U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: RADIONUCLIDE BEHAVIOR AT ELEVATED TEMPERATURES; COLLOID BEHAVIOR

PRESENTER: DR. DAVID E. HOBART

PRESENTER'S TITLE AND ORGANIZATION: STAFF SCIENTIST, LOS ALAMOS NATIONAL LABORATORY LOS ALAMOS, NEW MEXICO

PRESENTER'S TELEPHONE NUMBER: (505) 667-9313

DECEMBER 11-12, 1989
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RADIONUCLIDE BEHAVIOR AT ELEVATED TEMPERATURES

- THE SOLUBILITY STUDIES HAVE PROVIDED SOLUBILITY OR CONCENTRATION LIMITS FOR DISSOLVED SPECIES OF SEVERAL KEY RADIONUCLIDES UNDER EXPECTED CONDITIONS AT YUCCA MOUNTAIN

- STUDIES (LANL, LLNL, LBL) INDICATE THAT RADIONUCLIDE MIGRATION MAY BE CONTROLLED BY

  - DISSOLUTION OF WASTE FORM
  - PRECIPITATION OF SOLUBILITY CONTROLLING SOLIDS
  - FORMATION OF SOLUBLE SPECIES
    * SPECIATION (OXIDATION STATES)
  - FORMATION OF COLLOIDS
THE NATURE OF COMPOUNDS AND SOLUTION SPECIES DEPENDS ON SEVERAL PARAMETERS

- OXIDATION STATE OF RADIONUCLIDE
- NATURE AND CONCENTRATION OF
  - PRECIPITATING IONS
  - COMPLEXING LIGANDS
- pH
- Eh
- TEMPERATURE
TWO PRINCIPAL METHODS ARE USED TO DETERMINE SOLUBILITY

- **UNDERSATURATION**
  - WELL-DEFINED SOLID PHASE PLACED IN CONTACT WITH AQUEOUS PHASE
  - DISSOLUTION OF SOLID IS MONITORED

- **SUPERSATURATION**
  - EXCESS AMOUNT OF COMPOUND IN SOLUBLE FORM IS ADDED TO AQUEOUS SOLUTION
  - PRECIPITATION OF INSOLUBLE MATERIAL IS MONITORED

- BOTH METHODS SHOULD LEAD TO THE SAME RESULTS
EXPERIMENTAL APPROACH TO SOLUBILITY MEASUREMENTS

![Graph showing concentration over time with phases of oversaturation, equilibrium, and undersaturation.](image)
APPLICATION OF SOLUBILITY INFORMATION

SOLUBILITY DATA ARE USED TO

- Obtain good estimates on the upper limit of radionuclide concentrations in solution
- Provide a source term for sorption studies

SOLUBILITY DATA WILL BE USED TO

- Validate models
  * Chemical component of transport model
  * Data base validation for reliable predictions and extrapolation of thermodynamic functions to higher temperatures
EXPERIMENTAL DETAILS FOR THE SOLUBILITY MEASUREMENTS

- USED FILTERED GROUNDWATERS FROM YUCCA MOUNTAIN REGION (J-13 AND UE-25p#1; BROAD RANGE IN CARBONATE CONCENTRATION AND IONIC STRENGTH)

- SUPERSATURATED SOLUBILITY CONDITIONS (Np, Pu, Am)

- pH
  - 6, 7, AND 8.5

- TEMPERATURE
  - 25°, 60°, AND 90°C

- TOTAL CARBONATE HELD CONSTANT
  - SATURATION WITH Ar-CO₂ MIXTURES OF DEFINED CONTENTS FOR EACH pH AND TEMPERATURE
APPROACH OF J-13 WATER SOLUTIONS OF Am(III) TO EQUILIBRIUM AT pH 7 AND 25°C

INITIAL Am/Nd CONCENTRATION: 1.3X10^-6 (M)
Pu(IV) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C

SOLID PHASES CONTAIN Pu(IV)-POLYMER AND CARBONATE
PLUTONIUM OXIDATION STATE DISTRIBUTIONS FOR pH 8.5 J-13 GROUNDWATER SOLUTIONS AT 25°, 60°, AND 90°C
Np(V) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C

CHEMICAL COMPOUNDS:

A: $\text{Na}_{x.8}\text{NpO}_2(\text{CO}_3)_{0.8}\cdot\text{H}_2\text{O}$
B: $\text{Na}_{x.8}\text{NpO}_2(\text{CO}_3)_{0.8}\cdot2.5\text{H}_2\text{O}$
C: $\text{Na}_{x.8-1}\text{NpO}_2(\text{CO}_3)_x\cdot\text{nH}_2\text{O}$
D: $\text{Np}_2\text{O}_5$

CONCENTRATION OF Np-237 (M)

PH VALUES:

- pH 5.9
- pH 7
- pH 8.5

THERMAL CONDITIONS:

- 25°C
- 60°C
- 90°C
PLUTONIUM OXIDATION STATE DISTRIBUTIONS FOR J-13 AND UE-25p#1 GROUNDWATERS AT pH 6 AND 25°C

PERCENTAGE OF OXIDATION STATE

OXIDATION STATE

Pu(III)+POLYMER  Pu(IV)  Pu(V)  Pu(VI)

J-13  UE-25p#1
Am(III) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°C AND 90°C

AmOHCO₃
A : HEXAGONAL
B : ORTHORHOMBIC
COLLOID FORMATION, CHARACTERIZATION, AND STABILITY

- PLUTONIUM RADIOCOLLOIDS HAVE BEEN STUDIED

- COLLOIDS MAY CONTRIBUTE TO RADIONUCLIDE MIGRATION
WHAT ARE COLLOIDS?

**COLLOID** - SMALL PARTICLES WHICH WILL REMAIN SUSPENDED INDEFINITELY

**RADIOCOLLOID** - COLLOID FORMED FROM RADIONUCLIDE

**NATURAL COLLOID** - COLLOID FORMED FROM GEOLOGIC MEDIA

**COMPLEX COLLOID** - COLLOID RESULTING FROM COMBINATION OF NATURAL COLLOID AND RADIOCOLLOID (DEH 1989)
PHOTOGRAPH: VIALS SHOWING VARIOUS SPECIES OF PLUTONIUM
RADIOCOLLOID (SOL) FORMATION

- THE FIRST STAGE IN SOL FORMATION IS THE HYDROLYSIS OF AQUO Pu(IV), WHICH FORMS MONOMERIC SPECIES SUCH AS Pu(OH)\(_3^+\), Pu(OH)\(_2^{2+}\), Pu(OH)\(_3^+\), AND Pu(OH)\(_4^0\)

- HYDROLYSIS IS FOLLOWED BY COLLOIDAL POLYMERIZATION RESULTING FROM FORMATION OF OXYGEN BRIDGES BETWEEN ADJACENT PLUTONIUM IONS TO THE EXTENT THAT LARGE AGGREGATES ARE FORMED

- PRECIPITATION CAN OCCUR BY A NUMBER OF METHODS
PLUTONIUM COLLOID CHARACTERIZATION

ABSORPTION SPECTRA OF PLUTONIUM (III), (IV), (V) AND (VI), AND POLYMERIC PLUTONIUM (IV)
COMPARISON OF SPECTRA FOR Pu(IV) COLLOID SOL AND HIGH-FIRED PuO₂

Pu(IV) COLLOIDAL SOL

HIGH-FIRED PuO₂
Pu(IV) COLLOID STABILITY
(ELECTROCHEMISTRY)

CONTROLLED POTENTIAL ELECTROCHEMICAL
METHODS USED ON Pu(IV) COLLOID PROVIDED
INFORMATION ON:

● CHEMICAL PROPERTIES
  - ELECTRON TRANSFER REACTIVITY
  - "REDOX POTENTIALS"

● PHYSICAL PROPERTIES
  - PARTICLE SIZE
  - PARTICLE CHARGE
SPECTRAL RESULTS FOR REDUCTION OF Pu(IV) COLLOID TO Pu(III)\textsubscript{aq}

![Spectral graph showing absorbance units against wavelength (nm)]
RATE OF ELECTROCHEMICAL REDUCTION OF Pu(IV)-COLLOID TO Pu(III)$_{aq}$
SUMMARY OF RESULTS FROM SOLUBILITY EXPERIMENTS

- Pu, Np, Am

- IDENTIFIED CONTROLLING SOLIDS

- SOLUBILITY BEHAVIOR OF Pu DOES NOT VARY AS A FUNCTION OF DIFFERING GROUNDWATERS (J-13, UE-25p#1)

- Pu(V) IS DOMINANT SPECIE IN J-13 GROUNDWATER AT pH OF 8.5 AT VARIOUS TEMPERATURES

- Pu(IV) SOLUBILITY DECREASES AS A FUNCTION OF INCREASING TEMPERATURE

- Np(V) SOLUBILITY DECREASES WITH INCREASING pH (NO TEMPERATURE DEPENDENCE OBSERVED)

- NO GENERAL TREND OBSERVED FOR Am (LOW SOLUBILITY)
SUMMARY OF RESULTS FOR COLLOID STUDIES

- Pu(IV)-COLLOID IS SIMILAR TO HIGH-FIRED PuO₂

IMPLICATIONS:

- Pu(IV)-COLLOID IS OBSERVED IN GROUND WATER SOLUTIONS; IMPORTANT TO SORPTION AND TRANSPORT STUDIES

- IN TIME, Pu(IV)-COLLOID MAY STABILIZE TO PuO₂; IMPORTANT IN ASSESSING RADIONUCLIDE MIGRATION

- Pu(IV)-COLLOID IS STABLE UNDER EXPECTED CONDITIONS (Eh)
ONGOING WORK

- SOLUBILITY EXPERIMENTS TO BE EXTENDED TO OTHER RADIONUCLIDES (i.e., Zr, Ni, Th, Ra, Cd)

- COLLOID WORK TO INCLUDE Am

- EFFECTS OF NATURAL ORGANICS TO BE CONSIDERED