

Yucca Mountain Project Far-Field Sorption Studies and Data Needs

# Los Alamos

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

9201090144 911224 PDR WASTE WM-11 PDR This work was supported by the US Department of Energy, Office of Nuclear Energy.

An Affirmative Action/Equal Opportunity Employer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

LA-11671-MS

UC-510 Issued: September 1990

## Yucca Mountain Project Far-Field Sorption Studies and Data Needs

Arend Meijer

LOS Alamos Los Alamos National Laboratory Los Alamos, New Mexico 87545

## CONTENTS

ABSTRACT1
I. INTRODUCTION AND STATEMENT OF PURPOSE
II. CONSTANT SORPTION COEFFICENTS IN TRANSPORT CALCULATIONS . 7
<ul> <li>III. REVIEW AND EVALUATION OF ALTERNATIVE PROCEDURES FOR DERIVATION OF SORPTION COEFFICIENTS</li></ul>
IV. REVIEW AND EVALAUTION OF YMP SORPTION DATABASE 15
V. SORPTION MECHANISMS
VI. SIGNIFICANCE OF NRC CONCERNS THAT RELATE TO SORPTION STUDIES         A. Experimental Aspects       21         B. Applications Aspects       23
<ul> <li>VII. STRATEGY FOR ADDRESSING NRC CONCERNS REGARDING EXPERIMEN- TAL AND APPLICATIONS ASPECTS OF SORPTION SUTDIES</li></ul>
VIII. POSITION ON SORPTION TASK
REFERENCES

iv

## YUCCA MOUNTAIN PROJECT FAR-FIELD SORPTION STUDIES AND DATA NEEDS

by

## Arend Meijer

#### ABSTRACT

Batch sorption experiments in which radionuclides dissolved in groundwaters from Yucca Mountain were sorbed onto samples of crushed tuff have resulted in a substantial database of sorption coefficients for radionuclides of interest to the repository program. Although this database has been useful in preliminary evaluations of Yucca Mountain as a potential site for a nuclear waste repository, the database has limitations that must be addressed before it can be used for performance assessment calculations in support of a license application for a waste repository. The limitations result in part from conceptual problems and in part from the experimental approach used to obtain the existing database of sorption coefficients.

The dominant conceptual question concerns the validity of using a constant sorption coefficient for a given radionuclide in transport calculations. A constant sorption coefficient approach is viable if the composition and physical characteristics of the flow system do not change significantly over the interval modeled in the calculations and if the sorption coefficient used accurately represents the natural system. If the composition of the system is likely to change with time, the effects of the compositional changes on the sorption coefficient must be determined either by empirical and/or theoretical approaches. An empirical approach could follow along the lines of the previous studies. The drawbacks of this approach are that (1) it would require a very large number of experiments in which each compositional change is evaluated separately for each important radionuclide, and (2) synergistic effects among various compositional changes could not be fully evaluated. The "theoretical" approach could involve studies of the mechanisms by which the important radionuclides sorb to the mineral phases Such studies would concentrate on in Yucca Mountain tuffs.

elucidating sorption reactions of the important radionuclides on pure mineral separates. If the sorption reactions of the important radionuclides could be elucidated, it would be possible to develop models that predict the effects of compositional changes in the system on sorption coefficients. Such models could also be used to test the validity of sorption coefficients in the existing database.

Database limitations resulting from the experimental approach include aspects such as the use of crushed vs solid rock, oversaturation of feed solutions, imperfect solid/liquid separations, the use of feed solutions containing all of the important radionuclides, and sorption kinetics. An evaluation of the existing database suggests these aspects are most critical for experiments involving the actinide elements. By studying sorption reaction mechanisms on pure mineral phases, it is possible to address indirectly many of these experimental limitations. The result would be greater confidence in the existing database and in our ability to extrapolate to conditions not addressed directly by the experimental program.

## I. INTRODUCTION AND STATEMENT OF PURPOSE

The sorption task of the Yucca Mountain Project (YMP) [work breakdown structure (WBS) 2.3.4.1.5A] has the responsibility for obtaining data on the sorptive behavior of important radionuclides (Kerrisk, May 1984; Oversby, 1987) for use in the evaluation of the future performance of a proposed nuclear waste repository at Yucca Mountain, Nevada. Since 1977, the Isotope and Nuclear Chemistry Division of Los Alamos National Laboratory has been conducting experiments on the sorptive behavior of radionuclides on tuffaceous rock samples from the Nevada Test Site. These experiments have produced a set of average sorption coefficients for important radionuclides (Table I) that has been included in the Environmental Assessment (1986) and the Site Characterization Plan (1988) for the Yucca Mountain site. Many coefficients, particularly those for the actinides and several of the fission products, are poorly constrained and may reflect processes other than sorption (for example, precipitation).

Now that Yucca Mountain has been chosen for site characterization, more quantitative and technically defensible studies must be carried out to obtain a more detailed understanding of the sorptive behavior of important radionuclides in relation to the various rock and mineral types present in the far field (between the proposed repository and the accessible environment). In addition to improving the reliability of performance assessment calculations, such an understanding will provide a basis for responding to various regulatory and public concerns over potential releases of radionuclides from the repository horizon over the proposed containment period. In this regard, the Nuclear Regulatory Table Ia. Average sorption ratios (distribution coefficients) from batch sorption experiments on crushed tuff for americium, plutonium, uranium, selenium, technetium, and neptunium<sup>a,b</sup>

Stratigraphic <sup>c</sup>		Depth			Sorption (mi	n Ratios		
Unit	Sample	(ft)	Am	Pu	U	Se	Tc	Np
Трс	JA-8 YM-5	606 251			<u> </u>			
Трр	G2-547 G2-723	547 723	13 000(110) 890 000 (49 000)	1200(120) >4500	9.4(0.1) 2.4(0.6)	2(2) 19(2)	0 <sup>f</sup> 0 <sup>f</sup>	
	GU3-433 GU3-855 GU3-916	433 855 916	3400(200) <sup>d</sup>	330(60) <sup>\$</sup>	0 10(0.7)	15(3) 10(0.4)	0	7.9(0.1)
Tpt	YM-22 GU3-1203 G1-1292	848 1203 1292	1200(130) <sup>d,e</sup> 1100(120) <sup>g</sup>	64(20) <sup>d</sup> 360(40) <sup>g</sup>	1.8(0.2) <sup>d</sup> 0	1(1)	0.72(0.2) $0.3(0.14)^{d}$ 0	$\frac{4.9(1)}{7.0(1.0)}$ 2.7(0.1)
	GU3-1301 YM-30	1301 1264	1800(160) <sup>g</sup>	290(40) <sup>g</sup>	0	7(2)	0.03(0.001)	5.0(0.1)
<u></u>	JA-18 C1 1496	1420	180(30)	120(20)	2.5(0.4)			
1 116	G2-1952 GU3-1436	1436 1952 1436	1700(70) <sup>f</sup>	66(6) <sup>f</sup>	10(2) 0 20(2)	$     \begin{array}{r}       10(3) \\       2(1) \\       3     \end{array} $		2.7(0.1)
bt	GU3-1531 YM-38 YM-42	1531 1504 1824	14 600(1000)	140(30)	54(9) 5.3(0.2)	5(1)		11.0
Тср	G1-1854 YM-45 G1-1883 YM-46 G1-1982 YM-49	1854 1930 1883 2002 1982	4700(300)	77(11)		2.5		6.4 2.4
	YM-49 JA-26	2114 2221 1995	4300(1400)	230(50) <sup>e</sup>			$\begin{array}{c} 0.15(0.02) \\ 0.21(0.02) \end{array}$	9(3)
Тсь	JA-28 G1-2233 G1-2289 YM-54 G1-2333 G1-2363	2001 2233 2289 2491 2333 2363	153(6)	80(20)	5 2.5 1.3(0.3)	10 9(1)	4.2(0.5) <sup>b</sup>	
	G1-2410 JA-32 G1-2476	2410 2533 2476	130(30)	110	2.2(0.9)	20(9)		
Tct	G1-2698 G1-2840 G1-2854	2698 2840 2854			0.5	3.1		
	G1-2901 G1-3116 JA-37	2901 3116 3497	28 000 (10 000) <sup>e</sup>	400(70) <sup>e</sup>	4.3 3.7 4.6(0.3)	5.5 3.3		22
Tl	G1-3658	3658						······
Tba	G2-3933	3923	6600(400)	1600(30)	0		0.1(0.06)	

<sup>a</sup>Data from Daniels et al. (December 1982); Ogard et al. (1983); Wolfsberg et al. (1983). If no footnote is indicated, the sorption ratio in parentheses represents the standard deviation of the mean.

<sup>b</sup>Ambient conditions, air,  $20 \pm 4^{\circ}$ C; fractions do not contain particles smaller than 75  $\mu$ m in diameter except in fractions designated by footnote f.

<sup>c</sup>Stratigraphic units are as follows: Tpc = Tiva Canyon Member; Tpp = Pah Canyon Member; Tpt = Topopah Spring Member; Tht = tuffaceous beds of Calico IIills; bt = bedded tuff; Tcp = Prow Pass Member; Tcb = Bullfrog Member; Tct = Tram Member; Tl = older tuffs; Tba = bedded tuff.

<sup>d</sup>Nonweighted average; value in parentheses is the standard deviation of the mean.

<sup>e</sup>Some data were rejected in averaging.

<sup>f</sup>Average of data for the fraction with particles smaller than 500  $\mu$ m in diamter (contains some particles smaller than 75  $\mu$ m).

<sup>6</sup>Nonweighted average of samples taken in two different positions.

<sup>h</sup>Performed under controlled atmospheric conditions of nitrogen with  $\leq 0.2$  ppm O<sub>2</sub> and  $\leq 20$  ppm CO<sub>2</sub>.

Table Ib. Average sorption ratios (distribution coefficients) from batch sorption experiments on crushed tuff for strontium, cesium, barium, radium, cerium, and europium<sup>a,b</sup>

.....

C		Donth	Sorption Ratios $(m\ell q)$					
Unit	Sample	(ft)	Sr	Cs	Ba	Ra	Ce	Eu
Tpc	JA-8	606	270(5) <sup>d</sup>	2700(400) <sup>d</sup>	435(15) <sup>d</sup>			2100(300) <sup>d</sup>
	YM-5	251	280(80)	5800(800)	1100(200)		450 000 <sup>d</sup> (240 000)	2 300 000 (40 000)
Трр	G2-547	547	265(10) <sup>f</sup>	13 300	3490(30) <sup>f</sup>			340(30) <sup>f</sup>
	G2-723	723	290(40) <sup>f</sup>	4100 (600)f	3500			>10 000 <sup>f</sup>
	GU3-433 GU3-855	433 855	45(9) <sup>g</sup>	630(20) <sup>s</sup>	(400) <sup>s</sup> 810(100) <sup>s</sup>			100(14) <sup>g</sup>
Tpt	YM-22 GU3-1203	848	53(4) 42(1)	290(30)	900(30) 640(40)		1270(40)	1390(110)
	G1-1292	1200	200(6)	430(28)	$2100(300)^{f}$	1500(100)	66(8) <sup>d</sup>	$140(14)^{d}$
	GU3-1301	1301	28(4) <sup>g</sup>	160(40)	570(60) <sup>\$</sup>	~ /	000.000	45(12) <sup>g</sup>
	Y.M-30	1204	260(80)	855(5)	3400(1500)		230 000 (100 000)	(50,000)
	JA-18	1420	17 000 (3000)	16 000 (1000)	38 000 (18 000)		2800 (1400) <sup>e</sup>	1400(200) <sup>e</sup>
Tht	G1-1436	1436	36 000 (3000)	7800	150 000 (24 000)		59 000 (7000)	30 000 (2000)
	G2-1952	1952	2200(400) <sup>f</sup>	63 300	25 000		(1000)	(2000) 89(14) <sup>gf</sup>
	GU3-1436	1436		(1100) <sup>f</sup>	(4000) <sup>f</sup>			. ,
ht	GU3-1531	1531						
50	YM-38	1504	$17\ 000$ (2000)	13 000 (2000)	100 000 (10 000)		760(140)	1600(200)
	YM-42	1824	3900(600)	17 000 (1000)	94 000 (14 000)		49 000 (7000)	52 000 (4000)
Тср	G1-1854	1854	60 000 (14 000)	13 000	45 000			. 15 000
	YM-45	1930	195(14)	520(90)	1200(100)		730(100)	1600(200)
	G1-1883 VM-46	1883	22(0.2) 190(60)	187(3) 840(6)	183(12)		1420(20)	207.000
		2002	100(00)	040(0)	(6000)		$(110\ 000)$	(110 000
	G1-1982	1982	55(4)	1120(110)	700(50)		560(40) <sup>gf</sup>	970(150)
	X_M-48	2114	2100(400)	9000(4000)	18 000		1400(500)	2200(500)
	YM-49	2221	3200(300)	36 000	42 000		550(100)	1200(100)
-	JA-26	1995	95(35)	(3000) 1500(600)	(8000) 800(300)			
Tcb	JA-28	2001	94(20)	1640(210)	820(50)			2100(1000)
	G1-2233	2233	48 000 (2000)	13 500	250 000		1400(300)	900(200)
	G1-2289	2289	7300(500)	37 000	66 000	46 000		797(10)
	YM-54	2491	62(12)	$(13\ 000)$ 180(40)	(9000) 400(150)	$(20 \ 000)$	150(40)	470(40)
	G1-2333	2333	180(20)	1400(130)	1500(200)		100(40)	2300(400)
	G1-2363	2363	64(3)	470(40)	235(9)	540(60)		730(50)
	JA-32	2533	57(3)	1230(30) 123(4)	380(30)		82(14)	440(80) 90(20)
	G1-2476	2476	41(1)	700(40)	385(11)		02(11)	3200(100)
Tct	G1-2698	2698	42 000 (2000)f	7700(400) <sup>f</sup>	63 000		240(30) <sup>f</sup>	$200(30)^{f}$
	G1-2840	2840	860(1)	2200(200)	2070(70)			4900(400)
	G1-2854	2854	94(1)	1080(120)	1000(50)			1300(200)
	G1-2901	2901	68(1) <sup>1</sup>	1290(110) <sup>1</sup>	1600(200) <sup>f</sup>		42 000	160 000
	G1-3116	3116	2400(17) <sup>f</sup>	6600(500)	12 000		(3000) <sup>1</sup> 100(10) <sup>f</sup>	(50 000) <sup>f</sup> 760(60) <sup>f</sup>
	JA-37	3497	287(14)	610(40)	(4000) <sup>•</sup> 760(150)			6000(800)
Tl	G1-3658	3658	13 000(0)	4950(50)	13 500 (500)		$1000(200)^{f}$	530(40)
Tba	G2-3933	3933	240(60) <sup>f</sup>	2500(1000) <sup>f</sup>	1700(500) <sup>f</sup>		··· · · · · · · · · ·	1500(700) <sup>f</sup>

4

... --

Table Ic. Average sorption ratios (distribution coefficients) from batch desorption experiments on crushed tuff for strontium, cesium, barium, cerium, and europium<sup>a,b</sup>

,-

Stratigraphic <sup>c</sup>		Depth	(De)Sorption Ratios (mℓ/g)					
Unit	Sample	(ft)	Sr	Cs	Ba	Ce	Eu	
Tpc	JA-8	606	311(3)	4600(400)	480(50)		10 000(3000)	
	YM-5	251	320(30) <sup>d</sup>	8900(600)	1200(120) <sup>d</sup>	31 000(30 000) <sup>d</sup>	36 000(14 000) <sup>d</sup>	
Tpp	G2-547	547	$210(10)^{f}$	8700(550) <sup>f</sup>	2900(200) <sup>f</sup>		1700(600) <sup>f</sup>	
	G2-723 GU3-433	723 433	330(4) <sup>1</sup> 40(10)\$	4300(4) <sup>1</sup> 520(20) <b>5</b>	$4200(10)^{1}$ $460(20)^{8}$		$>10\ 000^{1}$	
m (	176.00				400(20)-		140(10)*	
Tbr	GU3-1203	848 1203	59(2) 47(1)	365(7) 340(10)	830(100) 720(30)	6500(800)	3500(200) 650(50)	
	G1-1292	1292	120(5) <sup>f</sup>	$510(20)^{f}$	1500(100) <sup>e,f</sup>	600(200) <sup>f</sup>	600(70) <sup>f</sup>	
	GU3-1301 YM-30	1301	80(20) <sup>8</sup> 210(30)	185(20) <sup>8</sup>	675(60) <sup>8</sup>	170 000(15 000)	$100(20)^{g}$	
	JA-18	1420	15 000(2000)	17 500(700)	280 000	1600(500) <sup>e</sup>	$2400(300)^{\circ}$	
			· · ·	· · ·	(50  000)	()		
Tht	G1-1436	1436	87 000	24 000(2000)	340 000	6700(600)	5300(600)	
	G2-1952	1952	$(12000)^{f}$	46 000(1400) <sup>f</sup>	(90 000) 40 000		1600(200) <sup>f</sup>	
			1200(200)	10 000(1 100)	$(1000)^{f}$		1000(200)	
	YM-38 VM-42	1540	22 000	13 000	260 000	2600	7300	
	1.91-92	1042	4100(1000)	21 000(2000)	90 000	44 000(5000)	64 000(3000)	
Тср	G1-1854	1854	72 000 (13 000)e	14 000(2000)	$150\ 000$		4800(700)	
	YM-45	1930	210(20)	620(110)	1310(60)	5800(600)	7300(900)	
	G1-1883	1883	59(1) <sup>f</sup>	430(4)	$440(10)^{f}$	$2200(100)^{f}$	1350(50) <sup>f</sup>	
	<b>I</b> _VI-40	2002	260(20)	1800(300)	210 000 (3000)	300 000 (50 000)	31 000(2000)	
	G1-1982	1982	322(8) <sup>f</sup>	$2300(200)^{f}$	2780(120) <sup>f</sup>	7000(800) <sup>f</sup>	6370(130) <sup>f</sup>	
	Y.M-48	2114	2700(200)	27 000(4000)	34 000(7000)	128 000	8100(1200)	
	YM-49	2221	4400(100)	39 000(1000)	65 000(7000)	1040(40)	2100(500)	
	JA-26	1995	39(3)	1580(90)	450(13)		2900(200)	
Teb	JA-28	2001	114(3)	2400(100)	1160(20)		12 300(500)	
	G1-2233	2233	90 000	$23\ 000(6000)^{f}$	240 000	20 000	$5000(2000)^{f}$	
	G1-2289	2289	$(40\ 000)^{4}$		(80 000)*	$(13 \ 000)^{e}$		
	YM-54	2491	97(9)	310(20)	660(20)	1000(200)	1840(110)	
	G1-2333	2333	140(13)	1230(100)	1460(130)		9900(1200)	
	G1-2000	2303	190(0).	1200(30)*	820(20)*	130 000 (6000) <sup>f</sup>	$6100(200)^{1}$	
	G1-2410	2410	140(14)	1120(100)	1760(150)	(0000)	6000(3000)	
	JA-32 G1-2476	$2533 \\ 2476$	53(3) 200(40)	175(11) 1520(0)	490(40)	530(120)	850(130)	
Tet	C1-2608	2608	210.000	17.000(1100)[	100.000	0000(400)f		
100	01-2030	2030	$(50\ 000)^{f}$	17 000(1100).	190 000 (80 000) <sup>f</sup>	2000(400)*		
	G1-2840	2840	1540(4)	2300(130)	2500(200)		9000(1100)	
	G1-2854 G1-2001	2854	96(1) 67(1)e.f	1160(20)	1330(0)	80.000(1000)f	5000(200)	
	91-2901	2901	01(1)***	1300(30).	1880(30),	39.000(1000) <sub>1</sub>	210 000 (50 000)	
	G1-3116	3116	24 000(13 000) <sup>f</sup>	11 000	160 000	3000(1000) <sup>f</sup>	8000(3000) <sup>f</sup>	
	JA-37	3497	312(9)	(3000) <sup>r</sup> 850(50)	(80 000) <sup>f</sup> 920(40)		11 000(2000)	
Tl	G1-3658	3658	12 000(3000) <sup>f</sup>	12 000(2000) <sup>f</sup>	10 000(4000) <sup>f</sup>	9000(4000) <sup>f</sup>	9000(3000) <sup>f</sup>	

Stratigraphic <sup>c</sup>		Depth	(De)Sorption Ratios (m\ell/g)						(De)Sorpt		
Unit	Sample	(ft)	Am	Pu	Ŭ	Tc	Np				
Трс	JA-8 YM-5	606 521									
Tpp	G2-547	547	17 000(1400)	1200(170) <sup>f</sup>							
	G2-723	723	$2.8 \times 10^{6}$	>4700							
	GU3-433	433	9300(1780) <sup>g</sup>	920(40) <sup>g</sup>							
Tpt	YM-22	848	2500(400) <sup>d</sup>	1330(140) <sup>d</sup>	5(2) <sup>d</sup>	1.2(0.3) <sup>d</sup>	33(5) <sup>d</sup>				
	GU3-1203	1203	1300(200) <sup>s</sup>	920(15) <sup>g</sup>							
	GU3-1301	1292	2500(600)5	1300(460)5		U					
	YM-30	1264		1000(100)							
	JA-18	1420	1100(300)	350(140)	9.4(1.4)						
${ m Tht}$	G1-1436	1436	E000(1100)E	950/4518			15(0)				
	G2-1952 YM-38	1952	7100(1200)	350(45)° 1600(300)	14.8(1.0)		15(2) 24(2)				
	YM-42	1824	()		(1)		- (-)				
Tcp	G1-1854	1854									
	YM-45	1930	5000(000)	000(00)			00(10)				
	G1-1883 VM-46	1883	7200(900)	890(60)			36(10)				
	G1-1982	1982			4.1						
	YM-48	2114				1.6(0.2)					
	YM-49 IA-26	2221	3400(400) <sup>e</sup>	720(90)		2.0(0.3)	12(4)				
Tch	JA 28	2001			·						
100	G1-2233	2001			8(2)						
	G1-2289	2289			0(-)						
	YM-54	2491	550(80)	720(40)	12(8)						
	G1-2333 G1-2363	2333									
	G1-2410	2410									
	JA-32	2533	2200(600)		8(2)						
	G1-2476	2476			1.5(0.2)						
Tct	G1-2698	2698									
	G1-2840 G1-2854	2840									
	Ğ1-2901	2901									
	G1-3116	3116	80.000/10.000	1 400 (000)	1.7(0.3)						
	JA-37	3497	32 000(10 000)	1400(300)	9.9(0.40)	·	170(50)				
<u></u>	G1-3658	3658									
Tba	G2-3933	3933	12 000(410)	530(130)		0					

Table Id. Average sorption ratios (distribution coefficients) from batch desorption experiments on crushed tuff for americium, plutonium, uranium, technetium, and neptunium<sup>a,b</sup>

<sup>a</sup>Data from Daniels et al. (December 1982); Ogard et al. (1983); Wolfsberg et al. (1983). If no footnote is indicated, the sorption ratio in parentheses represents the standard deviation of the mean.

<sup>b</sup>Ambient conditions, air,  $20 \pm 4^{\circ}$ C; fractions do not contain particles smaller than  $75 \ \mu$ m in diameter except in fractions designated by footnote f.

<sup>c</sup>Stratigraphic units are as follows: Tpc = Tiva Canyon Member; Tpp = Pah Canyon Member; Tpt = Topopah Spring Member; Tht = tuffaceous beds of Calico IIills; bt = bedded tuff; Tcp = Prow Pass Member; Tcb = Bullfrog Member; Tct = Tram Member; Tl = older tuffs; Tba = bedded tuff.

<sup>d</sup>Nonweighted average; value in parentheses is the standard deviation of the mean.

Some data were rejected in averaging.

<sup>f</sup>Average of data for the fraction with particles smaller than 500  $\mu$ m in diamter (contains some particles smaller than 75  $\mu$ m).

<sup>g</sup>Nonweighted average of samples taken in two different positions.

<sup>h</sup>Performed under controlled atmospheric conditions of nitrogen with  $\leq 0.2$  ppm O<sub>2</sub> and  $\leq 20$  ppm CO<sub>2</sub>.

Commission (NRC) has formulated a technical position on sorption (Nuclear Regulatory Commission, 1987) that establishes various guidelines on the types of information and level of understanding of sorption processes that "will be needed in order to assess the effects of radionuclide sorption upon performance of a high-level waste repository." The NRC contracted with Oak Ridge National Laboratory to conduct a series of experiments independent of the US Department of Energy (DOE) program to evaluate the "potential geochemical behavior of radionuclides" at the Yucca Mountain site. Evaluation of the YMP sorption coefficient database through duplication of experiments performed by the YMP formed a major part of the Oak Ridge program (Meyer et al., 1987). Other concerns about the YMP sorption coefficient database have been expressed in public comments on the Environmental Assessment, Yucca Mountain (1986) and on the Site Characterization Plan (1988).

With this background in mind, the purpose of this paper is to

- (1) review the applicability of simple (constant) sorption coefficients in transport calculations,
- (2) review and evaluate alternative methods for the derivation of sorption coefficients,
- (3) summarize and evaluate the present YMP sorption database to identify areas of data sufficiency and significant data gaps,
- (4) summarize our current understanding of pertinent sorption mechanisms and associated kinetic parameters,
- (5) evaluate the significance to the YMP of potential problems in the experimental determination and field application of sorption coefficients as enumerated by the NRC (Nuclear Regulatory Commission, 1987) in its technical position paper on sorption,
- (6) formulate and evaluate strategies for the resolution of NRC concerns regarding experimental problems, and
- (7) formulate a position on the sorption coefficient database and the level of understanding of sorption mechanisms likely to be required in the licensing application.

Several aspects of sorption in relation to the potential repository at Yucca Mountain will not be addressed in this paper. These include: (1) sorption in the near-field of the potential repository, (2) sorption or complexation of radionuclides by microorganisms or other organic materials, and (3) quantitative estimates of transport based on sorption coefficients discussed in this paper. These topics are covered under WBS numbers 1.2.2.5.2.L, 2.3.4.1.9.A, and 2.3.4.1.7.A, respectively.

## II. CONSTANT SORPTION COEFFICIENTS IN TRANSPORT CALCU-LATIONS

The rate of transport of a given chemical component through a porous medium is typically calculated using a constant sorption coefficient (Abriola, 1987). This is the approach that has been used in performance assessment by the YMP (Environmental Assessment, 1988). Various authors have questioned the validity of this approach in recent years (for example, Reardon, 1981; Tripathi, 1983; Cederberg, 1985; Valocchi, 1985), leading to confusion over the applicability of sorption coefficients in transport calculations. As concluded in the following discussion, the issue is not whether sorption coefficients are applicable but the manner in which they are obtained and applied (also see Serne, 1982).

Some authors have argued that different species of a particular element in solution (for example,  $Ca^{++}$ ,  $CaCl^+$ , etc.) may have different sorption coefficients in a given medium and will therefore be transported at different rates (Tripathi, 1983; Cederberg, 1985). In "equilibrium" systems, this argument is not valid because individuals in a population of chemical species have short lifetimes relative to the solvent flow rate (Vermuelen et al., 1984). As a result, a strongly sorbing species of the element may convert into a weakly sorbing species and vice versa so that an average sorption coefficient for the various species of the element can be used to model the transport behavior of the element. Calculations presented in support of the the speciation argument (Cederberg, 1985) do reflect a change in the average sorption coefficient in the "equilibrium" system modeled. However, this change is due primarily to a prescribed change in the composition of the feed solution (that is, the solvent).

Most other arguments against the use of constant sorption coefficients are also predicated on changes in the system with time. These changes fall into two categories: (1) changes in the composition of the system with time [for example, changes in the concentration of the solute, changes in the composition and/or identity of the sorbing phase(s), etc.], and (2) changes in the physical state of the system (for example, temperature, permeability, flow rate, etc.). There is no consensus at present on how the effects of these changes should be incorporated into transport calculations (codes). One possibility would be to retain the simple  $K_d$  approach in the transport calculation but provide an independent procedure to obtain the K<sub>d</sub> values for a given set of conditions. Changes in the sorption coefficient caused by changes in the concentration of the solute could be handled with empirical isotherm equations (for example, Langmuir, Freundlich, etc.). Changes in sorption coefficients resulting from dispersion (Rubin and James, 1973) could also be handled this way. More complex chemical changes could be handled either by calculations based on geochemical codes such as EQ3/6 (Viani, 1988) or MINEQL (Westall et al., 1976) or by a series of predetermined three-dimensional  $K_d$  matrices representing the K<sub>d</sub> values for a given radionuclide at different points within Yucca Mountain at different times or under a variety of different environmental conditions. The  $K_d$  calculations could also be embedded directly within the transport code (Abriola, 1987); however, this would increase the computation time dramatically.

One reason no consensus exists on how to include the effects of changes in chemical conditions in transport calculations is that our present understanding of sorption mechanisms is rather limited. In fact, prediction of the effects on sorption of compositional changes in the system (for example, pH and composition of the substrate) is a major objective of current research (Davis and Hayes, 1986; Stumm, 1987).

The impact of changes in the physical state of the system on the transport of chemical components often requires some understanding of kinetic factors. For instance, an increase in the flow rate may preclude the attainment of equilibrium during the sorption process (Reardon, 1981). To quantify the effects of these changes, kinetic rate constants are required for the appropriate sorption mechanisms. Because natural flow systems are physically as well as compositionally heterogeneous, these constants are generally obtained on a site-specific basis (for example, Rundberg, 1987). Changes in the temperature of a flow system can lead to changes in sorption coefficients with or without kinetic effects. There are no theoretical equations for predicting the effects of temperature on sorption coefficients so these effects must be measured experimentally. In the near field of a repository, the structure of the sorbing substrates may be altered as a result of temperature increases. Under these conditions, modeling of element transport will involve a complex set of problems that goes well beyond the scope of this review.

In summary, unless the chemical parameters (except sorbing components) or physical parameters in a flow system vary significantly, a constant sorption coefficient ( $\pm$  isotherms) may be adequate for modeling waste element transport. If the system parameters vary as stepfunctions or if the variations have very long time constants relative to the flow rate, the transport calculations can be carried out in steps by using different values for the sorption coefficients in each step. If the changes in system parameters are continuous, sorption coefficients used in the transport calculation could be changed at intervals corresponding in time to some threshold change in the value of a system parameter. Sorption reaction kinetics could also be included in this approach in an approximate fashion. Full coupling of the effects of continuous changes in chemical and physical variables on transport would dramatically increase the complexity of the problem and calculation time (Tsang and Mangold, 1984; Abriola, 1987).

## III. REVIEW AND EVALUATION OF ALTERNATIVE PROCEDURES FOR. DERIVATION OF SORPTION COEFFICIENTS

Sorption coefficients have traditionally been obtained in the laboratory by empirical methods (for example, Serne and Relyea, 1981). Although the coefficients obtained by these methods have been useful in evaluating the behavior of various chemicals on a local scale and over relatively short time intervals, the problem of long-term storage of nuclear wastes calls for more quantitative and theoretically defensible methods of evaluation and prediction. Alternative strategies for obtaining sorption coefficients are summarized in Fig. 1. To date, the YMP has followed the first strategy, in which selected groundwater compositions, spiked with radionuclides, are reacted with a limited number of rock types. This strategy provides sorption coefficients at different radionuclide concentrations for a limited set of groundwater compositions.

A major criticism of the whole-rock approach to the derivation of sorption coefficients is that it does not lead to an extrapolation capability. That is, it does not provide a means to estimate sorption coefficients under physical conditions or rock and water compositions not directly included in the experimental program. One way to enhance this predictive CONCEPTUAL STRATEGIES FOR OBTAINING Rd's



Fig. 1. Conceptual strategies for obtaining R<sub>d</sub>'s.

capability is to carry out sorption experiments on pure mineral phases over the range of physical and chemical conditions anticipated in the system (Fig. 1). The results of such experiments would allow prediction of sorption coefficients in rock types that were not directly included in the experimental program by weighting sorption coefficients for the mineral phases present in the rock according to their modal abundance (Serne and Relyea, 1981). This approach might be attractive for the estimation of sorption coefficients of mineralogically variable fracture fillings in Yucca Mountain (see, for example, Carlos, 1985). It could also be used to provide a finer grid of sorption coefficient data over the repository block if a grid of sufficiently detailed mineralogic information is available. However, the capability to model sorption coefficients as a function of rock mineralogy (given a constant water composition) only addresses part of the problem.

Under ambient conditions in a flow system such as that associated with Yucca Mountain, the mineralogy of the rock matrix is unlikely to change much over periods of tens to hundreds of thousands of years. The parameters most likely to vary through time include the chemical composition of groundwaters and the concentration of waste elements they may carry. If present and future groundwater compositions are sufficiently well characterized, the experimental grid used for the pure mineral sorption experiments can simply be enlarged to include a greater number of water compositions. However, to derive an extrapolation capability for the prediction of sorption coefficients involving groundwaters ( $\pm$  contaminants) not included in the experimental matrix, a more theoretical approach is required.

This approach requires various types of information as input, as shown on Fig. 1 and discussed in more detail below. The advantage to this approach is that it provides a capability for extrapolation to conditions not included in the experimental matrix of the empirical studies. In the following discussion, the empirical and theoretical approaches will be reviewed separately.

## A. Review and Evaluation of Empirical Techniques for Derivation of Sorption Coefficients in the Laboratory

In the empirical batch method (Fig. 1) used at Los Alamos (Daniels et al., December 1982), a sample of crushed rock or soil material is reacted with a solution representing the *in situ* groundwater, which has been spiked with an radioisotope of the element of interest. The crushed rock is "equilibrated" with a separate aliquot of *in situ* groundwater before the spiked water is added. The final radioactivity of the spiked element in the solution and the radioactivity on the solid phase are measured after some appropriate contact time. The ratio of the activity per gram of solid to the activity per milliliter of solution is calculated and is called the experimental sorption coefficient, denoted by  $R_d$ . The appropriate contact time is determined in a series of experiments carried out over different time intervals with the same sample and spike solution. In these experiments, the sorption coefficient generally approaches a steady state value with time. If the solution is not oversaturated with a stoichiometric compound of the radionuclide spike(s), the experimental sorption coefficient obtained is probably close to the equilibrium  $K_d$ .

Batch experiments can be carried out at different temperatures if the substrate composition and structure remain unchanged except for the elements exchanging on the sorption sites. Experiments are often carried out over a range of element concentrations appropriate to the intended application. Because these experiments are carried out at constant temperature, the best fit line through the data in a plot of the solid concentrations vs the solution concentrations is called an isotherm. If the sorption coefficient does not vary over the measured range (that is, constant sorption coefficient), the isotherm is said to be linear. If the coefficient is not constant over this range, various isotherm equations, such as the Langmuir, Freundlich, and others, are available to fit the data (Vermeulen et al., 1984).

The wafer technique is a modification of the batch technique in which a solid wafer of rock is used instead of a crushed sample. Conceptually, the wafer technique more closely reflects the *in situ* sorption processes that would retard the transport of radionuclides in solid rock. Although the wafer technique has been used successfully with more permeable materials such as bedded tuffs, it is difficult to apply successfully to materials with low permeabilities (for example, Topopah Springs tuff).

The column technique offers a somewhat more sophisticated approach to the derivation of sorption data; it is very similar in operation to a typical ion exchange column (Vermuelen et al., 1984). A spiked groundwater solution is eluted through a column packed with crushed rock or soil material. Because of its dynamic aspect, the column technique provides information not obtainable through the batch technique. For instance, if the sorption reaction between the solid and the solution is slow relative to the column flow rate, the solute front will exit the column earlier than predicted on the basis of "equilibrium" batch sorption data. Mathematical analysis of these types of experiments can, therefore, yield information on the kinetics of sorption reactions (Rundberg, 1987). For elements that are slow to equilibrate among possible complexes in solution or for elements that form colloids (for example, plutonium), the column technique may result in apparent sorption coefficients that are substantially different from coefficients obtained through the batch technique (see, for example, Thompson, 1988). Such results emphasize potential problems in the application of batch sorption coefficients to the prediction of element transport in the absence of additional data on colloid behavior and the kinetics of complex formation/destruction in solution.

Conceptually, the most satisfactory approach to the determination of sorption coefficients in the laboratory involves the use of solid rock columns. Unfortunately, experiments involving solid rock columns are limited in a practical sense to rock samples with substantial permeability and elements with rather low sorption coefficients. Experiments involving rocks with low permeabilities or elements with high sorption coefficients generally cannot be completed within a reasonable period of time. The high reliability required of the experimental equipment used in long-term experiments is problematic, as are the potential imperfections (such as fractures) in the rock sample chosen for a given experiment. To model transport processes in a heterogeneous flow system such as that associated with the Yucca Mountain site, empirical sorption coefficients must be obtained over a range of conditions that bound those anticipated in the system over the lifetime of the proposed repository. Regardless of the chosen technique, experiments should be carried out using (1) all the major rock types found in the system, (2) all the major water compositions either existing or anticipated in the system, (3) the anticipated range of temperatures, and (4) the anticipated ranges of waste element concentrations. Consideration of other variables such as the fugacity of reactive gases and the speciation of radionuclides in solution may also be appropriate if warranted by anticipated conditions. To model a system as complex as Yucca Mountain, a large number of experiments are required even if all experimental difficulties (for example, colloid formation) can be taken into account.

## B. Review and Evaluation of Theoretical Approaches to Derivation of Sorption Coefficients

Until recently, developments in the quantitative understanding of sorption reactions have been driven largely by the needs of the industrial and agricultural sectors. For example, zeolites are widely used in the chemical industry, where the need for particular chemical separations has encouraged the development of theoretical models for ion exchange in zeolites (Barrer and Klinowski, 1977). Similarly, agricultural chemists have been concerned with the ion exchange behavior of clays and iron and manganese oxyhydroxides in relation to the effects of various chemical constituents on plant growth. This concern led to the development of ion exchange models for clays (Gaines and Thomas, 1953) and surface complexation models for the oxyhydroxides (Sposito, 1981; Davis et al., 1978; Davis and Leckie, 1978). These theoretical models for sorptive behavior are based on a more mechanistic treatment of the chemical reactions involved in the sorption process. These models are not strictly theoretical because they still require assumptions (see Sposito, 1981; Sposito, 1986; Stumm, 1987). The theoretical models assume that sorption of chemical species (sorbate) from a solution onto a solid substrate (sorbent) primarily involves ion exchange and/or surface complexation/precipitation processes in which the structure and composition of the substrate remain essentially unchanged. Ion exchange theory is well established theoretically (Sposito, 1981) and is extensively applied in industry (Vermeulen et al., 1984). The principal data required to apply the theory are selectivity coefficients that reflect the relative affinity of a given ion exchanger (substrate) for different ions (Triay and Rundberg, 1987). Surface complexation and precipitation theories are not as well grounded theoretically and require greater amounts of empirical data for their application (Sposito, 1986; Stumm, 1987). Nonetheless, if the composition and speciation of a solution are known or can be calculated, the theoretical models currently available allow the prediction of sorption coefficients for certain elements on selected minerals, including some iron and manganese oxyhydroxides (Hsi and Langmuir, 1985; Sanchez et al., 1985), zeolites (Breck, 1974; Benson, 1980), clays (Benson, 1980), and carbonates (Davis et al., 1987).

There are insufficient data available at present to apply this approach directly to the prediction of sorption coefficients for important radionuclides on rocks from Yucca Mountain. To derive sorption coefficients for Yucca Mountain rocks and fracture fillings, the following types of information will be required:

- (1) water (solution) compositions,
- (2) formation constants for solution species,
- (3) mineral compositions and structures,
- (4) mineral surface structures, surface compositions, and surface areas,
- (5) ion exchange constants (selectivity coefficients), and
- (6) Surface complexation constants.

At Yucca Mountain, water compositions have been obtained for the saturated zone (Ogard and Kerrisk, 1984), but the compositions of unsaturated zone waters are poorly known. Additional data on unsaturated zone waters should become available after the exploratory shaft has been sunk. Data available in the literature on formation constants for species of important radionuclides in waters typical of the Yucca Mountain area are currently being assembled as part of the solubility and EQ3/6 database development tasks within the YMP (WBS 2.3.4.1.4.A, and 1.2.2.5.2.L, respectively). In addition, experiments are in progress to determine the speciation and solubility of various radionuclides for which the available literature data are inadequate. Data on the abundance, composition, and structure of the major mineral phases present in Yucca Mountain have been published (Bish and Vaniman, 1985). Additional data will be required on the abundance, composition, and structure of trace mineral phases, including iron and manganese oxides and/or oxyhydroxides. These will be obtained as part of the mineralogy of transport pathways task (WBS 2.3.4.2.3.A). The availability of data on the surface properties of the major and trace minerals present in Yucca Mountain has not been evaluated to date. This subject must be addressed before theoretical sorption models can be applied to the Yucca Mountain site. Some data on ion exchange constants for zeolites and clays are available in the literature, and additional work is in progress to obtain constants applicable to ion exchange minerals in Yucca Mountain. Data on the surface complexation mechanisms for important radionuclides on minerals present within Yucca Mountain are sparse at the present time. Additional studies will be required to identify the nature of surface complexes on these minerals and their binding constants.

In summary, sorption coefficients can be derived on either an empirical or theoretical basis. If the present and future physical and compositional characteristics of the system are known or can be calculated, the empirical approach may be adequate if a sufficient number of experiments are conducted. On the other hand, if there is uncertainty regarding the present or future characteristics of the system, development of a more continuous predictive capability would be advantageous.

## IV. REVIEW AND EVALUATION OF YMP SORPTION DATABASE

The YMP sorption database contains data from various types of experiments that address different aspects of sorption behavior. Most of the sorption coefficient data were obtained in batch experiments involving crushed rock samples and a reference water composition (Well J-13). Data have also been obtained in experiments with solid rock wafers, crushed rock columns, and solid rock columns. The database will be reviewed and evaluated to identify the most reliable data and for any insight provided on sorption mechanisms, sorption reaction kinetics, and various concerns expressed by the NRC regarding sorption experiments and processes.

Thomas (1987) has tabulated and reviewed the YMP database for batch crushed rock sorption experiments involving the following elements: americium, barium, cerium, cesium, europium, neptunium, plutonium, radium, selenium, strontium, technetium, thorium, tin, and uranium (see also Daniels et al., December 1982; Environmental Assessment, 1986; Site Characterization Plan, 1988). The tabulated data reflect various permutations of the following experimental parameters: mineralogy and particle size of the crushed rock samples, temperature, sorption time, desorption time, degree to which equilibrium was attained, atmospheric composition, sorbing tracer concentration, water/rock ratios, tracer preparation techniques, and other experimental procedures. In a separate publication, Knight and Thomas (1987) discussed the results of batch sorption experiments in which groundwater composition was a variable.

As noted by Thomas (1987), some of the data were obtained while experimental techniques were being developed. Therefore, not all the data included in her tabulation are equally reliable. With this in mind, Beckman et al. (1987) used statistical techniques in an attempt to quantify and separate the effects of experimental technique, temperature, particle size, waste-element concentration, and sorption time on the measured sorption coefficients for barium, cerium, cesium, europium, and strontium. These elements were chosen because they make up the largest experimental data set and because they are generally thought to exhibit sorption behavior that is less complicated than that of the other elements included in the Thomas (1987) tabulation. Beckman et al. (1987) concluded that particle size had only a small effect on measured sorption coefficients, whereas temperature and the length of sorption experiment had more significant effects. Further, Beckman et al. (1987) noted no significant effect of tracer concentration although sufficient data to test for this effect were only available for barium for one rock sample. These conclusions will be evaluated below.

Data obtained to date indicates that the mineralogy of the substrate is an important variable in the sorption of the alkali and alkaline earth elements (Daniels et al., December 1982, pp. 92-103). Rock samples containing abundant zeolites and/or clays generally have much higher sorption coefficients for these elements than do devitrified or glassy samples. On the other hand, sorption coefficients for the fission products cerium, europium, and tin show large variations that do not appear to be correlated with rock type (Daniels et al., December 1982). The coefficients for cerium and europium may be correlated with the

abundance of primary phosphates such as apatite, secondary carbonates (see, for example, Caporuscio et al., 1985), and/or sulfates (Jonasson et al., 1988). Tin sorption coefficients are fairly consistent in all but one sample (G1-2901). In the latter sample, the coefficient is 2 orders of magnitude higher for an undetermined reason. Sorption coefficients for the elements neptunium, selenium, technetium, and uranium are generally small (1 to 5 ml/g), except in samples that contain certain accessory minerals. Neptunium and selenium sorption coefficients are larger in samples with carbonate minerals. Sorption coefficients for technetium are generally near zero, except for samples that contain significant amounts of iron oxides. Uranium coefficients are larger in samples with significant amounts of iron and/or manganese oxides and/or oxyhydroxides (Zielinski et al., 1986) and possibly in samples with carbonates.

Batch data for the elements americium and plutonium are more difficult to interpret because the experimental techniques used in the sorption studies on these elements evolved with time and experience (Daniels et al., December 1982, pp. 72-80). Further, preliminary data on the solubilities of americium and plutonium compounds (Kerrisk, July 1984; Nitsche et al., 1987) suggest many of the sorption experiments were performed with oversaturated feed solutions. On the basis of the most recent results (Thomas, 1987), it appears that sorption coefficients for americium and plutonium are lowest for glassy and zeolitic samples, somewhat higher for devitrified samples, and highest for samples with significant amounts of secondary clays, iron oxides, and/or calcite. The question of whether the results for glassy and zeolitic samples represent true sorption coefficients. precipitation, or both, has not been adequately resolved, even though these results are generally consistent with sorption coefficients reported in the literature (Means et al., 1978; Allard and Beall, 1979; Sanchez et al., 1985). Some of the detailed variation in measured americium and plutonium sorption coefficients, particularly in devitrified and glassy samples, could be due to the presence of secondary clays, iron and/or manganese oxides and oxyhydroxides, and calcite at levels below the detection limits of the x-ray diffraction techniques used to determine relative mineral abundances (Caporuscio and Vaniman, 1985; Bish and Vaniman, 1985). The unusually high values measured in a calciterich sample (G2-723) may be due to surface precipitation of americium hydroxycarbonate (Nitsche, 1986; Nitsche et al., 1987) on calcite. The ion association product (IAP) for surface precipitation can be substantially smaller than the IAP for precipitation of the pure phase.

Except in the case of the smallest size fractions ( $<75 \ \mu$ m), particle size does not appear to exert a major influence on the values for sorption coefficients obtained in the experiments (Daniels et al., December 1982, pp. 110-118; Daniels et al., January 1982, pp. 18-23). Sorption coefficients measured for the smallest size fractions ( $<75 \ \mu$ m) are generally somewhat greater than those obtained on the larger fractions (Wolfsberg et al., April 1982, pp. 22-26). This effect has been attributed to preferential concentration of fine grained sorptive minerals (such as clays) in the smaller fractions (Daniels et al., January 1982, pp. 19-22).

The effect of temperature on sorption coefficients was investigated in a limited number of experiments at 70°C (Wolfsberg et al., 1979; Vine et al., 1980) and at 85°C (Ogard et al., 1983). In general, measured sorption coefficients are higher at elevated temperature for all the elements included in the experiments (americium, barium, cerium, cesium, europium, plutonium, strontium, and uranium). The temperature effect is as much as an order of magnitude for the alkali and alkaline earth elements, americium, and plutonium but somewhat smaller for uranium; the elements cerium and europium showed little if any effect (Wolfsberg et al., 1979; Ogard et al., 1983). The early high-temperature experiments involving alkali and alkaline earth elements yielded sorption coefficients that showed monotonic increases with time. Although no additional high-temperature experiments have been carried out to evaluate experimental uncertainties, it appears likely that much of the variation in early high-temperature results reflects incomplete recrystallization of the rock material (see Daniels et al., January 1982, pp. 2-6) as well as any temperature dependencies the pertinent sorption coefficients may have. Because the reaction products in the early experiments were not characterized in detail, this possibility cannot be fully evaluated.

Although the early high-temperature experiments involving americium and plutonium also suffered from large experimental uncertainties, more recent experiments at 85°C showed some clear trends. Experiments on a devitrified sample (GU3-0433) showed little or no temperature effect for americium but as much as a factor of 7 increase in the sorption coefficient for plutonium. Sorption coefficients for glassy samples were increased by factors of at least 2 to 7 for both elements at high temperature (Ogard et al., 1983). Perhaps the glassy samples were altered during the higher temperature experiments to secondary phases such as clays, iron oxyhydroxides, and possibly other phases (Daniels et al., January 1982, p. 4) that had high sorption coefficients for these elements. Alternatively, the higher temperatures lead more readily to equilibration, which appears to be difficult to achieve for these elements at ambient temperatures.

Knowledge of the degree to which sorption equilibrium is attained during a given experiment is critical to the proper interpretation and application of the measured sorption coefficient. The measured coefficient may be either smaller or larger than the equilibrium coefficient if sorption equilibrium is not attained. Indications of the degree to which sorption equilibrium has been attained can be derived from the trend in measured sorption coefficients with time in a given experiment and by comparison of coefficients obtained in sorption vs desorption experiments. Assuming the correct experimental technique has been used, the gradual approach to a constant value for the sorption coefficient with time suggests sorption equilibrium has been approximated. Equal values for sorption and desorption coefficients, within the experimental error, also would suggest sorption equilibrium has been approximated. A lack of consistency in the measured coefficients could reflect problems with sorption equilibrium, analytical technique, or some sort of irreversible reaction(s) (Davis and Hayes, 1986).

Because most of the early experiments on alkali and alkaline earth elements did not attain steady state concentrations even over periods up to 90 days (see Figs. 1 through 28 in Wolfsberg et al., 1979), the sorption coefficients calculated from these experiments are unlikely to represent equilibrium values. More recent ambient temperature experiments have yielded consistent results and suggest sorption equilibrium is attained for these elements within 3 weeks or less (Daniels et al., January 1982). Devitrified samples appear to equilibrate more rapidly than zeolitic and glassy samples. Further, cesium appears to equilibrate more rapidly than strontium, which in turn appears to equilibrate somewhat faster than barium. Why the measured sorption coefficients obtained in the early experiments did not achieve steady state values over 6- to 8-week periods is uncertain but may be related to the procedure used to separate the solution from solid residue. The early experiments with cesium on devitrified samples came closest to achieving steady state values. They show a rapid increase in R<sub>d</sub> in the first 3 weeks, followed by a more gradual increase to the end of the experiment. Although the desorption coefficients show more variation, they appear to converge on a steady state value that is similar to that approximated by the sorption coefficients (Wolfsberg et al., 1979; Vine et al., 1980; Erdal et al., 1981; Wolfsberg et al., 1981). Similar results are reported by Daniels et al. (January 1982) and Bryant and Vaniman (1984) for barium, cesium, and strontium.

Although data from early batch (crushed rock) experiments with americium and plutonium showed inconsistencies, more recent (ambient temperature) experiments performed with improved techniques have yielded more consistent results. Time-series experiments involving a zeolitic tuff (G4-1502) at ambient temperature show that a near steady state value for the americium sorption coefficient was obtained after 20 days (Bryant and Vaniman, 1984). Six-week (single time step) experiments on other zeolitic and glassy tuffs yielded sorption coefficients broadly consistent with the time-series experiments (Ogard et al., 1983). However, the fact that desorption coefficients for americium differed from sorption coefficients by as much as a factor of 2 in glassy samples and as much as a factor of 5 in zeolitic samples suggests the results from the time-series experiments may not be representative and that the time required to achieve sorption equilibrium in experiments involving americium may be longer than 6 weeks, at least for some rock types. Other explanations for these observations include the possibility that (1) part of the americium sorbs by some irreversible reaction (Sposito, 1986), or (2) colloidal or other particulate material was present in the sorption but not in the desorption experiments. Sorption and desorption coefficients obtained for plutonium (Ogard et al., 1983) in the 6-week experiments are less consistent than those obtained for americium but are still within a factor of 6. Until the experimental problems with oversaturation are resolved, no reliable data on the kinetics of americium and plutonium sorption will be obtained.

The results of batch experiments with solid-rock wafers have been used to derive kinetic rate constants for sorption reactions involving simple cations. Rundberg (1987) has evaluated the rate of uptake of barium, cesium, and strontium by wafers of zeolitic and devitrified rock obtained from Yucca Mountain cores. He was able to fit the experimental data by assuming the sorption process includes two diffusion-limited steps. The first step involves the diffusion of a given element through the rock matrix to the mineral, and the second step involves diffusion within the mineral. This approach was used to derive the matrix diffusion coefficients and the forward and backward rate constants for the "sorption reaction" for barium, cesium, and strontium in several experiments involving different rock samples and water from well J-13. Although the data for actinide sorption are less reliable, this approach was also applied to a set of data for plutonium. The calculated rate constants were several orders of magnitude smaller than the constants for the alkali and alkaline earth elements (Rundberg, 1987).

The experimental data on crushed-rock columns (Treher and Raybold, 1982) can also be used to obtain information on the kinetics of sorption reactions. However, data from these experiments are more difficult to interpret because they reflect physical parameters (for example, porosity and dispersion) as well as sorption processes. Rundberg (1987) has successfully modeled the breakthrough behavior for barium, cesium, and strontium in columns with different crushed-rock compositions and flow rates. At flow velocities  $\leq 10^{-4}$ cm/s, the broadening of the elution curve was concluded to be largely due to longitudinal diffusion of the cations in solution and not to slow mass transfer kinetics. Thompson (1988) has reported on crushed-rock column experiments involving zeolitic tuffs in which a substantial fraction of the plutonium (V and VI) loaded on the columns was eluted in a noncolloidal form along with the nonsorbing reference tracer. When compared with batch data for the same samples, these results suggest the kinetics of actinide sorption and solution reactions are very slow relative to the flow rates in these columns.

The effects of atmospheric composition on sorption coefficients were investigated in two different types of experiments. In one, the natural atmosphere was replaced with nitrogen with  $\leq 0.2$  ppm O<sub>2</sub> and  $\leq 20$  ppm CO<sub>2</sub>. This atmosphere had no measurable effect on the sorption coefficients for americium, barium, cerium, cesium, europium, selenium, and strontium; it lowered the coefficients for manganese (factors of 3 to 4) and tin (factor of 2); and it increased the coefficients for neptunium and plutonium by a factor of 2, uranium by a factor of 2 to 3, and technetium by a factor of 10 or more. These variations presumably reflect the less oxidizing nature of the nitrogen atmosphere. In the other set of experiments, the amount of  $CO_2$  in the atmosphere was controlled at a level corresponding to a solution (J-13 groundwater) pH of 7.0. This resulted in slightly lower (less than factor of 2) selenium sorption coefficients in all but one sample and higher (factors of 2 to 5) uranium coefficients. It had no apparent effect on neptunium coefficients in glassy and zeolitic samples, although it decreased the coefficient in a devitrified sample by a factor of 18. The latter decrease may reflect a lower sorption coefficient for neptunium on iron oxide at lower pH (Kent et al., 1988). The increased uranium sorption coefficients at lower pH may reflect a decrease in the importance of carbonate complexing of the uranyl ion (Ogard and Vaniman, 1985). Although thorium was also included in these experiments, no experimental data are available at ambient atmosphere for comparison because thorium is very insoluble at pH > 7.0.

As discussed earlier, sorption coefficients for a given element can vary with the concentration of the element in the solution. To determine the effect of this parameter on radionuclide transport, sorption experiments have been carried out over a range of radionuclide concentrations to obtain isotherms. To date, data that allow the testing of isotherm equations have been obtained for plutonium on a devitrified and a partially zeolitized tuff under ambient conditions (Daniels et al., December 1982), cesium (Daniels et al., 1983) and strontium (Wolfsberg et al., October 1982) on a devitrified welded tuff (G1-2840) under ambient conditions, and neptunium and protactinium on a zeolitic tuff (G-4-1608) under a  $CO_2$  controlled atmosphere (Rundberg et al., 1985). The plutonium data were not sufficiently consistent to allow selection of an isotherm equation. A Langmuir isotherm was fit to the strontium data for the welded tuff sample (Wolfsberg et al., October 1982). The cesium data for this sample could not be fit with a Langmuir isotherm because of a lack of data required to correct for the indigenous (nonradioactive) cesium in the sample.\* However, Fuentes et al. (August 1987) have fit these data with a Freundlich isotherm. Data for neptunium on the zeolitic sample appear to fit a Langmuir isotherm, whereas the protactinium data are not sufficiently consistent to fit with any isotherm.

Fuentes et al. (August 1987; September 1987) and Polzer and Fuentes (1987) have used the data set selected by Beckman et al. (1987) to calculate isotherm parameters for the elements barium, cesium, europium, and strontium in various rock types. Their results for barium corroborate the conclusion reached by Beckman et al. (1987) regarding the lack of a tracer concentration effect for this element. However, for other elements in their study, Fuentes et al. (August 1987; September 1987) did observe concentration effects that they chose to model with a modified Freundlich isotherm. Unfortunately, for many if not most of the isotherms fit by these authors, there were not enough measurements to make a statistically meaningful distinction among the various isotherm equations available (see Daniels et al., December 1982, p. 133). Further, fitting the experimental data with a modified Freundlich isotherm does not provide much insight into sorption mechanism(s) for the elements involved nor does it provide for significant extrapolation capabilities.

The effect of different water/rock ratios on sorption coefficients has been measured for the elements barium, cerium, cesium, europium, and strontium in a devitrified sample and a zeolitic sample (Wolfsberg et al., 1981). Data for the elements cerium and europium will not be discussed because of problems with reaction kinetics. The data for the elements barium, cesium, and strontium suggest the effect of changes in water/rock ratios are relatively minor for the devitrified sample but may be more significant for the zeolitic sample, particularly for barium. The data for the devitrified sample have been evaluated and a Freundlich isotherm was used to compare them with the results of isotherm measurements on the same sample. Within the limitations of the data (kinetics, analytical errors, etc.), the variations in the sorption coefficients with changes in water/rock ratios can be modeled with a Freundlich isotherm equation for the devitrified sample (Wolfsberg et al., April 1982, p. 27-30). The data for the zeolitic sample could not be successfully modeled using this approach. More experiments will be needed to resolve this issue.

The results of experiments on the effect of variations in groundwater composition on sorption coefficients for barium, cerium, cesium, europium, strontium, and tin have been reported by Vine et al. (1980) and Knight and Thomas (1987). The overall effects were

<sup>\*</sup> Information received from S. Knight, Los Alamos National Laboratory (1988).

generally small and within a factor of 5 of the J-13 results. An analysis of these variations has not been attempted but should be pursued in the future.

## V. SORPTION MECHANISMS

Although very little information has been obtained in the YMP sorption task on sorption mechanisms at the atomic or molecular level, clear correlations have been defined between sorption coefficients for elements in a given chemical group (such as alkaline earths) and the mineralogy of different rock samples. For example, rock samples high in zeolites and/or clays have large sorption coefficients for the alkali and alkaline earth elements. This is consistent with the known ion exchange behavior of these minerals (see, for example, Benson, 1980). Devitrified welded tuffs composed of alkali feldspar and cristobalite, with and without quartz and without zeolites and/or clays, have much smaller sorption coefficients for these elements. This presumably reflects a smaller number of available sorption sites in these rocks.

Knowledge of the mechanisms by which the rare earth and actinide elements sorb remains a major area of uncertainty in the sorption task. The batch sorption coefficients for americium and plutonium are often large and appear to be relatively insensitive to variations in the abundances and compositions of the various framework silicates found in the Yucca Mountain tuffs. This may reflect oversaturation of the experimental feed solutions leading to precipitation of actinide compounds and/or colloids, or it may suggest these elements sorb by some sort of nonspecific surface complexation reactions (Schindler et al., 1976). Primary nonsilicate trace minerals (such as magnetite, apatite, monazite, and ilmenite) and many of the secondary alteration minerals (such as clay, calcite, hematite, manganese-oxyhydroxides) found in Yucca Mountain samples often have much higher affinities for the rare-earth and actinide elements than do the framework silicates (Allard and Beall, 1979) and can therefore be of great importance to their retardation. The mechanisms by which these trace and secondary phases preferentially bind these elements appear to be dominated by surface complexation reactions (Means et al., 1978; Sanchez et al., 1985; Jonasson et al., 1988). Further studies of this topic will be required to gain an adequate understanding in relation to the proposed repository at Yucca Mountain.

## VI. SIGNIFICANCE OF NRC CONCERNS THAT RELATE TO SORPTION STUDIES

The NRC (1987) has formulated a position on radionuclide sorption in relation to nuclear waste repositories and has enumerated various concerns regarding the experimental determination of sorption coefficients and their application in transport calculations (that is, for performance assessment). In the following discussion, those concerns enumerated by the NRC that apply to the Yucca Mountain site have been separated into two groups—one emphasizing the experimental aspects, the other emphasizing applications aspects.

#### **A.** Experimental Aspects

The NRC concerns involving the experimental determination of sorption coefficients include topics below.

#### (1) Kinetics

- Colloid formation
- Sorption equilibrium
- Species equilibrium in solution
- (2) Precipitation vs sorption
- (3) Reactive surfaces that result from grinding
- (4) Multitracer sorption experiments
- (5) Effect of trace minerals with high sorptive capacity
- (6) Sorption mechanisms
- (7) Realistic error analysis

As noted above, kinetics have been a problem principally in experiments involving the actinide elements. In these experiments, there are potential problems with precipitation, colloid formation, equilibrium among complexes in solution, and probably sorption kinetics. These problems need to be resolved before the sorptive behavior of the actinides can be delineated with any degree of certainty.

The problem of reactive surfaces, produced either during the rock-crushing process or during agitation over the course of the experiments, is of concern because these surfaces may result in enhanced sorption of radionuclides in the experiments relative to what may be expected in the natural environment at Yucca Mountain.

The YMP sorption experiments are generally carried out with, at most, a few of the important radionuclides included in any single experiment (Thomas, 1987); therefore, the extent to which the sorption coefficient for a given radionuclide may be affected by competition for sorption sites among various radionuclides and between radionuclides and nonradioactive solution species in the repository environment has not been fully evaluated. However, the relatively small changes in sorption coefficients observed in batch experiments with solutions of considerably higher ionic strength than J-13 (Knight and Thomas, 1987) suggest this aspect may be of secondary importance.

The effect of trace minerals on the bulk sorption coefficient for a given radionuclide in a various rock samples from Yucca Mountain has not been adequately investigated even though it could be of substantial importance for some radionuclides. For instance, the iron oxyhydroxide mineral goethite readily sorbs uranium (Hsi and Langmuir, 1985), plutonium (Sanchez et al, 1985), and neptunium (Meijer et al., 1989). It also has a significant sorption coefficient for technetium (Palmer and Meyer, 1981). Because secondary iron oxides are ubiquitous in Yucca Mountain samples (Caporuscio and Vaniman, 1985), these phases could be very important in the sorption of these elements. The same argument applies to several other secondary trace phases (such as manganese oxides) reported in Yucca Mountain samples (Carlos, 1985). Some knowledge of the mechanism(s) by which the important radionuclides are sorbed is essential to proper interpretation of the experimental results. Based on the discussion in the previous section, it appears that the alkali and alkaline earth elements are sorbed primarily through simple ion exchange mechanisms. This knowledge provides greater confidence in our predictions for these elements and allows some extrapolation of the experimental results. This sort of confidence has not been developed for the actinide elements and most of the other elements considered to date. The general lack of information concerning the mechanisms by which these elements sorb on Yucca Mountain materials precludes quantitative interpretation of the experimental results.

The derivation of realistic error estimates associated with the experimental determination of sorption coefficients is an important aspect of this task. Error estimates typically provided with the published sorption data (Thomas, 1987) represent only the counting statistics associated with the radioactivity measurements in the experimental products. The total error associated with these experiments is likely greater than reported. More realistic error estimates should include errors caused by blanks, efficiency of solution-solid separation, colloid formation, etc.

## **B.** Applications Aspects

The NRC concerns regarding application of experimentally determined sorption coeficients in transport calculations include aspects that are not entirely within the scope of the sorption task. Although most of the concerns discussed by the NRC are included in the following list, only those that relate to the YMP sorption task will be discussed in detail. These include:

- (1) Kinetics
  - Colloid formation/destruction (sorption equilibrium) (species equilibrium)
- (2) Crushed vs intact-rock sorption coefficients
- (3) Water/rock ratio
- (4) Unsaturated flow conditions
- (5) Matrix vs fracture flow
- (6) Representative experimental conditions
- (7) Lack of extrapolation capability
- (8) Lack of corroborating field test
- (9) Realistic error analysis

The kinetics of sorption processes and speciation reactions in solution are likely to be less of a problem during transport of radionuclides in Yucca Mountain than they are in the sorption experiments because of the greater amount of time available for equilibration in the natural flow system given the current estimates of water velocities in the saturated and unsaturated zones within Yucca Mountain (Site Characterization Plan, 1988). Rundberg (1987) has estimated the impact sorption kinetics could have on the retardation of barium, cesium, strontium, and plutonium during rapid water flow in a porous medium. He finds that "the kinetics of adsorption for simple cations is fast enough to provide an ample safety factor in the velocity limit ( $10^5$  to  $10^7$  m/yr) to allow neglect of adsorption kinetics in porous flow scenarios." In contrast, the calculated velocity limit for plutonium is ~230 m/yr, assuming a sorption coefficient of 10. According to Rundberg (1987), this value does not provide a sufficient safety factor to allow the neglect of plutonium sorption and solution kinetics in all porous and fracture flow scenarios. The same conclusion will likely be drawn for americium. Uncertainties regarding the behavior of actinide colloids further limit the safety factor.

The question of the applicability of sorption coefficients obtained on crushed-rock material to sorption behavior within the rock unit from which the crushed material was derived is of concern because crushed material may have a greater number of sorption sites available than intact rock.

As noted earlier, sorption experiments with barium, cerium, cesium, europium, and strontium on two different tuff samples (YM-22 and YM-38) over a range of water/rock ratios suggested tuff sorption coefficients might be sensitive to this parameter (Wolfsberg et al., 1981). Similar observations have been reported by other authors (Allard et al., 1977; Bradbury and Stephen, 1986). Although Wolfsberg et al. (1981) showed that barium, cesium, and strontium sorption data for YM-22 (devitrified tuff) at different water/rock ratios could be related to isotherm measurements on the same rock sample at a given water/rock ratio, through a Freundlich isotherm equation, this approach does not explain the results obtained by the other authors cited. Although the latter results may reflect experimental artifacts such as imperfect solution/solid separations or coprecipitation reactions, a firm conclusion cannot be drawn on this topic without more definitive data.

Although sorption experiments under unsaturated (vadose) conditions have not been performed by the YMP to date, sorption coefficients in the unsaturated zone will likely be different from those in the saturated zone because of differences in the groundwater compositions in these zones. Available data on the chemistry of unsaturated zone waters from Yucca Mountain (Yang et al., 1988) suggest these waters have higher ionic strengths (total dissolved solid contents) than do waters common to the saturated zone (Ogard and Kerrisk, 1984). On the basis of experiments to date (Knight and Thomas, 1987), it appears that sorption coefficients for alkali and alkaline earth elements tend to be slightly lower in experiments involving waters with higher ionic strengths than the J-13 reference water; however, sorption coefficients for the elements europium and tin appear to increase with the ionic strength of the solvent. Few data are available at present on the influence of water composition on the sorption coefficients of the actinide elements. The available data (Thomas, 1988) suggest this influence may be minimal for neptunium. However, because the data are difficult to interpret unambiguously, more definitive data must be obtained before sorption of actinides in the unsaturated zone can be evaluated with confidence.

Scenarios involving the rapid flow of water through fractures (Site Characterization Plan, 1988) require special consideration. This problem can be broken down into two parts,

one dominantly physical and the other dominantly chemical. In the case of a nonsorbing species, the physical aspect, which involves the rate of dispersion of chemical species within a fracture and into the adjacent matrix, dominates transport. For sorbing species, the importance of the chemical aspect depends on the value of the sorption coefficient and the reaction kinetics. Neretnieks (1980) has shown that in the absence of kinetic effects, sorbing species travel along a fracture slower than nonsorbing species. This suggests that simple cations should be more retarded than nonsorbing species because the reaction kinetics of the simple cations are relatively fast (Rundberg, 1987). However, solution and sorption reaction kinetics may become important factors in the transport of actinide species in scenarios involving high water flow rates because less time is available for equilibration with the matrix. Although Rundberg (1987) has shown that large sorption coefficients can partly offset the effect of relatively slow reaction kinetics and high fluid velocities on the retardation of a given radionuclide, for radionuclides with small sorption coefficients and slow reaction kinetics the impact of high fluid velocities could be substantial and must be determined.

As discussed in an earlier section, until now, the YMP has followed an empirical approach to the determination of sorption coefficients (Fig. 1). This approach is valid as long as the parameters within the experimental matrix are representative of all the scenarios and associated conditions anticipated for the repository and its environment over the required containment period (Site Characterization Plan, 1988). Because the environment of the repository block is only partly characterized at the present time, this approach may require a number of additional sorption experiments as new data (for example, unsaturated zone water compositions) become available. Further experiments may also be required if new investigations lead to predictions of future conditions not represented within the experimental matrix of the sorption task. These observations emphasize that the inability to extrapolate the present database to a larger range of physical and chemical conditions is a major limitation of the empirical approach.

Field studies of radionuclide transport in the Yucca Mountain area would be useful in developing public and scientific confidence in the models and experimental data used by the YMP to assess the future performance of the proposed repository. Although the amount of time available for such studies may restrict their success and possibly their usefulness, the obvious need for model validation would seem to outweigh the limitations that may be associated with such studies. Tests planned to address this issue are described in the reactive tracer testing study plan (WBS 2.3.4.1.8.A).

Estimates of errors in predictions of radionuclide transport will probably be derived as part of the performance assessment task through sensitivity analysis. Although a discussion of this type of analysis is beyond the scope of this review, the results of sensitivity analyses involving the transport of important radionuclides in Yucca Mountain under various scenarios would be very useful in identification of those parameters that should be emphasized in the experimental sorption program. Plans to carry out the types of sensitivity analyses required are described in the study plan for the retardation sensitivity analysis task (WBS 2.3.4.1.7.A).

### VII. STRATEGY FOR ADDRESSING NRC CONCERNS REGARDING EXPERIMENTAL AND APPLICATIONS ASPECTS OF SORPTION STUDIES

#### A. Experimental Aspects

The question of the impact of sorption reaction kinetics on experiments involving the actinides and certain rare earth elements (REE) will be addressed in several different ways. To minimize the possible effects of precipitation and/or colloids on these experiments, the concentration of a given radionuclide in the feed solutions will be determined by the detection limit of the most sensitive means of measurement for the appropriate radionuclide. For example, in the case of the actinide elements, the most sensitive analytical technique is mass spectrometry. Mass spectrometric techniques for the actinides have been developed by the Isotope and Nuclear Chemistry Division for other programs at Los Alamos and can be used without further development by the YMP. This allows use of actinide feed solutions that are up to 4 orders of magnitude lower in concentration than most of the solutions used in the experiments reported by Thomas (1987). The saturation state of these feed solutions with respect to known actinide compounds will be checked with the EQ3 geochemical code.

If problems with precipitation and/or colloid formation can be alleviated with this approach, questions relating to solution and sorption reaction kinetics of the actinides and the REE can be addressed by standard batch and column experiments run over a range of time intervals (Rundberg, 1987). However, even if colloids remain a problem, other experiments can be carried out to obtain useful data. One possible approach planned as part of the dynamic transport task (WBS 2.3.4.1.6.A) is to infiltrate solid-rock beakers, formed out of tuff samples from Yucca Mountain, with the actinide and REEbearing solutions. Assuming tuff samples with sufficiently small pore sizes are used in these experiments, colloids will be preferentially retained near the solution/rock interface, whereas soluble species will be transported into the rock. Measurement of concentration profiles within the rock beakers after appropriate intervals would provide data on sorption coefficients and the kinetics of the sorption reactions.

The question of the influence of reactive surfaces on measured values for sorption coefficients can be answered partly with available data. As Rundberg (1987) has noted, alkali and alkaline earth sorption coefficients obtained by batch (crushed-rock) techniques compare favorably with coefficients obtained on the same samples using the solid-rock wafer technique (Table II). This suggests that crushing or grinding of the rock material either before or during the experiments does not introduce a significant bias in the measured sorption coefficients for the alkali and alkaline earth elements. This can be explained through the following observations. First, the crushed rock used in these experiments is equilibrated with unspiked groundwater (such as J-13) for weeks before the sorption experiments. As a result, any reactive surfaces produced during grinding of the rock sample will react and eventually equilibrate with constituents in the ambient groundwater. Second, the individual mineral grains in the rock samples (~1  $\mu$ m) are much smaller than the multimineral grains used in the experiments (75 to 500  $\mu$ m). Therefore, the percentage

increase in mineral grain surface area produced by grinding is not large in comparison to the increases produced in the grinding of granites, sandstones, limestones, or basalts. Finally, unlike the latter rock types, the tuffs commonly contain minerals (for example, zeolites and clays) with large intracrystalline ion exchange capacities. These capacities should not be significantly affected by the grinding processes. Whether or not reactive surfaces are a problem in experiments involving the actinide elements remains to be determined through experiments similar to those used for the alkali and alkaline earth elements.

Tuff Sample	Element	${ m KR_d}$ (Wafer) (m $\ell/g$ )	${ m KR_d}$ (Batch) (m $\ell/g$ )
G-1-1883	$\mathbf{Sr}$	27	22
	$\mathbf{Cs}$	230	190
	$\operatorname{Ba}$	210	180
G-1-1982	Sr	80	62
	$\mathbf{Cs}$	1000	1200
	Ba	800	800
G-1-1436 (desorption)	Sr	95 500	87 000
· - •	Cs	14 900	$2 \ 400$

Table II. KRd Comparison: Tuff Wafers vs Crushed Tuff.

The question of the degree to which the presence of one radionuclide may influence the sorption coefficient measured for another radionuclide will be difficult to resolve in a quantitative manner. Sorption experiments in which all of the important radionuclides are mixed in the same feed solution will be difficult to handle in the laboratory from a radiological point of view; they will also be difficult to analyze and interpret. Plans to carry out experiments that address this issue are discussed in the study plan for the integrated testing task (WBS 1.2.2.3.4.1.L). If experiments of this type are to be carried out as part of the sorption task, considerable development of laboratory and analytical techniques will be required because of the highly radioactive nature of the feed solutions and the complex gamma-ray spectra of the experimental products.

To gain a better understanding of (1) the mechanisms by which the actinides and other radionuclides sorb on tuff and (2) the importance of trace minerals to sorption in Yucca Mountain, batch and column experiments will be carried out using pute separates of the major and trace minerals, as well as glasses found in the Yucca Mountain tuffs (Bish and

Vaniman, 1985). Mineral samples will be obtained either directly from Yucca Mountain samples or from classic localities. It is highly desirable to conduct such experiments with known species of the sorbing radionuclides because the sorption behavior is thought to be strongly dependent on this parameter. This is particularly important for the actinides because they can exhibit multiple oxidation states with a wide variety of possible metastable species including polymers and colloids. Recent advances in photoacoustic and fluorescence spectroscopic techniques may provide the means to study actinide speciation at the low concentration levels relevant to geologic migration studies. Other spectroscopic techniques such as extended x-ray absorption fine structure (EXAFS) will be used to study the complexation of radionuclides on the surfaces of well-characterized mineral phases pertinent to Yucca Mountain.

The data and insight into sorption mechanisms obtained in these experiments will (1) provide data to respond to NRC concerns on this issue, (2) aid in the interpretation of previous YMP sorption experiments on whole rocks, (3) provide a means to estimate sorption coefficients for fracture fillings of variable mineralogy and whole rocks not included in sorption experiments to date, and (4) provide basic information needed for the modeling of sorption behavior with geochemical codes such as EQ3/6. Once sorption mechanisms are better understood, more reliable estimates can be derived of the total errors associated with a given sorption coefficient. These estimates should include the analytical errors as well as errors arising from the mineralogic characterization of the tuffs, analysis of groundwater compositions (especially pH and Eh), and other potential sources.

#### **B.** Applications Aspects

Resolution of the application aspects will mostly be carried out within other YMP tasks including dynamic transport (WBS 2.3.4.1.6.A), solubility determination (WBS 2.3.4.1.4.A), retardation sensitivity analysis (WBS 2.3.4.1.7.A), mineralogy of transport pathways (WBS 2.3.4.2.3.A) and field testing (WBS 2.3.4.1.8.A and 2.3.4.1.11.A).

Questions regarding the kinetics of sorption reactions and solution speciation are addressed in the previous section on experimental aspects. Questions relating to the formation, destruction, and transport of colloids will be addressed in the dynamic transport and the retardation sensitivity tasks.

As discussed in the previous section, the use of crushed *vs* intact rock in sorption experiments is less critical for tuffaceous rocks than it is for other rock types, particularly for the simple cations. However, considerable uncertainty exists at present regarding the degree to which this conclusion applies to sorption experiments involving the actinide elements and certain fission products. This uncertainty should be resolved in the course of sorption experiments carried out to obtain data on other aspects such as reaction kinetics.

The water/rock ratio question will be addressed by a limited number of additional experiments involving the sorption of barium, cesium, and strontium on both devitrified and zeolitic tuffs. In these experiments, alternative procedures such as ultrafiltration will be used for solid/liquid separations.

The sorption of actinide elements and fission products during fracture flow will also be studied as part of the dynamic transport task. Experiments are planned using solidrock columns with fractures that go through the column. Radionuclides will be injected at the top of the columns and their transport along the fracture and penetration into the fracture surface will be measured using autoradiographic techniques. Although these experiments will likely be carried out under saturated conditions, data from experiments in which colloid-bearing actinide feed solutions are infiltrated into unsaturated rock beakers can be used in combination with the solid-rock core experiments to estimate fracture flow transport under unsaturated conditions.

As discussed earlier, to estimate sorption coefficients for conditions not currently included within the experimental matrix for the sorption task, two separate approaches are possible: (1) direct measurement and (2) theoretical extrapolation from available data. The direct approach may yield short-term results but may not be practicable at some future date after termination of the experimental program. This and other aspects discussed earlier suggest some capability for extrapolation will be required for long-term prediction of radionuclide transport. Measurement of sorption isotherms on pure mineral phases will provide some capability for interpolation. Isotherm data will be combined with data on solution speciation, surface complexation (from EXAFS), and selectivity coefficients for ion exchangers to develop theoretical models of sorption mechanisms and to strengthen our capability for extrapolation. Even if a complete theoretical understanding is not achieved, the insight into sorptive behavior gained with this approach will improve our confidence in any predictions of transport behavior of important radionuclides.

Field-based transport experiments involving both sorbing and nonsorbing tracers will be very useful in the validation of the data and approach used by the YMP in performance assessment. Such studies might include fracture flow experiments, diffusion experiments, and unsaturated flow experiments. Detailed plans for such studies will be formulated as part of the geochemical field tests for the validation task (WBS 2.3.4.1.11.A).

An analysis of overall errors likely to be associated with the application of sorption data in transport calculations lies outside of the sorption task. As noted above, this analysis will be addressed by the sensitivity analysis task (WBS 2.3.4.1.7.A).

## VIII. POSITION ON SORPTION TASK

The following brief list of conclusions and recommendations is based on the previous discussion. The items on the list address concerns regarding sorption behavior of important radionuclides as expressed by the NRC and the State of Nevada.

- The  $R_d$  approach (± isotherms) is valid as long as the water and rock compositions remain constant.
- The present database for alkali and alkaline earth elements is usable but needs augmentation with further batch experiments and kinetic studies of actinides and certain fission products (for example, technetium).

- The present database shows zeolites and clays strongly sorb alkalies and alkaline earths but do not appear to have special affinity for actinides or rare earth elements.
- Secondary and trace primary phases may have special affinity for actinides, rare earth elements, technetium, and other important radionuclides.
- Batch experiments with pure primary and secondary minerals are needed to understand sorption mechanisms of actinides and rare earth elements.
- Actinide and rare earth element batch experiments should be carried out with more dilute (undersaturated) feed solutions.
- Additional studies on water/rock ratio effects are needed.
- Kinetic data obtained as part of dynamic transport task will be very useful in interpretation of batch experiments.
- An experimental program, in which waste-form leach solutions or a synthetic equivalent are used directly in batch experiments, should be initiated.
- Theoretical modeling of sorptive behavior of radionuclides within Yucca Mountain will be feasible with additional data on solution speciation, selectivity coefficients, mineral surface characteristics, the identity of surface complexes, and detailed host rock mineralogy.

### REFERENCES

- 1. L. M. Abriola, "Modeling Contaminant Transport in the Subsurface: An Interdisciplinary Challenge," Rev. of Geophys. 25, 125-134 (1987).
- B. Allard and G.W. Beall, "Sorption of Americium on Geologic Media," J. Environ. Sci. Health A14 (6), 507-518 (1979).
- 3. B. Allard, H. Kipatsi, and J. Rydberg, "Sorption of Long-Lived Radionuclides in Clay and Rock. Part I. Determinations of Distribution Coefficients," KBS-TR-55 Käunbränslesäkerhet, Stockholm report CTH 1977-10-10 (1977).
- 4. R. M. Barrer and J. Klinowski, "Theory of Isomorphous Replacement in Aluminosilicates," Phil. Trans. R. Soc. London, Ser. A285, 637-676 (1977).
- 5. R. Beckman, K. Thomas, and B. Crowe, "Preliminary Report on the Statistical Evaluation of Sorption Data: Sorption as a Function of Mineralogy, Temperature, Time, and Particle Size," Nevada Nuclear Waste Storage Investigations Milestone R311 (1987).
- 6. L. V. Benson, "A Tabulation and Evaluation of Ion Exchange Data on Smectites, Certain Zeolites and Basalt," Lawrence Berkeley Laboratory report LBL-10541 (1980).
- 7. D. L. Bish and D. T. Vaniman, "Mineralogic Summary of Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-10543-MS (October 1985).
- 8. D. W. Breck, Zeolite Molecular Sieves (Wiley Interscience, New York, 1974).
- M. H. Bradbury and I. G. Stephen, "Diffusion and Permeability Based Sorption Experiments in Intact Rock Samples," in Scientific Basis for Nuclear Waste Management IX, Materials Research Society Symposia Proceedings, Stockholm, L. O. Werme, Ed. (Materials Research Society, Pittsburgh, 1986), pp. 81-90.
- E. A. Bryant and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1-September 30, 1983," Los Alamos National Laboratory report LA-10006-PR (July 1984).
- F. A. Caporuscio and D. T. Vaniman, "Iron and Manganese in Oxide Minerals and in Glasses: Preliminary Consideration of Eh Buffering Potential at Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-10369-MS (April 1985).

12. F. A. Caporuscio, R. G. Warren, and D. E. Broxton, "Detailed Petrographic Descriptions and Microprobe Data for Tertiary Silicic Volcanic Rocks in Drill Hole USW G-1, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-9323-MS (December 1985). ł

- B. A. Carlos, "Minerals in Fractures of the Unsaturated Zone from Drill Drill Core USW G-4, Yucca Mountain, Nye County, Nevada," Los Alamos National Laboratory report LA-10415-MS (April 1985).
- 14. G. A. Cederberg, "TRANQL: A Ground-Water Mass-Transport and Equilibrium Chemistry Model for Multicomponent Systems," Ph.D. Dissertation, Stanford University (March 1985).
- W. R. Daniels, K. Wolfsberg, R. S. Rundberg, A. E. Ogard, J. F. Kerrisk, C. J. Duffy, et al., "Summary Report on the Geochemistry of Yucca Mountain and Environs," Los Alamos National Laboratory report LA-9328-MS (December 1982).
- W. R. Daniels, K. Wolfsberg, D. T. Vaniman, and B. R. Erdal, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1– September 30, 1981," Los Alamos National Laboratory report LA-9095-PR (January 1982).
- W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1-September 30, 1982," Los Alamos National Laboratory report LA-9577-PR (March 1983).
- J. A. Davis, R. O. James, and J. O. Leckie, "Surface Ionization and Complexation at the Oxide/Water Interface, I. Computation of Electrical Double Layer Properties in Simple Electrolytes," J. Colloid Interface Sci. 63, 3 (1978).
- 19. J. A. Davis and J. O. Leckie, "Surface Ionization and Complexation at the Oxide/Water Interface, II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions," J. Colloid Interface Sci. 67, 1 (1978).
- J. A. Davis, C. C. Fuller, and A. D. Cook, "A Model for Trace Metal Sorption Processes at the Calcite Surface: Adsorption of Cd<sup>2+</sup> and Subsequent Solid Solution Formation," *Geochim. Cosmochim. Acta* 51, 1477-1490 (1987).
- 21. J. A. Davis and K. F. Hayes, Eds., *Geochemical Processes at Mineral Surfaces*, American Chemical Society Symposium Series 323 (American Chemical Society, Washington, DC, 1986).
- 22. "Environmental Assessment, Yucca Mountain Site, Nevada Research and Development Area, Nevada," US Department of Energy report DOE/RW-0073 (May 1986).

- B. R. Erdal, W. R. Daniels, and K. Wolfsberg, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, January 1-March 31, 1981," Los Alamos National Laboratory report LA-8847-PR (July 1981).
- 24. H. R. Fuentes, W. L. Polzer, J. Gruber, B. Lauctes, and E. H. Essington, "Preliminary Report on Sorption Modeling," Los Alamos National Laboratory report LA-10952-MS (August 1987).
- H. R. Fuentes, W. L. Polzer, B. E. Barnes, C. A. Dicke, and G. J. Langhorst, "Progress Report on Sorption Modeling," Los Alamos National Laboratory document TWS-HSE12-9/87-41, R3 (September 1987).
- G. L. Gaines and H. C. Thomas, "Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption," J. Chem. Phys 21, 714-718 (1953).
- 27. C-K D. Hsi and D. Langmuir, "Adsorption of Uranyl Onto Ferric Oxyhydroxides: Application of the Surface Complexation Site-Binding Model," *Geochim. Cosmochim. Acta* 49, 1931-1941 (1985).
- R. G. Jonasson, G. M. Bancroft, and L. A. Boatner, "Surface Reactions of Synthetic, End-Member Analogues of Monazite, Xenotime and Rhabdophane, and Evolution of Natural Waters," *Geochim. Cosmochim. Acta* 52, 767-770 (1988).
- 29. D. B. Kent, V. S. Tripathi, N. B. Ball, and J. O. Leckie, "Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments," US Nuclear Regulatory Commission report NUREG/CR-4807 (March 1988).
- 30. J. F. Kerrisk, "Solubility Limits on Radionuclide Dissolution at a Yucca Mountain Repository," Los Alamos National Laboratory report LA-9995-MS (May 1984).
- 31. J. F. Kerrisk, "Americium Thermodynamic Data for the EQ3/6 Database," Los Alamos National Laboratory report LA-10040-MS (July 1984).
- S. D. Knight and K. W. Thomas, "Sorption of Radionuclides Using Different Groundwater Compositions," Nevada Nuclar Waste Storage Investigations Milestone M316 (1987).
- J. L. Means, D. A. Crerar, and M. P. Borcsik, "Adsorption of Co and Selected Actinides by Mn and Fe Oxides in Soils and Sediments," *Geochim. Cosmochim. Acta* 42, 1763-1773 (1978).

- 34. A. Meijer, I. Triay, S. Knight, and M. Cisneros, "Sorption of Radionuclides on Yucca Mountain Tuffs," in Proceedings of the Topical Meeting on Nuclear Waste in the Unsaturated Zone Focus '89, September 17-21, 1989, Las Vegas Nevada (American Nuclear Society, LaGrange Park, 1989), pp. 113-117.
- 35. R. E. Meyer, W. D. Arnold, J. G. Blencoe, G. D. O'Kelley, F. I. Case, J. F. Land, and G. K. Jacobs, "Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects Semi-Annual Report for October 1985-March 1986," US Nuclear Regulatory Commission report NUREG/CR-4708 (January 1987).
- 36. I. Neretnieks, "Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation?" J. Geophys. Res. 85, 4379-4397 (1980).
- 37. H. Nitsche, "Determination of the Solubilities and Complexation of Waste Radionuclides Pertinent to Geologic Disposal at the Nevada Tuff Site, II. Solubility of AmOHCO<sub>3</sub> in Aqueous Solution Under Atmospheric Conditions," Lawrence Berkeley Laboratory report LBL-21237 (1986).
- 38. H. Nitsche, E. M. Standifer, S. C. Lee, R. C. Gatti, and D. B. Tucker, "Solubility and Speciation Studies of Waste Radionuclides Pertinent to Geologic Disposal at Yucca Mountain: Results on Neptunium, Plutonium, and Americium in J-13 Groundwater," Lawrence Berkeley Laboratory letter report R707 (September 1987).
- 39. Nuclear Regulatory Commission, "Determination of Radionuclide Sorption for High-Level Nuclear Waste Repositories," US Nuclear Regulatory Commission technical position paper (January 1987).
- A. E. Ogard, K. Wolfsberg, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1–June 30, 1983," Los Alamos National Laboratory report LA-9846-PR (December 1983).
- 41. A. E. Ogard and J. F. Kerrisk, "Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment," Los Alamos National Laboratory report LA-10188-MS (November 1984).
- 42. A. E. Ogard and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1-September 30, 1984," Los Alamos National Laboratory report LA-10299-PR (May 1985).
- 43. V. M. Oversby, "Important Radionuclides in High Level Nuclear Waste Disposal: Determination Using a Comparison of the US EPA and NRC Regulations," *Nucl. Chem. Waste Management* 7, 149-161 (1987).

- 44. D. A. Palmer and R. E. Meyer, "Adsorption of Technetium on Selected Inorganic Ion-Exchange Materials and on a Range of Naturally Occurring Minerals Under Oxic Conditions," J. Inorg. Nucl. Chem. 43 (11), 2979-2984 (1981).
- 45. W. L. Polzer and H. R. Fuentes, "The Use of a Heterogeneity-Based Isotherm of Interpret the Transport of Reactive Radionuclides in Volcanic Tuff Media," *Radiochim. Acta* 44/45, 361-365 (1988).
- 46. E. J. Reardon, "Kd's—Can They be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration?" *Groundwater* **19** (3), 279-286 (1981).
- 47. J. Rubin and R. V. James, "Dispersion-Affected Transport of Reacting Solutes in Saturated Porous Media: Galerkin Method Applied to Equilibrium-Controlled Exchange in Unidirectional Steady Water Flow," Water Resour. Res. 9 (5), 1332-1350 (1973).
- 48. R. S. Rundberg, "Assessment Report on the Kinetics of Radionuclide Adsorption on Yucca Mountain Tuff," Los Alamos National Laboratory report LA-11026-MS (1987).
- R. S. Rundberg, A. E. Ogard, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1– June 30, 1984," Los Alamos National Laboratory report LA-10297-PR (May 1985).
- 50. A. L. Sanchez, J. W. Murray, and T. H. Sibley, "The Adsorption of Plutonium IV and V on Goethite," *Geochim. Cosmochim. Acta* 49, 2297-2307 (1985).
- P. W. Schindler, B. Fürst, R. Dick, and P. U. Wolf, "Ligand Properties of Surface Silanol Groups. I. Surface Complex Formation with Fe<sup>3+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>," J. Coll. Inter. Sci. 55, 2 (1976).
- 52. R. J. Serne and J. F. Relyea, "The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program," in *The Technology of High-Level Nuclear Waste Disposal*, P. L. Hofmann and J. J. Breslin, Eds. (US Department of Energy, Washington, DC, 1981).
- 53. R. J. Serne, "Discussion of 'K<sub>d</sub>'s—Can They Be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration?" *Groundwater* 20, 232-233 (1982).
- 54. "Site Characterization Plan, Yucca Mountain Site, Nevada Research and Development Area, Nevada," US Department of Energy report DOE/RW-0199 (December 1988).
- 55. G. Sposito, The Thermodynamics of Soil Solutions (Oxford Clarendon Press, Oxford, UK, 1981).

- 56. G. Sposito, "Distinguishing Adsorption from Surface Precipitation," in Geochemical Processes at Mineral Surfaces, J. A. Davis and K. F. Hayes, Eds., Proceedings of the 190th Meeting of the American Chemical Society, Chicago, September 8-13, 1985, Washington DC (American Chemical Society, Washington, DC, 1986).
- 57. W. Stumm, Ed., Aquatic Surface Chemistry (Wiley & Sons, New York, 1987).
- 58. K. W. Thomas, "Summary of Sorption Measurements Performed with Yucca Mountain, Nevada, Tuff Samples and Water from Well J-13," Los Alamos National Laboratory report LA-10960-MS (December 1987).
- 59. K. W. Thomas, "Research and Development Related to the Nevada Nulcear Waste Storage Investigations, October 1-December 31, 1984," Los Alamos National Laboratory Report LA-11443-PR (November 1988).
- 60. J. L. Thompson, "Actinide Behavior on Crushed Rock Columns," J. Radioanalyt. Nucl. Chem. 130 (Z), 353-364 (1989).
- 61. E. N. Treher and N. A. Raybold, "The Elution of Radionuclides Through Columns of Crushed Rock from the Nevada Test Site," Los Alamos National Laboratory report LA-9329-MS (October 1982).
- 62. I. R. Triay and R. S. Rundberg, "Determination of Selectivity Coefficient Distributions of Deconvolution of Ion-Exchange Isotherms," J. Phys. Chem. 91, 5269-5274 (1987).
- 63. V. S. Tripathi, "Uranium(VI) Transport Modeling: Geochemical Data and Submodels," Ph.D. Dissertation, Standard University (December 1983).
- 64. C-F. Tsang and D. C. Mangold, Eds., "Coupled Thermo-Mechanical-Hydro-Chemical Processes Associated with a Nuclear Waste Repository," Lawrence Berkeley Laboratory panel report LBL-18250 (July 1984).
- A. J. Valocchi, "Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils," Water Resour. Res. 21 (6), 808-820 (1985).
- 66. T. Vermeulen, M. D. LeVan, N. K. Hiester, and G. Klein, "Adsorption and Ion Exchange," in *Perry's Chemical Engineers' Handbook*, R. H. Perry, D. W. Green, and J. O. Maloney, Eds. (McGraw-Hill, New York, 1984).
- 67. B. Viani, "Interim Report on Modeling Sorption With EQ3/6," Lawrence Livermore National Labortaory report UCID-2308 (January 1988).

- 68. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, et al., "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies from Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (January 1980).
- 69. J. C. Westall, J. L. Zachary, and F. M. M. Morel, "MINEQL—A Computer Program for the Calculations of Chemical Equilibrium Composition of Aqueous Systems," Massachusetts Institute of Technology Technical Note 18 (1976).
- K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. R. Erdal, F. O. Lawrence, A. E. Norris, and J. R. Smyth, "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos National Laboratory report LA-7480-MS (April 1979).
- 71. K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, et al., "Sorption-Desorption Studies on Tuff. III. A Continuation of Studies With Samples from Jackass Flats and Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).
- 72. K. Wolfsberg, W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1– June 30, 1982," Los Alamos National Laboratory report LA-9484-PR (October 1982).
- 73. K. Wolfsberg, W. R. Daniels, D. T. Vaniman, B. R. Erdal, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1– December 31, 1981," Los Alamos National Laboratory report LA-9225-PR (April 1982).
- 74. I. C. Yang, A. K. Turner, T. M. Seyre, and P. Montazer, "Triaxial-Compression Extraction of Pore Water from Unsaturated Tuff, Yucca Mountain, Nevada," US Geological Survey Water-Resources Investigation report 88-4189 (1988).
- 75. R. A. Zielinski, C. A. Bush, R. W. Spengler, and B. J. Szabo, "Rock-Water Interaction in Ash-Flow Tuffs, Yucca Mountain Nevada—The Record From Uranium Studies," Uranium 2, 361-386 (1986).

## This report has been reproduced directly from the best available copy.

#### Available to DOE and DOE contractors from the Office of Scientific and Technical Information P.O. Box 62 Oak Ridge, TN 37831 prices available from (615) 576-8401, FTS 626-8401

#### Available to the public from the National Technical Information Service U.S. Department of Commerce 5285 Port Royal Rd, Springfield, VA 22161

#### Microfiche A01

	NTIS		NTIS		NTIS		NTIS
Page Range	Price Code						
001025	A02	151-175	A08	301-325	A14	451-475	A20
026-050	A03	176-200	A09	326-350	A15	476-500	A21
051-075	A04	201-225	A10	351-375	A16	501-525	A22
076-100	A05	226-250	A11	376-400	A17	526-550	A23
101-125	A06	251-275	A12	401-425	A18	551-575	A74
126-150	A07	276-300	A13	426-450	A19	576-600	A25
						601-up*	A99

\*Contact NTIS for a price quote.