DT#48115 QA·NA 087/17/06

SANDIA REPORT

MOL.20060825.0188

Yucca Mountain Project Getter Program Results (Year 1):

I-129 and Other Anions of Concern

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ABSTRACT

Although high level nuclear wastes (HLW) contain a daunting array of radioisotopes, only a restricted number are long-lived enough to be problematic, and of these many are either effectively insoluble or are likely to be scavenged from solution by minerals indigenous to all aquifers. Those few constituents likely to travel significant distances through aquifers either form colloids (and travel as particulates) or anions – which are not sorbed onto the predominantly negatively charged mineral surfaces. Iodine (^{129}I) is one such constituent and may travel as either iodide (I^-) or iodate (IO_3^-) depending on whether conditions are mildly reducing or oxidizing. Conventionally, ^{99}Tc (traveling as TcO_4^-) is regarded as being of greater concern since it is both more abundant and has a shorter half life (e.g., has a higher specific activity). However, it is unclear whether TcO_4^- will ever actually form in the mildly reducing environments thought likely within degrading HLW canisters. Instead, technetium may remain reduced as highly insoluble Tc(IV), in which case ^{129}I might become a significant risk driver in performance assessment (PA) calculations.

In the 2004-2005 time frame the US Department of Energy (DOE) – Office of Civilian Radioactive Waste Management (OCRUM), Office of Science and Technology International (S&T) funded a program to identify "getters" for possible placement in the invert beneath HLW packages in the repository being planned by the Yucca Mountain Project (YMP). This document reports on progress made during the first (and only) year of this activity. The problem is not a new one and the project did not proceed in a complete vacuum of information. Potential leads came from past studies directed at

developing anion getters for a near surface low-level waste facility at Hanford, which suggested that both copper-containing compounds and hydrotalcite-group minerals might be promising. Later work relating to closing HLW tanks (Hanford and Savannah River) added layered bismuth hydroxides to the list of candidates.

In fact, even in the first year the project had considerable success in meeting its objectives (Krumhansl, et al., 2005). "Batch Kd" testing was used to screen a wide variety of materials from the above-mentioned groups. Some materials tested were, in fact, archived samples from prior studies but a significant amount of effort was also put into synthesizing new - and novel - phases. A useful rule of thumb in judging getter performance is that the "Kd" , should exceed a value of roughly 1000 before it's placement can materially decrease the potential dose at a hypothetical (distant) point of compliance (MacNeil, et al., 1999). Materials from each of the groups met these criteria *for both iodide and iodate* (though, of course, the actual chemistry operating in "batch Kd" runs is unknown, which casts a rather long shadow over the meaning of such comparisons). Additionally, as a sideline, a few materials were also tested for TcO_4^- and occasionally Kd values in excess of 10^3 were also found for this constituent.

It is to be stressed that the "batch Kd" test was used as a convenient screening tool but in most cases nothing is known about the chemical processes responsible for removing iodine from the test solutions. It follows that the real meaning of such tests is just as a relative measure of iodine scavenging ability, and they may say nothing about sorption processes (in which case evaluating a Kd is irrelevant). Numerous questions also remain regarding the longevity and functionality of materials in the diverse environments in, and around, the proposed YMP repository. Thus, although we had a highly successful first year, we are still far from being able to either qualify any material for placement in the repository, or quantify a getter's performance for use in PA assessments.

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I.   INTRODUCTION

A key element in fielding a high level nuclear waste repository at Yucca Mountain, Nevada is to demonstrate through the use of performance assessment (PA) models that dose rates at some distant point of compliance will not exceed regulatory limits. Implicit in this approach is the fact that the most mobile radionuclides present in natural groundwaters are likely to play a large role in determining the eventual suitability of the proposed facility. Although radioactive wastes have large radioisotope inventories, considerations of relative abundance, half life, solubility, and aqueous chemistry dictate that the chief elements of concern are technetium, neptunium, and iodine. Long-lived isotopes of selenium and cesium may also play a role in such assessments. However, they will not be of primary importance unless they are concentrated into some peculiar waste form prior to placement in a repository.

The current generation of PA models generally assigns higher priorities to technetium and neptunium than to iodine. However, such models universally overlook important chemical processes that may take place within waste packages as they deteriorate (Brady, et al., 2005). In particular, the waste canisters will contain vast amounts of metallic iron (along with Ni and Cr), and the waste itself contains significant amounts of uranium dioxide; all of which are potential reducing agents. Although the conditions in the proposed repository are postulated to be oxidizing, there is every reason to believe that at least mildly reducing conditions will persist within, and around, waste packages for long after the first breach occurs (and leaching of the more soluble constituents is initiated). There is a substantial body of evidence suggesting that in such a setting both the Tc and Np will reduce to the tetravalent form and that these constituents (unlike TcO_4^- and NpO_2^+) will sorb strongly onto the rust formed as the waste packages degrade. Further, additional iron liberated by later corrosion will cover the sorbed constituents, effectively precluding the release of these constituents. If this scenario is verified, performance of the repository may depend largely on the behavior of more mobile, though less radioactive, [129]I.

The objective of this document is to report on early success in developing materials that scavenge [129]I. The rationale behind developing such scavengers ("getters") is that such materials could be placed beneath the waste with the crushed rock liner on the proposed repository floor (e.g., the "invert"). Here, they would then immobilize or delay the radioiodine before it could leave the repository facility (Jow et al., 2005). Although PA model development is an ongoing activity, some preliminary results (MacNeil et al., 1999) suggest that a rough metric for a "successful" getter (e.g., one that could impact the dose at the point of compliance) is that it will have an adsorption coefficient "K_d" greater than 10^3.

A getter's performance generally depends on the environment within the repository. This issue is discussed separately in some detail (Krumhansl, *et al.*, 2006) but the main features of the environment are summarized below. The mountain "breathes" (e.g., changes in air pressure are noted within the mountain in response to outside changes in atmospheric pressure), so the YMP program position is that the repository will be as oxidizing as the earth's surface. It is also presumed that the UO_2 fuel and metallic waste packages (or portions thereof) will be present in the repository for many thousands of years. This is relevant because iodine can travel in groundwaters as iodide (I^-), elemental iodine ($I_2(aq)$), and iodate (IO_3^-). Iodate is the stable form in surface groundwaters. However, with all the metal and fuel presumed to be present (and its

potential for locally producing reducing environments), a pragmatic choice is to focus on initially developing getters that effectively sequester I^-.

Any successful getter must survive the thermal cycle of the repository and withstand several decades of dehydration. It is expected that the temperatures will peak at 120-160 $^\circ$C and persist for several decades before slowly cooling below the boiling point of water. After that the temperature continues to fall slowly to about 50 $^\circ$C after 10,000 years. During this period the getter probably will have to withstand prolonged "stewing" in mildly oxidizing or reducing aqueous fluids.

The fluids in contact with the getter are another important variable in determining getter performance. A survey of YMP literature defines three general classes of fluids:

> (1) Indigenous groundwaters. All have low ionic strengths, are mildly basic and contain only the normal constituents of drinking water;
> (2) Derivatives of normal groundwaters arrived at by evaporation. Depending on initial compositions, fluids may develop that contain high concentrations of alkali halide or nitrate with some carbonate and sulfate, or that are rich in alkaline earth metals with appreciable sodium, chloride and nitrate, but minimal sulfate and carbonate;
> (3) Fluids whose chemistries are dominated by constituents derived from waste package corrosion processes. If interactions with the rust particle surfaces are not considered these fluids will be mildly to strongly acidic with appreciable nickel and chromate concentrations. Including the surface chemistry of the rust particles in the model, however, suggests that much less aggressive fluids will be formed. In fact, fluids will not differ greatly from the indigenous groundwaters except for having slightly elevated chromate concentrations. The chromate, of course, will only form if fully oxidizing conditions persist on the corroding metal surface. If oxygen is not freely available insoluble trivalent chromium compounds will form that are analogous to iron corrosion products.

The second type of fluids will have mostly left the repository before much of the radionuclide inventory could be leached out of the waste. Consequently, the greatest immediate concern for getter performance (and the only topic addressed in this report) is how potential getters perform in (more or less) normal YMP repository groundwaters. Parenthetically, had the study had continued for an additional two years (as initially anticipated) we would have also explored: (1) whether the early-formed waters might pre-load the getters with constituents that would later interfere a getter's ability to scavenge iodine and, (2) whether the early waters might react with a getter to make completely new phases – possibly leading to a complete loss of iodine-scavenging ability.

Our primary objective initially was to identify the most promising candidates from a rather extensive list of possibilities gleaned from past experience and from the literature. To simplify this process we employed a "batch Kd" technique and our test matrix was limited to assessing getter performance in a single fluid, "J-13 surrogate" (Appendix A, Table A-1 and Krumhansl, et al., 2006, *in press*) that resembles dilute groundwaters found near the YMP repository site. Further, the experiments usually had a short duration (days to weeks of contact time), and no

attempt was made to thermally treat materials beyond what was inherent in their various synthetic procedures.

II. BACKGROUND

Sequestration of ^{129}I is not, at least formally, a very difficult problem and we had many leads going into the project (see the topic review by Mattigod et al., 2003). It has been known for some years that metal sulfides, and the mineral cinnabar (HgS) in particular, have a strong affinity for iodine (Ikeda et al., 1994; Balsley et al., 1996). Further, cinnabar is clearly stable for geological periods of time in mildly acidic and oxidizing surface groundwaters indigenous to central Nevada (Fig. 1). However, the inclusion of large amounts of a powdered mercury-containing material in a working repository is probably not economically feasible, nor environmentally tractable.

Fig. 1 Cinnabar (red) collected from a surface outcrop in north-central Nevada (Humboldt County). The orange staining results from the acidic iron-containing fluids formed as the iron pyrite (FeS$_2$) deposited along with the cinnabar was oxidized. Although the rock is, in general, highly weathered the cinnabar has remained untouched by the process.

Although using cinnabar to sequester iodine fails the "giggle test", the chemistry implicit in its behavior suggests a list of other potential iodide getters. Other metals, such as Pb, Ag, and Cu also form both essentially insoluble sulfides and sparingly soluble iodide salts. However there are draw-backs for lead and silver compounds. Placing lead compounds in the repository would raise many of the same environmental issues associated with mercury (though, parenthetically, central Nevada is dotted with natural ore deposits which expose considerable amounts of Pb and Hg (along with Cu and Ag) on the surface so any conceivable activity at Yucca Mountain could only be a trivial perturbation on what nature has already created). For silver, there are obvious cost considerations (particularly given the 2006 silver market!). Further, AgI is unstable with regard to photo-dissociation, which places any AgI – related scavenging mechanisms at a clear disadvantage in a high radiation environment. Copper, on the other hand, is less environmentally problematic and less expensive. Reasoning along these lines motivated an earlier, partly successful, effort to develop copper-based iodine getters for use in a near-surface low level waste facility being contemplated at Hanford (Balsley et al., 1998).

Part of the reason both iodine and technetium travel well in groundwater is that they form anions and, at normal groundwater pH values, the negatively charged mineral surfaces do not sorb anions. An alternate approach to finding iodine getters (also initially explored for potential Hanford applications, Balsley et al, 1998) was to survey the geologic literature for exceptional minerals with positive surface charges. In doing this, two classes of materials emerged: imogolite-type silicates and hydrotalcites (Fetter et al., 1997; Kang et al., 1999). Imogolite proved impractical because it was difficult to synthesize and the natural material (found as an impurity in some volcanic soils) had only a very limited capacity and specificity for iodide. Several hydrotalcite-group minerals, however, were found to have significant potential as iodide getters. The zinc-aluminum derivative is particularly easy to synthesize and therefore was used in most early studies. In the course of that work it was also found that the nature of the anions used to counterbalance the zinc and aluminum in the synthesis fluid affected the iodine-scavenging ability of the getter.

Several years elapsed before the search for anion getters resumed; this time the motivation came from DOE-sponsored Tank Focus Area (TFA) efforts (in the 2001-2002 time frame) to place getters in decommissioned high level waste tanks. The primary focus of the research was to find sequestering agents for technetium (rather than iodine), but the materials advances, as well as scoping "sorption" studies made in the context of this investigation are noteworthy (Krumhansl, et al., 2002; selected TFA study results are also abstracted in Appendix B. Also see Harbour et al., 2004). Of help in guiding this study were several papers describing new "hydrotalcites" based on the use of heavier metals hydroxides (Velu et al., 1998,1999) and particularly the Se-scavenging ability of a "hydrotalcites" fabricated from bismuth, in conjunction with zinc and magnesium (Tsuji et al., 2000).

The conventional hydrotalcite structure can be described as a layered metal hydroxide in which a portion of the octahedrally-coordinated divalent metal is replaced with a trivalent metal. The substitution imparts a net positive charge to the layer and creates a material capable of exchanging anions. In the mineral "hydrotalcite" {formally: $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$} layers are composed of magnesium hydroxide with aluminum substitutions to impart a net positive layer charge. The carbonate resides in the interlayer position to balance the positive charges on the hydroxide layers. This basic structural template also characterizes the other members of the hydrotalcite mineral group, in which almost all the various combinations of the first row transition metals with dominant +2 and +3 valences are observed. One unusual derivative of the conventional hydrotalcite structure involves exposing layered $Al(OH)_3$ to concentrated Li^+-containing solutions. Some lithium ions diffuse into vacant octahedral sites and impart a net positive charge to the layer (Devyatkina et al., 1983; Lei et al., 2000).

A large ion such as Bi^{+3} (1.03 Å) cannot, obviously, be accommodated on the octahedral site of a conventional hydrotalcite lattice. Although, the unusual bismuth "hydrotalcite" compounds posses structural similarities to the hydrotalcites, the materials described by Tsuji et al. (2000) cannot actually be members of the hydrotalcite mineral family. Thus, in addition to hydrotalcites, there are other apparently layered hydroxides that may provide additional avenues for developing iodide (and technetium) getters. Tests done in 2002 confirmed the basic radionuclide-scavenging ability of such Bi-materials (Appendix B). Later work has shown that several different layered pure Bi-hydroxide structures can be synthesized (Bontchev et al., 2005).

Thus, in the two-metal mixtures it is not even certain that the second metal in the mix actually plays a role in the structure.

III. BATCH TEST EVALUATION PROCESS

The bulk of this report reviews the relative performances of the different classes of materials alluded to above. These comparisons are based on the results from what are commonly referred to as batch "sorption" tests – though mechanistic insights (sorption or not) are not actually implicit in data obtained in this manner. A brief description of the test process is given here, and a more detailed coverage of the underlying rationale can be found in a companion document (Krumhansl et al., 2006 – *in press*).

The batch sorption (or K_d) approach is particularly good at providing an efficient, cost-effective method for *differentiating between poorly performing getters and those with some potential* for iodide sequestration. The environment for the tests was chosen to superficially resemble what might be found in the YMP repository. Toward this end the test fluid contained reasonable concentrations of normal groundwater anions that might compete with iodide "sorption,". Experiments were also designed so that the iodine (and other contaminants of interest) would never be a major component in the dissolved load of the fluid. Thus, if something in a normal groundwater "interfered" with iodine sequestration then the empirical result obtained would show that this material had little potential as a getter (though any insight as to why the material had performed poorly would, of course, be unavailable). Finally, within the limits imposed by analytic sensitivities, the tests were conducted so that all the samples in a particular suite of experiments would be run at essentially the same solid to liquid ratios. The actual ratio, however, varied from suite to suite (typically 0.05 to 0.25 grams of solid in 25-60 ml of fluid), and changed as our understanding of getter performance advanced.   Experience gained during the performance of these tests ultimately led to the protocols described in Krumhansl et al., 2006.

Analytical techniques vary depending on the constituent and analytic range desired. For iodide, the specific ion electrode was occasionally employed, but this was limited to a sensitivity of about 0.05 ppm. However, the specific ion electrode has the advantage of uniquely identifying the iodine species in solution since it is insensitive to both elemental iodine and iodate. Inductively coupled plasma – mass spectroscopy (ICP-MS) is more sensitive to iodine but suffers from two shortcomings. Unlike the specific electrode, ICP-MS is indifferent to aqueous speciation and so measures the total iodine content of the fluid being sampled. Also, in the case of iodide, the surface chemistry of the machine's internal plumbing is such that iodide is retained; resulting in serious memory effects (e.g. iodine is carried over from previous samples). This can be overcome by not acidifying the samples *or standards,* and using a rinse fluid consisting of one part (by volume) concentrated NH_4OH in 19 parts de-ionized water and spiked with an AA standard to contain 5 to 10 ppm Ag^+. Once the iodine analyses have been completed, the samples (and standards) can be acidified for the analysis of other elements that may also be of concern. Iod*ate* is less strongly retained on the machine's internal surfaces than is iod*ide,* and can generally be run without a special (basic) rinse.

IV. RESULTS

Several different classes of materials were identified at the onset of this study as potential iodide getters. In fact, there is some overlap because some of the criteria used in grouping materials are structural and some are compositional. The performance of the delafossites and their related compounds are discussed first. This is followed by a discussion of layered compounds: a) presumably, true multi-metal hydrotalcites and b) Bi-based getters. The last section reviews the performance of miscellaneous materials that don't fall into the other main categories. The main body of the text is largely in the form of tables and emphasizes the performance characteristics of the materials.

a.   Copper Delafossites and Spinels

Delafossites have the general chemical formula ABO_2 and can be described as alternating layers of edge-shared BO_6 octahedra and two-coordinate noble metal A-site cations. This structure type can accommodate various monovalent A-site cations (Cu, Pd, Pt and Ag) and trivalent B-site cations ($0.53 < r$(six coordinate B^{3+}) < 1.09 Å). The delafossite structure as an iodide scavenger is interesting because the copper is monovalent (thus resembling Ag^+), and it is only 2-coordinated (suggesting the potential for additional bonding – possibly with iodide). It was thought that Cu(I) might have an affinity to iodide that was similar to that of Ag, and form a similarly insoluble compound. Furthermore, the iodine might have relative access to the layered copper. After initial synthesis was completed select compositions were also oxidized because of the uncertainty of the environment inside the repository. The structure of the oxidized materials is spinel-like. The spinel structure can be described as layers of close-packed oxygen atoms with tetrahedral copper and octahedral tri-valent cations (M^{3+}).

Synthesis and Structural Characterization: Seven polycrystalline delafossites and three compositionally-related spinels were synthesized by solid state reaction (Table 1). Stoichiometric amounts of Cu_2O (Alfa Aesar, 99.9%), CuO (Alfa Aesar, 99.7%), Al_2O_3 (Alfa Aesar, 99.9%), V_2O_3 (Alfa Aesar 99.7%), Cr_2O_3 (Alfa Aesar, 99%), Mn_2O_3 (Alfa Aesar, 98%), Fe_2O_3 (Alfa Aesar, 99.9%), Ga_2O_3 (Alfa Aesar, 99.99%), and Y_2O_3 (Alfa Aesar, 99.9%) were ground with an agate mortar and pestle. The delafossites and spinels were calcined in flowing N_2 and air, respectively, between 750 – 1100 °C for 24 h. The materials were ground to a fine powder.

The samples' structures were identified using powder X-ray diffraction (XRD). The XRD patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer (Cu Kα radiation, Kevex detector, 40 kV, 30 mA; 2θ) 5-60°, 0.05° step size and 3 s count time) and used for crystalline phase identification. The phases were identified by comparison with the data reported in the JCPDS (Joint Committee of Powder Diffraction Standards) database.

Table 1. Physical Properties and Sorption Coefficients of the Delafossites and Spinel Compounds[a]

Composition	Structure Type	Calcination Temp. (^{o}C)	Log K_d I^-	Log K_d IO_3^-	Log K_d ReO_4^-	Log K_d TcO_4^-
$CuAlO_2$	Delafossite	1090	1.5	< 1.40	< 1	-
$CuCrO_2$	Delafossite	1000	0.54	1.64	1.23	-
$CuMnO_2$	Delafossite	960	< 1	< 1.40	< 1	-
$CuMn_2O_4$ + Impurity	Spinel	750	0.94	0.00	0.00	-
$CuFeO_2$	Delafossite	1050	1.5	< 1.40	< 1	-
$CuFe_2O_4$	Spinel	750	0.99	0.00	0.00	-
$CuGaO_2$	Delafossite	1070	1.3	< 1.40	< 1	-
$CuYO_2$ + Cu_2O	Delafossite	1050	1.49	1.48	0.75	-
CuY_2O_5	Spinel	1050	1.04	0.27	0.00	-
$CuV_{0.5}Fe_{0.5}O_2$	Delafossite	850	-	< 1.40	< 1	-

a.   Dash (-) indicates no test was performed.

Results and Discussions: The physical properties and sorption coefficients of the delafossites and spinels are summarized in Table 1 (Pless et al., 2006). The sorption capacities of the delafossites and spinels are relatively small. Most of the iodide Log(K_d) values fall between 1 and 1.5. Interestingly, the iodate Log (K_d) values of the delafossites is similar to the iodide Log(K_d) values, but the iodate Log (K_d) values of the spinel-like compounds become significantly smaller. The difference might be related to the local structure of the copper. The copper in delafossite is relatively open with only two bonds to oxygen, whereas the copper in the spinel is more surrounded with bonds to four oxygen atoms. So it is more difficult for the larger IO_3^- anion to coordinate/bond to the copper. Finally, the ReO_4^- Log(K_d) values are unremarkable, falling between 1.25 and 0.75 for the delafossites and are 0 for the spinels. The difference again can be explained by the local environment of the copper atoms.

b.   Hydrotalcites

As stated above, hydrotalcites (HTCs) are well known for their ion exchange abilities. A variety of hydrotalcites were synthesized by changing the divalent and trivalent cations in order to more fully study the sorption properties. In addition, it has been shown that the hydrotalcite structure collapses upon calcining due to anion and water loss. The collapsed material can be dispersed into an aqueous solution containing an ion and the HTC structure recrystallizes including the "new" ion. Select compositions were calcined because of the uncertainty of the environment inside the repository.

Synthesis and Structural Characterization: Nineteen polycrystalline hydrotalcites were synthesized by direct co-precipitation of the divalent and trivalent cations at room temperature. Stoichiometric amounts of $Mg(NO_3)_2 \cdot 6\ H_2O$ (Alfa Aesar, 98%), $Co(NO_3)_2 \cdot 6\ H_2O$ (Aldrich, 98%), $Ni(NO_3)_2 \cdot 6\ H_2O$ (Aldrich, 98.5%), $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (Aldrich, 98%), $Zn(NO_3)_2 \cdot 6\ H_2O$ (Aldrich, 99%), $Pd(NO_3)_2$ solution (Alfa Aesar, Pd 8.5% w/w) or $Cd(NO_3)_2 \cdot 4\ H_2O$ (Alfa

Aesar, 98%) and $Al(NO_3)_3 \cdot 9 H_2O$ (Alfa Aesar, 98%), $Cr(NO_3)_3 \cdot 9 H_2O$ (Aldrich, 99%), $Fe(NO_3)_3 \cdot 6 H_2O$ (Aldrich, 98%), $Ga(NO_3)_3 \cdot X H_2O$ (Alfa Aesar, 99.9%), or $La(NO_3)_3 \cdot 6 H_2O$ (Alfa Aesar, 99%) were dissolved in 400 mL of DI water. The pH of the solution was adjusted to ~ 10 with NH_4OH (Fisher, Reagent), precipitating an HTC and turning the solution into a thick opaque suspension. This mixture was allowed to age for approximately 24 hours at room temperature. The product was filtered and washed until the conductivity of the filtrate was approximately 100 microsiemens. The product was dried overnight in air at 100 °C. Select samples were calcined at 550 °C between 1 and 24 hours. The materials were ground to a fine powder.

The samples' structures were identified using powder X-ray diffraction (XRD). The XRD patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer (Cu Kα radiation, Kevex detector, 40 kV, 30 mA; 2θ) 5-60°, 0.05° step size and 3 s count time) and used for crystalline phase identification. The phases were identified by comparison with the data reported in the JCPDS (Joint Committee of Powder Diffraction Standards) database.

Results and Discussions: The physical properties and sorption coefficients of the hydrotalcites (HTCs) are summarized in Table 2. The sorption coefficients (Log K_d) for iodide fall in a rather large range, from 10^1 - 10^4. The iodide sorption does not appear to be significantly affected by the identity of the trivalent cation, except for La^{3+}. This is not surprising as the ionic radius of six-coordinate lanthanum (1.032 Å) is significantly larger than those of six-coordinate aluminum, chromium, iron and gallium (0.535 Å, 0.615 Å, 0.645 Å, and 0.620 Å, respectively). Samples containing Cu^{2+} exhibited the highest sorption for iodide, followed by the samples containing Co^{2+} and Ni^{2+}. These three metals are classified as "border region" elements of the hard/soft acceptor properties. The difference in sorption capacity between these three elements could be due to their electronic structures or that Cu^{2+} exhibits Jahn-Teller distortions. It was thought that the soft acceptor, Pd^{2+}, would exhibit a higher iodide (soft) sorption capacity than the analogous Ni^{2+} compound, however, the sorption capacity of the palladium structure was about an order of magnitude smaller. This might be due to the larger ionic radius of six-coordinate Pd^{2+} (0.86 Å) compared to Ni^{2+} (0.690 Å).

Nearly all of the HTCs' iodate sorption capacities were larger than the respective iodide sorption capacities, except for the Mg/Al – HTC. Interestingly, the iodate sorption values for all but four HTCs (Mg/Al, Pd/Al, Co/La and Cu/La) were 10^3 or higher. The sorption capacities followed the same trends for iodate as for iodide. Several of the Co, Ni and Cu HTCs exhibited sorption capacities greater than 10^2. Select samples were measured for their ability to sorb TcO_4^-. All of the samples tested exhibited higher values for TcO_4^- than for the ReO_4^-. The calcination times and sorption properties of the selected calcined HTCs are listed in Table 3. It can be seen that calcination of the samples decreased the sorption capacities for all of the anions tested. The length of calcination does not have a large effect on sorption values.

The HTC class of materials offers much promise for sequestering radioactive anions. Two HTC samples (Cu/Al and Cu/Cr) exhibited sorption capacities of 10^3 or greater for iodide, iodate and pertechnetate. Further studies are needed to determine the affects of composition, particle properties, radiation damage, the time of the HTC in the ionic test simulant, the composition of the test simulant, etc. on the ability of these materials to sorb radioactive anions.

Table 2. Physical Properties and Sorption Coefficients of the Hydrotalcites[a]

Targeted Composition	Structure Type[b]	Log K_d I^-	Log K_d IO_3^-	Log K_d ReO_4^-	Log K_d TcO_4^-
$Mg_6Al_2(OH)_{18}$	HTC	1.60	0.52	0.887	-
$Co_6Al_2(OH)_{18}$	HTC	2.36	4.00	2.18	-
$Ni_6Al_2(OH)_{18}$	HTC	2.51	4.70	2.55	3.40
$Cu_6Al_2(OH)_{18}$	HTC	3.98	> 4.66	2.44	3.05
$Zn_6Al_2(OH)_{18}$	HTC	2.26	3.82	2.00	-
$Pd_6Al_2(OH)_{18}$	HTC	1.55	1.93	0.00	-
$Cd_6Al_2(OH)_{18}$	HTC	1.20	-	-	-
$Co_6Cr_2(OH)_{18}$	HTC	1.99	4.51	2.13	-
$Ni_6Cr_2(OH)_{18}$	HTC	2.63	> 4.66	2.55	3.22
$Cu_6Cr_2(OH)_{18}$	HTC	3.62	> 4.66	2.69	3.32
$Co_6Fe_2(OH)_{18}$	HTC	1.53	3.89	2.02	-
$Ni_6Fe_2(OH)_{18}$	HTC	2.15	4.78	2.16	3.20
$Cu_6Fe_2(OH)_{18}$	CHN	2.89	4.22	1.90	-
$Ni_6Ga_2(OH)_{18}$	HTC	2.02	3.79	2.14	-
$Cu_6Ga_2(OH)_{18}$	CHN	3.22	4.72	2.18	-
$Zn_6Ga_2(OH)_{18}$	HTC	1.36	3.19	1.47	-
$Co_6La_2(OH)_{18}$	HTC	1.82	2.66	0.95	-
$Ni_6La_2(OH)_{18}$	HTC	1.83	3.17	2.51	2.44
$Cu_6La_2(OH)_{18}$	CHN	1.62	1.77	0.26	-

a. Dash (-) indicates no test was performed.
b. HTC indicates the conventional hydrotalcite structure and CHN indicates $Cu_2(NO_3)(OH)_3$.

Table 3. Physical Properties and Sorption Coefficients of the Calcined Hydrotalcites[a]

Targeted Composition	Calcination Time	Log K_d I^-	Log K_d IO_3^-	Log K_d ReO_4^-	Log K_d TcO_4^-
$Ni_6Al_2(OH)_{18}$	1 hour	-	1.99	1.02	-
$Ni_6Al_2(OH)_{18}$	24 hours	1.56	1.93	0.93	-
$Ni_6Ga_2(OH)_{18}$	1 hour	0.89	2.42	1.23	-
$Ni_6Ga_2(OH)_{18}$	24 hours	1.33	1.92	1.13	-
$Zn_6Ga_2(OH)_{18}$	1 hour	1.36	-	-	-
$Zn_6Ga_2(OH)_{18}$	22 hours	1.04	-	-	-

a.   Dash (-) indicates no test was performed.

c.   Layered Bismuth Hydroxides

From the onset, developing anion getters based on bismuth seemed an attractive alternative given the considerable insolubility of many bismuth-oxide-anion combinations (e.g., those with sulfate,

chloride, bromide, iodide, carbonate, nitrate, fluoride, iodate etc.). When alleged "hydrotalcites" (Tsuji et al., 2000) based on Bi-Mg-Zn-hydroxide formulations appeared it became apparent that the such materials might also have the high surface areas and positive surface charges required to selectively scavenge anions from solution. These materials were first evaluated as part of a DOE-Tank Focus Area effort (2001-2002) to find getters for use in HLW tank decommissioning. These results were encouraging enough (Appendix B) to warrant revisiting the topic in the context of finding getters for deployment in the YMP repository invert.

General Synthesis: Because of their historical affiliation with hydrotalcites, it is not surprising that the Bi-based materials are synthesized using methods similar to those used to prepare hydrotalcites. Typically, an acidified bismuth nitrate solution is prepared separately from that of the second metal salt. Care must also be exercised in the choice of the other metal salt since many anions (such as chloride, acetate, sulfate, carbonate etc.) will immediately react with bismuth and precipitate insoluble bismuth compounds that differ from the desired synthesis product. The fluids are then mixed and immediately titrated with sodium hydroxide until the pH stabilizes at about 9, though overshooting, even up to pH 12, does not appear to make any difference. Traditional hydrotalcite preparation methods may also employ sodium carbonate rather than sodium hydroxide to raise the pH. However, the bismuth oxy-carbonate salt which then forms has little affinity for scavenging the radionuclides in question (iodide Kd of just 16). As the pH increases a thick, white, pasty slurry forms immediately, which is then cured in the synthesis fluid at about 90° C oven for times ranging from overnight to over the weekend. (For the record, no significance could be ascribed to curing times, or to whether the process was even carried out.) However, since a successful getter in the YMP repository environment will have to withstand elevated temperatures, it seemed a sensible precaution to incorporate a heating step into the synthesis procedure.) The residual salt solution is then washed out and the residue dried (either at room temperature or in a drying oven) producing a cohesive mass of material that can be ground to give the very fine powder used in batch K_d testing. Appendix A (Table A-4) gives additional details on the synthesis of materials used in this study while Appendix B provides some details on materials from the previous TFA study.

Performance of archived Bi-based iodine getters: The current study was initiated by re-examining the performance of the archived getters developed earlier under TFA sponsorship. Particular concerns were whether the passage of time (and possible aging of materials), or the use of a different test fluid (e.g., J-13 surrogate vs. 1% to 5% DSSF-7 HLW tank simulant fluid – see Appendix B, Table B-1 for composition) would negate the promise evident in the earlier study. Secondary objectives were to: (a) extend the database on their performance to include the sorption of iodate as well as iodide, and (b) assess if these materials had also retained some ability scavenge ReO_4^-.

After aging for more than a year, these materials did, indeed, retain their ability to scavenge both iodide and ReO_4^-, though in the latter case the performance was insufficient to meet the $10^3 K_d$ criteria that defines a "useful" getter. We also established that these aged materials were good iodate getters – occasionally performing at levels that exceeded their ability to scavenge iodide (Table 4).

In some cases arsenate sorption was also assessed as a "probe" for a getter's propensity for forming inner sphere surface sorption complexes, and because treating drinking water is currently of great topical interest. Generally, these materials proved to be very effective arsenic scavengers with "batch K_d" values in the range of 10^5-10^6. This performance is significantly better than what was measured for As in the earlier (TFA-sponsored) tests (compare Table 7, 8, and 9 with Appendix B, Table B-4). This improvement presumably reflects a higher pH present in the 1%-5% DSSF-7 fluid as compared to that of the "J-13 surrogate" – which is the trend which might be expected with changing pH, where an anionic constituent was scavenged by a surface complexation process (Davies and Kent, 1990).

Table 4. Batch "Kd's" for previously synthesized materials in a J-13 simulant (NT = not tested)

0.25 g solid sample to 25 ml J-13 simulant, shaken for 24 - 48 hours. Sample designation with occasionally X-ray data and chemistry See appendix 2 for additional details on materials.	I⁻ Log(Kd)	IO₃⁻ Log(Kd)	ReO₄⁻ Log(Kd)
HT-0	NT	1.6	Kd<10
HT-1, Zn >Sn+2Al, SO4, HT peaks broad but well defined	NT	1.6	Kd<10
HT-2, Zn >Sn+2Al, SO4, HT peaks broad but well defined	NT	Kd<25	Kd<10
HT-3, Zn-Bi, SO4, Almost no HT peaks	2.3, 2.4	2.5, 2.5	Kd<10
HT-4 , Mg-Bi, CO3, Almost no HT peaks	1.2	1.4, 1.1	Kd<10
HT-5 (fines), Zn-Al, SO4, HT peaks well developed	NT	Kd<25	1.2
HT-6, Mg-Bi, SO4, Almost no HT peaks	Kd<10	1.6	Kd<10
HT-7, Zn-Bi, Ac(Ac =Acetate), HT peaks broad but prominent	3.7, 3.8	3.3	2.1
HT-8, ZnAl, Ac, HT peaks broad but prominent	NT	2.9	2.1
HT-9, MgAl, Ac, well crystallized HT	NT	3.6	1.9, 2.0
HT-10, ZnBi, Ac, HT peaks broad but prominent	3.7, 4.0	2.3	1.4
HT-11 (dried 90-97°C), Mg > CuBi, Ac, well crystallized HT	1.7	2.8	1.8
HT-11 (lime green), Zn >CuBi, Ac, multiple broad HT peaks	3.9, 3.9	3.4	1.5
HT-12 (low temp drying), Mg > Cu, Bi, Ac, well crystallized HT	1.7	2.8, 1.9	1.8
HT-14 (batch 1), Mg Al, Ac, poorly crystallized HT	NT	3.2	2
HT-15, Zn >Cu, Sn+2La>Sn+4, Ac, Small broad well defined HT	3.1	2.9,4.0	1.7, 2.5
HT-16, Mg >Cu,Sn+2La>Sn+4, Ac, poorly crystalline HT	1.5	2.8	1.4
HT-17/18? Zn >Sn+2, La, Ac (NA)	Kd<10	NT	NT
HT-17, Zn >Sn+2La, Ac, no HT, ZnO and Sn6O4(OH)4	Kd<10	3	1.9
HT-18, Mg >Sn+2La, Ac, no HT, good Sn6O4(OH)4 poor Mg2La2SnO7	Kd<10	1.8	2.3
HT-19, Mg >Cu, Sn+2Al>Sn+4, Ac, small broad HT peaks	NT	3.4, 3.3	2.2,2.3
HT-20 Zn >Cu, Sn+2Al>Sn+4, Ac, small broad HT peaks	3.1	4	2.4, 2.5
HT-20 (Split of Apricot colored precipitate)	2.9, 3.2	3.9	2.5, 2.5
HT-20 (blue, settled on top)	1.5	2.5	1.4
HT-21 (split), Mg >Cu, Sn+2Al>Sn+4, Ac, small broad HT peaks	NT	3	2.1, 2.0
HT-21 (settled on top)	NT	1.6	1.3
HT-22 (Turquoise colored from top of batch)	NT	3.8	2.3, 2.3
HT-22 (split), Zn>Cu and Al>Sn	NT	3.8	2.4, 2.4
HT -22 (settled on top)	NT	2.4	1.3
HT -23 (Hot split)	NT	1.5	0.4

NT = not tested
A log(Kd) of about 4.2 means the analytic instrumentation is about at the lower limit of its detection.

Newly Developed Bi-based Iodine Getters (Round 1): Studies on the archived materials clearly demonstrated that Bi-based materials were promising getters. However, a number of unanswered questions remained:

    (a) would a second synthesis also result in successful getters or were the initial result some sort of an experimental fluke;

    (b) does the presence of a second metal have a strong impact on the performance of such materials;

    (c) how sensitive is the performance with respect to changes in test solution pH;

    (d) what is the maximum loading of the secondary metal that could be tolerated;

    (e) how important is the anion mix (e.g. anions needed to counterbalance the metals in the synthesis) in the original synthesis?

To address these questions, additional batches of materials were synthesized (Appendix A) and tested using the familiar "batch Kd" methodology and the "J-13 simulant" solution that was doped with ppm levels of various radionuclide surrogates (Table 5, and Appendix A).

Table 5: Synthesis details and Kd results for various Round 1 - Bi-based getters
(The balance of these tests would have been performed with what would turn out to be a relatively high solid:liquid ratio; approximately 0.1 g of getter in 25 ml of J-13 simulant solution. Colors group result from different batches of analyses.)

Sample Desiganation	# grams Bi(NO3)3- Pentahydrate	Other Salts	grams salts	Base Used*	I- Log(Kd)	IO3- Log(Kd)	ReO4- Log(Kd)
P5-J	8.13	Ni(NO3)2 ¥	15.15	Ni(OH)2	2.9, 3.4, 2.90, 2.8	3.4	1.4, 1.2
P5-K	8.30	Zn(NO3)2 ¥	20.97	ZnO	3.8, 4.0, 3.6, 3.5	4.9	2.4
P5-L	8.12	Zn(NO3)2 ¥	1.54	NH4OH	5.2, 4.0, 3.8, 4.1	4.9	3.8, 3.8
Pepto Bismol - dried	N/A	N/A	N/A	N/A	3.0	2.7	2.1
Bi-subcarbonate	N/A	N/A	N/A	N/A	2	2.0	1.0
Bi2O3 untreated	N/A	N/A	N/A	N/A	3	1.7	Kd<10
P5-A	Bi2O3	in fused LiNO3		N/A	3.6, 3.5	2.3, 2.3	1.3, 1.2
P5-B & C	8.25	LiNO3	10.84	NH4OH	4.26, 4.4, 4.4	4.2	3.8, 3.8
P5-D	8.31	LiNO3	0	NH4OH	4.1, 3.9, 3.9, 4.2	4.6	2.3, 2.3
P5-H	8.25	KNO3	15.52	KOH	3.7, 3.8, 3.4, 4.0	3.5	2.1, 2.2
P5-I	8.17	NaNO3	13.35	NaOH	3.3, 3.7	2.5	0.9
P9-1	8.37	LiNO3	1.08	Na(OH)	3.8	NT	NT
P9-2	8.29	KNO3	15.65	Na(OH)	3.8	NT	NT
P9-3	8.21	KNO3	1.56	Na(OH)	3.9	NT	NT
P9-4	8.27	NaNO3	13.36	Na(OH)	4.0	NT	NT
P9-5	8.23	NaNO3	1.38	Na(OH)	3.8	NT	NT
# The bismuth ntirate hydrate was dissolved in roughly 5 g concentrated HNO3 mixed with 25 ml DI H2O							
* Titrated to roughly pH 9.5							
¥ Hexahydrate salt							NT = Not Tested

One set of the new materials (P5-J, K, L) resembled the old mixes in that the synthesis fluid contained both a M^{+2} metal and bismuth. Since among the TFA-sponsored samples the performance of Mg^{+2} - based materials was inferior to that of Zn based materials, the decision was made to substitute a different divalent metal, Ni^{+2}. The results from these tests confirmed the robust nature of the synthesis since, with minimal care; it was again possible to prepare

materials that were excellent scavengers for both iodide and iodate. In addition, this time some materials (P5- B,C and L) performed "acceptably" for ReO_4^- removal.

The possibility of gaining insights into the impact of the second metal, as well as the type of base used to neutralize the initial metal mix, was also built into this early experimental matrix. Thus, the relative performance of Zn and Ni-based materials were assessed alongside of a variety of combinations where the second metal was a monovalent alkali cation (Li, K, Na). The concept arose out of the observation that if $Al(OH)_3$ - also a layered lattice - is placed in a concentrated lithium salt solution some lithium ions diffuse into the vacant octahedral sites in the $Al(OH)_3$ lattice, creating an anion exchange medium (Devyatkina *et al.*, 1983; Lei *et al.*, 2000). Given that the size of the sites in a predominantly Bi-hydroxide lattice would not necessarily be the same as those in aluminum hydroxide, it seemed reasonable to try other monovalent cations as well - hence Na^+ and K^+; ammonium was also added by default since large amounts of ammonium hydroxide were occasionally employed to neutralize the nitric acid required to initially keep the bismuth in solution.

The results of these substitutions were not particularly dramatic, at least with regard to the ability of the materials to scavenge iodide. Most of the iodide $Log(K_d)$ values still fell between 3 and 4 and about the only clear trend is that the Ni-based material is not quite as good as the others. The picture with regard to iodate and perrhenate scavenging is more interesting. $Log(K_d)$ values for iodate range from about 2.5 to 4.9, a factor of 250 difference in performance. For perrhenate, the spread was even larger with $Log(K_d)$ values from 0.9 to 3.8 – a factor of almost 800 difference in performance. The highest ReO_4^- K_d values were sufficiently anomalous to warrant some follow-up experimentation employing actual TcO_4^-. In a J-13 solution spiked with tracer levels of pertechnetate the K_d was measured as 7,350 for the P5-B&C material, while in a solution spiked initially to a level of 12.8 ppm Tc (1.3×10^{-4} molar) the K_d still had a surprisingly high value of 338. These results directly support the concept of using ReO_4^- as a surrogate for TcO_4^-, at least as a qualitative technique for identifying promising candidate Tc-getters. A quantitative correspondence between getter responses to the two anions remains to be established.

Finally, a few scoping tests were performed on materials that were commercially available to assess whether just any bismuth compound was likely to work (Pepto-Bismol (dried) - bismuth subsilicate, from the drug store, and reagent grade bismuth oxide and subcarbonate). Nothing dramatic showed up here but is may be significant that treating the Bi_2O_3 in molten $LiNO_3$ did enhance the overall scavenging ability of the residue.

Samples prepared independently by the second author (J.D.P. rather than J.L.K.) also show similar results (Table 6), again confirming that the synthesis is, indeed, robust. It is also evident that the bismuth oxyhalides have significantly smaller sorption capacities than do the bismuth oxides (Table 6).

Table 6. Sorption Coefficients of Bismuth Compounds

Structures Identified By XRD	Log K_d I^-	Log K_d IO_3^-	Log K_d ReO_4^-
$Mg(OH)_2 + Bi_xO_y$	3.18	3.42	2.75
$Co_5(O_{9.48}H_{8.52})NO_3 + Bi_xO_y$	2.75	4.09	3.56
$NiO(OH) + Bi_xO_y$	2.44	3.46	3.31
$ZnO + BiOCl$	1.74	1.99	0.96
$ZnO + Bi_xO_y$	3.78	3.94	3.71
$Cu_4(NO_3)_2(OH)_6 + Bi_6(NO_3)_4(OH)_2O_6\ 2H_2O$	4.06	3.36	2.18

To summarize, based on these studies it appears that Bi-based getter materials have the following characteristics:

1. The synthesis is relatively robust and reproducible;
2. At least for iodide, the second metal in the mix did not have a large effect on performance;
3. Materials were identified that scavenged iodate as effectively as they scavenged iodide;
4. Although not the direct objective of this research, there are indications that these materials may also be effective at scavenging perrhenate (and hence technetium);
5. The nature of the alkali metal base, as well as high initial alkali metal concentrations in the synthesis fluid had little impact on the ability of getters to scavenge iodide, but did impact scavenging ability of the getter toward other anions.

Follow-On Studies (Round 2): The large spread in Kd values for iodate and perrhenate, and the small, though significant, difference between the performance of the Zn and Ni based materials even for iodide, prompted additional research into mixes rich in divalent and trivalent metals. Toward this end a variety of multi-metal mixes were prepared in pairs. Mixes designated "-1" (Table 7) were fabricated from a synthesis solution containing a 1:10 molar ratio of metal to bismuth while those designated "-2" had equal amounts of the second metal and bismuth in the synthesis solution prior to the neutralization step.

It was obvious at the onset that in most cases much of the second metal was not incorporated into the precipitates. This follows from the fact that for the highly colored ions the post-precipitation solution remained colored, while the precipitate (after being washed appropriately) was white. Those solids with obvious coloration included mixes with iron (brown), manganese (black), and chromium (III - green). However, even in these cases, the co-precipitation of a second hydroxide is a more likely explanation than formation of a mixed-metal hydroxide material and only small amounts would actually be needed to color the mix.

Even when placed on a shaker table, the solids in the first K_d runs did not appear to stay suspended very well. A second set of experiments was, therefore, performed after the materials had been ground to a fine powder. The liquid:solid ratio was also decreased by a factor of four since in the first round of testing some materials had removed essentially all of the radionuclide surrogate (leaving dissolved concentrations almost at the detection limit of the ICP-MS). Quite surprisingly, the K_d values from the second pass were *significant less,* in spite of the grinding, which should have made more surfaces available (Fig. 2 and Table 7).

This odd behavior apparently arises because by decreasing the solid:liquid ratio we (inadvertently) entered the realm where the sorption capacity of the solids was approaching saturation. This explanation is consistent with the observation that the overall iodide loading was similar in the pre and post grinding experiments even though the K_d values differed significantly. For, example, for iodide, the K_d values in most cases differed by at least a factor of ten (an average difference factor is 13.3), while the loadings differed by significantly smaller factors (an average of 2.7). Thus, in addition to providing K_d values for iodide sorption at low iodine concentrations, these results also, fortuitously, provide rough estimates of material loading capacities *in a concentration range relevant to assessing performance in YMP-related environments.*.
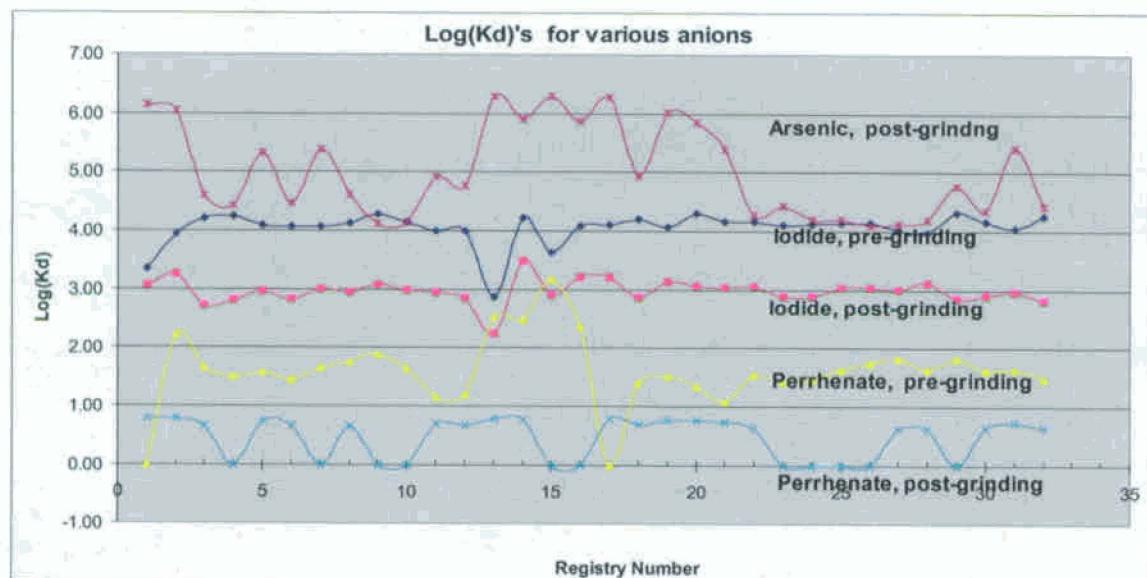
Fig. 2. Comparative behavior before and after grinding iodide, perrhenate and arsenate. (post-grinding only, pre grinding analyses were mostly non-detects with the implication of values greater also than those for the post-grinding, though by how much cannot be quantified). Registry numbers provide sample identification; see Table 7.

A second odd behavior noted in the course of these experiments was that the pH of the equilibrated K_d experiments was distinctly acidic, in spite of the fact that the recipe used for making these materials generally involved titrating the synthesis fluid to a distinctly basic pH and then aging the precipitate overnight in this fluid. Studies performed early in the program (Fig. 3) had indicated that Kd values were higher in more acidic solutions – but it was unclear how large the decrease would be in mildly basic YMP-related groundwaters, and whether this behavior applied to iodate and perrhenate as well as iodide.

Table 7: Kd values before and after grinding

Registry Number		Before Grinding Iodide Log Kd	pH of "Before" Kd Expt. Fluids	After Grinding Iodide Log Kd	Kd/Kd Pre/post	Relative Loading Post/pre	Before Grinding ReO4- Log Kd	After Grinding ReO4- Log Kd	After Grinding As Log Kd
1	FeAc-1	3.34	5.74	3.07	1.86	2.95	NT	1.98	6.14
2	Fe II Ac 1	3.93	5.682	3.26	4.68	3.09	2.20	1.58	6.05
3	NiAc-1	4.19	5.38	2.73	28.84	2.88	1.65	1.73	4.60
4	NiAc-2	4.24	5.143	2.82	26.30	2.51	1.50	NS	4.44
5	BaNO3 1	4.09	4.786	2.99	12.59	2.63	1.58	1.69	5.32
6	BaNO3 2	4.07	5.111	2.85	16.60	2.51	1.43	1.32	4.47
7	CuAc 1	4.06	4.861	3.03	10.72	2.75	1.64	NS	5.38
8	CuAc 2	4.12	5.364	2.97	14.13	2.75	1.75	1.04	4.61
9	MgNO3 1	4.27	5.523	3.09	15.14	2.95	1.88	NS	4.13
10	MgNO3 2	4.14	5.3	3.00	13.80	2.69	1.62	NS	4.15
11	ZnAc 1	4.00	4.918	2.96	10.96	2.29	1.15	2.13	4.92
12	ZnAc 2	3.99	5.714	2.87	13.18	2.19	1.19	1.66	4.78
13	CrNO3 1	2.89	5.311	2.24	4.47	2.57	2.53	1.68	6.29
14	CrNO3 2	4.22	5.86	3.50	5.25	3.47	2.47	1.81	5.91
15	ZrNO3 1	3.63	5.033	2.92	5.13	2.69	3.19	NS	6.29
16	ZrNO3 2	4.08	5.555	3.24	6.92	3.02	2.36	NS	5.88
17	LaNO3 1	4.10	6.336	3.23	7.41	3.02	Log(Kd)>5	2.01	6.27
18	LaNO3 2	4.20	5.078	2.88	20.89	2.45	1.39	0.82	4.95
19	Mn II Ac 1	4.06	5.275	3.16	7.94	2.75	1.51	1.96	6.03
20	Mn II Ac 2	4.29	5.465	3.08	16.22	2.75	1.35	2.19	5.86
21	ZnNO3 1	4.16	4.933	3.05	12.88	2.51	1.07	1.71	5.40
22	ZnNO3 2	4.17	5.104	3.08	12.30	2.75	1.54	0.32	4.28
23	MgAc 1	4.11	5.496	2.90	16.22	2.88	1.42	NS	4.43
24	MgAc 2	4.13	5.395	2.90	16.98	2.75	1.46	NS	4.20
25	CaNO3 1	4.13	5.639	3.05	12.02	2.88	1.63	NS	4.20
26	CaNO3 2	4.15	5.525	3.06	12.30	2.82	1.73	NS	4.11
27	SrNO3 1	4.01	5.734	3.02	9.77	2.69	1.82	1.88	4.12
28	SrNO3 2	3.97	5.857	3.13	6.92	2.82	1.63	2.02	4.20
29	NiNO3 1	4.31	5.467	2.87	27.54	2.45	1.83	NS	4.78
30	NiNO3 2	4.15	5.452	2.93	16.60	2.69	1.61	1.49	4.35
31	CuNO3 1	4.04	5.302	2.99	11.22	3.02	1.63	0.93	5.42
32	CuNO3 2	4.26	4.759	2.82	27.54	2.63	1.47	0.89	4.44
			Average is		13.29	2.75			
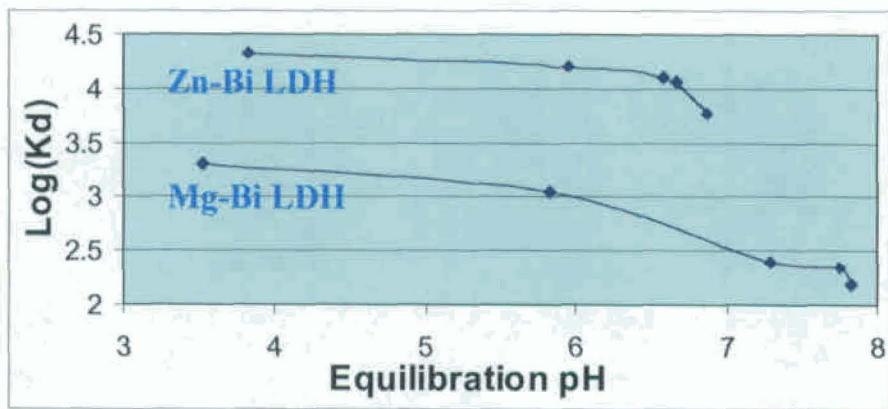
Fig. 3. Iodide Log Kd vs pH behavior for two mixed-metal layered double hydroxides synthesized early in the program.

Several mechanisms may be involved in scavenging iodide (and other radionuclides). If the bismuth hydroxide sheets in the lattice have a residual positive charge then an anion must reside on the surface of the sheets to maintain overall electrical neutrality of the mineral – but the nature of the anion is not particularly important. This is the setting where traditional kinds of anion exchange reactions may occur, and pH has a minimal impact on the process.

Alternatively, radionuclides may also be scavenged by a process (actually a collection of processes) broadly termed "surface complexation" (Davies and Kent, 1990). This occurs where incompletely bonded atoms left exposed on mineral surfaces interact with ions from the surrounding solutions. Typically, the hydrogen ion is strongly bonded to such surfaces so the overall surface charge (as well as the ability of the surface to exchange anions or cations) depends strongly on the pH of the surrounding fluid. In strongly acidic solutions a net positive surface charge develops and materials become good anion scavengers, while the opposite happens in basic solutions. It is this implicitly strong pH dependence that is of concern. Given the acidic nature of the final K_d solutions it is quite possibly that the generally auspicious high Kd values observed might not be representative of performance in the mildly basic indigenous YMP-related groundwaters.

To resolve this uncertainty several samples were selected for more detailed studies. In the first round of tests (Table 8, Fig. 4) the J-13 surrogate was spiked with iodide, perrhenate, and arsenate. A second set of tests was done with iod*ate* to complete the experimental matrix (Table 9 and Fig. 5).

For iodide and perrhenate a strong pH dependence is not apparent, except for the two extreme points for Fe and Zr. Thus, it is reasonable to surmise that anion exchange (onto charged metal hydroxide sheets) dominates over a surface complexation mechanism. For the more strongly held arsenate, however, there is evidence for a mixture of scavenging mechanisms in some cases. The NiAc-1 samples still appears to be dominated by a purely anion exchange mechanism. However, the BaNO3-1, FeAc-1, CrNO3-1, and ZrNO3-1 materials exhibit a weak pH dependency, though not nearly as large as would be expected if surface complexation were the

only scavenging mechanism involved. ("Ac" is an abbreviation for acetate.) The suite of experiments evaluating the impact of pH on iodate sorption produced a similar picture, with little variation in Kd over the pH range relevant to normal YMP-related groundwaters. However, the first few steps to increment the pH upward did typically result in a slight decrease in Kd (about half a log unit).

To summarize, it does not appear that generally the acid pH values reported earlier invalidate the generally favorable picture of iodide getter performance that seems to be developing. In all, a number of materials were identified that still retained iodine Kd values close to 10^3 in mildly basic fluids such as might be encountered under repository conditions. Unfortunately, because the program was ended sooner than anticipated we were unable to establish why acidic conditions developed during batch Kd testing, or why there was such a large spread between the behaviors of the different materials.

Table 8. Summary of pH dependent Kd (I^-, IO_3^-, ReO_4^- and AsO_4^{-3})

Getter	pH	Log Kd Iodide *	Log Kd ReO4	Log Kd AsO4
FeAc-1	7.2	3.18	2.98	GT 7
FeAc-1	7.4	3.18	1.70	6.96
FeAc-1	7.5	3.32	1.59	7.33
FeAc-1	7.8	3.32	1.68	7.70
FeAc-1	9.3	3.00	1.33	6.30
CrNO3-1	6.3	2.78	2.09	6.67
CrNO3-1	6.6	2.78	2.07	6.71
CrNO3-1	6.7	2.77	1.99	6.54
CrNO3-1	7.1	2.83	2.17	5.94
CrNO3-1	8.7	2.82	1.96	6.05
NiAc-1	6.1	3.42	1.95	4.71
NiAc-1	6.2	3.43	1.99	4.73
NiAc-1	6.5	3.46	2.20	4.71
NiAc-1	7.0	3.52	2.08	4.71
NiAc-1	8.9	3.55	1.85	4.76
BaNO3-1	5.4	3.64	1.96	5.03
BaNO3-1	5.8	3.61	2.05	4.86
BaNO3-1	6.3	3.58	1.99	5.00
BaNO3-1	6.7	3.58	1.99	4.46
BaNO3-1	6.9	3.57	1.81	4.23
ZrNO3-1	6.8	3.34	2.11	6.41
ZrNO3-1	7.0	3.36	2.21	6.40
ZrNO3-1	7.4	3.41	1.92	6.00
ZrNO3-1	7.6	3.36	2.05	6.12
ZrNO3-1	9.0	3.19	2.12	5.46

Material	rest pH	Log(Kd) for IO_3^-	Material	rest pH	Log(Kd) for IO_3^-
ZnAc1	5.565	3.00	CuNO31	5.412	3.56
ZnAc1	5.535	2.82	CuNO31	5.598	3.51
ZnAc1	6.099	2.86	CuNO31	6.153	3.15
ZnAc1	6.959	2.81	CuNO31	6.6	3.23
ZnAc1	10.511	2.71	CuNO31	10.501	2.65
ZnAc2	5.811	2.96	CuNO32	6.931	2.77
ZnAc2	6.464	2.59	CuNO32	7.033	2.79
ZnAc2	7.354	2.27	CuNO32	8.451	2.86
ZnAc2	9.337	2.27	CuNO32	10.247	2.43
ZnAc2	10.694	0.69	CuNO32	10.749	1.63
ZnNO31	5.429	3.31	CrNO32	6.874	4.15
ZnNO31	5.419	3.55	CrNO32	7.146	4.00
ZnNO31	6.228	3.17	CrNO32	7.867	4.10
ZnNO31	7.338	2.28	CrNO32	8.29	3.82
ZnNO31	10.454	2.81	CrNO32	9.938	3.31
ZnNO32	6.947	2.70	NiAc2	6.609	1.71
ZnNO32	7.363	2.70	NiAc2	7.387	2.50
ZnNO32	8.298	2.68	NiAc2	8.634	2.55
ZnNO32	10.088	2.50	NiAc2	9.908	2.69
ZnNO32	10.729	2.48	NiAc2	10.747	no sorption
ZrNO32	6.938	3.13	BaNO32	5.788	2.92
ZrNO32	7.337	3.15	BaNO32	6.859	2.45
ZrNO32	8.476	3.08	BaNO32	7.966	2.73
ZrNO32	9.508	2.70	BaNO32	9.701	2.48
ZrNO32	10.522	2.76	BaNO32	10.677	2.13

GT = greater than, * Values presented in Fig. 4
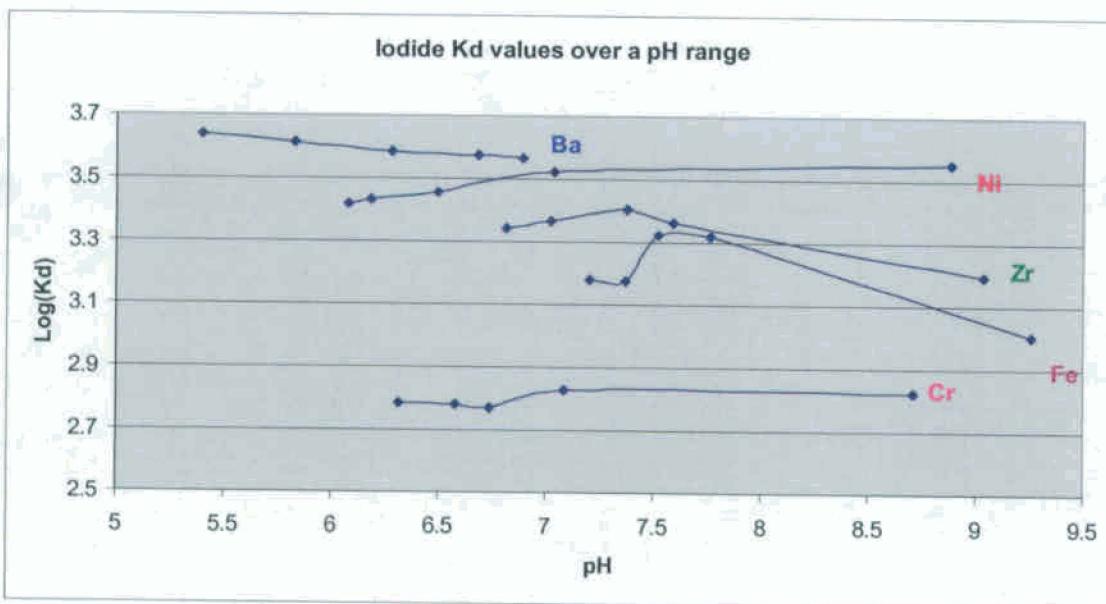
Fig. 4. Iodide Kd values determined with the post-grinding ratio of solid to liquid; 0.05 g solid to 50 ml of fluid. (from 4-26-05 pH adjustments)
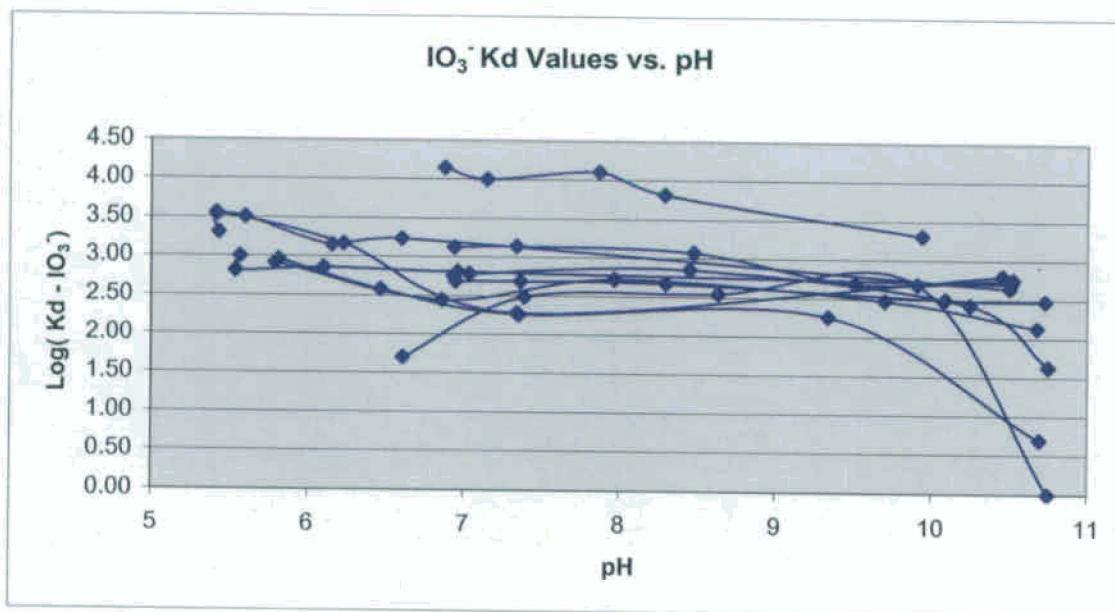
Fig. 5. Iodate Kd values determined with the post-grinding ratio of solid to liquid; 0.05 g solid to 50 ml of fluid. (from 4-26-05 pH adjustments)

Materials Characterization: All materials from this study were characterized using a batch "sorption" test process with "J-13 surrogate" water. Some materials synthesized early in the program (principally Round 1 materials from Table 5) were also characterized by X-ray diffraction (Appendix A, Table A-3 and Fig. A-1 to A-4.) and SEM (scanning electron microscope). In large measure, the X-ray diffraction studies showed these materials to be similar to the bismuth-containing samples produced years earlier for the TFA-funded study (Krumhansl *et al.*, 2006; and Appendix B, Table B-3). Detailed examination, however, did allow for segregating some of the early synthesized (Round 1) materials into tentative groupings (designated Types I, II and III – Appendix A, Table A-3 and Fig. A-1 to A-4). Three classes of materials were discernable, none of which exactly match the relatively uniform materials produced by the standardized recipe used in the second round of mixed-metal synthesis studies (Tables 7 and 8). The distinctions between the performances of the different groupings are not large for iodide and arsenate. But, the Type II sorbers work substantially better for perrhenate, perchlorate and iodate. This suggests that a simple anion exchange process is involved for the monovalent oxy-anions, while a (stronger) surface complexation mechanism is involved in scavenging iodide and arsenate.

Table 9. Kd values for select Round 1 materials grouped by X-ray diffraction type (Appendix A).(These were very early tests that used an Albuquerque tap water matrix, 0.1 g sample to 10 ml tap water with initially 2 ppm of I, Re and As, or 20 ppm ClO_4^-. Analytical techniques were generally still in the developmental stages at this time as well.)

	"Type"	Kd-not Log ClO_4^-	Log Kd ReO_4^-	Log Kd I^-	Log Kd AsO_4^{--}
p83α	II	25.1	3.78	3.70	5.20
p83β	?	0	0.02	ns	1.53
p83γ	?	4.6	-0.23	1.67	4.29
p9-1	I	5.5	0.57	2.92	5.29
p9-2	I	12.3	0.20	2.86	5.64
p9-3	I	11.8	0.39	2.71	5.58
p9-4	I	11.8	0.53	3.12	5.62
p9-5	I	7.9	0.75	2.84	4.85
p5-C orig.	II	19.1	3.43	3.37	5.27
p5-C labled	II	20.7	3.27	3.99	5.11
p5-D	I	8.4	0.73	2.97	6.03
p5-H	I	0	0.11	ns	5.17
p5-I	I + ?	3.6	0.05	ns	3.83
p5-J	II	4.6	0.84	1.80	5.30
p5-K	misc	7.9	2.18	2.89	4.48
p5-L	II?	20.2	3.85	3.10	4.72
BiNO3.5W	?	nt	1.15	3.92	5.24
p85μ	III	nt	2.44	3.48	5.19
p85v	II	nt	3.30	3.67	5.11
p85δ	III	nt	2.36	3.80	5.72
Bi subsal.		nt	1.40	2.43	4.40
nt - not tested					
ns - no sorption found					

Some X-ray work was also done on the Round 2 materials, though the abrupt termination of the program precluded going very far with this study. Apparently the more standardized synthesis produced a material which can be distinguished by consistently having its strongest diffraction line being at about 7.5 deg. two-theta, while for the best crystallized early materials (Type I) the low angle peak is at about 8.5 deg. two-theta and it is not the strongest reflection.

SEM/EDS studies revealed that the solids precipitating from the mixed salt solutions only contained evidence of the second (non-bismuth) metal if the second metal formed an exceedingly insoluble hydroxide on its own (e.g., Fe^{+3}, Cr^{+3} Zr^{+4}, Mn^{+4}). In the other cases the effect of the second metal was apparently to influence the type of bismuth hydroxide layer structure that nucleated, though the second metal does not seem to have actually been incorporated into the structure. These distinctions seemed to be most pronounced among the materials produced by the less standardized processes used in Round 1. Most of the mixed-metal pairs produced during the Round 2 studies resembled P5-C (below, Fig. 6).

P5-C   P9-2   P5-E

Fig. 6. SEM photographs showing different textures of Bi-based getters; see Table 5 for performance and synthesis details. Occasionally a bladed structure results that is suggestive of layered materials (middle, P9-2). Often, however, the results are granular (left) or needle-like (right).

d.   Miscellaneous Materials

Assorted materials that do not fit into any of the above categories are discussed below. Several of the samples consist of naturally occurring minerals, tungstates, phosphates or simple metal oxides or hydroxides. Some of the naturally occurring minerals studied contain copper in the hopes that the copper compounds generally could be shown to aid in sequestring iodide. The tungsten bronzes were studied because of their stability under a various oxidation states. The Cs-Cu-phosphates/arsenates were of interest because they are mesoporous materials. The simple metal oxides or hydroxides were studied to determine if the individual components of the complex materials studied above contributed to the sorption capacities.

Table 10. Sorption Coefficients of Miscellaneous Compounds[a]

Targeted Composition	Log K_d I^-	Log K_d IO_3^-	Log K_d ReO_4^-
Malachite	1.2	2.5	< 1
Azurite	1.3	-	
Chrysocolla	1.1	-	
Montmorillonite - SWy-1 w/ Sn(II)	-	1.0	2.3
Montmorillonite w/ Sn(II)	-	1.5	3.1
Kaolinite w/ Sn(II)	-	< 1.4	1.4
Saponite w/ Sn(II)	-	< 1.4	1.3
$MgWO_4 + WO_3$	1.28	1.09	0.84
$Fe_2WO_6 + WO_3$	1.25	1.09	0.95
$CoWO_4$	0.98	1.13	1.11
$NiWO_4$	0.59	1.10	1.08
$CuWO_4$	1.46	0.87	0.63
$ZnWO_4$	1.28	0.96	0.67
$CsCu_5O_2(AsO_4)_2Cl$	1.38	-	-
$K_2Cs_3Cu_3(P_2O_7)_2Cl_3$	1.68	0.86	1.14
$Cs_2Cu_3(P_2O_7)_2 \, xH_2O$	1.72	2.00	1.90
$CuZr_2(PO_4)_3$	2.42	1.34	1.33
$Cu_2P_2O_7 + Zr_2P_2O_7$	1.32	1.29	1.19
$SnHPO_3$ (JLK)	< 1.0	0.5	1.4
$Al(OH)_3$ Pure	< 1.0	-	-
$Al(OH)_3$ w/$SnCl_2$ (0.5 g)	1.1	-	-
MnO_3	-	< 1.4	< 1.0
NiO	0.88	0.00	0.42
$Ni(OH)_2$	0.84	2.73	0.62
Cu_2O	1.5	< 1.4	< 1.0
CuO	1.0	< 1.4	< 1.0
$Sn(OH)xOx$ acid titration (NA)	< 1.0	< 1.3	<1.0
$Sn(OH)_x$, $SnCl_2$, Base titrat. (NA)	< 1.0	-	-
$BaCO_3$(syn) (N.A.)	1.0	< 1.4	< 1.0
Fe metal with $CuSO_4$	2.6	-	-
W w/ Zn shot (NA)	-	< 1.4	1.3

a. Dash (-) indicates no test was performed.

Synthesis and Structural Characterization: The naturally occurring minerals were purchased at local mineral shops. They were then ground to a fine powder with an agate mortar and pestle.

Six polycrystalline tungstates were synthesized by solid state reaction. Stoichiometric amounts of MgO (Alfa Aesar, 95%), Fe_2O_3 (Alfa Aesar, 99.9%), CoO (Alfa Aesar, 95%), NiO (Alfa Aesar, 99%), CuO (Alfa Aesar 99.9%) and WO_3 (Alfa Aesar, 99.8%) were ground with an agate mortar and pestle. The samples were calcined in air between 850 – 1000 °C for 24 h. The materials were ground to a fine powder. Note: WO_3 is present in both the magnesium sample

because $Mg(OH)_2$ was present in the MgO and the iron sample because the author failed to realize that Fe_2WO_6 would form.

Three Cs-Cu/phosphates/arsenates were supplied by Mutlu Kartin. The Cu-Zr-phosphates were were synthesized by solid state reaction. Stoichiometric amounts of $(NH_4)H_2PO_4$ (Aldrich, 98%), CuO (Alfa Aesar 99.9%) and ZrO_2 (Aldrich, 99%) were ground with an agate mortar and pestle. The samples were calcined in air at 350 °C for 4 h, at 850 °C for 16 h, and at 1200 °C for 12h. The samples were removed after each heating step and reground to ensure mixing. The materials were ground to a fine powder.

The samples' structures were identified using powder X-ray diffraction (XRD). The XRD patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer (Cu $K\alpha$ radiation, Kevex detector, 40 kV, 30 mA; 2θ) 5-60°, 0.05° step size and 3 s count time) and used for crystalline phase identification. The phases were identified by comparison with the data reported in the JCPDS (Joint Committee of Powder Diffraction Standards) database.

Results and Discussions: The physical properties and sorption coefficients of the miscellaneous materials are summarized in Table 10. Most of the iodide, iodate and perrhenate sorption capacities (K_d) of these miscellaneous materials are unremarkable ($< 10^2$). Two samples have iodide sorption capacities that are greater than 10^2; $CuZr_2(PO_4)_3 - 10^{2.42}$ and Fe metal with $CuSO_4 - 10^{2.6}$. Three samples have IO_3^- sorption capacities great than 10^2; Malachite $- 10^{2.5}$, $Cs_2Cu_3(P_2O_7)_2 - 10^2$ and $Ni(OH)_2 - 10^{2.73}$. Finally, Montmorillonite exhibits a sorption capacity for ReO_4^- of $10^{2.3-3.1}$, though reduction of the Re(VII) may lie at the heart of the sequestration mechanism – in which case re-oxidation is a concern..

The range of adsorption for Montmorillonite demonstrates that sorption coefficients of minerals are strongly affected by impurities found in natural systems (and ferrous iron might be expected to play a similar role). It is not surprising that the tungstates did not exhibit high adsorption coefficients as these materials are structurally compact and are stable under a variety of oxidation states. Finally, occasional results found in the literature suggested that phosphates might play a significant role in radionuclide sorption (Anderson, 1998; Moore et al., 2001). Although no single phosphate exhibited multiple K_ds greater than 2, as a class they showed promise for the sorption of I^- and IO_3^-. Further investigation of several types of phosphates might yield promising materials for radioiodine sorption.

V. SUMMARY AND CONCLUSIONS

The principal objective of this study was to evaluate a wide range of potential iodine getters under conditions relevant to their placement in the invert beneath waste canisters in the Yucca Mountain repository. Toward this end, numerous potential getters were identified from the literature, and from the first author's past research activities. Their relative performance was judged using a batch "K_d" technique that employed a surrogate YMP-related groundwater ("J-13"). Two classes of materials appeared to be particularly promising; members of the hydrotalcite-mineral family and similarly layered materials comprised (principally) of hydrous bismuth hydroxide. Both classes of materials produced several candidates with "K_d" values greater than 10^3, (the metric set by performance assessment studies, MacNeil et al., 1999. as

defining a useful getter), and numerous materials that performed less well. Unfortunately, the getter program only lasted a year, making it impossible to develop an explanation for why similar materials performed so differently, or how one might optimize the best performing materials.

It is also ***extremely important*** to note that although these tests did use the "J-13" groundwater surrogate, these tests were far too limited in scope to be useful in defining how such getters would actually function inside a repository. The first step in addressing that issue would be to develop an extended test protocol that addresses difficult issues such as:

(1) How to show long term getter performance when only a few months (or at best years) are available to perform direct experimental observations on the getters;
(2) How to evaluate overall performance since the getter will have to function in a significant number of different environments;
(3) What actually defines acceptable getter performance?

Finally, although much remains to be learned about getter performance, a good start has been made at identifying potentially useful materials useful should a future need arise to further develop getters (or waste forms) to sequester the radionuclides targeted in this report.

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APPENDIX A
Selected supplementary data for this study:

Table A-1: Comparison of recipe for "J-13 surrogate" with literature "J-13" composition:

	mg/kg Recipe	mg/kg Ref. J-13
Na	57.0	45.8
K	5.00	5
Ca	13	13
Mg	2.0	2
SiO_2	see note	28.5
Cl	7.1	7.1
SO_4	22.6	18.4
HCO_3	152	152
NO_3	8.78	8.78
F	2.18	2.18
Na*	**78.8**	**45.8**

* If silica is added in the soluble form of $Na_2SiO_3 \cdot 9H_2O$ the Na concentration increases to 78.8 mg/kg, and the acid needed to bring the pH back into line will alter one of the anion concentrations.

Table A-2: Supplemental TcO_4^- Kd information:

Earliest Testing - Page 5

Solid	Initial Activity	After 72 hours	% Sorbed	Kd
"Bi(OH)3" ppted with no Li	221000	166000	24.89	41.4
"Bi(OH)3" ppted with Li	221000	58700	72.99	**337.7**
Bi2O3 As received	221000	187000	15.38	22.7
	pCi/ml			

221000 pCi/ml is 12.8 ppm Tc or 1.29×10^{-4} molar

Later Kd TcO_4^- Kd values

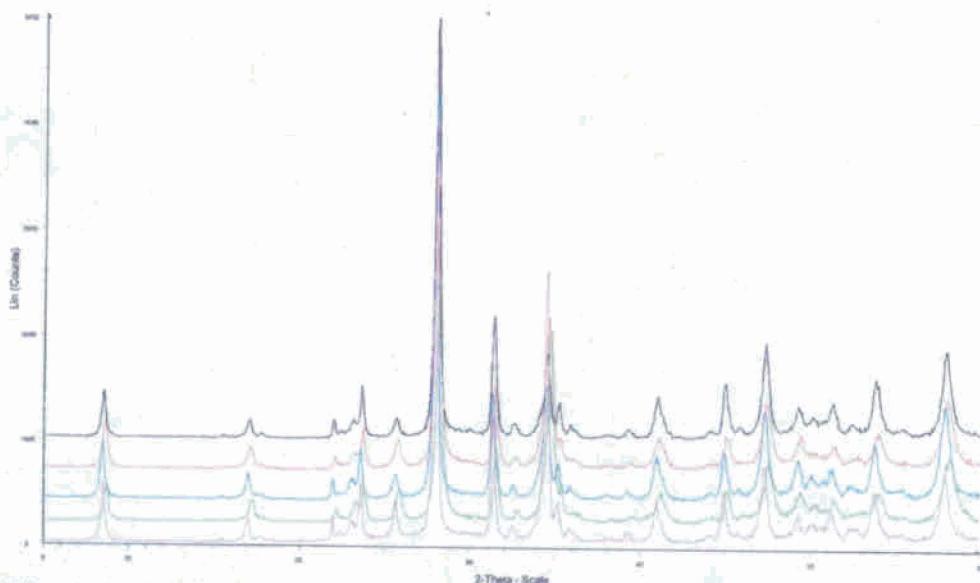| Sample	Beta activity (pCi/mL)	% sorbed	% remaining	"Kd"
Pepto bismol	7.80E+02	52	48	163.4615
P5D	1.47E+03	10	90	16.32653
P5H	1.74E+03	-7	107	-9.48276
P5I	2.02E+03	-24	124	-28.9604
P5J	2.04E+03	-25	125	-30.1471
P5K	1.24E+03	24	76	47.17742
P5L	8.78E+02	46	54	128.4738
P5F*	1.70E+03	-4	104	-6.17647
Blank	1.63E+03	0	100	0

Each sample 0.2g, added to 30mL Yucca Mtn. water. Spiked with Tc.
Sample P5F: only 0.05g sample used in 30mL water

Table A-3: X-ray diffraction characteristics of early-synthesized materials (numbers refer to peak positions - 2θ, Cu Kά X-radiation.

	"Type"	"hydrotalcite" Peaks?							
86-1	p83α	I	7-9 trace	none	none	none	24.5 trace		none	28.2 main
86-2	p83β	?								
86-3, no 4	p83γ	?								
86-5, no 4	p9-1	I	8.50	17	21.8	23	23.7	25.6		28.0 main
86-6	p9-2	I	9.00	17.4	22.2	23.3	23.9	25.9		28.0 main
86-7	p9-3	I	7.50	16.9	22	23.1	23.5	25.5		28.0 main
86-8	p9-4	I	7.70	17	22.2	23.3	23.6	25.8		28.0 main
86-9	p9-5	I	7.60	17	21.1	23.3	23.5	25.8		28.0 main
86-10	p5-C orig.	II	8.60	none	19.7tr	none	24.1 small	none	none	28.3 main
86-11	p5-C labled	II	6.0, 8.4	none	none	none	23.8 small	none	none	28.0 main
86-12	p5-D	I	8.2 sharp	15.5, 17, 17.7		22	23.0 tr	23.5 sharp	25.6 small	none	28.0 main
86-13	p5-H	I	7.6 sharp	14,15.1,16.5	19.8, 21.7	none		24.3 small	25.8 trace	27.0sharp	27.5 main
86-14	p5-I	I + ?	7.7 sharp		7.6	11.0, 15.4,		22.9 none		none	27.6 sharp
86-15	p5-J	II	6 small	none	19.4 tr		24.0 small	none	None	None
86-16	p5-K	misc	9 trace	10.5, 11.2, 11.7, 18.2, 19.5, 21.2, 22.0,			none	25, 25.6	none	28, 28.2(main),
86-17	p5-L	II?	7.2, nice		10.2	none	none	none	none	none	29.5 main
86-18	BiNO3.5W	?								
86-19	p85μ	III	7.0, nice	none	none	none	24.0 small	none	27.0 poor	28.4 trace
86-20	p85ν	II	7.0, nice	none	none	none	24.0 small	none	27.0 good	28.4 trace
86-21	p86δ	III	none	none	none	none	24.0 trace	none	none	28.4 main

86-1	p83α	I	none	31.9 Sharp		42 trace	45-48 hump	none	54.5 sharp	58 poor
86-2	p83β	?								
86-3, no 4	p83γ	?								
86-5, no 4	p9-1	I		31.3	34.5	40.8	44.8	47.2	53.6	57.8
86-6	p9-2	I		31.6	34.6	41.2	45.2	47.4	54	58.2
86-7	p9-3	I		31.3	34.5	40.7	44.9	47.1	53.6	57.8
86-8	p9-4	I		31.5	34.4	41.1	45.1	47.3	53.8	57.9
86-9	p9-5	I		31.4	34	41	44.9	47.2	53.7	57.9
86-10	p5-C orig.	II	none	31.9		41.3	45.7 sharp	47.6 broad	54.6 sharp	58.1 sharp
86-11	p5-C labled	II	none	31.8 sharp		41.5 trace	45.4 sharp	47.5 broad	54.2 sharp	58.5broad
86-12	p5-D	I	none	31.3 sharp	41.0 small		44.5 shapp	47.0 sharp	53.8 sharp	58.0 sharp
86-13	p5-H	I	28.0 sharp	29.5, 30.6, 33.4	35.0 etc		46.0, 46.4	47.6 trace	52.4, 53.5, 54.0,54.5,55.5 6,56.8,59, 59	
86-14	p5-I	I + ?	28.5 small	30.5 main		32.7, 38.4,40.3, 45.0, 45.5,46.5,50.0		52.8 large	
86-15	p5-J	II	25-31 hump	32.5 main		38.6 broad	46.7sharp	47.2 small	53-58 hump	
86-16	p5-K	misc	28.7, 29.5, 30.231.5, etc looks to be pretty well crystalline							
86-17	p5-L	II?	28-33 hump	32.5 sharp		42 trace	46.5 broad	48 sharp	52-58 hump	
86-18	BiNO3.5W	?								
86-19	p85μ	III	28-33 hump	33.0 sharp		43.5 trace	47.0 sharp	48 trace	52-58 hump	
86-20	p85ν	II	28-33 hump	33.0 sharp		43.5 trace	47.0 sharp	none	52-58 hump	
86-21	p86δ	III	28-33 hump	33.0 small		none	47.0 sharp	none	52-58 hump	

86-1	similar to p5L but shfited
86-2	
86-3, no 4	
86-5, no 4	
86-6	
86-7	
86-8	
86-9	intermediate small peats at 49 and 51
86-10	wide little at 34.4
86-11	wide little at 31.2, 41.5
86-12	yellow -Bi2O3?? - ell xline, decent small peaks at 12.0, 22.0, 23.2, 25.5, 32.4, 34.5 (pretty large), and 35.2
86-13	other peaks at 14.0, 15.0, 16.6, 19.7, 22.0, 22.6, 24.3, 26
86-14	
86-15	
86-16	
86-17	sharp salt peaks at 10.5 and 31.5, similar to p83α but shifted
86-18	
86-19	
86-20	
86-21	

Typical X-ray diffraction patterns for various kinds of Bi based getter materials

Fig. A-1: Typical "Type I" diffraction patterns (from the bottom up: p9-1 (purple), p9-2 (green), p9-3 (blue), p9-4 (brown), p9-5 (black).
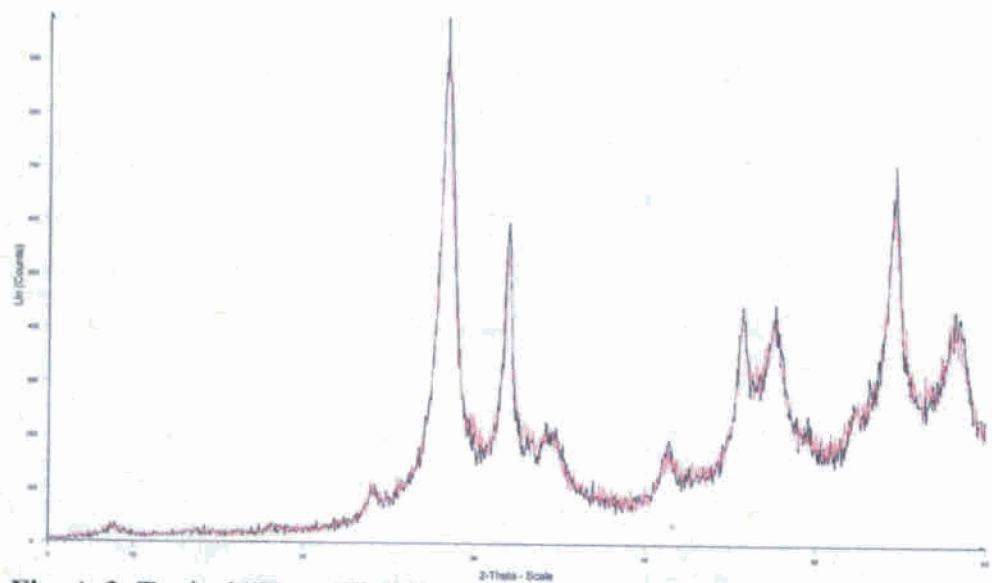
Fig. A-2: Typical "Type II" diffraction pattern (p5-C). Marginally better for ClO_4^-, I^- and ReO_4^-.
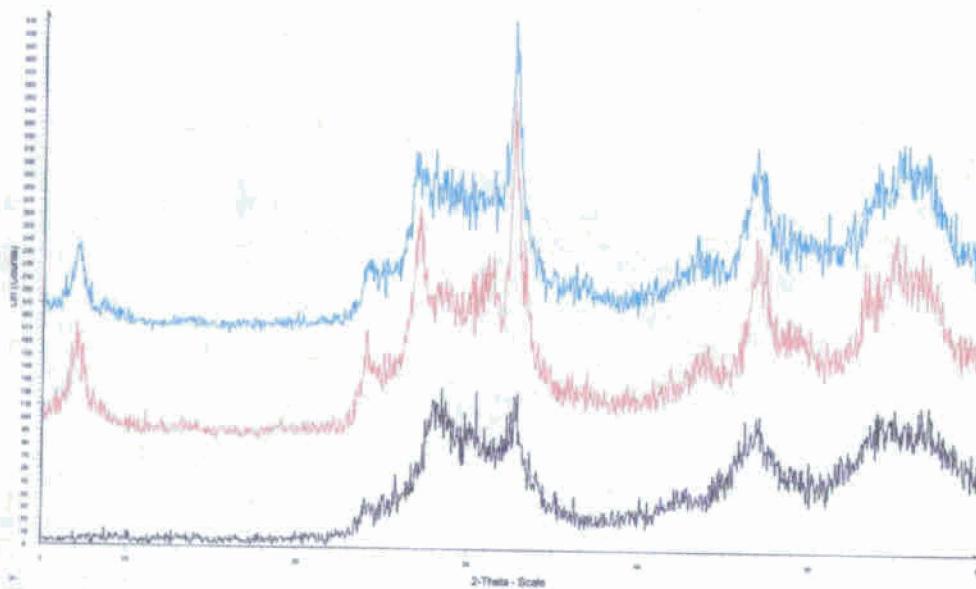
Fig A-3: Top: "Type III" diffraction patterns p85-m (blue, top) and p85-δ (red, middle), with a poorly expressed "Type II" pattern, p85-ν (black, bottom) below for comparison.
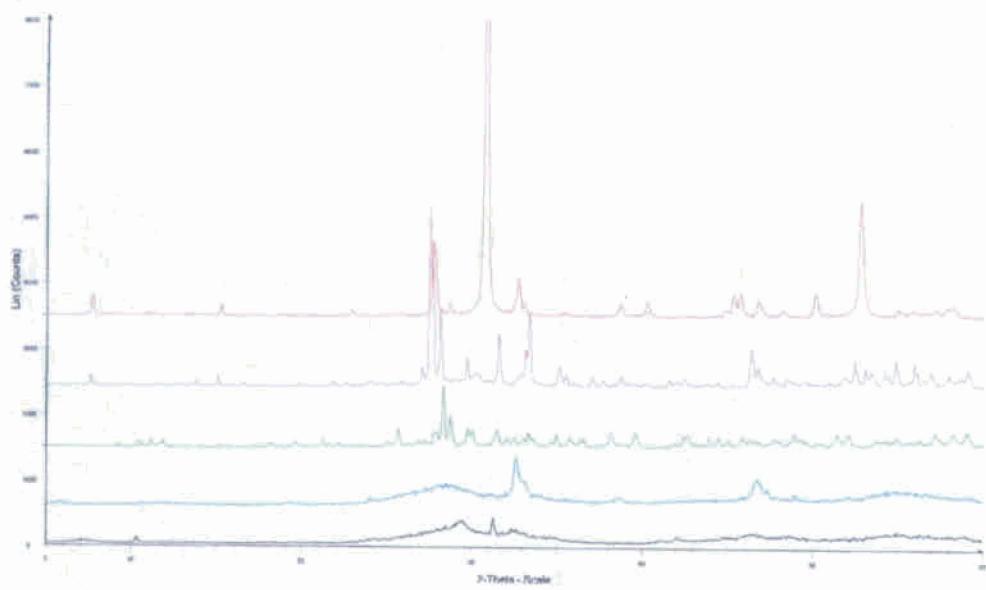
Fig A-4: Additional Bi getter diffraction patterns: from the bottom up; p5-L (black), p5-J (blue), p5-K (green), p5-H (purple) and p5-I (brown)

Table A-4: Synthesis notes and supplemental Kd values for materials synthesized in the first round of testing for this project:

		Material synthesis and performance notes
		Step 1
86-1	p83α	8.758 g BiNO3.5W, 5.145 g HNO3 (30%), 17.416 g H2O, 10.345 g LiNO3
86-2	p83β	8.784 g BiNO3.5W, 5.129 g HNO3 (30%), 17.264 g H2O, 10.346 g LiNO3, dissolves
86-3, no 4	p83γ	8,902 g BiNO3.5W, 5.370 g HNO3(30%), 17.216 g DI, 10.692 g LiNO3
86-5, no 4	p9-1	8.368g Bi(NO3)3.5W, 5.217 g HNO3(30%) 25.221 g H2O 1.083 g LiNO3
86-6	p9-2	8.279 g Bi(NO3)3.5W, 5.205 g HNO3(30%) 25.318 g H2O 15.646 g KNO3
86-7	p9-3	8.205 g Bi(NO3)3.5W, 5.255 g HNO3(30%) 26.370 g H2O 1.565 g KNO3
86-8	p9-4	8.273 g Bi(NO3)3.5W, 5.230 g HNO3(30%) 25.631 g H2O 13.363 g NaNO3
86-9	p9-5	8.266 g Bi(NO3)3.5W, 5.386 g HNO3(30%) 25.723 g H2O 1.383 g NaNO3
86-10	p5-C orig.	8.25 g Bi(NO3)3.5W, 10.845 g LiNO35.350 g HNO3(30%) 17.343 g H2O?
86-11	p5-C labled	8.25 g Bi(NO3)3.5W, 10.845 g LiNO35.350 g HNO3(30%) 17.343 g H2O
86-12	p5-d	8.3 g Bi(NO3)3.5W, 5.15 g HNO3(30%) 17.409 g H2O
86-13	p5-h	8.249 g Bi(NO3)3.5W, 4.698 g HNO3(30%) 54.507 g H2O 15.525 g KNO3
86-14	p5-I	8.179 g Bi(NO3)3.5W, 5.15 g HNO3(30%) 29.408 g H2O, 13.350 g NaNO3
86-15	p5-j	8.129g Bi(NO3)3.5W, 12.566 g HNO3(30%) 18.863 g H2O, 15.141 g Ni(NO3)2.6W
86-16	p5-k	8.3 g Bi(NO3)3.5W, 5.876 g HNO3(30%) 20.191 g H2O, 20.972 g Zn(NO3)2.6W
86-17	p5-I	8.116 g Bi(NO3)3.5W, 2.083 g HNO3(30%) 20.069g H2O, 1.542 g Zn(NO3)2.6W
86-18	BiNO3.5W	0.0168 g of Bi(NO3)3.5W [equivalent to 0.0090 g Bi(OH)3] added to the fluid with no ammendments
86-19	p85μ	8.268 g BiNO3.5W, 5 g HOAc, 5 g H2O
86-20	p85ν	8.340 g BiNO3.5W, 5.051 HOAc, 5.289 g H2O, 10.407 g LiNO3, 9.230 g NH4Acetate
86-21	p86δ	8.710 g BiNO3.5W, 8.8 g HOAc, 19.32 g H2O
86-22	Bi-Subsal.	0.203 g Bi-subsalicylate added to the fluid without other ammendments
		Step 2, sometimes
86-1	p83α	None
86-2	p83β	Next, add 6.056 g Na benzonate sat, 36.123 g di, 39.46 g HNO3(30%)
86-3, no 4	p83γ	6.13 g Na-benzoate in NH4OH - maybe about 6.5 grams??
86-5, no 4	p9-1	None
86-6	p9-2	None
86-7	p9-3	None
86-8	p9-4	None
86-9	p9-5	None
86-10	p5-C orig.	None
86-11	p5-C labled	None
86-12	p5-d	None
86-13	p5-h	None
86-14	p5-I	None
86-15	p5-j	None
86-16	p5-k	None
86-17	p5-I	None
86-18	BiNO3.5W	None
86-19	p85μ	5.563g Li2CO3, 17.05 g HOAc, 7.8 g H2O.
86-20	p85ν	None
86-21	p86δ	5.529 g Li2CO3, 9.25 g HOOAc, 25 ml H2O
86-22	Bi-Subsal.	None

APPENDIX B
Results from earlier TFA-sponsored getter studies

The TFA-sponsored study was carried out in the 2001-2002 time-frame and laid the groundwork for many of the approaches exploited in the current study. However, since copies of contractor letter reports can be difficult to obtain (particularly when the funding entity was later disbanded) the effort was made to extract the main findings from that report and summarize them here. The basic venue of the work was to support the decommissioning of HLW tanks at Hanford by providing a sorbant barrier to prevent radionuclides remaining in decommissioned tanks from migrating into local groundwaters. In this setting both concrete and diluted (mildly basic) HLW fluid (DSSF-7) could be presumed to exist together with the getter. These were the chemical parameters which defined the performance envelope for the materials tested for the TFA application. Notably, many materials synthesized for this study were archived (those given "HT-#" designations) and served as starting materials referenced in the current study. The additional performance data (relative to mildly elevated pH values and the presence of ordinary Portland cement, "OPC"), could also be applicable in the future if structural concrete ever becomes a more prominent feature in the YMP repository design.

"A Preliminary Assessment of Tc, I and Se Getter Development Activities for Hanford Tank Closure Applications"

Letter Report to US – DOE Tank Focus Area, Oct 14, 2002:

J.L. Krumhansl
Kathleen Holt (6849) and
Francois Bonhomme (6118)

Abstract:

Controlling the migration of residual radionuclides is an important step in solving the high level waste (HLW) tank closure problem at Hanford and Savannah River. One strategy is to place materials in the tanks prior to or during closure operations that will radically lower the solubility of radioisotopes left in the tanks. Performance assessments have often identified ^{99}Tc, and to a lesser degree ^{129}I and ^{79}Se, as being likely to migrate from decommissioned tanks. An experimental program was undertaken to assess if various mixed metal hydroxides (similar to hydrotalcites) could provide effective barriers. Tc was tested in full strength tank simulant solutions as well as their diluted equivalents. In full strength solutions the highest Tc Kd obtained with a seven day exposure time is about 18 L/kg, while in the diluted tank liquors (1% DSSF-7) a few materials yielded much higher Tc Kd values in the range of several thousand. *While potentially useful in some applications, none of these Tc Kd values are competitive with the results obtained in a parallel study evaluating the use of stannous chloride treated apatite (calcium hydroxyphosphate) getters.* Getters for I and Se were only tested in 1% DSSF-7 solutions. The highest Kd values obtained with 26-day exposure times were $10^{+4.9}$ L/kg for I and $10^{+3.9}$ L/kg for Se. Portland cement was found to not adversely effect this performance and may alone provide a barrier to the migration of I and Se. Compositional trends were identified that could provide improved materials if performance assessment calculations demonstrated a need for further materials development.

Table B-1: Formulation for DSSF-7 (7 M Na^+) Hanford Tank Simulant

Component	Molarity	g/L
$NaNO_3$	1.162	98.77
KNO_3	0.196	19.82
KOH	0.749	42.03
Na_2SO_4	.008	1.09
$Na_2HPO_4 \cdot 7H_2O$	.014	3.75
NaOH	3.885	155.40
$Al(NO_3)_3 \cdot 9H_2O$	0.721	270.48
Na_2CO_3	0.147	15.58
NaCl	0.102	5.98
$NaNO_2$	1.512	104.33

Table B-2: Summary of mixed metal hydroxides synthesized for this study

HT-#	M^{+2}, and substitutions	M^{+3}, and substitutions	Anions that were present
1	$Zn > Sn^{+2}$	Al	$SO_4^= > CO_3^=$, OH^-, Cl^-
2	$Zn > Sn^{+2}$	Al	$SO_4^= > OH^-$, Cl^-
3	Zn	Bi	$SO_4^= > OH^-$, Cl^-, NO_3^-
4	Mg	Bi	$CO_3^= > OH^-$
5	Zn	Al	$SO_4^= > OH^-$, NO_3^-
6	Mg	Bi	$SO_4^= > OH^-$, NO_3^-
7	Zn	Bi	$Ac > OH^-$, NO_3^-
8	Zn	Al	$Ac > OH^-$, NO_3^-
9	Mg	Al	$Ac > OH^-$, NO_3^-
10	Zn	Bi	$Ac > OH^-$, NO_3^-
11	$Zn > Cu^{++}$	Bi	$Ac > OH^-$, NO_3^-, $SO_4^=$
12	$Mg > Cu^{++}$	Bi	$Ac > OH^-$, NO_3^-, $SO_4^=$
13	$Zn > Cu^{++}$ overheated	Bi	$Ac > OH^-$, NO_3^-, $SO_4^=$
14	Mg	Al	$Ac > OH^-$, NO_3^-, Cl^-
15	$Zn > Cu^{+2} \to Cu^{+1}$	$La > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-
16	$Mg > Cu^{+2} \to Cu^{+1}$	$La > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-
17	Zn	$La > Sn^{+2}$	$Ac > OH^-$, Cl^-
18	Mg	$La > Sn^{+2}$	$Ac > OH^-$, Cl^-
19	$Mg > Cu^{++}$, and $Cu^{+2} \to Cu^{+1}$	$Al > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-, NO_3^-
20	$Zn > Cu^{++}$, and $Cu^{+2} \to Cu^{+1}$	$Al > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-, NO_3^-
21	$Mg > Cu^{+2} \to Cu^{+1}$	$Al > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-, NO_3^-
22	$Zn > Cu^{+2} \to Cu^{+1}$	$Al > Sn^{+2} \to Sn^{+4}$	$Ac > OH^-$, Cl^-, NO_3^-
23	$Cu^{+2} \to Cu^{+1}$	$Sn^{+2} \to Sn^{+4}$	Cl^-, OH^-

Ac = acetate

Table B-3: X-Ray diffraction characteristics of materials synthesized

Sample Number and Composition, HT-#	Quality of Hydrotalcite Peaks	Main Hydrotalcite Peak Positions - Å	Well Crystalline Phases
1 $Zn > Sn^{+2}$ $Al, SO_4^=$	Broad but well defined	7.7, 4.6, 3.3	None, sample is mostly poorly crystalline to amorphous materials.
2 $Zn > Sn^{+2}$ $Al, SO_4^=$	Broad but well defined	8.0, 4.1, 2.6	$Sn_3O_2(OH)_2$
3 Zn $Bi, SO_4^=$	Almost none	Poorly defined shoulder at 10.4. A well developed $Bi(OH)_3$ peak at 6.8.	$Bi(OH)_3$ and/or $Bi_2O_3CO_3$
4 Mg $Bi, CO_3^=$	Almost none	Poorly defined shoulder at 10.4. A well developed $Bi(OH)_3$ peak at 6.8.	$Bi(OH)_3$ and/or $Bi_2O_3CO_3$
5 Zn $Al, SO_4^=$	Relatively well Developed; mixture of, two types of hydrotalcite?	7.2, 3.54, 3.20, 2.71, 2.53 < 8.7, 4.37, 2.64	None
6 Mg $Bi, SO_4^=$	Almost none	Poorly defined shoulder at 10.4. A well developed $Bi(OH)_3$ peak at 6.8.	$Bi(OH)_3$ and/or $Bi_2O_3CO_3$
7 Zn Bi, Ac (Ac =Acetate)	Broad but well defined	7.0, 3.7, 2.1 < 3.2, 3.0, 1.64	Sharper peaks at 2.74 and 1.91 Å may be salts or off-spec. $Bi(OH)_3$ and/or $Bi_2O_3CO_3$
8 Zn Al, Ac	Well crystallized hydrotalcite plus broad peaks	12.6, 8.7, 4.35, (all broad)	Analogue to Mg-Al-OH, see #9 below.
9 Mg Al, Ac	Well crystallized hydrotalcite	7.6, 3.83, 2.6 (all sharp)	PDF #48-0601 Hydroxy-Hydrotalcite - $Mg_2Al(OH)_7$ $Mg(OH)_2Al(OH)_3$
10 Zn Bi, Ac	Broad but well defined	12.3, 3.7, 3.3	ZnO and/or $Zn(OH)_2$ – same as 11
11 $Zn > Cu$	Multiple broad low angle peaks	12.4, 9.3, 7.3 << 3.45, 3.30, 2.9, 2.7	ZnO and/or $Zn(OH)_2$ – same as 10

Bi, Ac			
12 Mg > Cu Bi, Ac	Similar to Tsuji, et al.(2000) but peaks are offset	8.8, 4.8< 3.5, 3.2, 2.9, 2.64, 2.36, 1.98, 1.89	Nothing obvious – may have off-spec. $Bi(OH)_3$ and/or $Bi_2O_3CO_3$
13 Zn >Cu Bi, Ac	Similar to Tsuji, et al.(2000) but peaks are offset	8.8, 4.8< 3.5, 3.2, 2.9, 2.64, 2.36, 1.98, 1.89	Nothing obvious – may have off-spec. $Bi(OH)_3$ and/or $Bi_2O_3CO_3$
14 Mg Al, Ac	Like to Mg-Al-OH (#9) but not well crystallized	7.9, 3.9, 2.56, 2.31 (all broad)	None
15 Zn >Cu, Sn^{+2} La>Sn^{+4}, Ac	Small broad well defined	Only one peak at 12.6	ZnO all good sharp peaks
16 Mg >Cu,Sn^{+2} La>Sn^{+4}, Ac	Very poorly crystalline	5.6, 3.2, 2.3, 1.85 (all very broad)	None
17 Zn >Sn^{+2} La, Ac	None	None	ZnO and four small sharp peaks at 3.5, 3.28, 2.98, 1.98; may be $Sn_6O_4(OH)_4$
18 Mg >Sn^{+2} La, Ac	None	None	$Sn_6O_4(OH)_4$ – well expressed $Mg_2La_2SnO_7$ - poorly expressed
19 Mg >Cu, Sn^{+2} Al>Sn^{+4}, Ac Low Sn^{+4}	Small broad peaks	7.9, 4.0	$MgSn(OH)_6$ and/or$CuSn(OH)_6$
20 Zn >Cu, Sn^{+2} Al>Sn^{+4}, Ac Low Sn^{+4}	Small broad peaks	8.0, 4.0, 2.6	$CuSn(OH)_6$ and Cu_2O .
21 Mg >Cu, Sn^{+2} Al>Sn^{+4}, Ac High Sn^{+4}	Small broad peaks	7.9, 4.0, 2.55	$CuSn(OH)_6$, Cu_2O, and CuO

Significant differences in peak height is indicated by the < symbol, with listings for the smaller peaks being to the left of the symbol.

Table B-4: Log Kds for I^-, $SeO_4^=$, ReO_4^-, and AsO_4^{-3}:
1% DSSF-7 fluid matrix and 1-day contact times.

HT-#	Metals	Log Kd Iodine	Log Kd Selenium	Log Kd ReO_4^-	Log Kd Arsenic
0	Zn, $Bi^{+3} \rightarrow$ **Bi metal** $Sn^{+2} \rightarrow Sn^{+4}$	No removal	No removal	No removal	2.27
1	Zn > Sn^{+2}, Al	No removal	No removal	No removal	3.17
2	Mg > Sn^{+2}, Al	No removal	1.44	0.71	2.80
3	Zn, Bi	2.16	No removal	No removal	3.05
4	Mg, Bi	1.95	No removal	No removal	3.52
5	Zn, Al	No removal	0.64	No removal	3.53
6	Mg, Bi	2.29	0.68	No removal	3.20
7	Zn, Bi	2.96	1.64	1.77	3.00
8	Zn, Al	No removal	3.15	No removal	4.31
9	Mg, Al	No removal	2.58	No removal	3.82
10	Zn, Bi	2.72	1.28	1.43	3.35
11	Zn > Cu^{++}, Bi	3.25	1.51	1.55	3.04
12	Mg > Cu^{++}, Bi	**3.53**	1.40	0.81	3.28
13	Zn > Cu^{++}, Bi (hot)	1.73	**3.94**	No removal	4.6
14	Mg, Al	No removal	3.41	1.24	4.34
15	Zn >$Cu^{+2} \rightarrow Cu^{+1}$, La > $Sn^{+2} \rightarrow Sn^{+4}$	2.00	0.99	No removal	3.60
16	Mg >$Cu^{+2} \rightarrow Cu^{+1}$, La > $Sn^{+2} \rightarrow Sn^{+4}$	No removal	1.55	No removal	3.20
17	Zn, La > Sn^{+2}	No removal	0.69	No removal	3.50
18	Mg, La > Sn^{+2}	1.72	2.40	**2.35**	3.95
19	Mg > Cu^{++}, and $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	2.12	3.63	1.08	5.43
20	Zn > Cu^{++}, and $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.79	3.37	0.56	4.84
21	Mg > $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.81	3.22	0.66	4.84
22	Zn > $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.17	3.49	0.72	**6.12**
23	$Cu^{+2} \rightarrow Cu^{+1}$, $Sn^{+2} \rightarrow Sn^{+4}$	2.90	No removal	No removal	1.69

Table B-5: Comparison of Log Kd values for 1-day (left) and 26-day contact times (right)

HT-#Metals	Log Kd I^-	Log Kd $SeO_4^=$	Log Kd ReO_4^-
0 Zn, $Bi^{+3} \rightarrow$ *Bi metal* $Sn^{+2} \rightarrow Sn^{+4}$	N.S., N.S.	N.S., 1.54	N.S., N.S.
	N.S.,	N.S., N.S.	N.S., N.S.
1 Zn > Sn^{+2}, Al	0.64		
2 Mg > Sn^{+2}, Al	N.S., N.S.	1.44, N.S.	0.71, 0.81
3 Zn, Bi	2.16, 2.75	N.S., 1.59	N.S., N.S.
4 Mg, Bi	1.95, 2.081	N.S., N.S.	N.S., N.S.
5 Zn, Al	N.S., N.S.	0.64, 1.70	N.S., N.S.
6 Mg, Bi	2.29, 2.84	0.68, 1.61	N.S., N.S.
7 Zn, Bi	2.96, 3.79	1.64, N.S.	1.77, 1.75
8 Zn, Al	N.S., 0.92	3.15, N.S.	N.S., 0.34
9 Mg, Al	N.S., N.S.	2.58, 2.67	N.S., 0.40
10 Zn, Bi	2.72, 3.90	1.28, 1.02	1.43, 1.56
11 Zn > Cu^{++}, Bi	3.25, 4.90	1.51, 1.78	1.55, 1.50
12 Mg > Cu^{++}, Bi	**3.53**, ----	1.40, 1.97	0.81, 1.12
13 Zn > Cu^{++}, Bi (hot)	1.73, 1.62	**3.94, 3.86**	N.S., 0.32
14 Mg, Al	N.D. 1.66	3.41, 2.58	1.24, 0.46
15 Zn > $Cu^{+2} \rightarrow Cu^{+1}$, La > $Sn^{+2} \rightarrow Sn^{+4}$	2.00, N.S.	0.99, 1.74	N.S., N.S.
16 Mg > $Cu^{+2} \rightarrow Cu^{+1}$, La > $Sn^{+2} \rightarrow Sn^{+4}$	N.D., 1.91	1.55, 1.92	N.S., N.S.
17 Zn, La > Sn^{+2}	N.D., 0.16	0.69, 1.37	N.S., N.S.
18 Mg, La > Sn^{+2}	1.72, N.S.	2.40, 1.97	**2.35, 1.98**
19 Mg > Cu^{++}, and $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	2.12, 0.86	3.63, 3.56	1.08, 0.84
20 Zn > Cu^{++}, and $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.79, 2.14	3.37, 2.28	0.56, N.S.
21 Mg > $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.81, 1.58	3.22, 3.20	0.66, 0.77
22 Zn > $Cu^{+2} \rightarrow Cu^{+1}$, Al> $Sn^{+2} \rightarrow Sn^{+4}$	1.17, 1.39	3.49, N.S.	0.72,. N.S.
23 $Cu^{+2} \rightarrow Cu^{+1}$, $Sn^{+2} \rightarrow Sn^{+4}$	2.90, 1.39	N.S., 1.58	N.S., N.S.

N.S. = no evidence for sorption.

Table B-6: Effect of ordinary Portland cement on iodine and selenium sorption:
Log Kd values and final concentrations in - parts per billion;
5 day contact time with OPC, 26 days without OPC, 1% DSSF-7 matrix)

Spl. #	Results of **Iodine** Sorption Experiments				Results of **Selenium** Sorption Experiments			
	With Portland Cement		No Cement		With Portland Cement		No Cement	
	Log Kd	PPB-Final	Log Kd	PPB-Final	Log Kd	PPB-Final	Log Kd	PPB-Final
0	0.87	948	NS	1015	3.45	46	1.54	794
1	1.64	748	0.64	967	2.06	533	NS	1031
2	1.36	882	NS	1058	1.97	574	NS	1165
3	2.73	196	2.75	191	3.41	49	1.59	773
4	2.81	169	2.08	523	3.48	41	NS	7466
5	0.18	990	NS	1333	2.34	407	1.70	726
6	2.95	133	2.84	159	3.37	55	1.61	761
7	**4.13**	**9.0**	**3.79**	**21**	2.96	120	NS	1430
8	1.77	675	0.92	940	3.22	69	NS	5721
9	1.79	690	-0.04	993	**3.74**	**24**	2.67	222
10	**3.79**	**20**	**3.90**	**16**	2.48	297	1.02	926
11	**5.27**	**0.69**	**4.90**	**1.6**	1.98	568	1.78	679
12	1.25	880	Not Analyzed		2.77	182	1.97	588
13	1.76	698	1.62	759	**3.71**	**25**	**3.86**	**18**
14	1.83	663	1.66	739	**3.70**	**26**	2.58	256
15	1.70	726	NS	1018	2.35	373	1.74	695
16	2.21	440	1.91	611	3.53	36	1.92	605
17	1.63	750	0.16	989	2.39	342	1.37	849
18	1.66	735	NS	1046	3.47	41	1.97	585
19	1.70	721	0.86	946	3.68	27	**3.56**	**34**
20	1.99	567	2.14	486	2.79	174	2.28	405
21	1.76	699	1.58	774	3.60	32	**3.20**	**77**
22	1.51	802	1.39	837	2.98	121	NS	2646
23	1.73	719	1.39	839	3.54	38	1.58	772
CEMENT	0.43	788			2.35	43	NS = No Sorption	

Table B-7: Effect of ordinary Portland cement ("OPC") on perrhenate sorption: Log Kd values and final concentrations in - parts per billion; 5 day contact time with OPC, 26 days without OPC, 1% DSSF-7 matrix)

	Results of ReO$_4^-$ Sorption Experiments			
	With Portland Cement		No Cement	
HT- #	**Log** Kd	PPB-Final	**Log** Kd	PPB-Final
0	1.19	899	NS	1008
1	NS	1065	-0.28	996
2	0.44	979	0.81	954
3	0.58	972	NS	1003
4	0.34	984	NS	1012
5	NS	1026	NS	1029
6	0.65	969	0.03	992
7	**1.98**	**566**	**1.75**	**702**
8	NS	1050	0.34	984
9	0.43	981	0.40	982
10	1.63	746	1.56	783
11	1.45	817	1.50	802
12	1.09	914	1.12	908
13	NS	1019	0.32	984
14	0.81	954	0.46	978
15	NS	1059	NS	1001
16	0.24	986	NS	1002
17	1.28	872	0.08	991
18	**2.34**	**365**	**1.98**	**579**
19	0.94	938	0.84	948
20	NS	1032	NS	1013
21	0.89	945	0.77	957
22	NS	1042	NS	1019
23	NS	1011	NS	1011
CEMENT	NS	1012	NS = No Sorption	

Table B-8: Pertechnetate sorption test results.
Solution concentrations (pCi/ml) at 1 hour, 1 day, 3 days and 7 days. Except for the last tests Kd values are based on 7-day test results. Desorption concentrations were measured at 1 hour, 1 day and 3 and 7 days. Complete release would result in a concentration of 1,9400 pCi/ml.

Sample	Sorption Data					Desorption Data			
	1hr	1 day	3 days	7 days	Kd-7Days	1 hr	1 day	3 days	7 Days
DI water + Tc BLANK	1.95E+04	1.85E+04	1.94E+04	1.93E+04	N/A				
DSSF-7 BLANK	1.89E+04	1.40E+04	1.66E+04	1.64E+04	N/A				
DSSF-7 + HT4	1.83E+04	1.65E+04	1.53E+04	1.14E+04	1.87E+01				
DSSF-7 + HT1	8.40E+03	1.69E+04	1.71E+04	1.37E+04	1.10E+01				
DSSF-7 + HT2	1.31E+04	1.11E+04	1.74E+04	1.40E+04	1.02E+01				
1% DSSF-7 BLANK	1.93E+04	1.84E+04	1.93E+04	1.94E+04	-1.39E-01				
1% DSSF-7 + HT4	1.94E+04	1.82E+04	1.82E+04	1.83E+02	2.82E+03	2.92E+02	1.58E+03	1.58E+03	1.55E+03
1% DSSF-7 + HT1	2.33E+01	9.85E+00	1.51E+01	1.66E+02	3.11E+03	4.64E+01	4.16E+01	1.46E+02	6.59E+02
1% DSSF-7 + HT2	5.93E+02	1.40E+01	1.56E+01	9.82E+01	5.28E+03	2.72E+01	1.27E+01	1.69E+01	2.44E+01
DSSF-7 + (concrete) BLANK	1.94E+04	1.64E+04	1.84E+04	1.71E+04	3.47E+00				
DSSF-7 + (concrete) + HT4	1.86E+04	1.75E+04	1.68E+04	1.55E+04	6.62E+00				
DSSF-7 + (concrete) + HT1	1.09E+04	1.80E+04	1.75E+04	1.73E+04	3.12E+00				
DSSF-7 + (concrete) + HT2	1.48E+04	9.80E+02	1.76E+04	1.54E+04	6.84E+00				
1% DSSF-7 + (concrete) BLANK	1.96E+04	1.89E+04	1.93E+04	1.94E+04	-1.39E-01				
1% DSSF-7 + (concrete) + HT4	1.94E+04	1.82E+04	1.83E+04	1.92E+04	1.41E-01				
1% DSSF-7 + (concrete) + HT1	3.19E+01	4.79E+04	2.90E+01	2.84E+02	1.81E+03	1.07E+02	1.56E+02	4.29E+02	1.05E+03
1% DSSF-7 + (concrete) + HT2	4.83E+01	6.61E+02	8.15E+01	2.96E+02	1.73E+03	1.09E+02	1.13E+02	1.26E+02	8.44E+01
1% DSSF-7 + (concrete/pH reduce) BLANK	1.97E+04	1.93E+04	1.91E+04	1.95E+04	-2.77E-01				
1% DSSF-7 + (concrete/pH reduce) + HT4	1.82E+04	1.79E+04	1.78E+04	1.89E+04	5.71E-01				
1% DSSF-7 + (concrete/pH reduce) + HT1	1.16E+04	1.24E+04	4.74E+03	1.88E+03	2.50E+02	1.10E+01	1.82E+01	2.98E+01	1.93E+02
1% DSSF-7 + (concrete/pH reduce) + HT2	1.47E+04	2.23E+03	4.32E+01	8.92E+01	5.81E+03	2.53E+01	3.51E+00	1.14E+01	5.13E+00

Sample	Sorption Data					Desorption Data			
	1hr	1 day	3 days	7 days	Kd-7Days	1 hr	1 day	3 days	7 Days
DSSF-7 + HT7	1.60E+04	1.10E+04		1.58E+04	5.98E+00				
DSSF-7 + HT8	1.69E+04	1.68E+04		1.83E+04	1.48E+00				
DSSF-7 + HT9	1.67E+04	1.64E+04		1.86E+04	1.02E+00				
DSSF-7 + HT10	1.56E+04	1.55E+04		1.55E+04	6.62E+00				
1% DSSF-7 + HT7	8.62E+03	1.07E+03		7.89E+02	6.33E+02	3.52E+02	9.35E+02	9.65E+02	9.82E+02
1% DSSF-7 + HT8	1.34E+04	6.99E+03		7.02E+03	4.72E+01	3.09E+03	8.77E+03	9.20E+03	8.92E+03
1% DSSF-7 + HT9	1.45E+04	1.50E+04		1.55E+04	6.62E+00				
1% DSSF-7 + HT10	1.25E+04	3.63E+03		9.27E+02	5.35E+02	4.00E+02	1.33E+03	1.41E+03	2.49E+03
DSSF-7 + (concrete) + HT7	1.60E+04	1.53E+04		1.72E+04	3.28E+00				
DSSF-7 + (concrete) + HT8	1.68E+04	1.50E+04		1.87E+04	8.66E-01				
DSSF-7 + (concrete) + HT9	1.61E+04	1.86E+04		1.89E+04	5.71E-01				
DSSF-7 + (concrete) + HT10	1.70E+04	1.61E+04		1.77E+04	2.44E+00				
1% DSSF-7 + (concrete) + HT7	5.37E+03	6.63E+02		6.02E+02	8.39E+02	2.83E+02	6.75E+02	6.94E+02	6.85E+02
1% DSSF-7 + (concrete) + HT8	1.36E+04	8.62E+03		8.91E+03	3.15E+01	2.86E+03	8.72E+03	8.95E+03	8.62E+03
1% DSSF-7 + (concrete) + HT9	1.51E+04	1.48E+04		1.55E+04	6.62E+00				
1% DSSF-7 + (concrete) + HT10	6.14E+03	1.53E+04		9.43E+02	5.26E+02	3.09E+02	7.29E+02	7.60E+02	7.16E+02
1% DSSF-7 + (concrete/pH reduce) + HT7	1.58E+04	1.31E+04		1.38E+04	1.08E+01				
1% DSSF-7 + (concrete/pH reduce) + HT8	1.39E+04	1.13E+04		1.30E+04	1.31E+01				
1% DSSF-7 + (concrete/pH reduce) + HT9	1.71E+04	1.64E+04		1.71E+04	3.47E+00				
1% DSSF-7 + (concrete/pH reduce) + HT10	1.78E+04	1.65E+04		1.44E+04	9.19E+00				

Sample	Sorption Data					Desorption Data			
	1hr	1 day	3 days	7 days	Kd-7Days	1 hr	1 day	3 days	7 Days
DSSF-7 + HT11	1.56E+04	1.61E+04	1.61E+04	1.63E+04	2.15E+00				
DSSF-7 + HT12	1.54E+04	1.52E+04	1.37E+04	1.53E+04	4.06E+00				
DSSF-7 + HT12 Low Temp	1.60E+04	1.49E+04	1.45E+04	1.38E+04	7.43E+00				
DSSF-7 +HT14	1.70E+04	1.71E+04	1.70E+04	1.68E+04	1.29E+00				
1% DSSF-7 + HT11	1.10E+04	2.58E+03	2.19E+03	2.36E+03	1.74E+02	2.20E+02	1.58E+03	1.92E+03	2.11E+03
1% DSSF-7 + HT12	1.40E+04	9.16E+03	7.89E+03	7.51E+03	3.63E+01	4.05E+02	2.68E+03	3.16E+03	2.99E+03
1% DSSF-7 + HT12 Low Temp	1.69E+04	1.59E+04	1.57E+04	1.58E+04	3.08E+00				
1% DSSF-7 + HT14	1.02E+04	8.31E+03	8.51E+03	9.26E+03	2.43E+01	7.70E+02	5.31E+03	5.83E+03	6.21E+03
DSSF-7 + (concrete) + HT11	1.60E+04	1.70E+04	1.66E+04	1.67E+04	1.46E+00				
DSSF-7 + (concrete) + HT12	1.59E+04	1.60E+04	1.63E+04	1.60E+04	2.70E+00				
DSSF-7 + (concrete) + HT12 Low Temp	1.61E+04	1.46E+04	1.50E+04	1.66E+04	1.63E+00				
DSSF-7 + (concrete) + HT14	1.74E+04	1.65E+04	1.72E+04	1.72E+04	6.28E-01				
1% DSSF-7 + (concrete) + HT11	1.03E+04	2.34E+03	2.12E+03	2.18E+03	1.91E+02	4.79E+02	2.42E+03	2.70E+03	2.65E+03
1% DSSF-7 + (concrete) + HT12	9.94E+03	5.30E+03	4.16E+03	4.50E+03	7.86E+01	3.23E+02	1.85E+03	2.13E+03	3.22E+03
1% DSSF-7 + (concrete) + HT12 Low Temp	1.56E+04	1.38E+04	1.21E+04	8.20E+03	3.10E+01	7.98E+02	1.95E+03	1.87E+03	2.07E+03
1% DSSF-7 + (concrete) + HT14	9.76E+03	8.63E+03	9.19E+03	9.01E+03	2.57E+01	9.53E+02	5.18E+03	5.72E+03	6.19E+03
1% DSSF-7 + (concrete/pH reduce) + HT11	1.57E+04	1.35E+04	1.32E+04	1.47E+04	5.33E+00				
1% DSSF-7 + (concrete/pH reduce) + HT12	1.66E+04	1.61E+04	1.63E+04	1.73E+04	4.68E-01				
1% DSSF-7 + (concrete/pH reduce) + HT12 Low T	1.63E+04	1.60E+04	1.62E+04	1.75E+04	1.54E-01				
1% DSSF-7 + (concrete/pH reduce) + HT14	1.33E+04	1.15E+04	1.10E+04	1.19E+04	1.29E+01				

Table B-8 Continued

Sample	Sorption Data 1hr	1 day	3 days	7 days	Kd-7Days	Desorption Data 1 hr	1 day	3 days	7 Days
DSSF-7 + HT15	1.73E+04	1.54E+04	1.57E+04	1.67E+04	1.46E+00				
DSSF-7 + HT16	1.69E+04	8.36E+03	1.31E+04	1.56E+04	3.46E+00				
DSSF-7 + HT17	6.45E+03	4.73E+03	1.01E+04	1.80E+04	-6.00E-01				
DSSF-7 + HT18	5.82E+03	2.94E+03	5.04E+03	1.65E+04	1.80E+00	1.12E+03	1.53E+03	1.83E+03	2.43E+03
1% DSSF-7 + HT15	1.43E+04	8.58E+03	8.11E+03	7.75E+03	3.43E+01				
1% DSSF-7 + HT16	1.06E+04	4.43E+03	3.55E+03	3.27E+03	1.18E+02				
1% DSSF-7 + HT17	1.38E+04	7.45E+02	2.23E+03	2.14E+01	2.22E+04	9.59E-02	-3.69E-01	6.86E-01	-2.87E-01
1% DSSF-7 + HT18	8.15E-01	-7.86E-01	1.57E+03	1.39E+00	3.42E+05	-1.29E-01	6.04E-01	3.14E+00	8.14E-01
DSSF-7 + (concrete) + HT15	1.74E+04	1.51E+04	1.53E+04	1.73E+04	4.68E-01				
DSSF-7 + (concrete) + HT16	1.54E+04	9.07E+03	1.13E+04	1.53E+04	4.06E+00				
DSSF-7 + (concrete) + HT17	7.34E+03	5.04E+03	1.02E+04	1.75E+04	1.54E-01				
DSSF-7 + (concrete) + HT18	6.12E+03	3.08E+03	5.01E+03	1.76E+04	0.00E+00	6.97E+02	1.13E+03	1.41E+03	1.89E+03
1% DSSF-7 + (concrete) + HT15	1.43E+04	1.02E+04	8.94E+03	9.65E+03	2.22E+01				
1% DSSF-7 + (concrete) + HT16	1.08E+04	4.81E+03	4.77E+03	4.38E+03	8.15E+01				
1% DSSF-7 + (concrete) + HT17	3.40E+00	1.56E+00	-7.38E-01	2.27E+00	2.09E+05	7.67E-01	-3.21E-01	1.07E+00	2.72E+01
1% DSSF-7 + (concrete) + HT18	-2.59E-01	-1.15E-01	4.08E+02	4.79E-02	9.92E+06	4.94E-01	7.19E+00	4.46E-01	1.32E+02
1% DSSF-7 + (concrete/pH reduce) + HT15	1.49E+04	1.09E+04	1.16E+04	9.08E+03	2.53E+01				
1% DSSF-7 + (concrete/pH reduce) + HT16	1.29E+04	6.75E+03	6.86E+03	6.77E+03	4.32E+01	6.79E+02	1.10E+03	1.42E+03	1.88E+03
1% DSSF-7 + (concrete/pH reduce) + HT17	1.42E+04	1.07E+04	1.36E+04	1.43E+04	6.23E+00				
1% DSSF-7 + (concrete/pH reduce) + HT18	8.76E+01	2.40E+01	5.07E+01	1.83E+01	2.59E+04	7.46E+00	2.35E+01	1.96E+01	1.65E+01

Sample	Sorption Data 1hr	1 day	3 days	7 days	Kd-7Days	Desorption Data 1 hr	1 day	3 days	7 Days
DSSF-7 + HT19	1.67E+04	1.49E+04	1.70E+04	1.63E+04	2.15E+00				
DSSF-7 + HT20	1.65E+04	1.50E+04	1.64E+04	1.62E+04	2.33E+00				
DSSF-7 + HT21	1.47E+04	9.75E+03	1.61E+04	1.62E+04	2.33E+00				
DSSF-7 + HT22	1.64E+04	1.48E+04	1.63E+04	1.67E+04	1.46E+00				
DSSF-7 + HT23	1.64E+04	1.49E+04	1.61E+04	1.65E+04	1.80E+00				
DSSF-7 + bone char	1.65E+04	1.35E+04	1.53E+04	1.49E+04	4.89E+00				
DSSF-7 + BiZnOH HT	1.64E+04	1.46E+04	1.51E+04	1.49E+04	4.89E+00				
1% DSSF-7 + HT19	1.41E+04	7.96E+03	8.15E+03	8.68E+03	2.77E+01	2.34E+03	4.01E+03	4.81E+03	5.43E+03
1% DSSF-7 + HT20	1.49E+04	1.08E+04	7.73E+03	8.10E+03	3.17E+01	1.37E+03	3.82E+03	4.97E+03	5.70E+03
1% DSSF-7 + HT21	5.40E+03	3.24E+02	2.78E+02	5.05E+02	9.14E+02	1.27E+02	8.62E+02	1.69E+03	4.18E+03
1% DSSF-7 + HT22	1.53E+04	9.82E+03	5.51E+03	5.73E+03	5.59E+01	1.50E+03	3.99E+03	5.36E+03	6.34E+03
1% DSSF-7 + HT23	1.67E+04	1.69E+04	1.72E+04	1.71E+04	7.89E-01				
1% DSSF-7 + bone char	1.65E+04	1.66E+04	1.67E+04	1.64E+04	1.98E+00				
1% DSSF-7 + BiZnOH HT	1.63E+04	1.67E+04	1.70E+04	1.70E+04	9.53E-01				
DSSF-7 + (concrete) + HT19	1.64E+04	1.38E+04	1.63E+04	1.62E+04	2.33E+00				
DSSF-7 + (concrete) + HT20	1.63E+04	1.50E+04	1.63E+04	1.61E+04	2.52E+00				
DSSF-7 + (concrete) + HT21	1.43E+04	8.82E+03	1.64E+04	1.65E+04	1.80E+00				
DSSF-7 + (concrete) + HT22	1.60E+04	1.52E+04	1.61E+04	1.61E+04	2.52E+00				
DSSF-7 + (concrete) + HT23	1.64E+04	1.54E+04	1.64E+04	1.64E+04	1.98E+00				
DSSF-7 + (concrete) + bone char	1.62E+04	1.45E+04	1.53E+04	1.45E+04	5.77E+00				
DSSF-7 + (concrete) + BiZnOH HT	1.64E+04	1.40E+04	1.60E+04	1.62E+04	2.33E+00				
1% DSSF-7 + (concrete) + HT19	1.58E+04	1.10E+04	8.57E+03	8.22E+03	3.08E+01	2.01E+03	3.98E+03	4.52E+03	5.01E+03
1% DSSF-7 + (concrete) + HT20	1.64E+04	1.52E+04	1.07E+04	9.13E+03	2.50E+01	6.48E+02	2.53E+03	4.71E+03	6.07E+03
1% DSSF-7 + (concrete) + HT21	1.28E+04	5.18E+03	1.51E+03	6.96E+02	6.56E+02	1.69E+02	8.86E+02	1.13E+03	1.78E+03
1% DSSF-7 + (concrete) + HT22	1.73E+04	1.53E+04	9.76E+03	6.88E+03	4.21E+01	9.11E+02	3.69E+03	5.05E+03	6.09E+03
1% DSSF-7 + (concrete) + HT23	1.70E+04	1.70E+04	1.70E+04	1.71E+04	7.89E-01				
1% DSSF-7 + (concrete) + bone char	1.66E+04	1.71E+04	1.70E+04	1.70E+04	9.53E-01				
1% DSSF-7 + (concrete) + BiZnOH HT	1.76E+04	1.74E+04	1.71E+04	1.62E+04	2.33E+00				
1% DSSF-7 + (concrete/pH reduce) + HT19	1.61E+04	1.46E+04	1.12E+04	9.54E+03	2.28E+01	9.82E+02	2.56E+03	3.62E+03	4.33E+03
1% DSSF-7 + (concrete/pH reduce) + HT20	1.66E+04	1.35E+04	1.15E+04	1.02E+04	1.96E+01				
1% DSSF-7 + (concrete/pH reduce) + HT21	1.54E+04	1.05E+04	5.25E+03	5.60E+02	8.22E+02	2.55E+01	3.40E+01	5.74E+01	1.62E+02
1% DSSF-7 + (concrete/pH reduce) + HT22	1.65E+04	1.54E+04	1.23E+04	9.68E+03	2.21E+01	1.05E+03	2.79E+03	3.39E+03	4.08E+03
1% DSSF-7 + (concrete/pH reduce) + HT23	1.63E+04	1.63E+04	1.64E+04	1.56E+04	3.46E+00				
1% DSSF-7 + (concrete/pH reduce) + bone char	1.64E+04	1.49E+04	1.46E+04	1.40E+04	6.94E+00				
1% DSSF-7 + (concrete/pH reduce) + BiZnOH HT	1.68E+04	1.67E+04	1.67E+04	1.59E+04	2.89E+00				

Table B-9: TcO$_4$- Kd values (not Log Kd) for selected HT samples: 5% DSSF-7 fluid matrix and 4 months equilibration time

Sample #	Replicate Kd values	Average Kd (ml/g)
HT-1	7.9, 9.0	8.4
HT-3	1.1, .9	1.0
HT-4	256, 73	164
HT-7	139, 151	145
HT-8	No sorption	No Sorption
HT-10	88, 96	92
HT-11	20,21	20.5
HT-12	51, 55	53
HT-14	No Sorption	No Sorption
HT-15	No Sorption	No Sorption
HT-16	86, 209	147
HT-17	22, 65	43
HT-18	31, 31	31
HT-19	2.2, 2.6	2.4
HT-20	No sorption	No sorption
HT-21	3.4, 2.8	3.1
HT22	2.4, 0.5	1.5
Bone Char	7.3, 4.5	5.9

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