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

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: THERMODYNAMIC DATABASE FOR THE SOURCE TERM

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Objectives

- Evaluate speciation (indication of migration fate) and solubility (upperbound of solution concentration) of waste actinides (Pu, Am, Np, U) under proposed repository groundwater conditions

For example, one can predict the concentration of the ion UO_2^{2+} in equilibrium with solid $UO_2(OH)_2 \cdot H_2O$ from the solubility constant,

$$UO_2(OH)_2 \cdot H_2O \text{ (solid)} + 2H^+ = UO_2^{2+}\ 3H_2O,\ \log K = 5.40$$

However, UO_2^{2+} is a minor solution component in the pH range of natural systems, and the formation constants for the following hydrolysis reactions are needed (Lemire and Tremaine, 1980):

$$UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$$
$$UO_2^{2+} + 2H_2O = UO_2(OH)_2^0 + 2H^+$$
$$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$$
$$3UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^+$$
$$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$$
$$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$$
$$4UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$$

All these equations must be solved simultaneously to calculate the concentrations of the individual solution species, since they can occur together in solution. In addition, if other solution complexes are present, they must be included. For example, if carbonate is present in the uranium system, reactions involving the carbonate complexes of uranyl must be included, i.e.,

$$UO_2^{2+} + CO_3^{2-} = UO_2CO_3^{o}$$

$$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$$

$$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$$

Priority List for the Determination of Thermodynamic Data for Waste Elements

Priority	Element	Priority	Element
1	Americium	2	Antimony
1	Plutonium	2	Selenium
1	Neptunium	2	Cesium
1	Uranium		
1	Technetium	3	Palladium
1	Zirconium	3	Curium
1	Nickel	3	Iodine
		3	Molybdenum
2	Carbon	3	Thorium
2	Niobium		
2	Tin		

1. Top Priority. Will need thermodynamic data
2. Second priority. Will probably need some thermodynamic data
3. Third Priority. Probably will not need further thermodynamic data

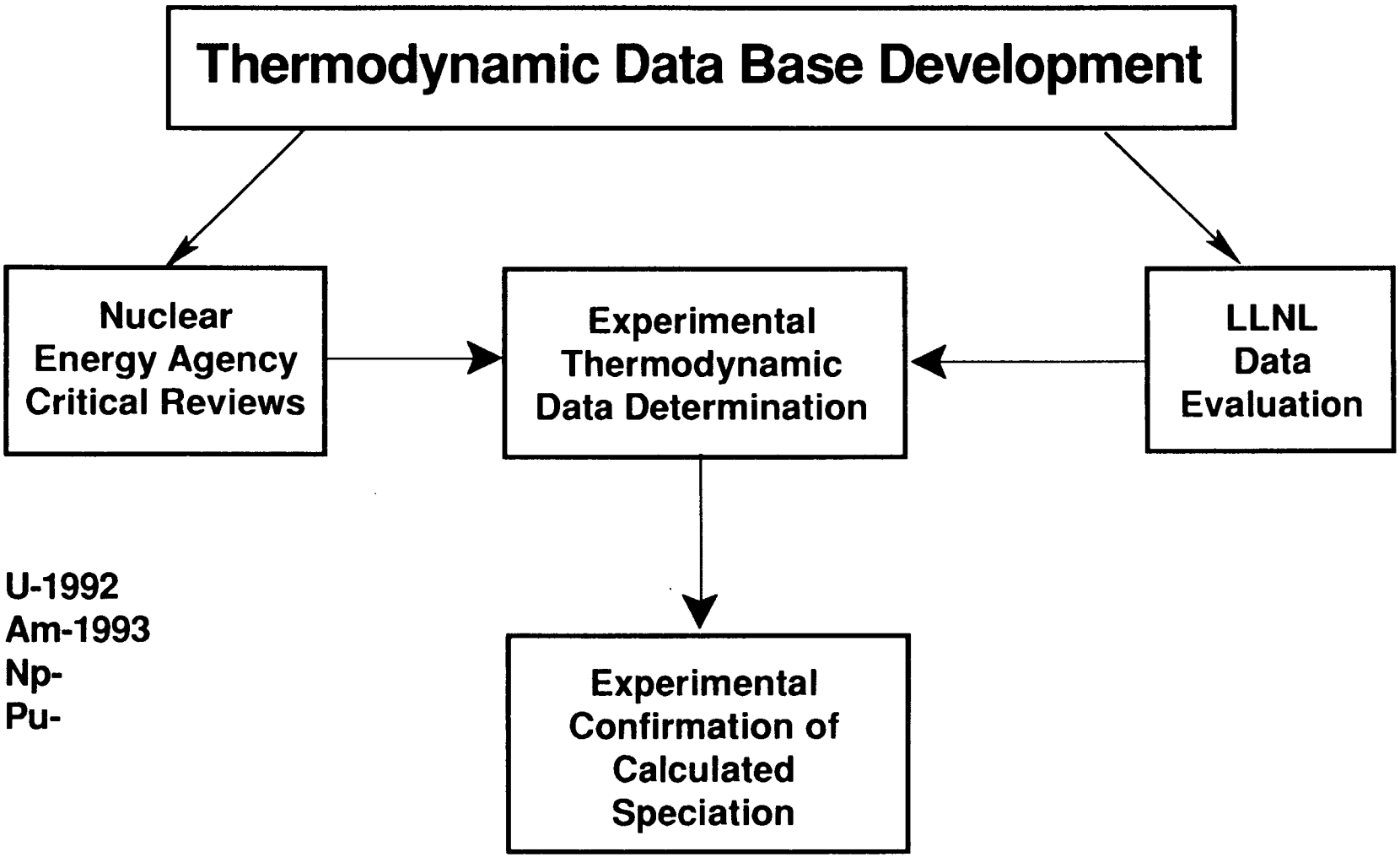
Solids and Complexes

- Hydroxide
- Carbonate
- Silicate
- Fluoride
- Sulfate
- Phosphate
- Chloride
- Nitrate

Solution Parameters

- pH
- Eh
- Temperature
- Ionic Strength
- Water Composition

Strategy



U-1992
Am-1993
Np-
Pu-

Phase 1: Thermodynamic Data Review

Review data base for experimentally determined thermodynamic values

- 25°C
- J-13 groundwater ions
- Oxidation states

J-13 Well Water Values (Initial Conditions)

Fluoride	2.1 mg/L
Chloride	6.4 mg/L
Sulfate	18.1 mg/L
Bicarbonate	143.0 mg/L
Nitrate	10.1 mg/L
Oxygen	5.7 mg/L
Phosphate	118.7 ug/L
pH	6.9
Actinide	1e-5 M

Log β for Reaction of Radionuclide (+3 State) with J13 Groundwater Ligand

Species	# Ligands	Ligand								
		OH^-	F^-	Cl^-	NO_3^-	$H_2PO_4^-$	CO_3^{--}	SO_4^{--}	HPO_4^{--}	PO_4^{---}
Am^{+++}	1	7.97	3.73	1.13	1.41	2.68	7.90	3.93		
Np^{+++}	1	7.19				2.39				
Pu^{+++}	1	8.51		0.98	1.09	2.68		3.78		
U^{+++}	1									
Am^{+++}	2	11.98	7.83	0.82	1.92	3.98	12.20	5.45		
Np^{+++}	2					3.73				
Pu^{+++}	2				2.22	4.08		6.32		
U^{+++}	2									
Am^{+++}	3	18.08	11.08			4.99	12.70			
Np^{+++}	3					5.64				
Pu^{+++}	3				2.52	5.04				
U^{+++}	3									
Am^{+++}	4					5.55				
Np^{+++}	4									
Pu^{+++}	4					5.65				
U^{+++}	4									

Log β for Reaction of Radionuclide (+4 State) with J13 Groundwater Ligand

Species	# Ligands	Ligand								
		OH^-	F^-	Cl^-	NO_3^-	$H_2PO_4^-$	CO_3^{--}	SO_4^{--}	HPO_4^{--}	PO_4^{---}
Am^{++++}	1									
Np^{++++}	1	12.95	8.68	1.15	1.50			6.58		
Pu^{++++}	1	13.67	8.45	1.62	1.87	4.92	12.30	6.76	16.00	
U^{++++}	1	13.45	9.24	1.71	1.45			6.40		
Am^{++++}	2									
Np^{++++}	2		15.70	1.68	2.31			9.79		
Pu^{++++}	2	28.20	15.82	2.16	3.36	8.30	23.35	10.36	28.13	
U^{++++}	2		16.03		2.26			10.26		
Am^{++++}	3									
Np^{++++}	3		21.36	2.41	3.51					
Pu^{++++}	3	38.85	20.70	0.09	3.15		30.00	8.30	37.90	
U^{++++}	3		21.06							
Am^{++++}	4									
Np^{++++}	4		25.25		2.75					
Pu^{++++}	4	49.02	25.00			13.85	33.00		45.65	
U^{++++}	4	51.45	25.29				32.82			
Am^{++++}	5									
Np^{++++}	5									
Pu^{++++}	5	53.80					34.00		48.60	
U^{++++}	5	54.42	26.83				33.90			
Am^{++++}	6									
Np^{++++}	6									
Pu^{++++}	6									
U^{++++}	6		28.86							

Phase 1: Findings

- Good shape for solution species--
  (except silicates and phosphates--need data)
- Solubilities need continued effort
- Experimental efforts continue in U.S. and internationally
- NEA Critical Reviews--internally consistent data sets for U, Am, Pu, Np (not guaranteed to be complete)
  - U in data base
  - Am ready for addition to data base
  - Pu, Np draft reviews forthcoming

Phase II: Data Evaluation at 25°C

- Evaluate sensitivity of speciation (solubility) to
  - Thermodynamic constants
  - Anion concentration
- Evaluate quality of thermodynamic data base
  - Internal consistency
  - Estimates of "missing" data
    - ionic charge
    - ionic radius
- Calculate speciation of actinides as function of anion concentration, pH
- Identify important species (oxidation state, anions)

Log β for Reaction of Radionuclide (+3 State) with J13 Groundwater Ligand

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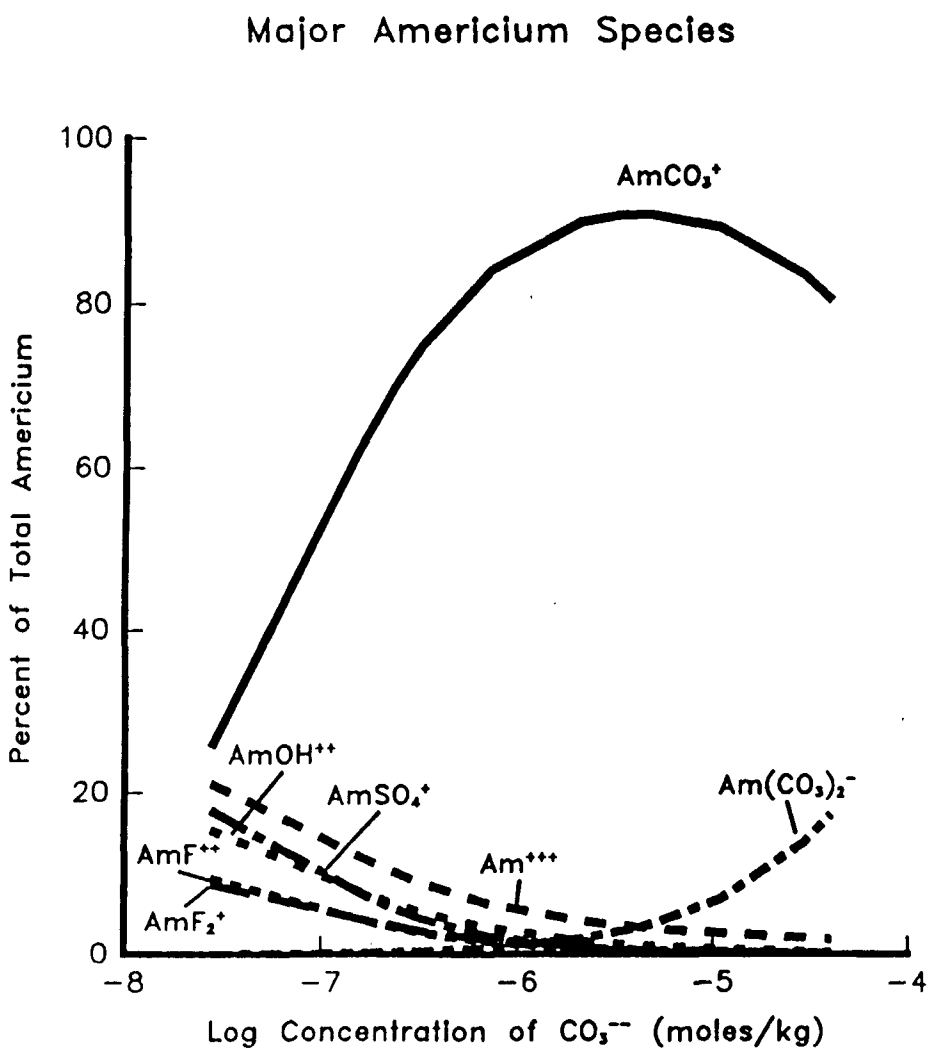
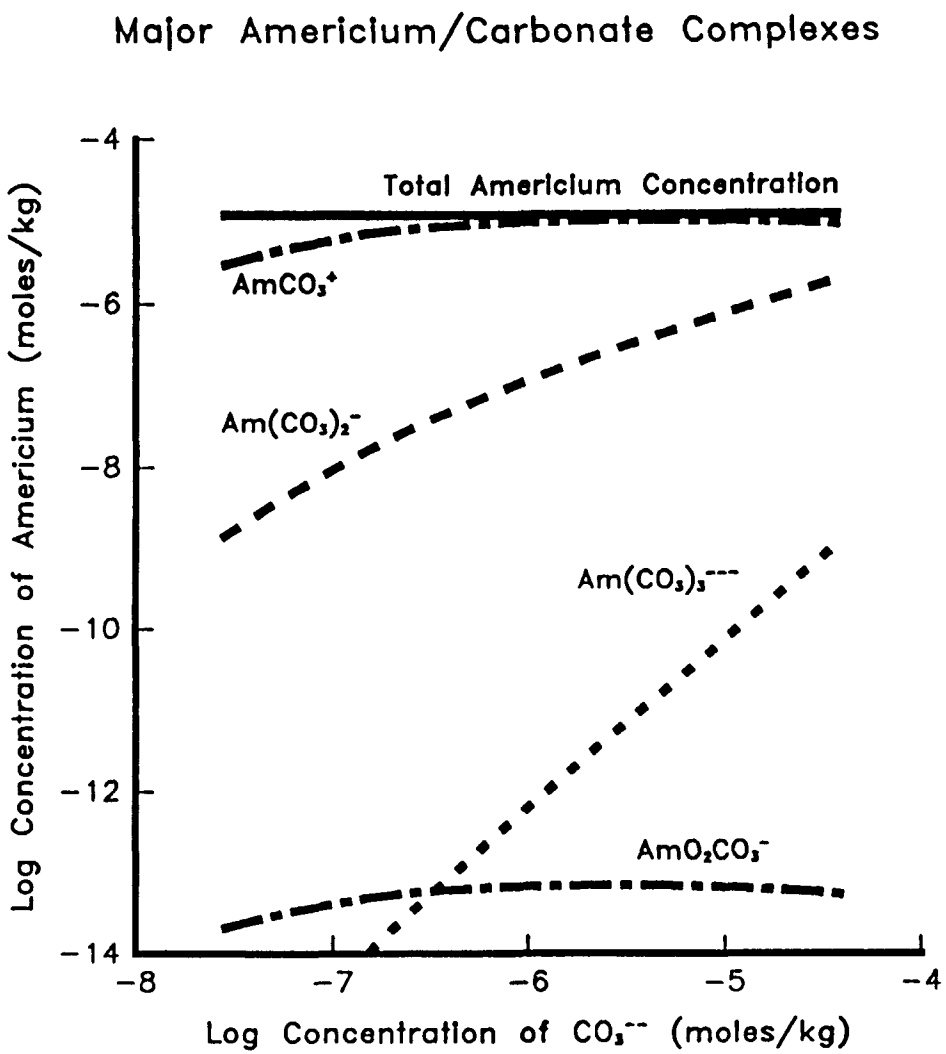
U^{+++}	2	11.98	7.83	0.82	1.92	3.98	12.20	5.45		
Am^{+++}	3	18.08	11.08		2.52	4.99	12.70			
Np^{+++}	3	18.08	11.08		2.52	5.64	12.70			
Pu^{+++}	3	18.08	11.08		2.52	5.04	12.70			
U^{+++}	3	18.08	11.08		2.52	4.99	12.70			
Am^{+++}	4					5.55				
Np^{+++}	4					5.55				
Pu^{+++}	4					5.65				
U^{+++}	4					5.55				

Americium Species as Function of CO_3^{--} Concentration
pH = 5.9





Phase II: Findings (Speciation Only, 25°C)

- Carbonate formation and hydrolysis dominate the chemistry under J-13 conditions at 25°C. Thermodynamic data primarily experimentally determined
- Phosphate/hydrogen phosphate complexes appear to compete with carbonate formation and hydrolysis. Experimental work needed to determine formation constants
- Silicates not addressed in this work because no experimental data exists. Experimental work required
- Cl^-, F^-, $SO_4^=$, NO_3^- not significant species, even at anion concentrations much greater than J-13 well water. Estimates provide adequate information. No further experimental work recommended
- Update analysis incorporating solid phases

Phase III: Repository Conditions

- To understand speciation and solubilities near the waste package, we need thermodynamic values at elevated temperatures
- Iterate on previously described (25°C) process
- Little experimentally determined thermodynamic data at elevated temperatures

Phase III: Recommendations

- Begin thermodynamic measurements at elevated temperatures
  - initially focus on $CO_3^{=}$, OH^-
  - able to do photoacoustic spectroscopy at 60, 90°C
- Initiate solubility measurements at elevated temperatures using J-13 well water (modified), coordinate with H. Nitsche to investigate solid phases