

EVALUATION AND SELECTION OF ^{99}Tc GETTERS FOR SEQUESTRATION OF LIQUID SECONDARY WASTES RESULTING FROM VITRIFICATION OF RADIOACTIVE WASTES FROM HANFORD – 11167

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ABSTRACT

Getters are most commonly inorganic materials that selectively adsorb radionuclide and metallic contaminants. Typically, these materials have been deployed in two different modes to immobilize and retard contaminant release from monolithic waste forms. One mode is to first use getters to selectively scavenge the radionuclide of interest from a liquid waste stream, and then incorporate the radionuclide-loaded getters in cementitious or other monolithic waste forms. The other mode consists of mixing getters and liquid waste together during formulation of monolithic waste forms. Desirable characteristics for a getter material include, 1) specific adsorption of radionuclide of interest and very high selectivity toward radionuclides of concern in concentrations that would be several orders of magnitude less than the concentrations of competing anions and cations, 2) adsorption capacity that should be sufficient for the mass and volume of the material that will be deployed to be within practicable limits, 3) long-term adsorption and retention of radionuclide, 4) sufficient physical and chemical stability that its radionuclide retention performance will not degrade significantly during the designed life span of the waste form, 5) chemical stability under the range of Eh, pH, and solution conditions that exist in the waste form environment, and 6) should not adversely affect chemical and physical integrity of waste forms. We conducted a literature review to identify getters that are suitable for effectively sequestering ^{99}Tc in monolithic waste forms that are being evaluated for stabilizing secondary liquid waste streams resulting from treatment and vitrification of radioactive tank wastes at Hanford. As a result of this review, we identified a set of getters that warrant further evaluation for this specific application.

INTRODUCTION

For several decades, the Hanford Site in southeastern Washington State was used by the United States government to produce nuclear materials. The resulting radioactive and mixed wastes are currently stored in 177 underground single- and double-shell tanks at this site [1]. Currently, the US Department of Energy (DOE) Office of River Protection (ORP) is proceeding with plans to permanently dispose of the liquid and solid wastes by processing and vitrifying these wastes. The high-level waste (HLW) glasses will be disposed of at an off-site repository, and the immobilized low-activity waste (ILAW) will be disposed of in the Integrated Disposal Facility (IDF) at the Hanford site [2]. The liquid secondary wastes generated from the waste vitrification activities contain a portion of the ^{99}Tc inventory and will be treated at the Hanford's Effluent Treatment Facility (ETF) and solidified into waste forms for disposal at the IDF.

Pacific Northwest National Laboratory (PNNL)¹ was contracted to initiate a Waste Form Testing Program to support the evaluation of the long-term durability of a number of solidified secondary waste forms. The purpose of PNNL's work was 1) to find suitable candidate stabilization technologies that have the potential to successfully treat liquid effluents and 2) to identify getters that would improve the radionuclide retention performance of these solidified waste forms. As part of the objective, a review of ^{99}Tc getters was conducted² and the results are presented in this paper.

GETTERS

Getters are most commonly inorganic materials that selectively adsorb radionuclide and metallic contaminants. Typically, these materials have been deployed in two different modes to immobilize and retard contaminant release. One application of getters is to reduce the release of radionuclides from monolithic waste forms. This is accomplished either by first using getters to selectively scavenge the radionuclide of interest from a liquid waste

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² Pierce et al. 2010. Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams. PNNL-19122, Pacific Northwest National Laboratory, Richland, WA.

stream, then subsequently incorporating the loaded getters in to cementitious or other monolithic waste forms. The other method consists of mixing getters and liquid waste together during formulation of monolithic waste forms. Another mode of getter use consists of deploying the materials in near-field barriers of repositories to adsorb and attenuate any long-lived radionuclides that may be released from physically degrading and chemically weathering waste packages.

Considerable research effort has been expended during the last several decades to identify suitable getter materials that can immobilize or delay the transport of pertechnetate ($^{99}\text{TcO}_4^-$) that would be released from degrading waste packages [3 – 23].

Based on intended application, getters can be grouped into two categories: getters used as monolithic waste form additives and getters used as repository backfills. The typical characteristics of each category of getters are tabulated in Table 1. The aforementioned investigations indicate that deployment of suitable getter materials can be an important aspect of effective long-term containment of contaminants in monolithic waste forms.

Table 1. Characteristics of Getters

| Getters Characteristic | Waste Form Getter | Backfill Getter |
|---|---|-----------------------------|
| Adsorptive Capacity | Moderate to high (K_d 1000 – 5×10^4 ml/g) | Low (K_d 10 - 1000 ml/g) |
| Contaminant Selectivity | High | Low |
| Contaminant Desorption | Very low | Low to high |
| Long-term Stability: Chemical physical, and radiation | High | Low to medium |
| Waste Form Compatibility | Medium to high | Not applicable |
| Cost | Moderate to high | Low |

Getter Properties

Adsorbent materials need to possess certain critical properties to be designated as a getter material. Several investigators have identified a number of important performance characteristics that getter materials should possess for effective deployment [20, 24 -27]. Viani [20] provided a more comprehensive list of criteria (described below) that can be used to assess the properties of potential getter materials.

Adsorption Potential: The getter material should specifically adsorb the radionuclide of interest and should exhibit very high selectivity toward radionuclides of concern in concentrations that would be several orders of magnitude less than the concentrations of competing anions and cations. The adsorption capacity of the getter materials should be sufficient for the mass and volume of the material that will be deployed to be within practicable limits. Based on laboratory experiments, it should be feasible to reliably predict the long-term adsorption and retention behavior of the getter material.

Physical Stability: The getter material should possess sufficient physical and chemical stability that its radionuclide retention performance will not degrade significantly during the designed life span of the waste form. It should be physically robust so that its particles will not disintegrate when subjected to moisture, temperature, and the expected radiation regime. The getter media should also be chemically stable over the range of Eh, pH, and solution conditions that are predicted to exist without noticeable degradation in its functionality. The getter material should not adversely affect chemical and physical integrity of waste forms. It should be possible to predict the physical and chemical stability of the getter material from a combination of laboratory-scale, field-scale, and natural analog studies.

Deployment: The getter material deployment should be technically feasible. If the getter material is difficult to deploy and needs special handling, the cost of deployment may preclude its use.

Material Cost: The cost of a getter material should be commensurate with its performance. The getter material cost/performance ratio is critical for the deployment decision.

For a getter material to be selected, it should substantially meet all of the above criteria. In the following review, we will examine the published data and suggest a scheme for evaluating and selecting suitable getter materials.

TECHNETIUM GETTERS

Several types of natural and modified minerals have been tested for their suitability as getters for ^{99}Tc . These getters include minerals and synthetic adsorbent materials such as oxides, hydroxides, natural and modified aluminosilicates, synthetic magnesium silicates, sulfides, and coal. Recently, novel getter materials designed specifically to remove radioiodine have been synthesized and tested for their getter properties. Published data on technetium getters from various sources are listed in Table 2.

Oxide and Hydroxide Minerals

Adsorption tests have shown that iron oxides and hydroxides have relatively low affinity (K_d : 0 – 5 mL/g) for the pertechnetate ion (TcO_4^-) [18, 23, 28, 29]. Under anoxic conditions, iron oxides exhibit relatively higher K_d values (0 – 190 mL/g) [29]. The increases in K_d values were attributed to the potential reduction of Tc(VII) to the less soluble Tc(IV) form. Precipitating Fe(II) hydroxide in a Tc(VII) spiked raffinate simulant may yield K_d values ranging from 1.3×10^3 to 2.8×10^3 mL/g reflecting potential reduction of ^{99}Tc and co-precipitation [41]. This was confirmed by the fact that after exposure to air for 11 days about 30% of the co-precipitated ^{99}Tc was released into solution.

The immobilization of ^{99}Tc immobilization by magnetite results in K_d values ranging from 4 to 490 mL/g [29]. The presence of Tc(IV) complexing ligands such as chlorides and phosphates however, results in lower K_d values (<0.1 – 57 mL/g). The latter effects have been confirmed by other investigators [7, 15, 28, 30]. Based on detailed studies, [8,31] concluded that the specific surface area, the Fe(II) content, and the mode of bonding of Fe (II) in the mineral were the principal factors that influenced the rate of ^{99}Tc reduction by Fe(II)-bearing minerals. They found that among Fe(II)-bearing minerals, magnetite was the most efficient reductant for Tc(VII) due to its low band gap between valence and conduction bands. Metallic iron is also known to promote immobilization of ^{99}Tc through reduction reaction (K_d values from about 200 to more than 200,000 mL/g) [13, 28, 29, 32-34]. Inexplicably, in another test, metallic iron showed very low K_d values (0 – 14 mL/g) [34].

Other oxide and hydroxide minerals exhibit relatively low K_d values for Tc adsorption (0 – 55 mL/g) [5, 30, 35, 18, 36]. Reported K_d values for synthetic hydrotalcites range from 137 – 6,160 mL/g [5, 11, 12]. However, Zn-hydrotalcite showed significantly lower K_d values (1 – 84 mL/g) [5].

These studies indicate that relatively poor capacity and selectivity and a potential lack of chemical stability preclude using many of the oxide and hydroxide minerals as effective getter materials for technetium. Synthetic layered double hydroxide (LDH) compounds appeared to exhibit better getter properties than natural materials. Similarly, magnetite and metallic iron under certain limited conditions appear to be effective getters for ^{99}Tc . However, the chemical stability and the tendency for ^{99}Tc mobilization from radiolysis effects and potential influx of oxic groundwaters and/or leachates (reflecting site-specific conditions) need to be evaluated for LDH, magnetite, and metallic iron materials.

Sulfide Minerals

Published data indicate that the ^{99}Tc attenuation performance of sulfide minerals is highly variable and appears to depend on a number of factors, such as the type of mineral, particle size, type of contacting solution, pH, ionic strength, and Eh [5, 6, 15, 18, 19, 23, 37, 38, 58]. It is generally recognized that the principal mechanisms of ^{99}Tc attenuation by sulfide minerals are through either reduction of Tc(VII) to low solubility Tc(IV) phases such as $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ [6] or by direct precipitation of Tc(VII) as the sparingly soluble sulfide mineral Tc_2S_7 [15, 38, 39]. However, spectroscopic work (extended x-ray absorption fine structure [EXAFS] and x-ray adsorption near-edge

spectroscopy [XANES]) on reducing grouts indicated that Tc(IV) may exist as Tc_3S_{10} [40]. Although some sulfide minerals show better ^{99}Tc attenuation characteristics, their long-term stability for deployment as ^{99}Tc getters has not been established. It is also necessary to establish the rate of oxidation and the concomitant rate of release of Tc(VII) from various sulfide getters.

Other Minerals

When used as a part of cementitious waste forms, blast furnace slag (BFS) is known to attenuate Tc(VII) release through reduction of Tc(VII) to Tc(IV) [41- 43, 43- 49, 60]. Typically, BFS has reductive capacities that range from 0.82 to 4.79 meq/g [40, 41, 43]. Test data indicate that unless protected from oxygen intrusion, the BFS getter-based waste forms tend to release ^{99}Tc by oxidation of Tc_3S_{10} [40, 41].

Materials such as activated carbon (charcoal) have been tested for their capacity to adsorb pertechnetate [27, 50]. Activated carbon tests conducted in 5-M sodium chloride solution showed moderate affinity (K_d : 310 – 380 mL/g) for Tc(VII) [27]. However, other tests [50] have indicated that although activated carbon showed very high affinity for Tc(VII) in a DI water matrix (K_d : 8,000 – 10,000 mL/g), the affinity decreased in 1M sodium chloride solution (K_d : 300 – 5,000 mL/g) and in $NaClO_4$ solution (K_d : 10 – 300 mL/g).

Other minerals (gypsum, dolomite, apatite, and monazite, zirconium phosphate and Sb silico-phosphate, bone black, fishbone, and Fe(III) phosphate) have relatively low affinity (K_d : <0.1 – 11 mL/g) for Tc(VII) [18, 34, 36]. When treated with a reductant such as, Fe(II) sulfate, bone black, fishbone, and Fe(III) phosphate showed higher selectivities (1800 – 6400 mL/g). Tests conducted on Sn(II)- apatites in concentrated salt solutions showed Tc K_d values of 5,140 – 6,510 mL/g [17].

Novel Synthetic Getters

Scoping tests conducted on Sn(II)-bearing nanoporous phosphates in dilute $NaHCO_3$ solution indicated K_d values exceeding 90,000 mL/g [21]. However, more extensive tests are needed to fully evaluate the ^{99}Tc getter potential of these novel synthetic materials. Synthetic sodalite is also considered to be an effective getter for ^{99}Tc . Several studies have shown that the cage-like structure of sodalite can trap and immobilize up to 9 mol% of oxyanions that include Tc (VII) [51- 57]. However, further study is needed to demonstrate the effectiveness of sodalite as a stable getter for long-term sequestration of Tc(VII).

Getter Selection and Evaluation Process

Good adsorption performance (capacity, kinetics, and selectivity for contaminants of interest) is an essential characteristic that potential getter materials must exhibit. However, additional criteria should be met by any potential getter material before it can be effectively deployed in a waste form. Additional proposed evaluation steps taken to assure that the criteria are met are shown in the flow chart (Figure 1). The proposed tiered approach for the getter selection and evaluation scheme is based on the critical performance factors listed below:

- adequate selectivity and capacity for radionuclide of concern
- low desorption characteristics
- chemically and physically stable
- compatibility with waste form
- cost effectiveness.

If getters are needed to improve the performance of a waste form, a preliminary screening of currently available mineral and synthetic getters needs to be conducted. During the first tier testing, the getters would be evaluated for their adsorption capacity, weathering kinetics, and the contaminant specificity. For reductive getters, it may be appropriate to measure reductive capacity. These tests are typically conducted using the actual waste stream or a simulant. After these tests, desorption tests can be conducted on contaminant-loaded getters. It is appropriate to conduct desorption tests using a simulant of the pore water of selected monolithic waste forms to provide better understanding of potential contaminant release and partitioning that may occur between getters and the waste form

matrix. Getters meeting the previously established performance specifications can then be subjected to the next tier of tests.

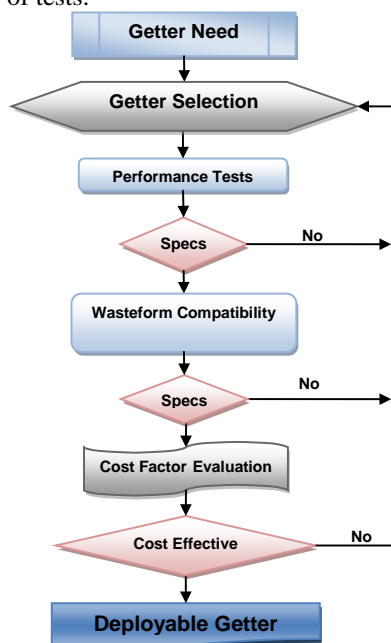


Figure 1. Flowchart for Getter Selection and Evaluation

thoroughly characterized these interactions. Recent studies [48, 49] demonstrated that including BFS as a getter in the Containerized Cast Stone (CCS) formulation did not degrade the performance of this monolithic waste form. However, the compatibility of various effective getter materials with selected monolithic waste forms needs to be studied and better understood before the composite waste form can be deployed. Therefore, such a compatibility evaluation has been suggested as part of getter selection criteria (Figure 1).

CONCLUSIONS

The literature review generated comprehensive lists of technetium getters (Tables 2). Based on existing test data, the most promising getters that need additional evaluation include, nanoporous tin phosphates, Sn(II)-treated apatite, nano zero-valent iron (nano ZVI), and ground BFS as ⁹⁹Tc getters.

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For screening purposes, the waste form compatibility tests at this level may consist of leach tests, such as ANSI/ANS 16.1 [59] and the EPA's recently developed test methods [66-69]. Although TCLP testing [70] is also conducted as part of Waste Acceptance Criteria [71], the typical suite of waste-form testing is not needed in this testing tier. If the results of the leach tests [59, 66-69] of the getter-containing waste forms show lowered leachability of the ⁹⁹Tc than leachability in the waste form with no getter, it would be appropriate to consider the use of getters. Finally, the cost effectiveness of getter deployment in a selected waste form needs to be assessed, including factors such as the cost per mass of contaminant sequestered, any reduction in waste form loading of ⁹⁹Tc caused by the need to add getters, and the cost savings realized from disposal of waste forms with lowered leachability of contaminants.

GETTER-WASTE FORM INTERACTIONS

Typically, when incorporated into monolithic waste forms, getters interact both physically and chemically with the encapsulating matrix. Ideally, while performing the targeted task of sequestration and attenuation of radionuclides, getters should not adversely affect the physical and leaching performance of the monolithic waste forms. Although the getters and waste forms have been studied extensively, the published literature includes a limited number of studies that have

Table 2. Technetium Distribution Coefficient Data for Natural and Synthetic Getter Materials

| Getter Material | K _d (mL/g) | Matrix Solution | Eq. pH | SO ₄ /TcO ₄ M Conc Ratio | Ref |
|--|---|--|---|---|-----|
| Iron Sulfide (Am) | >6000 | 0.1 M NaCl | 6.1 – 9.0 | -- | 61 |
| Bone Black UT: untreated, T: Fe(II) treated Fishbone Metallic Iron Fe(III) Phosphate | 0- 5 (UT), 6,070 (T) 0- 5 (UT), 6,400 (T) 0-14 (UT), 9,200 (T) 0-2 (UT), 1,820 (T) | TcO ₄ solution | 5 to 6 and 12 | -- | 34 |
| Fe Hydroxide | 1280 - 2770 | Savannah River site alkaline raffinate simulant | 12.37 – 12.60 | -- | 41 |
| Nanoporous tin phosphates | >90,000 | 0.002M NaHCO ₃ | 8 | -- | 21 |
| Bismuth hydroxides (with and without Li) | 23 - 340 | J-13 simulant (Yucca Mt., groundwater) | 7 | -- | 62 |
| Sn(II) treated Apatite | 475,000 – 3,202,100 5,140 – 6,510 | 9.11 x 10 ⁻⁶ – 1.15 x 10 ⁻⁵ M Tc in groundwater 9.11 x 10 ⁻⁶ – 9.11 x 10 ⁻⁵ M Tc in conc. NaNO ₃ -NaNO ₂ , NaOH-NaAlO ₂ solution | 6 – 10 13 | -- | 17 |
| Hydroxaltes [Al, Bi, Cu(I, II), La, Sn(II), Sn (IV), Zn] | 137 – 4,890 | Dilute NaNO ₃ -NaNO ₂ , NaOH-NaAlO ₂ Solution | -- | -- | 12 |
| Sn(II), Fe(II) treated Synthetic & Bovine Apatites | 7,110 – 357,100 | 0.1M KNO ₃ | 8 | -- | 63 |
| Fe Metal | 1,800 - >200,000 | 0.1M NaCl, NaClO ₄ , NaNO ₃ | 6.4 – 7.0 | -- | 33 |
| Cu-EDA SAMMS Cu-EDA Resin | 50 – 440 66 – 790 340 -720 3,400 – 7,300 8,400 – 37,500 1 – 30 | Groundwater Groundwater Glass leachate simulant Groundwater Groundwater Glass leachate simulant | 5.83 – 7.44 7.76 – 8.04 | 6 x 10 ³ 7 x 10 ² 1 x 10 ² | 64 |
| Boehmite, Al hydroxide | 0 – 110 | 0.001 M ReO ₄ in 0.001 M NaNO ₃ | 5.2 – 9.7 | -- | 35 |
| Cu Oxides Chalcocite Covellite Zn hydroxaltes CMSA Imogolite | 43 – 55 31 67 1 – 84 134 23 | TcO ₄ solution | 6.8 – 7.1 8.6 5.4 5.3 – 7.7 11.7 6.4 | -- | 5 |
| Hydroxaltes | 265 – 6,160 | 0.3 M NH ₄ TcO ₄ , 0.1 M NH ₄ OH, 0.1 M HTcO ₄ | 10.59 – 12.51 | | 11 |
| Fe metal | ~121,700 | 1x10 ⁻⁵ M TcO ₄ in ~6 – 12 M MgCl ₂ brine | -- | 60 – 1.8 x10 ⁴ | 13 |
| Ti Oxide Greeknockite (CdS) Zr Phosphate Sb silicophosphate Li-Mn-Al hydroxide Li-Ti-Cr hydroxide | 1 – 31 2 – 13 1-11 <0.1 – 9 2 – 10 2 – 11 | TcO ₄ solution | 1.3, 6.5, 12.7 | -- | 36 |

| Getter Material | K _d (mL/g) | Matrix Solution | Eq. pH | SO ₄ /TcO ₄ M Conc Ratio | Ref |
|--|--|---|--|---|----------|
| Fe Metal Greigite | 1,490 – 18,700 110 – 6,100 | 13. mg/L TcO ₄ in heavy metal sludge filtrate | 8.5 | -- | 32 |
| Magnetite Magnetite | 0.3 – 1.3 1 – 343 | 5x10 ⁻⁹ M Tc in oxic, anoxic syn & natural groundwater 6x10 ⁻⁶ M Tc & 6 mg/L Fe ²⁺ in oxic & anoxic syn & natural groundwater | 7.4 – 8.8 7.4 – 8.8 | 6 x 10 ³ – 6.6 x 10 ⁵ 5.2 – 550 | 7 |
| Activated carbon | 8,000 – 10,000 300 – 5,000 90 – 300 10 – 90 | TcO ₄ solution 1 M NaCl 0.001M NaClO ₄ 0.1 M NaClO ₄ | 10 – 2 10 – 2 10 – 2 10 – 2 | -- | 50 |
| Fe Metal Greigite Hematite Magnetite | 33233 1166 5 3 | 0.2. mg/L TcO ₄ in surrogate raffinate solution | 7 – 9 8.1 – 8.3 3.9 – 6.9 3.9 – 8.9 | 1.3 x 10 ⁴ | 28 |
| Pyrrhotite Stibnite Galena Pyrite Loellingite Chalcocite Sphalerite | ~50000 ~2000 – 50,000 ~50 – 1,000 ~70 – 100 ~0.4 – 400 ~0.4 – 5 ~0.1 – 0.3 | TcO ₄ solution in 0.007 M bicarbonate groundwater | ~5.2 – 7.2 ~7.2 – 7.5 ~6.8 – 7.2 ~2.5 – 7.2 ~6.8 – 7.2 ~5.2 – 7.2 ~7.2 – 9.8 | -- -- -- -- -- -- -- | 6 |
| Stibnite | ~200 | TcO ₄ (2x10 ⁷ Bq/ml) in 0.1 M NH ₄ OH | -- | -- | 58 |
| Stibnite Molybdenite REE hematite | 143 – 1,980 0.6 – 2.7 1.0- 5.1 | TcO ₄ (2x10 ⁷ Bq/ml) in 0.1 M NH ₄ OH | 3.84 – 6.22 -- 8.02 - 8.04 | -- | 23 |
| Silicate minerals (oxic conditions) Silicate minerals (anoxic conditions) | 0.2 – 5 13 -71 | TcO ₄ in 0.16 M NaNO ₃ solution | -- | -- | 9 |
| Pyrrhotite Pyrite Magnetite | 443 – 667 <0.1 <0.1 | 10 ⁻⁶ M TcO ₄ in groundwater | 3.5 – 5.4 5.2 – 5.9 6.6 – 7.6 | -- | 15 |
| Hematite, limonite, goethite, ilmenite, Fe metal Hematite, limonite, goethite, ilmenite Fe metal Magnetite | 0 - 5 4990 0 – 190 ~190 4 – 490 | 3x10 ⁻¹² M TcO ₄ in oxic granite ground-water 3x10 ⁻¹² M TcO ₄ in anoxic granite groundwater 3x10 ⁻¹² – 1x10 ⁻⁴ M TcO ₄ in DI water, granite groundwater, WN-1 saline, Can. Shield saline, Na ₂ HPO ₄ solution, humic acid | ~6.5 ~6.5 – 8.2 | 2x10 ⁷ 2x10 ⁷ 2x10 ⁷ – 2 x 10 ⁹ | 29 |
| Na bentonite , Fe silicate | 132 – 2,269; 0 | 4.187 x 10 ⁻¹⁴ M TcO ₄ in DI water | 5.68 – 10.1 | -- | 65 |
| Silicates, oxides, hydroxides Chalcocite, Chalcopyrite, Galena, molybdenite, Pyrite Gypsum Dolomite Phosphates (Apatite, monazite) | 0 – 26 1.6 – 3.2 1.8 0.3 0.8 – 6.3 | TcO ₄ in 0.01 – 4 M NaCl solutions | -- -- | -- -- | 18 |
| Chrysocolla Chalcopyrite, Enargite, bornite, pyrite, tennantite, Ag- tetrahedrite Galena Tetrahedrite, Bournonite | 10 – 20 ≤3 1 – 10 2 – 2,000 200 – 2,000 | 5x10 ⁵ dpm TcO ₄ solution | -- -- -- -- -- | -- -- -- -- -- | 19 37 |
| Activated Charcoal | 310 -380 | 6- 6 x 10 ⁻⁵ M TcO ₄ in ~5 M NaCl brine | -- | -- | 27 |

| Getter Material | K _d (mL/g) | Matrix Solution | Eq. pH | SO ₄ /TcO ₄ M Conc Ratio | Ref |
|---|-----------------------|--|--------|--|-----|
| Bentonite, hectorite | 0 - 1 | | -- | -- | |
| Augite Biotite Galena, sphalerite ,Smithsonite,CuO, Cu ₂ O, PbO Magnetite, graphite | 23 1 0 0 | 1 x 10 ⁻⁴ M TcO ₄ solution | -- | -- | 30 |

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