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

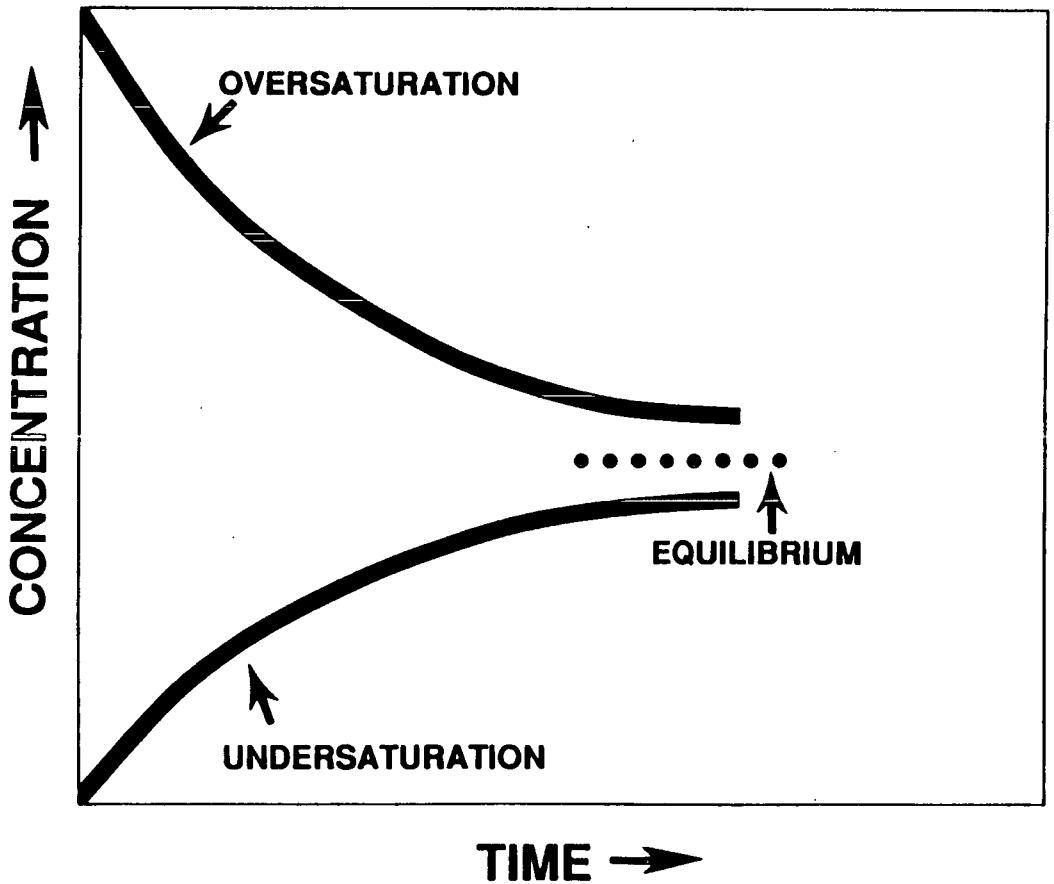
TWO PRINCIPAL METHODS ARE USED TO DETERMINE SOLUBILITY

- **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



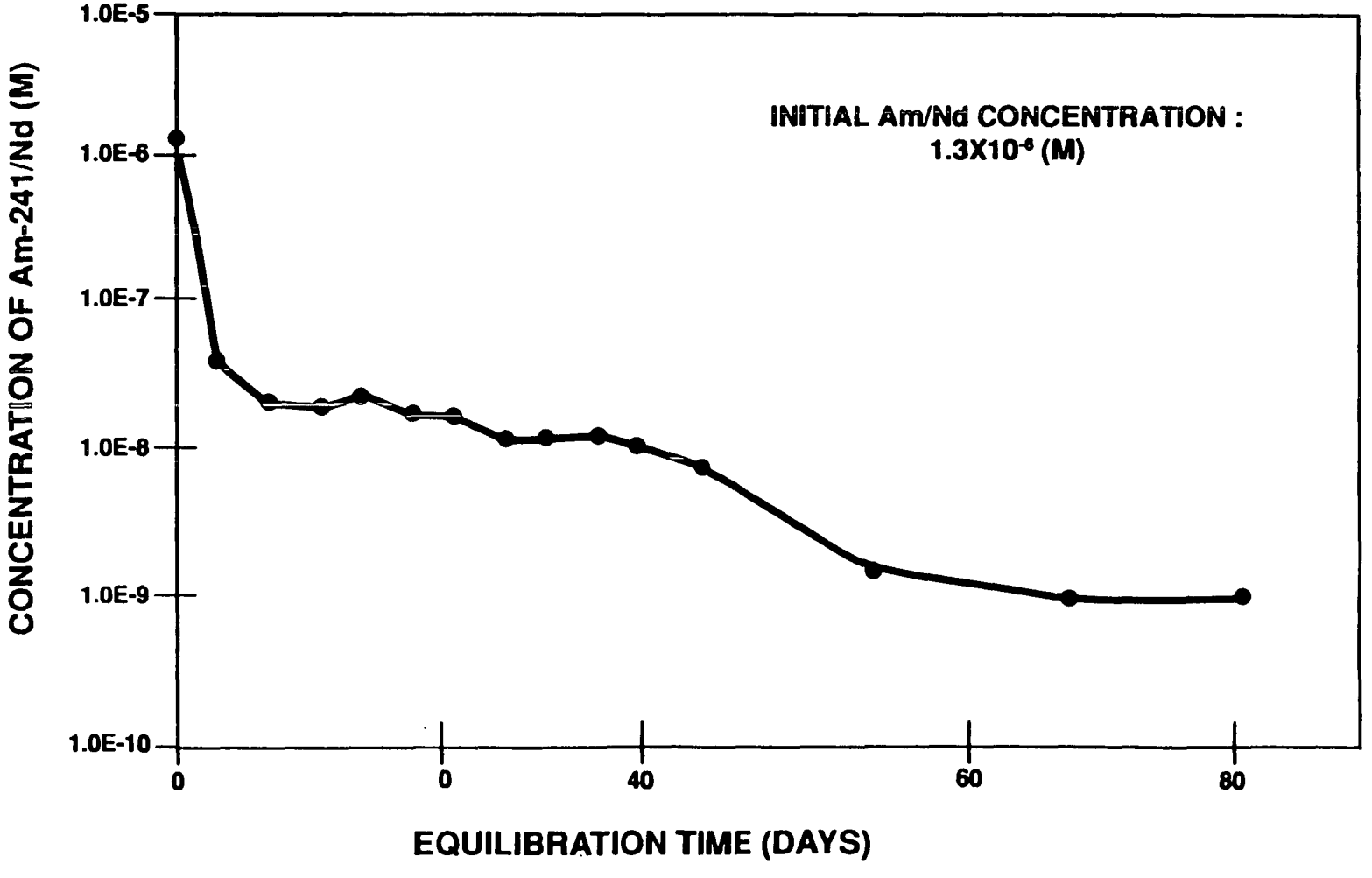
APPLICATION OF SOLUBILITY INFORMATION

- 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

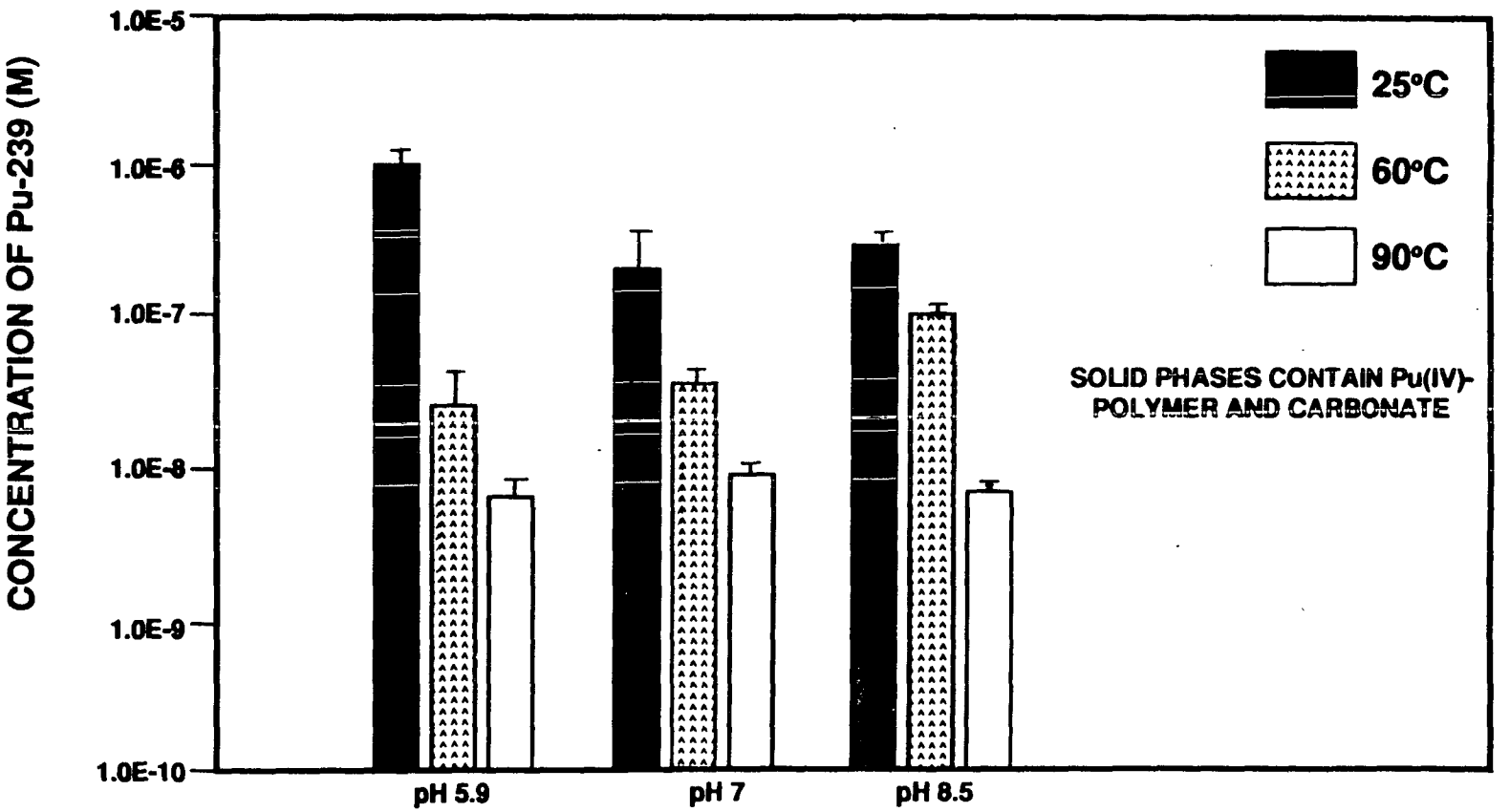
EXPERIMENTAL DETAILS FOR THE SOLUBILITY MEASUREMENTS

- 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-CO_2 MIXTURES OF DEFINED CONTENTS FOR EACH pH AND TEMPERATURE

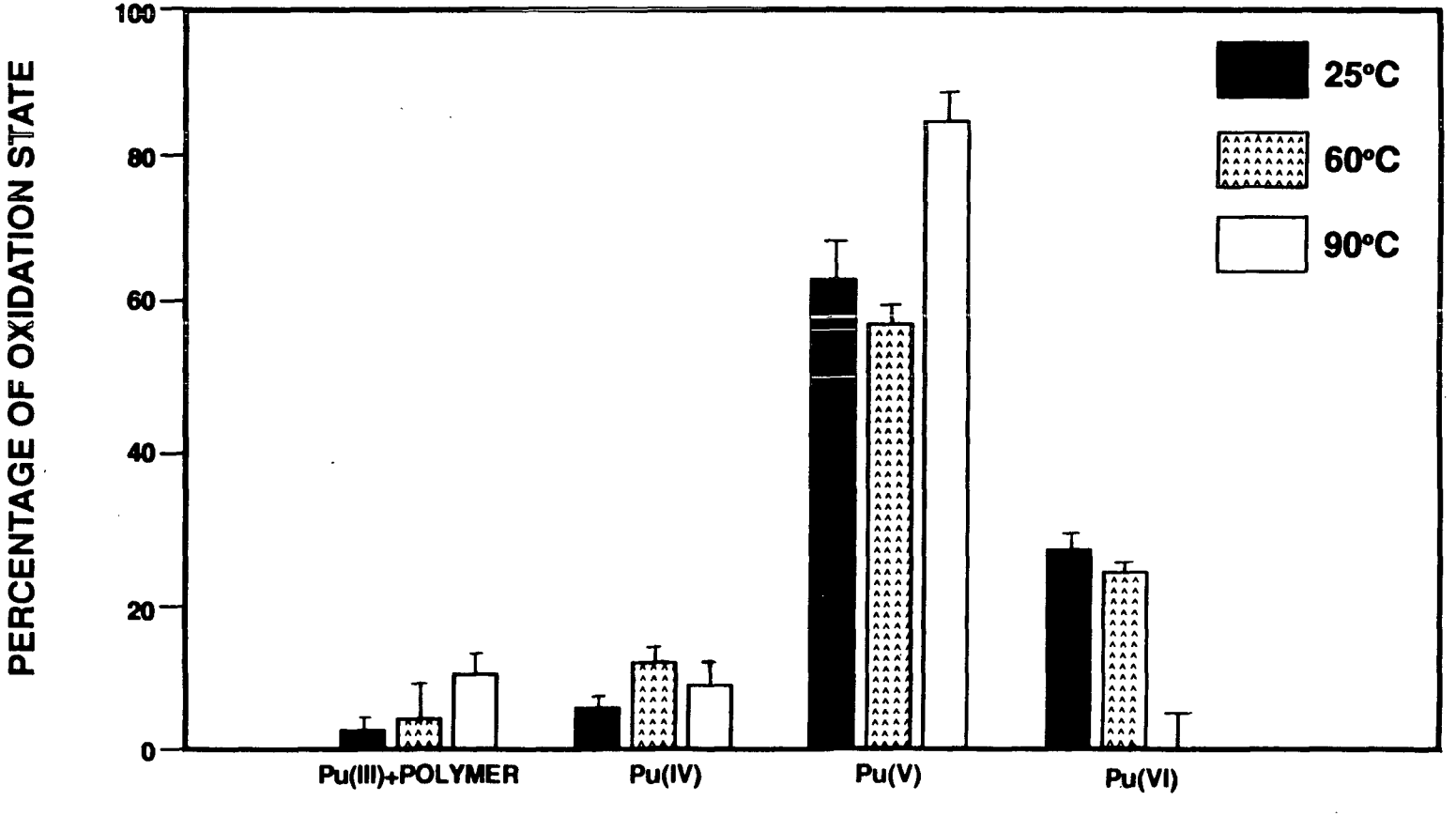
APPROACH OF J-13 WATER SOLUTIONS OF Am(III) TO EQUILIBRIUM AT pH 7 AND 25°C



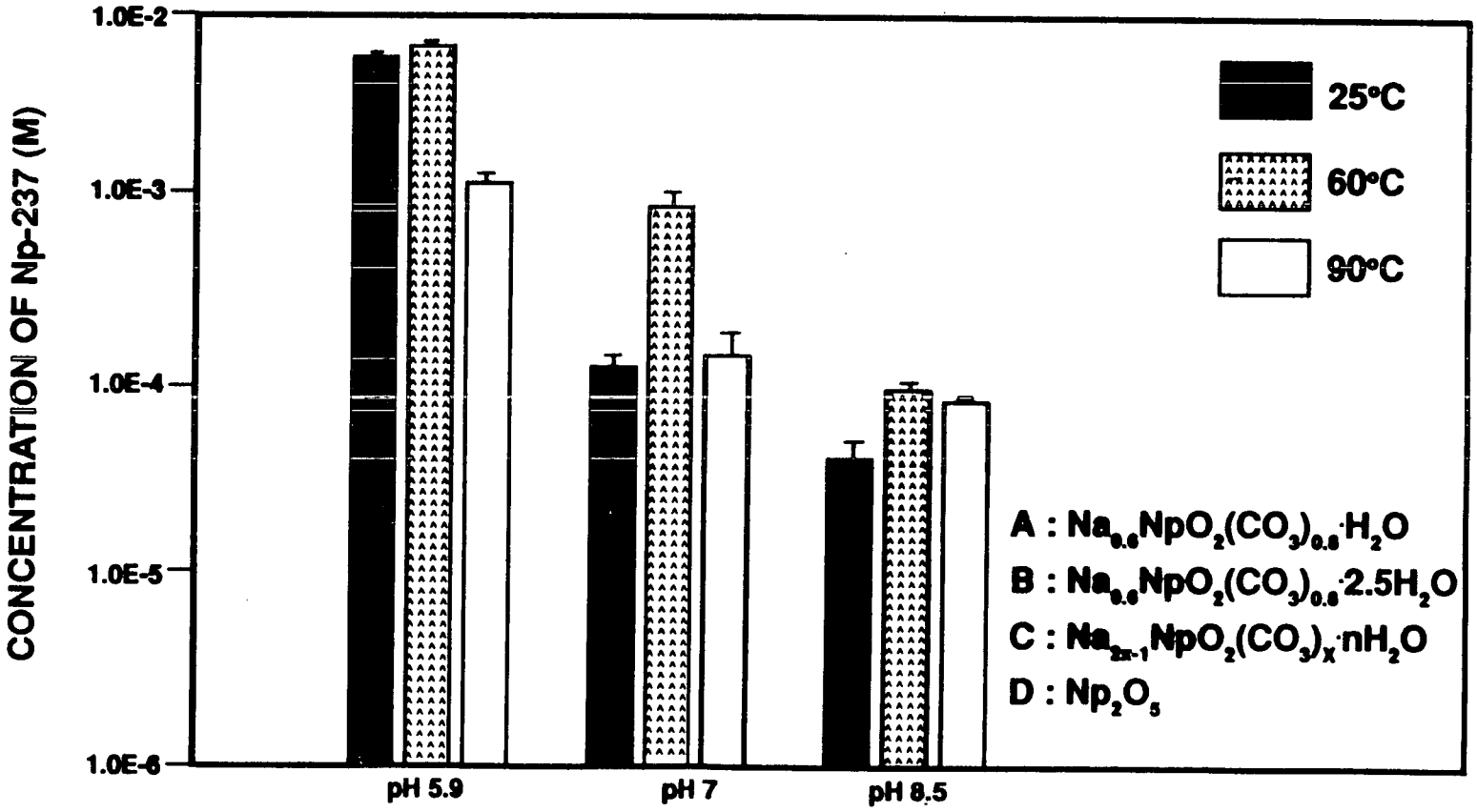
Pu(IV) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C



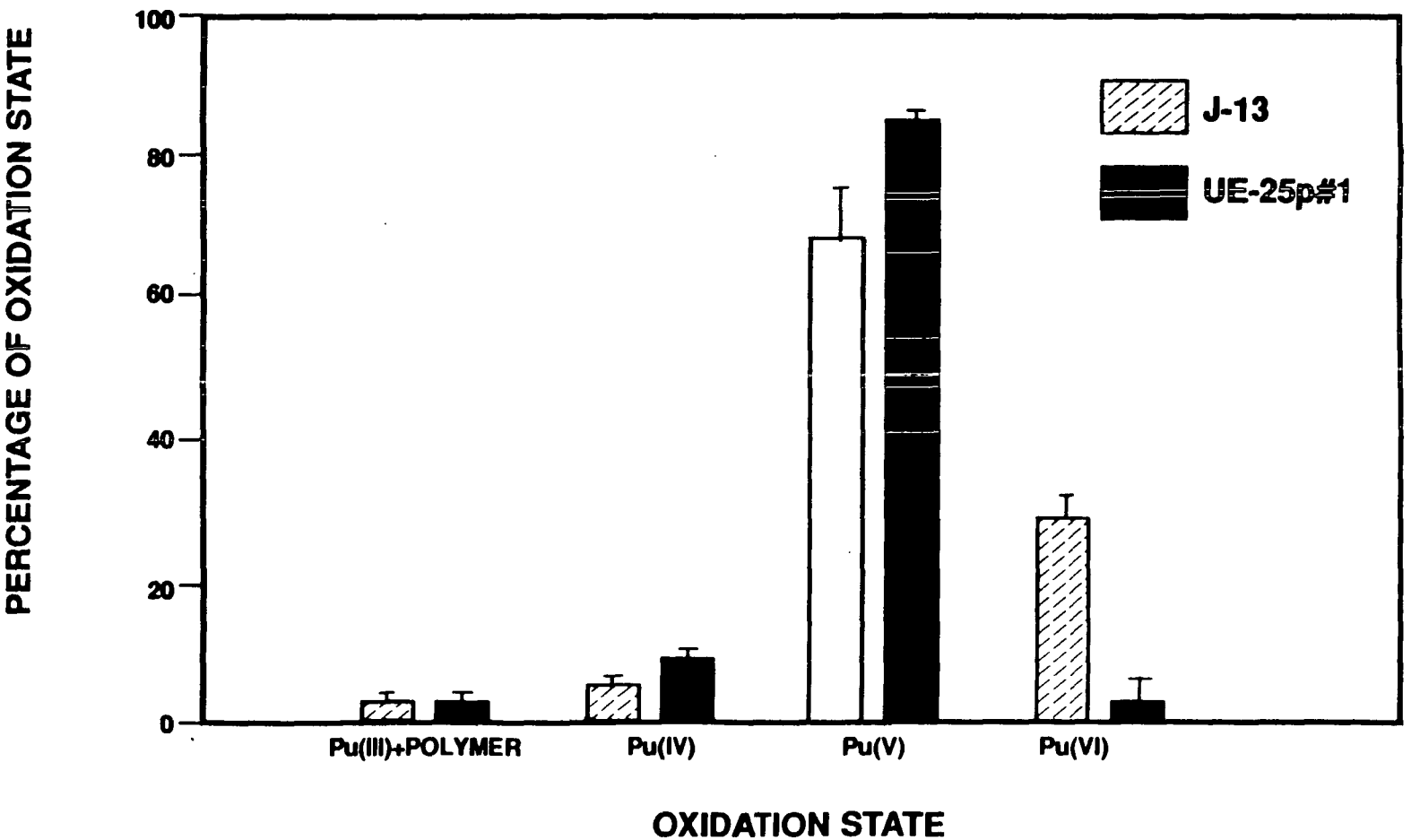
PLUTONIUM OXIDATION STATE DISTRIBUTIONS FOR pH 8.5 J-13 GROUNDWATER SOLUTIONS AT 25°, 60°, AND 90°C



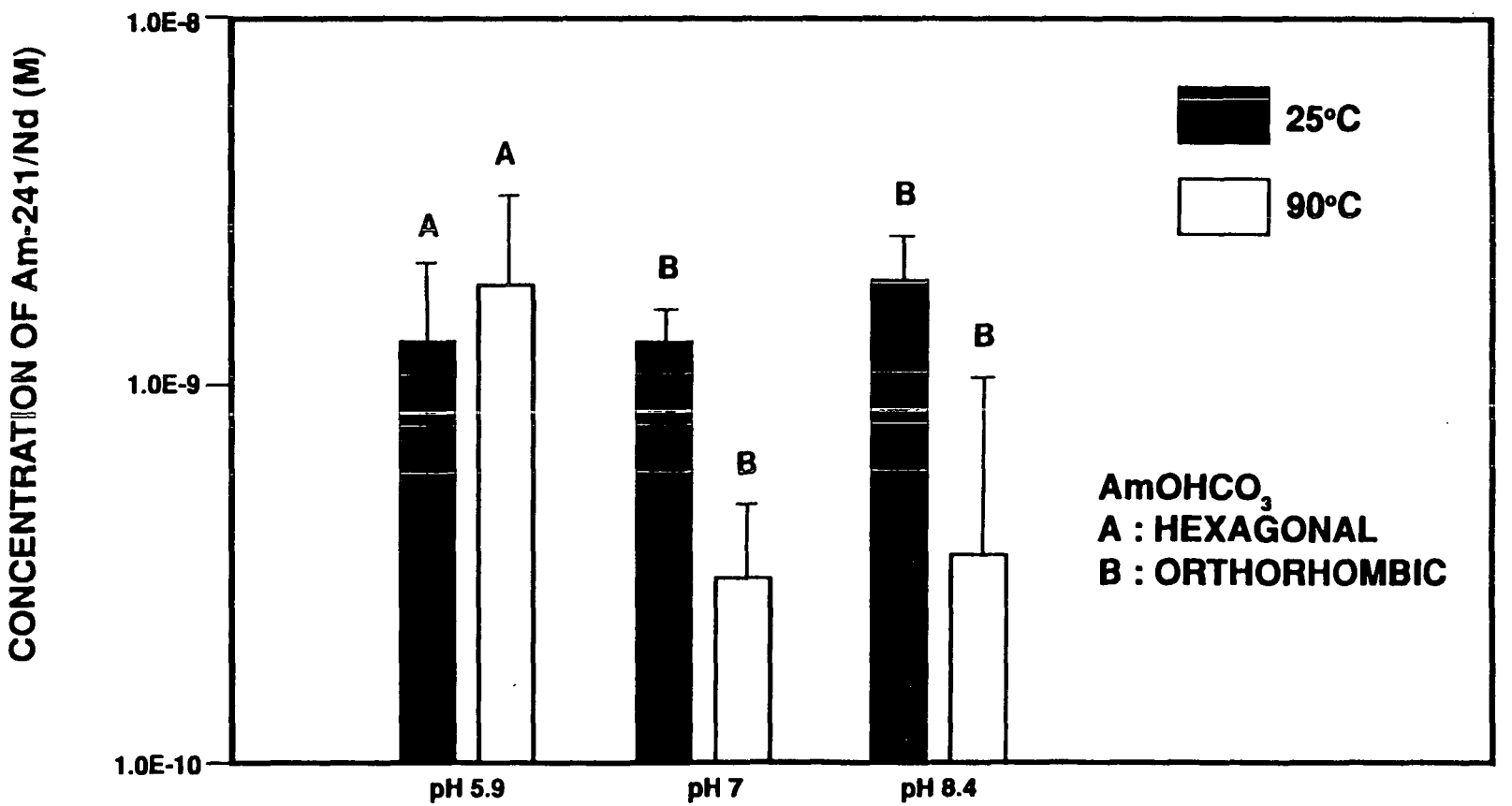
Np(V) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER AT 25°, 60°, AND 90°C



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

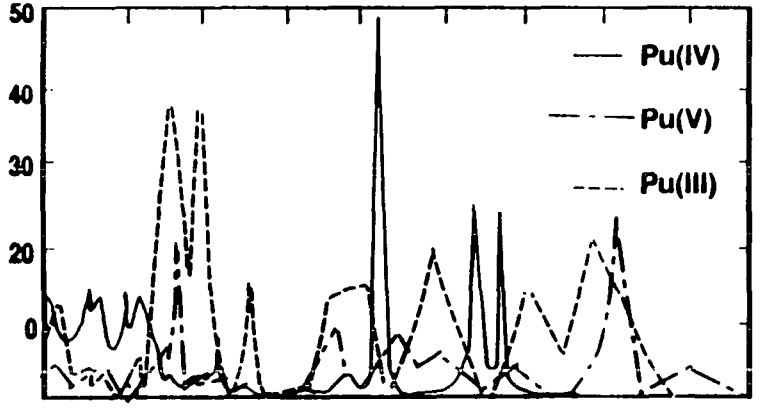
RADIOCOLLOID (SOL) FORMATION

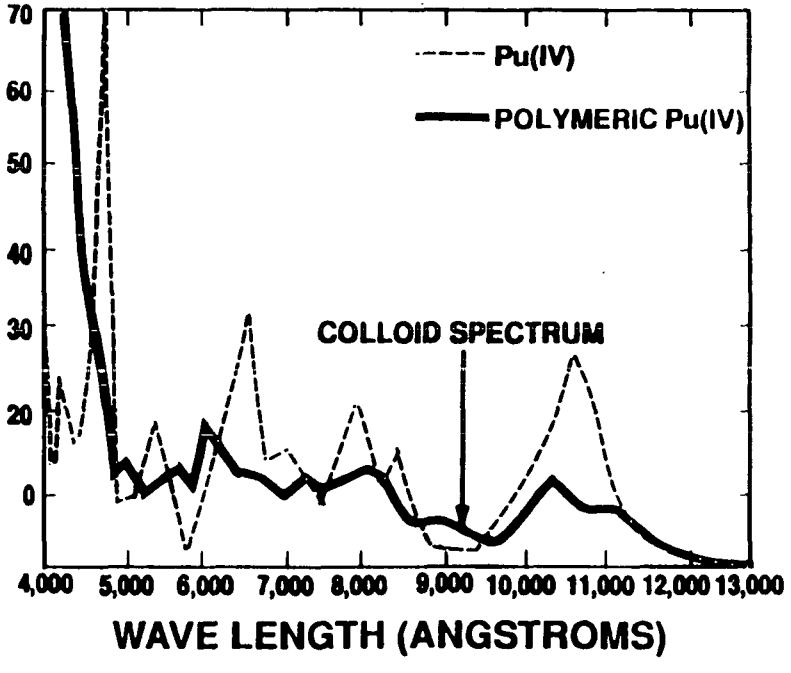
- THE FIRST STAGE IN SOL FORMATION IS THE HYDROLYSIS OF AQUO Pu(IV), WHICH FORMS MONOMERIC SPECIES SUCH AS $Pu(OH)^{3+}$, $Pu(OH)_2^{2+}$, $Pu(OH)_3^{+}$, AND $Pu(OH)_4^{0}$

- 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

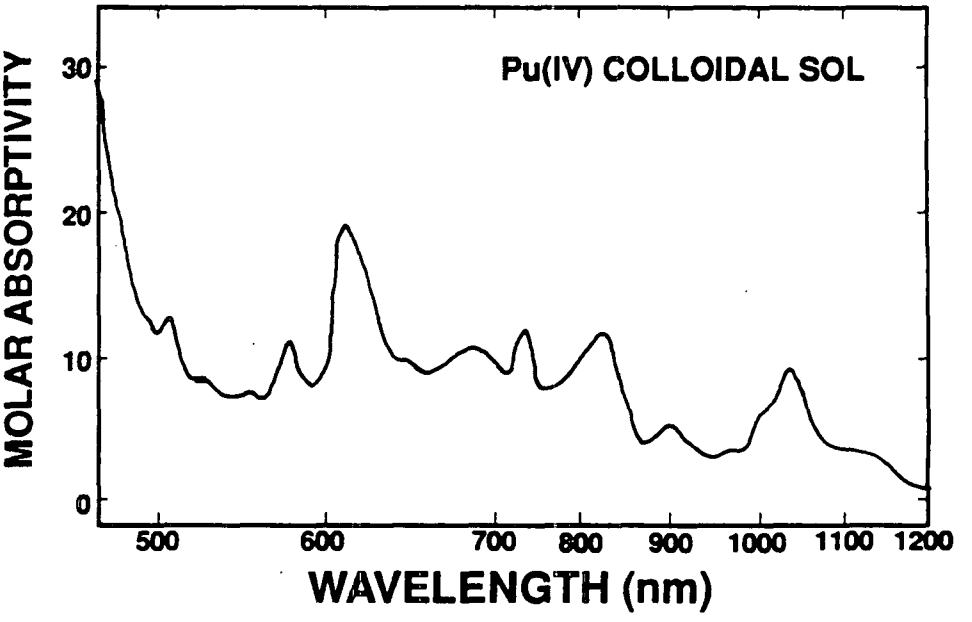
PLUTONIUM COLLOID CHARACTERIZATION

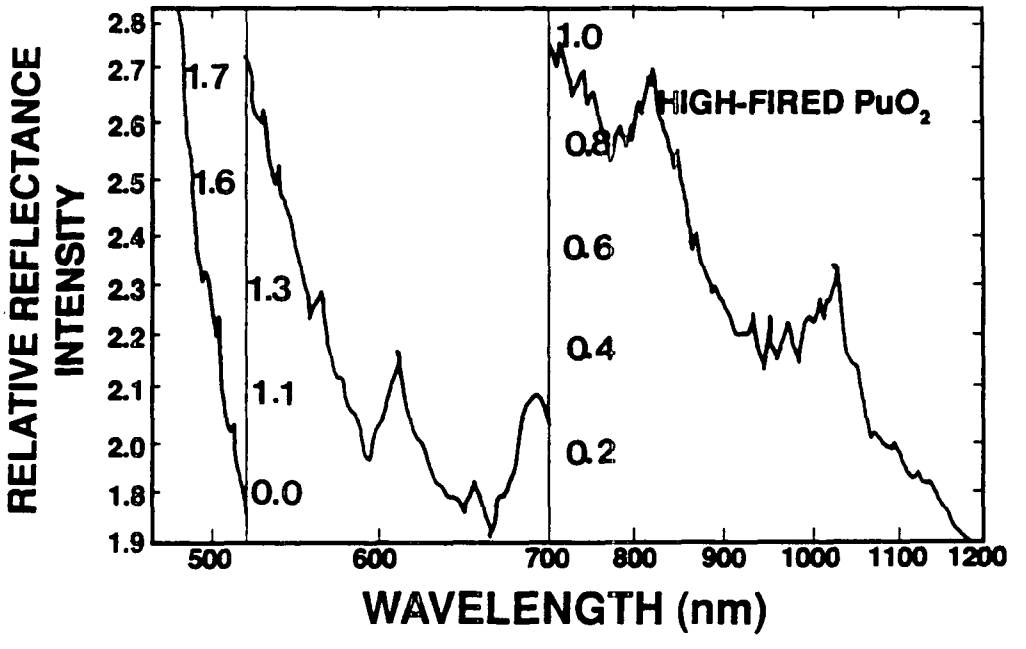




ABSORPTION SPECTRA OF PLUTONIUM (III), (IV), (V) AND (VI), AND POLYMERIC PLUTONIUM (IV)

COMPARISON OF SPECTRA FOR Pu(IV) COLLOID SOL AND HIGH-FIRED PuO_2



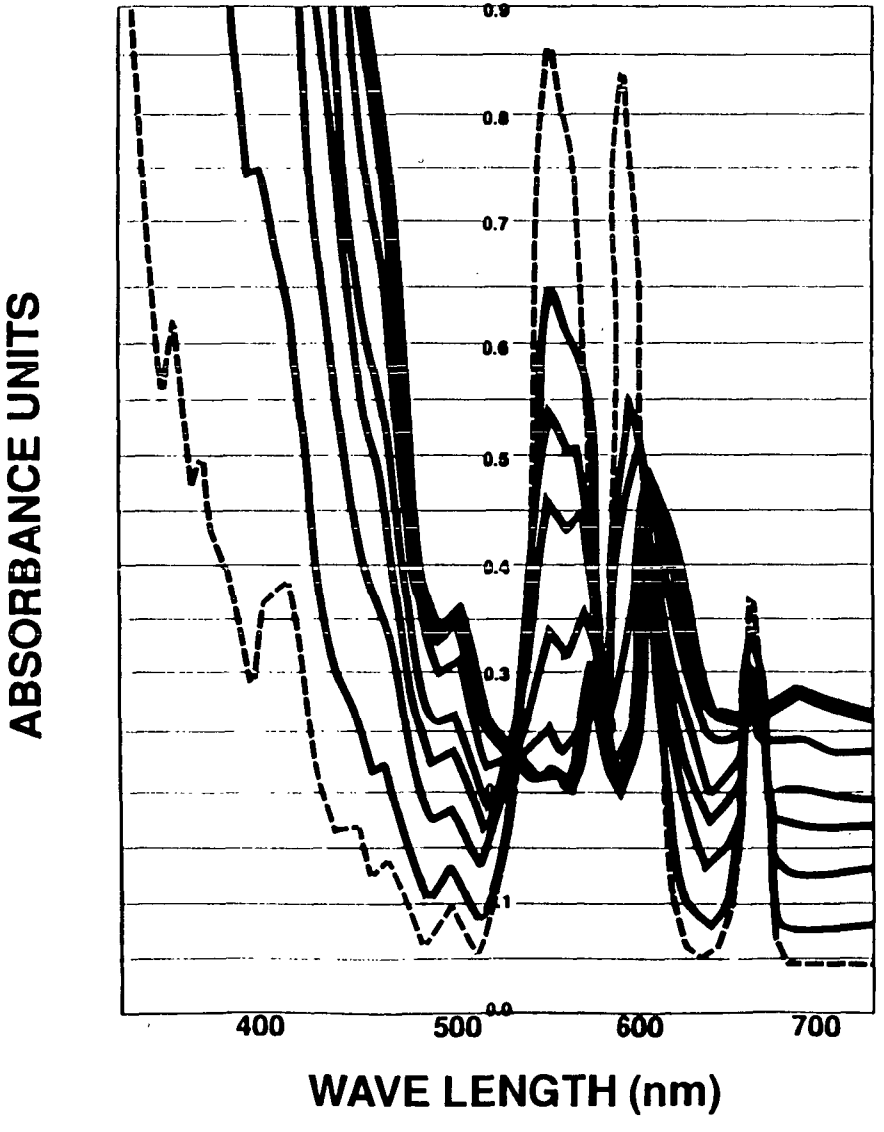


Pu(IV) COLLOID STABILITY (ELECTROCHEMISTRY)

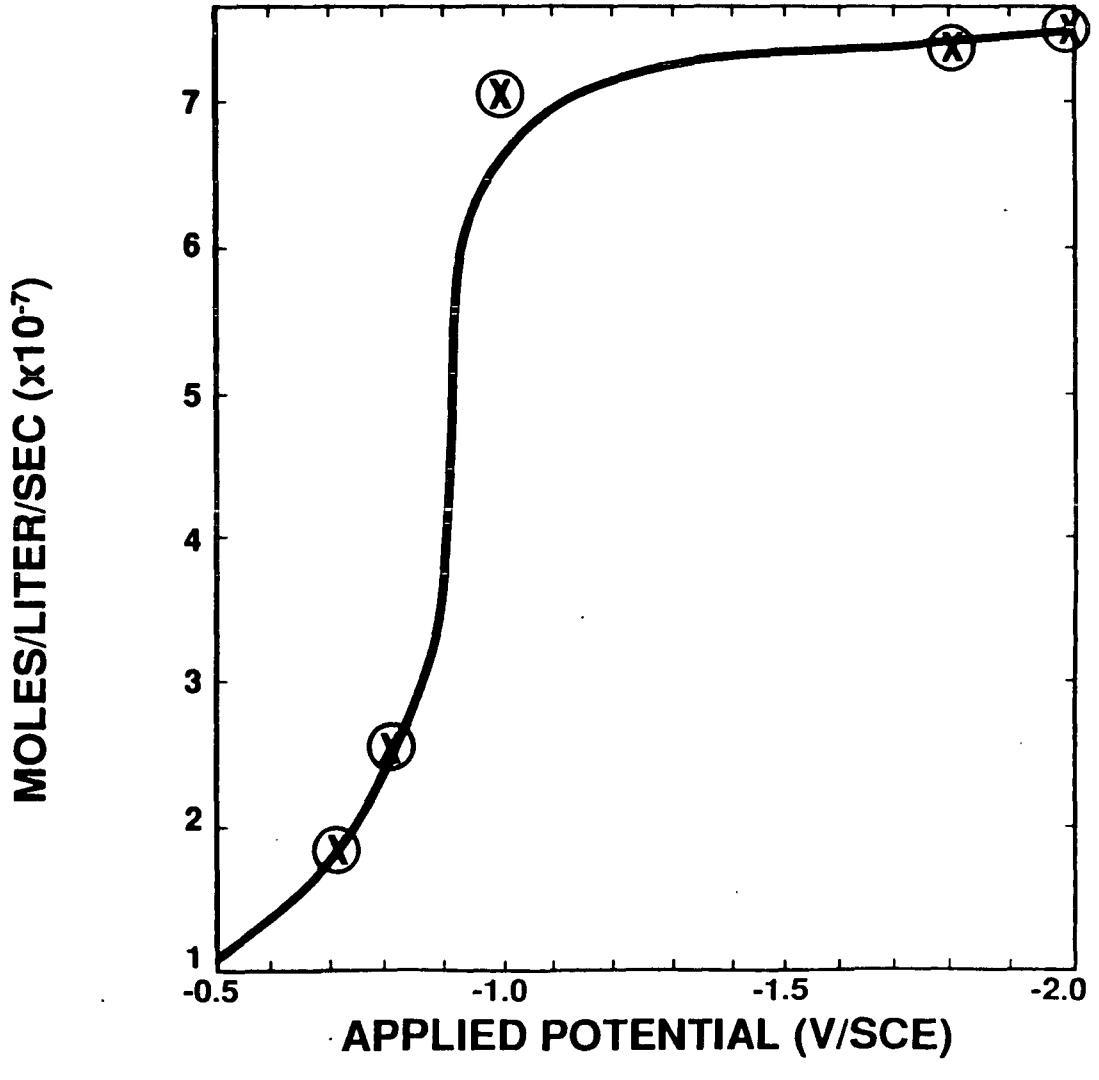
CONTROLLED POTENTIAL ELECTROCHEMICAL METHODS USED ON Pu(IV) COLLOID PROVIDED INFORMATION ON:

- 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 PuO_2

  IMPLICATIONS:

  - Pu(IV)-COLLOID IS OBSERVED IN GROUND WATER SOLUTIONS; IMPORTANT TO SORPTION AND TRANSPORT STUDIES
  - IN TIME, Pu(IV)-COLLOID MAY STABILIZE TO PuO_2; 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