Status and Priorities Regarding Sorption of Long-Lived Radionuclides

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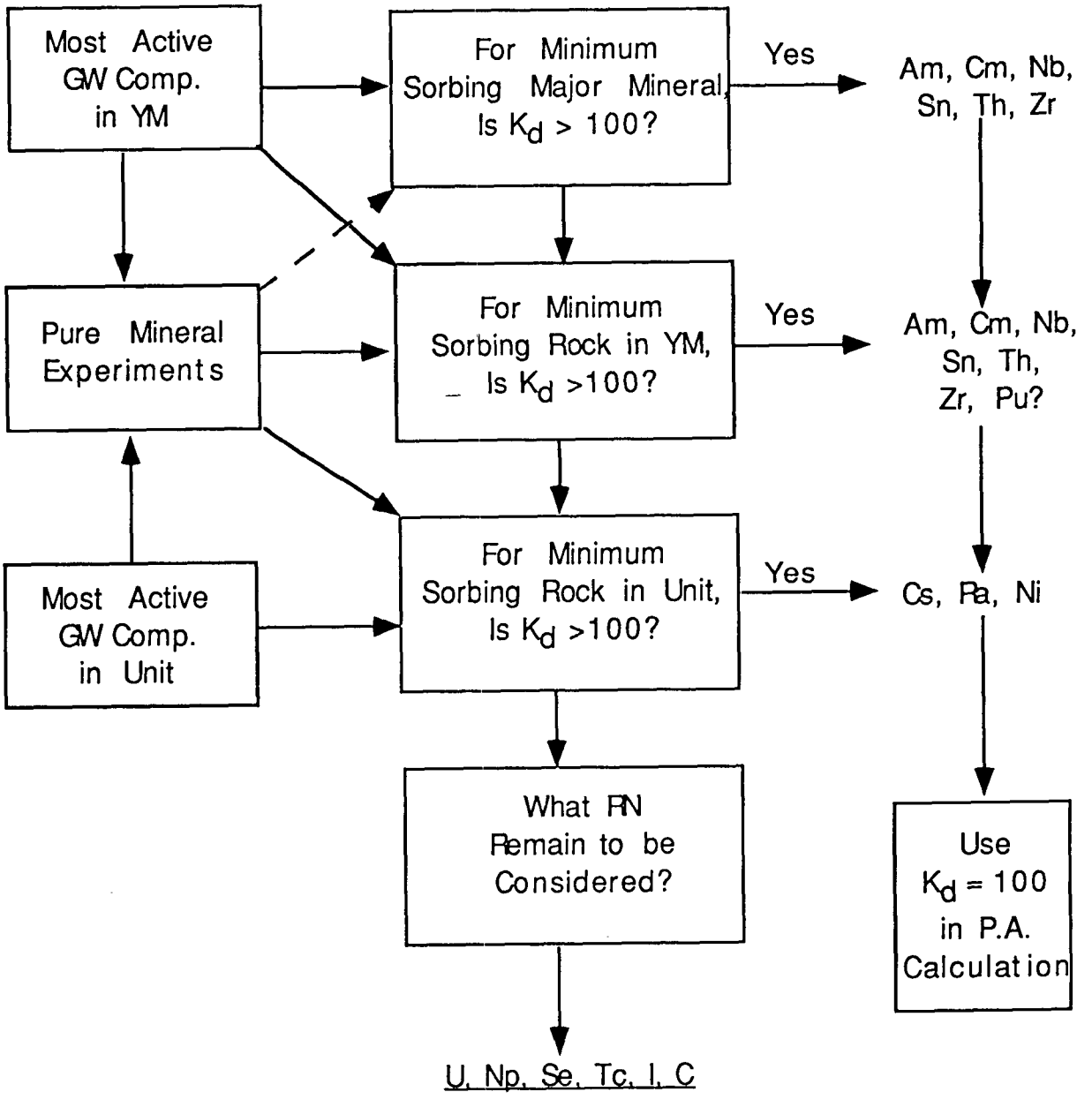
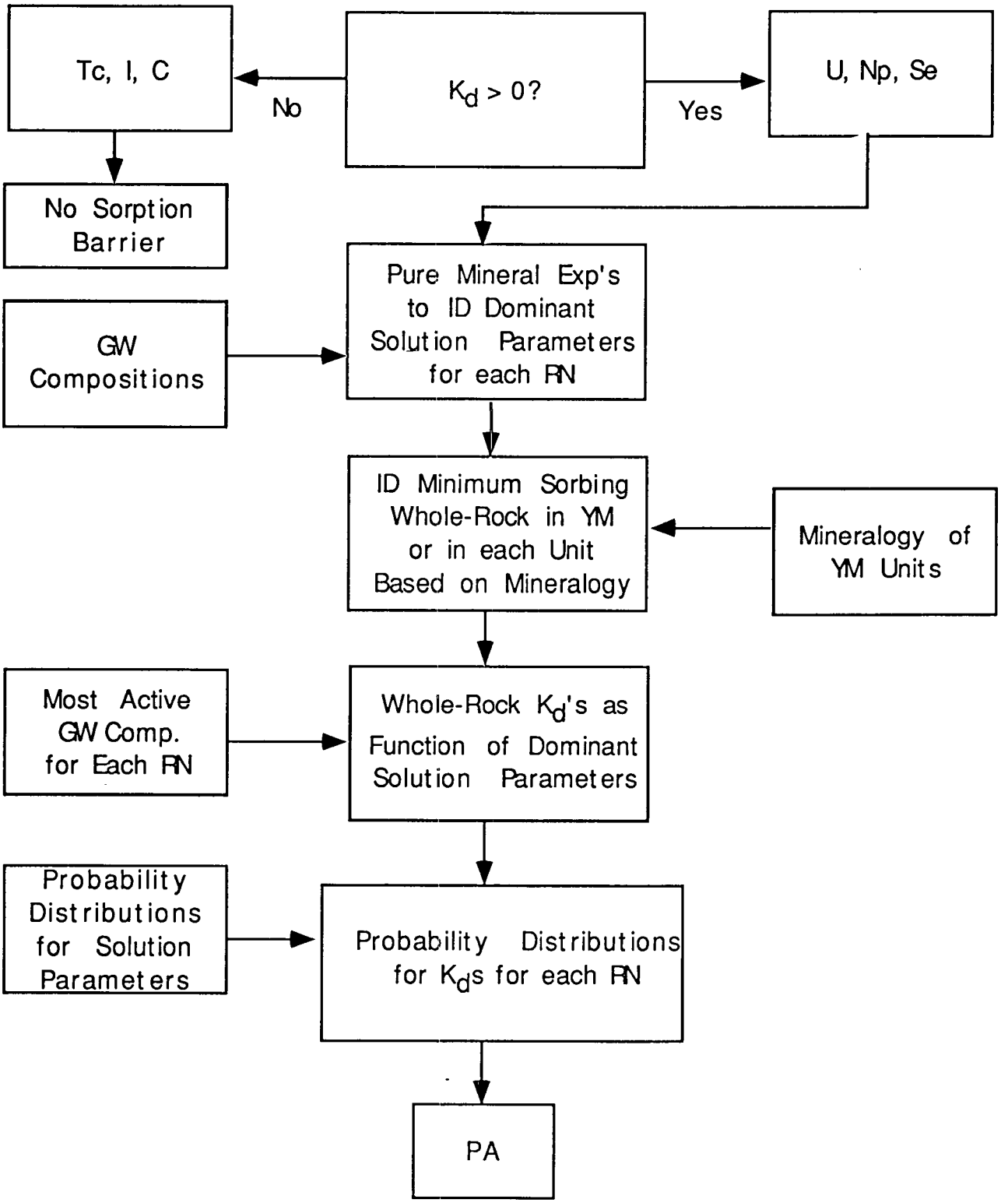
LANL

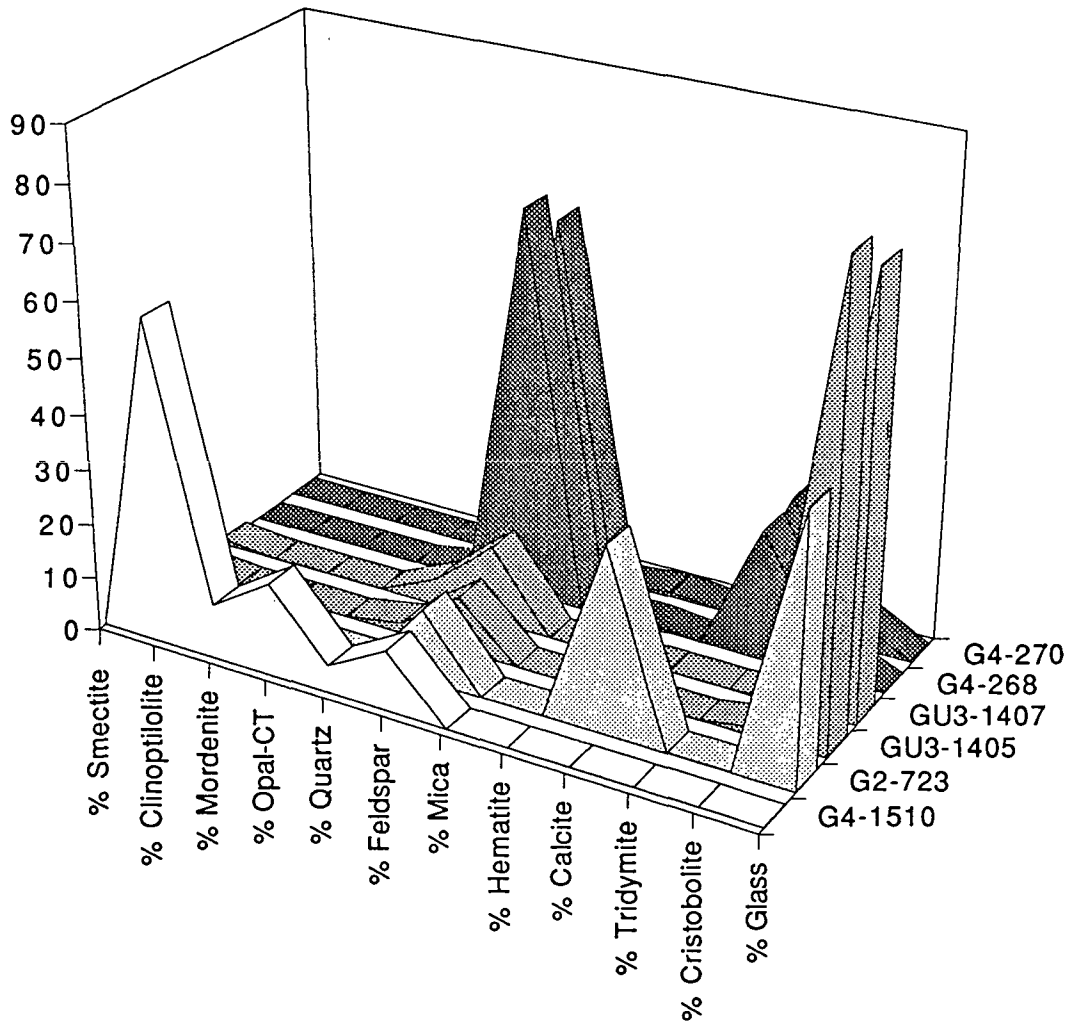
MINIMUM K_d STRATEGY



STRATEGY FOR "POORLY SORBING" RN (i.e., U, Se, Np, Tc, I, C)



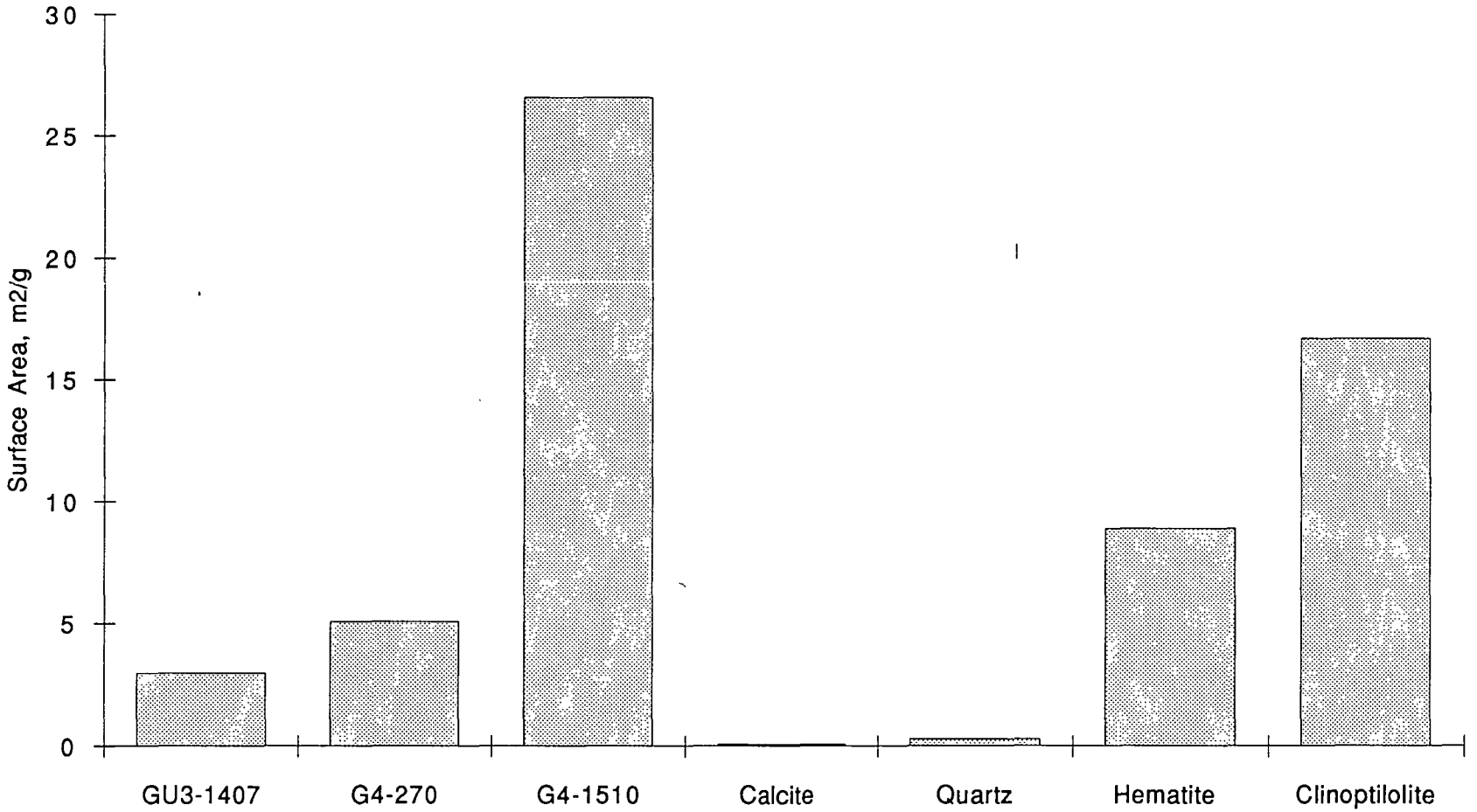
Mineralogy of Tuff Samples



XRD Data Plotted for Tuffs Wet Sieved with J-13 (if available); G2-723 Dry Sieved; GU3-1405 Not Ground

Surface Area of Tuffs and Minerals

BET Data Plotted for Wet-Sieved Samples; Hematite and Clinoptilolite Not Sieved



XRD and BET Results

Tuff or Mineral	Sieving Information	Groundwater used for sieving	Particle size (if ground and sieved) in micrometers	Surface Area, m2/g	% Smectite	% Clinoptilolite
USW G2-723	Dry	N/A	75 - 500		4 ± 1	0
USW G4-268	Not Ground	N/A	N/A		0	0
USW G4-268	Wet	J-13	75 - 500		0	0
USW G4-270	Not Ground	N/A	N/A	2.0	Trace	0
USW G4-270	Dry	N/A	75 - 500	6.4	0	0
USW G4-270	Wet	J-13	75 - 500	5.1	0	0
USW G4-270	Wet	UE-25 p#1	75 - 500	5.0	0	0
USW G4-1510	Wet	J-13	75 - 500	26.6	1 ± 1	59 ± 7
USW GU3-1405	Not Ground	N/A	N/A		1 ± 1	0
USW GU3-1407	Not Ground	N/A	N/A	1.7	1 ± 1	0
USW GU3-1407	Dry	N/A	75 - 500	3.3	1 ± 1	0
USW GU3-1407	Wet	J-13	75 - 500	3.0	1 ± 1	0
USW GU3-1407	Wet	UE-25 p#1	75 - 500	3.2	1 ± 1	0
Calcite	Dry	N/A	75 - 500	0.6	0	0
Calcite	Wet	J-13	75 - 500	0.1	0	0
Calcite	Wet	UE-25 p#1	75 - 500	0.1	0	0
Synthetic Hematite	Not Sieved	N/A	N/A	8.9	0	0
Montmorillonite	Dry	N/A	75 - 500		95+	0
Purified Clinoptilolite	Not Sieved	N/A	N/A	16.7	0	95+
Quartz	Dry	N/A	75 - 500	0.2	0	0
Quartz	Wet	J-13	75 - 500	0.3	0	0
Quartz	Wet	UE-25 p#1	75 - 500	0.4	0	0
Albite	Not Ground	N/A	N/A		0	0

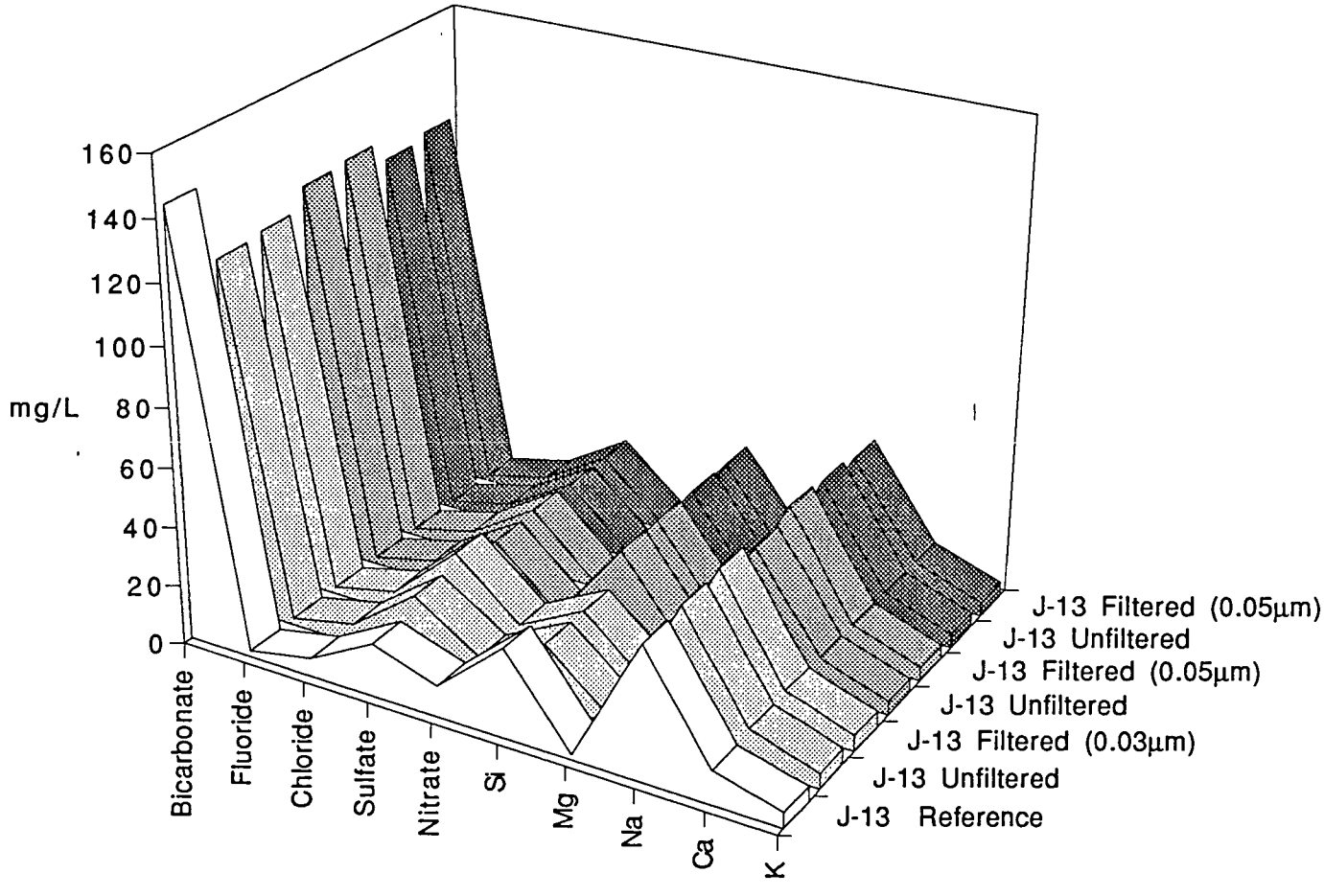
XRD and BET Results

Tuff or Mineral	% Mordenite	% Opal-CT	% Quartz	% Feldspar	% Mica	% Hematite	% Calcite
USW G2-723	0	0	Trace	13 ± 2	Trace	0	34 ± 2
USW G4-268	0	0	1 ± 1	69 ± 10	Trace	1 ± 1	0
USW G4-268	0	0	2 ± 1	71 ± 10	Trace	1 ± 1	0
USW G4-270	0	0	0	66 ± 16	Trace	1 ± 1	0
USW G4-270	0	0	0	64 ± 16	Trace	1 ± 1	0
USW G4-270	0	0	0	65 ± 16	Trace	1 ± 1	0
USW G4-270	0	0	0	65 ± 16	Trace	1 ± 1	0
USW G4-1510	10 ± 3	17 ± 4	5 ± 1	11 ± 3	0	0	0
USW GU3-1405	0	0	2 ± 1	10 ± 1	0	Trace	0
USW GU3-1407	0	0	5 ± 1	11 ± 2	Trace	0	0
USW GU3-1407	0	0	4 ± 1	14 ± 2	Trace	Trace	0
USW GU3-1407	0	0	5 ± 1	14 ± 2	Trace	0	0
USW GU3-1407	0	0	5 ± 1	11 ± 2	Trace	0	0
Calcite	0	0	0	0	0	0	100
Calcite	0	0	0	0	0	0	100
Calcite	0	0	0	0	0	0	100
Synthetic Hematite	0	0	0	0	0	100	0
Montmorillonite	0	0	Trace	Trace	0	0	0
Purified Clinoptilolite	0	0	0	0	0	0	0
Quartz	0	0	100	0	0	0	0
Quartz	0	0	100	0	0	0	0
Quartz	0	0	100	0	0	0	0
Albite	0	0	0	95	Trace	0	0

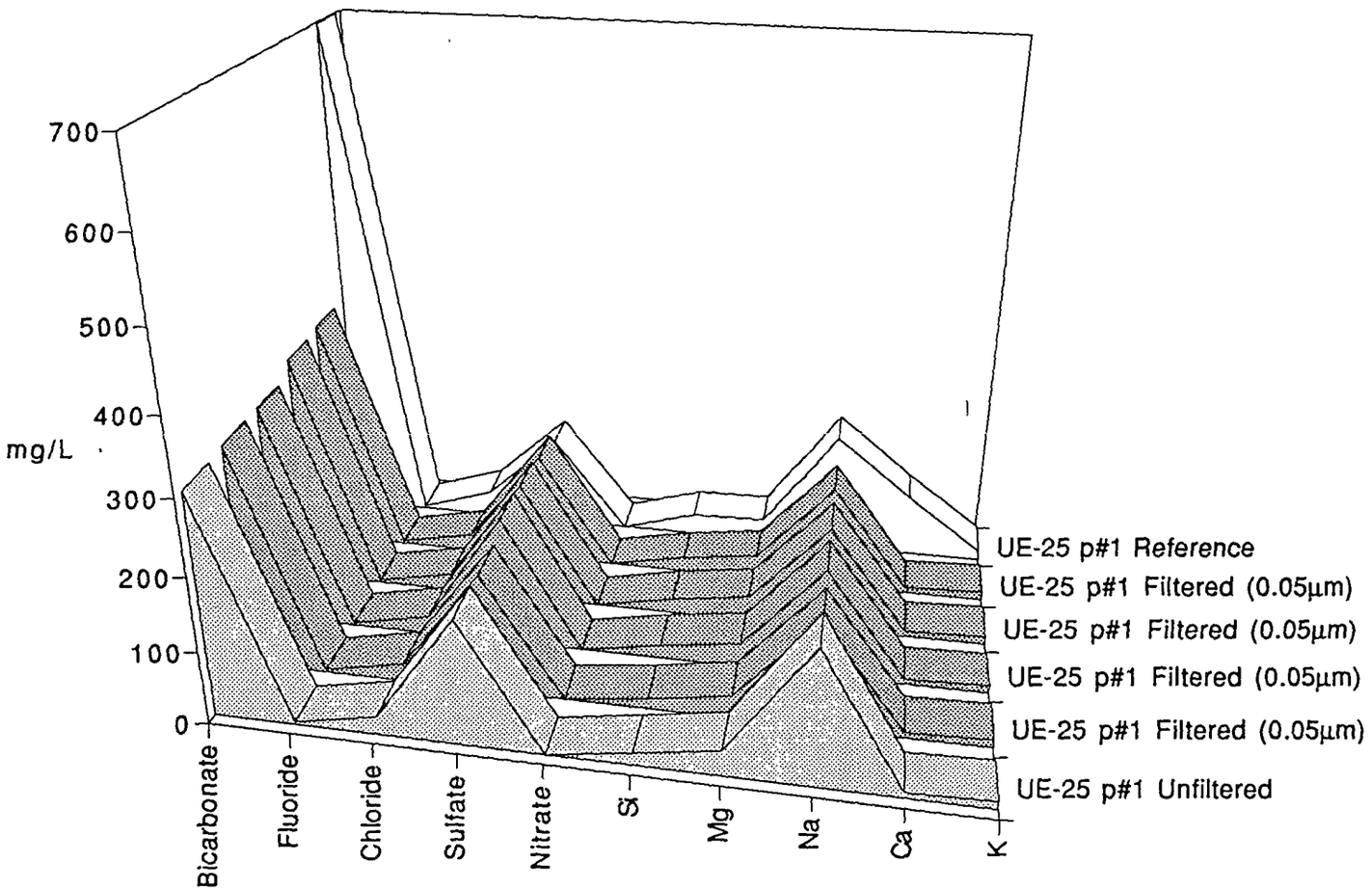
XRD and BET Results

Tuff or Mineral	% Tridymite	% Cristobolite	% Glass
USW G2-723	0	Trace	49 ± 3
USW G4-268	24 ± 2	4 ± 2	0
USW G4-268	24 ± 2	5 ± 3	0
USW G4-270	25 ± 3	7 ± 4	0
USW G4-270	25 ± 2	7 ± 3	0
USW G4-270	25 ± 3	6 ± 3	0
USW G4-270	26 ± 3	7 ± 4	0
USW G4-1510	0	0	0
USW GU3-1405	0	2 ± 1	85 ± 2
USW GU3-1407	0	2 ± 1	81 ± 2
USW GU3-1407	0	1 ± 1	80 ± 2
USW GU3-1407	0	1 ± 1	79 ± 2
USW GU3-1407	0	2 ± 1	81 ± 2
Calcite	0	0	0
Calcite	0	0	0
Calcite	0	0	0
Synthetic Hematite	0	0	0
Montmorillonite	0	0	0
Purified Clinoptilolite	0	0	0
Quartz	0	0	0
Quartz	0	0	0
Quartz	0	0	0
Albite	0	0	0

Chemical Analysis of J-13



Chemical Analysis of UE-25 p#1 Water



J-13 and UE-25 p#1 Chemical Analysis

mg/L	J-13 Unfiltered (Analyzed at Site)	J-13 SPC00007994 Unfiltered	J-13 SPC00007994 Filtered	J-13 SPC00007995 Unfiltered	J-13 SPC00007995 Filtered	J-13 SPC00007996 Unfiltered	J-13 SPC00007996 Filtered
Si	30	20	20	23	23	29.8	29.8
Al	0.03	<0.1	<0.1	<0.3	<0.3	<0.15	<0.15
Fe	0.04	<0.01	<0.01	<0.1	<0.1	<0.4	<0.4
Mn	0.001	<0.01	<0.01	<0.1	<0.1	<0.01	<0.01
Mg	1.76	1.7	1.6	1.7	1.6	1.92	1.95
Ca	11.5	12.8	13.3	12.7	12.3	12.7	12.7
Na	45	46	47	46	47	43.5	47
K	5.3	5.2	5.4	4.4	4.4	4.62	4.66
Cs		<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Li	0.06	0.044	0.043	<0.04	0.04	0.46	0.05
Carbonate		2.5	1.5		1.57	<0.1	<0.1
Bicarbonate	143	118	119		121	126	127
Fluoride	2.1	2.25	2.2	2.2	2.3	2.3	2.4
Chloride	6.4	6.9	7.2	5.7	7.7	7.4	7.6
Sulfate	18.1	23	27	15	17	20.6	21.4
Nitrate	10.7	9	8.6	15	7.5	1.5	1.7
TOC		0.44	0.58		0.47	1.62	1.1
pH	6.9	8.5	8.4		8.5	8.0	7.8
Date Collected	1984	4/27/92	4/27/92	4/27/92	4/27/92	4/27/92	4/27/92
Date Filtered	N/A	N/A	5/8/92	N/A	5/8/92	N/A	2/24/93
Filter Size, µm	N/A	N/A	0.03µm	N/A	0.03µm	N/A	0.05µm

J-13 and UE-25 p#1 Chemical Analysis

mg/L	J-13 SPC00100297 Unfiltered	J-13 SPC00100297 Filtered	UE-25 p#1 Unfiltered (Analyzed at Site)	UE-25 p#1 Unfiltered	UE-25 p#1 Filtered	UE-25 p#1 Filtered	UE-25 p#1 Filtered	UE-25 p#1 Filtered
Si	30	29.8	30	17	14.1	19	20.4	20.8
Al	<0.15	<0.15	0.1	<0.3	<0.3	<0.3	<0.15	<0.15
Fe	<0.4	<0.4	<0.1	<0.1	<0.05	<0.1	1.2	0.54
Mn	<0.01	<0.01	<0.1	<0.1	<0.01	<0.1	0.075	<0.01
Mg	1.9	1.92	31.9	34.6	32	34	35.6	35.1
Ca	12.6	12.6	87.8	7	8	7.2	7.4	7.5
Na	45.5	43.5	171	184	148	151	147	147
K	4.62	4.56	13.4	10.7	11.2	10.3	11.9	11.9
Cs	<0.2	<0.2		<0.2	<0.2	<0.2	<0.2	<0.2
Li	0.044	0.044	0.32	0.41	0.5	0.4	0.54	0.54
Carbonate	<0.1	<0.1		28.7	30.5	23.2	17.3	15.3
Bicarbonate	120	122	698	299	303	302	320	324
Fluoride	2.3	2.3	3.5	4	4	4	4.3	4.1
Chloride	7.4	7.3	37	24	25	25	23.8	24.8
Sulfate	20.4	20.5	129	170	162	178	168	156
Nitrate	1.4	1.5	<0.1	0.11	0.5	0.06	<0.1	<0.1
TOC	1.67	0.85		0.96	1.89		2.51	1.43
pH	7.9	7.8	6.7	9.0	9.0	9.0	8.7	8.6
Date Collected	7/8/93	7/8/93	N/A	N/A	N/A	N/A	N/A	N/A
Date Filtered	N/A	8/4/93	N/A	N/A	7/20/83	7/20/83	7/20/83	2/24/93
Filter Size, µm	N/A	0.05µm	N/A	N/A	0.05µm	0.05µm	0.05µm	0.05µm

Batch Sorption Experimental Procedure

Pre-treatment Step

- 1g of solid equilibrated with 20 ml of groundwater
- Phases separated by centrifugation

Sorption Step

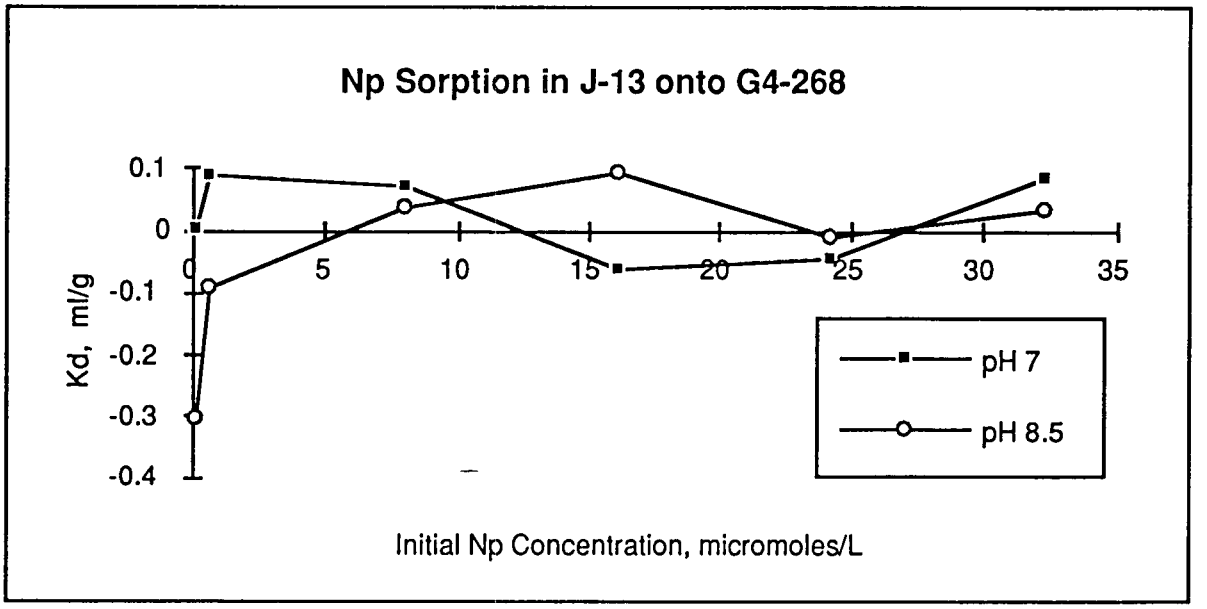
- Pre-treated solid equilibrated with 20 ml of solution containing radionuclide
- Phases separated by centrifugation
- Amount of radionuclides in liquid phase determined by radioanalytical techniques
- Amount of radionuclide in solid phase calculated by difference

Controls

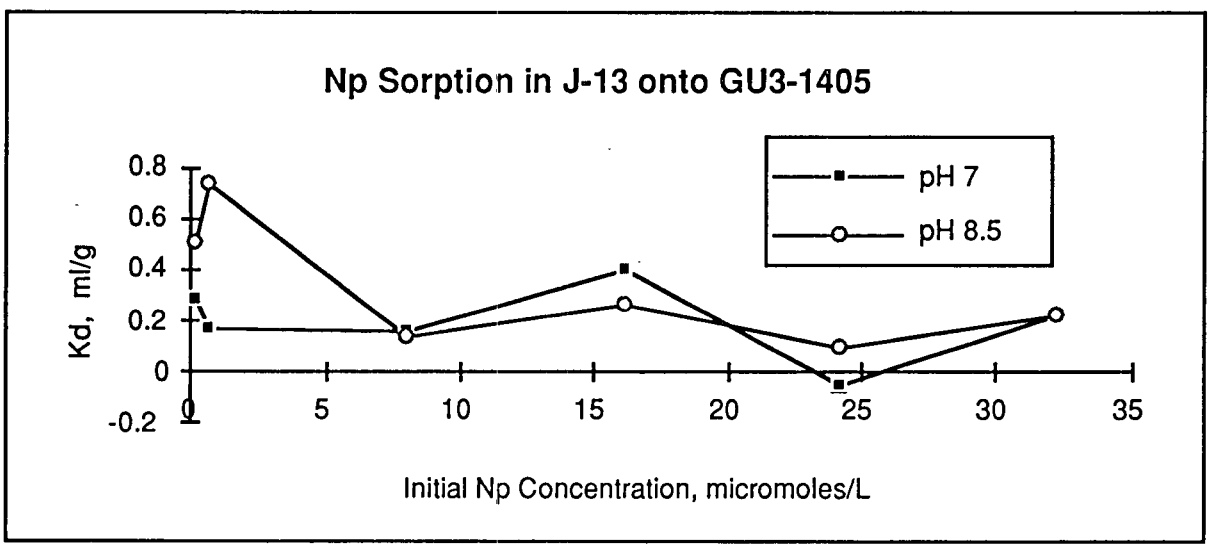
- Containers without solid phases utilized to monitor radionuclide precipitation and/or sorption onto walls

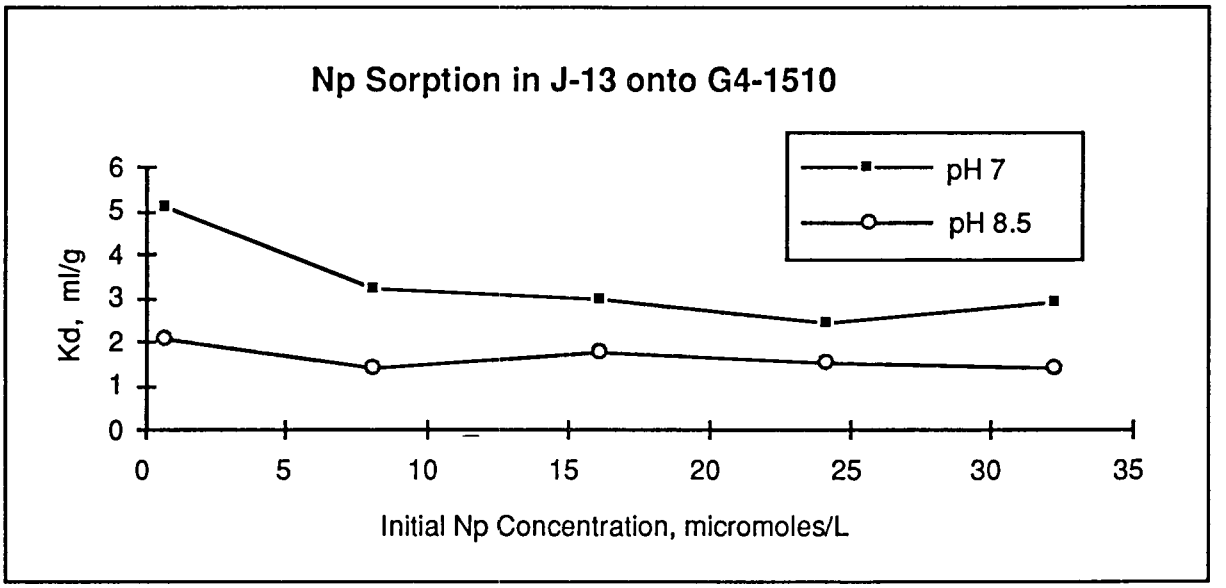
Definition of Batch Sorption Distribution Coefficients, K_d

$$K_d = \frac{\text{moles of radionuclide per g of solid phase}}{\text{moles of radionuclide per ml of solution}}$$

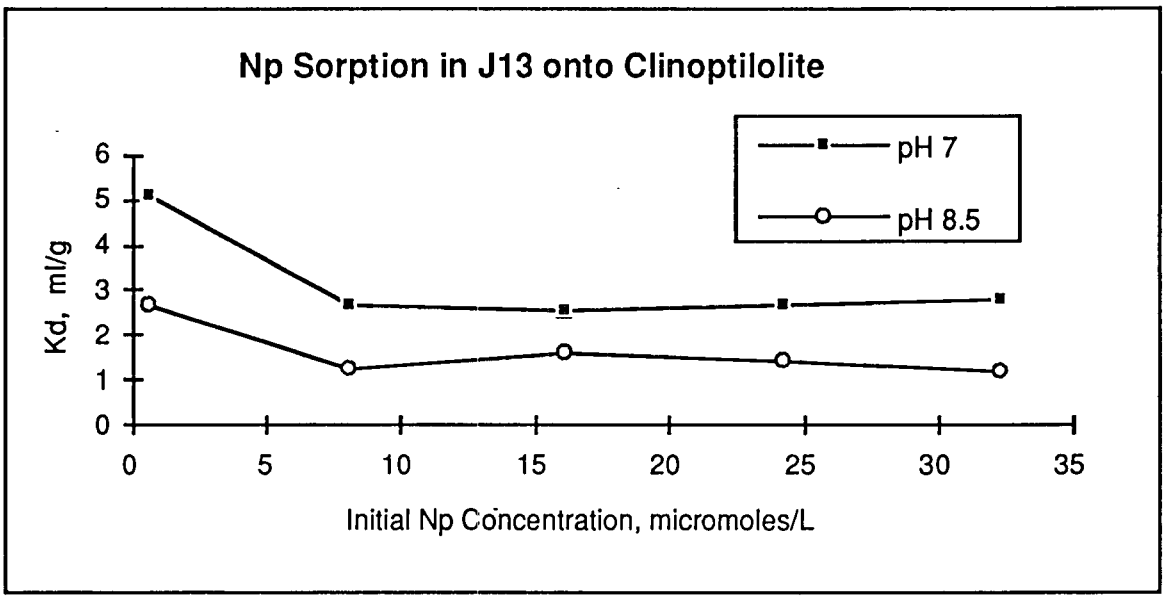


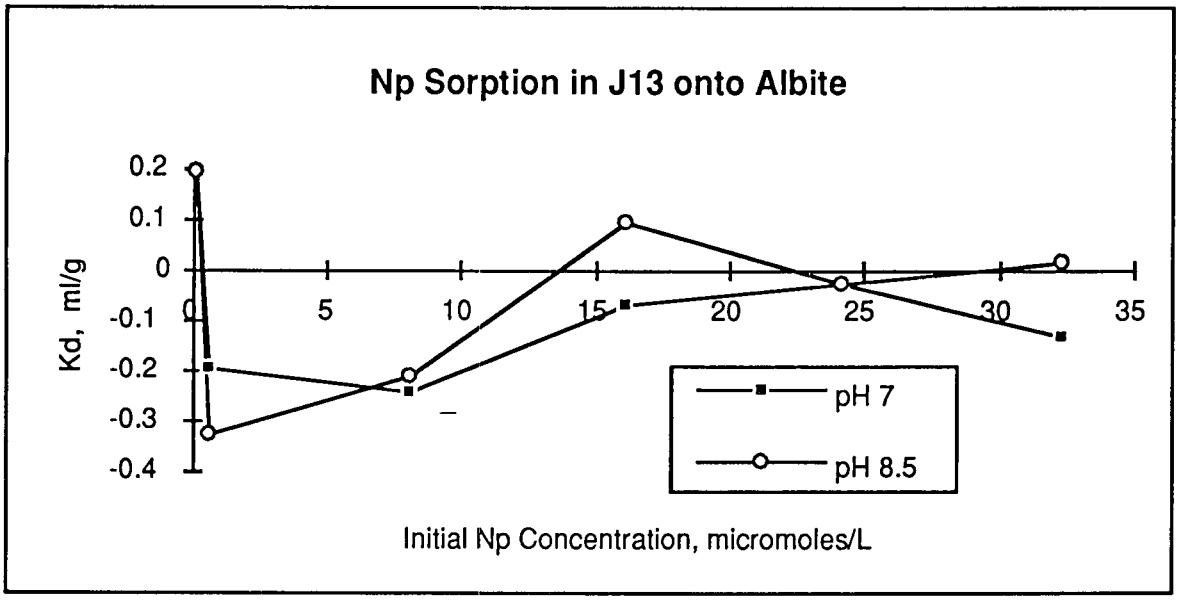
Tuffs Wet Sieved; Particle Size = 75 - 500 micrometers;
Period of Pretreatment = 2-3 d; Period of Sorption = 3-5 d



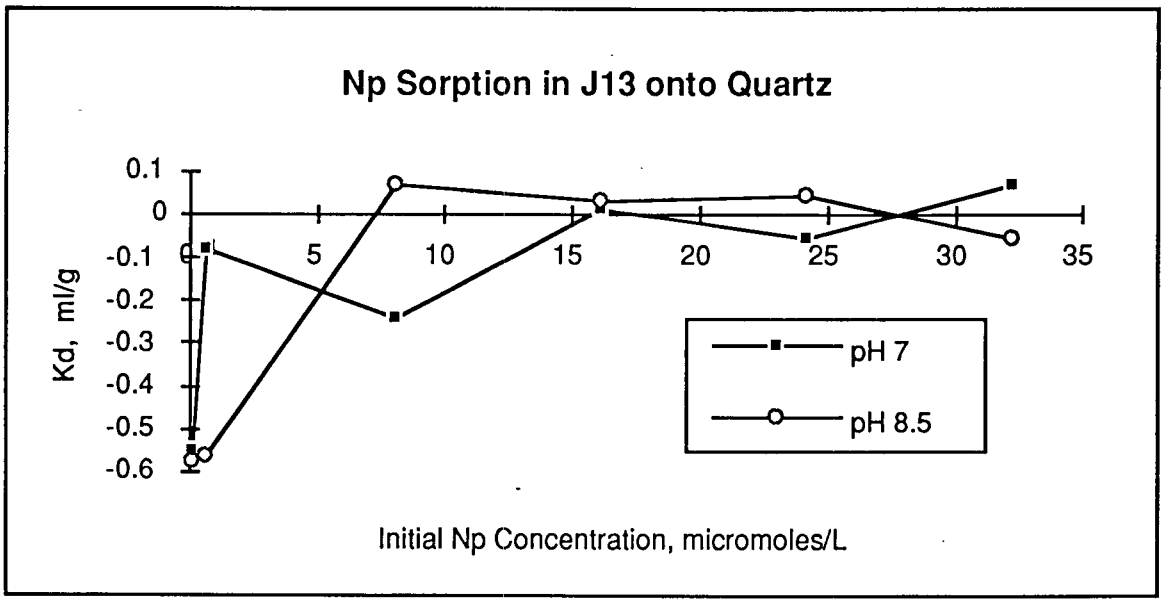


Tuff Wet Sieved; Particle Size = 75 - 500 micrometers;
Clinoptilolite Not Sieved;
Period of Pretreatment = 2-3 d; Period of Sorption = 3-5 d



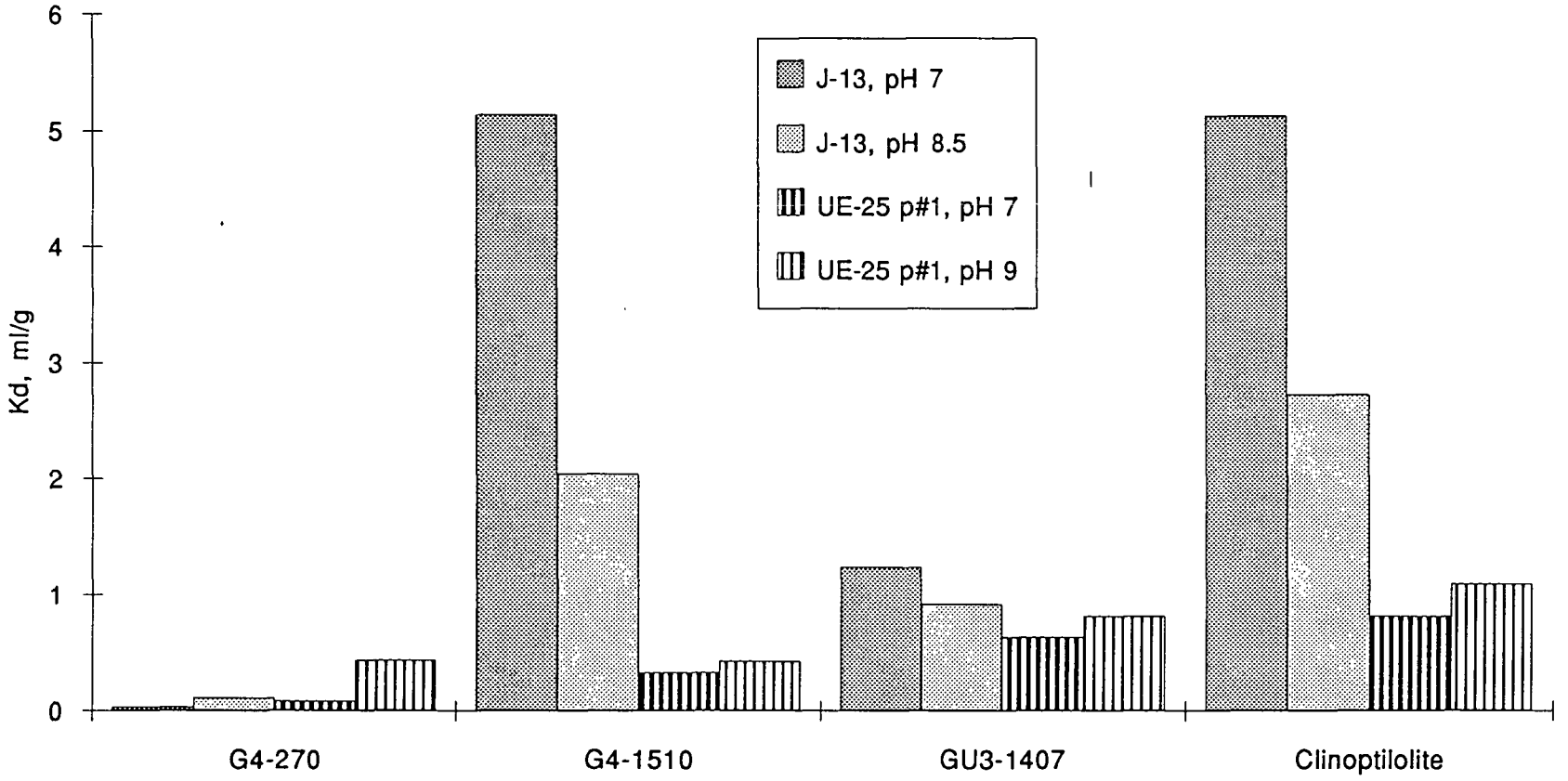


Albite Not Sieved;
Quartz Wet Sieved; Particle Size = 75 - 500 micrometers;
Period of Pretreatment = 2-3 d; Period of Sorption = 3-5 d



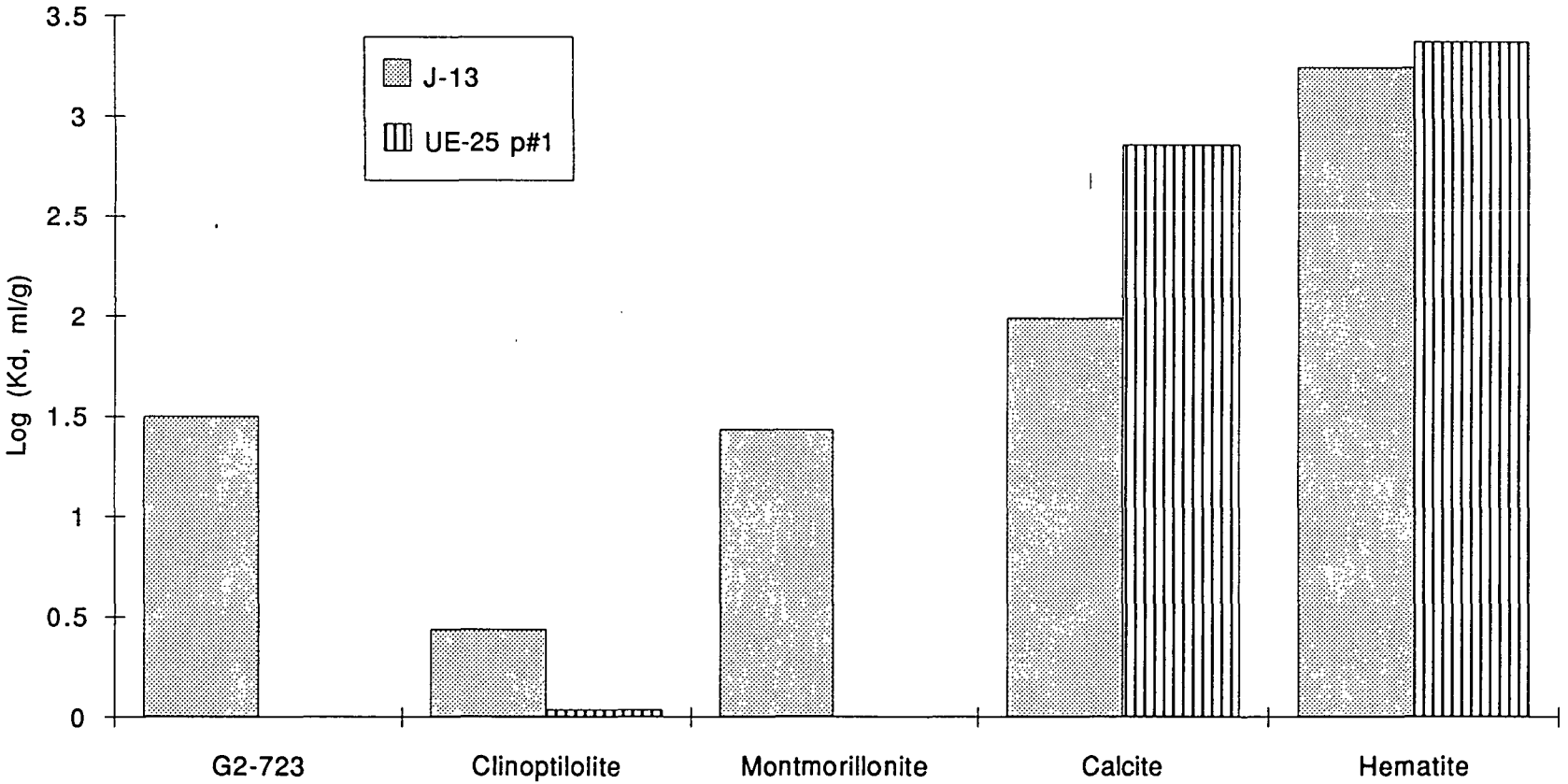
Np Sorption onto Tuffs and Clinoptilolite in J-13 and UE-25 p#1

Initial [Np] ranging from 6 to 8 E-07 M; Tuffs Wet Sieved; Tuffs Particle Size = 75-500 micrometers; Clinoptilolite Not Sieved; Period of Pretreatment = 2-14 d; Period of Sorption 3-23 d



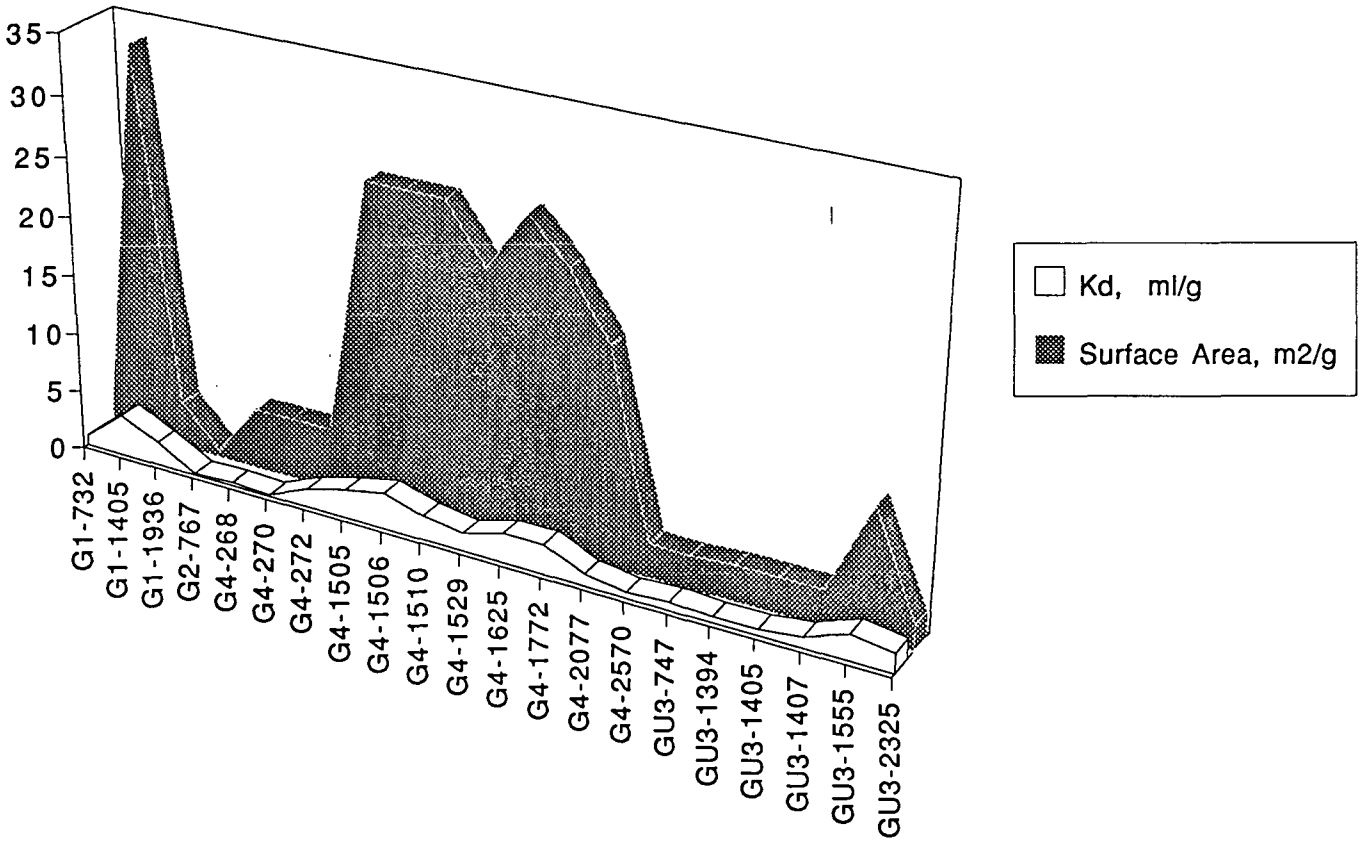
Np Sorption in J-13 onto Tuff and Minerals

Sorption (under atmospheric conditions) at an initial [Np] ranging from 6 to 8 E-07 M; Tuff and Calcite Wet Sieved; Montmorillonite Dry Sieved; Particle Size = 75 -500 micrometers; Clinoptilolite and Hematite Not Sieved; Sorption for 17-22 d



Np Sorption in J-13 onto Tuffs as a Function of Surface Area

Sorption (under atmospheric conditions) at an Initial [Np] ranging from 6 to 8 E-07 M; Tuffs Wet Sieved; Tuffs Particle Size = 75 - 500 micrometers; Period of Pretreatment = 2-14 d; Period of Sorption = 3-23 d



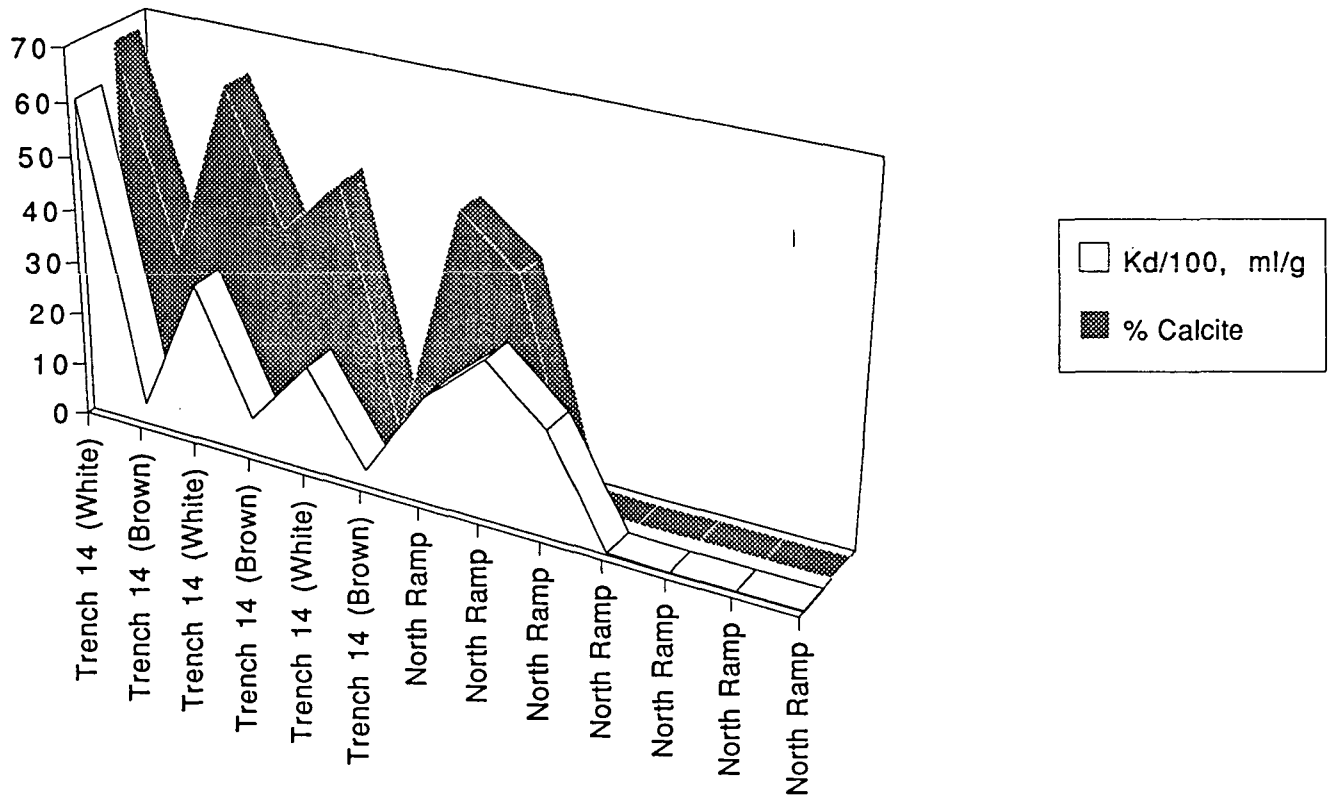
Np Sorption in J-13 onto Tuffs (under atmospheric conditions)

Solid	Ka, m	Predicted Ka, m	% Clinoptilolite	% Hematite
G1-732	3E-07		0	Trace
G1-1405	1E-07	1E-07	68 ± 7	0
G1-1936	5E-07		0	0
G2-767	3E-07		0	1 ± 1
G4-268	6E-08		0	1 ± 1
G4-270	2E-08		0	1 ± 1
G4-272	3E-07		0	1 ± 1
G4-1505	9E-08	1E-07	74 ± 7	0
G4-1506	1E-07	1E-07	62 ± 7	0
G4-1510	8E-08	1E-07	59 ± 7	0
G4-1529	7E-08	1E-07	59 ± 8	0
G4-1625	9E-08	1E-07	61 ± 7	0
G4-1772	1E-07	1E-07	63 ± 5	0
G4-2077	5E-08	8E-08	51 ± 8	0
G4-2570	2E-07		0	Trace
GU3-747	3E-07		0	Trace
GU3-1394	2E-07		0	0
GU3-1405	2E-07		0	Trace
GU3-1407	3E-07		0	0
GU3-1555	2E-07		1 ± 1	0
GU3-2325	8E-07		0	1 ± 1

Initial [Np] ranging from 6 to 8 x 10^{-7} M;
Tuffs Wet Sieved; Tuffs Particle Size = 75-500 micrometers;
Period of Prettreatment = 2-14 d; Period of Sorption = 3-23 d

Np Sorption in J-13 onto Near-Surface Samples

Sorption (under atmospheric conditions) at an initial [Np] of 7 E-07 M; Material Dry Sieved; Particle Size = 75-500 micrometers; Period of Pretreatment = 2-3 d; Period of Sorption = 3-5 d



Sorption Data (from LA-11671-MS)

Stratigraphic Unit	Sample	Sorption Ratios (mL / g)		
		Pu	U	Se
Tiva Canyon Member				
Pah Canyon Member	G2 - 547	1,200 ± 120	9.4 ± 0.1	2 ± 2
	G2 - 723	> 4,500	2.4 ± 0.6	19 ± 2
	GU3 - 433	330 ± 60	0	15 ± 3
	GU3 - 855		10.7 ± 0.7	10 ± 0.4
	GU3 - 916	250 ± 25		
Topopah Spring Member	YM - 22	64 ± 20	1.8 ± 0.2	
	GU3 - 1203	360 ± 40	0	1 ± 1
	GU3 - 1301	290 ± 40	0	7 ± 2
	JA - 18	120 ± 20	2.5 ± 0.4	
tuffaceous beds of Calico Hills	G1 - 1436		10 ± 2	10 ± 3
	G2 - 1952	66 ± 6	0	2 ± 1
	GU3 - 1436		20 ± 2	3
bedded tuff	GU3 - 1531		54 ± 9	5 ± 1
	YM - 38	140 ± 30	5.3 ± 0.2	
Prow Pass Member	G1 - 1883	77 ± 11		
	G1 - 1982			2.5
	YM - 49	230 ± 50		
Bullfrog Member	G1 - 2233		5	10
	G1 - 2289		2.5	9 ± 1
	YM - 54	80 ± 20	1.3 ± 0.3	
	G1 - 2363		0	25 ± 5
	JA - 32	110	2.2 ± 0.9	
Tram Member	G1 - 2840		0.5	3.1
	G1 - 2901		4.3	5.5
	G1 - 3116		3.7	3.3
	JA - 37	400 ± 70	4.6 ± 0.3	
older tuffs				
bedded tuff	G2 - 3933	1,600 ± 30	0	

Summary

- Minimum K_d Strategy reduced radionuclides that need to be studied further to Np, Se, U, and Pu
- Conclusions on Np
  - Sorption is very high onto calcite and calcite-rich tuffs
  - Sorption is negligible onto devitrified and vitric tuffs in J-13 and UE-25 p#1 in the pH range 7 - 9
  - Sorption is negligible onto zeolitic tuffs in UE-25 p#1 in the pH range 7 - 9
  - K_ds are in the range 2 - 5 ml/g for clinoptilolite-rich zeolitic tuffs in J-13 water in the pH range 7 - 8.5
  - Sorption increases with decreasing pH in zeolitic tuffs in J-13
  - Sorption onto clinoptilolite-rich zeolitic tuffs is correlated to surface area and amount of clinoptilolite and can be predicted
  - Iron Oxides appear to be passivated in Tuffs
  - Work remaining is to acquire data for Np sorption onto calcite and clinoptilolite as a function of pH, I, and $[HCO_3^-]$
- Conclusions on Se and U
  - Se and U sorb poorly onto most tuffaceous materials
  - Work remaining is to identify the minerals dominating sorption and the solution parameters that influence sorption behavior
- Conclusions on Pu
  - Sorption appears high onto tuffaceous materials; If this is not an experimental artifact as a result of colloid formation, only confirmation of the Pu batch sorption results will take place