308 - - - Q200405250001

Scientific Notebook No. 300: 1. A Quantitative Geochemical Model for the Ambient Natural System at Yucca Mountain, Nevada; 2. A Reactive Transport Model for Geochemical and Hydrological Evolution of the Near Field Environment at Yucca Mountain due to

21
150

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CNWRA
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Windows NT
OS

Input/Output files for EQ3/6
MULTIFLO, MS WORD, MS EXCEL
Individual files referenced in
S. Notebook 300 text

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Initial Entry

12-15-98

This notebook describes the construction of: 1) a quantitative geochemical model for the ambient natural system at Yucca Mt, Nevada, and 2) a reactive transport model for the geochemical and hydrological evolution of the Near Field Environment at Yucca Mt due to repository-induced perturbations to the ambient system. The main collaborators are William M. Murphy & Debra Hughson. In-Process entries will identify additional collaborators, if necessary.

The primary codes used in this analysis are EQ3/6 V7.2b and MULTIFLO1. The EQ3/6 software package was installed on a WindowsNT platform, and its control issues are documented in the scientific notebook CNWRA controlled copy # 037, issued to William M. Murphy. Initial Multiflo runs were generated & documented by Debra Hughson.

This notebook will be maintained by Lauren Browning, who is identified as LaBrowning or LB.

LaBrowning
12-15-98

Benchmarking: EQ3/6 with Multiflo 12-16-98

It is necessary to test the reliability of MULTIFLO to calculate a variety of geochemical processes, such as precipitation and aqueous speciation. This can be accomplished by entering similar problems into both codes, and comparing the results.

Benchmarking exercises were done mostly in collaboration with Debra Hughson.

The general procedure is as follows. Debra H. set up a Multiflo run with:

2 1 m^3 blocks
0.11 porosity
1.0 = saturation level
⇒ 1.78 m^3 of solid material total
220 kg H_2O

The solid material is made of an inert substance, plus calcite and an amorphous SiO_2. The setup for these is initially:

	Calcite	SiO_2(am)
volume fraction:	0.01	0.01
reaction Rate:	$10^{-11.34}$ $\frac{mol}{cm^2 s}$	$10^{-12.5}$ $\frac{mol}{cm^2 s}$
specific surface:	1 cm^2/cm^3	1.00^{-4} cm^2/cm^3
activation enthalpy:	35 kJ/mol	62.9 kJ/mol

These values are not real, and will be used for benchmarking only.

LB 12-16-98

Benchmarking: EQ3/6 with Multiflo 12-17-98

The parameters used in MULTIFLO must be equated with those needed to run EQ3/6. the procedure is shown here.

1) EQ3/6 requires surface area input as $\frac{cm^2}{kg\ H_2O}$

so, for SiO_2(Am):

$1 \cdot 10^{-4}\ \frac{cm^2}{cm^3} * 2.00^6\ cm^3 = 200\ cm^2$ LB 12-17-98 = Total SiO_2(Am) surface in system

want the surface area in contact with 1 kg H_2O, so:

$\frac{200\ cm^2}{220\ kg\ H_2O} = \boxed{0.9091\ \frac{cm^2\ SiO_2(Am)}{kg\ H_2O}}$

2) EQ3/6 requires $\frac{\text{moles reactant}}{\text{Kg } H_2O}$ for input, so:

$\frac{200\ cm^2\ (\text{total } SiO_2 \text{ surface})}{1.78 \cdot 10^4\ cm^3\ (\text{total volume } SiO_2(am))} \Rightarrow 89.0\ \frac{cm^3}{cm^2}\ SiO_2(Am)$

we have 0.9091 cm^2, so $89.0\ \frac{cm^3}{cm^2} \cdot .9091\ cm^2 = 80.91\ cm^3$

and $80.91\ cm^3_{SiO_2(Am)} \cdot \frac{1\ mol\ SiO_2(Am)}{29\ cm^3} = \boxed{2.79 \text{ moles } SiO_2(Am)}$

3) EQ3/6 requires activation enthalpies in $\frac{kcal}{mol}$, so:

for SiO_{2am}: $62.9\ \frac{kJ}{mol} \cdot \frac{kcal}{4.186\ kJ} = 15.026\ \frac{kcal}{mol}$

Using the same procedures for Calcite, I obtain: $9091.0\ \frac{cm^2}{kg\ H_2O}$ = surface area, calcite

2.1991 moles calcite
8.361 kcal/mol = activation H

LB 12-17-99

Benchmarking: EQ6 with Multiflo 46 3-24-99 ~~12-17-98~~

A daily log of Benchmarking exercises has been kept by Debra Hughson. The accompanying EQ3 input and output files are located in:

D:\EQ3-MFBench\Basic\EarlyBench\

The 'bill25a.*' series may be compared with those in:

UNIX: ~lbrowning/gem-eq3.1/

Differences between the EQ3/6-MULTIFO outputs were deemed by Spainter to be insignificant for the bill25a.* series with the non-isothermal kinetic dissolution of Calcite and Amorphous SiO_2.

LB
3-24-99

Benchmarking EQ3 with Multiflo 3-31-99

The closest match between EQ3 and Multiflo results was obtained for the following files:

D:\EQ3-MFBench\Basic\U02\bill25au02.3ϕ

and

Unix: ~lbrowning/gem-eq3.2/

As shown on attached, differences are <ϕ.1%. This is the first result obtained after I started running multiflo, as well as EQ3/6.

LB
3-31-99

LB
3-24-99
~~12-17-98~~

Benchmarking: EQ6 with Multiflo

A daily log of Benchmarking exercises has been kept by Debra Hughson. The accompanying EQ3 input and output files are located in:

D:\EQ3-MFBench\Basic\EarlyBench\

The 'bill25a.*' series may be compared with those in:

UNIX: ~~~Hbrowning/~~gem-eq3.1/

Differences between the EQ3/6-MULTIFO outputs were deemed by Spainter to be insignificant for the bill25a.* series with the non-isothermal kinetic dissolution of Calcite and Amorphous SiO_2.

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3-24-99

Benchmarking EQ3 with Multiflo

EQ3: bill25auo2.3o
aqueous species.
3\31\99

--- Distribution of Aqueous Species ---

Species	MF	Molality	Log molality	Log gamma	Log activity
HCO3-		2.5034E-03	-2.6015	-0.0382	-2.6396
Ca++		2.5000E-03	-2.6021	-0.1536	-2.7557
Cl-		2.4919E-03	-2.6035	-0.0392	-2.6427
SiO2(aq)		1.0000E-03	-3.0000	0.0000	-3.0000
CO2(aq)		3.3908E-04	-3.4697	0.0008	-3.4689
O2(aq)		2.5171E-04	-3.5991	0.0008	-3.5983
CaCO3(aq)	5.9856E-6	5.9847E-06	-5.2230	0.0000	-5.2230
CO3--		2.2793E-06	-5.6422	-0.1522	-5.7944
OH-	1.6505E-4	1.6522E-07	-6.7819	-0.0392	-6.8211
H+		7.2813E-08	-7.1378	-0.0362	-7.1740
UO2(CO3)2--	5.5346E-10	5.5327E-10	-9.2571	-0.1562	-9.4132
UO2(CO3)3----	1.1312E-10	1.1707E-10	-9.9316	-0.6307	-10.5623
UO2(OH)2(aq)	1.9863E-11	1.9861E-11	-10.7020	0.0000	-10.7020
UO2CO3(aq)	1.3678E-11	1.3667E-11	-10.8643	0.0000	-10.8643
UO2(OH)3-	4.0097E-13	4.0080E-13	-12.3971	-0.0382	-12.4352
UO2OH+	1.8713E-13	1.8710E-13	-12.7279	-0.0408	-12.7687
UO2++	2.6546E-15	2.6546E-15	-14.5760	-0.1593	-14.7353
(UO2)2CO3(OH)3-	2.5176E-15	2.5171E-15	-14.5991	-0.0382	-14.6373
UO2Cl+	6.6055E-18	6.6061E-18	-17.1801	-0.0408	-17.2208
H4(H2SiO4)4----		2.4342E-19	-18.6136	-0.6307	-19.2444
UO2(OH)4--		1.2235E-19	-18.9124	-0.1562	-19.0686
(UO2)2(OH)2++		2.5235E-21	-20.5980	-0.1593	-20.7573
ClO3-		5.4600E-26	-25.2628	-0.0382	-25.3010
ClO4-		3.0963E-26	-25.5092	-0.0392	-25.5484
UO2+		2.3021E-27	-26.6379	-0.0408	-26.6786
(UO2)3(OH)4++		5.2505E-28	-27.2798	-0.1593	-27.4391
(UO2)3(OH)5CO2+		1.8689E-28	-27.7284	-0.0408	-27.7692
(UO2)3O(OH)2(HCO3)+		4.8887E-30	-29.3108	-0.0408	-27.8626
ClO2-		1.5071E-28	-27.8218	-0.0382	-29.3490
(UO2)4(OH)7+		2.3248E-31	-30.6336	-0.0408	-30.6744
HClO2(aq)		4.4340E-34	-33.3532	0.0000	-33.3532
UO2(CO3)3(5-)		1.9402E-36	-35.7122	-0.9873	-36.6995
U(OH)4(aq)		7.8097E-38	-37.1074	0.0000	-37.1074
UO2ClO3+		3.1358E-40	-39.5037	-0.0408	-39.5444
Formate		2.4674E-44	-43.6078	-0.0382	-43.6459
H2(aq)		4.9163E-45	-44.3084	0.0008	-44.3076
Formic acid(aq)		8.5710E-48	-47.0670	0.0000	-47.0670
U(CO3)4----		1.9131E-49	-48.7183	-0.6307	-49.3490
CO(aq)		1.9289E-50	-49.7147	0.0000	-49.7147
UOH+++		5.5728E-55	-54.2539	-0.3526	-54.6065

Pages 6 through 14 of this scientific notebook were intentionally left blank and therefore contain no information.

YM Pore Water Analyses 1-3-99

The goal of these analyses is to determine if the available analytical data for unsaturated zone pore water compositions at Yucca Mountain are thermodynamically consistent internally. If not, corrections must be made to restore internal consistency.

Unsaturated Zone Pore Water Compositions were obtained from:

Ref: In C. Yang, Gordon Rattray, & Pei Yu (1996) Interpretation of chemical and isotopic data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada, USGS Water-Resources Investigations Report 96-4058

and

Ref: In C. Yang, A. Keith Turner, Ted M. Sayre, & Parviz Montazer (1988) Triaxial-Compression Extraction of Pore Water, USGS Water-Resourses Investigations Report 88-4189.

Results show that the analytical data of Yang et al. are thermodynamically inconsistent. For well in E-25 UZ#16, analytical data for water compositions at different depths, were analyzed with EQ3 by inputting the analytical data, as reported, and not assigning any charge balancing species.

EQ3 input and output files for this analysis are located in the folder D:\YangYZ and are summarized in the Excel file: YangWellsYZ.xls

LB
1-3-99

LB 3-25-99

Ym Pore Water Analyses 1-3-99

Summary of Results in:

YangWells42.xls:

input: analytical data, no charge balance
Output:
→ $7 \leq pH \leq 9.2$ (same as input; fixed)

→ most analyses have excess cations; charge imbalances are significant (as high as 90% of the mean)

→ analytical $\frac{CO_3^{--}}{HCO_3^-}$ ratio is not equilibrated at the given analytical pH: [see pg 18 for plot]

We interpret these results as unsatisfactory. Thus, modifications to the analytical data are required.

A sample input file is given on page 19. This shows that:

1) HCO_3^- is input as a free component, so that the equilibrated $[CO_3^{--}]$ is calculated for comparison with the analytical $[CO_3^{--}]$.

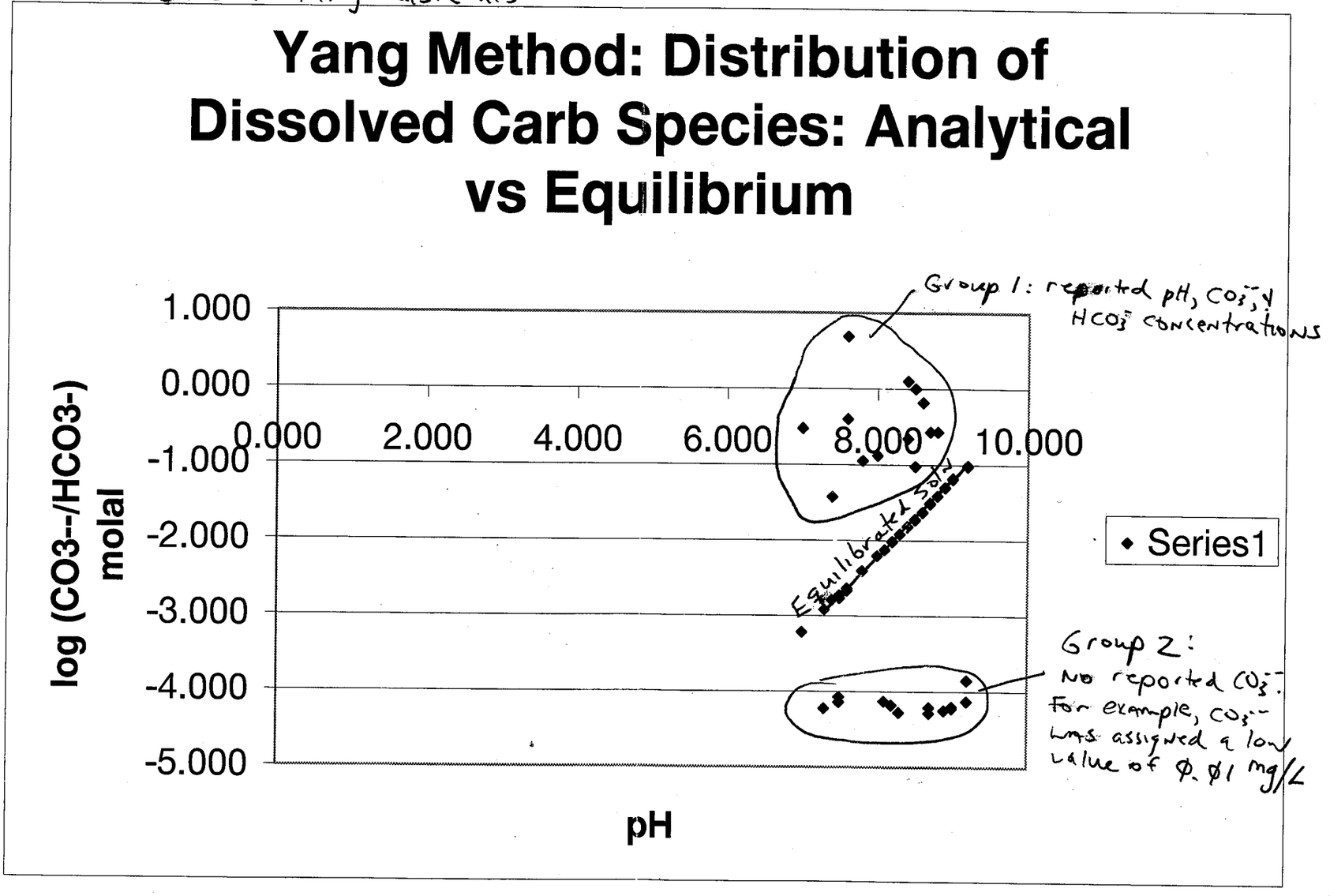
2) $fO_2(g)$ is set to atmospheric

3) $T(c) \equiv (\text{Depth in meters} + 1093.47)/156.31$ based on geothermal gradients measured by Sass & Lachenbruch (1982)

LB 1-3-99

YM Pore Water Analyses 1-3-99

data from YangWells42.xls



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1-3-99

YM Pore Water Analyses

UZ163y2.3i

```
|-----------------------------------------------------------------------|
|Version level= 7.2  (xcon3)                                            |
|EQ3NR input file name= UZ163Y2.3i                                      |
|                                                                       |
|Yang, WRIR 96-4058, 1996                                               |
|                                                                       |
| UZ well: UZ-16/163.5-163.9: 49.9 meters                               |
|                                                                       |
|   Yang Approach                                                       |
|   NOTE: Log fO2(g) set to atmospheric, scaled to P(tot) of 850 mbar   |
|   NOTE: Temperature (T) estimated from data in Sass                   |
|           & Lachenbruch (1982), by                                    |
|           T = (Depth in meters + 1093.47)/56.31                       |
|                                                                       |
|Computations by Lauren Browning December 30 1998                       |
|                                                                       |
|-----------------------------------------------------------------------|
|Temperature (C)         | 20.3         |Density(gm/cm3)|  1.00000      |
|-----------------------------------------------------------------------|
|Total Dissolved Salts   |              | mg/kg | mg/l  |*not used      |
|-----------------------------------------------------------------------|
|Electrical Balancing on |                       | code selects |*not performed|
|-----------------------------------------------------------------------|
| SPECIES                | BASIS SWITCH/CONSTRAINT| CONC/ETC  | UNITS OR TYPE |
|-----------------------------------------------------------------------|
|redox                   |                        |-.7706     |LogfO2         |
|H+                      |                        | 7.6       |pH             |
|Ca++                    |                        |42.5       |mg/L           |
|Mg++                    |                        |13.4       |mg/L           |
|Na+                     |                        |21.5       |mg/L           |
|SiO2(aq)                |                        |77.5       |mg/L           |
|Al+++                   |                        | 0.5       |mg/L           |
|HCO3-                   |                        |114.70     |free mg/L      |
|Cl-                     |                        |32.4       |mg/L           |
|NH3(aq)                 |NO3-                    |6.338      |mg/L           |
|SO4--                   |                        |72.3       |mg/L           |
|-----------------------------------------------------------------------|
|Input Solid Solutions                                                  |
|-----------------------------------------------------------------------|
| none                   |                        |           |                |
|-----------------------------------------------------------------------|
|SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value    |
|-----------------------------------------------------------------------|
| none                |         |                          |           |
|-----------------------------------------------------------------------|
|OPTIONS                                                                |
|-----------------------------------------------------------------------|
| - SOLID SOLUTIONS -                                                   |
|     ignore solid solutions                                            |
|   * process hypothetical solid solutions                              |
|     process input and hypothetical solid solutions                    |
| - LOADING OF SPECIES INTO MEMORY -                                    |
|   * does nothing                                                      |
|     lists species loaded into memory                                  |
| - ECHO DATABASE INFORMATION -                                         |
|   * does nothing                                                      |
|     lists all reactions                                               |
|     lists reactions and log K values                                  |
|     lists reactions, log K values and polynomial coef.                |
| - LIST OF AQUEOUS SPECIES (ordering) -                                |
|   * in order of decreasing concentration                              |
|     in same order as input file                                       |
| - LIST OF AQUEOUS SPECIES (concentration limit) -                     |
```

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1-3-99

YM Pore Water Analyses


```
|     all species                                                          |
|     only species > 10**-20 molal                                         |
|   * only species > 10**-12 molal                                         |
|     not printed                                                          |
| - LIST OF AQUEOUS SPECIES (by element) -                                 |
|   * print major species                                                  |
|     print all species                                                    |
|     don't print                                                          |
| - MINERAL SATURATION STATES -                                            |
|   * print if affinity > -10 kcals                                        |
|     print all                                                            |
|     don't print                                                          |
| - pH SCALE CONVENTION -                                                  |
|   * modified NBS                                                         |
|     internal                                                             |
|     rational                                                             |
| - ACTIVITY COEFFICIENT OPTIONS -                                         |
|   * use B-dot equation                                                   |
|     Davies' equation                                                     |
|     Pitzer's equations                                                   |
| - AUTO BASIS SWITCHING -                                                 |
|   * off                                                                  |
|     on                                                                   |
| - PITZER DATABASE INFORMATION -                                          |
|   * print only warnings                                                  |
|     print species in model and number of Pitzer coefficients             |
|     print species in model and names of Pitzer coefficients              |
| - PICKUP FILE -                                                          |
|    write pickup file                                                     |
|   *  don't write pickup file                                             |
| - LIST MEAN IONIC PROPERTIES -                                           |
|   * don't print                                                          |
|     print                                                                |
| - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -               |
|   * print                                                                |
|     don't print                                                          |
| - CONVERGENCE CRITERIA -                                                 |
|   * test both residual functions and correction terms                    |
|     test only residual functions                                         |
|--------------------------------------------------------------------------|
|DEBUGGING SWITCHES (0 = off, 1,2 = on                                     |
|--------------------------------------------------------------------------|
|0  generic debugging information                                          |2
|0  print details of pre-Newton-Raphson iteration                          |2
|0  print details of Newton-Raphson iteration                              |
|0  print details of stoichiometric factors                                |2
|0  print details of stoichiometric factors calculation                    |
|0  write reactions on RLIST                                               |
|0  list stoichiometric concentrations of master species                   |
|0  request iteration variables to be killed                               |
|--------------------------------------------------------------------------|
|DEVELOPMENT OPTIONS  (used for code development)                          |
|--------------------------------------------------------------------------|
| none                                                                     |
|--------------------------------------------------------------------------|
|TOLERANCES                   (desired values)        (defaults)           |
|--------------------------------------------------------------------------|
|      residual functions  |                      |1.0e-10  tolbt         |
|        correction terms  |                      |1.0e-10  toldl         |
|        saturation state  |                      |0.5      tolsat        |
|number of N-R iterations  |                      |30       itermx        |
|--------------------------------------------------------------------------|
```

Ym Pore Water Analyses 1-3-99

Modifications to the Yang et al. data were reported in:

J.A. Apps (1997) Hydrochemical Analysis; Chap 14 in The Site-scale unsaturated zone model of Yucca Mountain, Nevada for the Viability Assessment, LBNL-40376 UC-814

This work notes inconsistencies in the Yang Data, and suggests that the measured pH values alone are incorrect. To calculate new pH values, the well waters are assumed to be in equilibrium with calcite.

To examine the nature of these assumptions, we use the Apps approach to 'correct' the Yang water compositions reported for well UE25 UZ#16.

The results of these analyses are located in:

D:\YangA2\, and are summarized in D:\YangA2\YangWellsA2.xls

some results in YangWellsA2.xls are

input: input free HCO_3^- = Analytical HCO_3^-
NO charge balance
Calculate pH assuming equilibrium with Calcite

Output: ~7 ≤ pH ≤ 9.4
% charge imbalance ≲ 50% from mean
Trends appear: pH↑ until ~450 m, then ↓

LB 1-3-99

Ym Pore Water Analyses 1-3-99

These results are not satisfying because there should be no charge imbalance in the waters and the calculated pH range is larger than might be expected.

A new approach was devised. To correct for the likely chance that the analytical pH, HCO_3^-, & $CO_3^{=}$ are in err, we ① fix the fCO_2 at $10^{-2.991}$, an approximation of a curve for measured $CO_2(g)$ in a nearby well (Fig 18, Yang et al., 1996), and ② fix K^+ (mg/L) = 14 to account for the possibility that $[K^+]$ will affect the calculated pH. We ~~use~~ LB 1-3-99 Average $[K^+]$ analyses from the UZ-4 TP well at depths between 91.3 & 95.6 m, as reported by Yang et al. (1988)

The results of these analyses are located in:

D:\YangfixCO2+fixCO2&K, and are summarized in D:\YangfixCO2+fixCO2&K\YangfixCO2&K

a summary of these results is:

input: $K^+ \equiv 14$ (mg/L)
$CO_2(g) \equiv 10^{-2.991}$ atm
balance of H^+
[calcite equilibrium not assumed]

Output: - ~8 ≤ pH ≲ 8.5
- calcite saturation varies randomly, but remains ~close to saturated
- $[Ca^{2+}]/[Na^+]$ decreases to 425 m, then increases

PB 1-3-99

YM Pore Water Analyses 1-3-99

The plots given on pg 23 of this notebook compare the pH ranges that result from taking different approaches to the Yang analytical data.

These show results from analyses of well waters USW UZ#14 (Yang et al., 1996) with fCO_2 & K^+ fixed, as before.

The results of the UZ14 analyses are located in:

D:\YangWells\UZ14ck1 and are summarized in:
D:\YangWells\UZ14ck\Yang UZ14 qsp.xls

This approach tightens the analytical pHs, causes no charge imbalance, & ~~generates~~ LB 1-3-99 reveals useful trends. We therefore suggest modifying all UZ14 + UZ16 analyses by fixing $CO_2(g) = 10^{-2.991}$ & $[K^+] \equiv 14$ mg/L.

LB 1-3-99

YM Pore Water Analyses 1-3-99

LB
1-3-99

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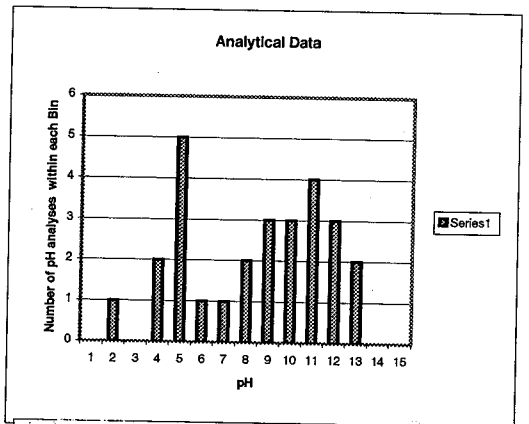
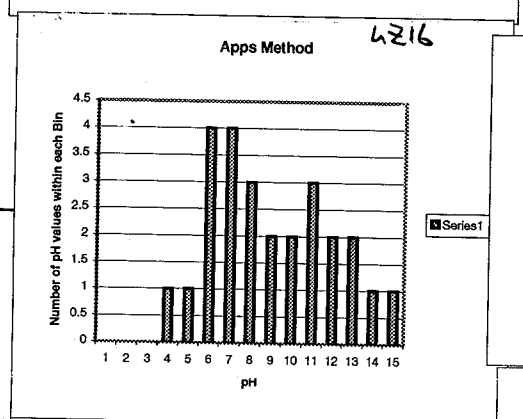
1-3-99

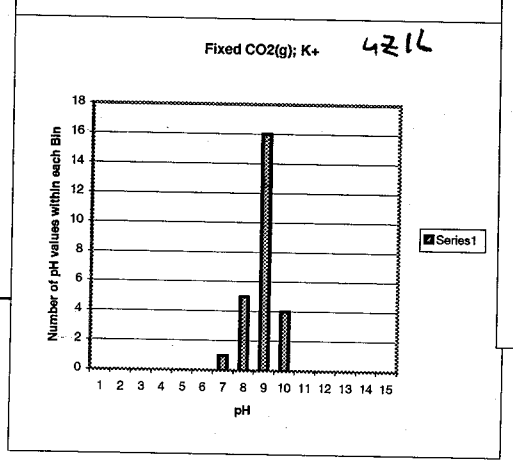
Yn Pore Water Analyses

File: YangPlotData.xls in D drive
Lauren Browning 1-3-99
Range of pH values for Yang data,
for modified and unmodified analytical data sets.

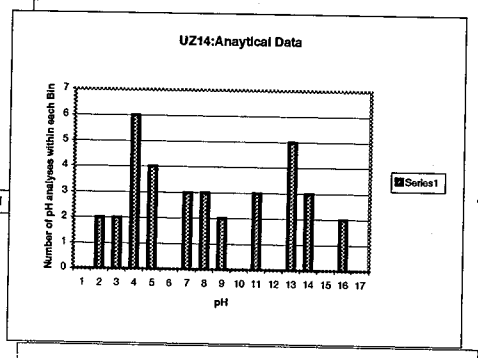
UZ 16 well

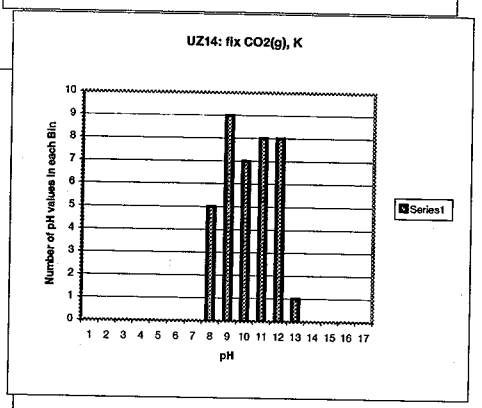






UZ 14 Well





UZ16 Well

Bin #	pH range
1	**6.61-6.8**
2	**6.81-7**
3	**7.01-7.2**
4	**7.21-7.4**
5	**7.41-7.6**
6	**7.61-7.8**
7	**7.81-8**
8	**8.01-8.2**
9	**8.21-8.4**
10	**8.41-8.6**
11	**8.61-8.8**
12	**8.81-9**
13	**9.01-9.2**
14	**9.210-9.4**
15	**>9.4**

UZ14 Well

Bin #	pH range
1	6.21-6.4
2	6.41-6.6
3	6.61-6.8
4	6.81-7
5	7.01-7.2
6	7.21-7.4
7	7.41-7.6
8	7.61-7.8
9	7.81-8
10	8.01-8.2
11	8.21-8.4
12	8.41-8.6
13	8.61-8.8
14	8.81-9
15	9.01-9.2
16	9.210-9.4
17	**>9.4**

Ym Pore Waters Analyses 1-3-99

In addition to the analyses discussed on pg 15-23 of this notebook, the Yang Data for UE25 UZ #16 was modified in 3 additional ways.

IN:

1) D:\YangToTA
summary D:\YangToTA\YangWellsToTA.xls

input: HCO_3^- (fice molal) = $\Sigma(HCO_3^- + CO_3^{--})_{Analytical}$
no charge balance
Assume calcite controls pH

2) D:\YangN2
summary: D:\YangToTN2\YangWellsN2.xls

input: balanced on HCO_3^-
Assume calcite equilibria controls pH

3) D:\Yang fixCO2 & fixCO2&K
summary: D:\YangfixCO2 & fixCO2&K\YangWellsfixCO2.xls

input: $fCO_2 \equiv 10^{-2.991}$
balance on H^+

Although these approaches are judged to be less satisfying than the one where fCO_2 and $[K^+]$ is fixed, and H^+ is used for charge balance, ~~data~~ LB 1-3-99 results from these analyses may be useful to help learn the source of the analytical uncertainties, or other issues.

LB 1-3-99

Rate Parameters for UO_2 3-15-99

The spent fuel at Yucca Mt is taken to be uraninite, UO_2.

Dissolution rate data from:

W.J. Gray, H.R. Leider, & S.A. Steward (1992) Parametric study of LWR spent fuel dissolution kinetics, J. of Nuclear Materials 190, 46-52.

was rewritten to fit the input parameter format used by EQ3/6.

$R\left(\frac{mg}{m^2 \cdot day}\right)$: $\log \vec{R} = 7.45 + 0.258 \log[C] + 0.142 \log[H^+] - \frac{1550}{T}$

$$R = 10^{7.45}[C]^{0.258}[H^+]^{0.142} - 10^{-\frac{1550}{T}}$$

$$R = 10^{7.45}[C]^{0.258}[H^+]^{0.142}\left(e^{\ln 10}\right)^{-\frac{1550}{T}}$$

$$R = 10^{7.45}[C]^{0.258}[H^+]^{0.142}\, e^{-\frac{1550}{T}\ln 10} \qquad [1]$$

We need K_+ and E_a:

for K_+: in general, $R = K_+ a_i^{\nu_i} a_j^{\nu_j}\left(1 - \frac{Q}{K}\right)$ [2]

compare equations 1 and 2.

K_+ includes all terms not related to the activity product. Setting $Q \equiv 0$ assures that our derivation will represent the maximum K_+ value for conditions far from equilibrium. So -

at $T = 298K$, $K_+ = 10^{7.45}\, e^{-\frac{1550}{T}\ln 10}$ [2a]

$K_+ = 177.28\left(\frac{mg}{m^2 \cdot day}\right)$ ~~[2a]~~ LB 3-15-99

LB 3-15-99

Rate Parameters for UO_2 3-15-99

for E_a: note $\vec{K} = a e^{-\frac{E_a}{RT}}$ [3]

for conditions of $Q \equiv \phi$, as here, K_+ is the forward reaction rate, $\vec{K}$.

compare equation [3] with the form of [2a]

$\Rightarrow$ $1550 \ln 10 = \frac{29697}{R}$ at any T

$3{,}569 = \frac{29697}{R}$ $\Rightarrow R = 8.321$

The value for $E_a = 29697 \frac{J}{mol}$ was given by Gray et al. (1992), so the above extrapolation of ~R shows our method of comparing the form of equations is valid.

$$\boxed{E_a = 29697 \frac{J}{mol} = 29.697 \frac{kJ}{mol}}$$

$$\bar{K} = 177.28 \frac{mg}{m^2 \cdot day} \cdot \frac{g}{1000\,mg} \cdot \frac{mol}{\cancel{238.03\,g}} \cdot \frac{m^2}{(100)^2 cm^2} \cdot \frac{day}{8.64 \cdot 10^4 s} =$$

LBB 3-15-99 < ~~254.03~~ g UO_2 270.03 g UO_2

$$\boxed{\bar{K} = 7.598 \cdot 10^{-13} \frac{mol}{cm^2 \cdot s}}$$

also- $H_A = E_A - RT$

$= \left(29697 \frac{J}{mol}\right) - 8.314 \left(\frac{J}{K \cdot mol}\right) 298$

$$\boxed{H_A = \text{Enthalpy of Activation} = 27.219 \frac{kJ}{mol}}$$

Assuming that it is constant at other Ts

LB 3-15-99

Estimating Thermodynamic parameters for GlassPC 3-26-99

goals: The multiflo database must be modified to include glass compositions associated with Yucca Mt Rocks. Thermodynamic data for YM glasses are not available from experiments, & must be estimated. Glasses are present in several geologic units at YM, including the Pah Canyon, Topapah Springs, & Calico Hills, ~~& P~~ LB 3-26-99. For simplicity, we select a single glass composition to represent the glasses present in all YM geologic Units – the Pah Canyon Glass (hereafter 'GlassPC'). We have analytical data for the composition of GlassPC in:

D.E. Broxton, B.L. Bish, & R.G. Warren Distribution & chemistry of Diagenetic Minerals at Yucca Mt., Nye County, Nevada. Clays & Clay Minerals, Vol. 35, No. 2, 89-110, 1987.
also in: D:\GlassPC\GlassBroxton.xls
and modified H_2O compositions in contact with this glass in well UE-25 UZ#16. (see pg. 21 - filename 'YangfixCO2&K.xls')

method:

I assume that GlassPC is equilibrated with the PC porewaters in contact with it. The log K value at 25°C can now be calculated in the following manner:

(1) a) A reaction was written for the dissolution of GlassPC. Although water compositions show that $AlOH^-$ is the dominant Al-bearing species in the PC pore waters, Al^{+++} is required by both the EQ3/6 v7.2b & Multiflo rxx databases, and is therefore used in the dissolution Reaction.

b) Activities of relevant species in the PC waters (files UZ160ck.30 & UZ180ck.30 in YangfixCO2&K.xls) were plugged into the mass action equation for the reaction in a) to calculate the log K for the reaction at 25°C.

LB 3-26-99

Estimating Thermodynamic Parameters for GlassPC - continued 3-26-99

c) Calculations and results from a & b are given in:
D:\GlassPC\4MGlassPC2withAl.xls

(2) Log k values are needed for temperatures of 0, 25, 60, 100, 150, 200, 250, & 300°C. The following method was used to obtain these estimates:

a) The enthalpy of formation for the glass was calculated as the sum of the solid oxide components plus the enthalpy of mixing. The enthalpy of mixing was estimated from data in:

Adam J. G. Ellison, & Alexandra Navrotsky (1990) Thermochemistry and structure of model waste glass compositions Mat. Res. Soc. Symp. Proc. Vol. 176, p. 193-207,

and was largely insignificant (e.g. -4.0 $\frac{kcal}{mol}$).

b) The enthalpy of the GlassPC dissolution reaction was determined by $\sum \Delta H_f^\circ$ products $- \sum \Delta H_f^\circ$ reactants

c) The Van't Hoff Equation, written as $\ln k_2 = -\left(\frac{H_{rxn}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_2}\right) + \ln k_1$, was used to estimate the Log k values for the GlassPC dissolution reaction at $T \neq 25°C$.

d) Calculations and results from a-c are given in:
D:\GlassPC\GlassPCwithFe,AlLogkwithT.xls

e) Modified Databases are:

EQ3/6 v7.26 D:\GlassPC\Data0.gls &
Multiflo v.xx D:\GlassPC\DatabaseAGU

LB
3-26-99

Estimating Kinetic Parameters for GlassPC with T 3-30-99

We use the Arhenius equation, $k = Ae^{-E_a/RT}$, to calculate rate constants as a function of T. Values of A & E_a were taken from

E_a:
Knauss K.G., Bourcier W. L., McKeegan K.D., Merzbacher C.I., Nguyen S.N., Ryerson F.J., Smith D.K., Weed H.C., and Newton L. (1990) Dissolution kinetics of a simple nuclear waste glass as a function of pH, time, and temperature. Mat. ~~S~~ LB 5-30-99 Res. Soc Symp. Proc.: 371-381.

A: Tompson A. F. B., Bruton C.J., and Pawlowski G.A. (1999) Evaluation of the hydrologic source term from underground nuclear tests in Frenchman Flat at the Nevada Test Site: The Cambric Test; Lawrence Livermore National Laboratory, (in press).

Our initial assumption about the pH dependence of the dissolution rate for GlassPC is that $a_{H^+}^{-0.5}$, based on the Feldspar dissolution results from William M. Murphy's disertation. $\Delta H_{activation} = \Delta E_a - RT$
Results are shown in D:\GlassPC\GlassPCRateswithT2.xls

LB
3-30-99

Database Entries for Clinoptilolite Solid Solution 4-21-99

Representative intermediate composition Clinoptilolite data was added to the Multiflo database:

D:|GlassPC|DatabaseAGU and
D:|DatabaseAGU|DatabaseAGU

Clinoptilolite compositions were obtained from Broxton et al (1987) [see pg 27 for full reference] for the Topapah Springs, Calico Hills & Prow Pass Units. Molar volumes were scaled from data in:

Chipera S.J. and Bish D.L (1997) Equilibrium modeling of Clinoptilolite-Analcime Equilibria at Yucca Mt., Nevada, USA. Clays & Clay Minerals Vol 45, No 2, 226-239.

Free energies of formation for endmember K, Na, & Ca clinoptilolite were obtained from the EQ36 V7.2b database. Mixing was assumed to be ideal.

Calculations and results of these mixing equations are shown in:

D:|~~Glass~~ LB 4-21-99 DatabaseAGU|ClinoptMixture4-21-99.xls

The phase names for these mixtures appear in the Database-AGU as: clinoptil-tp, clinoptil-ch, & clinoptil-pp. The suffixes refer to the lithologic units that they represent.

LB 4-21-99

Gem input file Development 4-21-99

An ambient steady state model for Yucca Mountain requires the development of a hydrostratigraphic conceptual model.

Our model for the ambient system is a 2-D, dual matrix/fracture continuum model with 12 different hydrostratigraphic units. ~~Each~~ LB 4-21-99 (See Attached)

UZ#16

Block #	ΔZ	ΔZ cumulative	Units
1	5		
2	5		
3	5.55	15.55	PTN 24
4	7.01	22.56	TSW 31
5	5		
6	5		
7	5		
8	5		
9	5		
10	5		TSW32
11	7.8	60.36	
12	6		
13	6		
14	6		
15	6		
16	6.23		TSW33
17	7		
18	7		
19	7		
20	7	118.59	
21	6		
22	6		
23	6		
24	6		TSW34
25	6		
26	6.5		
27	6.5	161.58	
28	6		
29	6		
30	6		
31	6		
32	6		TSW35
33	6		
34	6		
35	6.3		
36	6.3		
37	7.8		
38	7.8	230.18	
39	6		
40	6		
41	6		
42	6		
43	6		TSW36
44	6		
45	6		
46	6		
47	6		
48	6.37	290.55	
49	6.41		
50	7.0	303.96	TSW37
51	5		
52	5.37	314.33	CH3ZC ?
53	6		
54	6		
55	6		
56	6		
57	6		
58	6		CH3ZC
59	6		
60	6		
61	6		
62	6		
63	6		
64	5.11	390.55	
65	5.11		
66	5		
67	5		
68	5		TABT1 = CH4VC
69	8.04	411.59	
70	6		
71	6		
72	6		
73	6		PP3VP
74A	6		
75	6		
76	7	454.58	

LB 4-21-99

GEM input file development (continued) 4-21-99

The model attempts to simulate ambient conditions in borehole UE25 UZ#16. As such, the hydrostratigraphic units selected for the model, and their thicknesses were taken from borehole descriptions by:

S.J. Chipera, K. Carter-Krogh, D.T. Vaniman, D.L. Bish, and J.W. Carey (1997) Preliminary Three-Dimensional Mineralogic Model of Yucca Mountain, Nevada YMP Milestone # SP32IAM4

Geologic units described by Chipera et al. (1997) were converted into hydrostratigraphic unit terminology described in the Near-Field/Altered-Zone Models Report. Some adjacent units with similar mineralogy and/or hydrologic parameters were joined into a single hydrostratigraphic unit, for simplicity. [See Attached, pg. 31]

Mineral proportions were obtained from:

S.J. Chipera, D.T. Vaniman, R.A. Carlos, & D.L. Bish (1995) Mineralogic Variation in Drill Core UE-25 UZ#16, Yucca Mountain, Nevada; LA-12810-MS

For simplicity, minerals with similar compositions and/or thermodynamic properties were combined. 'Feldspar' was divided into Albite and K-feldspar, with relative proportions given by the bulk composition of the Topopah Spring Unit, as described by:
(Chapter 4)
W.M. Murphy & R.T. Pabalan (1994) Geochemical Investigations related to the Yucca Mountain Environment and Potential Nuclear Waste Repository CNWRA-94-006

LB 4-21-99

GEM input file development (continued) (4-21-99)

More information about the mineral volume percentages included in the model are given in:

D:\SpringAGU99\Metradata2.xls

Mineral dissolution rate information was originally obtained from:

Chapter 6: E. Sonnenthal, N. Spycher, J. Apps, & A. Simmons (1998) YMP Milestone SPY289M4 Thermo-Hydro-Chemical Predictive Analysis for the Drift Scale Heater Test

Although later, rate constants and reactive surface areas were slightly modified to improve the simulations.

The top of the Pah Canyon was taken as the upper boundary because H_2O chemistry data is available for that layer. [See Attached]

LB 4-21-99

Pah Canyon (PC) Water Compositions

Information (a table) potentially subject to copyright protection was redacted from this location. The redacted material is from Sonnenthal, et al. (1998) reference as listed above.

GEM input file Development (continued) 4-21-99

3 Pah Canyon water compositions were infiltrated into the model layers (see attached below) at ~13 mm/yr. A description of these waters is given on pages 15-24.

Information (a table) potentially subject to copyright protection was redacted from this location. The redacted material is from Sonnenthal, et al. (1998) reference as listed on page 33.

Results & Discussion 5-10-99

An abstract was written and accepted as an oral presentation at the Spring AGU (American Geophysical ~~AGU~~ LBS 5-10-99 Union) meeting in Boston.

The Abstract is located at:

D:\ SpringAGU\ AGU abstract.wpd

An example of the results is attached below.

Steady State 25°C Models

Information potentially subject to copyright protection was redacted from this location. The redacted material (a diagram) is from an abstract published by the American Geophysical Union in 1999.

LB 5-11

The boundary condition $SiO_2(aq)$ content was identical in the 3 infiltrating waters, & the models predict the same $SiO_2(aq)$ evolution with depth in the 3 cases.

Thermally-loaded RT model, & Results 5-10-99

We added a heat source of 60 MTU/Acre in the Topopah Spring Unit to simulate the emplacement of nuclear waste.

The diagram below shows the model pH predictions with depth for the 3 infiltrating water compositions after 50 years.

Unlike $SiO_2(Aq)$, the pH of the infiltrating waters ~~varies~~ vary. This diagram shows that variations or uncertainties in the infiltrating water composition may grow larger with heating.

Heated Models

Information potentially subject to copyright protection was redacted from this location. The redacted material (a diagram) is from an abstract published by the American Geophysical Union in 1999.

Initial Conclusions from RT model Development 5-10-99

MULTIFLO input and output files for this project are located at:

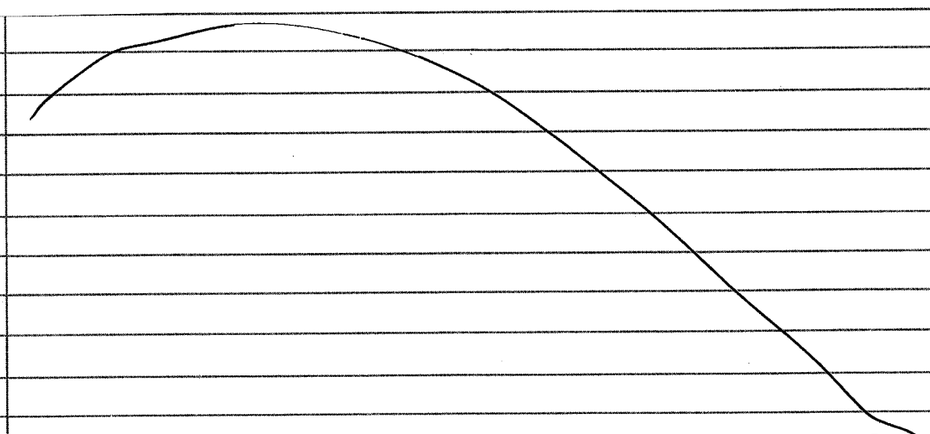
D:\SpringAGU99\Multiflo files*

General Conclusions of the Study include:

* **Prescribed water compositions at the upper boundary affect predicted water compositions under both ambient steady state and thermally loaded transient conditions.**

* **Further constraints on the THC properties of Yucca Mt. are needed to model accurately the ambient steady state, and therefore also the thermally perturbed conditions.**

LB 5-10-99



LB 5-10-99

Modification of Additional UZ H_2O Composition Data 8-15-99

LB 8-15-99
~~Data~~

Additional Measured UZ groundwater compositional data were obtained from:

In C. Yang, Pei Yu, G. W. Rattray, J. S. Ferarese, and J. N. Ryan (1998) Hydrochemical Investigations

Thermodynamic consistency was restored to these data by the method discribed on pages 21-22. The revised data are located at:

D:\YangAdditionalData*

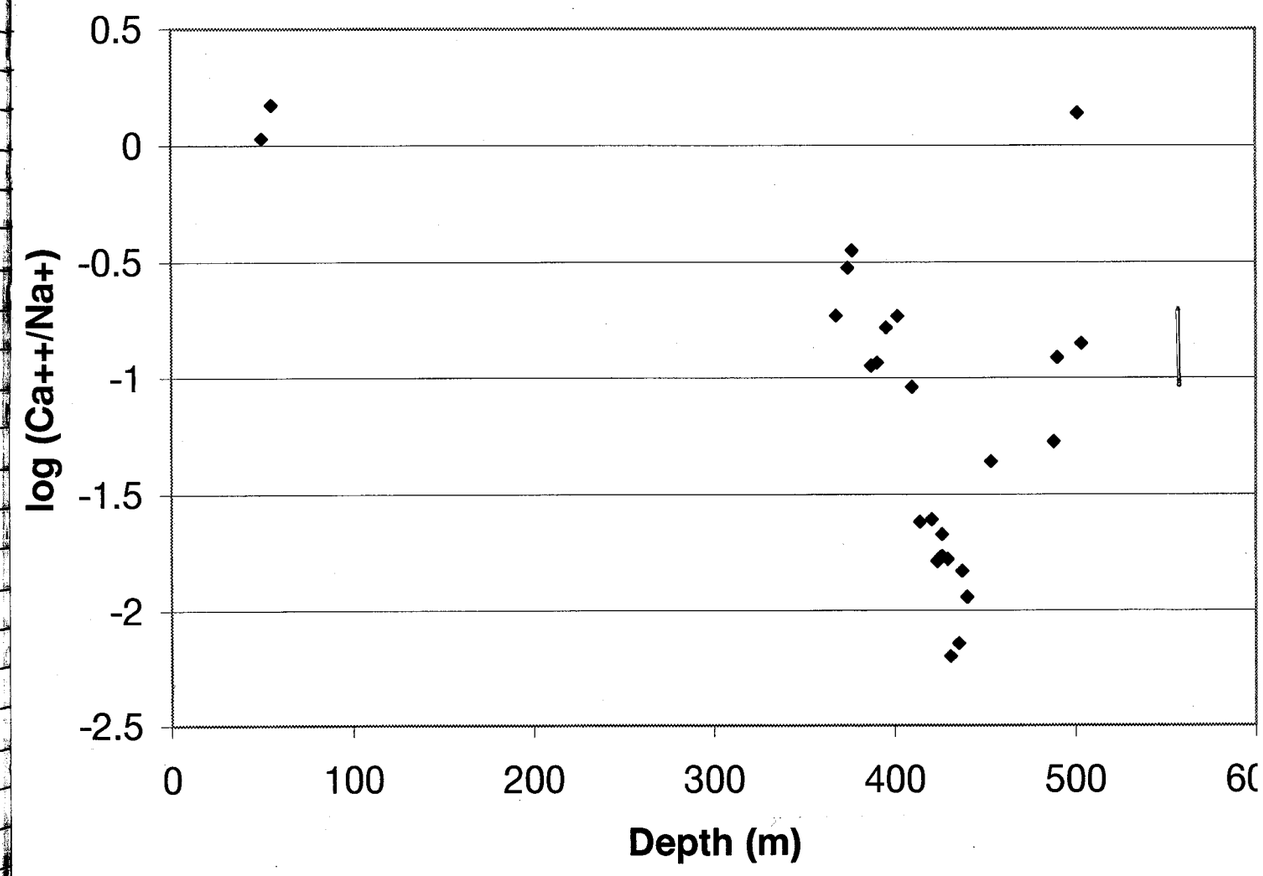
LB 8-15-99

Clinoptilolite Compositions Equilibrated with UZ Pore H_2O's 9-1-99

Goal: To determine how clinoptilolite compositions might vary with depth based on UZ pore water compositions.

For example, Ca^{++} & Na^{+} varies below the Topapah Spring Unit in the manner shown by the figure below.

LB 9-1-99



Clinoptilolite Compositions Continued... 9-1-99

Thermodynamic data for endmember clinoptilolite compositions were taken from:

Kerrisk, J.F. (1983) Reaction-Path Calculations of Groundwater Chemistry and Mineral Formation at Rainier Mesa, Nevada LA-10560-MS. Los Alamos, NM: Los Alamos National Laboratory.

Intermediate K-, Ca-, Na- clinoptilolite compositions were calculated assuming ideal mixing.

It is assumed that $X_{K\text{-clinoptilolite}} = 0.55$, in agreement with observations described by:

D.E. Broxton (1989) Clinoptilolite Compositions in Diagenetically-Altered tuffs at a Potential Nuclear Waste Repository, Nevada. in The Technology of High-Level Nuclear Waste Disposal, P.L. Hofmann, Ed. (Battelle Memorial Institute, Columbus, Ohio 1987) Vol. 3, pp. 179-194.

Values for $X_{Na\text{-Clinoptilolite}}$ & $X_{Ca\text{-Clinoptilolite}}$ were calculated from UE 25 UZ#16 water compositions with depth. The results are at:

D:\FallAGU99\Clinopt SS9-1-99.xls

LB 9-1-99 The revised Multiflo database is:
(vulcan) /home/wimurphy/databaseAGU2

Clinoptilolite Compositions Continued... 9-1-99

Volume $\left(\frac{cm^3}{mol}\right)$ for all ~~phases~~ LB 9-1-99 clinoptilolite compositions is estimated from data in:

S.J. Chipera & D.L. Bish (1997) Equilibrium modeling of Clinoptilolite-analcime equilibria at Yucca Mountain, Nevada, USA. Clays & Clay minerals vol 45, No. 2, 226-239.

These authors estimate 1264.1 $\frac{cm^3}{mol}$ for all clinoptilolite compositions in thier models. These contain 72 oxygen, & my clinoptilolite compositions (Kerrisk, 1983) all have 10 oxygen. I used the difference in oxygen to scale down the clinoptilolite molar volumes used in my database (databaseAGU2). This technique leads to a molar volume of

LB 9-1-99 ~~428~~ 421.37 $\frac{cm^3}{mol}$

LB 9-1-99

Akrotiri Project (first author: D. Hughson) 10-1-99

Data on the spatial distribution of metals derived from archeological artifacts at Akrotiri, Greece, were used to evaluate performance assessment model assumptions of radionuclide transport through unsaturated volcanic tuffs hosting the proposed repository at Yucca Mountain, Nevada.

D. Hughson is the lead on this project, and her work is described in the ENFE scientific notebook #305. The role of L. Browning in this project was to: 1) develop a simplified aqueous speciation model for atacamite solubility (Atacamite [$Cu_2Cl(OH)_3$] is an alteration mineral assumed to control Cu^{2+} concentrations near the artifacts), and 2) construct a reasonable GEM input file expressing the atacamite solubility controls on Cu^{2+} concentration.

L. Browning used 2 different computer codes to assist in the tasks described above:

1) MULTIFLO version X
   - executable located at ~sprinter/bin/multiflo
   - discussed earlier in this notebook

2) Geochemists Workbench (GWB)
   - commercially available set of software tools
   - developed by Craig Bethke (University of Illinois)
   - control issues reported in CNWRA scientific notebook #278 on Radionuclide Transport, and maintained by R. Pabalan.

LB 10-1-99

Akrotiri Project (continued) 10-1-99

The attached GWB input file describes the titration of Atacamite into a dilute solution of pH 7.96 (initial). The pH was allowed to vary in response to Atacamite dissoln.

```
                                   Akrotiri
# React script, saved Wed Aug 18 1999 by lbrowning
data = "C:\Program Files\Gwb\Gtdata\thermoEQ6V8.dat" verify
work_dir  =  D:\
temperature = 25
swap O2(g) for O2(aq)
1 kg free H2O
balance on Na+
total molality Na+ = 1e-7
pH = 7.96
total molality Cl- = .00776247117
total molality HCO3- = .00169824365
total molality SiO2(aq) = 1e-4
fugacity O2(g) = .158489319
total molality Cu++ = 2.51188643e-21
react 5 mol of Atacamite
```

GWB input and associated output files are located at:

D:\Akrotiri\Akrotiri (input)
D:\Akrotiri\~~Akrotiri~~ LB 10-1-99 React_output.txt

These calculations reveal aqueous speciation relations in the presence of Atacamite and fulfill L. Brownings task #1, discussed on pg. 42.

LB 10-1-99

Akrotiri Project (continued) 10-1-99

Results from the GWB aqueous speciation calculations were used to constrain chemical parameters used in GEM input.

The following GEM input file and associated output files are located at:

D:|Akrotiri|Akrotiri_GEM|*

GEM input

HB 10-1-99

Additional information regarding this project can be found in ENFE scientific notebook # 305.

HB 10-1-99

Akrotiri Project (continued) 10-1-99

Results from the GWB aqueous speciation calculations were used to constrain chemical parameters used in GEM input.

The following GEM input file, and associated output files are located at:

D:|Akrotiri|Akrotiri_GEM|* --

```
1D reactive transport of Cu phases at Akrotiri
June 25, 1999
:
:        geometry nx  ny  nz     mode  iprint idebug  iwarn
GRID      XYZ     52   1  30       2      1      1      3
:
DBASe
/home/wmurphy/databaseAGU2
:
:     method iops ifor iflxlim itmax ihalmax  ndteq loglin  istepdt
OPTS    1     1    2      1     32     16       1       0     1
:    isurf iact  isst wtup  cournr    dtcutf   delcmax  qkmax tpulse
      1     1     -1   0     1.e4      .500      ,03     500
:
:       isync  ipor iperm  perm-fac. porfac icksat slcutoff
COUPle   0      -1     0       3.     1.     0      0
:
PLTFiles
:iplot   a  s  t  m si sf  v  z  b in  e ex ti  g itex  err
    1    1  1  1  1  0  1  1  0  1  0  0  0  0  1   0    1
:
:      tol    ttol  tolneg tolpos tolstdste tolc
TOLR  1.d-7   1.e-1   1.e-0  1.e-2  1.e-6  1.e-12
:
:        mcyc  cc  c   flx r  sp  qk  pk  rk  a1  a2  a3
DEBUg    0       1  1   1   1   1   1   1   1
:
:       isat isothrm iread  por0  phir  sat  w  lambda toldelt  tolpor
ISYStem -1    0       0     0.52    0.    .01   1.   1.    1.e-3    1.e-3
:
:      vx0  vy0  vz0  vgx0  vgy0  vgz0[m/yr]  alphax   alphay   alphaz[m]
FLOW  0.   0.   .010   0.    0.    0.          0.       0.       0.
:
:   d0[cm^2/s]  delhaq[kJ/mol]  dgas[cm^2/s]  dgexp  tortaq  tortg idif
DIFF   7.5d-6     12.6            2.13d-1       1.8   1.d-1   1.d0    0
:
:       p (Pa) temp flag  a    b    c    d   x0   xlen
PTINit  101325   25.   0   25  300  250  125  1000.  2.d3
:
:master species for controlling time stepping
:MASTer all
:
DXYZ
0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2
0.2 0.2
0.2
0.2 0.2 0.2 0.2 0.2 0.13 0.07 0.05 0.05 0.05
0.05 0.05 0.05 0.04 0.05 0.05 0.05 0.05 0.05 0.08
0.13 0.2 0.2 0.2 0.2 0.2 0.3 0.3 0.4 0.5
:
:   isolv level north nitmax idetail rmaxtol rtwotol smaxtol
SOLV    3    1     4    100      0     1.e-12  1.e-12  1.e-12
:
```

Akrotiri Project (continued) 10-1-99

Results from the GWB aqueous speciation calculations were used to constrain chemical parameters used in GEM input.

The following GEM input file and associated output files are located at:

D:|Akrotiri|Akrotiri_GEM|*

```
:initial and boundary conditions: 1-conc., 2-flux, 3-zero gradient
COMP
:
:i1  i2  j1  j2  k1  k2
  1   52   1   1   1  30
.
:species itype   ctot  mineral  diffusion
cu+2       1     2.2887e-21
na+       -1     1.0e-2
h+         8     6
cl-        1     7.7363e-3
hco3-      1     1.7033e-3
sio2(aq)   1     1.0016e-4
.
.
:
BCON
:ibndtyp ifacx tmpbc dist  area    vell    velg  por  sl   porm  slm  imtx
    1      3    17.  0.02  1.6e-3 3.17e-10  0.  .6   0.08   .6   .08   1
: i1  i2  j1  j2  k1  k2
   1   52   1   1   1   1
.
:species  itype  guess  ctot  mineral
cu+2       1     2.2887e-21
na+       -1     1.0e-2
h+         8     6
cl-        1     7.7363e-3
hco3-      1     1.7033e-3
sio2(aq)   1     1.0016e-4
:
:ibndtyp ifacx tmpbc  dist   area   vell       velg  por    sl  porm  slm  imtx
    1      4    17.   0.04  1.6e-3  3.17e-10   0.   0.52  .08  .52   .08   1
: i1  i2  j1  j2  k1  k2
   1   52   1   1  30  30
.
:species  itype  guess  ctot  mineral
cu+2       1     2.2887e-21
na+       -1     1.0e-2
h+         8     6
cl-        1     7.7363e-3
hco3-      1     1.7033e-3
sio2(aq)   1     1.0016e-4
.
:
AQCX
co2(aq)
co3-2
hsio3-
oh-
cuco3(aq)
cuoh+
cucl+
cu(co3)2-2
.
:
MNRL
atacamite
```

Akrotiri Project (continued) 10-1-99

Results from the GWB aqueous speciation calculations were used to constrain chemical parameters used in GEM input.

The following GEM input file and associated output files are located at:

D:|Akrotiri|Akrotiri_GEM|*

```
.
:
:GASEs
:co2(g)
:o2(g)
:.
:
MNIR
:mineral  npar fkin delh  tau
atacamite    1   1.   35.   1.e-3
: itypkin  npri  sec sig  rk
   20     0     0     1.   -10.00
25  28  1  1  8  13   0.1  1.  0.    1.
/
.
:
BRKP   1
1 1 1
:
DTSTep[y]     5  1.e-16   1.e-6   1.e-5  1.e-3  1.e-2
1.e-15   1.e-4   1.e-3  1.e-2  1.e-1  1.e+2
:
TIME[y] 10  1. 5. 10. 25. 50. 100. 200. 300. 500.
510
:
ENDS
```

ELS Ambient Model 9-9-02

A set of files associated with the following draft journal article were saved at:

D:/AmbientModel2002;

Reactive Transport Model for the Ambient Unsaturated Hydrogeochemical System at Yucca Mountain, Nevada, by Lauren Browning, William M. Murphy, Chandrika Manepally, Randall Fedors, & Debra Hughson

The following text provides descriptions for the following set of files; hereafter refered to by their number (left margin) for name:

(1) ActivationEnthalpies.xls
(2) Beidellit-Ca, withTsdminwayAl.xls
(3) Beidellit-k " "
(4) Beidellit-Na " "
(5) ELSSept5.doc
(6) GlassCompBroxton.xls
(7) GlassPTN_rate_const.xls
(8) MetraDataELSJune18.xls
(9) PtnGlass, withTsd9midwayAL2.xls
(10) react_output.txt
(11) Sd9midwayAL
(12) SonnethalLogkConversions.xls
(13) thermoz.dat
(14) upTempExtrapolationfromSonnethalSiO2logks.xls
(15) Sd9mineralogic.xls

HB 9-9-02

ELS Ambient Model: 5) 9-9-02

The draft journal article (ELSSepts.doc) is going to be submitted to the journal ~~Computers & Geosciences~~ as part of a special issue on Reactive Transport Modeling in the Geosciences. I am the Guest Editor of that journal, with William M. Murphy.

The Revised analytical pH26 groundwater composition was calculated with:

(11) sdqmidwayAL ⇒ input file, GWB (aka Geochemist's Workbench code)

(13) thermoz.dat ⇒ GWB database

The file output are described in: (10) Reactoutput.txt

Thermodynamic data for Beidellite smectites were calculated, as described in the text, using:

(3) Beidellit-K, with Tsdmidway Al.xls
(4) " -Na, " " "
(2) " -Ca, " "

Thermodynamic data for the phase GLASSPTN were calculated using

(6) GlassCompBroxton.xls ⇒ glass composition used in dissolution reaction

(9) PTNGlass, with Tsdqmidway Al2.xls

Select Log k values for silica phases were recalculated in:

(12) SonnenthalLogkConversions.xls
(14) UpTempExtrapolationfromSonnenthalSiO2Logks.xls
KB 9-9-02

ELS Ambient Model 9-9-02

mineral volume fractions in various hydrostratigraphic model layers were calculated for the matrix & fracture continua using

(8) MetraData ELSJune18.xls, &
(15) Sd9Mineralogic.xls (Data provided by Randall Fedors, & is maintained in scientific notebook #432.

Kinetic Data were estimated in
(7) GlassPTN_rateconst.xls, and
(1) ActivationEnthalpies.xls

UNIX: The Ambient system model was run using MULTIFLO version 1.5, using the following input files:

MASIN.INP → GEM input file
sd9Nh.dat → METRA input file
sd9.INT → supporting METRA file; initialization
database6 → supporting GEM file; database

Calculations were performed on Idaho: Sun Cluster.
KB 9-9-02

Input & output files are located at:

~~H:\Browning\ELS~~ KB 9-9-02

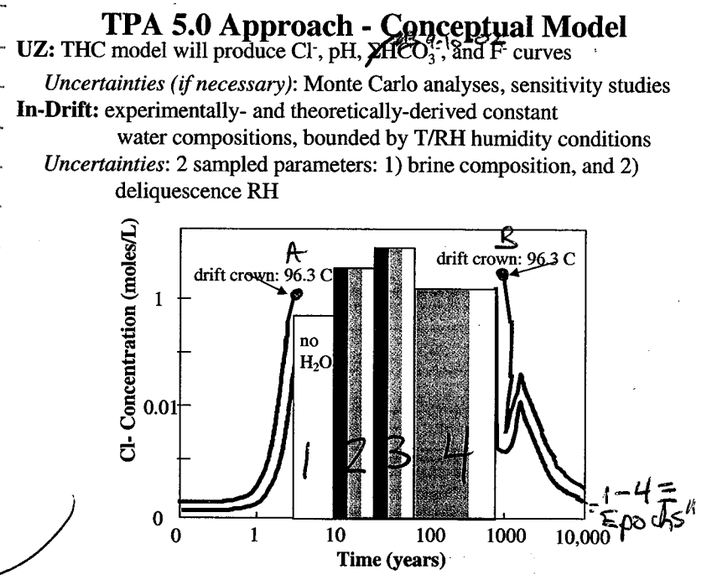
~ \browning\ELS\12xd

Unix files have also been copied to:

D:\AmbientModel2002\12xd; with xls data compilations
All Metra input & output files are maintained in Scientific Notebook #478E version 3 by Chandrika Manepally
KB 9-9-02

SALTS: 1st Approach for TPA5.0 9-10-02

The following cartoon summarizes the general approach for handling water chemistry above the drift & in the drift, for TPA5.0, that I suggested, based on conversations with Lietai Yang, Osvaldo Pensado, Ron Janetzke & Rob Pabalan & my own analysis.



LB 9-10-02

coupled thermal-hydrological-chemical (THC) processes are evaluated in TPA5.0 through a look-up table, giving [Cl⁻] pH Σ[CO₃²⁻] & [F⁻] as a function of T. Data for the Table may be generated from reactive transport models using, for example, MULTIFLO, and are depicted in the cartoon as red & black curves. LB 9-10-02 accidently

In-drift C processes cannot be reevaluated using reactive transport codes developed for porous media and dilute groundwater compositions.

LB 9-10-02

Salts: 1st approach for TPA5.0 9-10-02

When the T > boiling (93.6°C) above the drift, experimentally- and theoretically-derived constant water compositions are employed to describe in-drift chemical evolution of [Cl⁻][pH], ~~[ΣHCO₃⁻]~~ LB 9-10-02 and [F⁻], and Σ[CO₃²⁻].

The cartoon shows 4 "Epochs", but our current coded approach only utilizes 3, one dry-out and 2 water chemistry Epochs.

In the cartoon: Epoch 1 represents the dry-out period in the drift, defined by T > boiling (at drift ceiling), and the relative humidity RH < deliquescence point in the code.

Epochs 2-4 represent LB 9-10-02 periods that may be defined by different constant water compositions. The 2 in-drift chemistry epochs in TPA5.0 now are named Epoch 1 & Epoch 2, & have the following boundary conditions: LB 9-10-02

Epoch 1: T > boiling; RH > deliquescence RH, before peak T
Epoch 2: T > boiling; RH > deliquescence RH, after peak T

Deliquescence RH & brine compositions are uncertain & are treated in the code as sampled parameters with a Log uniform distribution.

Current input for these distributions are given in

D:\~~salts~~ LB 9-10-02

D:\TPA5.0, along with supporting files

Codes described in scientific notebook 170-16E (George Adams)

Work continues in data refinement, especially probability distributions

LB 9-10-02

11-20-02

GWB
Thermo2.dat
RxN

Cristobalite(beta) = SiO_2(Aq)

T = 20.8°C log k ≅ -3.103 k ≅ 7.89e-4
T = 27.3°C log k ≅ -3.009 k ≅ 9.98e-4

Quartz = SiO_2(Aq)

T = 20.8°C log k ≅ -3.75 k ≅ 1.78e-4
T = 27.3°C log k ≅ -3.64 k ≅ 2.29e-4

cristobalite (alpha) → SiO_2(Aq)

T = 20.8°C Log k ≅ -3.38 k ≅ 4.17e-4
T = 27.3°C Log k ≅ -3.31 k ≅ 4.90e-4

Amorphous silica = SiO_2(Aq)

T = 20.8°C Log k ≅ -2.68 k ≅ 2.09e-3
T = 27.3°C Log k ≅ -2.65 k ≅ 2.24e-3

TPA5.0 2-4-03

Re: subboiling temperature [Cl-], [F-], & pH

LB
2-4-03

51

2-4-03

TPA5.0

Re: Subboiling temperature [Cl-], [F-], + pH

Lauren Browning

Subject: FW: TPA5.0: Lower Cl-, F-, and pH

-----Original Message-----
From: Lauren Browning [mailto:lbrowning@cnwra.swri.edu]
Sent: Tuesday, February 04, 2003 4:58 PM
To: lbrowning@cnwra.swri.edu; 'Ronald Janetzke'; 'Osvaldo Pensado'
Cc: 'Roberto Pabalan'
Subject: TPA5.0: Lower Cl-, F-, and pH values
All:

The DOE examined the impact that different combinations of high vs low temperature repository design and high versus low CO2 (g) would have on the in-drift chemical environment. For any given combination, they used constants to describe chemical conditions for 6 different time periods: preclosure, boiling, cool down, extended cool down, transition to ambient, and ambient. Of the various combinations, the high temperature and high carbon dioxide case produced the highest concentrations of F- and Cl-. Those values were provided to you in an earlier note (see below). Those values represent the upper limits of Cl- and F- concentrations from the DOE's SSPA analysis of seepage water compositions. The ambient conditions, provided below, represent the lower limits of the DOE analyses of Cl- and F- concentrations from the SSPA. The following ambient temperature values (T = 23.2oC) were extracted from the same Table as before, i.e. Table 6.3.1-6.2:

[F-] = 2.97e-4 molal
[Cl-] = 3.31e-3 molal
pH = 8.41

Thus, we now have information to bound F- and Cl- concentrations in the sub-boiling regions of our own model. I hope that this addresses your comments, Ron and Osvaldo. Because the most corrosive conditions are expected to occur at higher temperatures (i.e. during the Epochs), I think that we should focus our future efforts on refining the Epochs data, rather than the data used to characterize chemical conditions in the sub-boiling portions of our model. Please let me know if you have other ideas or suggestions.

Thanks,
Lauren

-----Original Message-----
From: Lauren Browning [mailto:lbrowning@cnwra.swri.edu]
Sent: Tuesday, February 04, 2003 3:12 PM
To: lbrowning@cnwra.swri.edu; Ronald Janetzke; Osvaldo Pensado
Cc: Roberto Pabalan
Subject: RE: TPA5.0: Cl-, F-, and pH values

ps. The values that I provided below were estimated/calculated/abstracted by the DOE for a temperature of 95.80C.

Lauren

-----Original Message-----
From: Lauren Browning [mailto:lbrowning@cnwra.swri.edu]
Sent: Tuesday, February 04, 2003 2:19 PM
To: Ronald Janetzke
Cc: Roberto Pabalan
Subject: TPA5.0: Cl-, F-, and pH values

Hi Ron,

I suggest using the following constant values to depict water composition before and after the Epoch periods in TPA:

[Cl-] = 6.65e-3 molal
[F-] = 4.08e-4 molal
pH = 8.37

51

2-4-03

TPA5.0

Re: Subboiling temperature [Cl-], [F-], + pH

These values were taken from the SSPA, page 6T-4, Table 6.3.1-6.2. The reference is given below, for your viewing convenience. :-) The data came from a Table listing abstraction results for high temperature and high carbon dioxide partial pressure in the Tptpll lithology for seepage at the crown of the drift. If we obtain information indicating that these values should be modified, I will let you know.

I hope that helps.

Lauren

Supplemental Science and Performance Analyses Volume 1 Scientific Bases and Analyses. Rev. 00 U.S. Department of Energy TDR-MGR-MD-000007 Las Vegas, NV: June 2001

LB 2-4-03

2-02-03

LB

Re: Poster Presentation for EUG-AGU-EGS Assembly: Nice, France 3-9-03

The following ~~poster~~ Abstract was submitted to the EUG-AGU-EGS Joint Assembly 3-9-03, and is located in electronic format at: D:\meetings\Spring-2003-AGU (France) in the LUSK computer:

REACTIVE TRANSPORT SIMULATIONS OF ALTERNATIVE FLOW PATHWAYS IN THE AMBIENT UNSATURATED ZONE AT YUCCA MOUNTAIN, NEVADA.

Lauren Browning (1), William M. Murphy (2), Chandrika Manepally (1), and Randall Fedors (1).
(1) Center for Nuclear Waste Regulatory Analyses Southwest Research Institute, San Antonio, Texas,
(2) Department of Geosciences, California State University, Chico, California.
lbrowning@swri.edu/Fax: (210) 522-5155

Uncertainties in simulated ambient system unsaturated zone flow could have a significant impact on performance evaluations of the proposed nuclear waste repository at Yucca Mountain, NV. In addition to determining variations in the quantity of water available to corrode engineered materials and transport radionuclides, model assumptions regarding flow pathways may significantly affect predictions about groundwater chemistry. The manner and extent to which groundwater compositions evolve along a flow pathway is determined mainly by thermohydrologic conditions, the types of reactive materials encountered, and the interaction times with those materials. Simulated groundwater compositions can thus vary significantly depending on whether or not the flow model includes lateral diversion of infiltrating waters, or preferential flow pathways in variably–saturated materials. To assist a technical review of a application for a geologic repository, we developed a reactive transport model for the ambient hydrogeochemical system at Yucca Mountain (YM). The model simulates two phase, non-isothermal, advective and diffusive flow and transport through one dimensional, matrix and fracture continua (dual permeability) containing ten kinetically reactive hydrostatigraphic layers in the vicinity of the SD-9 borehole at YM. In this presentation, we describe how the model was used to evaluate alternative ambient UZ flow pathways proposed by the Department of Energy and Nuclear Regulatory Commission.

This abstract is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

LB
3-9-03

AGU Nice, (continued) 03-09-03

The presentation depicts results from 3 different reactive transport models, referred to in the poster presentation as Cases 1, 2, & 3.

MULTIFLO version 1.5 was used to run all 3 cases. Input & output files for all 3 cases are located on spock, at:

Case 1: (Calibrated Base case)

~ lbrowning | ~~Franceagu~~ | ~~LB 3-03~~
LB 3-9-03

~ lbrowning \ Els \ 12xd

Case 2: (Base case without PTN)

~ lbrowning \ Franceagu \ Noptn

Case 3: (Base Case with Thick PTN)

~ lbrowning \ Franceagu \ Thkptn

Supporting calculations were performed using the following codes & are located in the following directories on LBrowning's PC, Lusk:

Re: water composition: cases 2, 3
code: EQ3nr V7.2b
database: com
files: D:|meetings|Spring-AGU-2003(France)|eq3|EQ3|
colluv4.31
colluv4.30
colluv4.3p

AGU Nice (continued) 3-9-03

Re: development of figures
microsoft Excel: code
files: D:|meetings|Spring-AGU-2003(France)|Excel Calcs|

MASIN_~~MASIN~~ AQM LB 3-9-03_12xd, thkptn, noptn_aqm.xls

code: microsoft powerpoint 7.0
type of file: poster presentation
location: D:|meetings|spring-AGU-2003(france)|Poster

AGU-2003_Poster_Browning et al_ppt

LB
3-9-03

— AGU San Francisco, CA — Aug 1, 2003

This presentation focuses on an analysis of the hydrogeochemical differences between fracture & matrix materials at Yucca Mt. The abstract provides an introduction to the problem, & a summary of the approach taken to address it.

The abstract is located at:

Lusk = D:|Meetings|AGU 2003|Browning_AGU_2003.doc

The Ambient base case model applied to this work is described on page 45 of this scientific notebook.

Sensitivity studies are expected to expand beyond the base case model. At this time of this writing, one sensitivity study has been initiated in the following UNIX directory

Spock: ~lbrowning|Fract

The study includes the following input files for the first sensitivity study:

maoin.inp
sd9.int
sd9Nh.dat

LB

AGU 2003 [continued] Nov 3 2003

Files used in the construction of the AGU 2003 abstract by Browning et al — include those at:

Abstract & poster preparation files

Lusk: D:|Meetings|AGU2003|~~Browning AGU2003~~ LB 11/3/03

Spock: ~lbrowning/Fract2

Metra file name: afmvpold.dat
and Afm2.int

GEM files: maoin.inp

The D drive AGU2003 folder contains the subdirectories:

abstract: all text files leading to the development & acceptance of the AGU abstract

Data, Calc: files used to prepare figures for AGU 2003 poster

Poster: powerpoint files with the poster on them.

LB
11-3-03

MRS meeting Spring 2004 4-18-04

Estimated Effects of Temperature-Relative Humidity Variations on the Composition of In-Drift Water in the Potential Nuclear Waste Repository at Yucca Mountain, Nevada

Lauren Browning, Lietai Yang, Roberto Pabalan, Chandrika Manepally, and Randall Fedors
CNWRA - Southwest Research Institute

Information potentially subject to copyright protection was redacted from this location. The redacted material is an abstract that was published by the Materials Research Society in Spring 2004.

This paper is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

A symposium proceedings paper was prepared for submission & a powerpoint presentation was prepared. Calculations were performed on my office PC - "lusk", using the geochemists Workbench code V.4.0 and excel spreadsheets.

4-18-04

MRS meeting Spring 2004 - continued.

The following files document work completed for this project. File locations are for the Lusk computer:

*	D:\Meetings\MRS 2004\Final\MRS1
*	" " MRS2
	" " MRS Browning.doc
	" " DOE-6 Dust Bins1.doc
	" " MRS review5.ppt
	" " Salt Volume.xls
	" " Speciation Three Waters lowCO2.xls
	" " Speciation three_waters.xls
*	" " MRS2_hcl_rock_co2
*	" " MRS2_hcl
*	" " MRS2, T=25
*	" " MRS2_co2T

Excel files document speciation of evaporated water - as indicated within the spreadsheets plus estimated salt volumes. Files related to the use of Geochemists Workbench are indicated by asterisks in the left margin. The files MRSBrowning.doc and MRSreview5.ppt are the final draft versions of my symposium presentation paper + the presentation itself.

LB
4-18-04

I have reviewed this scientific notebook and find it in agreement with QAP-001. There is sufficient information regarding methods used for conducting tests, acquiring and analyzing data so that another qualified individual could repeat the activity.

E. C. Pearce
5/25/2004

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 300

Document Date:	12/15/1998
Availability:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
Contact:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
Data Sensitivity:	■"Non-Sensitive" □ Sensitive □"Non-Sensitive - Copyright" □ Sensitive - Copyright
Date Generated:	05/25/2004
Operating System: (including version number)	Windows NT OS
Application Used: (including version number)	MS Word; Multiflo; MS Excel
Media Type: (CDs, 3 1/2, 5 1/4 disks, etc.)	1- CD
File Types: (.exe, .bat, .zip, etc.)	Various
Remarks: (computer runs, etc.)	Media contains: Input/output files for EQ3/6; individual files referenced in the scientific notebook; and text files.