Novel Inorganic Complexes for Tc Management in the Tank Waste – 14345

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ABSTRACT

One of the U.S. Department of Energy (DOE) current challenges is to meet regulatory requirements for near term disposal of technetium-99 (Tc) present in DOE tank waste stored at Hanford site. Technetium is one of the most important radiotoxicity contributors during long-term waste storage. In the strongly alkaline environments typical for the Hanford tank waste, soluble Tc exists as Tc(VII) in the form of pertechnetate (TcO_4^-) and as non-pertechnetate species containing Tc in low oxidation states. It has been suggested that the dominant non-pertechnetate species are derived from Tc(I) tricarbonyl moiety $Tc(CO)_3^+$. Separation of these species from tank supernatants can't be performed by an ion exchange method and is problematic.   In our research we are exploring novel methods for the detection and separation of both TcO_4^- and non-pertechnetate species from the Hanford waste streams using inorganic composite materials. This paper describes our recent results on the selective detection and removal of TcO_4^- by these composites from both neutral and highly alkaline solutions consistent with tank-waste supernatants and groundwater.

INTRODUCTION

The radioisotope technetium-99 (Tc) is one of the most harmful long-lived products of uranium fission. Its complex redox chemistry, high solubility and volatility at elevated temperatures create the potential for leaching Tc in the environment. This, coupled with its ability to form anionic species, which are highly mobile in the subsurface environment, causes major concern when considering long-term disposal of high-level radioactive waste particularly found at Hanford and other DOE sites [1]. Removal of Tc from the Low Activity Waste (LAW) streams will eliminate vitrification and storage issues associated with volatility of Tc. Commercial anion exchange resins exhibit limited efficiency and selectivity for removing TcO_4^- from the LAW [2, 3]. Currently, SuperLig® 639, a patented resin manufactured and distributed exclusively by IBC Technologies is the preferred and most studied candidate material for the TcO_4^- removal from high ionic strength solutions [4]. This resin exhibits high separation selectivity and efficiency for TcO_4^- uptake. The major drawback of SuperLig® 639 is that its efficiency is limited to only TcO_4^- among Tc species.   In fact, neither SuperLig® 639 nor any other commercial ion exchange resin has the ability to remove non-TcO_4^- species from the aqueous streams. Based on these consideration, utilization of SuperLig® 639 will result in the removal of only a fraction of Tc leaving the non-TcO_4^- species in the solution. In addition, SuperLig® 639 is not cost-effective, and alternative more economical methods are attractive.

To address these needs, this project investigates a new class of inorganic sorbents and sensor materials with high selectivity for Tc, guided in part by models obtained from computational chemistry simulations. We specifically target Tc-selective materials possessing an inorganic

framework compatible with the vitrification process. Novel, inexpensive, and readily available transition metal-based materials promise new capability for the selective uptake of TcO_4^- and potentially of non-TcO_4^- species from LAW streams.   The proposed sorption composite materials are similar to the layered double hydroxides (LDH) and are based on the salts of transition metal complexes with the structure similar to hydrotalcite-like naturally occurring minerals and clays [5, 6]. LDH sorbents have been previously demonstrated as promising materials for the removal of hazardous oxyanions from the aqueous waste streams [7, and references therein]. These materials typically consist of two-dimensional, nanostructured, divalent cations, octahedrally coordinated by hydroxide ions, where some of the divalent cations are isomorphously replaced by tri- or tetravalent cations.   Such a replacement results in the charged sheets, where the net positive charge is compensated by anions in the interlayer region.

LDH materials can be tailored to achieve high selectivity and capacity for the uptake of an anion of interest [8]. The composite oxide/hydroxide composites possess superior characteristics including large surface area, high sorption capacity, and chemical/mechanical/thermal stability. Furthermore, these materials can be prepared in bulk amounts by efficient and simple single step syntheses from inexpensive starting reagents, making them promising candidates for large-scale treatment processes.   Since these composite oxide/hydroxide materials are of an inorganic nature, they exhibit excellent thermal and chemical stability, can be used in harsh environments, and potentially offer a simple, efficient and economic option for the selective removal of TcO_4^- anion.

Availability of sensing capabilities based on the chemical detection of Tc is imperative for an elucidation of the Tc sorption mechanism and its behavior in aqueous matrices, which in turn could lead to the design of new separation technologies. Under environmental conditions, Tc composition is dominated by TcO_4^-, which lacks a characteristic spectral signature preventing its rapid, sensitive and economic *in-situ* detection. This project investigates the potential of developing an inexpensive, solid-state, anion sensor that provides for colorimetric indication and easily detectable changes in spectroscopic properties upon exposure to TcO_4^-.   Such a sensor can be based on using the solid cationic complexes of the square-planar d^8-electron transition metals such as Pt(II), Pd(II), or Ni(II) as the potential colorimetric materials for TcO_4^-.   The reason for this choice is two-fold; (a) d^8-electron metal complexes exhibit a rich spectroscopy that can be tuned by carefully changing the non-covalent metal-metal interactions [9, 10] and (b) the spectroscopic response generated by the non-covalent metal-metal interactions between the square planar cations can be modulated by the size, charge and chemical composition of the counter-anion [11] and thus can be designed to generate unique response to TcO_4^-.

This report describes our current results on the separation and detection of TcO_4^-. We speculate that similar approaches can be used for the management of non-TcO_4^- species.

EXPERIMENTAL

Synthesis of the Composite Materials for TcO_4^- Uptake

The general synthetic procedure included weighing the appropriate starting transition metal salts for a specific composite synthesis.   The compounds were combined in ~50 mL deionized (DI) water.   The solution was stirred for about an hour and the pH measured.   Then 0.5M Na(K)OH was added to solution under stirring until the desired pH was achieved.   The mixture was then transferred to a Teflon-lined autoclave for hydrothermal synthesis at 110 °C for 72 hours in an oven to yield the LDH aggregate.   The set temperature variation was within ± 5 °C.   The resulting composite was filtered from the solution under gravity and allowed to air dry.   The dried compound was then ground into a fine powder with mortar and pestle and rinsed with water until the filtrate ran clear.   Then it was allowed to air dry before being ground into a fine powder again.

Testing of the Composite Materials for TcO_4^- Uptake

The affinity of the synthesized composite sorbents for TcO_4^- was initially assessed by monitoring TcO_4^- uptake from DI water and/or a caustic 1M $NaNO_3$/1M NaOH solution using liquid scintillation counting (LSC). Typical sample preparation involved mixing weighed amount (about 50 mg) of sorbent material with 1-4 mL of water or a caustic solution containing KTO_4 in a glass vial. The vial was then centrifuged at 4000 rpm for about 10 min until the sorbent settled at the bottom, leaving a clear solution at the top. The solution was periodically sampled for 24 hr to monitor TcO_4^- uptake by LSC.

Sensing of TcO_4^- by [Pt(tpy)Br]SbF_6 complex

The starting [Pt(tpy)Br]Br (tpy=2,2′:6′2″-terpyridine) material was prepared by the modified procedure reported elsewhere [12]. Solid [Pt(tpy)Br]SbF_6 (**1**·SbF_6) was prepared by precipitation upon adding a concentrated aqueous solution of $KSbF_6$ to an aqueous solution of [Pt(tpy)Br]Br and characterized by elemental analysis and ^{1}H NMR.

Bead-supported **1**·SbF_6 was prepared by sonicating dried Vycor porous glass beads in 50% v/v DMSO/acetone solution containing 20 mg of **1**·SbF_6 complex for 3 hours. The resulting yellow beads were submerged in water to induce precipitation of the complex within the glass matrix and air-dried. For anion exchange experiments, **1**·SbF_6 Vycor porous glass beads were immersed in aqueous TcO_4^- solutions of variable concentration for about 3 hr, washed with water, and air-dried before spectroscopy experiments.

RESULTS AND DISCUSSION

Tc uptake by the composite materials

To investigate new approaches of TcO_4^- removal from aqueous media, we synthesized and tested several inorganic composite materials of the formulae $[M_{1-x}^{2+}M_x^{m+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$ where M^{2+} is a divalent cation (Ni^{2+}, Sn^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ca^{2+}) and M^{m+} is a trivalent or tetravalent cation (Al^{3+}, Cr^{3+}, Zr^{4+}); the value of x is equal to the molar ratio of $M^{m+}/(M^{2+} + M^{m+})$, whereas A is the interlayer anion of valence n (e.g. hydroxide, oxide, phosphate). The TcO_4^- uptake was initially tested from water; Table 1 compares the 24 hr TcO_4^- sorption performance of

the tested composite materials.

Table 1. Preliminary evaluation of TcO$_4^-$ uptake by the synthesized composite materials. Reported values correspond to 24 hr uptake.

Sample ID	Composite material	Percent TcO$_4^-$ Sorption from	
		DI Water	Caustic
1	Sn(II)-Al(III)	99.5	95
2	Sn(II)-Al(III)-Zr(IV)	98	95
3	Ni(II)-Cu(II)-Al(III)	84	Not tested
4	Ni(II)-Cu(II)-Al(III)-Zr(IV)	83	11
5	Ni(II)-Al(III)-Zr(IV)	78	7
6	Sn(II)-Ni(II)-Al(III)-Zr(IV)	77	33
7	Ni(II)-Al(III)	70	9
8	Ni(II)-Fe(III)	37	Not tested
9	Ni(II)-Fe(III)-Zr(IV)	23	Not tested
10	Cu(II)-Al(III)	18	Not tested
11	Ni(II)-Fe(III)-Zr(IV)	11	7
12	Sn(II)-Fe(III)	10	20
13	Co(II)-Al(III)	9	Not tested
14	Co(II)-Fe(III)	0	Not tested
15	Sn(II)-Al(III) (PO$_4$)	Not tested	98
16	Zn(II)-Al(III)-Zr(IV)	Not tested	32
17	Sn(II)-Bonechar	Not tested	99.5
18	Sn(II)-Hydroxyapatite	Not tested	99
19	Bonechar	78	81
20	Hydroxyapatite	14	3

Examination of the TcO$_4^-$ sorption results obtained using water matrix revealed a few interesting trends. Most notably it was observed that Sn(II)-containing composites exhibited nearly quantitative uptake of TcO$_4^-$ (Samples 1 and 2) with exception of Sn(II)-Ni(II)-Al(III)-Zr(IV) composite (Sample 6), which showed only modest uptake of pertechnetate. Further, the kinetics of this uptake was fast (Figure 1). It can be suggested that the presence of Al(III) and/or Zr(IV) in the composite synergistically enhances TcO$_4^-$ uptake. Sn(II)-Fe(III) composite performed poorly, speculatively due to a reduction of Fe(III) to Fe(II) by Sn(II) during the synthesis. Ni(II)-Cu(II)-Al(III) composites with and without Zr(IV) (Samples 3 and 4) exhibited significant TcO$_4^-$ uptake.
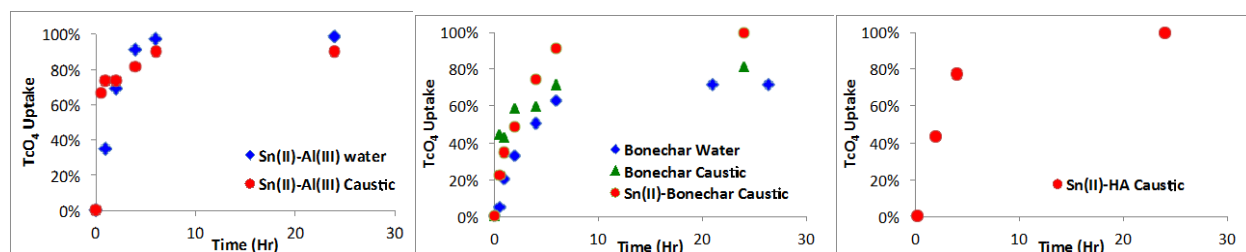
Figure 1. Time dependent TcO_4^- uptake by the representative composite materials monitored by LSC.

Selected composite materials were tested for the TcO_4^- uptake from caustic 1M $NaNO_3$/1M NaOH solutions, which are consistent with tank-waste supernatant conditions.   As with the water results, it was observed that the highest uptake capacity was exhibited by composites where Sn^{2+} was present (Table 1, Samples 1, 2, 15).

In addition to transition metal composites, commercial bonechar and hydroxyapatite sorbents were tested for the TcO_4^- uptake (Table 1, Samples 19 and 20).   Bonechar exhibited similar TcO_4^- sorption from water and caustic matrices (Figure 1).   Hydroxyapatite performed poorly. In an effort to enhance TcO_4^- uptake, both bonechar and hydroxyapatite were subjected to the reaction with $SnCl_2$ at 110 °C at pH of approximately 12.   The resulting materials exhibited nearly quantitative TcO_4^- uptake (Figure 1; Table 1, Samples 17 and 18).   To test if phosphate had an effect on the TcO_4^- uptake, phosphate anion was incorporated in the Sn(II)-Al(III) composite material.   The resulting product (Table 1, Sample 15) enhanced TcO_4^- uptake from the caustic solution in comparison with the parent composite (Table 1, Sample 1).

These results indicating that Sn(II)-containing composites exhibit efficient TcO_4^- sorption from both DI water and alkaline solutions are consistent with a literature report that described the application of Sn(II)apatite for the uptake and immobilization of TcO_4^- from tank waste simulants [13]. However, Sn(II)apatite exhibited only limited working pH range, 1 – 12, and was ineffective for the TcO_4^- sorption from highly alkaline solutions.   In this report, it was suggested that Sn(II) reduces TcO_4^- from the oxidation state of +7 to +4.   Based on this information, the proposed mechanism of TcO_4^- sorption using the Sn(II)-containing composites tested in this work is described in Figure 2.   It involves a two-step process, namely efficient TcO_4^- uptake followed by its reduction to Tc(IV).   If the insoluble Tc(IV) species are isomorphic with the composite structure, they are strongly retained within its matrix.

To test for uptake of the non-TcO_4^- species using commercial materials, the $[Tc(CO)_3(H_2O)_3]^+$ complex, which contains Tc as Tc(I), was synthesized as reported elsewhere [14].   Three commercial sorbents were tested, including bonechar, hydroxyapatite, and the silicontitanate ion exchanger IE-911.   When a water matrix was used, bonechar exhibited efficient uptake of Tc(I) while the other two sorbents performed only modestly (Table 2).   When a caustic matrix was used, Tc(I) sorption by all three materials was low.   This result was attributed to hydrolysis of the $[Tc(CO)_3(H_2O)_3]^+$ complex in the alkaline media and formation of the non-charged $[Tc(CO)_3(OH)(H_2O)_2]$ species [14], with has a poor affinity to the tested materials.
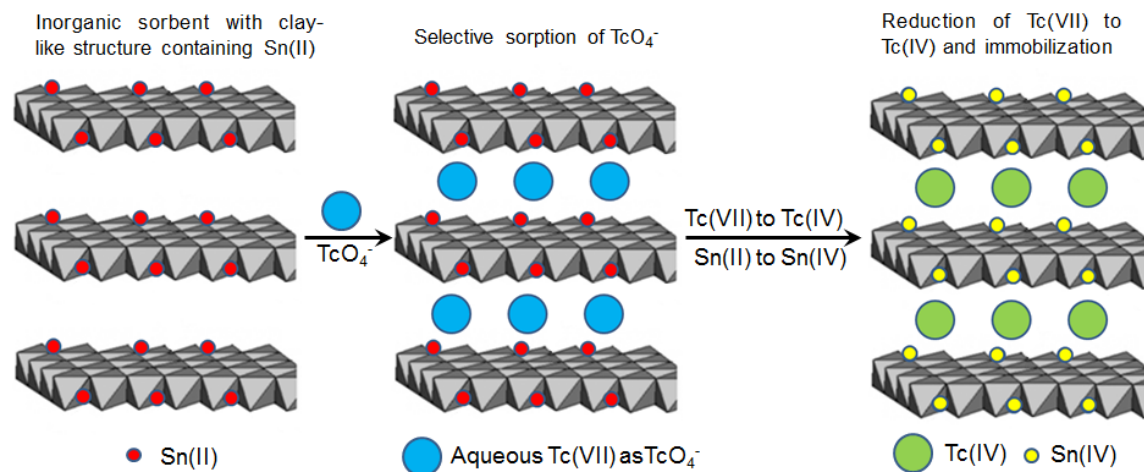
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Figure 2. Schematic representation of the TcO_4^- sorption by the clay-like material containing Sn(II). The sorption and immobilization of Tc-99 is achieved by (1) high affinity of the sorbent material to TcO_4^-, (2) reduction of Tc(VII) to Tc(IV) by Sn(II), and (3) formation of an insoluble Tc(IV) species isomorphic with the parent material.

Table 2. Preliminary evaluation of $[Tc(CO)_3]^+$ uptake by the synthesized composite materials. Reported values correspond to a 24 hr uptake.

Sample ID	Composite material	Percent Tc(I) sorption from	
		DI Water	Caustic
21	Bonechar	94	25
22	Hydroxyapatite	58	8
23	IE-911	56	8

TcO_4^- sensing

To quantify TcO_4^- in the liquid matrices, we designed a novel colorimetric and luminescence detection technique capable of detecting and quantifying nanomolar quantities of TcO_4^-. This method relies on the color change of the $[Pt(tpy)Br]SbF_6$ ($1 \cdot SbF_6$) complex and intense luminescence response upon SbF_6^- exchange with TcO_4^- due to concomitant enhancement of Pt•••Pt interactions. This spectroscopic response is highly selective for TcO_4^-. The TcO_4^- sensing mechanism is illustrated in Figure 3.
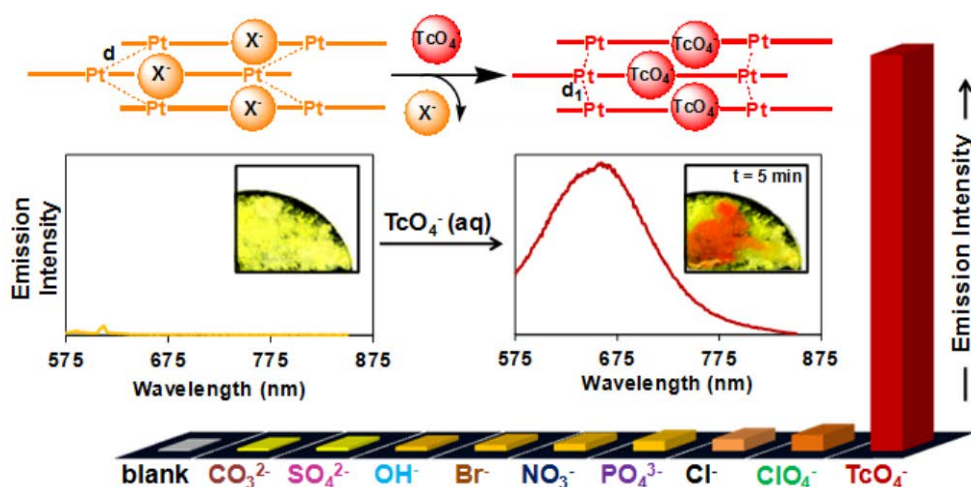
Figure 3. A schematic depicting selective detection of TcO_4^- in presence of other anions. Top: structural change of a generic square planar Pt(II) complex of upon selective TcO_4^- uptake leading to an increased Pt···Pt interaction and unique spectral response. Middle: the change of the color and emission profile of the solid Pt(II) complex upon contact with aqueous TcO_4^- solution. Bottom: the bar-graph demonstrating selectivity of TcO_4^- detection.

Compound **1**·SbF_6 (Scheme 1) is a sparingly water-soluble complex salt that crystallizes as yellow needles. To assess the colorimetric response, a yellow microcrystalline powder (~10 mg) or aqueous suspension (~10 mg/mL) of **1**·SbF_6 was exposed to 50 µL of 1.0 mM aqueous solution of TcO_4^-.
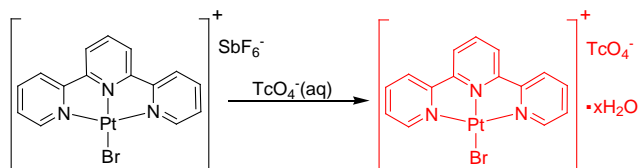
Scheme 1. Conversion of yellow [Pt(tpy)Br]SbF_6 (**1**·SbF_6) to red [Pt(tpy)Br]TcO_4·xH_2O (**1**·TcO_4·xH_2O) on exposure to aq. TcO_4^-.

This resulted in a distinct color change of the **1**·SbF_6 solid from yellow to red within 2-5 minutes. Results were indistinguishable irrespective of whether $KTcO_4$ or NH_4TcO_4 was used as the source of TcO_4^-. The presence of water is a key-factor in the color change; this is exemplified by the fact that when the powder 1·SbF_6 sample treated with aqueous TcO_4^- solution is allowed to dry, it changes from red back to yellow. The red color of **1**·TcO_4·xH_2O is restored upon re-equilibration with water.

To investigate the changes in electronic structure, **1**·SbF_6 was loaded on Vycor porous glass beads and absorption spectra were recorded (Figure 4). The absorption spectrum of the **1**·SbF_6-loaded beads shows an intense tpy-centered ⬚⬚* transition near 340 nm, and an

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MLCT band characteristic of the Pt(tpy)Br$^+$ chromophore near 400 nm that tails to longer wavelengths [15].

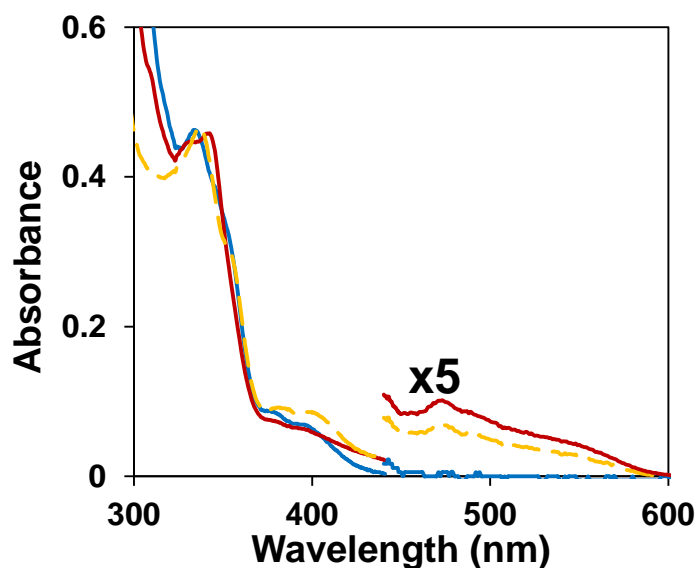**Figure 4.** Absorption spectra of Pt(tpy)Br$^+$ salts loaded into Vycor beads: (——)**1·**SbF$_6$, (——)**1·**TcO$_4$·xH$_2$O, (- - -)**1·**SbF$_6$ exposed to 1.0 mM TcO$_4^-$ for 3 hours.

Immersion of the glass beads in a 1.0 mM NH$_4$TcO$_4$ solution results in the appearance of a new band at longer wavelength.   The band is nearly identical to that observed when beads are loaded with **1·**TcO$_4$·xH$_2$O and is attributed to a metal–metal-to-ligand charge-transfer MMLCT [d π*(tpy)] transition [16].   Emission studies were performed on aqueous suspensions of **1·**SbF$_6$ and **1·**TcO$_4$·xH$_2$O as well as samples loaded onto Vycor glass using 532 nm light to selectively excite the MMLCT transition.   In both cases, **1·**SbF$_6$ exhibited extremely weak emissions.   On the other hand, the aqueous suspension of **1·**TcO$_4$·xH$_2$O displayed an intense emission at 592 nm with a shoulder at ~670 nm.   Vycor samples containing **1·**TcO$_4$·xH$_2$O showed an intense emission band with maximum at 655 nm (Figure 5a).   The emission in the 655-670 nm range is assigned to a predominantly spin-forbidden MMLCT transition.

To examine the selectivity of TcO$_4^-$ detection, solid **1·**SbF$_6$ material was suspended in aqueous 1 mM solutions of TcO$_4^-$, ClO$_4^-$, Cl$^-$, PO$_4^{3-}$, NO$_3^-$, Br$^-$, OH$^-$, CO$_3^{2-}$, or SO$_4^{2-}$.   The color of **1·**SbF$_6$ complex remains yellow in suspensions except the one containing TcO$_4^-$ (Figure 6).   To quantify the selectivity factors, Vycor glass beads loaded with **1·**SbF$_6$ were exposed to 1.0 mM aqueous TcO$_4^-$, ClO$_4^-$, Cl$^-$, PO$_4^{3-}$, NO$_3^-$, Br$^-$, OH$^-$, CO$_3^{2-}$, or SO$_4^{2-}$ solution.   Upon excitation at 532 nm, the glass beads loaded with TcO$_4^-$ exhibited an intense luminescence at 655 nm nearly identical to **1·**TcO$_4$·xH$_2$O.   Glass beads exposed to all other anions showed no or weak emission when excited with 532 nm laser light. The selectivity factors calculated as the ratio of the maximum emission intensities observed in presence of TcO$_4^-$ to that observed in presence of interfering anions range from 50 (for ClO$_4^-$) to 1200 (for CO$_3^{2-}$) (Figure 3, Table 3) confirming highly
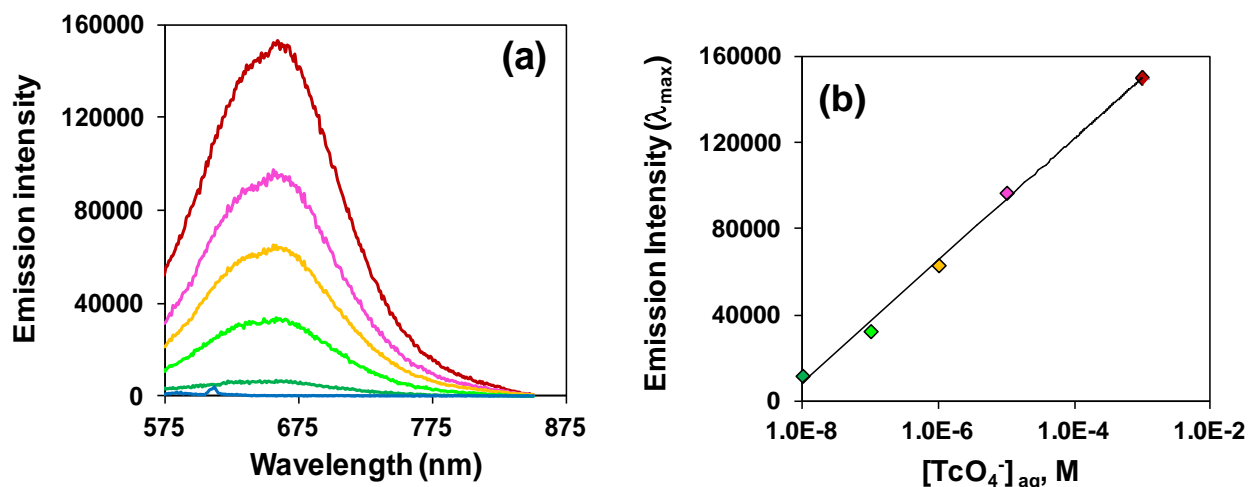
selective TcO_4^- detection.

Figure 5. (a) Luminescence spectra of $\mathbf{1 \cdot SbF_6}$ loaded Vycor beads upon exposure to varying concentrations of aqueous TcO_4^- for 1 hour: (——) 0 M, (——) 10^{-8} M, (——) 10^{-7} M, (——) 10^{-6} M, (——) 10^{-5} M, (——) 10^{-3} M. (λ_{ex}= 532 nm), (b) semilogarithmic plot of the maximum emission intensity (λ_{max}= 655 nm) of the loaded Vycor beads versus the concentration of solution TcO_4^- in solution.

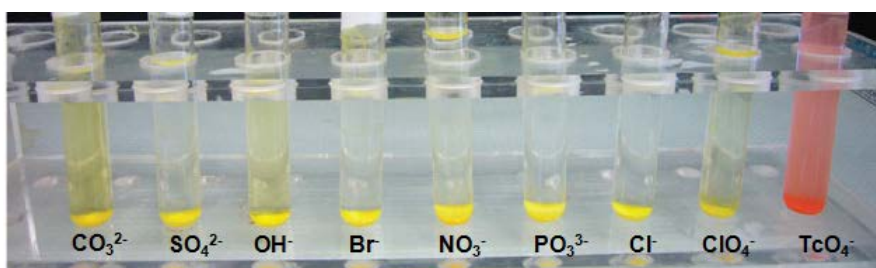**Figure 6**. Photograph of the $\mathbf{1 \cdot SbF_6}$ material in the 1 mM aqueous solutions of various potassium salts.

Table 3. Selectivity factors of TcO_4^- detection calculated as the ratio of the maximum emission intensity measured in presence of TcO_4^- to that observed in presence of interfering anions.

Anion	ClO_4^-	Cl^-	PO_4^-	NO_3^-	Br^-	OH^-	SO_4^-	CO_3^{2-}
Selectivity factor	50	100	165	185	500	750	1000	1200

To test whether the emission intensity can be used for the quantification of aqueous TcO_4^-, Vycor glass beads loaded with equal amounts of $\mathbf{1 \cdot SbF_6}$ were exposed to aqueous solutions containing different concentrations of TcO_4^- ranging from 10^{-8} to 10^{-3} M.   Upon excitation at 532 nm, the intensity of the characteristic 655 nm emission progressively increased with the increasing TcO_4^-

concentration. A preliminary working curve of the emission intensity (at 655 nm) as a function of the logarithm of TcO_4^- concentration shows a linear dependence for the entire TcO_4^- concentration range tested (Figure 5b).

CONCLUSIONS

Several inorganic composite materials were synthesized and tested for the TcO_4^- uptake from water and highly alkaline solutions consistent with tank-waste supernatant conditions.   It was observed that the highest uptake efficiency of 95-99% was exhibited by composites containing Sn(II).   This effect was attributed to the high affinity of the composite structure for the TcO_4^- anion and is responsible for its initial removal from the aqueous solutions.   Once incorporated in the composite, Tc(VII) was reduced to Tc(IV) by the Sn(II) present in the composite.   A few commercially available reagents (bonechar, hydroxyapatite) were chemically modified with Sn(II) and tested for TcO_4^- uptake as well. They too efficiently removed the TcO_4^- from caustic solution.

In a companion effort, a novel colorimetric and luminescence sensor material capable of selective measurements of nanomolar quantities of TcO_4^- was designed.   Quantitative measurement of aqueous TcO_4^- anion in the 10^{-8} - 10^{-3} M concentration range was achieved using solid [Pt(tpy)Br]SbF$_6$ salt (tpy=2,2′:6′2″-terpyridine).   This novel detection method relies on the color change of the Pt(II) complex and an intense luminescence response upon SbF$_6^-$ exchange with TcO_4^- due to concomitant enhancement of Pt•••Pt interactions.   This spectroscopic response was highly selective for TcO_4^-.

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