Nuclear Process & Radio-Analytical Chemistry

Class Notes – Part 3.0

Complexation Reactions
In Nuclear Separation

Chung-King Liu

SOME ELEMENTS AND ISOTOPES OF SPECIAL CONCERN IN FUEL CYCLE SEPARATIONS

Tc: (^{99}Tc)

U: (^{232}U, ^{233}U, ^{234}U, ^{235}U, ^{238}U)

Np: (^{237}Np)

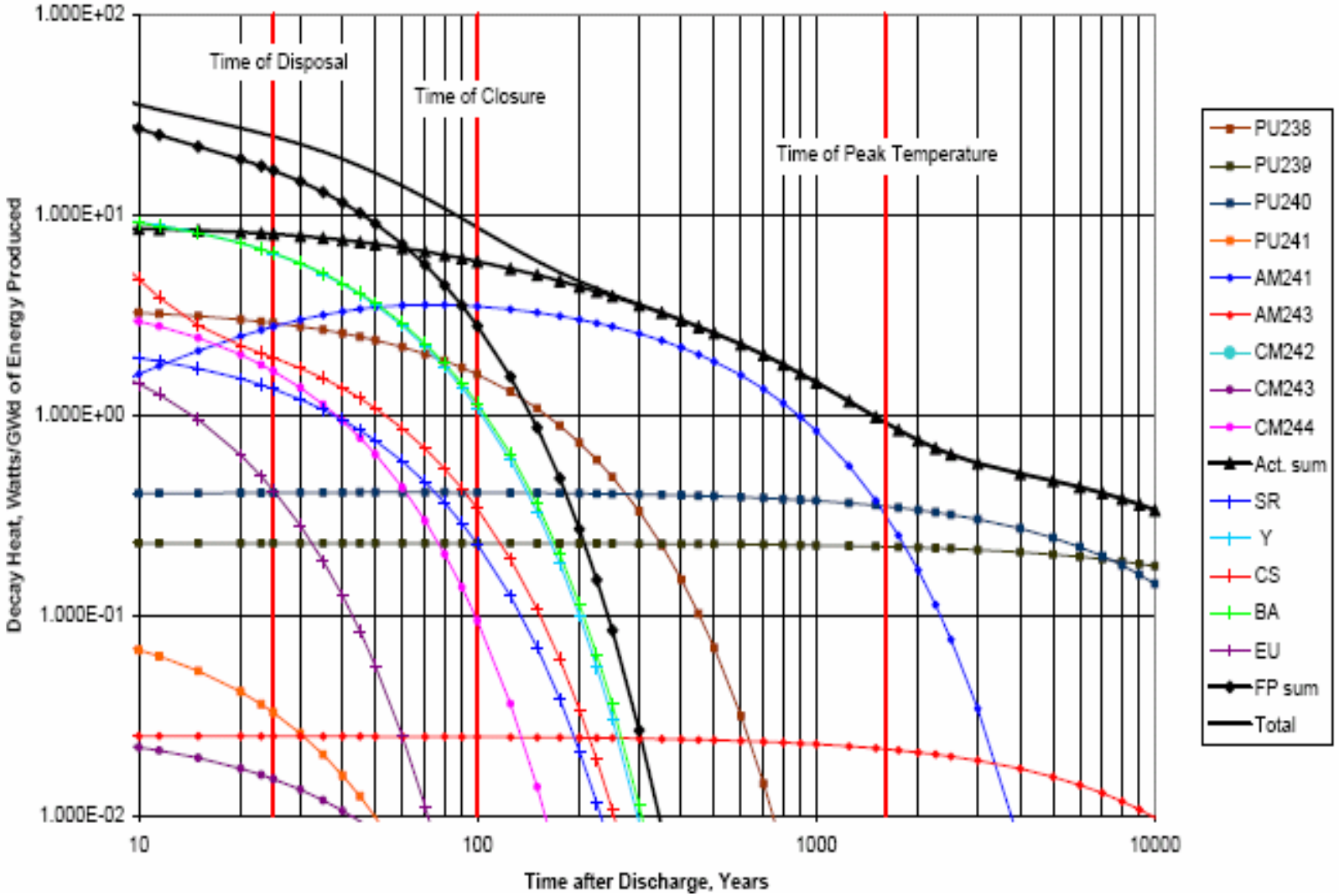
Pu: (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu)

Am: (^{241}Am)

Cm: (^{242}Cm, ^{244}Cm)

SOME REASONS FOR IMPORTANCE IN SEPARATIONS

- **U: FOUNDATION OF NUCLEAR ENERGY PRODUCTION AND NUCLEAR WEAPONS**
- **^{99}Tc: IMPORTANT DOSE LIMITING ISOTOPE IN REPOSITORY EXPOSURE PATH**
- **^{237}Np: IMPORTANT DOSE LIMITING ISOTOPE IN REPOSITORY EXPOSURE PATH**
- **^{238}Pu: HEAT PRODUCER IN REPOSITORY; SPACE ENERGY SOURCE**
- **^{239}Pu: FISSILE; IMPORTANT LONG TERM DOSE LIMITING ISOTOPE IN REPOSITORY EXPOSURE PATH; HEAT PRODUCER IN REPOSITORY**
- **^{240}Pu: HEAT PRODUCER IN REPOSITORY**
- **^{241}Am: IMPORTANT HEAT PRODUCER IN REPOSITORY**
- **^{244}Cm: HEAT PRODUCER IN REPOSITORY**


1.000E+02
1.000E+01
1.000E+00
1.000E-01
1.000E-02
Decay Heat, Watts/GWd of Energy Produced
Time of Disposal
Time of Closure
Time of Peak Temperature
10
100
1000
10000
Time after Discharge, Years
PU238
PU239
PU240
PU241
AM241
AM243
CM242
CM243
CM244
Act. sum
SR
Y
CS
BA
EU
FP sum
Total

IMPORTANT CHEMICAL ELEMENTS AND COMMON VALENCE STATES

- **Tc (IV, VII): ENVIRONMENTALLY MOBILE AS PERTECHNETATE ION (TcO_4^-)**
- **U (III, IV, VI): ENVIRONMENTALLY MOBILE; EXTRACTABLE; UBIQUITOUS**
- **Np (III, IV, V, VI): ENVIRONMENTALLY MOBILE AS NpO_2^-**
- **Pu (III, IV, V, VI): ENVIRONMENTALLY MOBILE AS +4 COLLOID POLYMER; EXTRACTABLE; CO-EXISTING VALENCE STATES**
- **Am (III, *IV, V, VI*): ALPHA HAZARD**
- **Cm (III): ALPHA HAZARD**

TECHNETIUM

- **TECHNETIUM DOES NOT OCCUR IN NATURE**
- **RHENIUM IS OFTEN USED AS ITS SURROGATE**
- **Tc (VII) OCCURS AS TcO_4^- (PERTECHNETATE ANION)**
- **NITRIC ACID AND HYDROGEN PEROXIDE OXIDIZE Tc TO TcO_4^-, AN OXIDIZING ANION THAT IS VERY MOBILE IN THE ENVIRONMENT**
- **TcO_4^- FORMS AN EXTRACTABLE COMPLEX WITH Zr(IV) THAT REACTS WITH UO_2^{2+} IN TBP TO FORM A COMPLEX ($UO_2NO_3TcO_4 \cdot 2TBP$) THAT IS SOLUBLE IN TBP**
- **Tc_2O_7 IS VOLATILE AND IS READILY FORMED BY EVAPORATING ACIDIC SOLUTIONS OF TcO_4^-**
- **Tc(IV) COMPOUNDS ARE MUCH LESS MOBILE THAN TcO_4^- IN THE ENVIRONMENT**
- **Tc(IV) SORBS ON UO_2**

URANIUM

(THE URANIUM LITERATURE IS HUGE AND ONLY A FRACTION OF IT IS ADDRESSED HERE)

- U AQUEOUS CHEMICAL SPECIES
- U^{3+}, U^{4+}, UO_2^{+}, UO_2^{2+}

U^{3+} IS THERMODYNAMICALLY UNSTABLE IN AQUEOUS SOLUTIONS BUT IS KINETICALLY STABLE IN THE ABSENCE OF CATALYSTS

U^{4+} FORMS COMPLEXES WITH Cl^-, CNS^-, SO_4^{2-}, F^-, et al AND HYDROLYZES EASILY

UO_2^{+} IS UNSTABLE AND DISPROPORTIONATES INTO U^{3+} AND UO_2^{2+}

UO_2^{2+} SALTS IN ACIDIC SOLUTIONS ARE OFTEN STABLE UP 300°C

STABLE U AQUEOUS CHEMICAL SPECIES

U^{3+}, U^{4+}, UO_2^{+}, UO_2^{2+}
(CONTINUED)

- UO_2^{2+} FORMS COMPLEXES WITH MANY ANIONS (e.g., Cl^-, SO_4^{2-}, F^-, NO_3^-, *et al*)
- UO_2^{2+} FORMS DIURANATES (e.g., $Na_2U_20_7$) WITH AMMONIUM AND SODIUM HYDROXIDES
- UO_2^{2+} PRECIPITATES THE PEROXIDE $U0_4 \cdot 2H_20$ FROM MILDLY ACIDIC SOLUTIONS
- UO_2^{2+} FORMS AN EXTRAORDINARILY STRONG AND USEFUL $[U0_2(CO_3)_3]^{4-}$ COMPLEX
- UO_2^{2+} FORMS A USEFUL AND UNUSUAL ACETATE COMPLEX: $NaZn[UO_2(C_2H_3O_2)_3]_3$
- UO_2^{2+} FORMS A NITRATE COMPLEX THAT EXTRACTS INTO TBP FROM CONCENTRATED NO_3^- SOLUTIONS AS THE $UO_2(NO_3)_2 \cdot 2TBP$ COMPLEX

NEPTUNIUM

STABLE Np AQUEOUS CHEMICAL SPECIES

- **Np^{3+}, Np^{4+}, NpO_2^{+}, NpO_2^{2+}**

Np^{3+} BEHAVES LIKE RARE EARTHS: SLIGHT COMPLEXATION; COMPLETE PRECIPITATION BY OH^{-}, PO_4^{3+} AND F^{-}

Np^{4+} BEHAVES LIKE Pu^{4+}: HYDROLYZES AND FORMS STABLE SO_4^{-2}, F^{-} AND $C_2O_4^{-2}$ COMPLEXES

NpO_2^{+} IS NOT EASILY COMPLEXED, PRECIPITATED, OR SOLVENT EXTRACTED

NpO_2^{2+} BEHAVES LIKE UO_2^{2+} AND PuO_2^{2+}; FORMS SIMILAR COMPLEXES AND IS EXTRACTED BY ORGANIC SOLVENTS

PLUTONIUM

STABLE Pu AQUEOUS CHEMICAL SPECIES

- Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}

Pu^{3+} IS MORE STABLE THAN U^{3+} OR Np^{3+}; STABLE IN ACIDIC SOLUTIONS; FLUORIDES AND HYDROXIDES ARE INSOLUBLE (LIKE RARE EARTHS); PRECIPITATED BY OXALATE AND CARBONATE; NOT EASILY SOLVENT EXTRACTED

Pu^{4+} PREDOMINATES IN ACIDIC SOLUTIONS BUT IS EASILY OXIDIZED OR REDUCED; APPRECIABLY COMPLEXED BY NITRATE, PEROXIDE, FLUORIDE AND CHLORIDE; ANIONIC COMPLEXES FORM AT HIGH CONCENTRATIONS OF NITRATE AND CHLORIDE; PRECIPITATED BY OXLALATE AND PEROXIDE; "IRREVERSIBLY" FORMS *PLUTONIUM POLYMER*; EXTRACTS INTO TBP AS $Pu(NO_3)_4 \cdot 2TBP$

PLUTONIUM

STABLE Pu AQUEOUS CHEMICAL SPECIES

Pu^{3+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+}

(CONTINUED)

PuO_2^{+} IS LESS COMPLEXED, LESS HYDROLYZED, LESS EASILY EXTRACTED, AND LESS EASILY PRECIPITATED THAN OTHER OXIDATION STATES OF Pu

PuO_2^{2+} IS EASILY EXTRACTED BY ORGANIC SOLVENTS WITH EXCESS NO_3^{-}; RESEMBLES UO_2^{2+} IN ITS HYDROLYSIS AND COMPLEX FORMATION; FORMS COMPLEXES WITH SULFATES AND CARBONATES,AMONG OTHERS

AMERICIUM

STABLE Am AQUEOUS CHEMICAL SPECIES

- Am^{3+}, *Am^{4+}*, *Am^{5+}*, *Am^{6+}*
- Am^{3+} IS THE ONLY OXIDATION STATE STABLE UNDER "ORDINARY" CONDITIONS
- Am(III) FORMS STABLE COMPLEXES WITH Cl^-, $NO3^-$,CNS^-, AND SiF_6^{2-} (RARE EARTHS ARE LESS PRONE TO FORM THEM)
- Am(III) FORMS A SOLUBLE CARBONATE COMPLEX [Cm(III) DOES NOT]
- Am(V) FORMS INSOLUBLE $KAmO_2CO_3$ (RARE EARTHS DO NOT)
- Am(VI) IS STRONGLY OXIDIZING AND DIFFICULT TO STABILIZE IN SOLUTION
- HYDROLYSIS COMPLICATES Am SOLUTION CHEMISTRY

CURIUM

- **STABLE Cm AQUEOUS CHEMICAL SPECIES**
- **Cm^{3+} IS THE ONLY OXIDATION STATE FOUND NORMALLY IN SOLUTION**
- **Cm(III) FLUORIDE, OXALATE, PHOSPHATE, IODATE, AND HYDROXIDE ARE INSOLUBLE**
- **Cm(III) IS VERY STABLE TOWARD OXIDATION**
- **Cm CHEMISTRY STUDIES ARE HAMPERED BY RADIOLYTIC AND HEATING EFFECTS**
- **CmF_3 CAN BE PRECIPITATED FROM SOLUTION**
- **Cm(III) FORMS COMPLEXES WITH α-HYDROXY-ISOBUTYRATE AND CNS^- THAT CAN BE SEPARATED FROM Am, OTHER TRU ELEMENTS, AND RARE EARTHS USING ION EXCHANGE ELUTION**