

**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**

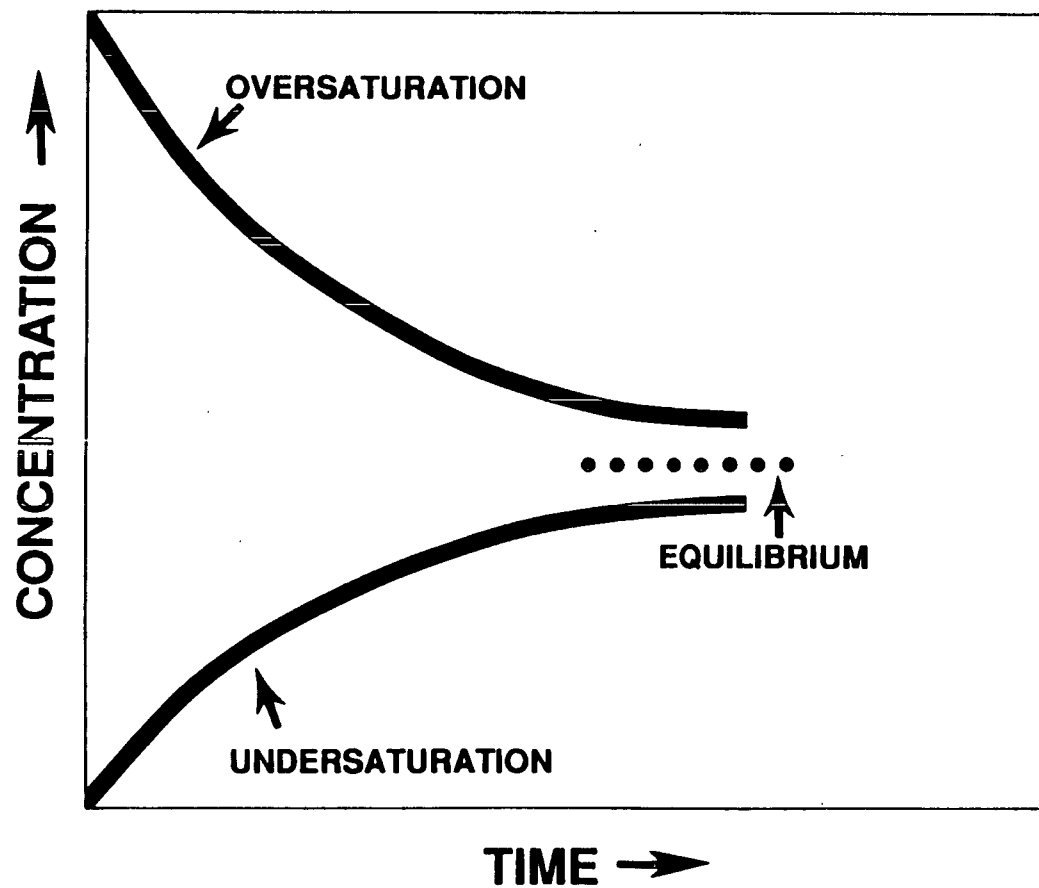
THE NATURE OF COMPOUNDS AND SOLUTION SPECIES DEPENDS ON SEVERAL PARAMETERS

- **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



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**

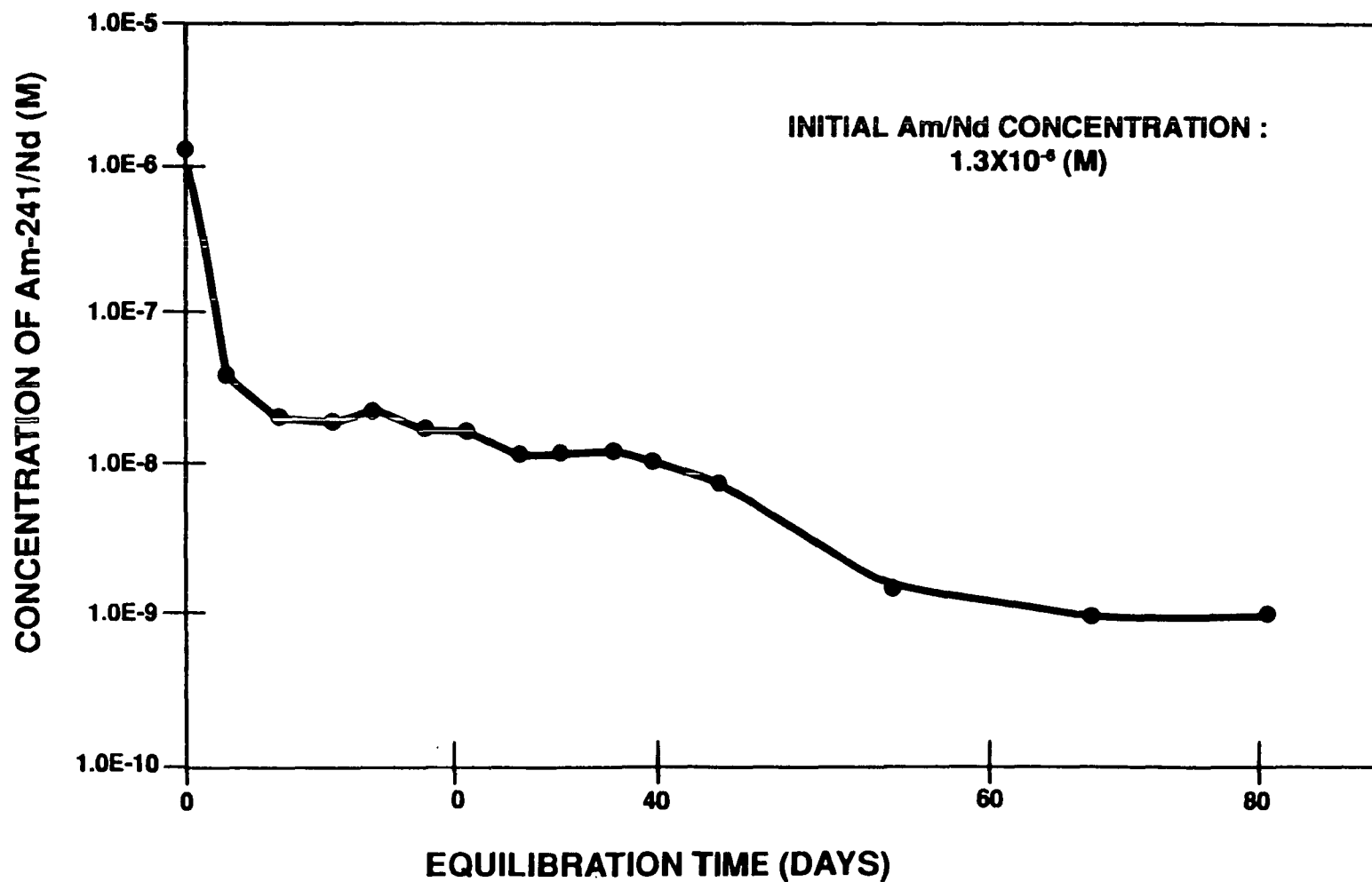
- **SOLUBILITY DATA WILL BE USED TO**

- **VALIDATE MODELS**
 - * **CHEMICAL COMPONENT OF TRANSPORT MODEL**
 - * **DATA BASE VALIDATION FOR RELIABLE PREDICTIONS AND
EXTRAPOLATION OF THERMODYNAMIC FUNCTIONS TO
HIGHER TEMPERATURES**

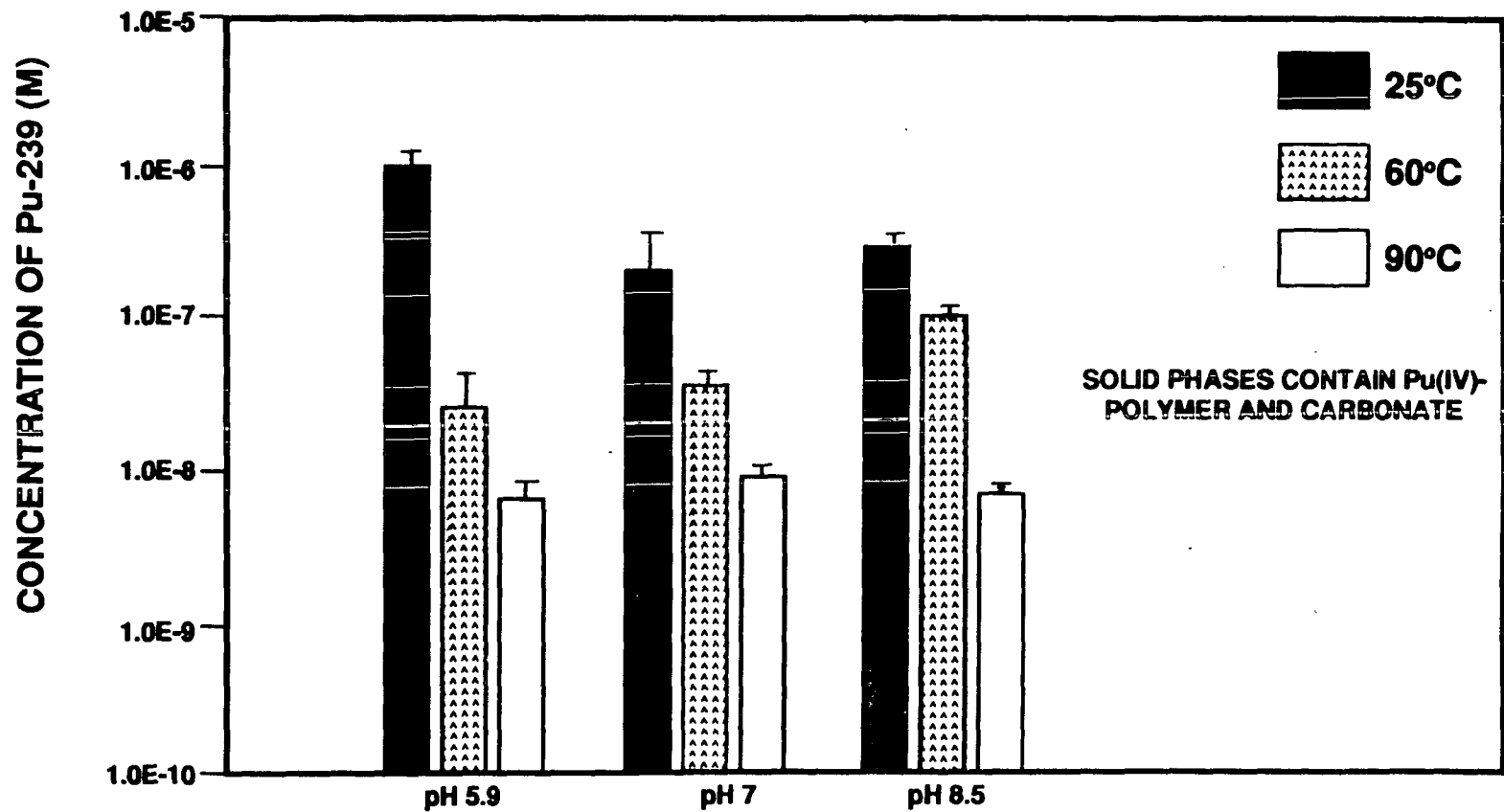
EXPERIMENTAL DETAILS FOR THE SOLUBILITY MEASUREMENTS

- **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

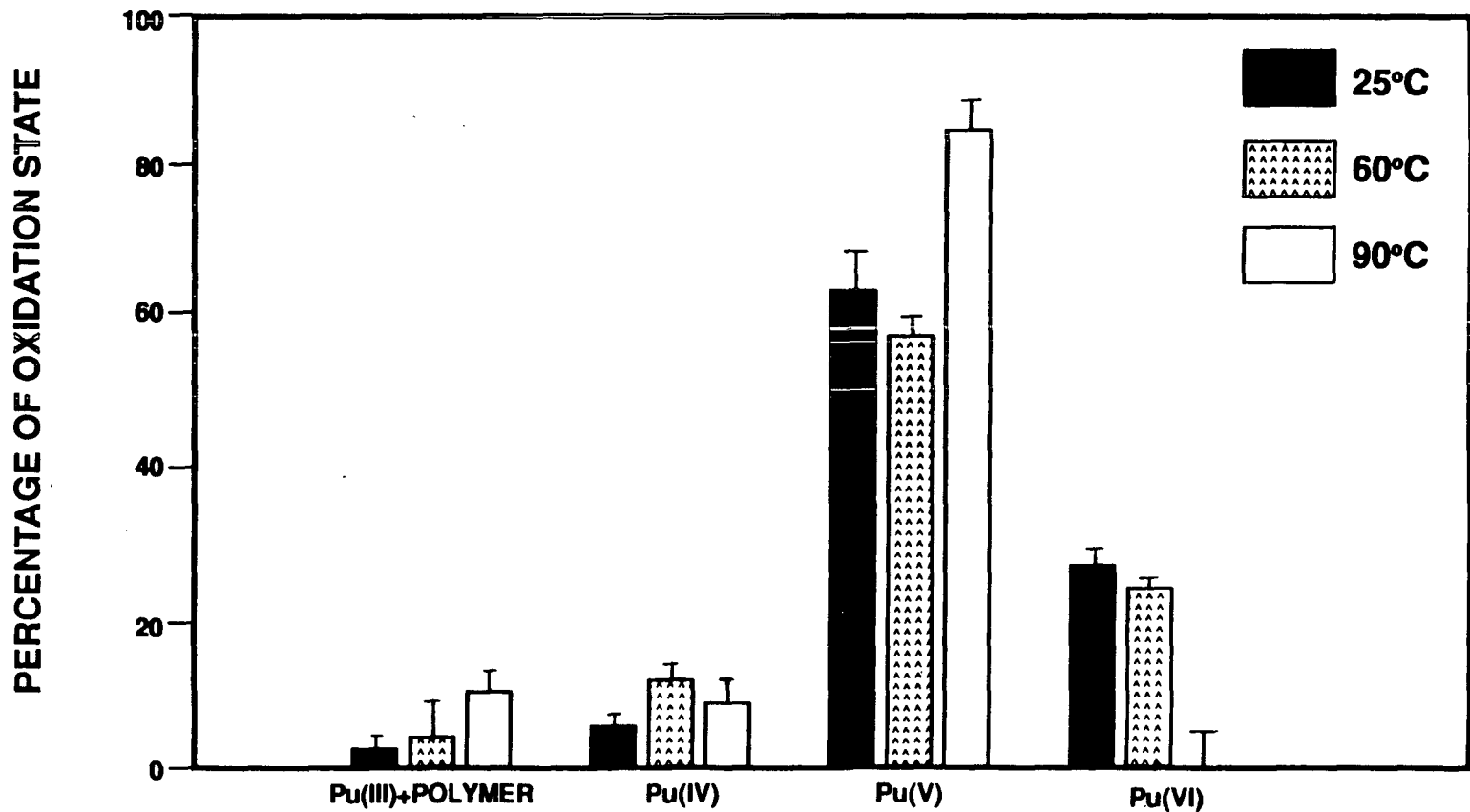
APPROACH OF J-13 WATER SOLUTIONS OF Am(III) TO EQUILIBRIUM AT pH 7 AND 25°C



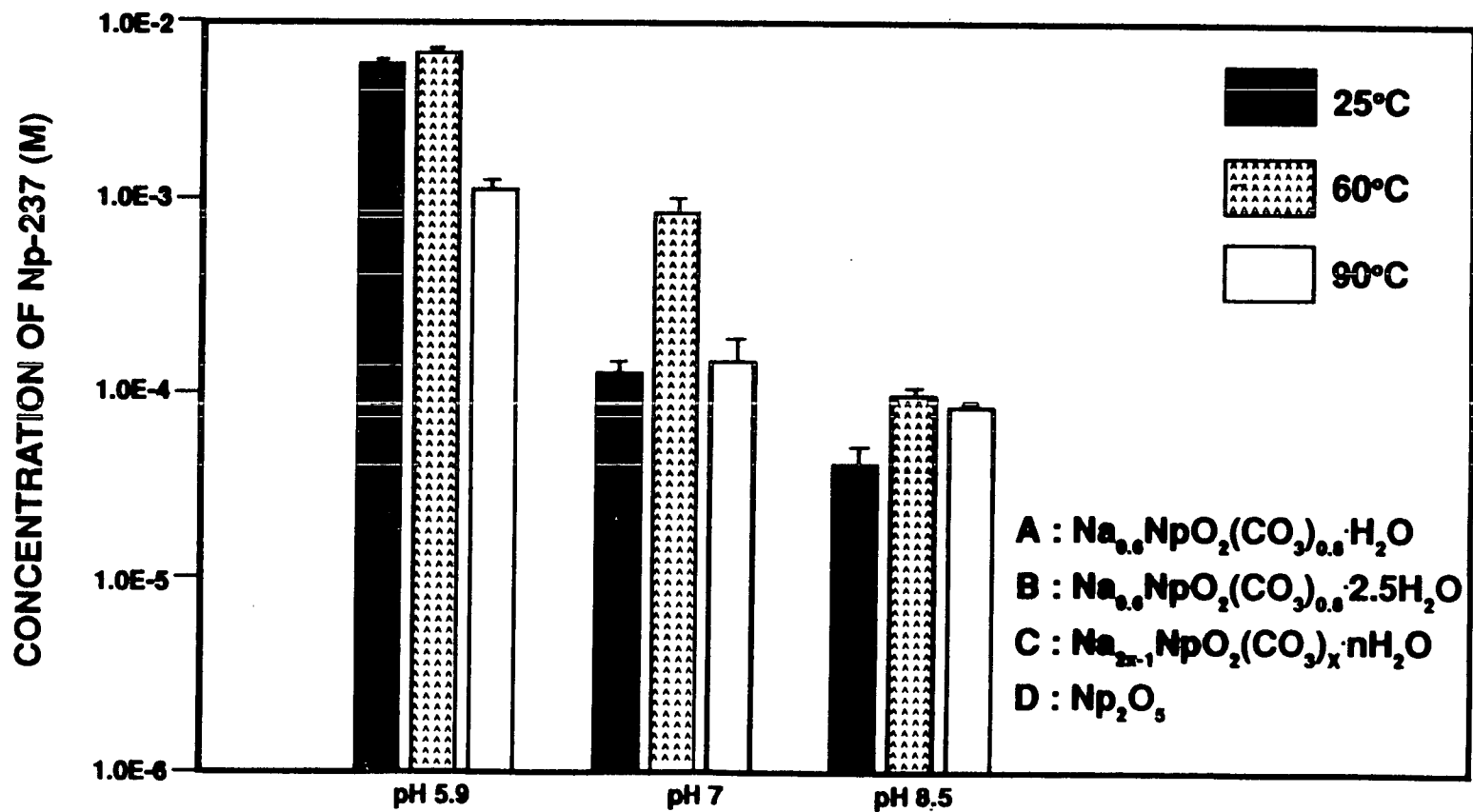
Pu(IV) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C



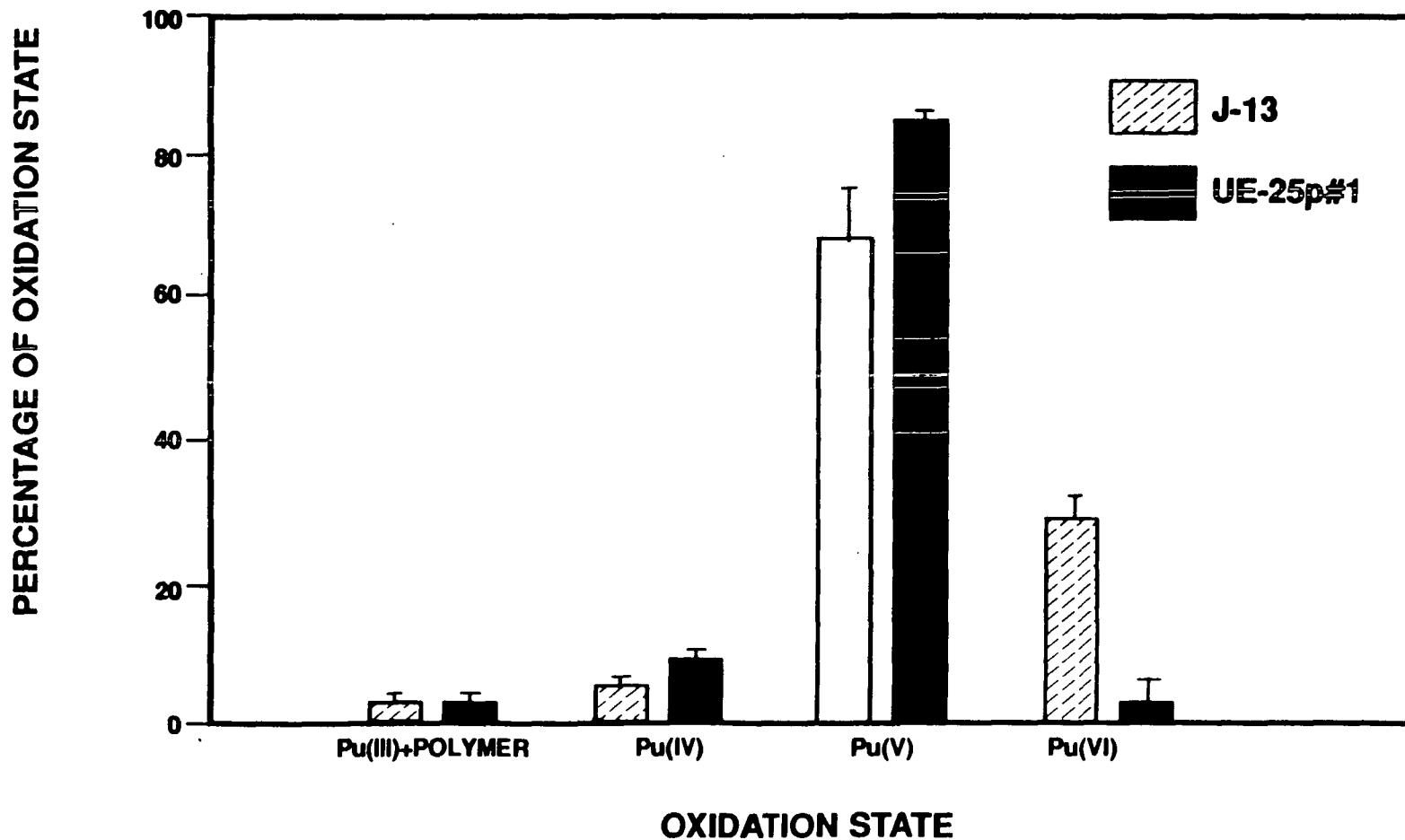
PLUTONIUM OXIDATION STATE DISTRIBUTIONS FOR pH 8.5 J-13 GROUNDWATER SOLUTIONS AT 25°, 60°, AND 90°C



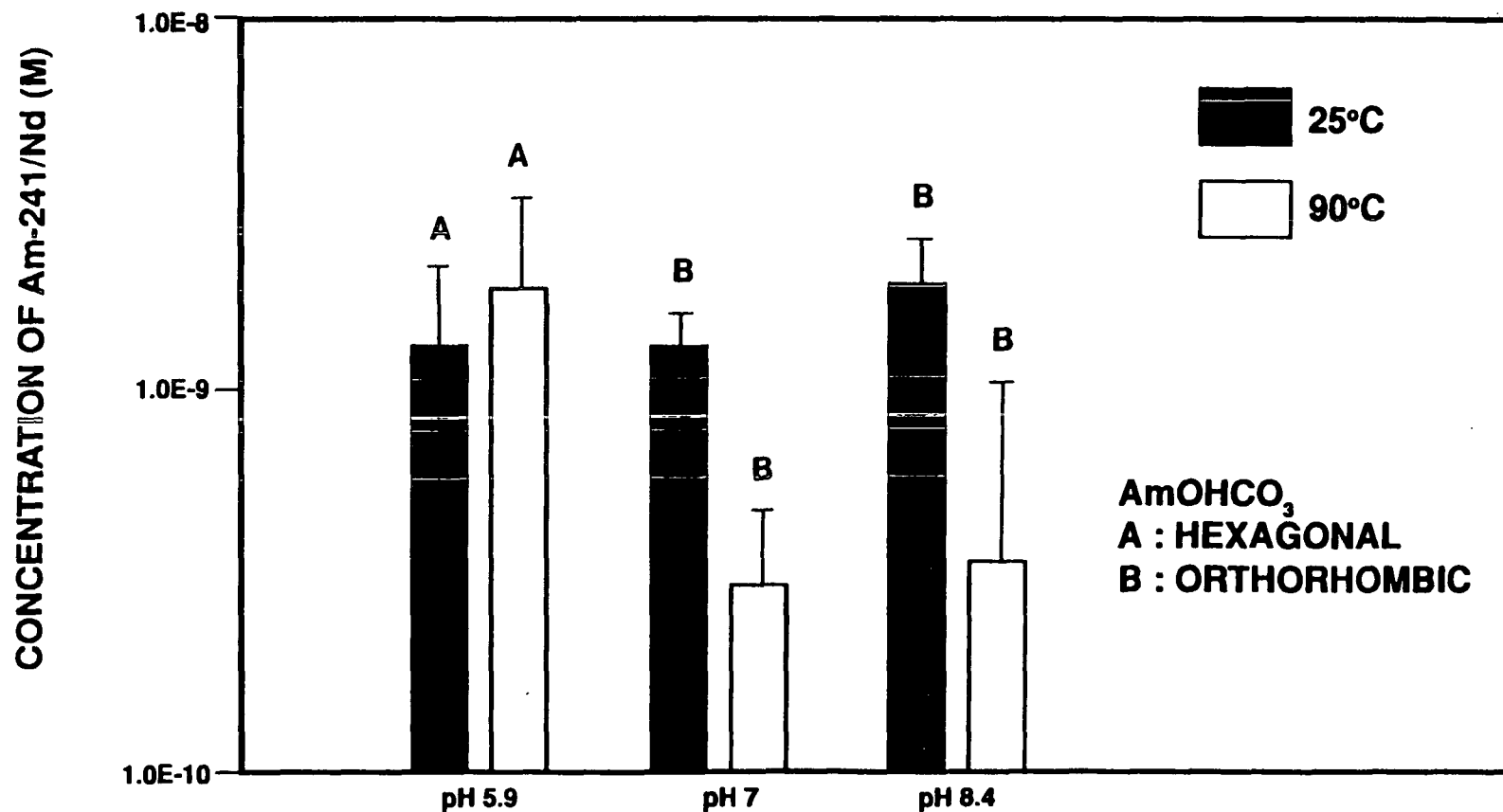
Np(V) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C



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



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



COLLOID FORMATION, CHARACTERIZATION, AND STABILITY

- **PLUTONIUM RADIOCOLLOIDS HAVE BEEN STUDIED**
- **COLLOIDS MAY CONTRIBUTE TO RADIONUCLIDE MIGRATION**

WHAT ARE COLLOIDS?

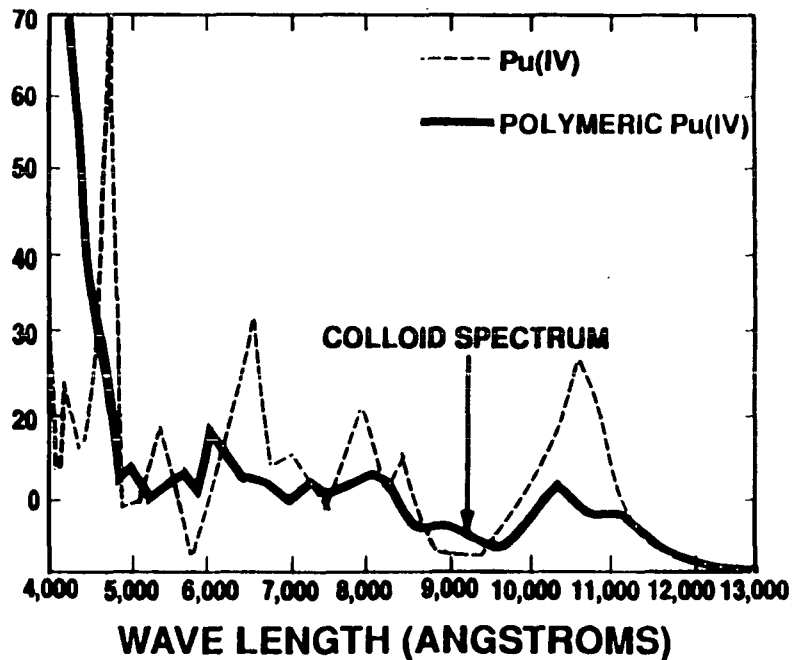
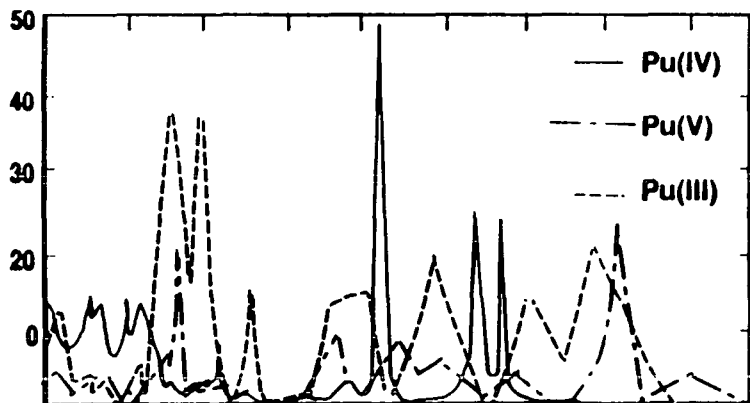
COLLOID -	SMALL PARTICLES WHICH WILL REMAIN SUSPENDED INDEFINITELY
RADIOCOLLOID -	COLLOID FORMED FROM RADIONUCLIDE
NATURAL COLLOID -	COLLOID FORMED FROM GEOLOGIC MEDIA
COMPLEX COLLOID -	COLLOID RESULTING FROM COMBINATION OF NATURAL COLLOID AND RADIOCOLLOID (DEH 1989)

**PHOTOGRAPH: VIALS SHOWING VARIOUS
SPECIES OF PLUTONIUM**

RADIOCOLLOID (SOL) FORMATION

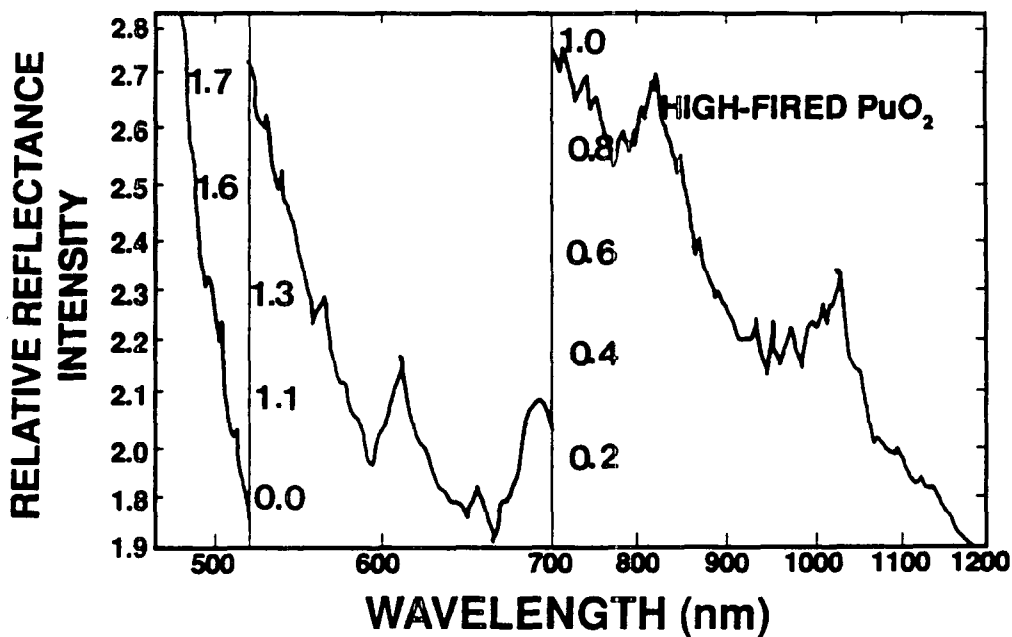
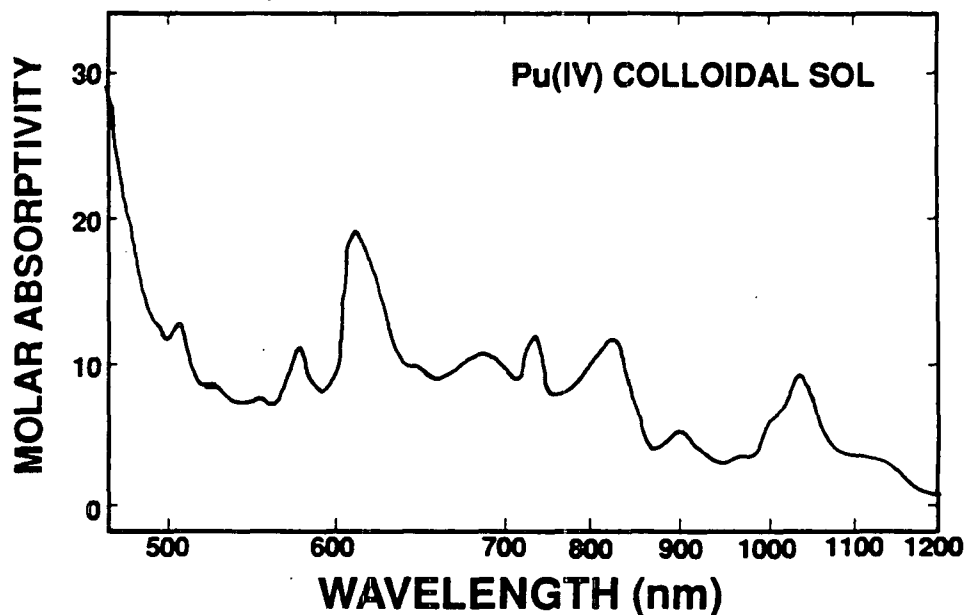
- THE FIRST STAGE IN SOL FORMATION IS THE HYDROLYSIS OF AQUO Pu(IV), WHICH FORMS MONOMERIC SPECIES SUCH AS $\text{Pu}(\text{OH})^{3+}$, $\text{Pu}(\text{OH})_2^{2+}$, $\text{Pu}(\text{OH})_3^+$, AND $\text{Pu}(\text{OH})_4^0$
- HYDROLYSIS IS FOLLOWED BY COLLOIDAL POLYMERIZATION RESULTING FROM FORMATION 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) COLLOID STABILITY (ELECTROCHEMISTRY)

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

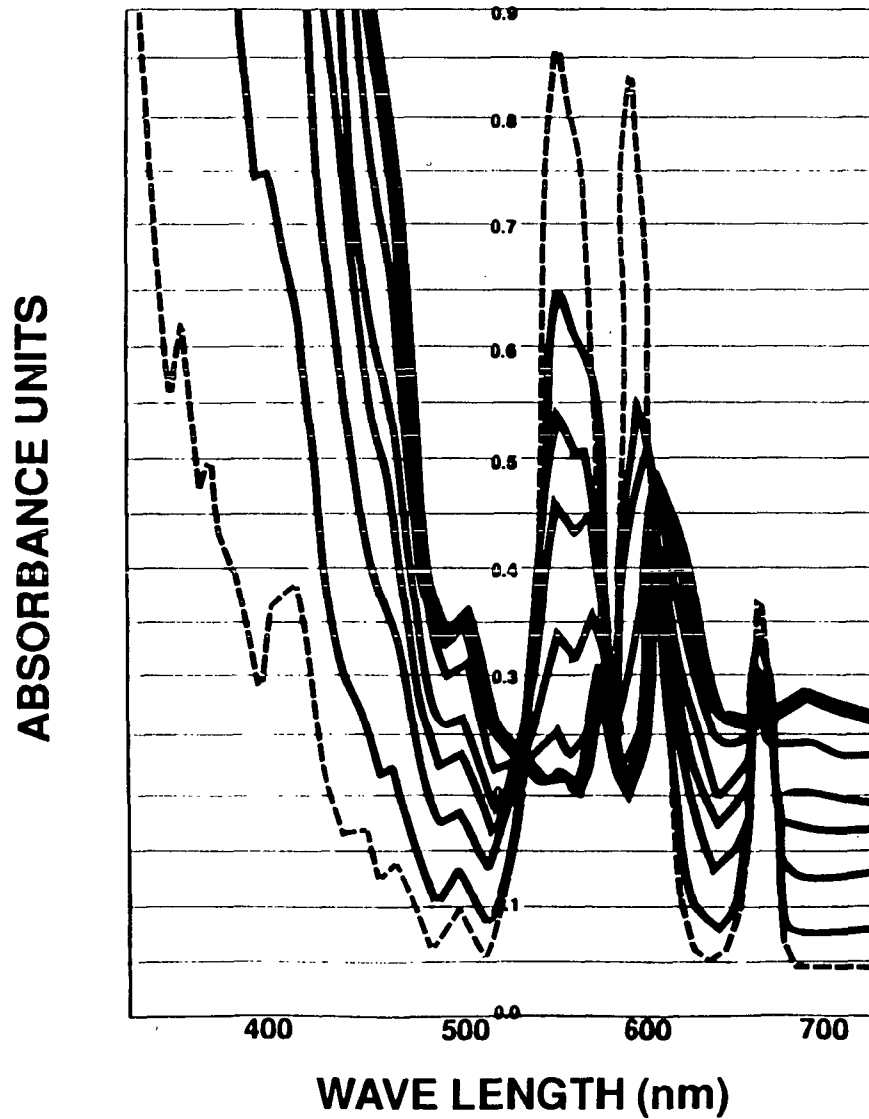
- **CHEMICAL PROPERTIES**

- **ELECTRON TRANSFER REACTIVITY**
- **"REDOX POTENTIALS"**

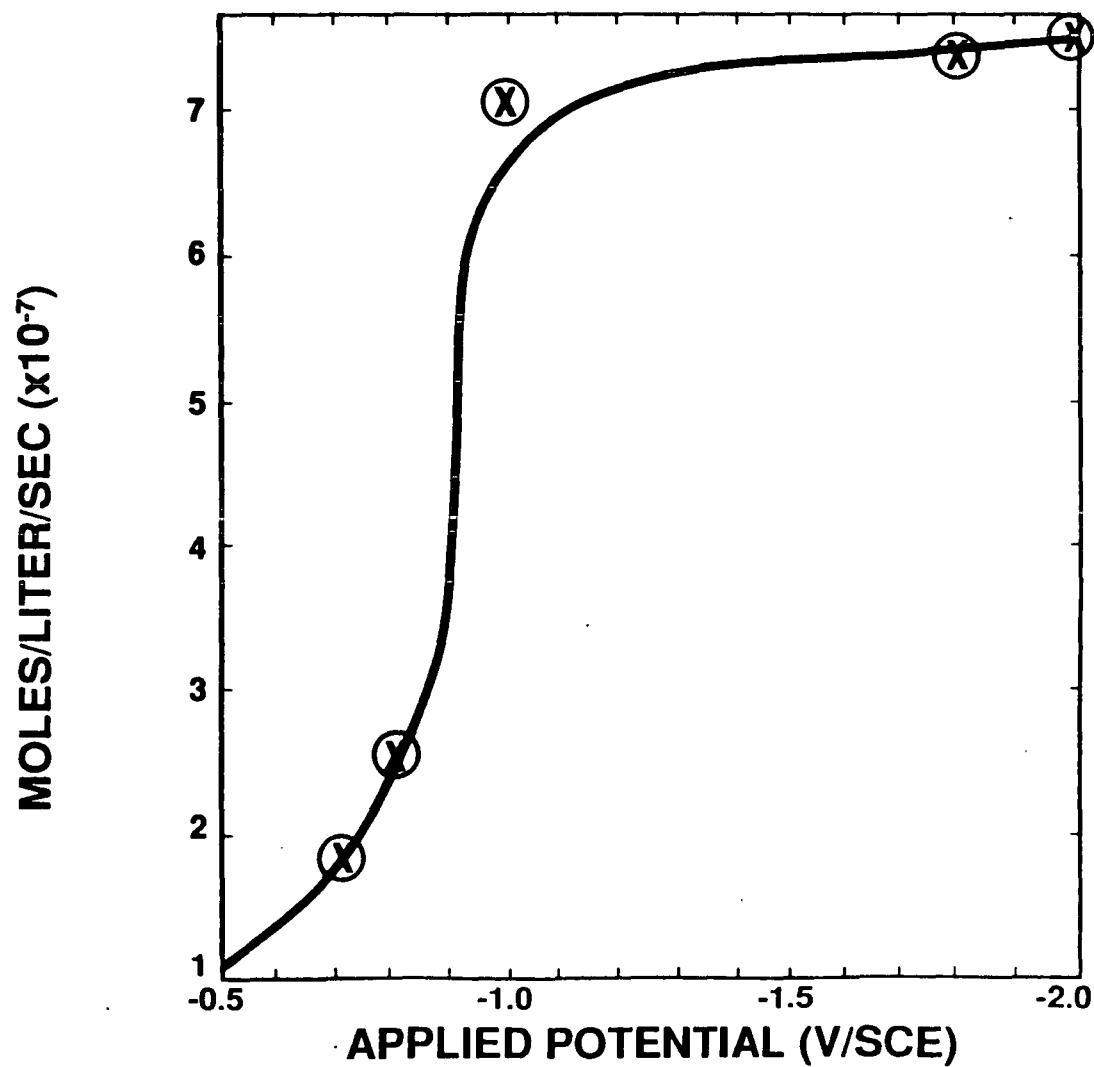
- **PHYSICAL PROPERTIES**

- **PARTICLE SIZE**
- **PARTICLE CHARGE**

SPECTRAL RESULTS FOR REDUCTION OF Pu(IV) COLLOID TO Pu(III)_{aq}



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**