15

GEOCHEMICAL RADIONUCLIDE SORPTION MODELS FOR TOTAL PERFORMANCE ASSESSMENT 3.2

Presented by
David R. Turner
210/522-2139 (dturner@swri.edu)
Center for Nuclear Waste Regulatory Analyses

May 26, 1999
San Antonio, Texas

DOE/NRC Technical Exchange on
Total System Performance Assessments for Yucca Mountain

Legacy/Main - RS

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

BACKGROUND

- Sensitivity analyses using TPA Version 3.1 indicate that an alternative conceptual model with no retardation in the geosphere results in the highest Mean Peak Annual Dose for both 10,000 and 50,000 year time periods (Nuclear Regulatory Commission, 1999)
- Current Performance Assessment (PA) models assume a constant sorption coefficient (K_D) for each radionuclide and each hydrostratigraphic unit
- In real systems, K_D is a complex function of system chemistry and mineralogy
- Stochastic approaches typically use probability distribution functions (PDFs) to represent variability in K_D
- K_D PDFs are based on expert judgement, limited laboratory experimental conditions and do not reflect possible covariance among radionuclides exhibiting similar sorption behavior
- Geochemical sorption models that can be combined with existing hydrochemical and mineralogical information can be used to provide better constraints on PA sorption parameters

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

OBJECTIVES

- Develop abstractions that incorporate, at least indirectly, the effects of chemistry on radionuclide sorption coefficients.
- Develop abstracted models based on site-specific hydrochemical information

ASSUMPTIONS:

- Sorption behavior of Np(V) and U(VI) as a function of pH and carbonate concentration is similar for aluminosilicate minerals when normalized to effective surface area (A'). It is assumed that it is also true for other actinides such as Am(III), Pu(V), and Th(IV).
- The mean pore size in the matrix at YM is 0.1 μm (Travis and Nuttall, 1987), which is assumed to be true for all hydrostratigraphic units used in TPA.
- The water chemistries of Perfect et al. (1995) as screened and culled in Turner (1998) represent the likely range in water chemistry at YM.
- As appropriate, mean values from tpa.inp for solubility limits, density, and porosity are used in DLM simulations.

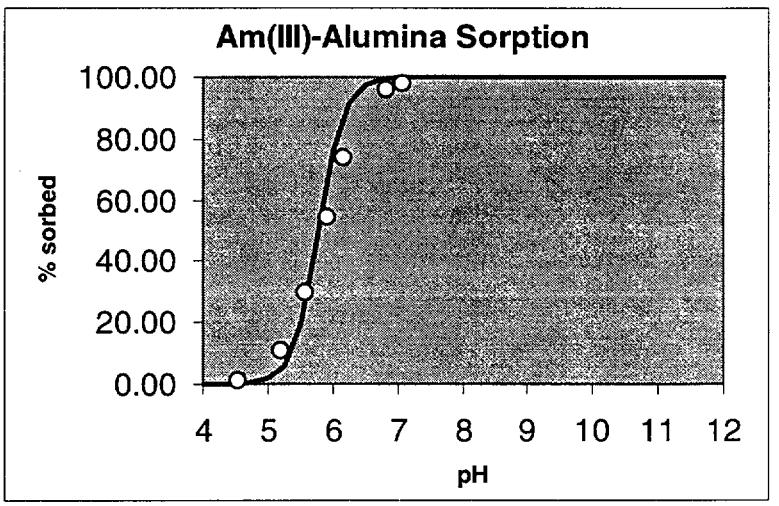
GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- **Identify sorption experiments that can be used to calibrate the DLM parameters.**
  - **Am(III), Th(IV), and Pu(V) sorption on γ-alumina (Righetto et al., 1988; 1991);**
  - **Np(V) and U(VI) sorption on montmorillonite (Turner et al., 1998a; Pabalan and Turner, 1997).**
- **Determine the DLM parameters for these experiments.**

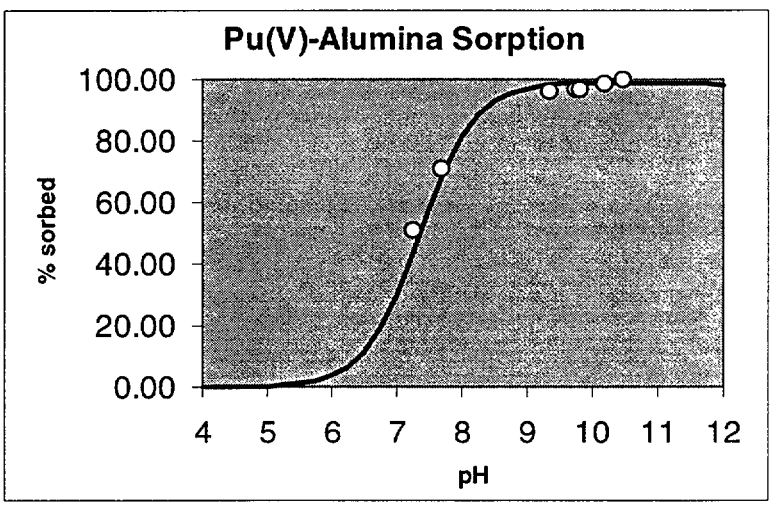
Radionuclide-Mineral	Surface Complex	Binding-Constant	Reference
Np(V)-montmorillonite	$>AlO^-$	-9.73	Turner et al. (1998a)
	$>AlOH_2^+$	8.33	Turner et al. (1998a)
	$>SiO^-$	-7.20	Turner et al. (1998a)
	$>AlO\text{-}NpO_2(OH)^-$	-13.79	Turner et al. (1998a)
	$>SiOH\text{-}NpO_2^+$	4.05	Turner et al. (1998a)
U(VI)-montmorillonite	$>AlO^-$	-9.73	Pabalan and Turner (1997)
	$>AlOH_2^+$	8.33	Pabalan and Turner (1997)
	$>SiO^-$	-7.20	Pabalan and Turner (1997)
	$>AlO\text{-}UO_2^+$	2.70	Pabalan and Turner (1997)
	$>SiO\text{-}UO_2^+$	2.60	Pabalan and Turner (1997)
	$>AlO\text{-}(UO_2)_3(OH)_5^\circ$	-14.95	Pabalan and Turner (1997)
	$>SiO\text{-}(UO_2)_3(OH)_5^\circ$	-15.29	Pabalan and Turner (1997)
Am(III)-γ alumina	$>AlO^-$	-9.73	Turner and Sassman (1996)
	$>AlOH_2^+$	8.33	Turner and Sassman (1996)
	$>AlO\text{-}Am^{2+}$	4.66	This study [Turner(1995)]
Pu(V)-γ alumina	$>AlO^-$	-9.73	Turner and Sassman (1996)
	$>AlOH_2^+$	8.33	Turner and Sassman (1996)
	$>AlO\text{-}PuO_2^\circ$	-2.18	This study [Turner(1995)]
Th(IV)-γ alumina	$>AlO^-$	-9.73	Turner and Sassman (1996)
	$>AlOH_2^+$	8.33	Turner and Sassman (1996)
	$>AlO\text{-}Th^{3+}$	15.3	This study [Turner(1995)]

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

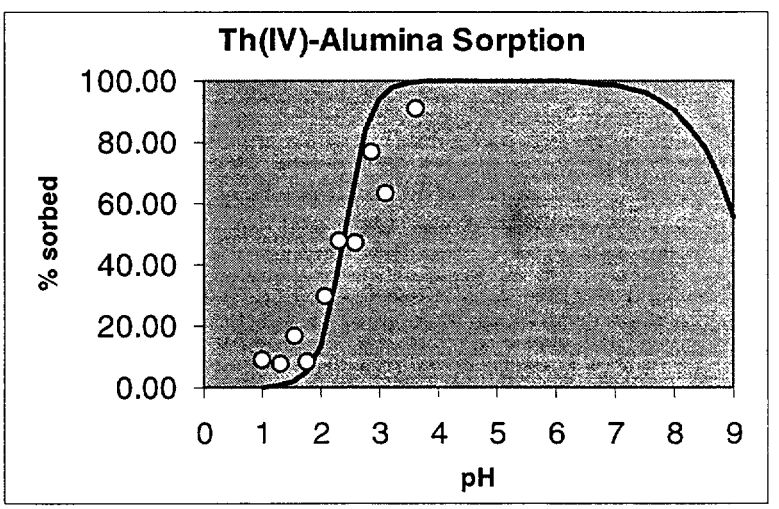
Righetto et al. (1988)
$Am(III)_{total}$ = 5E-11 M
M/V = 0.01 g/L (γ alumina)
BET = 130 m^2/g
A' = 13.0 m^2/g
T_{XOH} = 4.990E-07 M



Righetto et al. (1991)
$Pu(V)_{total}$ = 2e-10 M
M/V = 0.20 g/L (γ alumina)
BET = 130 m^2/g
A' = 13.0 m^2/g
T_{XOH} = 9.972E-06 M



Righetto et al. (1988)
$Th(IV)_{total}$ = 1e-11 M
M/V = 0.01 g/L (γ alumina)
BET = 130 m^2/g
A' = 13.0 m^2/g
T_{XOH} = 4.990E-07 M



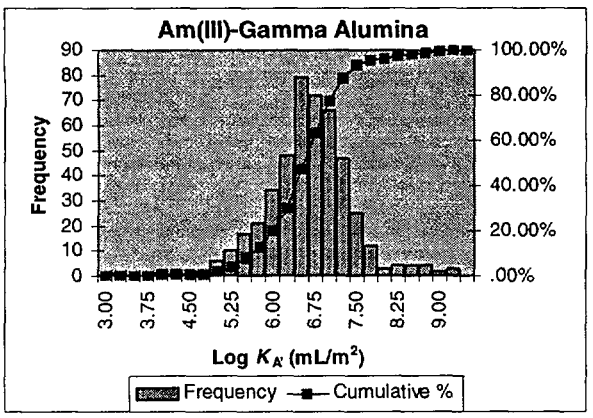
GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

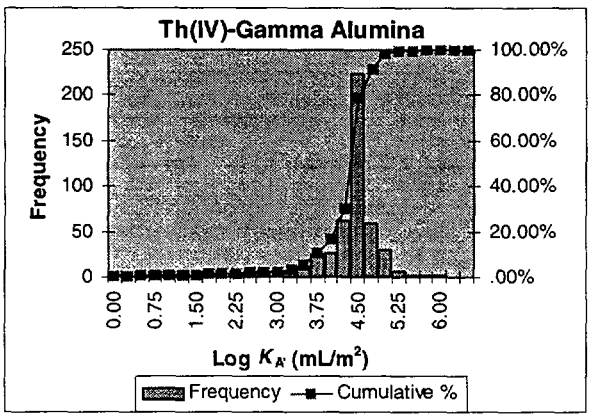
Descriptive Statistics:

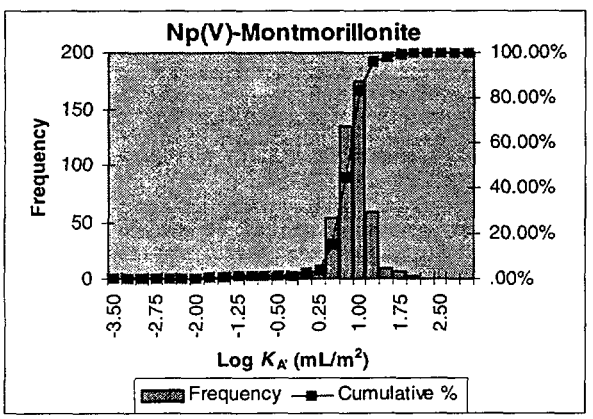
log K_A (mL/m^2)	*Am(III)*	*Np(V)*	*Pu(V)*	*Th(IV)*	*U(VI)*
Mean	6.549	0.742	2.707	4.248	-0.032
Median	6.539	0.773	2.715	4.330	0.002
Mode	6.337	0.738	2.650	4.439	-0.158
Standard Deviation	0.748	0.422	0.305	0.583	0.975
Sample Variance	0.560	0.178	0.093	0.340	0.951
Kurtosis	1.924	26.576	5.055	34.228	12.928
Skewness	0.118	-3.556	-0.148	-4.414	-2.318
Range	5.958	5.140	2.974	7.715	9.407
Minimum	3.160	-3.264	0.906	-1.780	-6.837
Maximum	9.119	1.876	3.881	5.935	2.570
Count	460	460	460	460	460

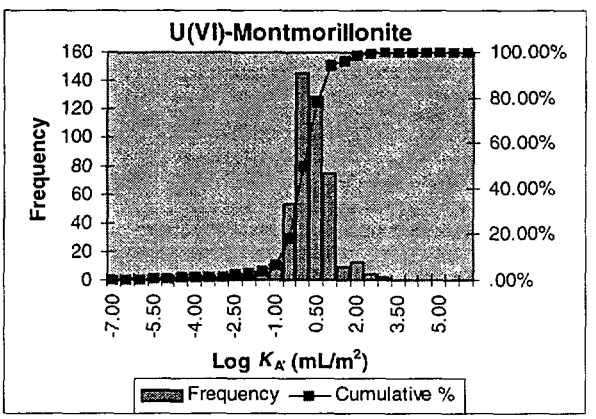
- **Normalized to effective surface area, K_A (in mL/m^2), these sorption coefficient distributions can be recast in terms of K_D for each of the hydrostratigraphic units used in TPA**

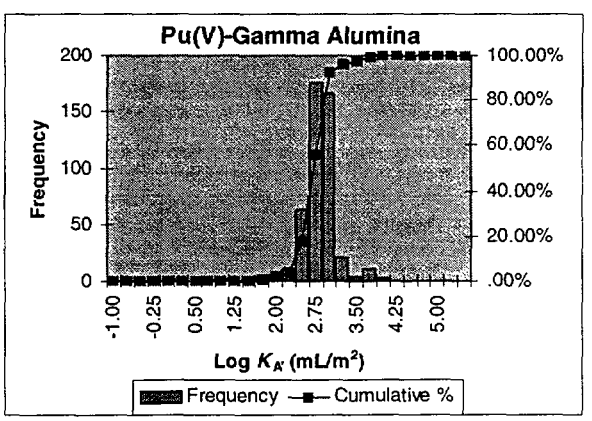
GEOCHEMICAL SORPTION MODELS FOR TPA 3.2











GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- The distributions for each radionuclide appear to be log normal, although the kurtosis of the distributions varies
- The final step in using this information in TPA is to apply this distribution to each hydrostratigraphic unit and transform the K_A into K_D (in mL/g)
- Arthur (1996) presents a relationship among porosity, dry density, and pore radius such that:

$$\text{Specific Surface Area} = \frac{3\phi_r}{\rho_r r}$$

where φ_r is porosity of the rock, ρ_r is density of the rock in g/m^3, and r is the radius of the pore in meters.

- Data Sources:
  - φ_r, ρ_r - input file for TPA 3.1.4
  - r - Travis and Nuttall (1987)

Unit	φ_r (m^3/m^3)	ρ_r (kg/m^3)	r (m)	SA (m^2/g)
TSw	0.12	2460	5.0E-08	2.9
CHnv	0.33	2260	5.0E-08	8.8
CHnz	0.32	2400	5.0E-08	8.0
PPw	0.28	2540	5.0E-08	6.6
UCF	0.28	2420	5.0E-08	6.9
BFw	0.12	2570	5.0E-08	2.8
UFZ	0.12	2630	5.0E-08	2.7
SAV	0.125	2470	5.0E-08	3.0

Measured surface areas: 2.6 to 10 m^2/g Triay et al. (1996):

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

$K_D = K_{A'} \times A'$ five radioelements for each of eight hydrostratigraphic units using water chemistry of Perfect et al. (1995) (n = 460 samples):

Log KD(m3/kg)	*Am(III)-TSw*	*Am(III)-CHnv*	*Am(III)-CHnz*	*Am(III)-PPw*	*Am(III)-UCF*	*Am(III)-BFw*	*Am(III)-UFZ*	*Am(III)-SAV*
Mean	4.011	4.493	4.452	4.368	4.387	3.996	3.980	4.026
Median	4.002	4.484	4.443	4.359	4.378	3.987	3.971	4.017
Mode	3.800	4.282	4.240	4.157	4.176	3.784	3.769	3.814
Std Deviation	0.748	0.748	0.748	0.748	0.748	0.748	0.748	0.748
Minimum	0.623	1.105	1.064	0.980	0.999	0.608	0.592	0.638
Maximum	6.581	7.063	7.022	6.938	6.957	6.566	6.550	6.596

Log KD(m3/kg)	*Np(V)-TSw*	*Np(V)-CHnv*	*Np(V)-CHnz*	*Np(V)-PPw*	*Np(V)-UCF*	*Np(V)-BFw*	*Np(V)-UFZ*	*Np(V)-SAV*
Mean	-1.796	-1.313	-1.355	-1.438	-1.419	-1.811	-1.827	-1.781
Median	-1.764	-1.282	-1.324	-1.407	-1.388	-1.780	-1.795	-1.750
Mode	-1.800	-1.318	-1.359	-1.443	-1.423	-1.815	-1.831	-1.785
Std Deviation	0.422	0.422	0.422	0.422	0.422	0.422	0.422	0.422
Minimum	-5.802	-5.320	-5.361	-5.445	-5.425	-5.817	-5.833	-5.787
Maximum	-0.661	-0.179	-0.221	-0.304	-0.285	-0.677	-0.692	-0.647

Log KD(m3/kg)	*Pu(V)-TSw*	*Pu(V)-CHnv*	*Pu(V)-CHnz*	*Pu(V)-PPw*	*Pu(V)-UCF*	*Pu(V)-BFw*	*Pu(V)-UFZ*	*Pu(V)-SAV*
Mean	0.169	0.651	0.610	0.527	0.546	0.154	0.138	0.184
Median	0.177	0.659	0.618	0.534	0.554	0.162	0.146	0.192
Mode	0.112	0.595	0.553	0.470	0.489	0.097	0.081	0.127
Std Deviation	0.305	0.305	0.305	0.305	0.305	0.305	0.305	0.305
Minimum	-1.631	-1.149	-1.190	-1.274	-1.255	-1.646	-1.662	-1.616
Maximum	1.343	1.825	1.784	1.700	1.719	1.328	1.312	1.358

Log KD(m3/kg)	*Th(IV)-TSw*	*Th(IV)-CHnv*	*Th(IV)-CHnz*	*Th(IV)-PPw*	*Th(IV)-UCF*	*Th(IV)-BFw*	*Th(IV)-UFZ*	*Th(IV)-SAV*
Mean	1.711	2.193	2.151	2.068	2.087	1.695	1.680	1.725
Median	1.792	2.274	2.233	2.149	2.168	1.777	1.761	1.807
Mode	1.901	2.383	2.342	2.259	2.278	1.886	1.870	1.916
Std Deviation	0.583	0.583	0.583	0.583	0.583	0.583	0.583	0.583
Minimum	-4.317	-3.835	-3.877	-3.960	-3.941	-4.333	-4.348	-4.303
Maximum	3.397	3.879	3.838	3.754	3.774	3.382	3.366	3.412

Log KD(m3/kg)	*U(VI)-TSw*	*U(VI)-CHnv*	*U(VI)-CHnz*	*U(VI)-PPw*	*U(VI)-UCF*	*U(VI)-BFw*	*U(VI)-UFZ*	*U(VI)-SAV*
Mean	-2.569	-2.087	-2.129	-2.212	-2.193	-2.584	-2.600	-2.555
Median	-2.536	-2.054	-2.095	-2.179	-2.160	-2.551	-2.567	-2.521
Mode	-2.695	-2.213	-2.255	-2.338	-2.319	-2.711	-2.726	-2.681
Std Deviation	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975
Minimum	-9.375	-8.893	-8.934	-9.018	-8.998	-9.390	-9.406	-9.360
Maximum	0.032	0.514	0.473	0.389	0.409	0.017	0.001	0.047

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- **For each radionuclide, this method results in the same distribution for each hydrostratigraphic unit, since K_D is determined by multiplying $K_{A'}$ by unit-specific constant (A')**

- **This information was used to develop correlation coefficients between each of the radionuclides for $K_{A'}$ (and therefore K_D):**

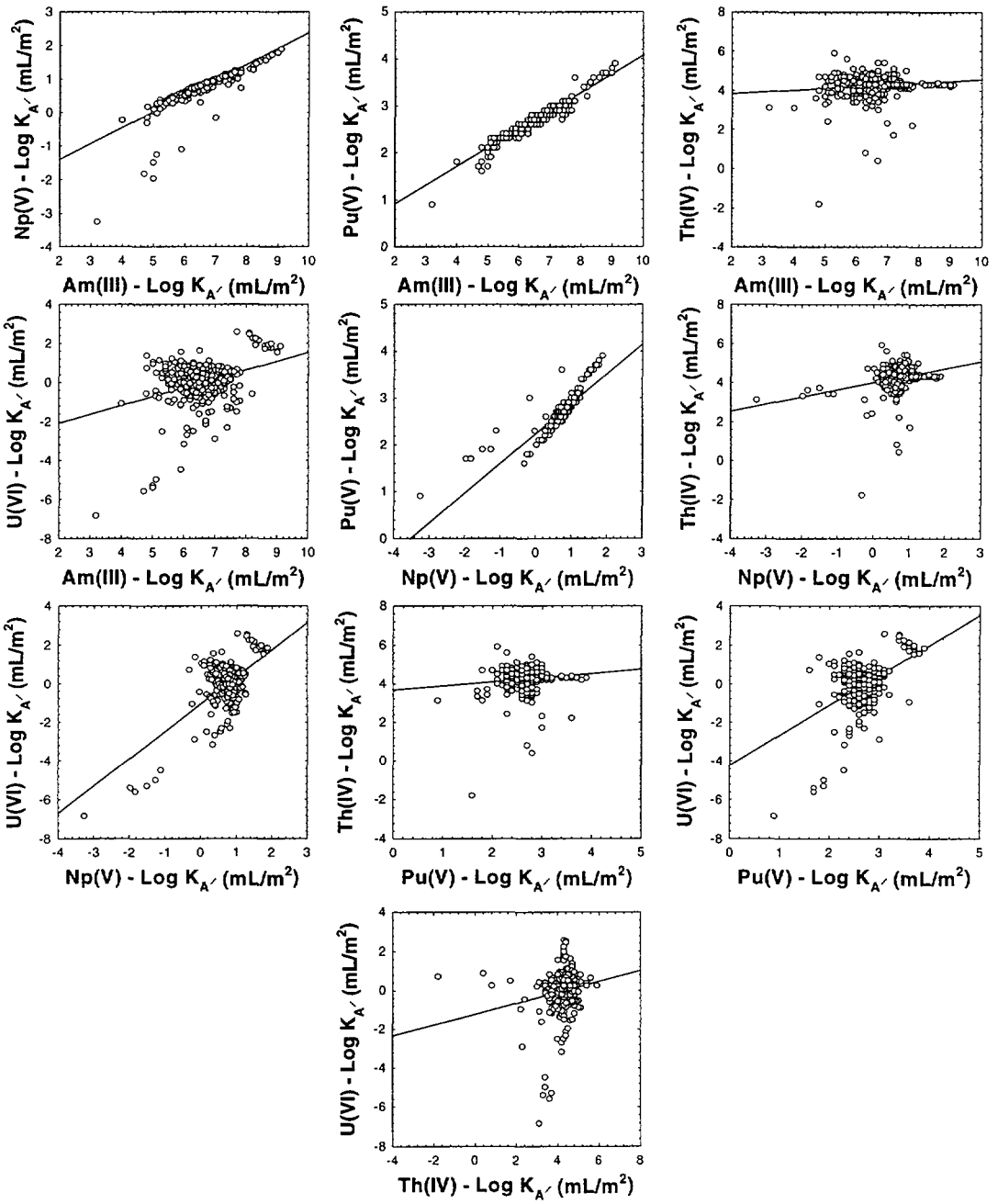
$K_{A'}$ (mL/m^2)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.9056	1			
Pu(V)	0.9025	0.9629	1		
Th(IV)	-0.0350	-0.0448	-0.0682	1	
U(VI)	0.3420	0.4073	0.4787	-0.0174	1

For log $K_{A'}$ (and log K_D), the correlation coefficients are different:

log $K_{A'}$ (mL/m^2)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.8373	1			
Pu(V)	0.9640	0.8814	1		
Th(IV)	0.1120	0.2599	0.1087	1	
U(VI)	0.3455	0.6097	0.4894	0.1648	1

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- **Implementation of the Geochemical Sorption Model in TPA 3.2**



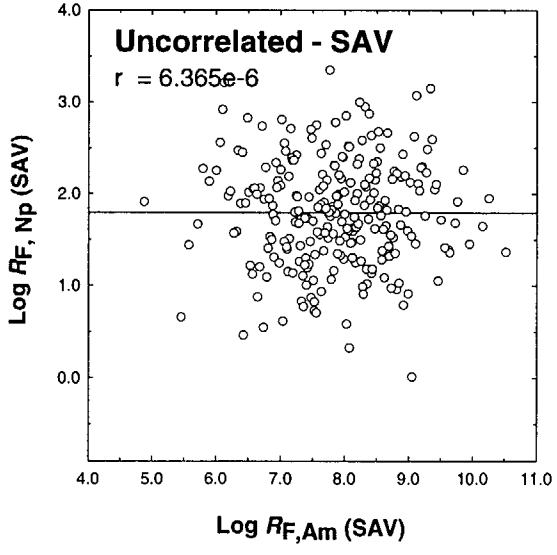
GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

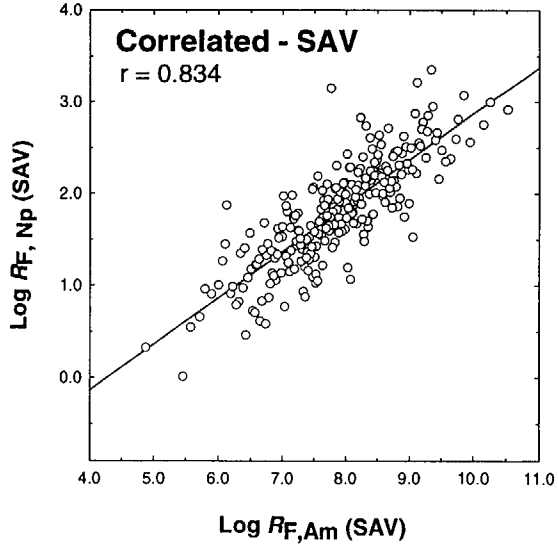
- **First step: Determine if correlations being properly implemented in TPA 3.2**
- **Four runs:**
  - **2 with correlations for SAV, 2 without correlations for SAV**
  - **50,000 years, 20 km, 250 realizations**
  - **Database tracking 20 radionuclides**

Am(III)-Np(V)

Input:

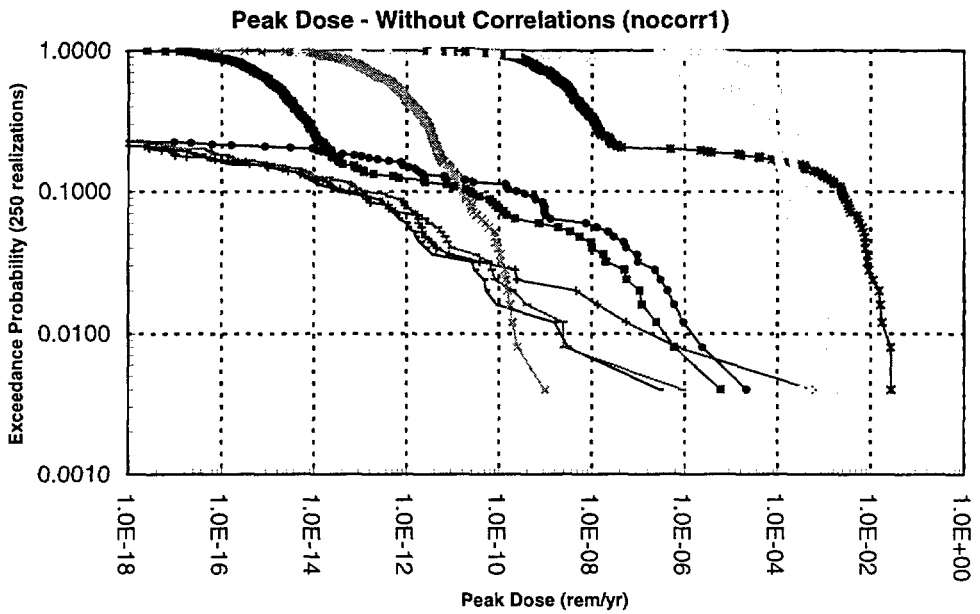
r = 0.8373

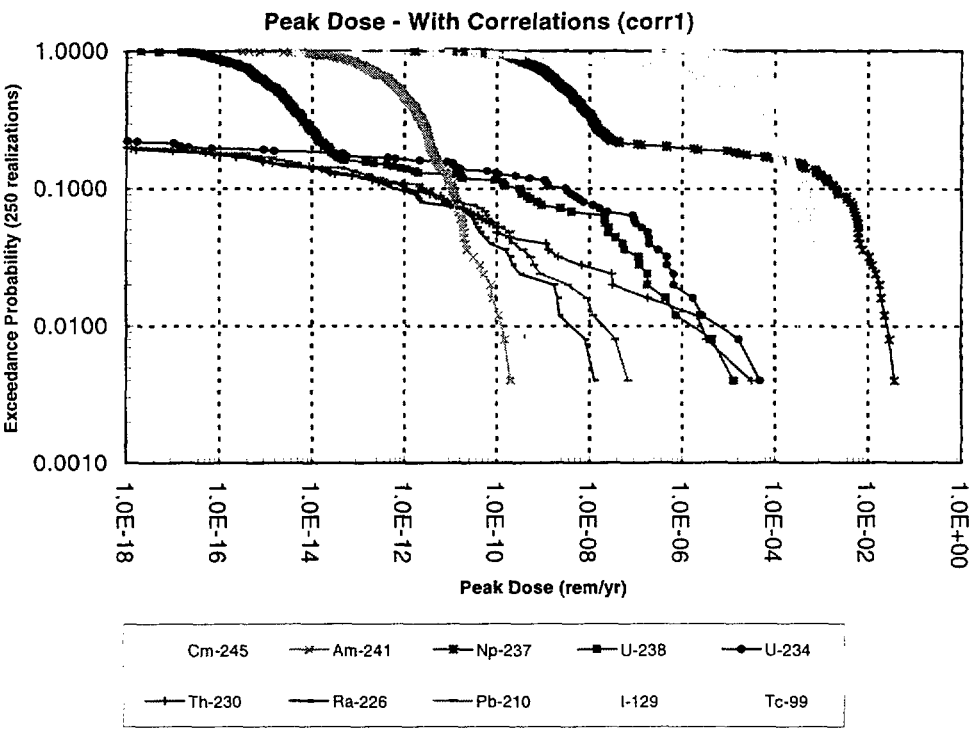




GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

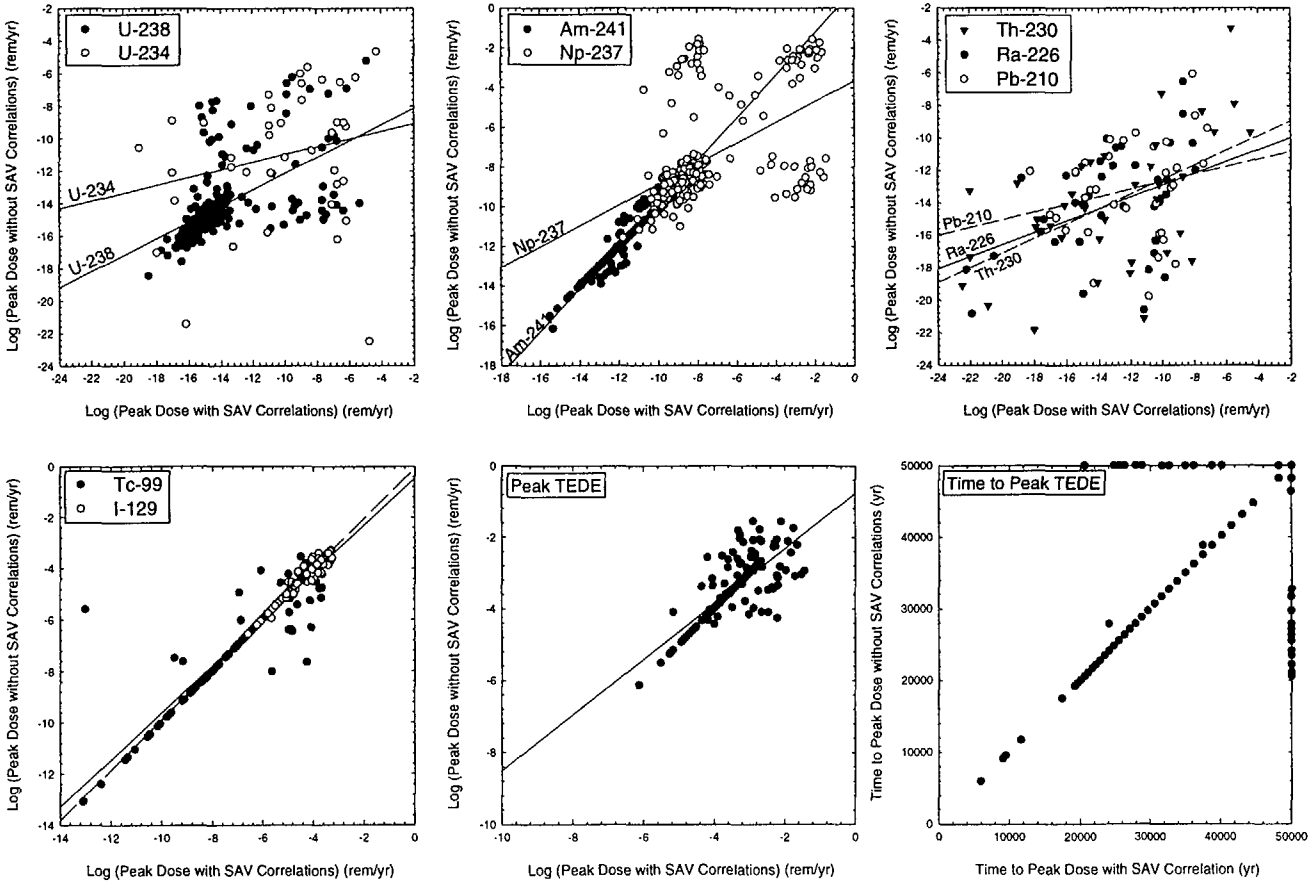
- **Comparison of Results:**





GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- **Comparison of Results (with and without SAV correlations):**



GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

- Radionuclides most affected include those with correlations:
  - U-238
  - U-234
  - Np-237
  - Th-230
  - Am-241
- Also affected:
  - Ra-226
  - Pb-210

  From the decay chain U-234 → Th-230 → Ra-226 → Pb-210
- Radioelements that do not show up at 50,000 y (Pu) may be more important at longer times
- Correlations may be relevant to radionuclides that TPA suggests are important (Cm-245,246) to dose at 50,000 y. These may be simulated using Am(III) as a homologue

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

SUMMARY AND CONCLUSIONS

- Geochemical sorption models (DLM) applied for Am, Np, Pu, Th, and U using site-specific hydrochemistry
- Limits established for PA sorption parameter PDFs for different hydrostratigraphic units
- Correlations (10 total) among five radioelements developed for sorption parameters in the alluvium
- TPA 3.2 correctly implemented correlations in LHS
- Presence of correlations produce effects on Peak Dose for TPA 3.2 simulations at 50,000 years, 20 km

GEOCHEMICAL SORPTION MODELS FOR TPA 3.2

Arthur, R.C. 1996. *SITE-94: Adaptation of Mechanistic Sorption Models for Performance Assessment Calculations.* SKI Report 96:34. Stockholm, Sweden: Swedish Nuclear Power Inspectorate.

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. 1998. Studies of neptunium^{V} sorption on quartz, clinoptilolite, montmorillonite, and α-alumina. E.A. Jenne. ed. *Adsorption of Metals by Geomedia.* New York, NY: Adademic Press, Inc.: 131-148.

U.S. Nuclear Regulatory Commission. 1999. *NRC Sensitivity and Uncertainty Analyses for a Proposed HLW Repository at Yucca Mountain, Nevada, Using TPA 3.1.* NUREG-1668, Vol. 2. Washington, DC: NRC.

Pabalan, R.T., and D.R. Turner. 1997. Uranium(6+) sorption on montmorillonite: Experimental and surface complexation modeling study. *Aqueous Geochemistry* 2: 203-226.

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. 1998. Uranium^{VI} sorption onto selected mineral surfaces. E.A. Jenne. ed. *Adsorption of Metals by Geomedia.* New York, NY: Adademic Press, Inc.: 99-130.

Perfect, D.L., C.C. Faunt, W.C. Steinkampf, and A.K. Turner. 1995. *Hydrochemical Data Base for the Death Valley Region, California and Nevada.* USGS Open-File Report 94-305. Denver, CO: U.S. Geological Survey.

Righetto, L., G. Bidoglio, B. Marcandalli, and I.R. Bellobono. 1988, Surface interactions of actinides with alumina colloids. *Radiochimica Acta* 44/45:73-75.

Righetto, L., G. Bidoglio, G. Azimonti, and I.R. Bellobono. 1991. Competitive actinide interactions in colloidal humic acid-mineral oxide systems. *Environmental Science and Technology* 25: 1913-1919.

Travis, B.J., and H.E. Nuttall. 1987. *Two-Dimensional Numerical Simulation of Geochemical Transport in Yucca Mountain.* LA-10532-MS. Los Alamos, NM: Los Alamos National Laboratory.

Triay, I.R., A. Meijer, J.L. Conca, K.S. Kung, R.S. Rundberg, and E.A. Strietelmeier. 1996a. *Summary and Synthesis Report on Radionuclide Retardation for the Yucca Mountain Site Characterization Project.* Milestone 3784. Los Alamos, NM: Chemical Science and Technology Division, Los Alamos National Laboratory.

Turner, D.R. 1995. *A Uniform Approach to Surface Complexation Modeling of Radionuclide Sorption.* CNWRA 95-001. San Antonio, TX: CNWRA.

Turner, D.R. 1998. *Radionuclide Sorption in Fractures at Yucca Mountain, Nevada: A Preliminary Demonstration of Approach for Performance Assessment.* CNWRA Letter Report. San Antonio, TX: CNWRA.

Turner, D.R. and S.A. Sassman. 1996. Approaches to sorption modeling for high-level waste performance assessment. *Journal of Contaminant Hydrology* 21: 311-332.

Turner, D.R., R.T. Pabalan, and F.P.Bertetti. 1998a. Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modeling study. *Clays and Clay Minerals* 46: 256-269.

Turner, D.R., G.W. Wittmeyer, and F.P. Bertetti. 1998b. *Radionuclide Sorption in the Alluvium at Yucca Mountain, Nevada: A Preliminary Demonstration of Approach for Performance Assessment.* CNWRA Letter Report. San Antonio, TX: CNWRA.

Turner, D.R., R.T. Pabalan, J.D. Prikryl, and F.P. Bertetti. 1999. Radionuclide sorption at Yucca Mountain, Nevada - Demonstration of an alternative approach for performance assessment. J. Lee and D. Wronkiewicz, eds. *MRS Symposium Proceedings: Scientific Basis for Nuclear Waste Management - XXII.* Pittsburgh, PA: MRS: (in press).

Turner, D.R., and R.T. Pabalan. 1999. Abstraction of mechanistic sorption model results for performance assessment calculations at Yucca Mountain, Nevada. *Waste Management.* (in revision).