroxide concentrations, the $[Tc(CO)_3]^+$ species undergo fast oxidative decomposition, most likely due to the hydrolytic destruction of the Tc-CO backbone via $OH^-$ nucleophilic attack at the carbonyl carbon. The presence of the high salt and relatively low $OH^-$ concentrations in LAW (typical for the majority of tanks) increases the stability of non-pertechnetate species. Increasing hydroxide concentration promotes decomposition of the $[Tc(CO)_3]^+$ species. Interestingly, the oxidative stability of the hydrolyzed $[Tc(CO)_3(OH)(H_2O)_2]$ species in the supernatant simulants containing 0.42, 0.83, or 1.47 M $OH^-$ was greater than that in the 5 M $NaNO_3$ solutions containing corresponding NaOH concentrations. In this study, under optimum conditions (0 to 0.01 M NaOH and 5 M sodium nitrate), almost 3 months have gone by either without any detectable pertechnetate formation or only about 10% conversion to pertechnetate, a half-life for reoxidation under conditions compatible with those found in actual Hanford tank sludge. This observation implies that if the conditions required for formation of the Tc(I)-tricarbonyl compounds exist in the tank, the organic complexants are not required for the product to be stable in conditions associated with Hanford tank supernatants. Alternatively, instead of Tc(I)-tricarbonyl/complexant species being required, *the Tc(I)-tricarbonyl hydrolysis products of general*

*composition $[Tc(CO)_3(OH)_n(H_2O)_m]^{1-n}$ that are anticipated to exist in the alkaline waste may be sufficient.*

Formation and oxidative stability of $[Tc(CO)_3]^+$/gluconate complex was tested in the pseudo-Hanford tank supernatant simulant solutions at variable hydroxide concentration. The oxidation rate of the $[Tc(CO)_3]^+$/gluconate complex was considerably slower in the supernatant simulant than in the simple 5 M $NaNO_3$/0.5 M NaOH/0.5 M NaGluconate solution.

These results indicate that a carbonyl complex is a viable candidate for the source of non-pertechnetate in tank waste. As indicated, testing has identified a range of conditions under which a significant portion of the carbonyl complex is stable for extended periods. Preliminary studies have shown a viable route for the formation of this complex under tank waste conditions. Also, since the range of concentration in tank waste varies from less than 0.1% to greater than 50%, the rates of production and destruction under these varying conditions obviously vary dramatically, and as such, the balance of these two reactions will be highly dependent upon tank waste chemistry.

A proof-of-principle demonstration corroborating the mechanism and feasibility of $[Tc(CO)_3]^+$ formation from pertechnetate using CO/$H_2$ reductant in the presence of an organic chelator and catalytic noble metals in the tank waste simulant was performed. The simulant used was based on the previously used Pretreatment Engineering Platform simulant formulation, albeit with altered free hydroxide concentrations and with the addition of some noble metals (simulating fission products) to catalyze any needed reduction of Tc(VII) by hydrogen and gluconate as a reductant/complexant. Reaction conditions were approximately 1300 psi atmosphere, at 80°C for about 12 days. The bulk of the pertechnetate was reduced following this treatment. Generated non-pertechnetate species included derivatives of Tc(VI), Tc(IV), and the Tc(I)-tricarbonyl/gluconate compounds as observed by Tc-99 electron paramagnetic resonance (EPR) and NMR spectroscopies. The same Tc(I) product can be prepared independently by the reaction of $[Tc(CO)_3]^+$ with gluconate in water, sodium nitrate, or supernatant simulant solutions. In short, this proof-of-principle test supports the concept of alkaline-soluble, low-valent Tc being formed by pertechnetate reduction under conditions consistent with those found in Hanford tank supernatants, albeit at intentionally high concentrations of carbon monoxide in this first proof-of-principle test. Redox stability of the generated non-pertechnetate species in the reacted simulant has been monitored for 1 year and currently ongoing. The results are briefly summarized in the table below (Table 1). Note remarkable stability of Tc(VI) and Tc(I) as $Tc(CO)_3(gluconate)^{n+}$ in the reacted simulant.

TABLE 1. Monitoring of Tc Oxidation State in Solutions Generated by the Reduction of $TcO_4^-$ in the $CO/H_2$-reacted Pseudo-Hanford Tank Supernatant Simulant.

| Reaction Medium | September 2014 Observations | September 2015 Observations |
|---|---|---|
| Simulant + 0.1M gluconate | Pink solution, no precipitate Tc-99 EPR: Tc(VI) in solution Tc-99 NMR: Solution contains 40% of initial $TcO_4^-$, no Tc(I) is found 60% is reduced to Tc(VI) non-$TcO_4$ | Pink solution, no precipitate Tc-99 EPR: Tc(VI) in solution Tc-99 NMR: Solution contains 50% of initial $TcO_4^-$ **50% remains as Tc(VI) non-$TcO_4$** |
| Simulant + catalytic metals | Brown solution + black precipitate Tc-99 EPR: Tc(IV) in both solution and precipitate Tc-99 NMR: no $TcO_4^-$ in solution (complete reduction), Tc(I) in solution as $Tc(CO)_3(H_2O)_2(OH)$ | Brown solution + black precipitate Tc-99 EPR: Tc(IV) in precipitate Tc-99 NMR: ~60% $TcO_4^-$ is regenerated in solution, Tc(I) decomposed |
| Simulant + 0.1M gluconate + catalytic metals | Brown solution + black precipitate Tc-99 EPR: Tc(VI) in solution, Tc(IV) in precipitate Tc-99 NMR: no $TcO_4^-$ in solution (complete reduction), Tc(I) in solution as $Tc(CO)_3(gluconate)^{n+}$ | Brown solution + black precipitate Tc-99 EPR: Tc(VI) in solution, Tc(IV) in precipitate Tc-99 NMR: ~40% regeneration of $TcO_4^-$ in solution **~25% of Tc(I) present in solution as $Tc(CO)_3(gluconate)^{n+}$** |

In conclusion, considerable achievements were made toward verifying that the Tc(I)-tricarbonyl species is a viable candidate for the source of alkaline-soluble, non-pertechnetate Tc in the Hanford tank supernatants. This work confirmed that the Tc species based on the $[Tc(CO)_3]^+$ center can be obtained by the laboratory synthetic route and that a potential route exists for their production in the alkaline tank wastes. These non-pertechnetate species are sufficiently stable under the conditions associated with Hanford tank supernatants. However, considerable work remains, specifically to achieve control over Tc redox behavior in the alkaline media, and to develop methods for the separation of non-pertechnetate species from LAW either by their conversion to pertechnetate or direct removal.

**Non-pertechnetate Sensor Development**

Development of a sensor to quantify the non-$TcO_4^-$ fraction will significantly improve the viability of methods to remediate non-pertechnetate species. This work will examine key features in the development of a non-pertechnetate sensor, including choice of electrode, choice of film, and choice of an optimized complexing agent,

needed to develop a spectroelectrochemical sensor to detect the $[Tc(L)_n(CO)_3]^+$ class of compounds.

The sensor's operation is based on the assumption that the non-pertechnetate (n-Tc) species of interest is of the structure $[Tc(L)_n(CO)_3]^+$. A recent review of all available studies found that the n-Tc species have not been definitively identified [6]. However, based on all investigations and detailed measurements, n-Tc species in the Hanford DST supernates are tentatively identified as Tc(I) carbonyl complexes. It is speculated that these are derived from either $Tc(CO)_3^+$ or $Tc(CO)_2(NO)^{2+}$ precursor molecules that may lead to final species such as $Tc(CO)_3(gluconate)^{2-}$ as a result of the radiolytic decomposition of organics and nitrite in those double-shell tanks that contain relatively high concentrations of dissolved organic carbon.

A proof of principle for the chemistry behind a fluorescence-based spectral/electrochemical sensor has been demonstrated with rhenium (Re) and Tc – tricarbonyl compounds [7]. We propose to examine other key features, including choice of electrode, choice of film, and choice of an optimized complexing agent, needed to develop a spectroelectrochemical sensor to detect the $[Tc(CO)_3]^+$ class of compounds. Work will be performed not only with Tc, but with Re analogs as needed.

This sensor concept combines electrochemistry, optical spectroscopy, and selective partitioning into a single device. Our group, a collaboration between PNNL and the University of Cincinnati, has been developing spectroelectrochemical sensors applicable to Hanford waste for many years. The sensor in its simplest form consists of an optically transparent electrode that is coated with a chemically selective film. The sensor functions according to the following steps: 1) pre-concentration of the Tc analyte by the chemically selective film on the electrode, 2) reaction of the target Tc complex with ligands immobilized within the selective film, 3) electrochemical oxidation and reduction of the fluorescent Tc-complex, and 4) detection of electrochemically modulated fluorescent complex using optical spectroscopy.

In one approach, the bipyridyl – Tc(I)-tricarbonyl complexation is a solution phase reaction followed by transfer of the complex into the polymer film followed by spectroelectrochemical detection; Fig. 3 summarizes these key aspects of this approach. In a second approach, the Tc(I)-tricarbonyl complex is introduced into the sensor film that already contains the bipyridyl ligands; the ligand binding then is performed within the polymer film followed by spectroelectrochemical detection. In both approaches, the tank waste sample will be added to a preconditioning solution that is tailored to do several things: 1) in the first approach, it offers the ligand in a high enough concentration that allows binding to the Tc(I) metal center, 2) by a high dilution factor, it reduces the effect of other competing ligands that may be present within the waste matrix, and 3) it adjusts the pH and ionic strength of the final solution to a predetermined concentration by effect of dilution of the waste sample in the preconditioning solution. While the composition of the "preconditioning" solution has not been determined, this basic method has worked well in our past work where we measured ferrocyanide in actual Hanford waste using our polymer-coated spectroelectrochemical sensor.
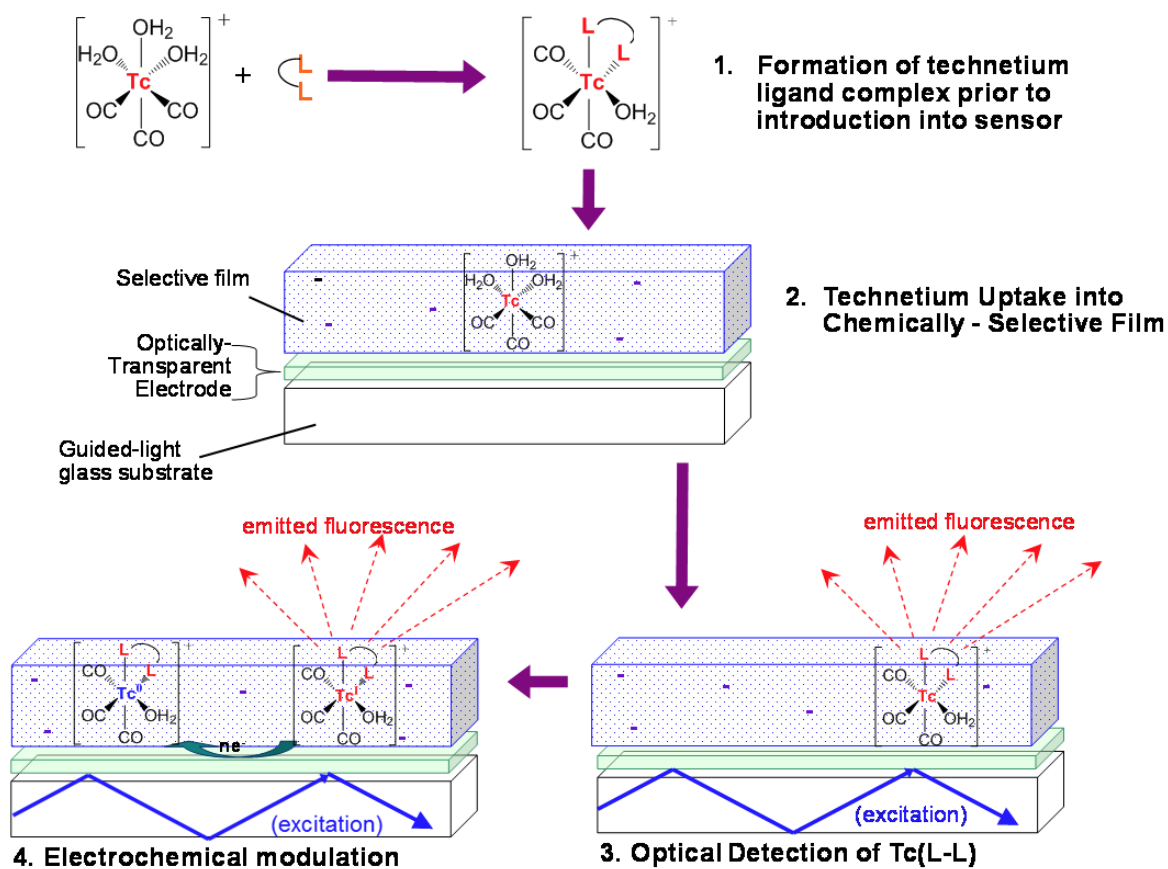
Fig. 3. Concept for Detection of the Tc(I)-tricarbonyl Species

Key outcomes of this work to date are [7]:

1.  Demonstrated the photoluminescence of a series of Re(I)-carbonyl complexes, which are direct analogs to the Tc(I)-carbonyl target complexes. These complexes are $[Re(L \frown L)(CO)_3(H_2O)]^+$ (where $L \frown L$ is a bidentate ligand = bpy, dbbpy, dmeobpy, dmbpy, phen, or bpym). The detection limit for $[Re(bpy)(CO)_3(H_2O)]^+$ was determined to be 9 Å~ 10-7 M. Synthesized the Tc(I)-carbonyl species $[Tc(bpy)(CO)_3(H_2O)]^+$ and $[Tc(phen)(CO)_3(H_2O)]^+$, and by comparison with the spectroscopic emission properties of the Re analogs, $[Re(bpy)(CO)_3(H_2O)]^+$ and $[Re(phen)(CO)_3(H_2O)]^+$, confirmed the formation of these target complexes. To achieve the desired detection limits, fluorescent molecules are needed because fluorescence detection methods are many orders of magnitude more sensitive than other optical techniques. The fluorescence measurement of $[Tc(bpy)(CO)_3(H_2O)]^+$ and $[Tc(phen)(CO)_3(H_2O)]^+$ was performed, which demonstrates the ability to use these molecules as target analytes within the proposed fluorescence-based spectroelectrochemical sensor.

2.  Demonstrated the reversible electrochemistry for the two classes of Re(I) carbonyl complexes, $[Re(L \frown L)(CO)_3(H_2O)]^+$ and $Re(L \frown L)(CO)_3Cl$, (where $L \frown L$ is a bidentate ligand = bpy, dbbpy, dmeobpy, dmbpy, phen, or bpym). To achieve the required

selectivity, reversible electrochemistry of target analyte complex is desired. Changing the oxidation state of the complex through reversible electrochemistry allows for the creation and quenching of the fluorescence signal from the sample. This changing signal, which is triggered through the electrochemical sensor, creates a modulated (on/off) signal within the sensor iv platform. The ability to monitor a changing (modulated) signal of the Tc analyte complex allows this signal to be distinguished from a constant fluorescence signal originating from a potential interfering species.

3. Demonstrated the spectroelectrochemical detection of several complexes, showing the reversible electrochemical behavior is exhibited in the modulated photoluminescence of the optical signal. By combining the reversible electrochemical reduction/oxidation of the target analyte complex while measuring the fluorescence signal spectroscopically, it is possible to monitor a changing (modulated) signal from the Tc analyte complex. The ability to perform combined spectroscopy and electrochemistry was demonstrated using fluorescence modulation of the $[Re(bpy)(CO)_3(H_2O)]Br$ in a spectroelectrochemical cell.

4. Evaluated several polymer films and thicknesses for the application of selective uptake of Tc target complexes for use in the sensor apparatus. The selective uptake of $[Re(dmeobpy)(CO)_3(H_2O)]^+$ and other model complexes into polymer films was successfully performed during spectroelectrochemical sensing, demonstrating the spectroelectrochemical sensor prototype. To increase sensitivity and selectivity, we are evaluating several polymer films for the application of selective uptake of Tc target complexes for use in the sensor apparatus. The selective uptake of $[Re(dmeobpy)(CO)_3(H_2O)]^+$ and other model complexes into polymer films was successfully performed during spectroelectrochemical sensing, demonstrating the spectroelectrochemical sensor prototype, including the selective partitioning film. The effect of varying the selective film thickness within the sensor was evaluated by using a series of ITO-electrodes, coated with variable thickness of Nafion® material. Compared to an uncoated electrode, the increase in electrochemical signal using a model compound for a 25-nm, 70-nm, and 200-nm Nafion coating was 10-, 70-, and 100-fold, respectively.

In summary, proof-of-principle work was successfully demonstrated for a prototype spectroelectrochemical sensor.

**Non-glass Waste Forms for Technetium Immobilization**

The objective of this task is to develop a waste form specifically for immobilization and disposal of Tc. Current Tc disposition pathways typically involve recycling any Tc captured in off-gas and WESP/SBS flush waters to the LAW treatment processes or sending it to HLW vitrification for immobilization in a glass waste form. Alternative

waste forms that can be used with Tc separated from the tank wastes or WTP process streams are being considered for immobilization of Tc for storage and final disposal.

Previous work included testing to evaluate the use of "getter" materials to improve the retention of Tc in cementitious waste forms. The results of the batch sorption tests conducted in deionized water and a LAW waste simulant are documented by Neeway et al. [8]. The current focus of this task is to identify waste forms for Tc separated from either LAW or melter off-gas. This task first evaluates the compositions and volumes of the SuperLig® 639 eluent and off-gas condensate. Based on this evaluation, the strategies for Tc management of these streams, including operations required for its immobilization in the Tc-specific waste form, will be proposed.

Within the WTP, the Tc will partition between both the HLW and LAW fractions of the tank waste. The HLW fraction will be converted to a glass waste form in the HLW vitrification facility and the LAW fraction will be converted to another glass waste form in the LAW vitrification facility. In both vitrification facilities, the Tc is incorporated into the glass waste form, but a significant fraction of the Tc volatilizes at the high glass-melting temperatures and is captured in the off-gas treatment systems at both facilities. The aqueous off-gas condensate solution containing the volatilized Tc is recycled and is added to the LAW glass melter feed. This recycle process is effective in increasing the loading of Tc in the LAW glass, but it also disproportionately increases the sulfur and halides in the LAW melter feed, which increases both the amount of LAW glass and either the duration of the LAW vitrification mission or the required supplemental LAW treatment capacity.

One option being considered to address this issue is to remove the Tc at one of several possible points within the tank waste processing flowsheet so that the LAW melter off-gas condensates do not need to be recycled. The separated Tc must then be dispositioned in a manner such that it can be safely disposed. One option would be to put the Tc in a waste form specifically designed to immobilize the Tc. A literature survey was conducted to identify candidate waste forms for the separated Tc waste stream [9].

The Tc waste-form alternatives can be divided into two categories. The first category includes waste forms for solidification of multiple components in a waste stream. Included are borosilicate and iron phosphate glasses, cementitious grouts, geopolymers, phosphate-bonded ceramics, the fluidized bed steam reforming aluminosilicate waste form, and the crystalline ceramic Synroc waste form. The second category includes waste forms specifically designed to immobilize Tc. Included are iron-technetium oxides, metal alloys, technetium oxides, silicate minerals, titanates, sulfides, phosphates, layered double hydroxides, and sulfur-based aerogels.

The current work is initially focused on conducting a follow-up literature review to provide insight into the compositions and volumes of the waste streams, including the Superlig 639 eluent and the off-gas condensate generated, using actual waste and simulants. The information obtained from this review will be used to examine the compatibilities of these waste streams with Tc-specific waste forms and operations

required for Tc immobilization in the candidate waste forms. While this evaluation considers the metal alloy and sodalite Tc waste forms as primary options, other alternative waste forms will be considered as well. The completion of this study will result in the design of experimental activities for testing incorporation of Tc removed from a particular waste stream into the candidate waste form. The fabricated waste forms will be characterized and the specific form and location of Tc in the waste form matrix will be investigated.

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