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Overview of Actinide Chemistry and Geochemistry[1]

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Topics to Be Addressed

Overview

General properties of actinide elements

Some important actinides in radioactive waste repositories

Some features of actinides important for studies for radioactive waste repositories

References

Topics to Be Addressed

Overview

- Review of the periodic table
- Review of oxidation states
- Some chemical conventions

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Review of the Periodic Table

Definition (see handout from IUPAC, 2007)

- A tabular display of the chemical elements
  - Element: a pure chemical substance consisting of one type of atom with a unique atomic number (Z), which is the number of protons in its nucleus
- Groups: the columns in the periodic table
  - Usually the most important method of classifying elements
- Periods: the rows of elements in the periodic table
  - Can also be important for classifying elements (for example, transition metals, lanthanides, and actinides)

History

- Russian chemist Dmitri Ivanovich Mendeleev credited with proposing the periodic table in 1869

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Review of the Periodic Table (cont.)

Mendeleev’s original (1869) periodic table:

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,1.
			Fe = 56	Rn = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

Д. Менделѣевъ

Today's Periodic Table

Some printable periodic tables

- http://chemistry.about.com/od/periodictableelements/a/print peridodic.htm
- http://old.iupac.org/reports/ periodic_table/IUPAC_Periodic_Table-22Jun07b.pdf
- http://periodic.lanl.gov/downloads/periodictable.pdf
- http://www.webelements.com/nexus/Printable_Periodic_Table

Some printable information on individual elements

- http://www.rsc.org/chemsoc/visualelements/pages/pertable_j.htm

Review of the Periodic Table (cont.)

Oxidation state

- Very important for actinide mobilities

Definition of oxidation state (Calvert, 1990)

- A measure of the degree of oxidation of an atom in a substance
- The charge an atom might have when electrons are counted according to agreed-upon rules

Review of the Periodic Table (cont.)

Rules for determining oxidation states (Calvert, 1990)

- The oxidation state of a free (uncombined) element is 0
- For a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion
- Hydrogen (H) has an oxidation state of 1 and oxygen (O) has an oxidation state of −2 in most compounds
- The algebraic sum of oxidation states of all atoms in a neutral molecule is 0
- The algebraic sum of oxidation states of all atoms in a charged ion is equal to the charge on the ion

Some Chemical Conventions

The periodic table (these and the following guidelines are from Coghill and Garson, 2006)

- Always use lowercase for the words “periodic table”
- Always use lowercase for the word “group,” even with a specific number, unless it is the first word in a sentence
  - “group IIIB elements” instead of “Group IIB elements”

Element name

- Use lowercase for element names, even if the element is named after a country or person, unless it is the first word in a sentence
  - “plutonium” instead of “Plutonium”
  - “americium” instead of “Americium”
  - “curium” instead of “Curium”

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Some Chemical Conventions (cont.)

Element symbol

- Always use uppercase for the first letters of element symbols
  - “Am” instead of “am”

Isotope

- To designate an isotope of an element, place its mass number after its name when written out
  - “plutonium-239” instead of “239-plutonium”
- But place the mass number before the element symbol
  - “^{239}Pu” instead of “Pu^{239}”

Some Chemical Conventions (cont.)

Compositional stoichiometry (the relative numbers of atoms in a molecule)

- Use right subscripts for the stoichiometry
  - "PuO_2" means one Pu atom and two O atoms per molecule of PuO_2

Ionic charge

- To designate the charge on an element or a complex, place it after the element symbol
  - "Pu^{4+}" instead of "Pu^{+4}" or "Pu^{++++}"
- Stagger the subscript used for the compositional stoichiometry and the superscript used for the ionic charge; do not align them. The subscript comes first
  - "$PuO_2{}^{2+}$" instead of "$PuO^{2+}{}_2$"

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Some Chemical Conventions (cont.)

Oxidation state

- Use superscript roman numerals for the oxidation state of an element
  - "Pu^{IV}" instead of "Pu^{4+}"
  - "Pu^{+IV}" is unnecessary because chemists and geochemists understand that Pu donates electrons to form oxides instead of accepting them
- You may also write oxidation states on the line in parentheses closed up to the element name or symbol
  - "Pu(IV)" instead of "Pu (IV)" or, worse yet, "Pu^{4+}"
  - "plutonium(IV)" instead of "plutonium (IV)"

Some Chemical Conventions (cont.)

Additional conventions

- See Coghill and Garson (2006) for additional conventions used by the American Chemical Society, and for help with technical writing and other forms of communication of chemical and geochemical information

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General Properties of Actinide Elements

Definition

- The 15 elements from actinium (Ac) (Z = 89) through lawrencium (Lr) (103)
- Some chemists exclude Ac from the actinides
- See handouts (RSC, undated)

Only Th and U occur naturally; all other actinides are man-made

- See handout (Seaborg, 1946) for historical overview

All actinides are radioactive and radiotoxic

- See handouts (Argonne National Laboratory, 2005)

Properties of Actinides (cont.)

Possible oxidation states[1]

- +II (Th, Pa, Am, Cf, Es, Fm, Md, and No)
- +III (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr)
- +IV (Th, Pa, U, Np, Pu, Am, Cm, Bk, and Cf)
- +V (U, Np, Pu, and Am)
- +VI (U, Np, Pu, and Am)
- +VII (Np and Pu)

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1. Includes oxidation states that can only be established and maintained in the lab using strong oxidizing or reducing agents

Properties of Actinides (cont.)

Favored oxidation states[1]

- +III (Ac, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr)
- +IV (Th, U, Np, and Pu)
- +V (Pa, U, Np, and Pu)
- +VI (U and Pu)

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1. Oxidation states expected in the environment and in radioactive waste repositories

Topics to Be Addressed

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- **Which actinides are important?**
- **Actinides included by the WIPP Project**

Some features of actinides important for studies for radioactive waste repositories

References

Which Actinides Are Important?

Sensitivity studies are required to identify and quantify which actinide elements are important in a repository

- Which actinides are important varies from repository to repository
- Np was an important element for the Yucca Mountain Project (Friese et al., 2003) but is not important for the WIPP (Brush and Garner, 2005)

Important factors

- Regulations with which the repository must comply
  - Regulations generally take into account relative radiotoxicities of radioelements and half lives of radioisotopes
- Waste inventory
  - Relative amounts of radioelements and radioisotopes

Which Actinides Are Important (cont.)

Other factors that could be important

- Which mobilization mechanisms are important
- Which release mechanisms are important
- Which offsite transport pathways are important
- Which transport mechanisms are important

Actinides Included by the WIPP Project

Important, less important, and unimportant actinide elements have been included

- Lab studies, process modeling, and PA were started before sensitivity studies were completed
- Factors such as the inventory could change, thereby increasing the importance of less important or unimportant actinides

Included in WIPP performance assessment (PA), WIPP process modeling, and/or WIPP lab studies

- Th, U, Np, Pu, Am, Cm, and Cf

Potential effects on WIPP PA

- Pu $\approx$ Am >> U > Th >> Np > Cm > Cf

Plutonium

Oxidation states expected in the enviornment and radioactive waste repositories

- Pu(III), Pu(IV), Pu(V), and/or Pu(VI)
  - Can occur in more than one of these oxidation states simultaneously

Oxidation states expected in the WIPP

- Only Pu(III) or Pu(IV)

Mobility in the enviornment and repositories

- Pu(V) > Pu(VI) > Pu(III) >> Pu(IV)

Plutonium (cont.)

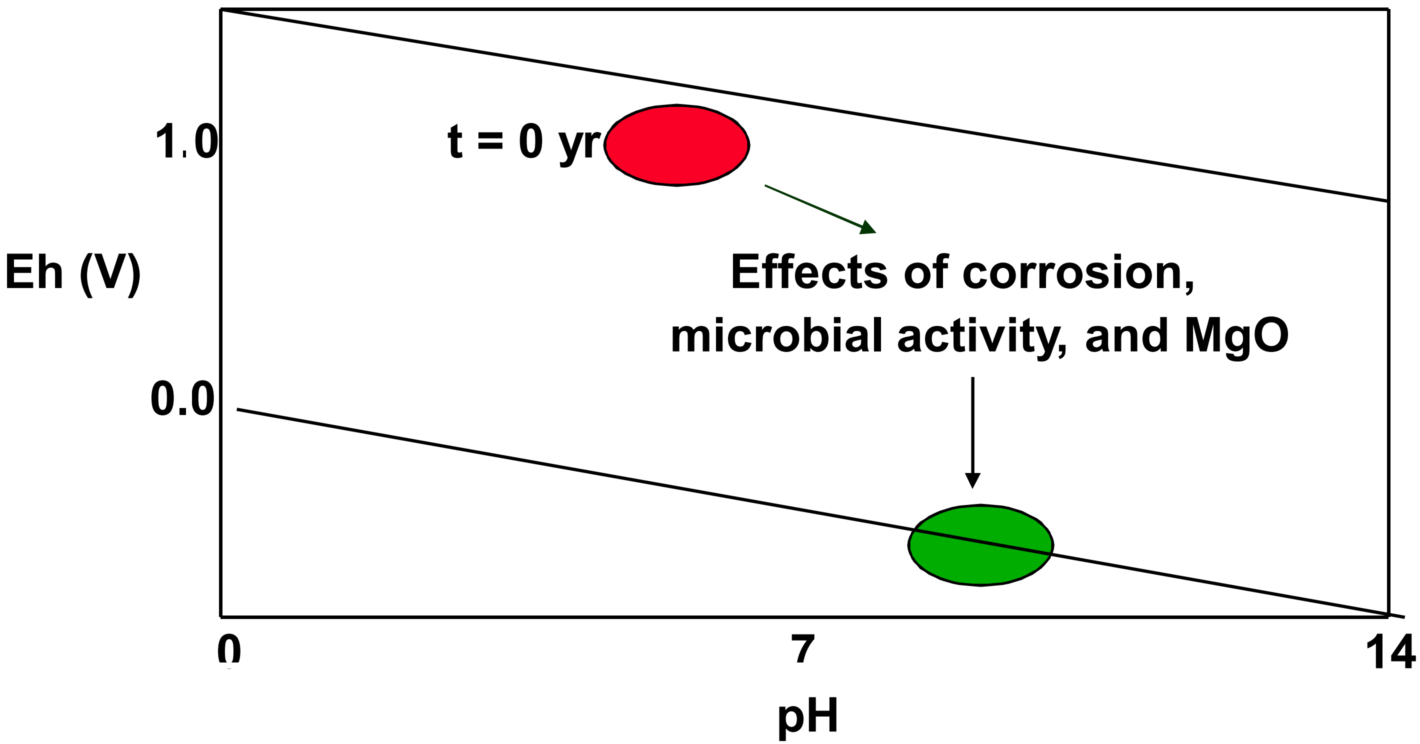
Pu chemistry especially complex

- See handout (Clark, 2000)

Use of Eh-pH diagrams to illustrate the effects of these chemical conditions on the speciation of Pu

- See handout (Runde, 2000)

Expected Evolution of Near-Field Conditions in the WIPP



Americium

Oxidation states expected in the enviornment and radioactive waste repositories

- Am(III), but could occur as Am(V) under some conditions
  - Am(V) is possible in brines, but reductants such as steel and other Fe-base metals in the WIPP will reduce Am(V) to Am(III)

Oxidation state expected in the WIPP

- Only Am(III)

Mobility in the enviornment and repositories

- Am(V) >> Am(III)

Uranium

Oxidation states expected in the enviornment and radioactive waste repositories

- U(IV) or U(VI)

Oxidation state expected in the WIPP

- U(IV) or U(VI)

Mobility in the enviornment and repositories

- U(VI) >> U(IV)

Thorium

Oxidation state expected in the enviornment and radioactive waste repositories

- Only Th(IV)

Oxidation state expected in the WIPP

- Only Th(IV)

Mobility in the enviornment and repositories

- Th(IV) generally very immobile
  - However, Th(IV) colloids can form under some conditions
  - Colloidal Th(IV) species are more mobile than other species (e.g., dissolved (Th(IV) species and Th(IV) species adsorbed by solids)

Neptunium

Oxidation states expected in the enviornment and radioactive waste repositories

- Np(IV) or Np(V), but could occur as Np(VI) under some conditions

Oxidation states expected in the WIPP

- Np(IV) or Np(V)

Mobility in the enviornment and repositories

- Np(V) >> Np(IV)

Curium

Oxidation states expected in the enviornment and radioactive waste repositories

- Only as Cm(III)

Oxidation state expected in the WIPP

- Only Cm(III)

Mobility in the enviornment and repositories

- Similar to Am(III)

Californium

Oxidation states expected in the enviornment and radioactive waste repositories

- Only as Cf(III)

Oxidation state expected in the WIPP

- Only Cf(III)

Mobility in the enviornment and repositories

- Similar to Am(III)

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Features of Actinides Important for Repository Studies

Laboratory studies of actinide elements are difficult, expensive and time consuming

- All actinides are radioactive and radiotoxic
- Strict licensing requirements for labs that use actinides in most countries
  - Only small quantities of actinides may be stored in the lab
- Strict environmental health and safety (ES&H) procedures required for lab experiments in most countries
  - Experiments require highly qualified personnel
  - Experiments must be carried out in glove boxes to ensure containment and eliminate the chances of worker exposure
  - Only very small quantities of actinides may be used in each experiment
  - Analytical equipment also subject to strict ES&H requirements

Features of Actinides Important for Studies (cont.)

Some of the most important actinides speciate in oxidation states that are difficult to establish and maintain during lab experiments

- **Actinide oxidation state strongly affects chemical behavior**
- **Pu: Pu(III), Pu(IV), Pu(V), and/or Pu(VI)**
  - **Pu(III) and Pu(IV) especially difficult to establish and maintain**
- **U: U(IV) or U(VI)**
  - **U(IV) especially difficult to establish and maintain**
- **Np: Np(IV) or Np(V)**
  - **Np(IV) especially difficult to establish and maintain**
- **Glove boxes with O_2-free conditions required to establish and maintain Pu(III), Pu(IV), U(IV), and Np(IV)**

Features of Actinides Important for Studies (cont.)

The Oxidation-State Analogy

- Chemical behavior of different actinide elements often very similar when they occur in the same oxidation state
  - Chemical behavior of Pu(III) ≈ Am(III) ≈ Cm(III) ≈ Cf(III)
  - Chemical behavior of Th(IV) ≈ U(IV) ≈ Np(IV) ≈ Pu(IV)
- See handouts (Choppin, 1999; Neck and Kim, 2001)

Use of the Oxidation-State Analogy

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