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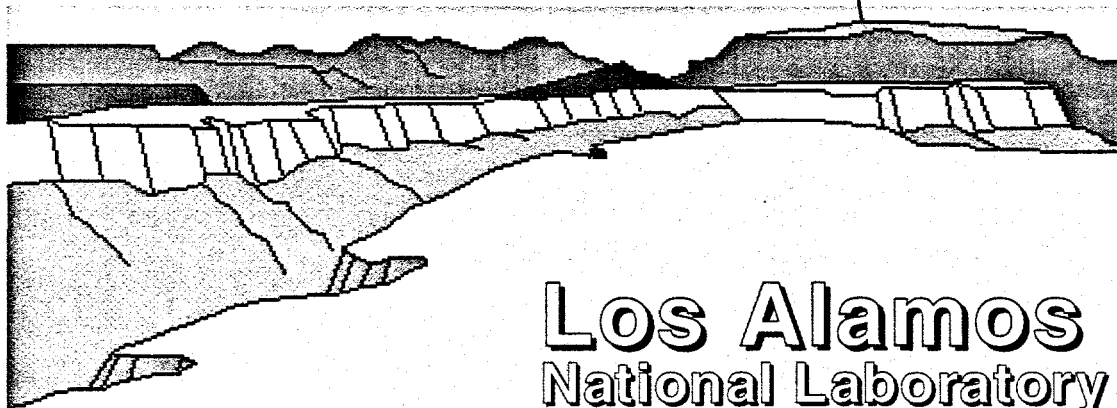
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SELECTION OF ACTINIDE CHEMICAL ANALOGUES FOR WIPP TESTS

by
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SUMMARY

Chemical characteristics of the actinides (Th, U, Np, Pu, Am) have been studied relative to nonradioactive chemical elements that have similar characteristics in an attempt to identify a group of chemical analogues that are nonradioactive. In general, the chemistry of the actinides, especially U, Np, Pu, and Am, is very complex and attempts to identify a single chemical analogue for each oxidation state were not successful. However, the rationale for selecting a group of chemical analogues that would mimic the actinides as a group is provided. The categorization of possible chemical analogues (tracers) with similar chemical properties was based on the following criteria. Categorization was studied according to

      1) molar volume,
      2) ionic radii, occurrence in nature, and hydrated ionic radii,
      3) electronegativities,
      4) electronic configuration,
      5) complexation and carbonate chemistry, and
      6) ion-exchange properties.

The group of tracers that are recommended for use in the field that would possess certain chemical properties that would be indicative of actinides are listed in the summary table.

SUMMARY TABLE

Th^{4+}	Ce^{3+}, Ce^{4+}, Gd^{3+}, Re^{7+}, Mo^{6+}
U^{4+}	Ce^{4+}, Y
U^{6+}	Ce^{3+}, Mg^{2+}, V^{5+}, Li^+, Mo^{6+}, W^{6+}, La
$Np^{3,4+}$	Nd, Er, Mo, Re, Mg, Li
Np^{5+}	Eu^{3+}, Gd^{3+}, Pr^{3+}, Sm
Pu^{3+}	Sm^{3+}, Ln, Y
Pu^{4+}	Nd^{3+}, Eu^{3+}
Pu^{5+}	Nd^{3+}, V^{5+}, Mo^{6+}
Pu^{6+}	Ce^{4+}, Re^{7+}, Mo^{6+}, Pr^{3+}
Am^{3+}	Eu^{3+}, Y^{3+}, Sm^{3+}, Fe^{3+}

Ce^{3+}, Ce^{4+}, V^{5+}, Mg^{2+}, Mo^{6+}, Eu^{3+} would be the top six with Nd^{3+}, Gd^{3+}, Y^{3+}, V^{5+}, Re^{7+}, and Li^+ as the second six recommended tracers for use in the field. The recommended tracers would be added as chloride, bromide, or nitrate salts

depending on the element. Li would be a good tracer that would mimic the size of the actinides, but not the chemistry. Perhaps the most effective set of tracers would be soluble carbonates of Re, Mo, or Eu. The rationale and criteria for selection of the tracers listed above is given in this report.

INTRODUCTION

The Department of Energy must demonstrate the effectiveness of the Waste Isolation Pilot Plant (WIPP) as a permanent repository for the disposal of transuranic (TRW) waste. Performance assessments of the WIPP require that estimates of the transportability and outcome of the radionuclides (actinides) be determined from disposal rooms that may become either partially or completely filled with brine. Federal regulations limit the amount of radioactivity that may be unintentionally released to the accessible environment by any mechanism during the post closure phase up to 10,000 years. Thermodynamic models have been developed to predict the concentrations of actinides in the WIPP disposal rooms under various situations and chemical conditions. These models are based on empirical and theoretical projections of the chemistry that might be present in and around the disposal room zone for both near and long-term periods. The actinides that are known to be present in the TRU wastes (and are included in the model) are Th, U, Np, Pu, and Am. Experiments are currently being conducted with actual TRU waste to verify the chemical conditions that might be present in the WIPP disposal rooms. Knowledge of the chemistry that might occur in the disposal rooms when the waste comes in contact with brine is important in understanding the range of oxidation states that might be present under different conditions.

There is a need to establish the mechanisms and resultant rate of transport, migration, or effective retardation of actinides beyond the disposal rooms to the boundary of the accessible environment. The influence of the bulk salt rock, clay sediments and other geologic matrices on the transport behavior of actinides must be determined to establish the overall performance and capability of the WIPP in isolating waste from the environment. Tests to determine the capabilities of the WIPP geologic formations in retarding actinide species in several projected oxidation states would provide a means to demonstrate the effectiveness of the WIPP in retaining TRU wastes. The most effective method of determining the retardation capabilities of WIPP geological matrices would be to conduct in-situ tests with each actinide species. However, environmental regulations would disallow addition of radionuclides to the environment for such tests. Since actual radionuclides (actinides) cannot be injected into the actual geologic formations at WIPP to follow their transport or migration, nonradioactive compounds (analogues) that have similar chemical and transport properties to the actinides must be identified. The selection of these nonradioactive chemical analogues,

hereafter called tracers, must be based on criteria showing the similarity of these tracers to actinides under the conditions of the experiments. The similarities can be assessed by evaluating the different physical and chemical properties of actinides and comparing them to analogous chemical compounds that are not radioactive. This report will provide the rationale for selecting a suite of nonradioactive tracers that can be used to mimic the behavior of radioactive actinides in the environment.

ACTINIDE TRANSPORT MECHANISMS

Actinides being transported from the disposal room environment can be present in many forms. Actinides that are dissolved or are present in brines are solutes, and the brine is the solvent. Brine having dissolved or entrained actinides (solutes) flowing in porous geologic media will transport the actinides in various forms as the brine flows. This method of transport of actinide contaminants is termed advection. Advection is the transport of contaminant solutes along stream lines at the average seepage flow velocity. The pore size, tortuosity, and type of media along with the pressure head on the solution governs the flow rate and direction of flow. If the porous media is either homogeneously or heterogeneously fractured, the flow of liquid will be through either the path of least resistance or the interconnected porosity. If the solid phase geologic media has a small particle size and the media volume is large, the mechanical or hydrodynamic dispersion of the solution is great and contact with the solid phase is maximized. The discrete location or area within the disposal room that is the source of release of actinides to the geologic media is termed the point source. A singular volume or mass of brine containing a known concentration of entrained actinide contaminants that is presented to the geologic media at a source point is called a slug. The concentration of actinides in a one-time point source or a continuous source can decrease as the front passes through the geologic media and is dispersed through the path by mechanical and hydrodynamic means.

There are many mechanisms that can influence the migration of actinides through the porous geologic media and result in a retardation or enhancement of the actinide concentration at the downgradient side of the geologic formation before breakthrough to the accessible environment. The distribution and extent of the actinides in the normal brine flow path (plume) relative to time gives an indication of the velocity and retardation/enhancement of the transport mechanisms. Actinide contaminants can migrate across transport zones according to their chemical kinetic activity. The movement of actinides from areas or volumes of higher concentration (disposal rooms) to lower concentrations (far field zones) is termed diffusion and is sometimes called specifically ionic or molecular diffusion. The difference in concentration between the disposal room and the downgradient formation that is a known distance away is called concentration gradient.

The flow of brine through geologic media can be by a dispersed front through homogeneous porous media or alternatively, by channel flow through fractured media (fractured media flow). Of course, it is possible to have both porous and fractured media flow in an sequential arrangement across a geologic gradient. As actinide contaminants move from the disposal room to a far-field formation via advection, hydrodynamic dispersion, and molecular or ionic diffusion, there are a variety of processes that can effect the concentration gradient across the porous and/or fractured media flow path. Table I gives a list of chemical or physical processes that could have a retardation effect or enhancement influence on actinides along the length of the flow path.

TABLE I. PROCESSES THAT INFLUENCE ACTINIDE TRANSPORT

Process	Overall Effect
Sorption by Organic Ligands (humics*)	Retardation
Precipitation	Retardation
Ion Exchange by Clay Minerals	Retardation
Colloid Primary Particles Formation	Mobility Enhancement
Colloid Agglomerates (stable), Gels, etc.	Retardation
Chemical Oxidation (Eh)	Mobility Enhancement
Chemical Reduction/Precipitation	Retardation
Hydrolysis	Retardation
Dissolution/Re-solution	Mobility Enhancement
Co-solvation by Organic Solvent	Mobility Enhancement
Filtration	Retardation
Complexation	Mobility Enhancement
Microbial Activity	Both ME and Retardation
Chemical Conditions (pH)	Both ME and Retardation

* Humic substances are polyelectrolytic and polyaromatic organic acids of high molecular weight (~800 to 4,000 g/mol, or higher) that occur in natural systems. Humic substances are operationally divided in humic acids and fulvic acids on the basis of solubility in water as follows: fulvic acids are water soluble at all pH levels; humic acids are water soluble above pH 2 and water insoluble below pH 2.

The structure of the geologic media around the WIPP disposal rooms would consist of consolidated rock and unconsolidated formations. The consolidated rock would act as a containment medium, while the unconsolidated formations, or fractured zones, could typically contain retardation media including rock fragments, gravel-sized particles, sand granules and mineral particles, silt particles containing mineral aggregates, and fine clay particles

consisting of microscopic mineral colloids. The size of the different unconsolidation fragments could be defined as below.

Classification	Size. diem in mm
Rock Fragments	> 75 mm
Gravel Particles	2 mm to 75 mm
Sand Fractions	0.075 mm to 2 mm
Silt Particles	2 μm to 75 μm
Clay Colloids	< 2 μm

The clay particles usually have the greatest surface area and active sites for ion exchange and sorption. Most clays are formed from silicates and are categorized as kaolinites, illites and smectites (montmorillonite).

The nature of the geologic media and the chemical processes occurring in the flow path system must be considered in assessing the suitability of a nonradioactive chemical analogue that can be used as a surrogate or tracer in place of a radioactive actinide.

PHYSICAL AND CHEMICAL CHARACTERISTICS OF ACTINIDES AND POTENTIAL TRACERS

CHARACTERISTICS FROM EXTRANUCLEAR STRUCTURES

Chemical and physical characteristics of the elements are determined by the extranuclear structures of the atoms and ions from which they are derived. More specifically, these characteristics are largely the result of the electrons in the highest quantum levels or outer electron shells. Perhaps the simplest means of perusing the elements as a whole is the periodic chart of the elements. There are certain generalizations that can be made in comparing elements within the periodic chart. Since the extranuclear electrons have such a dominant role in determining the chemical and physical characteristics of elements, the electronic structure of a portion of the seventh period or family is included in Table II.

TABLE II. ELECTRONIC STRUCTURE OF ACTINIDES

Element	Electronic Configuration			
Fr	[Rn]			$7s^1$
Ra	[Rn]			$7s^2$
Ac	[Rn]		$6d^1$	$7s^2$
Th	[Rn]		$6d^2$	$7s^2$
Pa	[Rn]	$5f^2$	$6d^1$	$7s^2$
U	[Rn]	$5f^3$	$6d^1$	$7s^2$
Np	[Rn]	$5f^4$	$6d^1$	$7s^2$
Pu	[Rn]	$5f^6$		$7s^2$
Am	[Rn]	$5f^7$		$7s^2$
Cm	[Rn]	$5f^7$	$6d^1$	$7s^2$

In general, there is an increase in size of an atom with increase in atomic number when a new electron shell is added to the electronic structure of elements. The spatial arrangement of electrons and their distance from the nucleus provides a parameter that can be considered in comparing the sphere of influence, and therefore the chemical properties of an atom. The radius of an atom, given in picometers, is dependent on several factors such as oxidation state, degree of ionization, and coordination number. When the atom is part of a molecule, two radii are defined: the covalent radius, which refers to the role it plays in forming bonds, and the van der Waals radius, which refers to the radius it presents to the world outside of the molecule. The atomic volume is defined as the ratio of gram-atomic weight to density; likewise, molecular volume is the ratio of gram-molecular weight to density.

It is known that no ion or atom has a precisely defined radius. The only way radii can be assigned to an atom or ion is to determine how closely the centers of two atoms or ions approach each other in solid substances and then to assume that such a distance is the sum of the radii of the two atoms or ions. Even with this summation of radii, there is no absolute way to know where one ion ends and a neighboring one begins. However, with the availability of relatively recent and accurate electron density maps, reasonably consistent trends of ionic radii provide a means to make generalizations concerning the periodicity that results from comparing the size of atoms and ions. Some of the important trends and correlations that have been developed based on ionic radii are as follows:

1)   the radius of a cation increases with increasing coordination number for the cation;

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2)   for an isoelectronic series such as Na^+, Ca^{2+}, Al^{3+} and Si^{4+}, the radius decreases with increasing charge;

3)   for a single element, the radius decreases with increasing charge $(Pu^{4+}, Pu^{5+}, Pu^{6+})$; and

4)   for elements in the transition series, especially lanthanides and actinides, the radius decreases as the nuclear charge (atomic number) increases while inner electronic shells are filled (lanthanide and actinide contractions).

As with ionic radii, attempts have been made to determine the atomic radius of an atom in a free element or covalently bonded compounds. These attempts have resulted in providing a relative indication of the size of an atom or ion. Table III illustrates the difference in the size of atoms and ions of selected actinides.

TABLE III. PERIODICITY AND SIZE OF ATOMS AND MULTI-CHARGED IONS

		$\underline{M}^0$	$\underline{M}^{3+}$	$\underline{M}^{4+}$	$\underline{M}^{5+}$	$\underline{M}^{6+}$
Th						
	Molar Volume	19.8				
	Density	11.72				
	Atomic/Ionic Radii	179.8		99		
U						
	Molar Volume	12.56				
	Density	18.95				
	Atomic/Ionic Radii	138.5	103	97	89	80
Np						
	Molar Volume	11.71				
	Density	20.25				
	Atomic/Ionic Radii	131	110	95	88	82
Pu						
	Molar Volume	12.3				
	Density	19.84(α)				
	Atomic/Ionic Radii	151(α)	108	93	87	81
Am						
	Molar Volume	17.78				
	Density	13.67				
	Atomic/Ionic Radii	184	107	92	86	80

One of the properties of transition elements that varies more or less systematically within the periodic table is atomic radius. Across a period (K to Kr and Rb to Xe), there is only a small change in size because the outer s electrons are shielded from the gradually increasing nuclear charge by the electrons that are added to the underlying d subshell. In general, there is a gradual decrease in size from left to right, with a minimum near the center of each row of transition elements. Going down a column (Group), the size of an atom increases for the first two columns; then in Group III and beyond (except for Group IIIB) there is very little change in the size of atoms. The reason for the Group IIIB deviation in size relationship is a phenomenon called the lanthanide contraction. Lanthanum, in Group IIIB, is slightly larger than yttrium as expected, but just to the right of Y is Zr, which has a slight decrease in size, which is not expected. The reason for the decrease in size is that going from La to Hf there is an increase in nuclear charge (atomic number) of 15 due to the entire series of lanthanide elements. Because the inner 4f shell of 14 electrons are sequentially added as the lanthanides are completed, they do not effectively shield the outer 5d and 6s electrons from the nucleus and the outer electrons of Hf experience an extra large nuclear charge. This draws the electrons closer to the nucleus and makes Hf smaller than expected. This unexpected shrinking across the lanthanides is called the lanthanide contraction. The result of the lanthanide contraction is the similarities in chemistry between the congeneric pairs Zr-Hf, Nb-Ta, Mo-W, and Tc-Re. All of these congeners have the same charge and size between each other and make their chemistry very similar and thus very hard to separate from each other in aqueous systems. The lanthanide contraction leads to relatively high densities of the post-lanthanide transition metals Hf (13.1), Ta (16.6), W (19.3), Re (21.0), Os (22.4), Ir (22.5), Pt (21.4), and Au (19.3). These elemental densities are about twice the density of the corresponding 5th period congeners. The increased density of the post-lanthanide elements results in their resistance to oxidation. The emphasis on the similarity of chemistry due to size relationships between elements and the influence of the lanthanide contraction is to call attention to the chemistry of the actinides which are also influenced by an actinide contraction.

Table IV lists the molar volume of elements. Based on a size criteria of molar volume only, it appears that Th and Am are similar to rare-earth elements; and U, Np, and Pu are similar to Li and perhaps Ti. Of course, this similarity will change when consideration is given to oxidation states of each element. If a grouping is made of those elements with similar ionic radius, there appears to be a coincidental grouping of these elements as they occur together in nature. Elements with similar ionic radii tend to prefer association in minerals that occur in nature.

TABLE IV. CATEGORIZATION ACCORDING TO MOLAR VOLUME

1st Period		2nd Period		3rd Period		4th Period	
He	24.6	Ne	16.7	Ar	28.5	Kr	38.9
H₂	13.6	Li	13.1	Na	23.7	K	45.5
		Be	9.3	Mg	14	Ca	30
		B	8.3	Al	10	Sc	15
						Ti	10.6
						V	8.8
						Cr	7.2
						Mn	7.4
						Fe	7.1
						Co	6.7

6th Period		7th Period	
Xe	37	Rn	50.5
Cs	71	Fr	--
Ba	39	Ra	45.20
La	20.7	Ac	22.54
Ce	20.7	**Th**	**19.9**
Pr	20.8	Pa	15.0
Nd	20.6	U	**12.6**
Pm	22.4	**Np**	**11.6**
Sm	20	**Pu**	**12.3**
Eu	28.9	**Am**	**17.9**
Gd	19.9	Cm	18.3
Tb	19.2		

TABLE V. IONIC RADII OF SPECIES OCCURRING TOGETHER IN NATURAL MINERALS RELATIVE TO ACTINIDES

Size Group	Ionic Radius	
1	0.1-0.3	B^{3+}, C^{4+}, N^{5+}, S^{6+}
2	0.3-0.5	Be^{2+}, Si^{4+}, P^{5+}, V^{5+}
3	0.5-0.7	Li^+, Mg^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Ti^{4+}, Mo^{6+}, W^{6+}
4	0.7-0.9	Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Sc^{3+}, In^{3+}, Zr^{4+}, Hf^{4+}, Sn^{4+}, Nb^{5+}, Ta^{5+}
5	0.9-1.1	Na^+, Ca^{2+}, Cd^{2+}, Y^{3+}, Gd^{3+}, Lu^{3+}, Ce^{4+}, Th^{4+}, U^{4+}
6	1.1-1.4	K^+, Sr^{2+}, La^{3+}, Eu^{3+}
7	1.4-1.7	Rb^+, Cs^+, Tl^+, Ba^{2+}, Ra^{2+}

	$Th^{4+}=0.99$		
	$U^{4+}=0.97$		$U^{6+}=0.80$
$Np^{3+}=1.10$	$Np^{4+}=0.95$	$Np^{5+}=0.88$	$Np^{6+}=0.82$
$Pu^{3+}=1.08$	$Pu^{4+}=0.93$	$Pu^{5+}=0.87$	$Pu^{6+}=0.81$
$Am^{3+}=1.07$	$Am^{4+}=0.92$	$Am^{5+}=0.86$	$Am^{6+}=0.80$

The relative size relationships in Table V show that the actinides, if present in nature, would prefer to be grouped in size groups 4, 5, and 6, with a predominance in 5. Elements with similar ionic radii to actinides that might show similar chemistry would be Gd^{3+}, Y^{3+}, and Ce^{4+} in the size group 5 and La^{3+} to Eu^{3+} in size group 6. It would be difficult to suggest an analogue from size group 4. However, uranium is present together with V^{5+} in carnotite.

The relative attraction of an atom for the electrons in a bond is termed the electronegativity of the atom. The electron pair of a covalent bond spends more time around the more electronegative atom, which acquires a partial negative charge. Electronegativity can be regarded as the balance between the tendency for an atom to gain an electron (electron affinity) and the tendency for an atom to lose an electron (ionization potential). The greater the magnitude of the tendency of an element to gain an electron, the greater is its oxidizing power. In general, the small atoms, such as Group VII halogens, have greater attraction for electrons are, therefore, more electronegative. Table VI is a list of elements with electronegativities.

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TABLE VI. TABLE OF ELECTRONEGATIVITIES

Element	Electronegativity	Element	Electronegativity	Element	Electronegativity
F	4.1	Zn	1.7	Mg	1.3
O	3.5	Co	1.7	Ti	1.3
N	3.1	Fe	1.7	Nb	1.3
Cl	2.9	Cr	1.6	Mo	1.3
Br	2.8	Mn	1.6	Sc	1.2
Se	2.5	Ir	1.6	Zr	1.2
C	2.5	Pb	1.6	Hf	1.2
S	2.4	V	1.5	Ca	1.1
I	2.2	Al	1.5	Y	1.1
As	2.2	Rh	1.5	La	1.1
P	2.1	Cd	1.5	Lanthanides	1.1 to 1.3
H	2.1	In	1.5	Actinides	1.2 to 1.4
At	2.0	Re	1.5	Li	1.0
Te	2.0	Os	1.5	Na	1.0
B	2.0	Pt	1.5	Sr	1.0
Ge	2.0	Be	1.5	Ac	1.0
Po	1.8	Hg	1.5	K	0.9
Sb	1.8	Tl	1.5	Rb	0.9
Ga	1.8	Tc	1.4	Ba	0.9
Cu	1.8	Ru	1.4	Ra	0.9
Ni	1.8	Pd	1.4	Cs	0.9
Bi	1.7	Ag	1.4	Fr	0.9
Sn	1.7	Ta	1.4		
		W	1.4		
		Au	1.4		

The elements included in Table VI can be compared with the electronegativities of the actinides which are listed below.

Th	1.3
U	1.38
Np	1.36
Pu	1.28
Am	1.3

Elements that have electronegativities similar to the actinides include Li, Na, Sr, Ac, rare-earths, Y, Ca, Hf, Zr, Sc, Mo, Nb, Ti, and Mg.

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ELECTRONIC CONFIGURATION OF THE ACTINIDES

Electrons are added to fill each shell, which results in an inert gas structure that is the most stable structure within each period (family). In general, Group I and II fill the respective s shell electrons while Group VIII, the inert gases, are the most stable electronic arrangements. All applicable electronic shells are filled to give an inert structure. Because atoms prefer to return to the most stable inert gas electronic configuration, elements that follow the inert gas structure will tend to lose electrons to yield a multi-positive ion with an inert gas structure. Electronic structures that tend to also be stable are when the f shell electronic level is half-filled or at the f^7 configuration (pseudo filled shell). The chemical characteristics of both lanthanides and actinides are strongly influenced by the tendency of elements to remain with the inert gas structures or pseudo-inert gas configurations at the f^7 level. Table VII shows the electronic configuration of actinides and lanthanides to illustrate this phenomenon.

TABLE VII. ELECTRONIC CONFIGURATIONS OF ACTINIDES AND LANTHANIDES AT DIFFERENT OXIDATION STATES

Actinide	Electronic Configuration				M^{3+}	M^{4+}	M^{5+}	M^{6+}
Ac	[Rn]		$6d^1$	$7s^2$	**[Rn]**	--	--	--
Th	[Rn]		$6d^2$	$7s^2$		**[Rn]**		
Pa	[Rn]	$5f^1$	$6d^2$	$7s^2$			**[Rn]**	
U	[Rn]	$5f^3$	$6d^1$	$7s^2$		$5f^3$		**[Rn]**
Np	[Rn]	$5f^5$		$7s^2$		$5f^3$	**[5f²]**	
Pu	[Rn]	$5f^6$		$7s^2$	$5f^5$	**[5f⁴]**	$5f^3$	$5f^2$
Am	[Rn]	$5f^7$		$7s^2$	**[5f⁶]**	$5f^5$		
Cm	[Rn]	$5f^7$	$6d^1$	$7s^2$	**[5f⁷]**			

Select Lanthanides	Electronic Configuration				M^{+2}	M^{+3}	M^{+4}
La	[Xe]		$5d^1$			**[Xe]**	
Ce	[Xe]	$4f^1$	$5d^1$	$6s^2$		$4f^1$	**[Xe]**
Pr	[Xe]	$4f^3$		$6s^2$		$4f^2$	
Nd	[Xe]	$4f^4$		$6s^2$		$4f^3$	
Pm	[Xe]	$4f^5$		$6s^2$		$4f^4$	
Sm	[Xe]	$4f^6$		$6s^2$	$4f^6$	$4f^5$	
Eu	[Xe]	$4f^7$		$6s^2$	**$4f^7$**	$4f^6$	
Gd	[Xe]	$4f^8$	$5d$	$6s^2$		**$4f^7$**	
Tb	[Xe]	$4f^9$		$6s^2$		$4f^8$	**$4f^7$**

Table VII illustrates the reason the first four actinides have stable oxidation states of Ac^{3+}, Th^{4+}, Pa^{5+}, and U^{6+} in the attempt of the individual actinide elements to retain the stable [Rn] inert gas configuration. Later in the period, Am attempts to achieve a pseudo-inert gas configuration of $5f^7$ but cannot go to Am^{2+} so settles for Am^{3+} and $5f^6$. Curium attains the $5f^7$ half-filled shell configuration and retains a singular 3+ oxidation state. Np, Pu, and Am have multiple oxidation states because they cannot achieve an inert gas configuration and are beginning to be pulled toward the Cm $5f^7$ half-filled shell stability. A look at Table VII shows that Ce^{4+} has a very similar electronic configuration to Th^{4+} and should make a good chemical analogue provided there is not a concentration of easily reduced compounds because of the electron affinity of Ce^{4+}. Eu^{3+} has a similar electronic structure to Am^{3+} and should make a good analogue for Am^{3+}. U^{4+} should have a chemistry similar to the lanthanides, Y^{3+} and Ce^{4+}. U^{6+}, Np^{5+}, Np^{6+}, Pu^{5+} and Pu^{6+} are rather unique in their chemistry and all form dioxo-compounds that have a complex structure.

SEARCH FOR CHEMICAL SIMILARITIES

The most stable oxidation state of uranium in aqueous systems is U^{6+} because of the tendency of U to maintain the stable electronic configuration of the nearest inert gas, radon. The U^{6+} (uranyl) ion, when in aqueous solution, combines with oxygen to give a dioxouranium compound UO_2^{2+}. Although the uranyl ion only carries a charge of 2+, it behaves more like an ion that carries a 4+ charge.

There are four cationic types of actinides in acidic aqueous solution: M^{3+}, M^{4+}, MO_2^+, and MO_2^{2+}. The MO_2^+ and MO_2^{2+} ions are remarkably stable with respect to the binding of the oxygen atoms and are essentially unique in this characteristic within the periodic chart. All positively charged ions in aqueous solution tend to be associated with water or other coordinating groups. The greatest degree of hydration, hydrolysis, and complex ion formation within the actinides occurs with the small highly charged M^{4+} ions. Pu^{4+} ions begin to hydrolyze to form polymerized or colloidal products in solutions that are less than 0.1 M in HNO_3. Pu^{4+} forms such strong anion complexes that the uncomplexed ion is an exception. These anions can be called ligands. A ligand is any molecule or ion that has at least one electron pair that can be donated. When a ligand becomes attached to two or more atoms it is a bidentate, tridentate, tetradentate or simply multidendate. Bidentate ligands when bound entirely to one atom are termed chelates. The process of displacing one set of ligands (aqua ions) from an atom in an aqueous system with a different set is what is called complex formation.

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It is common to write the solvated proton of dissociated water as H_3O^+. For Group IIA elemental salts of Mg and Ca mixed with water, oxo salts will form depending on the level of hydration of the salts, e.g., $2CaSO_4 \cdot H_2O$ (plaster of Paris) and $CaSO_4 \cdot 2H_2O$ (gypsum). However, Sr, Ba, and Ra form insoluble sulfates that are anhydrous. The carbonates of the Group IIA elements are rather insoluble in water and the solubility products decrease with increasing size of M^{2+}. For water solutions of Mg^{2+}, the coordination number is 6 to give an ion that can be described as $[Mg(H_2O)_6]^{2+}$. The complexity constants for Mg, Ca, Sr, and Ba vary greatly depending on the ligand.

For small or highly charged anions and certain unidentate and bidentate ligands the complex strengths decrease with increasing crystal radii, Mg > Ca > Sr > Ba.

For oxoanions like NO_3^-, SO_4^- and IO_4^-, the order is reversed according to the hydrated radii and Ba > Sr > Ca > Mg.

For actinides, the degree of hydrolysis or complex ion formation is $M^{4+} > MO^{2++} > M^{3+} > MO^{2+}$. The actinides, when mixed with carbonates, tend to form soluble complexes with the MO_2^{++} species and form precipitates in the M^{3+} and M^{4+} states (except for $Np^{3+,4+}$ which seems to form soluble carbonate complexes). The UO_2^{2+} ion is more like the Mg^{2+} (small ion) and less like Sr^{2+} and Ba^{2+} (larger ion) in the tendency to form soluble carbonate complexes, while Mg^{2+} precipitates are sparingly soluble. Thorium, as well as Group IVA elements, tends to form totally soluble carbonates. PuO_2^{2+}, like UO_2^{2+}, forms totally soluble carbonate complexes. Pu^{3+}, Pu^{4+}, Am^{3+} all form carbonate precipitates at low concentrations of carbonates and all are complexed at high concentrations of carbonates. Essentially all actinides in all stable oxidation states are complexed in concentrated carbonate solutions. In general, the lower oxidation states of the actinides will form carbonate precipitates at lower concentrations of carbonates and the higher oxidation states (6+) are complexed at all concentrations of carbonates. Np^{5+} formed soluble carbonate complexes at higher carbonate concentrations and precipitates at lower carbonate concentrations. Rare-earth elements and Y^{3+} form carbonates at low concentrations (like actinides) and soluble complexes at the higher concentrations of carbonates in solution. The lanthanides toward lanthanum tend to form carbonate precipitates while the heavy lanthanides and Y^{3+} tended to form soluble complexes. In general, the low molecular weight lanthanides were similar to An^{3+} and An^{4+} chemistry with carbonates while the higher molecular weight lanthanides and Y tended to complex as the U^{6+}, Np^{6+}, and Pu^{6+} ions. Table VIII summarizes the precipitation/complexation of actinides in different carbonate solutions. Table IX summarizes the precipitation/complexation of Y^{3+} and lanthanides. In general,

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the actinides have a greater tendency to form complexes than do the lanthanides. Perhaps, this is one of the major differences in the aqueous chemistry of the actinides relative to the lanthanides. The actinides form a variety of complexes with oxoanions including NO_3^-, SO_4^{2-}, CO_3^{2-}, halides, and other ligands, particularly chelating ligands. The general tendency to form complex ions is M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+. For anions, the tendency is to combine with singularly charged negative ions (CO_3^{2-} > oxalate^{2-} > SO_4^{2-}). The relatively large sizes of the actinide ions, coupled with the high electrostatic attraction because of the range of higher oxidation states of M^{3+}, M^{4+}, M^{5+} and M^{6+}, along with plentiful number of valence shell orbitals that are potentially available result in higher coordination numbers, such as 8 and 9.

The chemistry of actinides in general, especially U, Np, Pu, and Am, is very complex, and attempts to identify a single chemical analogue for these actinides will meet with failure. Formation of hydroxy compounds and polymers in solutions that are less than 0.05M HNO_3 or HCl complicates the chemistry of M^{4+} actinides, especially Pu^{4+}. The Th^{4+} ion is larger than succeeding M^{4+} ions and is more resistant to hydrolysis, but at pHs above 3 complex, polymeric hydrolysis products can form which complicates chemistry at neutral pHs.

ION-EXCHANGE CONSIDERATIONS

One of the characteristics that must be considered in selecting a chemical analogue for actinides is ion-exchange properties. Ion exchange has been defined as the reversible exchange of ions between a liquid phase and a solid phase which is not accompanied by any radical change in the solid structure. Ion-exchange processes are effected by contacting an ion-exchange material with a solution containing ions that are to be exchanged, that is, removed from solution. Most applications of ion-exchange materials utilize highly tailored synthetic resins and polymers that are designed to exhibit high exchange efficiency, capacity, and selectivity. Because the ion-exchange materials that are of interest in this study are natural inorganic minerals such as clays and aluminosilicates, this report will focus on ion-exchange of actinides and chemical analogues similar to actinides on natural inorganic ion-exchange minerals. The two primary types of ion-exchange materials that are presented to solutions are cationic exchangers that have fixed ionic groups that are negatively charged anions, and will exchange positively charged cations. Alternatively, anionic exchangers have fixed ionic groups that are positively charged cations that exchange negatively charged anions.
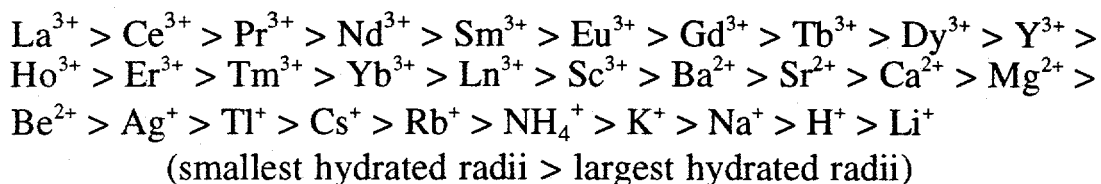
Solutions with mobile ions of opposite charge (counterions) to the fixed ionic groups can be passed through a mineral matrix containing natural ion exchangers. The mobile ions will be attracted to the fixed ionic groups and an exchange of ions will occur. A mobile ion with a charge of same sign as the fixed group is called a co-ion. Co-ions are electrostatically repulsed due to the

same charge. Cationic exchangers contain fixed ionic groups, which are proton donors, and behave similar to acids. They are, therefore, termed acidic exchangers. Similarly, anionic exchangers are proton acceptors and are termed basic exchangers (Bronsted concept of acid and base). In the Lewis concept of acid and bases, the acidic exchangers would be electron acceptors and the basic exchangers would be electron donors. Ion exchangers can be further classified as strong or weak acid (cationic) or base (anionic) ion exchangers, depending on the degree to which the ionizable group of the exchanger will dissociate. Strong acid and strong base ion exchangers completely dissociate over most pH values of a solution. As an example, the hydrogen ion of a solution does not compete with other cations for exchange sites of strong acids cationic exchangers (sulfonic acid groups), and, therefore, are effective for a wide range of pH values. Likewise, the hydroxyl in a solution does not compete with other anions for exchange sites of strong base ion exchangers. Thus, the ion-exchange capacities of strong acid and strong base ion exchangers do not vary significantly with pH.

Weak acid and weak base ion exchangers behave similar to weak acids and weak bases and do not dissociate completely over the pH range of most natural solutions. As a result, the number of sites available for ion exchange and the capacity of the exchangers are strongly influenced by pH. The capacity of weak acid ion exchangers (carboxylic acid groups) decrease as the pH goes toward the acid side beyond neutral while the capacity of weak base ion exchangers (amines) decrease as the pH goes toward the basic side beyond neutral.

Of great interest in natural ion exchange systems, is the selectivity of the available ion-exchange groups. Two important factors governing ion-exchange selectivity is the valence of the exchanging group and the effective hydrated ionic radius of the mobile ion. Ion exchangers generally prefer ions of higher valency (greater oxidation state) and smaller size. However, the effective size of a mobile phase ion must be taken as the ionic radius of the hydrated complex and not simply the ionic radius. This is important in that for a given sequence of ions, the ions of largest ionic radius are generally the ions of smallest hydrated ionic radius. Alternatively, the ions of smallest ionic radius generally have the larger hydrated radius. Consequently, the predicted preference of ion exchangers for counterions according to valency effects is $Th^{4+} > Nd^{3+} > Ca^{2+} > Na^+$ and $PO_4^{3-} > SO_4^{2-} > Cl^-$.

The effect of the hydrated counterion radius relative to the nonhydrated counterion radius is illustrated below.

$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Y^{3+} >$$
$$Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Ln^{3+} > Sc^{3+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} >$$
$$Be^{2+} > Ag^+ > Tl^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > H^+ > Li^+$$

(smallest hydrated radii > largest hydrated radii)

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According to the classic text by C.B. Amphlett, base exchange in soils could be traced to two principal causes: the presence of humins and humic acids that contain hydroxyl and carbonyl ligands which can act as ion exchange groups and the "colloid fraction" which consist chiefly of clay minerals.

The clay minerals comprise a complex series of aluminosilicate structures which possess ion exchange properties. The aluminosilicate basic structure consists of alternating, parallel, two dimensional layers formed from silicate tetrahedra and aluminate octahedra. The internal composition of the layers and the extent of isomorphous substitution within the layers determine, to a large extent, the chemical and physical properties of the clay minerals. In general, three basic types of clay minerals are recognized; kaolinite, montmorillonite, and illite. For kaolinite, the ion-exchange groups are hydroxyl ions that are weakly acidic and exchanged with anions. But the hydrogen ion also can exchange with cations, resulting in a limited exchange capacity for both cations and anions. The ion-exchange capacity of mineral clays depends on the chemical composition of the clay and decreases in order montmorillonite > illite > kaolinite for exchange for cations.

Another group of aluminosilicate minerals with different structures from the clay minerals are the zeolites. Like the mineral clays, they possess well-defined crystal structures that have ion-exchange groups available for exchange. The exchange capacity of the zeolites range from ~4 meq/gm to ~11 meq/gm which is considerably better than the clay minerals which have capacities that range from 0.02-0.10 meq/gm, for kaolinite, to ~ 1.0, for biotite and pure vermiculite.

Ion exchange properties of mineral clays, zeolites and other clay derivatives are strongly dependent on the concentration of anions and cations in the mobile phase. Also, the capacity of the natural inorganic ion exchangers for a particular cation can only be determined relative to the concentrations and compositions of the mobile phase. The actinides, in general, are expected to demonstrate ion exchange behavior according to the valency effect (great charge > small charge) and the hydrated ion radius effect (small hydrated ion > large hydrated ion.) If the valency effect is operative for actinide elements, the order of ion-exchange attraction should be $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$. If the hydrated ion radius effect is operative for actinides, then the hydrated ionic radii for M^{4+} would be $Am^{4+} > Pu^{4+} > Np^{4+} > U^{4+} > Th^{4+}$, and the attraction of those ions by ion exchange groups would be the opposite with $Th^{4+} > Am^{4+}$. If the preference of ion exchange groups is for more highly charged groups, then the valency effect would predominate and Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+} would be preferred to the dioxo uranyl, dioxo neptunyl and dioxo plutonyl complexes. In summary, the ion exchange behavior of actinides and potential actinide analogues would be as described below.

1) Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+} would tend to be similar to Ce^{4+}, Ln^{3+}, Hf^{4+}, and perhaps Ti^{4+}, and V^{5+}.

2) UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} would tend to be similar to Mg^{2+}, Li^+, and perhaps CrO_2^{2+} and MoO_2^{2+}.

3) Am^{3+} would tend to be similar to Eu^{3+}, Gd^{3+}, Nd^{3+}, or Y^{3+}.

4) Most naturally occurring inorganic ion-exchange minerals (clay minerals) would prefer cationic exchange and would be weak acids or weak bases.

5) Incorporation of the effects of natural humic acids would be dependent on the concentration and type of ligands available for ion-exchange or complexation.

STABLE ISOTOPES

One of the criteria that must be applied in assessing the suitability and applicability of a chemical analogue for actinides is the concentration of the tracer in the intrinsic geological environment that is to be tested. Sodium, potassium, magnesium, or chloride would not be appropriate tracers because the concentration of these elements in brine or the geologic media to be tested is very high and would interfere in establishing the elusion of the tracer. However, the analytical methodology projected to be used for analyses of the tracer is inductive-coupled argon plasma mass spectometry (ICP-MS). Because ICP-MS has the capability of performing analyses on an isotopic basis, elements and compounds that have multiple stable isotopes at constant ratios can be differentiated from tracers to be injected with elements enriched with specific isotopes to give different isotopic ratios. Magnesium, lithium, and several rare-earth elements would be included in the list of potentially effective tracers if enriched fractions of stable isotopes are commercially available for the elements to be used as tracers. Isotopes can be produced at ORNL and LANL for use in enriching certain elemental isotopes such as ^6Li (>95%), ^{26}Mg (>99%), ^{50}V (>35%), ^{58}Fe (>65%), ^{100}Mo (>95%), and ^{136}Ce (>35%).

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DISCUSSION

Catagorization of actinides and chemical analogues according to molar volume indicated the following similarities.

Th	19.9	La (20.7), Ce(20.7), Pr(20.8), Nd(20.6), Sm(20), and Gd(1 9.9)
U	12.6	Li(13.1), Mg(14)
Np	11.6	Li(13.1), Mg(14)
Pu	12.3	Li(13.1), Mg(14)
Am	17.9	Tb(19.2), Gd(19.9), Sm(20), Nd(20.6), La(20.7) and Ce(20.7)

Catagorization of actinides and potential chemical analogues according to ionic radii and occurrence together with minerals in nature gave the following similarities and tendencies.

Np^{3+}, Pu^{3+}, Am^{3+}	Rare-earths, Y^{3+}
Th^{4+}, U^{4+}, Pu^{4+}	Rare-earths, Hf^{4+}, Zr^{4+}, Sn^{4+}
Np^{5+}, Pu^{5+}	Nb^{5+}, Ta^{5+}, Hf^{4+}, Zr^{4+}, Sn^{4+}
U^{6+}	Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Zr^{4+}, Hf^{4+}, Nb^{5+}, Ta^{5+}, V^{5+}

Catagorization of actinides as a group has been compared with other elements according to electronegativities. The electronegativities of elements are given in Table VI and are compared to electronegativities of actinides. Elements that have electronegativities similar to actinides (1.28 to 1.38) include Li(1.0), Na(1.0), Sr(1.0), Ac(1.0), Ln(1.1 to 1.3), Y(1.1), Ca(1.1), Hf(1.2), Zr(1.2), Sc(1.2), Mo(1.3), Nb(1.3), Ti(1.3) and Mg(1.3).

Catagorization of actinides relative to other elements, especially rare-earths, according to extranuclear electronic configurations was shown in Table VII. A summary of the outer electronic shell configuration at different stable oxidation states is given below.

Th^{4+}	[Rn]		Ce^{4+} [Xe], La^{3+} [Xe], Hf [Xe] $4f^{14}$
U^{4+}	[Rn]		Ce^{4+} [Xe], Hf [Xe] $4f^{14}$, Ta [Xe] $4f^{14}$
U^{6+}	[Rn]		La^{3+} [Xe], Ce^{4+} [Xe], W^{6+} [Xe], Mo^{6+} [Kr]
Np^{4+}	[Rn]	$5f^3$	Nd^{3+} [Xe] $4f^3$
Np^{5+}	[Rn]	$5f^2$	Pr^{3+} [Xe] $4f^2$, Pr^{4+} [Xe] $4f^1$
Np^{6+}	[Rn]	$5f^1$	Ce^{3+} [Xe] $4f^1$, Pr^{4+} [Xe] $4f^1$
Pu^{3+}	[Rn]	$5f^5$	Sm^{3+} [Xe] $4f^5$
Pu^{4+}	[Rn]	$5f^4$	Pm^{3+} [Xe] $4f^4$
Pu^{5+}	[Rn]	$5f^3$	Nd^{3+} [Xe] $4f^3$
Pu^{6+}	[Rn]	$5f^2$	Pr^{3+} [Xe] $4f^2$, Pr^{4+} [Xe] $4f^1$
Am^{3+}	[Rn]	$5f^6$	Eu^{3+} [Xe] $4f^6$, Sm^{2+} [Xe] $4f^6$
Am^{4+}	[Rn]	$5f^5$	Sm^{3+} [Xe] $4f^5$
Cm^{3+}	[Rn]	$5f^7$	Gd^{3+} [Xe] $4f^7$

Catagorization of actinides according to carbonate chemistry is a unique but effective means to compare chemical properties of actinides with other elements. A comparison of carbonate complexation and precipitation reactions is given below.

1) • Actinides that form soluble complexes at all concentrations and pH levels (8-13) - U^{6+}, Np^{6+}, Pu^{6+}, Th^{4+}, $Np^{3,4}$ *.
 * Np oxidation state determined by dissolution in HCl and a blue violet color

1a) • Selected elements that form soluble carbonates at all concentrations and pH levels (8-13) - Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr^{3+}, Mo^{6+}, Re^{7+}, Ru, Rh, Pd, Group I elements.

2) • Actinides that form soluble complexes at higher carbonate concentrations and pH levels (~10) - Np^{5+}, Pu^{4+}.

2a) • Selected elements that form soluble carbonate complexes at higher carbonate concentrations and pH levels (~10) - rare-earth elements above Eu, Y, Mg.

3) • Actinides that form precipitates at low concentrations of carbonates - Pu^{3+}, Pu^{4+}, Am^{3+}, U^{4+}.

3a) • Elements that form precipitates at low concentrations of carbonates - rare-earths, Y, Ba, Sr, Ca, Fe, Co, Ni, Zn, Cd, Al, Pb.

4) • Actinides that form soluble carbonate complexes with NH_4HCO_3 and pH level 8-8.5 - U^{6+}, $Np^{3,4}$, Pu^{4+}(incomplete), Pu^{6+}, Th^{4+}.

4a) • Selected elements that form soluble carbonate complexes with NH_4HCO_3 - Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr, Mo, Re, Ru, Rh, Pd, Cu.

5) • Actinides that form precipitates when mixed with NH_4HCO_3 at pH 8-8.5 - Np^{5+}, Pu^{3+}, Pu^{4+} (incomplete).

5a) • Selected elements that form carbonate precipitates with addition of NH_4HCO_3 - Group II, Y, rare-earths, Mn, Fe, Co, Ni, Zn, Cd, Pb, Al.

6) • Actinides that form soluble complexes upon addition of ammonium carbonate at pH ~8.5 - All actinides, Np^{5+} (incomplete).

6a) • Selected elements that form soluble carbonate complexes upon addition of ammonium carbonate at pH ~8.5 - all rare-earths, Y, Ti, Zr, Hf, Cr, Mo, Re, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Cd.

7) • Actinides that form precipitates with addition of ammonium carbonate at pH ~8.5 - none.

7a) • Selected elements that form precipitates with addition of ammonium carbonate at pH ~8.5 - Group II elements, Mn, Al, Pb.

SUMMATION OF COMPARISONS

(1) U^{6+}, Np^{6+}, Pu^{6+}, Th^{4+}, $Np^{3,4+}$ similar within actinides

(1a) Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr, Mo^{6+}, Re^{7+} comparable analogues

(2) Np^{5+} and Pu^{4+} similar within actinides

(2a)   Eu and above, Y, Mg comparable analogues

(3) Pu^{3+}, Pu^{4+}, Am^{3+}, U^{4+} similar within actinides

(3a)   rare-earths, Y, Group II elements, Fe, Co, Ni, Zn, Al, Pb comparable analogues

(4) U^{6+}, $Np^{3,4}$, Pu^{6+}, Th^{4+} similar within actinides

(4a) Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr, Mo, Re, Ru, Rh, Pd, Cu comparable analogues

(5) Np^{5+}, Pu^{3+}, Pu^{4+} similar within actinides

(5a)   Group II, rare-earths, Y, Mn, Fe, Co, Ni, Zn, Al comparable analogues

(6)   All actinides similar within actinides

(6a)   All rare-earths, Y, Ti, Zr, Hf, Cr, Mo, Re, Fe, Ni, Co, Cu, Zn, Ru, Rh, Pd, (Cd comparable to (9))

(7)   No actinides

(7a)   Group II elements, Mn, Al, Pb

Catagorization according to complexation is difficult task because of the vast numbers of complexes that are formed by actinides, especially the dioxouranyl, neptunyl, and plutonyl complexes. A generalization is provided below.

Th^{4+}	-	similarity	-	Hf, Zr, Ti, Re, Cr, Mo
U^{6+}	-	similarity	-	Hf, Zr, Ti, Re, Cr, Mo, Mg
Np^{4+}	-	similarity	-	Like Th^{4+}
Np^{5+}	-	similarity	-	Am, Eu, Gd, Er
Np^{6+}	-	similarity	-	Somewhat like U^{6+}
Pu^{3+}	-	similarity	-	Rare-earths, Y
Pu^{4+}	-	similarity	-	Sm, Eu
Pu^{6+}	-	similarity	-	Somewhat like U^{6+}
Am^{3+}	-	similarity	-	Strongly similar to Sm, Eu, Gd

Th^{4+}

Molar Volume	rare-earths, especially Gd
Ionic Radii	rare-earths, Hf^{4+}, Zr^{4+}, Sn^{4+}
Electronegativities	Hf^{4+}, Zr^{4+}, Sc^{4+}, Mo^{6+}, Nb^{5+}, Ti^{4+}
Electronic Structure	Ce^{4+}, La^{3+}, Hf^{4+}
Carbonate Chemistry	Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr, Mo^{6+}, Re^{7+}
Complexes	Hf^{4+}, Zr^{4+}, Ti^{4+}, Re, Cr, Mo
Recommended analogues	rare-earths, Hf^{4+}, Zr^{4+}, Ti^{4+}, Re, Mo, Ce^{4+}

U^{6+}

Molar Volume	Li, Mg
Ionic Radii	Hf^{4+}, Zr^{4+}, V^{5+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Ta^{5+}
Electronegativities	Hf^{4+}, Zr^{4+}, Sc^{4+}, Mo^{6+}, Nb^{5+}, Ti^{4+}
Electronic Structure	La^{3+}, Ce^{4+}, W^{6+}, Mo^{6+}
Carbonate Chemistry	Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr, Mo^{6+}, Re^{7+}
Complexes	Hf^{4+}, Zr^{4+}, Ti^{4+}, Re^{7+}, Cr, Mo, Mg
Recommended analogues	Hf^{4+}, Zr^{4+}, Ti^{4+}, La^{3+}, W^{6+}, Mo^{6+}, Mg^{2+}

$$U^{4+}$$

Molar Volume	Li, Mg
Ionic Radii	rare-earths, Hf^{4+}, Zr^{4+}, Sn^{4+}
Electronegativities	Same as U^{6+}
Electronic Structure	Ce^{4+}, Hf^{4+}, Ta^{5+}
Carbonate Chemistry	Ce^{4+}, rare-earths, Y
Complexes	Uf_4 isomorphous with rare-earth F_4
Recommended analogues	Hf^{4+}, Ce^{4+}, Ta^{5+}, Y, Zr^{4+}

$$Np^{3+,4+}$$

Molar Volume	Li, Mg
Ionic Radii	Rare-earths, Y^{3+}
Electronegativities	Same as U^{6+}
Electronic Structure	Nd^{3+}, rare-earths
Carbonate Chemistry	Ti^{4+}, Zr^{4+}, Hf^{4+}, Mo, Re, Er
Complexes	Rare-earths
Recommended analogues	Nd, Hf^{4+}, Mo, Re, Er, Mg, Li

$$Np^{5+}$$

Molar Volume	Li, Mg
Ionic Radii	Hf^{4+}, Ta^{5+}, Nb^{5+}, Zr^{4+}, Sn^{4+}
Electronegativities	Same as U^{6+}
Electronic Structure	Pr^{3+}, Pr^{4+}
Carbonate Chemistry	Eu and above, Y, Mg
Complexes	Sm and above
Recommended analogues	Pr^{3+}, Pr^{4+}, Sm, Hf^{4+}, Y, Mg

Np^{6+}

Molar Volume	Li, Mg
Ionic Radii	Ni^{2+}, Co^{2+}, Fe^{2+}, Hf^{4+}, Zr^{4+}, Ta^{4+}, V^{5+}
Electronegativities	Same as U^{6+}
Electronic Structure	Ce^{3+}, Pr^{4+}
Carbonate Chemistry	Similar to U^{6+}
Complexes	Similar to U^{6+}
Recommended analogues	Ce^{3+}, Pr^{4+}, V^{5+}, Hf^{4+}, Mg, Li

Pu^{3+}

Molar Volume	Li, Mg
Ionic Radii	Rare-earths, Y^{3+}, Cd^{2+}
Electronegativities	Mg, Ti, Nb, Mo
Electronic Structure	Sm^{3+}
Carbonate Chemistry	Rare-earths, Y, Group II elements
Complex Formation	Rare-earths, Y
Recommended analogues	Sm^{3+}, Lanthanides, Mo, Y

Pu^{4+}

Molar Volume	Li, Mg
Ionic Radii	Lanthanides, Hf^{4+}, Zr^{4+}, Sn^{4+}
Electronegativities	Mg, Ti, Nb, Mo
Electronic Structure	Pm^{3+}, Nd^{3+}, Pr^{4+}
Carbonate Chemistry	Lanthanides, Y, Fe, Co, Ni, Al, Pb
Complex Formation	Hf, Zr, Ti, Re, Cr, Mo
Recommended analogues	Nd^{3+}, Pr^{4+}, Hf^{4+}, Ti^{4+}, Re, Mo

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Pu^{5+}

Molar Volume	Li, Mg
Ionic Radii	Nb^{5+}, Ta^{5+}, Hf^{4+}, Zr^{4+}, Sn^{4+}
Electronegativities	Mg, Ti, Nb, Mo
Electronic Structure	Nd^{3+}
Carbonate Chemistry	None available
Complex Formation	Hf^{4+}, Ti^{4+}, V^{5+}, Ta^{5+}
Recommended analogues	Nd, Mo, Hf^{4+}, V^{5+}, Ti^{4+}

Pu^{6+}

Molar Volume	Li, Mg
Ionic Radii	Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Sc^{3+}, In^{3+}, Hf^{4+}
Electronegativities	Mg, Ti, Nb, Mo
Electronic Structure	Pr^{3+}, Pr^{4+}
Carbonate Chemistry	Mo, Cr, Re, Ti, Zr, Hf
Complex Formation	Mo, Cr, Re, Ti, Zr, Hf, Mg
Recommended analogues	Pr^{3+}, Pr^{4+}, Mo, Cr, Re, Ni^{2+}, Co^{2+}, Fe^{2+}, Ti^{4+}

Am^{3+}

Molar Volume	Lanthanides, Tb, Gd, Sm, Nd, La, Ce
Ionic Radii	Lanthanides, Y^{3+}
Electronic Structure	Eu^{3+}, Sm^{3+}
Carbonate Chemistry	Lanthanides, Y, Group II elements, Fe, Co
Complex Formation	Sm, Eu, Gd
Recommended analogues	Eu^{3+}, Sm^{3+}, Ln, Y^{3+}, Fe^{3+}

CONSIDERATIONS OF SOLUBILITY, STABILITY, AVAILABILITY AND ANALYTICAL SENSITIVITY

The chemical analogues for actinides recommended under the "Discussion" section were selected on the basis of similar chemical and physical properties. In order for the recommended chemical analogues to be useful as tracers in the field, there must be a consideration of the solubility of an available salt, stability of the tracer in geologic media, and the capability to measure the tracer in samples taken after injection into the geologic system. Table X provides a list of compounds that contain a recommended tracer and gives the solubility of the parent compound in water. Potential tracer compounds with limited solubility are not included in the table. A potential tracer element that is complexed to the extent that the element no longer exhibits the characteristic of the tracer would not be included in the table. Potassium cyanotungstate ($K_4[W(CN)_8] \cdot 2H_2O$) with a solubility of 1300 gm/L would be an example of a highly complexed tracer element. Elements that have been designated as RCRA toxic elements are not included in the table because these elements would not be useable in a test in the natural environment. Compounds of Ba, Cr, Cd, Hg, and Pb are examples of compounds that have been eliminated for consideration.

Table VIII. Precipitation/Complexation of U, Np, Pu, Am

Salt	U^{+6}	Np^{+5}	Pu^{+3}	Pu^{+4}	Pu^{+6}	Am^{+3}
$NaHCO_3$	Complexed	Partial	Ppt	Partial	Complexed	Ppt
Na_2CO_3	Complexed	Complexed	Ppt	Ppt	Complexed	Ppt
NH_4HCO_3	Complexed	Ppt	Ppt	Partial	Complexed	Ppt
$KHCO_3$	Complexed	Ppt	Ppt	Complexed	Complexed	Ppt
$(NH_4)_2CO_3 \cdot H_2O$	Complexed	Partial	Complexed	Complexed	Complexed	Complexed
K_2CO_3	Complexed	Complexed	Complexed	Complexed	Partial	Complexed

Table IX.   Study of Precipitations

▨	Quantative Precipitation
▦	Total Complexation

NaHCO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Na₂CO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

NH₄HCO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

KHCO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

(NH₄)₂CO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

K₂CO₃

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Table X. Potential Tracer Solubilities

Compounds of Sodium

Formula	Name	Solubility (gm/L) °C
$NaCl$	Na chloride	357
$NaBr$	Na bromide	1160 @ 50
$NaClO_4$	Na perchlorate	soluble
$NaCHO_2$	Na formate	972 @ 20
$NaC_2H_3O_2$	Na acetate	1190 @ 0
Na_2MoO_4	Na molybdate	soluble
$NaReO_4$	Na perrhenate	1000 @ 20
$NaWO_4$	Na tungstate	575 @ 0
$Na_4[Si(W_3O_{10})_4 \cdot 20H_2O]$	Na silicotungstate	very soluble
$NaVO_3$	Na metavanadate	21.1 @ 25
$NaVO_4$	Na orthovanadate	soluble

Compounds of Potassium

Formula	Name	Solubility (gm/L) °C
KCl	K chloride	344
KBr	K bromide	535
$KCHO_2$	K formate	3310 @ 18
$KC_2H_3O_2$	K acetate	2530 @ 20
$KMoO_4$	K molybdate	1846 @ 25
$KReO_4$	K perrhenate	12.1 @ 20
$K_2[ReCl_6]$	K rhenium (IV) chloride	soluble
$K_2[ReOCl_4]$	K rhenium (V) oxychloride	soluble
$K_2WO_4 \cdot 2H_2O$	K tungstate	515
$K_6[H_2W_{12}O_{40}] \cdot 18H_2O$	K metatungstate	soluble
$K_4SiW_{12}O_{40} \cdot 18H_2O$	K silicotungstate	333 @ 20
KVO_3	K metavanadate	Sl soluble
$KV(SO_4)_2 \cdot 12H_2O$	K vanadium sulfate	1984 @ 10

Compounds of Ammonium

Formula	Name	Solubility (gm/L) °C
NH_4Cl	A. cloride	297 @ 0
NH_4Br	A. bromide	970 @ 25
NH_4CHO_2	A. formate	1020 @ 0
$NH_4C_2H_3O_2$	A. acetate	1480
$(NH_4)_2MoO_4$	A. molybdate	1846 @ 25
NH_4ReO_4	A. perrhenate	61 @ 20
NH_4VO_3	A. vanadate	5.2 @ 15
$NH_4V(SO_4)_2 \cdot 12H_2O$	A. vanadium sulfate	284 @ 20
$(NH_4)_2Ce(NO_3)_6$	A. ceric nitrate	1410 @ 25
$2(NH_4)_2NO_3 \cdot Ce(NO_3)_3 \cdot 4H_2O$	A. cerous nitrate	3182

(TABLE X. cont.)

	Halogens and Other Compounds	Solubility (gm/L) °C
$CeBr_3 \cdot H_2O$	Cerous bromide	very soluble
$CeCl_3$	Cerous chloride	1426
$Ce(NO_3)_3 \cdot 6H_2O$	Cerous nitrate	very soluble
$PrCl_3 \cdot 7H_2O$	Ln chloride	3340
$Gd(NO_3)_3 \cdot 6H_2O$	Ln nitrate	very soluble
$GdCl_3$	Ln chloride	soluble
$LiCl$	Lithium chloride	637 @ 0
$LiNO_3$	Lithium nitrate	898 @ 28
$TiCl_3$	Titanous chloride	soluble (unstable)
$TiBr_3 \cdot 6H_2O$	Titanous bromide	very soluble (unstable)
$ReCl_3$	Rhenium chloride	soluble
Re_2O_7	perrhenate	very soluble

Hf Compounds Generally Insoluble or Unstable

Pr^{4+}		unstable	
$MgBr_2$	Mg bromide	1015 @ 20
$MgCl_2$	Mg chloride	542.5 @ 20
$Mg(C_2H_3O_2)_2$	Mg acutate	1200 @ 15
$Mg(NO_3)_2 \cdot 2H_2O$	Mg nitrate	soluble

Prior to testing the recommended tracers, the compatibility of the tracers in brine must be established. The following tracer compounds should be tested with brine under the conditions of an injection test before conducting more extensive testing.

$CeCl_3$	for light fraction LnCl3
$GdCl_3$	for heavy fraction LnC13
$KMoO_4$	K molybdate or sodium molybdate
$NaReO_4$	Na perrhenate
Na_2WO_4	Na tungstate
$ReCl_3$	Re chloride
$Na_4[Si(W_3O_{10})_4] \cdot 20H_2O$	Na silicotungstate
Na_3VO_4	Na othovanadate
$(NH_4)_2Ce(NO_3)_6$	NH_4 ceric nitrate

One of the difficulties that can complicate a sorbing tracer test is that the tracers may be totally sorbed or retarded in the geologic matrix and not be measured at

all at some downflow location. The processes that influence actinide or tracer transport given in Table I can result in a concentration at a downgradient sample location that is too low to measure. To overcome this possibility, low sorbing tracers such as sodium formate or acetate can be injected along with the elemental tracer to give an indication of the concentration gradient of both a low sorbing tracer and a sorbing tracer. Alternatively, a deuterium spike can be injected along with the combined tracer to establish whether there is any flow via advection, hydrodynamic dispersion or molecular diffusion. The method of analysis of the different tracers or spikes can have a tremendous influence on the cost of conducting a field tracer test. The capabilities for analyzing elemental constituents at LANL is principally by Inductively-Coupled Mass Spectrometry (ICP-MS), Inductively-Coupled Atomic Emission Spectrometry (ICP-AES), Graphite Furnace Atomic Absorption Spectrophotometry (GFAA) and Ion-Chromatography (IC). ICP-MS allows the use of enriched stable isotopes. Tracers such as formates, acetates, or other organic-based compounds can be analyzed by GC methods with different detectors (FID or MSD). Also, a carbon analyzer (TOC) can be used as a screening tool. Deuterium analysis would have to be accomplished with a high resolution mass spectrometer. The sensitivity of most the methods is in the low parts per billion range.

CONSERVATIVE TRACERS

Conservative tracers, by definition, are agents that do not interact with the environment found in the flow path of the moving phase, and therefore can be used to determine the minimum transport time of injected tracers, as well as be used to determine the hydrologic flow conditions between the point of introduction and sampling. In practice, all agents interact to some degree, so that a better definition of a conservative tracer would be an agent that demonstrates minimum interaction with the environment along the flow path. The major uses of conservative tracers has been in the field of hydrology, where they are used to determine hydrogeologic flow characteristics of underground systems.

There are a variety of different types of compounds that have been used as tracers, including physical agents such as soil, silt, and microspheres. These agents will not be discussed in here, since they are not deemed applicable to the necessary characterization of the system. The discussion will be limited to the use of chemicals as conservative tracers whose primary function is to define the immediate hydrology of the sorbing tracer test and to serve as markers for the performance (degree of sorption) of the sorbing tracers.

These compounds can be grouped into the following categories:

Fluorescent dyes (Gaspar, 1987; Quinlan, 1992)

Applications: Aqueous transport evaluation, connectivity demonstration and mapping of detailed transport structure at high concentrations and in favorable soils.

Advantages: Relatively well known, inexpensive and commercially available tracers which are accepted as conventional in many environmental situations. Fluorescence detection provides a sensitive analytical approach for single tracers in most systems. Mapping and photography of transport paths is possible for high tracer concentrations and appropriate soils.

Disadvantages: Only a few tracers are available. Other organics and contaminants can interfere with quantitative analysis, particular for simple and rapid field spectroscopic techniques, while detailed and low level analyses are personnel intensive. Multiple tracer applications may result in interference with tracer identification and quantitative analyses. Interactions with soil materials can

hold up tracer or complicate interpretation. Biological degradation and interactions can hold up tracer and complicate interpretation.

Fluorinated organic compounds (Senum and Deitz, 1989; Benson and Bowman, 1994)

Applications: Transport evaluation and connectivity demonstration for solutions and gases in soils and rocks.

Advantages: Developed to provide multiple tracers with low detection limits. Perfluorocarbon gases are stable, nontoxic compounds which can be separated from air or water and analyzed to very low levels using gas chromatography with electron capture detection analyses (Senum and Deitz,1989). Similar fluorinated soluble anionic compounds (tri- and tetrafluorobenzoates) have been developed for water tracing utilizing high performance liquid chromatography analyses (Benson and Bowman, 1994). These compounds are resistant to biological interactions and degradation. Both types of compounds have seen growing use in tracer experiments, including in environmental systems. Where gas phase tracing is valuable or required, the perfluorocarbon tracers provide a distinct advantage.

Disadvantages: The number of tracers available is greater than that for fluorescent dyes, but still relatively limited. The compounds are commercially available, but less accessible and more expensive than fluorescent dyes. Volatilization of perfluorocarbon tracers can be a disadvantage in open environmental systems. Sorption in high organic soils may also impact tracer transport interpretations. Analytical instrumentation is more extensive than that required for fluorescent dyes and less fieldable.

Radioactive chemical tracers (Gaspar, 1987)

Applications: Aqueous transport evaluation and connectivity demonstration.

Advantages: Relatively well known tracer methodology with very low detection limits achievable. Commercially available tracers which are accepted as conventional in many situations. Detection equipment can be fieldable for real-time and continuous analyses. Analyses may be nondestructive and allow quantitation of multiple tracers simultaneously. Laboratory analyses (including extraction and separations) may be combined with analyses of other radioactive components from natural and anthropogenic processes.

Disadvantages: Injection of radioactive compounds is rapidly losing acceptability due to public sensitivity to radioactivity hazardous. Injection activities are often the most hazardous and transportation regulations and/or requirements to get tracer to the site may limit or exclude use. Analyses may require extensive processing and analytical efforts.

Natural Gases (Radon, Helium, C02, Methane, Hg)

Applications: Differencing of connectivity and transport structure.

Advantages: For these natural tracers no injection is necessary and sources are initially widely distributed within natural permeability and transport paths. Existing expertise in radon, natural gases, mercury and rare gases provides a baseline for comparison and application. Sensitive analytical techniques are available for a variety of such soil gases some of which are fieldable. Radon, in particular, has been extensively studied in recent years and can be relatively cheaply and effectively evaluated. A preliminary demonstration of radon utilization for barrier integrity testing has been recently completed (Janecky, 1995).

Disadvantages: A limited diversity of processes and heterogeneous natural distributions may produce equivocal or nonunique results. Little effort has been previously spent developing these components for environmental remediation system applications and integrity testing. Development will be required to evaluate sampling and quantitation strategies and technology, but significant background information can be obtained from geochemical process studies. Analytical cost and instrumentation requirements will vary widely depending on compound-technique couple. Fieldable techniques exist for quantification of mercury and some natural gases, but have not been examined for application to containment integrity testing. Rare gases and other uranium decay-series compounds will require more extensive analytical processing and more expensive equipment.

Natural Dissolved Compositions

Applications: Differencing of connectivity and transport structure; evaluation of chemical processes and variations due to remediation or barrier systems, such as mixing and freezing and reactive chemical introduction.

Advantages: Multicomponent analyses are now possible with modern analytical instruments, over wide dynamic ranges with very low detection limits and high

throughput (generally ppb levels). Major component compositions can provide information on physical processes, such as freezing, vapor extraction and mixing of disparate fluids. Minor and trace component compositions have more potential for providing information on chemical interactions, including subtle redox and complexation changes. Natural compositions and variations of some contaminants (i.e. elemental) or analogs can be evaluated to determine potential remedial and transport processes.

Disadvantages: Substantial site specific baselining and definition of optimal sampling and analysis strategy prior to remediation or containment activities will be required, along with careful monitoring of temporal variability due to storms, seasonal and other natural or imposed conditions. A chemical change across or due to the system being evaluated that can be effectively mapped or defined must also be present --- either homogeneous or highly heterogeneous systems will make evaluation complex. The variations present may require injected tracer(s) for baselining and quantification of differencing, connectivity and transport processes.

Metal-labeled stable isotopic compounds

Applications: Aqueous transport evaluation, connectivity demonstration and mapping of detailed transport and chemical structure. This approach develops from activatable tracer approaches (Gaspar, 1987), extended through the use of modern analytical instruments (e.g. ICP-MS) and methods.

Advantages: Coupling between natural and elemental contaminant characterization and tracer analyses can be exploited, utilizing modern multicomponent analytical instruments, such as ICP-MS, over wide dynamic ranges with low detection limits and high sample throughput. A wide range of mobile trace elements can potentially be used for injected tracers, and with extension to separated isotopic materials, the range is very wide with respect to both number of potential tracers and chemical behavior. Where solubility of a metal compound is limited and/or the problem to be examined involves organic molecules (including complexants), organic ligands can be labeled with metals. The modern analytical techniques provide a significantly expanded version of well established neutron activation techniques which were limited in the range of elements.

Disadvantages: Fieldable instrumentation is presently limited to only very high priority sites. These approaches are also not well established and will require baselining with other techniques. To achieve necessary analytical throughput, protocols and acceptance criteria for large numbers of analyses focused on trend

evaluation rather than strictly accurate and precise compositions of each specific sample may need to be developed, demonstrated and accepted. Separated isotopic materials can be expensive, even for small amounts of materials. This approach will probably require a component of site specific baselining and definition of optimal analysis strategy for each application.

Light-stable isotope labeled compounds (Janecky & Spall, 1990)

Applications: Aqueous transport evaluation, connectivity demonstration and mapping of detailed transport and chemical structure, mapping of subsurface chemical interaction, reaction and biologic processes, and quantification of contaminant amounts in the subsurface.

Advantages: Coupling between natural and elemental contaminant characterization and tracer analyses can be exploited, utilizing modern multicomponent analytical instruments, such as GC-MS, over wide dynamic ranges with low detection limits. Utilization of several separated isotopic materials (e.g. H, C, O, N, S) will allow a range of tracers to be applied, while limiting or avoiding use of radionuclides. A very wide range of tracers can be developed with respect to both number of potential tracers and chemical behavior. Labeling the same compound suite with several different isotopes can be used to provide compounds with distinguishable masses, but essentially identical chemical behavior. Identical chemical behavior to the contaminants of interest in a particular site could be achieved. These analyses could also be linked to regulatory requirements of organic contaminants, limiting the increase in analytical efforts associated with the tracer experiments. This approach builds on existing biomedical practice for determining residence times and processing behavior of specific compounds (Unkefer, 1986).

Disadvantages: These approaches are not well established and will require baselining with other techniques, while analytical protocols and acceptance criteria for large numbers of analyses focused on trend evaluation as opposed to strictly accurate and precise compositions of each specific sample will have to be developed. Separated isotopic materials can be expensive, even for small amounts of materials. This approach will probably require a component of site specific baselining and definition of optimal analysis strategy for each application. Fieldable instrumentation is becoming more available, though some combination of field spot checking and conventional laboratory analyses will probably be required on all but the very high priority sites due to analytical throughput considerations and existing certification approaches. Although any of these tracers might be used for the proposed test, the fluorinated acids have been extensively applied to the hydrological determinations already completed at the

WIPP site (Jones, T.L., et al, 1992), and therefore should be given the highest consideration for use as the conservative tracers for the sorbing tracer test.

The further recommendation is to utilize more than one conservative tracer. We recommend the use of two of the fluorinated benzoic acids, and at least two of the haloacids tracers used by Janecky and Spall (Janecky and Spall, 1990). The use of four tracers would obviate the difficulties which could arise from the potential sorption of the tracers when the evaluation of the data from the sorbing test is done.

The specific haloacids would be chosen from the following suite of compounds: chloroacetic acid, bromoacetic acid, dichloroactic acid, bromopropionic acid, fluoroacetic acid, 2-bromobutyric acid, trichloroacetic acid, 3-chloropropionic acid. The final selection will be based on materials compatibility, and potential interactions with the selected sorbing tracers.

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