TABLES

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Table 1. Results of Monitor Well Samples, February 2011

Well ID	MW-12	MW-9	MW-14	MW-108	MW-109	MW-74	MW-43R	MW-110	MW-111
Sample Date	2/11/2011	2/11/2011	2/11/2011	2/12/2011	2/12/2011	2/10/2011	2/12/2011	2/10/2011	2/10/2011
		Lang Draw			Northern Pathway				
Analyte								44 - C	
Major lons (mg/L)		an and party and the second		al deservices in the contract of the second s	New Sold Wheel States and States a		e trat Pagasi faraga sa mata sant Santa sa		
Calcium	883	883	824	868	552	686	739	769	520
Chloride	371	334	358	302	89	233	254	290	102
Magnesium	544	200	343	179	137	175	154	156	90
Nitrogen Nitrate + Nitrite as N	0.01	0.81	< 0.01	0.06	0.13	4.4	0.05	0.01	0.04
Phosphorus Total as P	< 0.005	0.006	0.058	0.013	0.029	0.008	0.009	0.064	0.01
Potassium	18	A	11	9	10	14	16	17	7
Sodium	297	257	268	180	127	122	66	43	24
Sulfate	2810	1880	2280	1620	1900	2000	1530	1720	1190
Metals Dissolved (mg/L)					S. C.				
Aluminum	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1
Arsenic	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Barium	<0.1	<0.1	< 0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Beryllium	< 0.001	N/A	N/A	N/A	N/A	< 0.001	N/A	N/A	N/A
Cadmium	< 0.001	N/A	N/A	N/A	N/A	< 0.001	N/A	N/A	N/A
Chromium	< 0.001	N/A	N/A	N/A	N/A	< 0.001	N/A	N/A	N/A
Iron	0.41	1.14	1.46	0.55	0.53	4.62	0.59	9.92	0.19
Manganese	6.62	0.18	1.19	0.43	0.04	2.11	1.04	0.53	<0.01
Molybdenum	< 0.001	N/A	N/A	N/A	N/A	< 0.001	N/A	N/A	N/A
Nickel	0.035	0.018	0.04	0.043	0.013	0.042	0.017	0.006	0.004
Selenium	0.002	< 0.001	0.004	N/A	N/A	0.021	0.003	N/A	N/A
Silica	28	23.7	25.9	26.2	14.1	29	19.6	23.6	18.1
Uranium (pCi/L)	420	195	439	135	61.3	15.4	38	1.6	17.6
Metals Total (mg/L)	an a		Ser parte la Prop						
Aluminum	<0.1	<0.1	<0.1	1.2	3.1	<0.1	0.3	3	2.1
Iron	0.57	1.25	1.55	1.53	2	4.96	1.55	12.9	1.23
Manganese	6.72	0.19	1.21	0.49	0.03	2.14	1.16	0.54	0.02
Silica	31.6	25.9	27.3	18.5	29	30.9	20.8	38.7	28.2
Radionuclides Dissolved (pCi/L)			f. and see the	pill And the		the state of the second	in and		
Radium-226	0.62	0.3	0.09	0.41	0.5	2.2	1.8	2.9	0.42
Radium-228	2.4	1.9	0.8	1.6	1.3	4	3.1	7.6	1.4
Thorium-230	-0.3	-0.06	<0.1	-0.1	-0.05	-0.09	-0.07	< 0.02	-0.06
Total Dissolved Solids (mg/L)	5770	4390	5050	3980	3050	3700	3410	3340	2260
pH (s.u.)	6.56	7.00	7.16	6.75	7.34	7.26	6.72	7.28	7.60

## Table 2. Saturation Indices for Water Samples on Lang Draw Flow Path, 2011

Phiese	Formula	MW-103	MW-109	MW-12	MW-143	. MIW-D
(UO2)3(PO4)2:4w	(UO2)3(PO4)2:4H2O	-36.01	-33.17		-36.37	-38.16
AI(OH)3(a)	AI(OH)3		-0.7			
Calcite	CaCO3	0.74	0.49	0.37	1.17	1.02
Chalcedony	SiO2	0.2	-0.07	0.23	0.2	0.16
CO2(g)	CO2 pressure (atmos.)	-0.91	-2.13	-0.74	-1.22	-1.11
Ferrihydrite	Fe(OH)3	2.23	2.49	1.97	2.86	2.69
Gypsum	CaSO4:2H2O	-0.01	-0.05	0.02	0.04	0.04
Magnesite	MgCO3	-0.19	-0.36	0.01	0.55	0.13
MnHPO4	MnHPO4	-0.28	-0.63		0.79	-0.97
Schoepite	UO2(OH)2:H2O	-7.67	-6.33	-6.64	-7.72	-7.88
Siderite	FeCO3	-7.03	-7.99	-7.12	-6.71	-6.77
U3O8(c)	U3O8	-38.21	-34.19	-35.12	-38.37	-38.83
UO2(OH)2(beta)	UO2(OH)2	-7.21	-5.87	-6.18	-7.27	-7.42
Uraninite(c)	UO2	-26.43	-25.09	-25.4	-26.48	-26.63

Note: SI less than 0 indicates undersaturation and SI greater than 0 indicates supersaturation.

### Table 3. Saturation Indices for Water Samples on Northern Pathway

Phase	Formula	XXX-110	MW-111	MW-49	MW-743
(UO2)3(PO4)2:4w	(UO2)3(PO4)2:4H2O	-40.91	-39.97	-35.5	-36.95
Calcite	CaCO3	0.93	1.05	0.44	0.59
Chalcedony	SiO2	0.15	0.03	0.07	0.24
CO2(g)	CO2 pressure (atmos)	-1.73	-2.14	-1.1	-1.96
Ferrihydrite	Fe(OH)3	3.74	2.1	2.24	3.4
Gypsum	CaSO4:2H2O	0.01	-0.19	-0.04	0.02
Magnesite	MgCO3	-0.01	0.04	-0.48	-0.25
MnHPO4	MnHPO4	0.7		0.03	0.45
Schoepite	UO2(OH)2:H2O	-9.16	-7.96	-7.45	-7.28
Siderite	FeCO3	-6.34	-8.39	-7.2	-6.91
U3O8(c)	U3O8	-42.69	-39.1	-37.54	-37.04
UO2(OH)2(beta)	UO2(OH)2	-8.71	-7.51	-6.99	-6.82
Uraninite(c)	U02	-27.92	-26.72	-26.2	-26.04

Note: SI less than 0 indicates undersaturation and SI greater than 0 indicates supersaturation.

# **ATTACHMENT I**

Temporal plots of chemical parameters measured in monitoring wells



а.






























































































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Date

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### ATTACHMENT II

Input PHREEQC data set for Long Draw

BC mod02 final Lang.pqi 8/8/2011 DATABASE Phreegcm.dat # Input dataset for Lang Draw model USER PUNCH -headings U pCi/L Radium pCi/L CELL DISTANCE m TIME YEARS DATE step ALKALINITY U ppm pH Ferri Cl ppm S(6) ppm Ra2(pCi/L) Ni ppm -start 5 USPECIES = MOL("Ca2UO2(CO3)3") + MOL("CaUO2(CO3)3-2") + MOL("UO2+2")+ MOL("U02C03") + MOL("U02C1+") + MOL("U02C12") + MOL("U02(C03)2-2")+ MOL("UO2(CO3)3-4") + MOL("UO2(OH)3-") + MOL("UO2(OH)2") + MOL("UO2OH+")+ MOL("UO2(OH)4-2")+MOL("UO2SO4")+ MOL("UO2(SO4)2-2") + MOL("(UO2)2(OH)2+2") 10 SURFCOMP = MOL("Hfo\_wOUO2+") + MOL("Hfo\_sOUO2+") + MOL("Hfo\_wOUO2(CO3)2-3") + MOL("Hfo wOUO2CO3-") 15 PUNCH USPECIES\*238\*1000\*.67\*1000 #Uranium in pCi/L 20 PUNCH (TOT("Ra")\*226\*1000)/(226\*2.8E-15\*1600) #Radium in pCi/L 25 PUNCH CELL NO 30 PUNCH CELL NO\*4 35 PUNCH TOTAL TIME/(3600\*24\*365) 40 PUNCH (TOTAL TIME/(3600\*24)+34578) # you can install an actual date by changing the 34578 value, WHICH is currently set for Sept 1 1994. 45 PUNCH step no # puts step number in column 7 50 PUNCH ALK\*50000 55 PUNCH TOT("U")\*238\*1000 60 PUNCH -LA("H+") 65 PUNCH EQUI("Fe(OH)3(a)") 70 PUNCH TOT("CL")\*1000\*35.453 75 PUNCH TOT("S(6)")\*1000\*96.064 80 SURFCOMP = MOL("Hfo\_wOUO2+") + MOL("Hfo\_sOUO2+") + MOL("Hfo\_wOUO2(CO3)2-3") + MOL("Hfo wOUO2CO3-") 90 PUNCH TOT("Ni")\*1000\*58.69 -end TITLE Transport: Bear Creek Lang Draw Model Phreeqc 2.0 SOLUTION 1000 solution MW-86 # Solution to mix with upgradient (MW-36) water for upgradient boundary condition units mg/L # Samplename MW-86 4.5 рН pe 12 temp 25 420 Ca 700 Mg 278 charge Na 42 K Fe 926 Mn 35.9 230 A1 S(6) 9040 600 Cl C(4) F 0.1 Ρ 0.01 #as SiO2 Si 21.4 Ni 0.08 # U-natural (pCi/L) 2038 U 3.303662 Ra 4.5e-09

END

1

SOLUTION clean wa	1 2000 iter	MW-36	background	d groundw	vater	#THIS	IS	WATER	FROM	MW-36
units mg # Sample pH pe temp Ca Mg Na K Fe Mn Al S(6) Cl Cl Cl Cl Cl Cl Ra	y/L ename 7.8 12 25 158 21 61 7 0.1 0.5 425 25 153 0.01 0.003 0.5E-0	MW-3	36							
END										
SOLUTION units mg # Sample pH pe Ca Mg Na K Fe Mn Al S(6) Cl Cl C(4) Ni U # U-natu Ra	J 3000 J/L ename 7.4 12 25 440 59 34 cha 2 0.1 0.49 0.5 1053 90 331 0.01 0.054 enal (P 1.2E-0	MW-14 MW-1 arge OCi/L)	14							
END										
MIX 1000 2000 SAVE SOI END	.59442 .4055 JUTION	27 73 0-30								
# CELL SETUP STARTS HERE FIRST SIMULATION										
EQUILIBR	LUM PH Al (OH) Fe (OH) Calcit Gypsur SiO2 (a	HASES 1 3(a) 3(a) 2e n a)	1.30 -1.36 0.0 1.69 1.0 0.0 0.0 0.0 0.2 0.0 0.0	) )000000E-4 ) 2 )						
SURFACE 1-30 -equilibrate with solution 1-30										

#### BC\_mod02\_final\_Lang.pqi

Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005

8/8/2011

```
SAVE EQUILIBRIUM PHASES 1-30
SAVE SURFACE 1-30
SAVE Solution 1-30
END
SOLUTION 31-55 Initial solution for column THIS IS MW-15
         units
                  ppm
units mq/L
# Samplename
                  MW-15
         6.0
pН
pe
         12
temp
         25
         650
Ca
Mq
         250
Na
         212 charge
Κ
         18
Fe
         2.18
Mn
         0.35
Al
         1.33
S(6)
         2420
C1
         375
C(4)
         1450
F
         0.3
Ρ
         0.01
         20.78
                                                                          #as SiO2
Si
Ва
         #
Ni
        0.025
U
         1.20000000
Ra
         2.5312E-09
EQUILIBRIUM PHASES 31-55
         Al(OH)3(a)
                      -1.36 0.1
                        1.69
                               1.000000E-4
         Fe(OH)3(a)
         Calcite
                        0.0
                               0.01
         Gypsum
                        0.0
                               0.2
         SiO2(a)
                        0.0
                               0.0
SURFACE 31-55
 -equilibrate with solution 31-55
Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is
surface area per mole of iron hydroxide
Hfo_sOH Fe(OH)3(a) equilibrium_phase 0.005
SAVE SURFACE 31-55
SAVE EQUILIBRIUM PHASES 31-55
SAVE Solution 31-55
END
SOLUTION 56-119 Initial solution for column MW-12
units mg/L
# Samplename
                  MW-12
рН
         7.0
pe
         12
temp
         25
         450
Ca
Mg
         150
         265 charge
Na
К
         14
```

BC\_mod02\_final\_Lang.pqi 8/8/2011 Fe 0.69 Mn 0.07 Al 1.15 S(6) 2000 Cl 275 C(4) 878 F 0.3 Ρ 0.01 Si 18 #as SiO2 Ni 0.025 U 0.16 1.5E-09 Ra EQUILIBRIUM PHASES 56-119 Al(OH)3(a) -1.36 0.01 1.69 Fe(OH)3(a) 1.00000E-4 0.0 Calcite 0.4 Gypsum 0.0 0.0 SiO2(a) 0.0 0.0 SURFACE 56-119 -equilibrate with solution 56-119 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005 SAVE EQUILIBRIUM PHASES 56-119 SAVE SURFACE 56-119 SAVE Solution 56-119 END SOLUTION 120-162 Initial solution for column MW-14 units mg/L # Samplename MW-14 рН 7.7 pe 12 temp 25 Ca 350 59 Mg Na 34 charge Κ 2 Fe 0.1 0.49 Mn Al 0.5 S(6) 800 C1 70 C(4) 331 F Ρ Si Ni 0.01 U 0.054 Ra 1.2E-09 EQUILIBRIUM PHASES 120-162 -1.36 0.01 Al(OH)3(a) 1.69 1.000000E-4 Fe(OH)3(a) Calcite 0.0 0.4 Gypsum 0.0 0.0

SiO2(a)

0.0

0.0

BC mod02 final Lang.pqi

SURFACE 120-162 -equilibrate with solution 120-162 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005 SAVE EQUILIBRIUM PHASES 120-162 SAVE SURFACE 120-162 SAVE Solution 120-162 END MIX 2000 0.5 3000 0.5 SAVE SOLUTION 163-210 END EQUILIBRIUM PHASES 163-210 -1.36 0.01 1.69 1.000000E-4 Al(OH)3(a) Fe(OH)3(a) Calcite 0.0 0.4 Gypsum 0.0 0.0 SiO2(a) 0.0 0.0 SURFACE 163-210 -equilibrate with solution 163-210 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005 SAVE SURFACE 163-210 SAVE Solution 163-210 END MIX 2000 0.8 3000 0.2 SAVE SOLUTION 211-242 END EQUILIBRIUM PHASES 211-242 Al(OH)3(a) -1.36 0.01 Fe(OH)3(a) 1.69 1.00000E-4 Calcite 0.0 0.4 Gypsum 0.0 0.0 SiO2(a) 0.0 0.0 SURFACE 211-242 -equilibrate with solution 211-242 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005

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8/8/2011
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SAVE EQUILIBRIUM PHASES 211-242 SAVE SURFACE 211-242 SAVE Solution 211-242 END PRINT -reset false -surface true SELECTED OUTPUT -file BC mod02.sel #can be SEL or XLS -reset false -step true #this # prints the time step in the first column, set to "false" in order to eliminate that column #1995 through 1997 Plateau 2 MIX 1000 .594427 2000 .405573 SAVE SOLUTION 0 # 1994 through 1995 TRANSPORT -cells 242 #235 is total cells -length #4 4 meter cells .10000000 40.000000 -shifts 9.00000 #6 yrs\*365\*24\*3600/2522880= 75 shifts; we start at the dam, John added a year for the diffence in length for the first water -time step 3155760.0 #This is 29.2 days in seconds and essentially indicates hydraulic conductivity -punch cells 1 20 52 98 121 159 181 242 -punch frequency 1 -flow direction forward -boundary conditions flux flux -correct disp true -dispersivity 235\*30.0000 -diffusion\_coef 0.0e-0 #NO diffusion -tempr 1.0 #NO heat retardation END #1995 through 1997 Plateau 2 MIX 1000 .349935 .650065 2000 SAVE SOLUTION 0 #Overwrite Solution 0 TRANSPORT -shifts 20.0000 END #1997 through 2000 Plateau 3 MIX .087363 1000 2000 .912637 SAVE SOLUTION 0 #Overwrite Solution 0. TRANSPORT -shifts 30.0000

BC\_mod02\_final\_Lang.pqi 8/8/2011 END #2000 through 2010 Plateau 4 MIX 1000 .004258 2000 .995742 SAVE SOLUTION 0 #Overwrite Solution 0. TRANSPORT 60.0000 -shifts END #2006 through 2010 Plateau 5 MIX 1000 1.25E-5 2000 .999988 SAVE SOLUTION 0 #Overwrite Solution 0. TRANSPORT 109.000 -shifts

```
END
```

END

## ATTACHMENT III

Input PHREEQC data set for Northern Pathway DATABASE C: Phreeqcm.dat

```
USER PUNCH
  -headings U pCi/L Radium pCi/L CELL DISTANCE m TIME YEARS DATE step
  ALKALINITY U ppm pH Ferri Cl_ppm S(6)_ppm RA_pCI/L NI_ppm
 -start
3 USPECIES = MOL("Ca2UO2(CO3)3") + MOL("CaUO2(CO3)3-2") + MOL("UO2+2")+
MOL("U02C03") + MOL("U02C1+") + MOL("U02C12") + MOL("U02(C03)2-2")+
MOL("UO2(CO3)3-4") + MOL("UO2(OH)3-") + MOL("UO2(OH)2") + MOL("UO2OH+")+
MOL("UO2(OH)4-2")+MOL("UO2SO4")+ MOL("UO2(SO4)2-2") + MOL("(UO2)2(OH)2+2")
4 SURFCOMP = MOL("Hfo wOUO2+") + MOL("Hfo sOUO2+") + MOL("Hfo wOUO2(CO3)2-3")
+ MOL("Hfo wOUO2CO3-")
5 PUNCH USPECIES*238*1000*.67*1000
#Uranium in pCi/L
7 PUNCH (TOT("Ra")*226*1000)/(226*2.8E-15*1600)
#Radium in pCi/L
11 PUNCH CELL NO
                                                                          #if
you want to eliminate a column, you remove it from the heading, then comment
out the line that applies to that column
13 PUNCH CELL NO*4
15 PUNCH TOTAL TIME/(3600*24*365)
17 PUNCH (TOTAL TIME/(3600*24)+34578)
                                                                         # you
can install an actual date by changing the 34578 value, WHICH is currently
set for Sept 1 1994.
19 PUNCH step no
                                                                          #puts
step number in column 7
21 PUNCH ALK*50000
23 PUNCH TOT("U")*238*1000
25 PUNCH -LA("H+")
26 PUNCH EQUI("Fe(OH)3(a)")
27 PUNCH TOT("CL")*1000*35.453
28 PUNCH TOT("S(6)")*1000*96.064
30 SURFCOMP = MOL("Hfo wOUO2+") + MOL("Hfo_sOUO2+") + MOL("Hfo wOUO2(CO3)2-3")
+ MOL("Hfo wOUO2CO3-")
32 PUNCH TOT("Ra")*226*1.0E12 # Ra in pCi/L
33 PUNCH TOT("Ni")*1000*58.69
 -end
TITLE
        Transport: Bear Creek North Path
SOLUTION 1000 solution MW-86
units mg/L
# Samplename
                MW-86
       4.5
рΗ
pe
        12
        25
temp
Ca
        420
Mq
        700
Na
        278 charge
Κ
        42
Fe
        926
Mn
        35.9
        230
Al
S(6)
        9040
Cl
        400
\mathbf{F}
        0.1
Ρ
        0.01
Si
       21.4
                                                                 #as SiO2
Ni
        .1
TT
        0.6
Ra
        1.51872E-08
END
```

8/8/2011
SOLUTION 2000 MW-36 background groundwater

units mg	J/L	
# Sample	ename	MW-36
рН	7.4	
pe	12	
temp	25	
Ca	158	
Mg	21	
Na	61	
K	7	
Fe	0.1	
Mn	0.11	
Al	0.5	
S(6)	425	
Cl	25	
C(4)	153	
Ni	0.01	
U	0.003	
Ra	2.5312E-	09

#### END

SOLUTION	1 3000 M	W-43	
# Sample	]/L	MW _ 1 2	11/10/04
H Sampre	7 7	14104 - 44 2	11/10/94
pn	10		
pe tomp	25		
Ca	23		
Ca Ma	9/4. 100		
Ma	190. 71 cha:		
Na	71. Cha.	rge	
ĸ	1/.		
Fe	7.91		
Mn	0.85		
Al	0.01		
S(6)	2080		
Cl	575.		
C(4)	854.		
F	.2		
Si	5.4		
Ba	#		
Ni	0.02		
IJ	0.0581		
Pa	5 164E-1	09	
****	2.1010	<u> </u>	

### END

MIX 1000 .334046 2000 .665954 SAVE SOLUTION 0-54 END

# CELL SETUP STARTS HERE FIRST SIMULATION

EQUILIBRIUM PHASES 1-54 Al(OH)3(a) -1.36 0.0 Fe(OH)3(a) 1.69 1.000000E-4 Calcite 0.0 0.0 Gypsum 0.0 0.2 SiO2(a) 0.0 0.0

SURFACE 1-54

,

### BC\_mod02\_north\_final.pqi

-equilibrate with solution 1-54 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo sOH Fe(OH)3(a) equilibrium phase 0.005

SAVE EQUILIBRIUM PHASES 1-54 SAVE SURFACE 1-54 SAVE Solution 1-54

### END

MIX 1000 .334046 2000 .665954 SAVE SOLUTION 55-84 END

# CELL SETUP STARTS HERE FIRST SIMULATION

EQUILIBRIUM PHASES 55-84 Al(OH)3(a) -1.36 0.0 Fe(OH)3(a) 1.69 1.000000E-4 Calcite 0.0 0.1 Gypsum 0.0 0.2 SiO2(a) 0.0 0.0

SURFACE 55-84 -equilibrate with solution 55-84 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005

SAVE EQUILIBRIUM PHASES 55-84 SAVE SURFACE 55-84 SAVE Solution 55-84

END

SOLUTION 85-125 Initial solution for column THIS IS MW-74 units ppm units mq/L # Samplename MW-74 9/94 6.7 pН pe 12 25 temp 450. Ca Mq 116. Na 67. charge Κ 12. Fe 0.66 Мn 0.48 Al 0.96 S(6) 1900. C1 200. C(4) 708. F 0.2 Ρ 0.01 Si 15.83 Ва # Ni 0.025 U 0.062

#as SiO2

#table 3-12

8/8/2011

BC\_mod02\_north\_final.pqi 8/8/2011 Ra 2.936E-09 EQUILIBRIUM PHASES 85-125 Al(OH)3(a) -1.36 0.1 Fe(OH)3(a) 1.69 1.000000E-4 Calcite 0.0 0.4 Gypsum 0.0 0.2 SiO2(a) 0.0 0.0 SURFACE 85-125 -equilibrate with solution 85-125 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium\_phase 0.005 SAVE SURFACE 85-125 SAVE EQUILIBRIUM PHASES 85-125 SAVE Solution 85-125 END SOLUTION 126-170 Initial solution for column MW-43 units mg/L # Samplename MW-43 11/10/94 7.7 рН pe 12 temp 25 Ca 974. 198. Mq Na 71. charge Κ 17. Fe 7.91 Мn 0.85 0.01 Al S(6) 2080 C1 575. C(4) 854. F . 2 Ρ Si 5.4 Ва # Ni 0.02 0.0581 U # U-natural (pCi/L) Ra 2.5E-9 EQUILIBRIUM PHASES 126-170 Al(OH)3(a) -1.36 0.01 Fe(OH)3(a) 1.69 1.000000E-4 Calcite 0.0 0.4 0.0 0.0 Gypsum SiO2(a) 0.0 0.0 SURFACE 126-170 -equilibrate with solution 126-170 Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 # 0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is surface area per mole of iron hydroxide Hfo\_sOH Fe(OH)3(a) equilibrium phase 0.005 SAVE EQUILIBRIUM PHASES 126-170 SAVE SURFACE 126-170 SAVE Solution 126-170

4

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BC_mod02_north_final.pqi
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```
END
MIX
2000 0.5
3000 0.5
SAVE SOLUTION 171-233
END
EQUILIBRIUM PHASES 171-233
                    -1.36 0.01
        Al(OH)3(a)
                    1.69 1.000000E-4
        Fe(OH)3(a)
        Calcite
                     0.0
                          0.4
        Gypsum
                     0.0
                          0.0
        SiO2(a)
                     0.0
                          0.0
SURFACE 171-233
 -equilibrate with solution 171-233
Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400 #0.2 sites per mole of Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is
surface area per mole of iron hydroxide
Hfo_sOH Fe(OH)3(a) equilibrium_phase 0.005
SAVE EQUILIBRIUM PHASES 171-233
SAVE SURFACE 171-233
SAVE Solution 171-233
END
MIX
2000 1.0
3000 0.0
SAVE SOLUTION 234-260
END
EQUILIBRIUM PHASES 234-260
        Al(OH)3(a) -1.36 0.01
        Fe(OH)3(a) 1.69 1.000000E-4
        Calcite
                     0.0
                           0.4
        Gypsum
                     0.0
                            0.0
        Si02(a)
                      0.0
                            0.0
SURFACE 234-260
 -equilibrate with solution 234-260
Hfo wOH Fe(OH)3(a) equilibrium phase 0.2 53400
                                                          #0.2 sites per mole of
Fe(OH)3(a) present; 53400=600x89 (89 is formula weight for goethite) is
surface area per mole of iron hydroxide
Hfo_sOH Fe(OH)3(a) equilibrium_phase 0.005
SAVE EQUILIBRIUM PHASES 234-260
SAVE SURFACE 234-260
SAVE Solution 234-260
END
END
PRINT
        -reset false
   -surface false
```

BC\_mod02\_north\_final.pqi 8/8/2011 SELECTED OUTPUT -file BC mod02.sel #can be SEL or XLS false -reset # -step true #this prints the time step in the first column, set to "false" in order to eliminate that column #1995 through 1997 Plateau 2 MIX .334046 1000 2000 .665954 SAVE SOLUTION 0 # 1994 through 1995 TRANSPORT -cells 260 #235 is total cells -length #4 4 meter cells .20000000 20.000000 -shifts 4.00000 #6 yrs\*365\*24\*3600/2522880= 75 shifts; we start at the dam, John added a year for the diffence in length for the first water 6311520.0 #This -time step is 29.2 days in seconds and essentially indicates hydraulic conductivity -punch cells 10 40 70 85 110 142 203 260 -punch frequency 1 -flow direction forward -boundary conditions flux flux -correct disp true -dispersivity 260\*20.000000 -diffusion\_coef 0.0e-0 #No diffusion -tempr 1.0 #No heat retardation END #1995 through 1997 Plateau 2 MIX 1000 .262052 2000 .737948 SAVE SOLUTION 0 #Overwrite Solution 0 TRANSPORT -shifts 11.0000 END #1997 through 2000 Plateau 3 MIX .166453 1000 .833547 2000 SAVE SOLUTION 0 #Overwrite Solution 0. TRANSPORT -shifts 14.0000 END #2000 through 2010 Plateau 4 MIX .069069 1000 2000 .930931 SAVE SOLUTION 0 #Overwrite Solution 0.

BC\_mod02\_north\_final.pqi TRANSPORT -shifts 29.0000 END #2006 through 2010 Plateau 5 MIX .010855 1000 2000 .989145 SAVE SOLUTION 0 write Solution 0. TRANSPORT 10 #00 -shifts END

8/8/2011

#Over-

END

# **ATTACHMENT IV**

Modifications to the Thermodynamic Database for Uranium and Radium

## Modifications to the Thermodynamic Database for Uranium and Radium

by

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## DATABASE

The thermodynamic database used for these calculations (summarized in Table 1) was a modified version of the WATEQ4F database provided with PHREEQC (Parkhurst and Appelo, 1999). Modifications were primarily based upon changes to the reactions in the SOLUTION\_SPECIES<sup>1</sup> portion of the database for the uranyl ( $UO_2^{+2}$ ) component. Additionally, reactions for radium were also added to the database; the solution reactions were originally taken from the MINTEQ.V4.dat database also provided with PHREEQC.

## Uranium

For uranium the revised data were from two sources. Reactions in solution were updated using the OECD NEA 2003 compilation (Guillaumont et al., 2003). This document is an update of an earlier compilation also done under the auspices of the NEA (Grenthe et al., 1992). The reactions that were updated primarily involved uranyl complexation reactions involving hydroxide and carbonate. Table 1 lists the NEA selected values along with the values in several of the unmodified databases included in the PHREEQC program package. The table also lists the values used in the revised database, called WATEQ\_NEA.dat in Table 1.

In addition to the NEA update reactions, three ternary uranyl complexes were also added to database. These complexes included  $CaUO_2(CO_3)_3^{-2}$ ,  $Ca_2UO_2(CO_3)_3^{\circ}$ , and  $MgUO_2(CO_3)_3^{-2}$ . The constants for these three reactions were reported in the literature after the 2003 NEA compilation was released. The values for these three complexation constants were taken from Dong and Brooks, (2006, 2008). The inclusion of these complexes will tend to increase

<sup>&</sup>lt;sup>1</sup> The term SOLUTION\_SPECIES is the keyword used in PHREEQC to define these reactions.

solubility concentrations estimates for uranyl and decrease adsorption of uranyl onto HFO in geochemical models (Mahoney et al., 2009b). Inclusion of the complexes improves model estimates by providing a more realistic set of complexation reactions in solution. Their presence will also tend to increase the model determined concentration of uranium in solution, which produces a more conservative model estimate. As this study was primarily aimed at adsorption reactions onto hydrous ferric oxide (HFO), no attempt was made to update uranyl bearing mineral phases in the database.

In addition to modifications to the SOLUTION\_SPECIES portion of the database, the reactions that defined the surface complexation of uranyl onto hydrous ferric oxide (HFO) were updated based upon the recently published results of Mahoney et al. (2009a). This set of four reactions replaced the estimated values for the two reactions that were originally presented in Dzombak and Morel, (1990). The following surface complexation reactions were used to describe uranium (as uranyl) adsorption onto hydrous ferric oxide:

$$\begin{array}{ll} Hfo\_sOH + UO_2^{+2} = Hfo\_sOUO_2^{+} + H^{+} & Log K_1^{int} = 3.736 \\ Hfo\_wOH + UO_2^{+2} = Hfo\_wOUO_2^{+} + H^{+} & Log K_2^{int} = 2.534 \\ Hfo\_wOH + UO_2^{+2} + CO_3^{-2} = Hfo\_wOUO_2CO_3^{-} + H^{+} & Log K_3^{int} = 9.034 \\ Hfo\_wOH + UO_2^{+2} + 2CO_3^{-2} = Hfo\_wOUO_2(CO_3)_2^{-3} + H^{+} & Log K_4^{int} = 15.28 \end{array}$$

These revised set of reactions correct the values reported by Dzombak and Morel for  $K_1^{int}$  and  $K_2^{int}$ , which were not based upon comparison to laboratory derived data. Rather Dzombak and Morel used a correlation between the log K for the first metal hydroxide complex and the log  $K_1^{int}$  and  $K_2^{int}$  values. When compared to experimental measurements the Dzombak and Morel estimated values for log  $K_1^{int}$  and  $K_2^{int}$  tended to significantly overestimate the amount of uranyl adsorption at low pH conditions and tended to underestimate uranium adsorption at high pH conditions particularly when carbonate was also present in solution. The newer values, published in Mahoney et al. (2009a), were based upon model based fits to laboratory measurements. Moreover, the revised data set included two surface complexation constants for uranyl carbonate complexes (the  $K_3^{int}$  and  $K_4^{int}$  reactions). Complexation constants for any type of uranyl carbonate surface complex were not included in the original Dzombak and Morel (1990) compilation that eventually became the basis for the surface complexation portion of the database included in the PHREEQC package. The existence of uranyl carbonate surface complexes has long been known, although various groups define them differently. The

Dzombak and Morel compilation was never meant to be a definitive treatise on surface complexation reactions involving uranium, and so this shortcoming can be excused. However, any detailed study involved with uranium adsorption must consider the reactions in some form or other. The revised database does consider these reactions.

In addition to the uranyl adsorption reactions, two additional surface complexation reactions were added to the database. These reactions are defined below:

$$\begin{array}{ll} Hfo\_wOH + CO_3^{-2} + H^+ = Hfo\_wOCO_2^{-1} + H2O \\ Hfo\_wOH + CO_3^{-2} + 2H^+ = Hfo\_wOCO_2H + H2O \\ \end{array} \qquad \begin{array}{ll} Log K^{int} = 12.78 \\ Log K^{int} = 20.37 \end{array}$$

These final two reactions were defined by Appelo et al. (2002), and will influence sorption at higher partial pressures of  $CO_2(g)$ . Specifically, these two additional reactions will tend to occupy sites on the surface that could complex with uranium. This will produce a concomitant increase in uranium concentrations in the pore waters (Mahoney et al., 2009b).

## Radium

Speciation reaction constants for radium were also added to this database. Values were obtained from Langmuir and Riese (1985). The following reactions were added to the database.

Species	Reaction	Log K
RaOH⁺	$Ra^{+2} + H_2O = RaOH^+ + H^+$	-13.5
RaSO <sub>4</sub>	$Ra^{+2} + SO_4^{-2} = RaSO_4$	2.76
RaCO <sub>3</sub>	$Ra^{+2} + CO_3^{-2} = RaCO_3$	2.5
RaCl⁺	$Ra^{+2} + Cl^{-} = RaCl^{+}$	-0.1
RaCl <sub>2</sub>	$Ra^{+2} + 2Cl^{-} = RaCl_2$	-0.05

Surface complexation reactions onto HFO for radium (as  $Ra^{+2}$ ) generally use the same values as  $Ba^{+2}$ . However, for this database values were recalculated and slight differences were noted. According to the model proposed by Dzombak and Morel, divalent cations form outer sphere complexes with the strong surface sites (designated as Hfo\_sOH) and inner sphere complexes

with the weak sites (Hfo\_wOH). Using only Ca, Ba and Sr, the correlation between log  $K_{MOH}$  the strong site surface complexes was

$$\log K_1^{int} = -0.6592 * \log K_{MOH} + 5.6719$$

a log  $K_1^{int}$  of 5.3424 was noted for radium<sup>2</sup>. The log  $K_1^{int}$  value for Ba<sup>+2</sup> was 5.46.

The value for the log  $K_2^{int}$  Reaction (Hfo\_wOH + Ra<sup>+2</sup> = Hfo\_wORa<sup>+</sup> + H<sup>+</sup>) was based upon the overall regression equation defined in Dzombak and Morel. The calculated value for log  $K_2^{int}$  was -7.333. The log  $K_2^{int}$  value for Ba<sup>+2</sup> was -7.2.

<sup>&</sup>lt;sup>2</sup> Langmuir and Riese (1985) write the radium hydrolysis reaction as  $Ra^{+2} + H_2O = RaOH^+ + H^+$ , however Dzombak and Morel removed water from their equations and used equations of the form  $Ra^{+2} + OH^- = RaOH^+$ , for their correlations. Therefore, for radium the log K<sub>MOH</sub> becomes 0.5, and the corresponding log K<sub>MOH</sub> for barium is 0.53.

Table 1. Continued.Surface complexation reactions for uranium adsorption onto HFOand solubility product constants for selected phases.

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		DAT	ABASE COMPARISON				
SPECIES	OECD NEA UPDATE	PHREEQC Databases					
2.000000000000000000000000000000000000	2003 Guillamont et al.	WATEQ4F.dat	WATEQ_NEA.dat Version for this project	lini.dat	minteq.v4.dat	minteq.da	
		SL	JRFACE COMPLEXES				
Hfo_sOUO2+	5.2 3.736 We are using the M		e Mahoney, Cadle and Jakubowski				
Hfo_wOUO2+	NEA does not discuss	2.8	2.534	(2009) constants plus two reactions for carbona surface complexation [Hfo_wOCO2-, and Hfo_wOCO2H]			
Hfo_wOUO2CO3-			9.034				
Hfo_wOUO2(CO3)2-3			15.28				
	1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	PHASES	(limited selection liste	ed)			
UO2SO4	Free Energy provided no value for K given			1.9681			
UO2SO4:2.5H2O	1.589			-1.4912			
UO2SO4:3.5H2O	1.585			-1.4805			
U02S04:3H2O *	-0.831* 0.754 (recalculated)			-1.4028			
U02S04:H20				-6.0233			
Schoepite (UO3:2H2O)	UO3 · 2H2O(cr) -> UO2 + 2 + 2 OH- + H2O(I) , 10 ,0 log s K = - (23.19 ± 0.43). Or 4.81 in proton form	5.404	5.404	4.8333	5.994	5.404	

 Table 1. Comparison of uranium solution complexation reactions in various databases

 provided with PHREEQC and selected values included in the updated database.

SPECIES	OECD NEA UPDATE			PHREEQC	Databases		
	2003 Guillamont et al.	WATEQ4F.dat	WATEQ_NEA.dat Version for this project	lini	.dat	minteq.v4.dat	minteq.da
II digits retained in table to facilitate traceability	Equation signs retained as in original; data is mainly from Table 3-2. To reduce error these values	CO3-2 is component		HCO3- is component	using CO3-2 as component		
CO3-2 HCO3- reaction	were mainly copied and pasted into cells	10.329		-10.3288		10.329	10.33
UO2OH+	-5.250	-5.2	-5.250	-5.2073		-5.897	-5.09
UO2(OH)2(aq)	-12.150		-12.150	-10.3146			
UO2(OH)3-	-20.250	-19.2	-20.250	-19.2218			
UO2(OH)4	-32.400	-33	-32.400	-33.0291			
UO2CO3(ag)	9,94	9.63	9.94	-0.6634	9.6654	9.6	10.071
UO2(CO3)2-	16.61	17.0	16.61	-3.7467	16.9109	16.9	17.008
UO2(CO3)3	21.84	21.63	21.84	-9.4302	21.5562	21.6	21.384
			ACTIVATION PLANE				
U02504(aq)	3.15	3.15	3.15	3.0703		3.18	2.709
U02(SO4)34-	3.02	4.14	4.14	3.5000			4.103
2							
(UO2)20H+++	-2.700	-2.7	-2.700	-2.7072			
(UO2)2(OH)2++	-5.620	-5.62	-5.620	-5.6346	A STREET	-5.574	-5.645
(UO2)3(OH)4++	-11.900	-11.9	-11.900	-11.929		10 100	
(UO2)3(OH)5+	-15.550	-15.55	-15.550	-15.5862		-15.585	-15.593
(UO2)4(OH)7+	-21.900	-21.9	-21.900	-21.9508			
(CC2)((C-1))					COMPANY R	Ser Charles	
(UO2)3(CO3)6(6-)			54.00	-8.0601	53.9127	Not present	Not presen
(UO2)2CO3(OH)3-	-19.010 CO2(gas) component		2UO2+2 + CO3-2 + 3H2O = (UO2)2CO3(OH)3- +3H+ log_k -0.86	-11.2229			
(UO2)3CO3(OH)3+	NOT IN NEA 2003 nor Grenthe et al. 1992						
(UO2)3(OH)5CO2+	NOT IN NEA 2003 Sames as (UO2)SO(OR)2(HCO3)+			-9.6194	42.0246		
(UO2)3O(OH)2(HCO3)+	-17.500 CO2(gas) component		3U02+2 + C03-2 + 3H2O = (U02)30 (OH)2(HC03)+ +3H+ log_k 0.65	- <del>9</del> .7129			
(UO2)11(CO3)6(OH)12	-72.500 CO2(gas) component		11U02+2 + 6C03-2 + 12H20 = (U02)11(C03)6(0H)12-2 +12H+ log_k 36.40	NA			
Ca2UO2(CO3)3(aq)	NEA did not select value some discussion in NEA VS they cite a range of 26.5 to 30.55. Dong and Brooks 2006 report 30.70, this value		30.7				
CaUO2(CO3)3	was selected Dong and Brooks 2006, report 27.18 this value was selected		27.18				
MgUO2(CO3)3-2	Dong and Brooks 2006, 25.8 This value was selected		25.8				



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