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Selection and Testing of "Getters" for Adsorption of Iodine-129 and Technetium-99: A Review

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Executive Summary

During the last several decades considerable research effort has been expended to identify suitable "getter" materials that can immobilize or delay the transport of anionic radionuclides (such as 129I and 99TcO4) that would be released from physically and chemically degrading waste packages. Several investigators have identified a number of important performance characteristics such as adsorption potential and chemical/physical stability that getter materials should possess for effective deployment in repository environments. A review of published literature indicated that various minerals and synthetic adsorbent materials such as, oxides, hydroxides, natural and modified aluminosilicates, sulfides, carbonates, phosphates, carbon, and functionalized novel sorbents have been tested for their getter properties.

Oxide/hydroxide solids and many silicate minerals have poor capacity and selectivity for iodide (Kd : 0 – 10 ml/g) and release iodide with increasing pH. A few silicate minerals such as illite exhibit better selectivity for iodide (Kd : ~30 ml/g). Significantly improved iodide selectivity (Kd : 5,000 ml/g) has been observed with organically-modified silicate minerals such as montmorillonite and vermiculite. Sulfide minerals such as cinnabar and argentite typically adsorb iodide with very high selectivity (Kd : 3,000 – 80,000 ml/g). Synthetic materials such as calcium monosulfate aluminate and hydrotalcite show moderate iodide selectivity (Kd: ~25 – 300 ml/g). A new class of specially-designed synthetic getters when tested in groundwater and simulated waste package leachate adsorbed iodide with very high specificity (Kd: 100,000 – 1,000,000 ml/g). The long-term stability of these mineral and synthetic getters in post-closure environment needs further evaluation.

Under oxic conditions and in groundwater or background salt solution, many of the oxide/ hydroxide solids and silicate minerals exhibit relatively poor capacity and selectivity (Kd: <5 ml/g) for Tc. Therefore, a potential lack of long-term stability precludes using many of the oxide and hydroxide minerals as effective getter materials for technetium. Although, magnetite and metallic iron under certain limited conditions appear to be effective getters for Tc (Kd: 350 – 122,000 ml/g), their chemical stability and their tendency for Tc mobilization from radiolysis effects and potential influx of oxic ground waters and/or leachates need to be evaluated on a site-specific basis. Among sulfide minerals, greigite appears to be best in immobilizing Tc (Kd: ~110 – 6100 ml/g). Principal mechanisms for Tc attenuation by sulfide minerals are through either reduction of Tc(VII) to low solubility Tc(IV) phases such as $TcO_2 \cdot xH_2O$ or by direct precipitation of Tc(VII) as a sparingly-soluble sulfide mineral, Tc_2S_7. Novel Cu-EDA SAMMS getters in groundwater and simulated waste package leachate have been shown to adsorb TcO_4^- (Kd: ~50 – 800 ml/g). The long-term stabilities and the adsorption performance of miscellaneous minerals and synthetic compounds under typical post closure conditions in any facility such as the Immobilized Low Activity Waste (ILAW) repository at Hanford need further evaluation.

A selection and evaluation scheme is proposed to identify appropriate getter materials that are i) chemically (including redox) and physically stable enough to be used as barrier materials, ii) not affected adversely by biotic factors that would compromise the contaminant adsorption performance to any measurable degree, and iii) cost effective and offer flexibility in deployment.

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1.0 Introduction

One of the preferred methods for safely disposing intermediate and low activity radioactive wastes involves vitrifying these wastes and sequestering the resulting waste glass forms in engineered shallow burial sites. One of the important factors for evaluating the long-term (~10,000 to 100,000 years) viability of such storage practices is the potential release of long-lived radionuclides such as ^{129}I, ^{237}Np, ^{79}Se, ^{99}Tc, and ^{233,235,238}U from the glass waste forms. Currently, a performance assessment (PA) is underway to evaluate the suitability of the unsaturated sediments at the Hanford Site for the long-term disposal of vitrified low-activity waste. This assessment includes predictions of the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. Previous analyses for proposed disposal actions on the Hanford site show that groundwater transport and consumption present the greatest potential for long-term dose uptake by humans (Mann et al. 1998 and Mann et al. 2001). Furthermore, these previous analyses have shown that the key risk drivers at the proposed disposal site include ^{129}I, ^{237}Np, ^{79}Se, ^{99}Tc, and ^{233,235,238}U.

It is anticipated that the leachate from glass waste forms (located in the Immobilized Low-Activity Waste [ILAW] facility) will have high ionic strengths (high concentrations of dissolved constituents, ~200 – 1500 mg/L) and will be extremely alkaline (pH 12- 13) (Mann et al. 1998). Under such extreme conditions several complex geochemical reactions are known to occur in waste forms, neighboring engineered structures, and the surrounding sediments that include: dissolution of several oxide/hydroxide and silicate minerals, precipitation of secondary and tertiary mineral phases, radionuclide adsorption onto minerals (primary, secondary, and tertiary), and sequestration of radionuclides into secondary and tertiary mineral phases (Mattigod et al. 1998, 2002).

During the last several decades, considerable research effort has been expended to identify suitable "getter" materials that can immobilize or delay the transport of anionic radionuclides (^{129}I and ^{99}TcO$_4$) that would be released from physically and chemically degrading waste packages. Metallic copper and its oxides (Haq et al. 1980), soils and soil minerals (Rancon 1988), cementitious forms (Atkins and Glasser 1990), various types of minerals (Coutore and Seitz 1983, Gradev 1987, Taylor 1990, Fetter et al. 1996, Kang et al. 1999, Krumhansl 2003), organophilic clays (Bors et al. 1994), modified montmorillonites (Sazarashi et al. 1995), and novel adsorbents (Mattigod et al. 2000; Kaplan et al. 2000b) have been tested and evaluated for their getter properties for radioiodine. Similar effort has been expended to identify suitable getters for Tc (Strickert et al. 1980; Palmer and Meyer 1981; Lieser and Bauscher 1988, Winkler et al. 1988, Ito and Kanno 1988, Zhuang et al. 1988, Bock et al. 1989, Byegard et al. 1992, Cui and Eriksen 1996, Kunze et al. 1996, Liang et al. 1996, Balsley et al. 1996, 1997, 1998; Kang et al. 1996, 1999; Viani 1999; Mattigod et al. 2000; Krumhansl 2003, Moore 2003).

These investigations indicate that deployment of suitable getter materials is considered to be an important aspect of effective secondary long-term containment of long-lived radionuclides. The objective of this study was to, 1) conduct a survey of the literature on I and Tc getters,

2) evaluate the efficacy of these materials to specifically adsorb the radionuclides of concern, and 3) assess and identify the needed research to fully evaluate the critical properties of getters before they can be deployed successfully.

2.0 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 in repository environments (Coons et al. 1980; Klingsberg and Duguid 1980; Nowak 1980a; Moak 1981; Viani 1999). Viani (1999) provided the most comprehensive list of criteria that can be used to assess the properties of potential getter materials. Following is a discussion of these criteria.

2.1 Adsorption Potential and Capacity

- The getter material should specifically adsorb the radionuclide of interest from the leachate generated from the chemical weathering of waste glass packages.
- The getter should exhibit very high selectivity towards radionuclides of concern present in the waste glass leachate 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 so that the mass and volume of the material that will be deployed will 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.

2.2 Physical and Chemical Stability

The getter material should:

- Possess sufficient physical and chemical stability so that its radionuclide retention performance in the post closure environment will not degrade significantly during the designed life span of the repository.
- Be physically robust so that the particles will not disintegrate when subjected to moisture, temperature, and the radiation regime within the repository.
- Be chemically stable under the range of Eh, pH, and solution conditions that are predicted to exist in the post closure environment without noticeable degradation in its functionality.
- Not adversely affect the vadose zone water chemistry by releasing toxic components into the waste leachate.

It should also 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.

2.3 Getter 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.

2.4 Getter 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 the above criteria. In the following review, we will examine the published data and evaluate the extent to which the potential getter materials meet these criteria. We will also discuss additional data needs to fully evaluate and identify suitable getter materials.

3.0 Iodine Getters

Under Eh-pH conditions typically encountered in ground waters, surface waters, glass and cement leachates, iodine exists mainly as iodide. Iodine can exist as iodate ions only under highly oxidizing conditions. Therefore, a significant fraction of iodine in glass and cement waste forms may also exist in the form of iodide.

Several types of natural and modified minerals have been tested as suitable getters for radioiodine. These 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 to specifically remove radioiodine have been synthesized and tested for their getter properties. Published data on iodine getters from various sources are listed in Table 1.

3.1 Oxides and Hydroxide Minerals

Oxide, hydroxide, and oxyhydroxide minerals typically exhibit low affinity for iodide ions. The distribution coefficient values for these minerals tested in distilled water matrices range from 0 – 6 ml/g (Rancon 1988; Zhuang et al. 1988). In one study involving copper oxides, a K_d value as high as 40 ml/g has been reported (Haq et al. 1980). When these minerals were tested either in groundwater or alkali chloride media, lower K_d values (0 – 3 ml/g) were observed (Allard et al. 1981; Hakem et al. 1996).

Recently, various layered double hydroxide (LDH) compounds (commonly known as hydrotalcites) with higher anion exchange capacities than natural minerals have been synthesized and tested for their ability to adsorb iodide (Balsley et al. 1996, 1999; Kang et al. 1999; Krumhansl 2003). Kang et al. reported K_d values that ranged from 38 – 31,000 ml/g for an Mg,Al hydrotalcite compound tested in competing anion free solutions. However, when various hydrotalcites were tested (Krumhansl 2003) in dilute sodium salt (nitrate, nitrite, aluminate, hydroxide) solutions the K_d values obtained (5 – 3,390 ml/g) were about an order of magnitude lower than the values obtained in tests without any competing anions being present (Kang et al. 1999). Similarly, lower K_d values that ranged from 25 – 290 ml/g were reported for iodide adsorption when samples of Zn-bearing hydrotalcites were tested in 0.01M sodium chloride solutions (Balsley et al. 1996, 1997).

The adsorption sites on these minerals are hydroxyls that ionize from either protonation or deprotonation; consequently, they exhibit adsorption capacities that vary as a function of pH. Typically, there is a critical pH (PZC) at which each of these minerals have an equal number of protonatated and deprotonated adsorption sites. Therefore, the anion adsorption capacities of these minerals increase with decreasing pH; whereas, the adsorption capacity decreases as pH values increase above the PZC. Also, because the anion adsorption sites on oxide/hydroxide are not very selective (except for LDH compounds), the adsorbed anions can be easily desorbed by other anions that are present in higher concentrations in contacting solution. If changes occur in

the post closure environment, such as pH increase and changes in contacting solution, radioiodine retained on oxide and hydroxide minerals would be mobilized with the concomitant loss in getter efficacy.

Due to their poor adsorptive capacity (under higher pH conditions predicted in the ILAW environment) and selectivity for radioiodine, and their potential lack of chemical stability, oxide and hydroxide minerals would not meet two important criteria to be reliable getter materials. Although synthetic LDH compounds exhibit better iodide adsorption characteristics, than oxide/hydroxide minerals, their desorptive properties have not been tested. Additional testing needs to be conducted to adequately evaluate the potential of the LDH compounds as iodine getters.

3.2 Silicate Minerals

Aluminum and magnesium silicate minerals such as allophane, montmorillonite, kaolinite, attapulgite, sepiolite, illite, halloysite, vermiculite, and clinoptilolite have been tested as potential iodine getters. These minerals typically have distribution coefficients that range from 0 – 10 ml/g (Allard et al. 1981; Rancon 1988; Sazrashi et al. 1994). In one case, a K_d value as high as 28 ml/g has been reported for illite (Kaplan et al. 2000a). These data show that the silicate minerals have similar selectivity for radioiodine as oxide and hydroxide minerals. This is not surprising considering that the major anion adsorption mechanism of silicates is similar to that of oxide-hydroxide minerals. Although in the case of illite, it is hypothesized that a minor fraction of radioiodine may substitute for structural hydroxides in the illite structure.

Several attempts have been made to improve the capacity and selectivity of the silicate minerals by treating them with organic compounds (Sazrashi et al. 1995; Bors 1990, 1992; Bors et al. 1994, 1996, 1998). Treated silicate minerals such as montmorillonite and vermiculite yielded K_d values as high as 5000 ml/g. Improved adsorption performance of these organic-modified minerals has been demonstrated in synthetic ground- and sea- water matrices in which the competing anions, such as chloride, were present in concentrations up to nine orders of magnitude higher than radioiodine in solution. (Bors 1992, Bors et al. 1998). However, the desorption characteristics of these organic-modified silicates are unknown. Additionally, the long-term chemical stability of these materials needs to be established because the organic component may be prone to microbial attack with resulting loss of getter functionality. Such microbial degradation could rapidly mobilize the adsorbed radioiodine. Therefore, desorptive properties, chemical stability, and cost of these organics-modified silicates need to be investigated further to assess their suitability as getter materials for radioiodine.

3.3 Sulfide Minerals

A number of sulfide minerals have been tested as potential iodine getters. These include copper sulfides, a variety of Cu-Fe bearing sulfides, and sulfides of Fe, Pb, Ag, and Hg. For Cu-sulfide minerals (covellite and chalcocite), Balsley et al. (1996, 1997) reported K_d values ranging from about 60 to 1400 ml/g. Tests on Pb sulfide indicate K_d values that range from 30 – 140

ml/g (Strickert et al. 1980; Zhuang et al. 1988; Rancon 1988). A number of Cu-Fe bearing sulfides were tested in a DI water matrix by Strickert et al (1980) for their iodide adsorption affinities. They reported K_d values for these minerals that ranged from 4 – 3,000 ml/g. The Cu-Fe sulfide minerals on average exhibit higher iodine K_d values than both oxide-hydroxide and unmodified silicate minerals. Among the sulfide minerals, the data indicate that Hg-sulfide (cinnabar) and Ag-sulfide (argentite) show high iodine selectivity. Tests conducted in different media such as groundwater, surface water, waste glass leachate, and concrete leachate showed that K_d values can be as high as ~3,000 ml/g for Hg-sulfide and ~80,000 ml/g for Ag-sulfide (Mattigod et al. 2000, Kaplan et al. 2000b).

One of the principal reasons for sulfide minerals' better performance in general can be ascribed to the nature of cationic species in the sulfide minerals. The cations that form sulfides typically have larger ionic radii, low electronegativity, and are highly polarizable. Such characteristics are categorized as soft acid behavior. According to the hard and soft acid and base (HSAB) principle (Sposito 1981), soft cations tend to bind strongly with soft bases (low electronegativity, high polarizability, prone to oxidation) such as iodine and sulfide. Therefore, relatively softer cations such as Hg and Ag have better iodine getter properties as compared to less soft cations such as Cu (I, II), Fe(II), and Pb.

Although sulfides show the best getter characteristics among all minerals, their long term chemical stability as getters has not been established. It is well known that sulfides oxidize and form highly soluble sulfate minerals. Such reaction would result in mobilization of not only radioiodine but also toxic constituents, such as Hg and Ag from these oxidized getters. Therefore, it is imperative to evaluate the rate of oxidation and concomitant release of radioiodine and the toxic components to evaluate the suitability of these minerals as potential getters for iodine.

3.4 Miscellaneous Minerals

Materials such as bituminous and lignitic coals have been tested for their capacity to adsorb radioiodine (Balsley et al. 1997). In these tests, coals exhibited higher K_d values at low pH values (~500 to 800 ml/g at pH 3.3 –3.9). At higher pH values (9.9) these materials showed a significant reduction in K_d values (0 –25 ml/g) indicating that coals behave very much like oxides and hydroxides in that their anion adsorption capacity declines drastically at pH values above PZC. Therefore, coals as iodine getters have the same limitations (low adsorption affinity under typical high pH post closure conditions in an ILAW facility) as oxide and hydroxide minerals. Additionally, coals have an inherent tendency to oxidize and release adsorbed constituents. Thus the long-term stability of these materials is practically unknown.

Tests conducted on the synthetic material calcium monosulfate aluminate in dilute sodium chloride solutions indicated that the radioiodine affinity (K_d) of this material ranges from 25 – 290 (Balsley et al. 1997). Other materials, such as a Pb-carbonate mineral (cerrussite) and metallic copper, have also been tested as iodine getters (Rancon 1988, Haq et al. 1980). Due to the limited test data on these miscellaneous materials, their potential as getters for iodine cannot be fully evaluated.

3.5 Novel Synthetic Mesoporous Silica Materials

During the last few years, a new class of getter materials has been developed. These consist of mesoporous ceramic substrates with specifically tailored pore sizes (from 20 - 100 Å) and very high surface areas (~1000 m^2/g).   These high-surface area substrates are functionalized with monolayers of well-ordered functional groups that have high affinity and specificity for specific types of free or complexed cations or anions (Figure 1). These self-assembled monolayers on mesoporous silica (SAMMS) materials with high adsorption properties have been successfully tested on a series of cations (Hg, Cu, Cd, and Pb), oxyanions (As, Cr, Mo, and Se), anions (I), and actinides (Pu, U, and Np). Detailed descriptions of the synthesis, fabrication, and adsorptive properties of these novel materials have been previously published (Fryxell et al. 1999a,b; Kemner et al. 1999; Liu et al. 1998, 2000; Mattigod et al. 1997, 1998).

Recently, some of the metal-capped thiol-SAMMS materials specifically designed to adsorb soft anions such as iodine have been tested for their getter properties. These tests included iodide adsorption from aqueous matrices that are expected to prevail in post closure environments such as groundwater, surface water, glass leachate and concrete leachate. The data showed that the metal-capped SAMMS materials had iodide K_d values as high as $10^5 – 10^6$ ml/g (Mattigod et al. 2000, 2003a,b; Kaplan et al. 2000b). These high values indicate the remarkable selectivity of these novel materials in adsorbing iodide in view of the fact that the contacting natural solution matrices contained competing halide ions such as Cl, Br, and F in concentrations that far exceeded (eight to ten orders of magnitude higher) the concentrations of radioiodine.

A reason for this selectivity can be explained on the basis of the Hard and Soft Acid and Base (HSAB) principle. According to the HSAB principle, hard acid cations preferentially bind with hard anions and similarly, soft cations form strong bonds with soft anions (Sposito 1981). The degree of hardness or softness is based on the ion size, oxidation state, electronegativity and polarizability. For instance soft cations and anions possess relatively large sizes, have lower oxidation states (= 2 ±), lower electronegativity, and high polarizability. The iodide ion is a softer anion among the halide anions and similarly, Ag and Hg are the softest cations (Sposito 1981) therefore, Ag and Hg SAMMS preferentially adsorb softer I ions even in the presence of higher concentrations of less soft anions such as, F, Cl, and Br.

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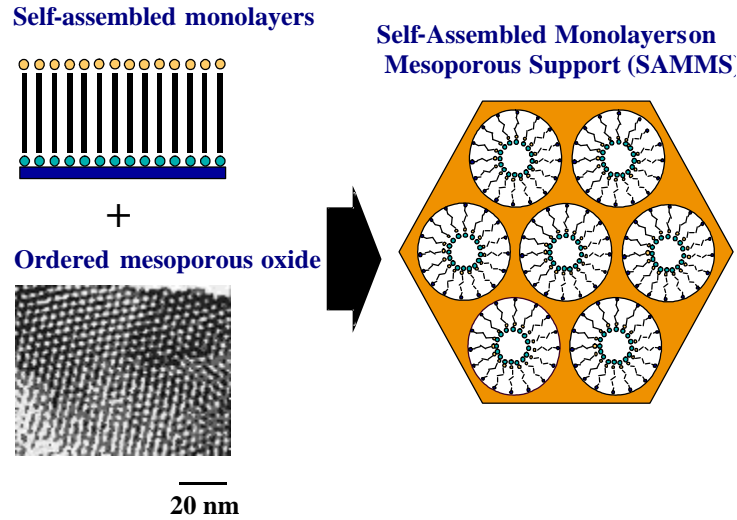
Figure 1. Technological Basis of Novel getters (SAMMS)

Presently, the long-term chemical stability of these novel materials has not been tested. However, it is expected that these materials would have significantly better stability than minerals because 1) the matrix of SAMMS materials are siliceous therefore, unlike sulfide minerals will not be affected by changes in redox conditions. 2) the specificities and capacities of functional groups in SAMMS materials are specifically designed to be relatively buffered from changing pH conditions whereas, the adsorption functionalities of minerals perform less efficiently above the pH PZC, and 3) the functional groups attached to the SAMMS materials are confined mainly within micropores (2 – 6 nm in diameter) as compared to functional groups that are on the external surfaces of minerals; consequently, the SAMMS functional groups are better protected from any potential microbial degradation. However, additional experiments need to be conducted on SAMMS materials to test these stability hypotheses.

Table 1. Iodide Distribution Coefficient Data for Natural and Synthetic Getter Materials

Getter Material	Kd (ml/g)	Matrix Solution	Eq. pH	Molar Conc Ratio (Cl, Br, F)/I	Reference
Hydrotalcites (Al, Bi, Cu2+, Cu+, La, Sn2+, Sn4+, Zn)	5 – 3,390	Dilute $NaNO_3$-$NaNO_2$, NaOH-$NaAlO_2$ Solution	--	--	Krumhansl 2003
Hg-thiol SAMMS	100,000	Groundwater	6.32 – 7.24	Cl/I: $3x10^{10}$ – $9x10^{10}$	Mattigod et al. 2000, 2003
	420,000	Glass Leachate	3.46 – 8.34	Br/I: $2x10^8$	
Ag-thiol SAMMS	99,000	Groundwater	6.79 – 7.37	F/I: $1x10^9$	
	100,000	Glass Leachate	4.41 – 8.35		
Cinnabar	2600	Glass Leachate	7.97 – 8.03		
Argentite	18,000	Glass Leachate	2.66 – 8.33		
Chalcocite	50 – 200	Glass Leachate	8.32 – 8.47		
Chalcopyrite	10 – 50	Glass Leachate	8.18 – 8.27		
Hg-thiol SAMMS	2,000 – 2,000,000	Surface water	3.00	Cl/I: $1x10^{10}$	Kaplan et al. 2000b
	8,000 – 600,000	Conc Leachate	9.55	Br/I: $2x10^7$- $1x10^8$	
Ag-thiol SAMMS	20,000 – 300,000	Surface water	3.72	F/I: $4 x 10^8$ - $1x10^9$	Mattigod et al. 2003 b
	9,000 – 600,000	Conc Leachate	11.94		
Cinnabar	700 – 3,000	Surface water	8.15		
	0 – 100	Conc Leachate	12.17		
Argentite	0 – 80,000	Surface water	5.98		
	20,000 – 700,000	Conc Leachate	11.94		
Ag-carbon	1,000 – 5,000	Surface water	7.56		
	2 0 – 4,000	Conc Leachate	11.18		
Illite	15 - 28	0.01M $CaCl_2$		Cl/I: $3 x 10^{12}$	Kaplan et al. 2000a
Hydrotalcite (Al)	38 – 31,000	$4.6 x 10^{-6}$ M ^{125}I in $1.8 x 10^{-5}$ – $5.3 x 10^{-2}$ M NaI and HI solution	10.62 -11.5		Kang et al. 1999
Titanium Oxide	0.25 – 3	0.001M NaCl	9.5 - 3.5	--	Hakem et al. 1996
Titanium oxide	0.05 – 0.11	0.1M NaCl	9.5 - 3.5		
Cinnabar	70 – 3,400	0.01M NaCl	10.0 – 4.0	Cl/I: 100	Balsley et al 1996 1997
Covellite	145 – 1,380	0.01M NaCl	8.3 – 4.0		
Chalcocite	60 – 1,290	0.01M NaCl	10.0 – 4.0		
CMSA 1	34 –110	0.01M NaCl	10.0 – 4.0		
CMSA2	30 – 100	0.01M NaCl	10.9 – 5.6		
Zn hydrotalcite-Cl	25 – 290	0.01M NaCl	10.0 – 4.1		
Zn hydrotalcite-SO_4	50 – 290	0.01M NaCl	10.0 – 4.1		
Zn hydrotalcite-CO_3	40 –80	0.01M NaCl	10.5 –4.8		
Lignite Coal	0 –520	0.01M NaCl	9.9 –3.9		
Subbituminous Coal	25 -840	0.01M NaCl	9.9 – 3.3		
Ag-thiourea mont	61 – 4,900	NaI and NaCl	~7.0	Cl/I: ~0 - 19	Sazarashi et al. 1994 1995
Allophane	2.1 – 3.6	0.01M KI	5.6 –6.0		
Attapulgite	0.2 – 0.9	0.01M KI	8.0		
Montmorillonite	0	0.01M KI	7.7 – 8.1		
Chalcopyrite	14.1 – 15.1	0.01M KI	6.3 – 6.6		
Cinnabar	4,000 – 20,000	0.01M KI	6.9 – 7.0		
Cinnabar	0 - 50	NaI and NaCl	9.4	Cl/I: 1	Ikeda et al. 1994

Table 1. (contd)

Getter Material	Kd (ml/g)	Matrix Solution	Eq. pH	Molar Conc Ratio (Cl, Br, F)/I	Reference
Org.treated bentonite	2 – 1,500	DI water	10.0 – 8.7	--	Bors 1990
Org-treated vermiculite	1 – 26,000	DI water	10.0 –9.4		
Org-treated Cretaceous clay	4 – 30,000	DI water	9.6 –8.4		
HDPY-vermiculite	10 – 5,500	DI water	--	--	Bors 1992
HDPY-vermiculite	10 – 4,500	syn groundwater	--	Cl/I: ~2x 10^{10}	
HDPY cretaceous Clay	10 – 5,500	DI water	--		
HDPY-cretaceous Clay	10 – 800	syn groundwater	--	Cl/I: ~2x 10^{10}	
HDPY-vermiculite	2 – 10,000	KI soln	--	--	Bors et al. 1994
HDPY-cretaceous Clay	1 – 10,000	KI soln	--		
HDPY-vermiculite	25 – 3,390	DI water	--	--	Bors et al. 1996
HDPY-MX80 bentonite	3 – 5,000	DI water	--	Cl/I: ~3 x 10^9	Bors et al. 1998
HDPY-MX80 bentonite	2 – 1,000	syn groundwater	--	Cl/I: ~4 x 10^6, F/I:~1x10^8	
HDPY-MX80 bentonite	10 – 450	natural water	--	Cl/I: ~5 x 10^6	
HDPY-MX80 bentonite	0 - 350	1/2 strength seawater	--		
Chalcopyrite	700	NaI solution	7.2	--	Rancon 1988
Chrysocolla	40	NaI solution	7.2		
Cerussite	8	NaI solution	7.0		
Galena	80	NaI solution	8.6		
Bauxite, goethite, hematite, laterite, limonite, siderite	0 – 6	NaI solution	6.5 – 7.6		
Quartz, attapulgite, bentonite, illite, clinoptilolite, kaolinite, sepiolite, vermiculite, zeolite	0 - 4	NaI solution	6.0 – 8.4		
Chalcopyrite	42 –97	DI water	7.73 – 8.24	--	Zhuang et al. 1988
Galena	62 – 137	DI water	3.53 – 6.14		
Pyrite	3 – 6	DI water	7.05 – 8.10		
Stibnite	2 – 3	DI water	4.52 - 5.66		
Molybdenite	1 – 3	DI water	7.62 – 7.89		
Rare-earth hematite	1 - 2	DI water	7.91 – 8.34		
Cinnabar	10 – 100	Groundwater, 4M NaCl	9.0 - 3.0	Cl/I: ~3x10^8 - 4x10^6	Allard et al. 1981
Chalcopyrite, Galena	0.1 –10		9.0 - 3.0		
Fe, Al, Pb hydroxides	0.1 - 100	Groundwater, 4M NaCl	9.0 - 3.0		
Olivine, attapulgite, sepiolite, halloysite, montmorillonite, quartz	0.1 – 10	Groundwater, 4M NaCl	9.0 - 3.0		
Metallic Cu	0.4 – 190	NaI soln	7.2	--	Haq et al. 1980
Cuprite	4 – 40	NaI soln	7.2		
Tenorite	0.5 -23	NaI soln	7.2		
Bournonite	200 – 1,000	DI water	--	--	Strickert et al. 1980
Pyrite	300 – 3,000	DI water	--		
Tetrahedrite	4 – 1,500	DI water	--		
Bornite	30 – 970	DI water	--		
Tennantite	100 – 350	DI water	--		
Enargite	150	DI water	--		
Chalcopyrite	190	DI water	--		
Galena	26	DI water			

4.0 Technetium Getters

Under Eh-pH conditions typically encountered in ground waters, surface waters, glass and cement leachates, technetium exists mainly in the 7+ redox state (TcO_4^-). Under reducing conditions, the stable form technetium is the less soluble Tc(IV). In oxidizing, alkaline leachates originating from glass and cement waste forms the stable form of technetium is expected to be pertechnetate ((TcO_4^-).

The same types of minerals that have been tested as getters for radioiodine have also been tested for their technetium getter properties.   A number of studies have been conducted to evaluate the getter properties of various oxides, hydroxides, silicates, sulfides and activated carbon. A novel getter that was developed for adsorption of tetrahedral oxyanions has also been tested for its ability to remove technetium from groundwater and glass leachate. Published data on technetium adsorption are listed in Table 2.

4.1 Oxides and Hydroxide Minerals

Adsorption tests have shown that iron oxides and hydroxides have relatively low affinity (K_d: 0.2 – 5 ml/g) for pertechnetate ion (Palmer and Meyer 1981). Their data also indicated that these minerals exhibited anion adsorption behavior that is typical for minerals with variable surface charge i.e., these minerals exhibited decreasing affinity for pertechnetate ion with increasing pH of the contacting solution. Studies conducted on hematite by Zhuang et al. (1988) and Bostick et al. (1990) resulted in K_d values that were similar in magnitude (1 – 5 ml/g) to that noted by Palmer and Meyer (1981). Another study involving extensive tests on various types of iron oxides in granitic groundwater indicated K_d values of (0 – 5 ml/g) under oxic conditions, and relatively higher K_d values of (0 – 190 ml/g) under anoxic conditions (Vandergraff et al. 1984). These increases in K_d values were attributed to potential reduction of Tc(VII) to the less soluble Tc(IV) form. Also, other experiments conducted to investigate the effects of various matrix solutions on Tc immobilization by magnetite indicated K_d values ranging from 4 – 490 ml/g (Vandergraff et al. 1984). However, lower K_d values (4 – 57 ml/g) were observed in matrix solutions containing Tc (IV) complexing ligands such as chlorides and phosphates. In another study, Bird and Lopata (1980) using only tracer solutions noted no measurable pertechnetate adsorption by magnetite. Studies by Lieser and Bauscher (1988) using groundwater and Bostick et al. (1990) using simulant raffinate also showed negligible adsorption of Tc (K_d: <0.1 – 3 ml/g) on magnetite. These observations were confirmed by Byegard et al. (1992) who observed that magnetite, when tested in synthetic and natural groundwater matrices (containing relatively high concentration of SO_4) under both oxic and anoxic conditions, showed relatively poor affinity for Tc (K_d: 0.3 – 1.3 ml/g). However, in tests conducted in groundwaters containing relatively low concentrations of SO_4 and fortified with 6 mg/L of ferrous iron, Byegard et al. (1992) observed enhanced attenuation of Tc (K_d: 1 – 343 ml/g), which was attributed to oxidation of Fe (II) coupled with reduction of Tc(VII) to more insoluble Tc(IV) species.

Detailed studies of the reductive immobilization mechanisms for Tc by Fe(II)-bearing minerals were conducted by Cui and Eriksen (1996). They found that 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 Tc reduction. 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.

A number of studies have been conducted to examine the effectiveness of metallic iron for promoting immobilization of Tc through reduction reaction (Vandergraff et al. 1984; Del Cul et al. 1993; and Kunze et al. 1996). Studies conducted by Vandergraff et al. (1984) with metallic iron substrate in granitic groundwater yielded relatively high K_d values of (190 – 4990 ml/g). The effectiveness of metallic iron for reductive immobilization of Tc (in heavy metal sludge filtrates and simulated raffinate solutions) was also confirmed by studies conducted by Del Cul et al. (1993); and Bostick et al. (1990), who observed K_d values as high as 18,900 – 33,233 ml/g. Metallic iron was also observed (Kunze et al. 1996) to successfully immobilize Tc in 6 -12 M magnesium chloride brine (K_d ~121,700 ml/g).

Adsorption tests conducted by Bird and Lopata (1980) indicated that Cu and Pb oxides (CuO, Cu_2O, and PbO) did not adsorb any pertechnetate. In contrast, recent studies conducted by Balsley et al. (1997) indicated that when tested in a DI water matrix, Cu oxides did adsorb (K_d: 43 – 55 ml/g) TcO_4^- ions. However, they did not test the affinity of these oxides for technetium in the presence of competing tetrahedral anions such as sulfate. In another study, Zhang et al. (2000) demonstrated that boehmite (Al oxyhydroxide mineral) can adsorb perrhenate (an analog for pertechnetate). Their data also showed significantly less adsorption with increasing pH with no adsorption at pH values greater than ~8. They also noted decreasing perrhenate adsorption in the presence of increasing concentrations (0.005 – 0.1M) of a competing oxyanion, such as NO_3, in solution. Palmer and Meyer (1981) also observed that, when tested in sodium chloride brine medium, a number of oxide/hydroxide minerals exhibited relatively low adsorption affinity (K_d: 0 -26 ml/g) for Tc.

Synthetic layered double hydroxide (LDH) compounds (hydrotalcites) have been tested for their ability to adsorb pertechnetate (Kang et al. 1996, Balsley et al. 1997; Krumhansl 2003). Kang et al. reported K_d values that ranged from 265 – 6,160 ml/g for an Mg,Al hydrotalcite compound tested in competing anion free solutions. Also, various hydrotalcites tested by Krumhansl (2003) adsorbed pertechnetate (K_d: 137 – 4,890 ml/g) from dilute sodium salt (nitrate, nitrite, aluminate, hydroxide) solutions. Significantly lower K_d values (1 – 84 ml/g) for pertechnetate adsorption were obtained for a sample of Zn-bearing hydrotalcite (Balsley et al. 1997).

These studies indicate that relatively poor capacity, selectivity and potential lack of chemical stability preclude using many of the oxide and hydroxide minerals as effective getter materials for technetium. Synthetic 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 Tc. However the chemical stability and the tendency for Tc

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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.

4.2 Silicate Minerals

Bird and Lopata (1980) tested a number of silicate minerals and found negligible pertechnetate adsorption from a tracer solution by biotite and kaolinite and limited adsorption by augite (K_d: 23 ml/g). A copper silicate mineral (chrysocolla) tested by Strickert et al. (1980) showed a limited degree of Tc adsorption (K_d: 10 -20 ml/g).   Palmer and Meyer (1981) also tested a number of primary silicate minerals and found that they had similar adsorption characteristics as oxide, hydroxide minerals in that they showed relatively low affinity for technetium (K_d: 0 – 3.4 ml/g). Similar results were obtained by Ito and Kanno (1988) using silicate minerals under oxidizing conditions (K_d: 0 – 3.4 ml/g). Another set of experiments conducted under reducing conditions yielded K_d values ranging from 13 –71 ml/g. These higher values under reducing conditions can be attributed principally to reduction of Tc(VII) and subsequent precipitation of Tc(IV) and not due to adsorption reactions. Tests conducted by Shade et al. (1984) on two silicate minerals in a groundwater matrix indicated K_d values of ~130 – 2270 ml/g for a sample of Na-bentonite, whereas, the synthetic Fe-silicate did not adsorb any Tc. Comparatively, studies conducted by Nowak (1980b) on samples of bentonite and hectorite in 5M sodium chloride brine (reflecting the Yucca Mountain repository environment) showed very low affinity for Tc (K_d: 0- 1 ml/g). These data suggest that the silicate minerals are not reliable getters for immobilizing Tc.

4.3 Sulfide Minerals

Studies conducted in DI water matrices (Strickert et al. 1980; Lieser and Bauscher 1988), in 0.1 – 4M sodium chloride solutions (Palmer and Meyer (1981), and in 0.1M ammonium hydroxide solution (Zhuang et al 1988) indicated that sulfide minerals such as chalcopyrite, chalcocite, enargite, bornite, galena, molybdenite, pyrite, tennantite, Ag- tetrahedrite, had relatively low affinity for pertechnetate ion (K_d: <0.1 - = 3 ml/g). However, using finely-ground (<63 µm) material in DI water matrix, Bock et al. (1989) noted galena and pyrite exhibited higher K_d values of 50 – 1000 and 70 -100 ml/g respectively. These investigators also observed that other sulfide minerals such as, pyrrhotite and stibnite had very high affinity (~50,000 ml/g) for the pertechnetate ion.   In studies using <10 µm particle size pyrrhotite in a groundwater matrix, Lieser and Bauscher (1988) showed that this mineral had only moderate affinity to attenuate Tc(VII). Similar adsorption affinity for Tc (VII) was measured (K_d: ~143 – 1980 ml/g) for sand-sized (125 - 250 µm) stibnite. Another sulfide mineral, greigite was also found to effectively remove technetium from raffinate simulant (K_d: ~1170 ml/g) and from heavy metal sludge filtrate (K_d: ~110 – 6100 ml/g) (Bostick et al. 1990; Del Cul et al. 1993).

Published data indicate that Tc adsorption performance of sulfide minerals are highly variable and appear to depend on a number of factors such as type of mineral, particle size, the type of contacting solution, pH, ionic strength, and Eh (Lee and Bondietti 1983; Bidoglio et al.

1985; Bock et al. 1989; Fried et al. 1978; Strickert et al. 1980; Palmer and Meyer 1981; Lieser and Bauscher 1988; Zhuang et al. 1988, 1995; Balsley et al. 1997a). It is generally recognized that the principal mechanisms of Tc attenuation by sulfide minerals are through either reduction of Tc(VII) to low solubility Tc(IV) phases such as $TcO_2 \cdot xH_2O$ (Bock et al. 1989) or by direct precipitation of Tc(VII) as a sparingly-soluble sulfide mineral, Tc_2S_7 (Lee and Bondietti 1983; Bidoglio et al. 1985, Lieser and Bauscher 1988). Although some sulfide minerals show better Tc attenuation characteristics, their long term stability (chemical, physical and microbiological) for deployment as Tc getters has not been established. It is also necessary to establish the rate of oxidation and concomitant rate of release of Tc(VII) from various sulfide getters.

4.4 Miscellaneous Minerals

Materials such as activated carbon (charcoal) have been tested for its capacity to adsorb pertechnetate (Nowak 1980b, Ito and Akiba 1991). Test results by Nowak (1980b) in 5M sodium chloride solution showed moderate affinity (K_d 310 – 380 ml/g) for Tc(VII). However, tests conducted by Ito and Akiba (1991) showed 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 a 1M sodium chloride solution (K_d: 300 – 5,000 ml/g), and in a $NaClO_4$ solution (K_d 10 – 300 ml/g).

Minerals such as, gypsum, dolomite, apatite and monazite have relatively low affinity (K_d 0.3 – 6 ml/g) for Tc(VII) (Palmer and Meyer 1981). Tests conducted on a synthetic compound (calcium monosulfate aluminate) in dilute sodium chloride solutions indicated that Tc(VII) adsorption (K_d) was ~134 ml/g. (Balsley et al. 1997). Recent tests by Moore (2003) indicate that a reductive compound (Sn(II)-treated apatite) was a very effective getter for pertechnetate (K_d: 475,000 – 3,202100 ml/g in a groundwater matrix, and in a concentrated sodium salt solution (K_d: 5,140 – 4,890 ml/g). Before these miscellaneous minerals and synthetic compounds can be deployed as Tc getters, additional evaluation, such as the long-term stabilities and the adsorption/ desorption performance under typical ILAW facility post closure conditions, needs to be conducted.

4.5 Tetrahedral Oxyanion-Specific Functionality Substrates

Recently, a self-assembled monolayer functionality (Cu-ethylenediamine complex) with high specificity for tetrahedral oxyanions has been synthesized (Fryxell et al. 1999a,b,c; Kemner et al. 1999; Liu et al. 1998, 2000). Substrates consisting of mesoporous silica and resin have been monolayered with Cu-EDA functionality and tested for their Tc(VII) affinity in matrix solutions that are expected to prevail in post closure environments such as groundwater, and glass leachate. The data indicate that Cu-EDA SAMMS material could specifically adsorb Tc from both groundwater (K_d: 50 - 790 ml/g) and simulated glass leachate (K_d: 340 - 720 ml/g). Comparatively, the same functionality (Cu-EDA) on a resin substrate exhibited very high specificity in a groundwater matrix (K_d: 3,400 – 37,500 ml/g) but poor specificity in simulated glass leachate (K_d: 1 - 30 ml/g). These differences indicate that the adsorption performance of the Cu-EDA functional monolayer is dependent on the type of substrate to which it is attached.

Therefore, the Tc adsorption performance of this novel functionality (Cu-EDA) can be maximized by choosing appropriate substrates. At present, the long-term physical and chemical stability of the novel combination of Cu-EDA functional monolayer and the substrate needs to be established.

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$_4$ Molar Conc Ratio	Reference
Sn(II) treated Apatite	475,000 – 3,202,100	9.11×10^{-6} – 1.15×10^{-5} M Tc in groundwater	6 – 10	--	Moore 2003
	5,140 – 6,510	9.11×10^{-6} – 9.11×10^{-5} M Tc in conc. NaNO$_3$-NaNO$_2$, NaOH-NaAlO$_2$ Solution	13		
Hydrotalcites (Al, Bi, Cu2+, Cu+, La, Sn2+, Sn4+, Zn)	137 – 4,890	Dilute NaNO$_3$-NaNO$_2$, NaOH-NaAlO$_2$ Solution	--	--	Krumhansl 2003
Cu-EDA SAMMS	50 - 440	Groundwater	5.83 – 7.44	6×10^3	Mattigod et al. 2000
	66 - 790	Groundwater		7×10^2	
	340 -720	Sim Glass Leachate		1×10^2	
Cu-EDA Resin	3,400 – 7,300	Groundwater	7.76 – 8.04		
	8,400 – 37,500	Groundwater			
	1 - 30	Sim Glass Leachate			
Boehmite, Al hydroxide	0 - 110	0.001 M ReO$_4$ in 0.001 M NaNO$_3$	5.2 - 9.7	--	Zhang et al. 2000
Cu Oxides	43 – 55	TcO$_4$ solution	6.8 -7.1	--	Balsley et al. 1997
Chalcocite	31		8.6		
Covellite	67		5.4		
Zn hydrotalcites	1 – 84		5.3 -7.7		
CMSA	134		11.7		
Imogolite	23		6.4		
Hydrotalcite	265 – 6,160	0.3 M NH$_4$TcO$_4$, 0.1 M NH$_4$OH, 0.1 M HTcO$_4$ solution	10.59 – 12.51		Kang et al. 1996
Fe metal	~121,700	1×10^{-5} M TcO$_4$ in ~6 – 12 M MgCl$_2$ brine	--	$60 – 1.8 \times 10^4$	Kunze et al. 1996
Fe Metal	1,490 – 18,700	13. mg/L TcO$_4$ in heavy metal sludge filtrate	8.5	SO$_4$/TcO$_4$	Del Cul et al. 1993
Greigite	110 – 6,100				
Magnetite	0.3 -1.3	5×10^{-9} M TcO$_4$ in Oxic and anoxic syn and natural groundwater	7.4 - 8.8	$6 \times 10^3 – 6.6 \times 10^5$	Byegard et al. 1992
Magnetite	1 - 343	6×10^{-6} M TcO$_4$ + 6 mg/ L Fe^{2+} in Oxic and anoxic syn and natural groundwater	7.4 - 8.8	5.2 – 550	
Activated carbon	8,000 – 10,000	TcO$_4$ solution	10 - 2	--	Ito and Akiba 1991
	300 – 5,000	1 M NaCl	10 - 2		
	90 –300	0.001M NaClO$_4$	10 - 2		
	10 - 90	0.1 M NaClO$_4$	10 - 2		
Fe Metal	33233	0.2. mg/L TcO$_4$ in surrogate raffinate solution	7 - 9	1.3×10^4	Bostick et al. 1990
Greigite	1166		8.1 - 8.3		
Hematite	5		3.9 - 6.9		
Magnetite	3		3.9 - 8.9		

Table 2. (contd)

Getter Material	K_d (ml/g)	Matrix Solution	Eq. pH	SO$_4$/TcO$_4$ Molar Conc Ratio	Reference
Pyrrhotite	~50000	TcO$_4$ solution in	~5.2 – 7.2	--	Bock et al. 1989
Stibnite	~2000 – 50,000	0.007 M bicarbonate	~7.2 – 7.5	--	
Galena	~50 – 1,000	groundwater	~6.8 – 7.2	--	
Pyrite	~70 – 100		~2.5 – 7.2	--	
Loellingite	~0.4 – 400		~6.8 – 7.2	--	
Chalcocite	~0.4 – 5		~5.2 – 7.2	--	
Sphalerite	~0.1 – 0.3		~7.2 – 9.8	--	
Stibnite	~200	TcO$_4$ (2x10^7 Bq/ml) in 0.1 M NH$_4$OH	--	--	Zhuang et al. 1995
Stibnite	143 – 1,980	TcO$_4$ (2x10^7 Bq/ml) in 0.1 M NH$_4$OH	3.84 – 6.22	--	Zhuang et al. 1988
Molybdenite	0.6 – 2.7		--		
REE hematite	1.0- 5.1		8.02 - 8.04		
Silicate minerals (oxic conditions)	0.2 - 5	TcO$_4$ in 0.16 M NaNO$_3$solution		--	Ito and Kanno 1988
Silicate minerals (anoxic conditions)	13 -71				
Pyrrhotite	443 – 667	10^{-6} M TcO$_4$ in	3.5 – 5.4	--	Lieser and Bauscher 1988
Pyrite	<0.1	groundwater	5.2 – 5.9		
Magnetite	<0.1		6.6 – 7.6		
Hematite, limonite, Goethite, ilmenite, Fe metal	0 - 5	3x10^{-12} M TcO$_4$ in oxic granite GW	~6.5	2x10^7	Vandergraff et al. 1984
Fe metal	4990				
Hematite, limonite, Goethite, ilmenite	0 -190	3x10^{-12} M TcO$_4$ in anoxic granite GW		2x10^7	
Fe metal	~190				
Magnetite	4 - 490	3x10^{-12} – 1x10^{-4} M TcO$_4$ in DI water, granite GW, WN-1 saline, Can. Shield saline, Na$_2$HPO$_4$ solution, humic acid	~6.5 – 8.2	2x10^7 – 2 x 10^9	
Na bentonite	132 -2,269	4.187 x 10^{-14} M TcO$_4$ in DI water	5.68 - 10.1	--	Shade et al. 1984
Fe- silicate	0				
Silicates, oxides, hydroxides	0 – 26	TcO4 in 0.01 – 4 M NaCl solutions		--	Palmer and Meyer 1981
Sulfides (Chalcocite, Chalcopyrite,	1.6 – 3.2			--	
Galena,	1.8			--	
Molybdenite,	0.3			--	
Pyrite)	0.8 – 6.3				
Gypsum Dolomite Phosphates (Apatite, monazite)					
Chrysocolla	10 – 20	5x10^5 dpm TcO$_4$	--	--	Strickert et al. 1980
Chalcopyrite,	=3	solution	--	--	Fried et al. 1978
Enargite, bornite,			--	--	
pyrite, tennantite,			--	--	
Ag- tetrahedrite	1 - 10		--	--	
Galena	2 – 2,000		--	--	
Tetrahedrite	200 – 2,000		--	--	
Bournonite					
Activated Charcoal	310 -380	6- 6 x 10^{-5} M TcO$_4$ in ~5 M NaCl brine	--	--	Nowak 1980b
Bentonite, hectorite	0 - 1		--	--	
Augite	23	1 x10^{-4} M TcO$_4$	--	--	Bird and Lopata 1980
Biotite	1	solution			
Galena, sphalerite	0				
Smithsonite	0				
CuO, Cu$_2$O, PbO,	0				
Magnetite, graphite	0				

5.0 Getter Selection and Evaluation

Good adsorption performance (capacity, kinetics, and selectivity towards contaminants of interest) is an essential characteristic that potential getter materials must exhibit.   However, there are additional criteria any potential getter material should meet before it can be effectively deployed in a waste repository environment. These additional proposed evaluation steps are shown in a flow chart (Figure 2). The proposed getter selection and evaluation scheme is designed to answer the following additional critical questions:

1) Are the getters chemically (including redox) and physically stable enough to be used as barrier materials in the anticipated repository environment?
2) Do biotic factors adversely affect and compromise the contaminant adsorption performance of these materials to any measurable degree?
3) Are the getters cost effective and offer flexibility in deployment?

Typically, an initial performance assessment (PA) conducted for a disposal facility such as the ILAW repository would be based on a number of factors that include the type of waste form, contaminant loading, the rate of physical and chemical weathering of the waste form and the concomitant rate of contaminant release, the geological setting of the repository (defined by soil and sediment characteristics, rainfall, rate of infiltration) etc. In some cases, the performance assessment may indicate that the contaminant release rates may be low enough to vitiate the need for getter materials. If however, the PA computations indicate a need for additional measures to further retard the mobility of contaminants, getters may be considered as one of the options to achieve that goal.

If getters are needed to improve the performance of the repository system, a preliminary screening of currently available mineral and synthetic getters needs to be conducted. The initial evaluation of the getters would consist of their adsorption capacity, weathering kinetics, and contaminant specificity. Further, laboratory tests should preferably be conducted in solution matrices consisting of surface and groundwater samples from the repository site, and leachates derived from the waste forms. The data from these tests would then be evaluated in the context of overall performance of the repository.

It is important to note that in the proposed getter testing flow chart (Figure 2)**,** all the conditional evaluations after each set of tests are to be based on the getter performance requirements (specification) established through the overall PA for the repository.

If the selected getters pass the adsorption performance criteria, chemical stability tests should be conducted to evaluate desorption characteristics and the stability of the getter substrates. If the getters meet the chemical stability criteria, other tests should be conducted sequentially to completely evaluate whether these materials meet all the specified performance characteristics. Lastly, the cost effectiveness for successful deployment of the selected getters in the near-field and/or the far-field of the repository should be evaluated. The following section contains a number of suggested test protocols for a comprehensive evaluation of getters.

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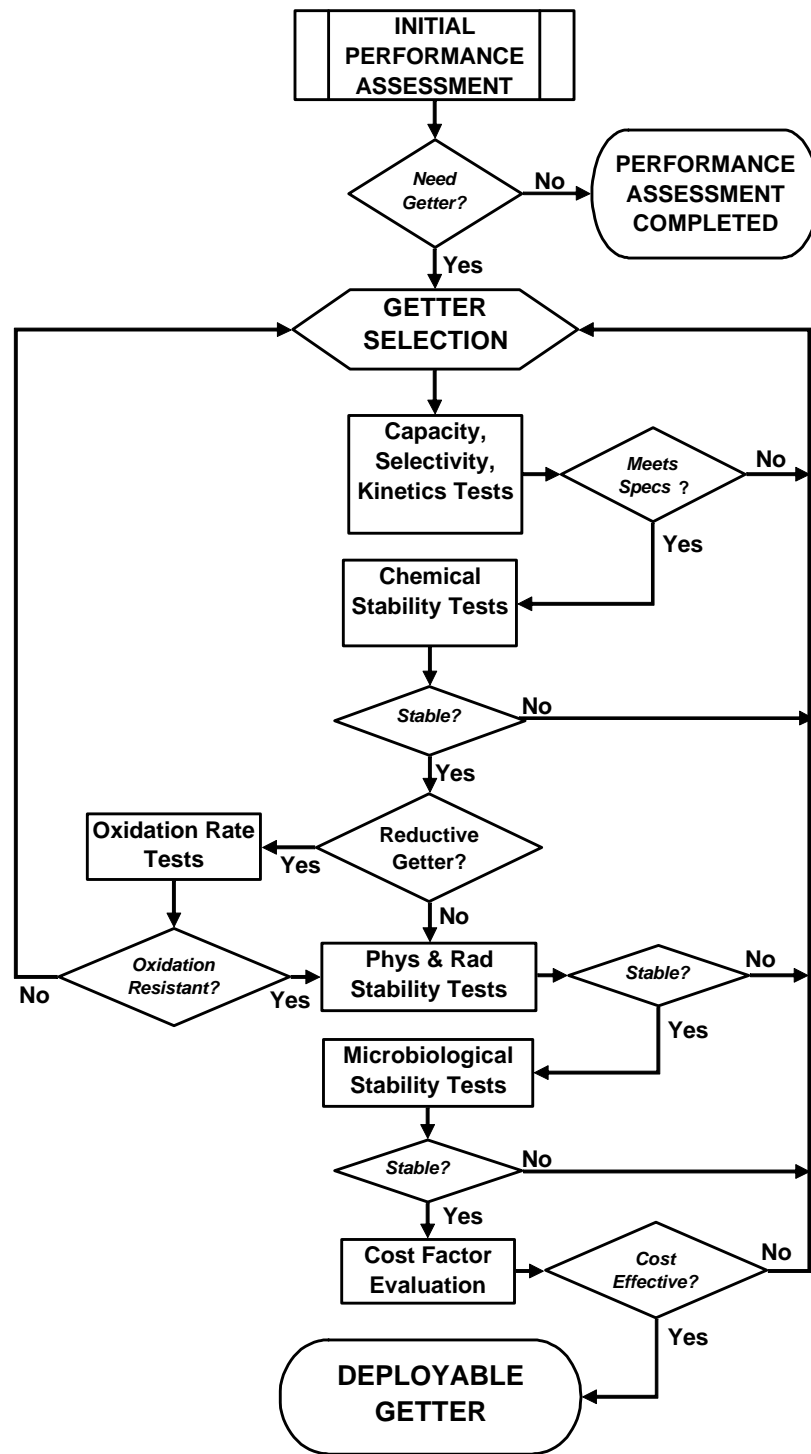
Figure 2. Flow Chart for Getter Selection and Evaluation as Part of Performance Assessment of Waste Repositories

5.1 Adsorption Capacity, Kinetics, and Selectivity Tests

Although initial getter screening tests are typically conducted using deionized, distilled or dilute salt solution matrices, a more rigorous series of test should be conducted to evaluate the ^{129}I and/or ^{99}Tc adsorption performance in water and leachate matrices typically encountered under repository conditions. Both static and dynamic tests should be used to better evaluate getter performance such as, adsorption capacity, adsorption kinetics, and selectivity using actual waters and simulated waste form leachates.

Static adsorption tests can be conducted by equilibrating getter samples with aliquots of water and leachates containing a range of activities of ^{129}I and/or ^{99}Tc. Solution-to-solid ratios (ml/g) of ~100 (0.1 g solid in 10 mL of spike solution), ~500 (0.1 g in 50 mL), ~1000 (0.1g in 100 mL), ~5000 (0.05 g in 250 mL), and ~10000 (0.025 g in 250 mL) can be used to evaluate the degree of ^{129}I and/or ^{99}Tc adsorption. A typical experimental protocol for such static radionuclide adsorption tests has been described by Kaplan et al. (1996). A positive control containing ^{129}I (or a combination of stable I and a short-lived tracer such as ^{125}I) and/or ^{99}Tc - spiked groundwater without any getter will help evaluate radionuclide sorption to labware and filters. Following overnight equilibration, residual radionuclide activities can be used to calculate getter adsorption capacities. Additionally, concentrations of competing major anions such as chloride, hydroxyls, carbonate, nitrate, and sulfate in equilibrated solutions can be measured to determine the getter selectivity for ^{129}I and/or ^{99}Tc.

The kinetics of adsorption by getters in water or leachate matrices for relevant repository conditions should also be evaluated by periodically sampling the contact solution during the experiment.

Saturated and/or unsaturated dynamic flow-through tests can be used to evaluate and predict the adsorptive performance of getters under conditions that are expected to exist in actual waste repositories. There are a number of experimental approaches that can be used evaluate the getter adsorption performance under saturated flow-thorough conditions (USEPA 1991; Relyea 1982, van Genuchten and Wierenga 1986). Typically, these methods use columns packed with getters (to a known bulk density) which allow radionuclide-spiked contact solutions (groundwater or waste form leachate samples) to flow-through under saturated conditions. The activities of radionuclides, and the competing anion concentrations in the column effluent can be monitored as a function of time to generate breakthrough curves. These data can be used to evaluate the getter adsorption characteristics such as, capacity, kinetics, and selectivity.

If the getters are to be deployed under unsaturated subsurface conditions, it is crucial to assess the ^{129}I and/or ^{99}Tc adsorption performance of these materials under the range of unsaturated flow conditions that are expected to exist in the near and far field vadose zones of a repository. Vadose zone conditions are typified by low moisture contents, a solid dominated matrix with gas-filled major pores, higher concentrations of dissolved solids, and unsaturated flow conditions. Such tests can be successfully conducted using a unique, patented, pressurized

unsaturated flow apparatus (PUF). The configuration of this PUF apparatus and its use to test nuclear waste glass reactions under simulated vadose zone conditions has been described in detail (McGrail et al. 1996, 1997).

The test apparatus basically consists of a column packed with material to be tested, a computer data acquisition and control system, fluid pump, and electronic sensors, as illustrated in Figure 3. The columns are made of chemically inert cubic zirconia for high temperature testing or PEEK (Poly ether ether ketone) for low temperature testing that precludes contaminant adsorption, and allows monitoring the adsorption reaction progress in real time using a laser Raman spectrometer (cubic zirconia columns do not have any interfering absorption bands). A porous titanium plate with a nominal pore size of 0.2 µm is sealed in the bottom of the column to ensure an adequate pressure differential for the conductance of fluid while operating under unsaturated conditions (Wierenga et al. 1993).

Figure 3. The Patented PUF System Hardware showing an array of control and data logging equipment (left) and an instrumented cubic zirconia column that contains test samples.

Titanium plate is highly corrosion-resistant and has excellent wetting properties. When water saturated, the porous plate allows water but not air to flow through it, as long as the applied pressure differential does not exceed the air entry relief pressure, or "bubble pressure," of the plate. The computer control system runs LabVIEW™ (National Instruments Corporation, Austin, Texas) software for logging test data to disk from several thermocouples, pressure sensors, inline sensors for effluent pH, and conductivity. The column is suspended from an electronic strain gauge to accurately track water mass balance and water saturation level. The column also includes a "PUF port," which is an electronically actuated valve that periodically vents the column gases at an interval specified by the operator. The purpose of column venting is to prevent reduction in the partial pressure of important gases, especially O_2 and CO_2, which are participants in a variety of homogeneous and heterogeneous chemical reactions.

Groundwater samples or waste form leachates containing known ^{129}I (or shorter lived tracers) and/or ^{99}Tc activities can be flowed through the columns under typical unsaturated conditions found in the vadose zone of a repository site. The solution pH, conductivity, and flow conditions can be monitored in real time with in line sensors. Periodically, the reaction progress can be monitored using laser Raman spectrometry (if the cubic zirconia column design is used). The activity of ^{129}I and/or ^{99}Tc and other dissolved constituents in the effluent can be used to generate breakthrough curves which can be used to evaluate important getter performance characteristics such as capacity, retardation factor (related to the K_d), selectivity versus other anions, and breakthrough pore volume.

5.2 Chemical Stability Tests

Hydrothermal tests can be used to evaluate the effects of abiotic factors such as temperature and time on the stability, durability, and contaminant desorption performance of getters. These tests can be conducted by reacting suspensions of pristine and contaminant-loaded getters in sterilized, simulated groundwater (1:500 w/v solid solution ratio) and/or glass or concrete leachates in closed Teflon™ containers for 6 months. If needed, the hydrothermal stability tests can be conducted at several elevated temperatures (50, 70, and 90 ºC) to enhance the rate of reaction. The extent of physical and chemical degradation of the sorbent material can be monitored by periodically taking aliquots of contacting solution and measuring the concentrations of substrate components and the desorbed contaminant. These data can be used to determine the rates of degradation as a function of temperature and time of reaction. Also, these temperature-dependent degradation data can be used to estimate enthalpies of reaction and to assess the long-term thermal stability of the getters.

Another test that could be used to evaluate getter stability is a modified form of the Toxicity Characteristics Leaching Procedure (TCLP). The TCLP procedure was developed by EPA to determine the fractions of organic and inorganic regulated contaminants that could be mobilized from solid and multiphasic wastes disposed of in landfills (USEPA 2000). Briefly, the method consists of extracting the waste form in a solution of acetic acid (pH ~3) for about 18 h at room temperature, and measuring the concentrations of dissolved constituents. However, the TCLP test is inappropriate for testing getter stability under ILAW conditions because the leachates generated from the waste forms are predicted to be highly alkaline in nature. Therefore, a suitable chemical stability test would consist of reacting under simulated repository conditions, natural water or leachates with getter materials and monitor the release of adsorbed and substrate components.

5.3 Oxidation Tests on Reductive Getters

A number of minerals and synthetic compounds such as ferrous iron containing minerals (e.g., biotite, magnetite, chlorite, olivine, hornblende, clays (Viani 1999), metal sulfides (Balsley et al. 1997), zerovalent-iron, and ferragels (Ponder et al. 1999), have been suggested as getters for Tc. These getters immobilize Tc by reducing soluble and highly mobile Tc(VII) to a low solubility Tc(IV) oxide form. Although these minerals are shown to be effective in

immobilizing Tc in laboratory scale and time experiments, their viability as getters on repository time scales is not well established. For instance, a few recent studies suggest that re-oxidation and mobilization may be encountered if reductive systems are used to immobilize highly mobile species such as Tc(VII) and U (VI) (Szecsody et al. 1998, McGrail and Mattigod 1999). Also, recent studies pointed out that the formation of highly electronegative, soluble Tc (IV) carbonate complexes in groundwaters might enhance the mobility of ^{99}Tc, and similarly, natural organic ligands such as oxalate and formate may also complex and increase Tc(IV) solubility (Wildung et al. 2000; Peretrukhin et al. 1996). Radiolysis is another suggested mechanism that can potentially mobilize Tc (Lieser et al. 1987). Therefore, these reductive getters should be tested under simulated repository conditions, in which re-oxidation and mobilization of the reduced contaminant species Tc(IV) may occur from radiolytic effects in the repository and from the potential influx of oxic groundwater or rainwater, atmospheric gases, and/or oxic leachates.

One of the methods to assess the redox stability of reductive getters is to use a Single Pass Flow-Through (SPFT) apparatus in which the contaminant-loaded substrates are subjected to a regulated flow of oxygenated water or leachate. The dissolved oxygen levels and the flow rates can be adjusted to simulate the conditions that may exist in a repository environment. The rate of release of oxidized contaminant species can be measured and used to assess the relative stabilities of reductive getters.

5.4 Physical and Radiological Stability Tests

Methods are available to test the physical stability of getter materials such as minerals, chemically modified minerals, and synthetic adsorptive substrates (ASTM, 2002c,d). These test methods can be readily adapted for evaluating the physical stability of getters. One of the tests that can be used to quantify the resistance of getters against physical degradation is an attrition test (ASTM 2002c), which consists of agitating (with a standard bladed rotor) a known quantity of material wetted to a known degree in a standard device for a set period of time (6 min.) and measuring the changes in particle size distribution. Another standard method that can be adapted to assess the physical stability of potential getters is the freeze-thaw test (ASTM 2002d). In brief, the test consists of subjecting a known quantity of material to a number of freeze-thaw cycles and measuring changes in the particle size distribution. The number of freeze-thaw cycles to be used in this test is based on the Severity Index for each geographical area compiled by the National Oceanic and Atmospheric Agency (NOAA).

Radiological stability tests need to be conducted if the getters are to be deployed in close proximity to the waste package in a repository. These tests can be conducted by subjecting the radionuclide-loaded getters to predicted radiation and temperature regimes and measuring any resulting physical and chemical degradation, and concomitant release of sequestered radionuclides using SPFT and/or PUF tests.

5.5 Microbiological Stability Tests

Studies of the vadose zone have revealed that subsurface zones are relatively devoid of microorganisms as compared to surface soils (Richter and Markewitz 1995). However, direct microscopic counts of vadose zone samples from several locations including the Hanford site have revealed both gram- positive and negative bacterial densities of $10^4 - 10^7$ cells/g (Kieft and Brockman 2001). These aphotic organisms catalyze reactions that can reduce and/or oxidize contaminants and may also degrade subsurface minerals (Ehrlich 1996; Kieft and Brockman, 2001). Clearly, it is necessary to evaluate the microbiological stability of any getter that would be deployed in subsurface barriers.

Protocols are available to test microbial degradation for various materials such as chemicals, plastics, synthetic polymers, and asphalt (ASTM 1995, 2002a, b; Luey and Li 1993). These protocols can be readily adapted for testing the stability of getters against microbial attack. As an example, the microbial degradation experiments can be set up using a series of 0.75 – 1.5 ml-size sterilized (using either gamma irradiation or autoclaving) teflon test tubes with air-tight screw caps and septa to aseptically remove aliquots of the solution for chemical analyses. It is preferable to obtain microorganisms to be used in the tests by extracting soil solutions from the subsurface sediments from potential repository sites. Alternatively, commercially available microorganisms prescribed for degradation studies can be used in these experiments (ASTM 1995; 2002a, b). According to ASTM methods, measured amounts of both pristine and contaminant-loaded getter materials can be inoculated with volumes of bacterial cultures in a specified nutrient broth (1:100 w/v ratio) and incubated for 6 months at predicted repository temperatures. The suspensions should not be mixed or stirred to simulate the mass transfer conditions that typically exist in a repository environment.

The microbiological degradation kinetics of getters can be monitored periodically by measuring solution concentrations of both getter substrate components and the desorbed contaminant. After each sampling, the volume of solution removed should be replaced with fresh nutrient broth to maintain the initial solid to solution ratio. Using such data, one can calculate the rates of degradation of sorbent components. These degradation rates can then be used to predict the long-term stability of the substrate materials when attacked by microorganisms that may be present in a repository environment.

5.6 Cost Factor Evaluation

Finally, the cost and ease of deployment of effective getters should be evaluated. Such evaluations would include a cost benefit analysis to examine whether getter deployment significantly enhances the predicted performance of the overall repository by reducing projected risk. The costs for getter deployment can be compared to other safety enhancing concepts per unit of dose or risk reduction.

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