Lecture 1: RDCH 710 Introduction

- Class organization
  - Outcomes
  - Grading
- Natural actinide species
  - Th
  - U
- Transuranic synthesis

Lecture notes based on LANL radiochemistry course
Course overview

The unique chemical properties of actinide elements are described and related to their electronic characteristics. Using nuclear properties in understanding actinide chemistry is provided. Presentations are given on exploiting the chemical behavior of the actinides in separation, the nuclear fuel cycle, environmental behavior, and materials. The goal of the course is to provide students with an understanding of the actinide elements for support in graduate education and research.
Course outcomes

• Understand the role of oxidation-reduction reactions in actinides
• Evaluation and utilizing actinide speciation and complexation
• Understanding the impact of f-orbitals on actinide chemistry
• Ability to interpret spectroscopy of the actinides
• Ability to discuss in detail the chemistry of various actinide elements
• Explain how to use actinide nuclear properties in experiments
• Understand the fundamental reactions that drive actinide environmental chemistry
• Understand and explain various separation methods for the actinides
• Describe and understand a range of actinide solid phases
• Understand the reactions behind synthesis of actinide compounds
• Basic understanding of computational actinide studies
Grading

• Classroom participation (15 %)
• 2 Exams (35 % each)
• Homework (15 %)

• The examinations are oral examination based upon subject matter presented in class. The first oral exam will be based on covered course material. The final oral exam will be a student presentation on recent actinide chemistry literature with questions based on material presented in class and designed to cover the course outcomes. Each oral exam will be 30 minutes. Homework questions will be given at the end of each topic.
Thorium

- natural thorium consists 100% of the isotope $^{232}\text{Th}$
- thorium is more common in nature than uranium
  - an average content in the earth's crust of 10 ppm
  - lead is about 16 ppm in the earth's crust
- the specific radioactivity for thorium is lower than that of uranium
- for radioactive tracer studies, $^{234}\text{Th} \ (t^{1/2} = 24.1 \text{ d})$ is used after separation from natural uranium
- Different Th minerals
  - Monazite (phosphate minerals)
    - Sm monazite, also contains U
  - Range of oxides
- thorium in sea water is $< 0.5 \times 10^{-3} \text{ g/m3}$, which is lower than uranium because of the lower solubility of tetravalent state of Th
Thorium minerals

• Monazite sands

• Thorianite, $\text{ThO}_2$
Monazite Analysis

X-Ray Fluorescence Spectrum

Element image of monazite sand grain
Alpha spectroscopy analysis
Uranium

- natural uranium consists of 3 isotopes
  - $^{234}\text{U}$, $^{235}\text{U}$ and $^{238}\text{U}$
  - members of the natural decay series
- earth’s crust contains 3 - 4 ppm U
  - about as abundant as As or B
- U is also chemically toxic and precautions should be taken against inhaling uranium dust for which the threshold limit is 0.20 mg/m³ air
  - about the same as for lead
- U is found in large granitic rock bodies formed by slow cooling of the magma about 1.7 - 2.5 $\times$ 9 years ago
- U is also found in younger rocks at higher concentrations called “ore bodies”
  - ore bodies are located downstream from mountain ranges
  - as atmosphere became oxidizing about 1E9 years ago
    - rain penetrated into rock fractures, oxidizing the uranium to U(VI)
    - dissolving it as an anionic carbonate or sulfate complexes
  - as the water and the dissolved uranium migrated downstream, reducing material was encountered
  - inorganic (pyrite) or organic (humic) matter
    - reduction to insoluble U(IV) ($U^{4+}$) compounds
Uranium

• in most minerals uranium is U(IV)
• most important mineral is uraninite (UO$_{2+x}$, $x = 0.01$ to 0.25)
  ▪ uranium concentration is 50 - 90%
• carnotite (a K + U vanadate) 54% U
• U is often found in lower concentrations, of the order of 0.01 - 0.03% in association with other valuable minerals such as apatite (phosphate rock), shale, or peat
Uranium minerals

URANINITE
$\text{UO}_2$
uranium oxide

CARNOTITE
$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1 - 3 \text{H}_2\text{O}$
hydrated potassium uranyl vanadate

AUTUNITE
$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10 \text{H}_2\text{O}$
hydrated calcium uranyl phosphate.
Uranium mining

URANIUM PROJECTS IN WYOMING
In situ mining

Acidic solution (around pH 2.5)
Ion exchange U separation
Uranium background

Uranium Concentrations

Source of data: U.S. Geological Survey Digital Data Series DDS-9, 1993
Np synthesis

• Neptunium was the first synthetic transuranium element of the actinide series discovered
  ▪ isotope $^{239}$Np was produced by McMillan and Abelson in 1940 at Berkeley, California
  ▪ bombarding uranium with cyclotron-produced neutrons
    $\rightarrow$ $^{238}$U(n,γ)$^{239}$U, beta decay of $^{239}$U to $^{239}$Np ($t_{1/2}$=2.36 days)
  ▪ Chemical properties unclear at time of discovery
    $\rightarrow$ Actinide elements not in current location
    $\rightarrow$ In group with W
• Chemical studies showed similar properties to U
• First evidence of 5f shell
• Macroscopic amounts
  ▪ $^{237}$Np
    $\rightarrow$ $^{238}$U(n,2n)$^{237}$U
    * Beta decay of $^{237}$U
    $\rightarrow$ 10 microgram
Pu synthesis

- Plutonium was the second transuranium element of the actinide series to be discovered
  - The isotope $^{238}\text{Pu}$ was produced in 1940 by Seaborg, McMillan, Kennedy, and Wahl
  - Deuteron bombardment of U in the 60-inch cyclotron at Berkeley, California
    \[ 238\text{U}(2\text{H}, 2\text{n})^{238}\text{Np} \]
    * Beta decay of $^{238}\text{Np}$ to $^{238}\text{Pu}$
  - Oxidation of produced Pu showed chemically different
- $^{239}\text{Pu}$ produced in 1941
  - Uranyl nitrate in paraffin block behind Be target bombarded with deuterium
  - Separation with fluorides and extraction with diethylether
  - Eventually showed isotope undergoes slow neutron fission
Am and Cm discovery

- Problems with identification due to chemical differences with lower actinides
  - Trivalent oxidation state
- $^{239}\text{Pu}(^{4}\text{He},n)^{242}\text{Cm}$
  - Chemical separation from Pu
  - Identification of $^{238}\text{Pu}$ daughter from alpha decay
- Am from $^{239}\text{Pu}$ in reactor
  - Also formed $^{242}\text{Cm}$
- Difficulties in separating Am from Cm and from lanthanide fission products
Bk and Cf discovery

• Required Am and Cm as targets
  ▪ Needed to produce theses isotopes in sufficient quantities
    \[\rightarrow\text{Milligrams}\]
    ▪ Am from neutron reaction with Pu
    ▪ Cm from neutron reaction with Am
• \(^{241}\text{Am}(^{4}\text{He},2n)^{243}\text{Bk}\)
  ▪ Cation exchange separation
• \(^{242}\text{Cm}(^{4}\text{He},n)^{245}\text{Cf}\)
  ▪ Anion exchange
Figure 2.8  Original elution data corresponding to the discovery of californium, 9 February 1950. Other activities were added for calibration purposes. Solid curve indicates α-particle counts/minute; dashed curve, conversion electrons and beta particles. (Dowex 50 resin at 87°C with ammonium citrate as eluting agent.)
Einsteinium and Fermium

• Debris from Mike test
  ▪ 1st thermonuclear test
• New isotopes of Pu
  ▪ 244 and 246
  → Successive neutron capture of $^{238}\text{U}$
  ▪ Correlation of log yield versus atomic mass
• Evidence for production of transcalifornium isotopes
  ▪ Heavy U isotopes followed by beta decay
• Ion exchange used to demonstrate new isotopes
Figure 2.13  Elution in original experiments of elements einsteinium (99) and fermium (100) relative to other actinide elements with a citrate eluant.
Md and No discovery

- 1st atom-at-a-time chemistry
  - $^{253}\text{Es}(^4\text{H},n)^{256}\text{Md}$
- Required high degree of chemical separation
- Use catcher foil
  - Recoil of product onto foil
  - Dissolved Au foil, then ion exchange
- No controversy
  - Expected to have trivalent chemistry
  - 1st attempt could not be reproduced
    - Showed divalent oxidation state
  - $^{246}\text{Cm}(^{12}\text{C},4\text{n})^{254}\text{No}$
    - Alpha decay from $^{254}\text{No}$
    - Identification of $^{250}\text{Fm}$ daughter using ion exchange
Lr discovery

- $^{249, 250, 251}$Cf bombarded with $^{10, 11}$B
- New isotope with 8.6 MeV, 6 second half life
  - Identified at $^{258}$Lr