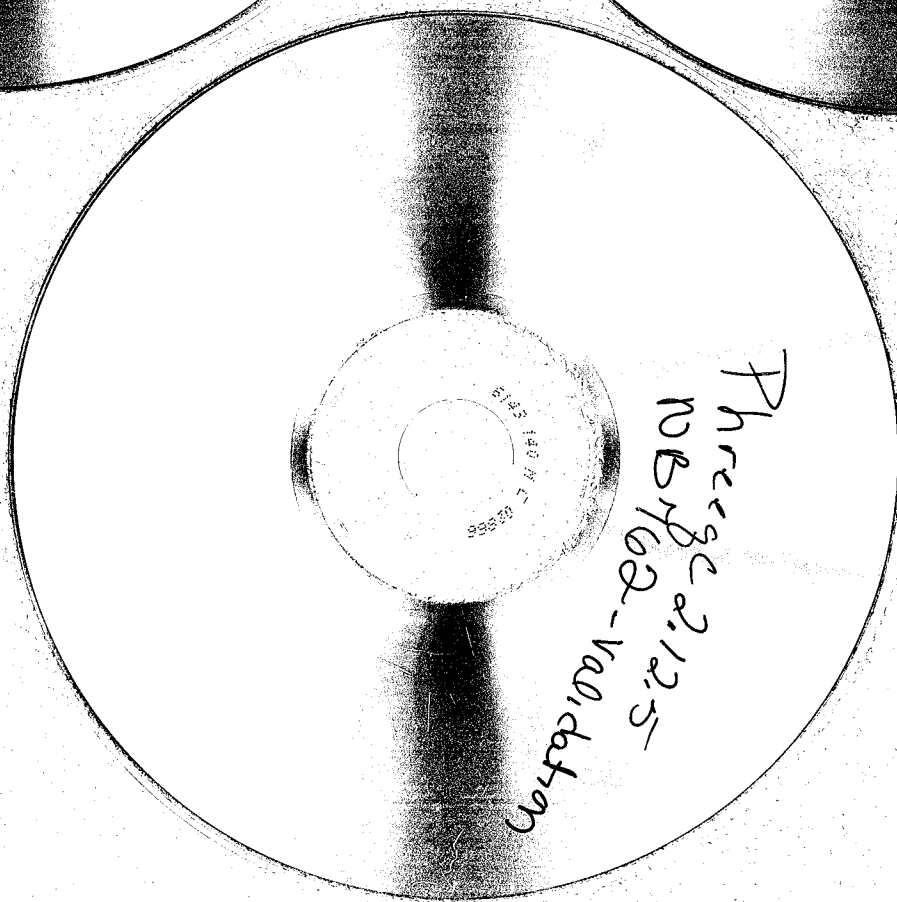
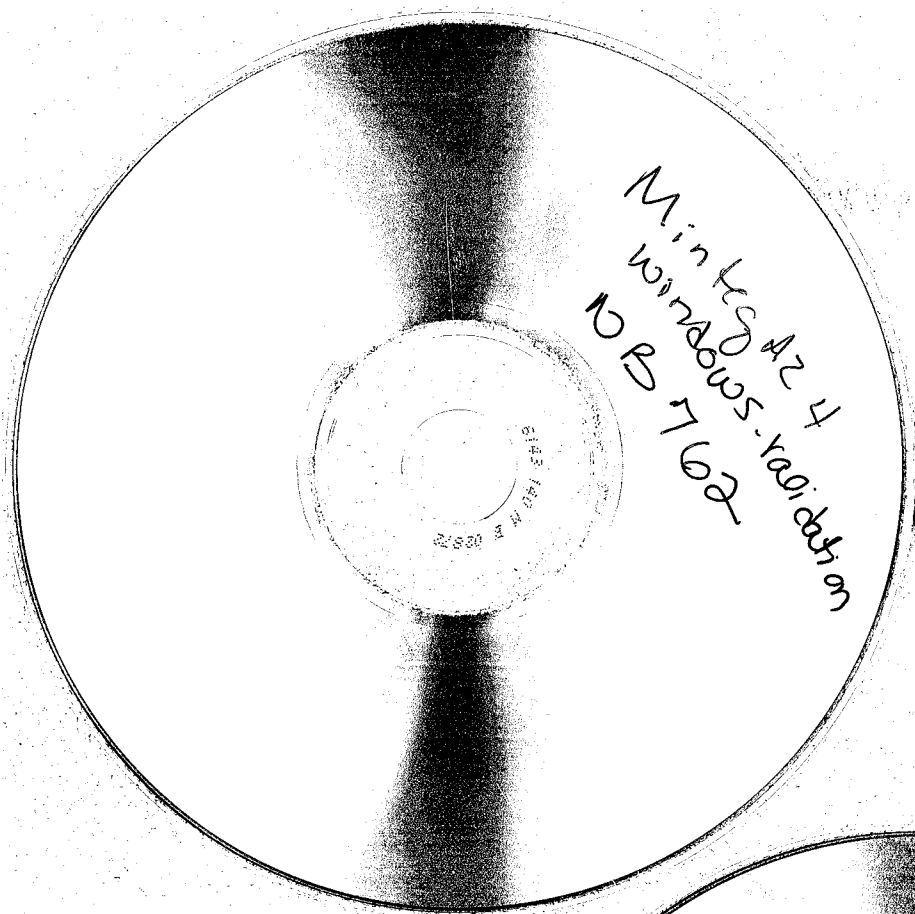


# LABORATORY NOTEBOOK



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Project ±  
20. 06062.01.212

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BOOK NO.

PAGE	SUBJECT	DATE
88	* Note All mentions of file location may be ignored for MintegA2 validation and all other projects. All pertinent files will be burned to CD's (sorted by project) and will accompany this notebook.	
3/22/07	- There are 3 separate CD's with this notebook. 1. MintegA2.4 windows validation 2. Phreeqc 2.12.5 validation 3. Multiflo-integrated project	

15  
3/22/07 BOOK NO. 1007  
PROJECT UP TO and including pg 83 all year 2007  
unless specified. JS

PAGE

Software Validation test plan for MintegA2 for windows version 1.5

by Lynn Sabick Janda JS 12/23/05 JS

Objective: to test MintegA2 for windows version 1.5 to make sure that the output of this updated model closely matches that of its previous form MintegA version 4.02. This will be achieved by running the same problems (Installation and various speciation/Adsorption/Titration problems) in both Model versions to see the degree of accuracy.

Training/qualification requirements: Familiarity with MintegA2 version 4.02 and windows version 1.5, also with PC computers, and a basic understanding of the specifics of various aqueous systems. See MintegA2 manual for 5/11/06 JS

Hypothesis - Although MintegA2 version 4.02 is a DOS program, has been updated to a windows format MintegA2 4 windows version 1.5 there should be no significant changes to the results of the same problems run in both models with the exception of small variations due to a slightly updated database in the windows version.

Approach - To use a series of input files to verify the two versions (DOS 4.02 and windows 1.5) are computing similar results. First a series of 11 files will be run on windows version 1.5 as an installation test. These results will be compared to those of the DOS 4.02 program, if compatible the program (windows 1.5) has been installed correctly. Secondly a series of various geochemical equilibrium problems will also be run through (after preparation) the windows version 1.5 and compared to previous output of DOS 4.02 to validate the windows version of MintegA2. The program will not be compared to others such as Phreeqc because DOS version 4.02 already has as is considered compatible and is already in accordance with DP-18 1



Program description - <sup>The</sup> ~~The~~ Windows V1.5 of MinteqA2 uses the same mathematical theory, Assumptions, initial ~~boundary~~ conditions, solution algorithms as MinteqA2 Dos version 4.02. Reference documents may be found on the internet at [www.allisonqscience.com/minteq.htm](http://www.allisonqscience.com/minteq.htm) 12/23/05

Status - This code, MinteqA2 Version Windows 1.5 is under review for compliance with TOP-018 and all tests performed will be done on a PC computer. The code will be in the directory marked `C:\Program Files\MinteqA2 For windows`

Input files Please see Software Validation Test Plan for MinteqA2 for windows Version 1.5 for the description and source of the data to be used to validate MinteqA2 N Windows V.1.5 to comply with TOP-018.

Installation Tests

There are 11 installation tests <sup>that were 12-23-05</sup> sent to me in updated form ready for MinteqA2 for windows with few modifications. The only modification made by me was to test 3, I had to add a species to the database and modify the log K's two others. See the folder marked installation test. There are <sup>12-23-05</sup> a few folders inside one marked input, contains the modified input files according to Jerry Allison's email, please see file marked email note in the input folder. These modified input files were run in MinteqA2 for windows and compared to the original output files (marked folder original output) from the Dos version 4.02. The newly created output files are also in the folder marked input. The newly created output files from windows version 1.5 are agreeable with the original output files from the Dos version 4.02, agreeable within a few percent.   
 J. Saub 12/23/05

12/26/05 JJ

Validation of MinteqA2 for windows Version 1.5

Files stored in folder marked Min4winV1.5, within this folder contains several sub folders  
 4.02 input - the original input files for MinteqA2 V. 4.02  
 4.02 output - the original output files for MinteqA2 V 4.02  
 Min4win input - the modified input files updated for the windows version 1.5. This folder also contains the output files obtained when using the updated files for Mint 4win V1.5  
 All files entered in Min4win interactive input session

Aqueous Speciation  
 Parkhurst + Appelo (1999)

Entered file as is (filename: valid62)  
 Changed log activity guesses to those found in the original output files, Problem converged, % difference of Aq. species such as  $CO_3^{2-}$  and Ca varied between 10-100%. However, the solubility indices varied a bit more. See comparison -

Jalid 12/26/05 JJ

Aqueous Species	4.02 Windows	%diff	updated win	%diff	
Valid62					
CO3-2	3.024E-05	3.372E-05	-11.51	4.137E-05	-36.81
Ca+2	8.785E-03	1.403E-04	98.40	1.692E-04	98.07
CaHCO3+	4.535E-05	1.386E-06	96.94	1.270E-06	97.20
CaCO3 (aq)	3.090E-05	9.253E-07	97.01	8.607E-07	97.21

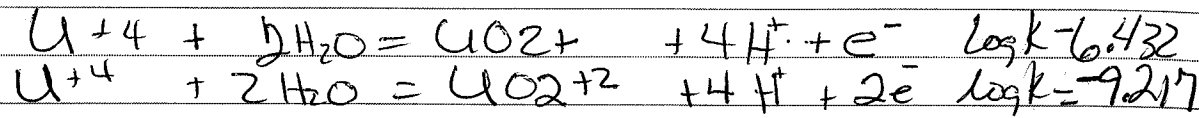
  

Saturation Indices	4.02 Windows	%diff	updated win	%diff	
calcite	0.879	-0.602	168.49	-0.67	176.22
halite	-2.427	-3.156	-30.04	-3.216	-32.51
sio2 (am,ppt)	-1.525	14.274	1036.00	20.038	1413.97

1/16/06 - opened phreeqc problem 1 to compare JJ ended up editing the thermo database for that problem for  $U(OH)_4$ ,  $U(OH)_5^-$ ,  $UO_2^{2+}$ ,  $UO_2(OH)^+$ ,  $(UO_2)_2(OH)_2^{2+}$ ,  $(UO_2)_3(OH)_3^{3+}$ ,  $UO_2(CO_3)_3^{4-}$   
 output not much different JJ

1/18/06

Changed actual database to include two reactions



and I changed the logK and enthalpy for the redox couples  $U^{+4}/UO_2^{+2}$  (old setting 9.04 / -143,86) and  $UO_2^{+2}/UO_2^{+2}$  (1.4800 / -6.1300) in the database. I then retyped up the problem and Equilibrated

The results are more off than the original run (see table on page 3, new results are under "Updated win")

1/18/06

took out value for  $O_2(g)$  I added. I found this value as part of a seawater composition from my thesis. Once removed the speciation is within a 1/2 percent of the MinteqA2 v.4.02 values. See table below.

**Aqueous Species**

Valid62	4.02 Windows	%diff	updated win/no O(g) value	%diff	
CO3-2	3.024E-05	3.372E-05	-11.51	3.024E-05	0.00
Ca+2	8.785E-03	1.403E-04	98.40	8.787E-03	-0.02
CaHCO3+	4.535E-05	1.386E-06	96.94	4.536E-05	-0.02
CaCO3 (aq)	3.090E-05	9.253E-07	97.01	3.091E-05	-0.03

Saturation Indices	updated win	%diff			
calcite	0.879	-0.602	168.49	0.879	0.00
halite	-2.427	-3.156	-30.04	-2.427	0.00
siO2 (am,ppt)	-1.525	14.274	1036.00	-1.525	0.00

1/25

when use Pe 7 set 250 kPa above and same ionic strength when use pe calc (assume) 12. the base of (stable) and ionic strength different, see page 6

Mineral Solubility

12/26/05

2 examples from Richardson + McSween (1989)  
 1) Barite Solubility (File: Valid63a)  
 2) Barite Solubility in 0.2M NaCl Solution (File: Valid63B)

Entered in cone, Barite as equilibrium constraint, and  $H_2SO_4^-$  and  $BaOH^+$  as excluded species. Please see Comparison chart. (5)

**Mineral Solubility Valid63a**

	4.02 Windows	%diff	
Ba++	1.055E-05	1.055E-05	0.00
Saturation Indices			
ba(oh)2:8h2o	-15.387	-15.592	-1.33
barite(baso4)	0	0	0.00

**Mineral Solubility Valid63b**

	4.02 Windows	%diff	
Ba++	3.675E-05	3.675E-05	0.00
Saturation Indices			
ba(oh)2:8h2o	-15.438	-15.438	0.00
barite(baso4)	0	0	0.00

1/9/06

In both examples the old (MinteqA v.4.02) and new (MinteqA2 for windows) calculates the same saturation indices within 1.5% difference

1/27/05 Agueous solution with U #valid62

an original problem pH 8.22 case IS = 6.653e-1  
Equilibrium pe 12.392 (case as specified)  
PO<sub>2</sub> = .21877 atm

When I specify pe 7, NO PO<sub>2</sub> I get the same Ionic Strength,  
Sat Indices, Concentrations.

I tried a few variations, however each one w/ a pe value  
the program will not allow you to calculate pe because redox  
couples are specified

Tried few examples

valid62 - pe = 7 NO O<sub>2</sub> conc / result <sup>page 3</sup> see table IS = 6.653e<sup>1</sup>

valid62bbb pe 12.392 PO<sub>2</sub> = .21877 atm / ionic strength 1.361

valid62ccc pe 12.392 PO<sub>2</sub> - not specified / IS = 6.653e<sup>1</sup>

Went back to valid62 pe 7 PO<sub>2</sub> = .21877 atm / IS = 6.653e<sup>1</sup>

Y3/10/05 Entered 1x10<sup>6</sup> U<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>3+</sup>, Fe<sup>2+</sup>, calc pe, entered PO<sub>2</sub> = .21877 - Correct

Answers → Same results as 4.02

4.02 compared to various input files for Windows version

	pe=7			pe=12.392			pe=12.392			pe=7		
	4.02	po2 NA	%diff	po2=0.2188	%diff	po2 NA	%diff	po2=0.2188	%diff	po2=0.2188	%diff	
Valid62	3.024E-05	3.024E-05	0.00	2.789E-05	7.77	3.02E-05	0.00	4.14E-05	-36.81			
CO3-2	8.785E-03	8.785E-03	0.00	1.162E-04	98.68	8.79E-03	0.00	1.69E-04	98.07			
Ca+2	4.535E-05	4.535E-05	0.00	1.479E-06	96.74	4.54E-05	0.00	1.27E-06	97.20			
CaHCO3+	3.090E-05	3.090E-05	0.00	9.883E-07	96.80	3.09E-05	0.00	8.61E-07	97.21			
CaCO3 (aq)												
Saturation Indices	updated win											
calcite	0.879	0.879	0.00	-0.547	162.23	0.879	0.00	20.03	-2178.73			
halite	-2.427	-2.427	0.00	-3.101	-27.77	-2.427	0.00	-3.216	-32.51			
sio2 (am, f)	-1.525	-1.525	0.00	-1.474	3.34	-1.525	0.00	-0.67	56.07			

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# Gas Chemistry

12/26/05 JS

Stumm & Morgan (1996) example 7.8 (file valid64a)  
to compare carbonate species entered PCO<sub>2</sub> as = 3.16e<sup>-4</sup>

Langmuir (1997) (file valid64b)

Effect of PCO<sub>2</sub> on Carbonate Species  
PCO<sub>2</sub> = 3.16e<sup>-4</sup>, 3.16e<sup>-3</sup>, 3.16e<sup>-2</sup>

See comparison charts <sup>88</sup> below

Handwritten signature (7)

## Gas Chemistry

Valid64a	4.02	Windows	%diff
Ca+2	1.01E-03	9.77E-04	3.03
CO3-2	3.54E-05	3.65E-05	-3.13
cahco3+	4.77E-06	4.40E-06	7.72
caco3 (aq)	4.10E-06	4.10E-06	0.00
hco3-	1.49E-03	1.42E-03	4.83
pH	8.32	8.36	-0.42
Alkalinity	1.53E-03	1.45E-03	4.65
alk=plusCO3-2and HCO3-			

## PCO2=3.16e-4

Valid64b	4.02	Windows	%diff
Ca+2	4.849E-04	4.849E-04	0.00
CO3-2	9.740E-06	9.739E-06	0.01
cahco3+	4.030E-06	4.030E-06	0.00
caco3 (aq)	4.759E-06	4.759E-06	0.00
hco3-	9.524E-04	9.523E-04	0.01
h2co3 (aq)	1.066E-05	1.066E-05	0.00
pH	8.284	8.284	0.00
Alkalinity	9.73E-04	9.73E-04	0.01
alk=CO3-2and HCO3-and h2co3 (aq)			

## PCO2=3.16e-3

Valid64b	4.02	Windows	%diff
Ca+2	1.070E-03	1.070E-03	0.00
CO3-2	5.149E-06	5.149E-06	0.00
cahco3+	1.857E-05	1.857E-05	0.00
caco3 (aq)	4.757E-06	4.757E-06	0.00
hco3-	2.148E-03	2.148E-03	0.00
h2co3 (aq)	1.066E-04	1.066E-04	0.00
pH	7.628	7.628	0.00
Alkalinity	2.260E-03	2.260E-03	0.00
alk=CO3-2and HCO3-and h2co3 (aq)			

## PCO2=3.16e-2

Valid64b	4.02	Windows	%diff
Ca+2	2.418E-03	2.418E-03	0.00
CO3-2	2.853E-06	2.853E-06	0.00
cahco3+	8.583E-05	8.583E-05	0.00
caco3 (aq)	4.752E-06	4.752E-06	0.00
hco3-	4.916E-03	4.916E-03	0.00
h2co3 (aq)	1.065E-03	1.065E-03	0.00
pH	6.976	6.976	0.00
Alkalinity	5.984E-03	5.984E-03	0.00
alk=CO3-2and HCO3-and h2co3 (aq)			

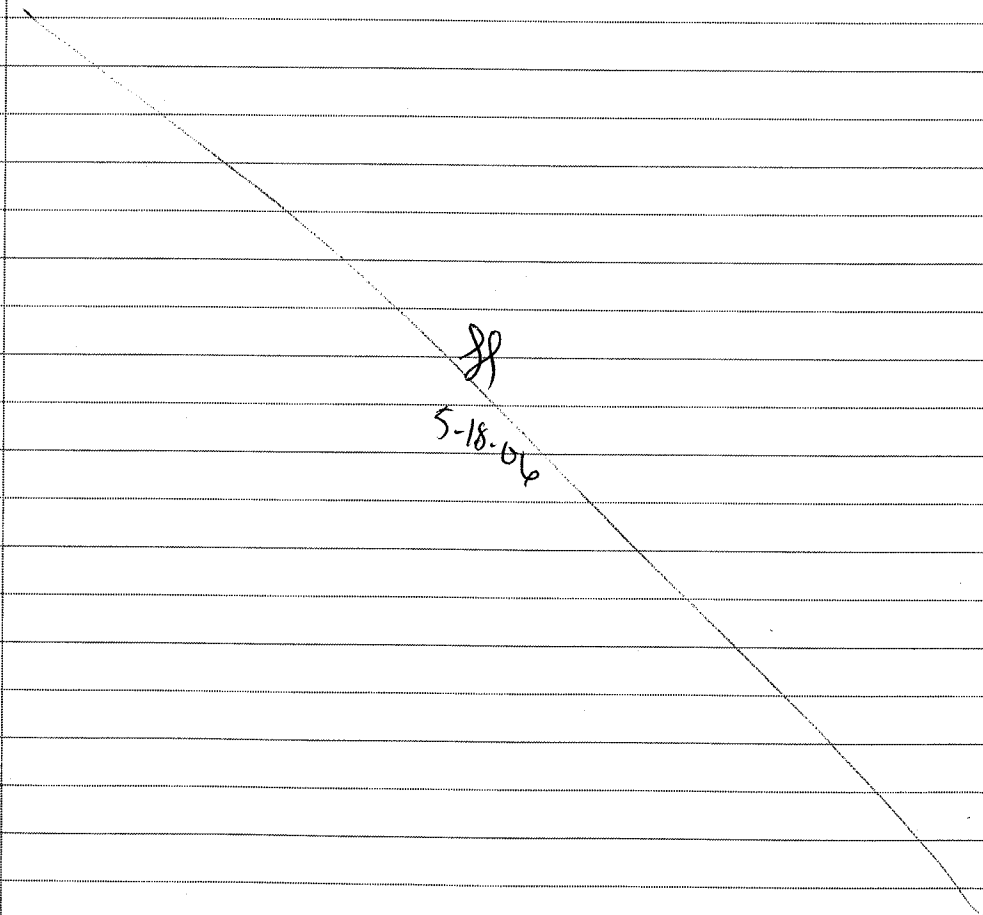
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1/10/06

Wt% entered as shown for (Version 4.02) output file.  
Two equilibrium constraints include Calcite, and  $\text{CO}_2(\text{g})$  as  $3.16 \times 10^{-4}$ . The % diff is order 10%. with the higher percents being on lowest concentrations

Wt% Very good comparison over the  $\text{P}_{\text{CO}_2}$  range

See chart on page 7. *js*



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- Sorption -

12/27/05 *js*

Parkhurst + Appelo (1999) - look at total dissolved  $\text{Zn}^{++}$  as a function of pH and total sorbed  $\text{Zn}^{++}$  as function of pH (file name: valid65)

2 <sup>different 5-18-06</sup> ~~different~~ concentrations for  $\text{Zn}^{++}$  1)  $1 \times 10^{-7}$  2)  $1 \times 10^{-4}$

pH varies. 5 to 8 in .25 increments.

1 surface for Double diffuse layer, 2 sites  
1 site  $\text{HfO-SOH}$  2nd site  $\text{HfO-WOH}$

Vary pH w/ 2 different Zinc Conc - probably 2 files

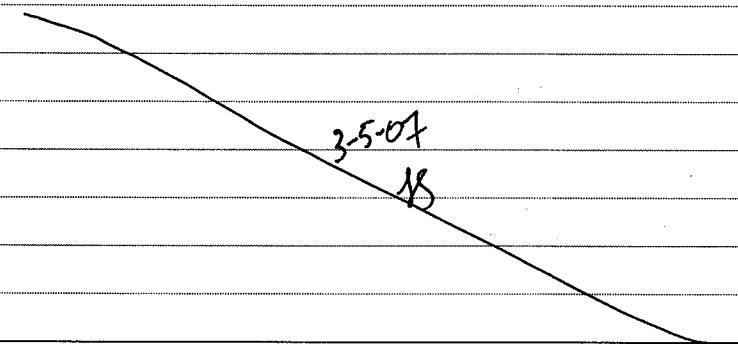
*js*

⑨

1/9/06

Pulled Phreeqc Example 8 for comparison to get specifics for problem (surface area, concentration)

had to run this problem as 2 separate problems because on top of the pH sweep, there are 2 Zinc Concentrations *js*



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Sorption	Zinc Concentration 1e-7		Windows Version		%diff	Diss	%diff	Sorb
Valid65	Dissol. Zn++	Sorbed Zn++	Dissol. Zn++	Sorbed Zn++				
5	9.968E-08	3.240E-10	9.968E-08	3.240E-10	0.00	0.00		0.00
5.25	9.911E-08	8.869E-10	9.911E-08	8.869E-10	0.00	0.00		0.00
5.5	9.761E-08	2.387E-09	9.761E-08	2.387E-09	0.00	0.00		0.00
5.75	9.376E-08	6.240E-09	9.376E-08	6.240E-09	0.00	0.00		0.00
6	8.469E-08	1.531E-08	8.469E-08	1.531E-08	0.00	0.00		0.00
6.25	6.704E-08	3.296E-08	6.704E-08	3.296E-08	0.00	0.00		0.00
6.5	4.271E-08	5.729E-08	4.270E-08	5.730E-08	0.02	-0.02		
6.75	2.133E-08	7.867E-08	2.133E-08	7.867E-08	0.00	0.00		
7	8.902E-09	9.109E-08	8.896E-09	9.110E-08	0.07	-0.01		
7.25	3.377E-09	9.662E-08	3.371E-09	9.663E-08	0.18	-0.01		
7.5	1.231E-09	9.877E-08	1.224E-09	9.878E-08	0.57	-0.01		
7.75	4.452E-10	9.955E-08	4.388E-10	9.956E-08	1.44	-0.01		
8	1.645E-10	9.984E-08	1.579E-10	9.984E-08	4.01	0.00		

Sorption	Zinc Concentration 1e-4		Windows Version		%diff	Diss	%diff	Sorb
Valid65	Dissol. Zn++	Sorbed Zn++	Dissol. Zn++	Sorbed Zn++				
5	9.969E-05	3.056E-07	9.969E-05	3.056E-07	0.00	0.00		0.00
5.25	9.924E-05	7.626E-07	9.924E-05	7.626E-07	0.00	0.00		0.00
5.5	9.833E-05	1.669E-06	9.833E-05	1.669E-06	0.00	0.00		0.00
5.75	9.699E-05	3.006E-06	9.699E-05	3.006E-06	0.00	0.00		0.00
6	9.551E-05	4.493E-06	9.551E-05	4.493E-06	0.00	0.00		0.00
6.25	9.377E-05	6.232E-06	9.377E-05	6.232E-06	0.00	0.00		0.00
6.5	9.079E-05	9.208E-06	9.079E-05	9.208E-06	0.00	0.00		0.00
6.75	8.493E-05	1.507E-05	8.493E-05	1.507E-05	0.00	0.00		0.00
7	7.516E-05	2.484E-05	7.515E-05	2.485E-05	0.01	-0.04		
7.25	6.263E-05	3.737E-05	6.260E-05	3.740E-05	0.05	-0.08		
7.5	4.959E-05	5.041E-05	4.952E-05	5.048E-05	0.14	-0.14		
7.75	3.765E-05	6.235E-05	3.748E-05	6.252E-05	0.45	-0.27		
8	2.773E-05	7.227E-05	2.731E-05	7.269E-05	1.51	-0.58		

*J. Salido*

2 zinc concentrations that were varied over a pH range of 5-8 in 25 increments. Good Comparison

3/5/07  
LS

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Redox Conditions 12/27/05 JS

Stumm and Morgan (1996) file valid66A - contains 3 separate redox files example 8.2

When entered into Mint Hwin had to create as three separate files, however pe calculated for all are comparable. Last example on Valid 66A - the pe was off not significantly see chart, however when log K was changed to match that of the old database for pyrolusite the pe calculated was the same as what was calculated in version 4.02.

Stumm and Morgan (1996) file (valid 66B) example 8.4 Redox HS<sup>-</sup> value entered pe = 7 pH = 10 and entered 3 excluded species.

*J. Salido JS 11*

REDOX  
Redox example 8.2 Stumm and Morgan (valid66a)

	4.02 Windows	%diff	windows file
pe #1	10.891	-0.293821	valid66a
pe #2	13.106	0	valid66a2
pe #3	6.925	-3.898917	valid66a3
note**	6.925	0	valid66a3

\*\* in the third case if the log K of pyrolusite is changed to -40.84 as it is show in the original input file the window version calculates the same pe

*J. Salido*

1/20/07

1/9/06 Creation of above table JS

1/24/06 Correction - result HS the same when pH is not specified (2/2 correction) in windows version JS change Fe redox couple to same as it had been in 4.02 (13,000) JS

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Redox example 8.4 Stumm and Morgan (valid66b)

			% diff	updated win	% diff
pE-9					
HS-1	1.000E-04	1.000E-04	0	9.991E-05	0.09
SO4-2	9.890E-21	2.266E-20	-129.1203	9.881E-21	0.09
H2S (aq)	8.642E-08	8.642E-08	0	8.634E-08	0.09
pE-8					
HS-1	1.000E-04	1.000E-04	0	9.991E-05	0.09
SO4-2	9.890E-13	2.266E-12	-129.1203	9.881E-13	0.09
H2S (aq)	8.642E-08	8.642E-08	0	8.634E-08	0.09
pE-7					
HS-1	5.000E-05	3.031E-05	39.38	4.998E-05	0.04
SO4-2	5.000E-05	6.969E-05	-39.38	4.998E-05	0.04
H2S (aq)	4.305E-08	2.607E-08	39.44251	4.303E-08	0.05
pE-6					
HS-1	9.913E-13	4.327E-13	56.35025	9.913E-13	0.00
SO4-2	1.000E-04	1.000E-04	0	1.000E-04	0.00
H2S (aq)	8.510E-16	3.715E-16	56.34548	8.510E-16	0.00
pE-5					
HS-1	9.913E-21	4.327E-21	56.35025	9.913E-21	0.00
SO4-2	1.000E-04	1.000E-04	0	1.000E-04	0.00
H2S (aq)	8.510E-24	3.715E-24	56.34548	8.510E-24	0.00
pE-4.3					
HS-1	2.490E-26	1.087E-26	56.34538	2.490E-26	0.00
SO4-2	1.000E-04	1.000E-04	0	1.000E-04	0.00
H2S (aq)	2.138E-29	9.331E-30	56.35641	2.138E-29	0.00

ggalide

10/06 initially the % difference was off. So we changed the hs-/so4-2 redox couple logK value - the results changed very little not sure why (value hs- redox couple changed in database)

11/8-06 retyped the input file and used it with the modified database. Once an input file is created + run (equilibrated) it most of return info. Because with the same modified database I retyped the problem and the results are very comparable within 0.1% See table above.

Temperature Effects

12/27/05

Parkhurst + Appelo (1999) valid67A solubility gypsum + Anhydrite in pure water Varying Temp valid67B solubility gypsum in pure water Varying Temp gypsum in equilibrium (Bard) (13) gg

Temperature Effects on Saturation Index

Valid67a	4.02	Windows	%diff	updatedwin	%diff
25					
Anhydrite	-0.175	-0.205	-17.1429	-0.175	0
Gypsum	0	0	0	0.03	100
35					
Anhydrite	-0.126	-0.158	-25.3968	-0.136	-7.93651
Gypsum	0	0	0	0.022	100
45					
Anhydrite	-0.061	-0.114	-86.8852	-0.1	-63.9344
Gypsum	0	0	0	0.014	100
55					
Anhydrite	0	-0.073	100	0.067	100
Gypsum	-0.019	0	100	0.007	136.8421
65					
Anhydrite	0	-0.035	100	-0.035	100
Gypsum	-0.112	0	100	0	100
75					
Anhydrite	0	0	0	-0.005	100
Gypsum	-0.216	-0.002	99.07407	-0.007	96.75926

ggalide

11/9/06 from after entering Anhydrite + gypsum as Equilibrium constraints. results off, so I updated the logK, enthalpy for the two to reflect version 4.02, results changed little and actually are worse. (changed for the problem only) gg

11/11/06 ran problem, once changing only changing logK gypsum then again (original logK) changing the enthalpy value for both Anhydrite + gypsum. This had little effect - answers not any better (Saturation index comparison = answers) gg

1/31 - Best 2 runs (1) using original model "as is" (2) changing enthalpy only

Cont' Page 16

Temperature Effects on Saturation Index

Valid67B	4.02	Windows	%diff	updated win	%diff
25					
Anhydrite	-0.22	-0.22	0	-0.19	
Gypsum	0	0	0	0.03	
35					
Anhydrite	-0.172	-0.173	-0.5814	-0.152	
Gypsum	0	0	0	0.022	
45					
Anhydrite	-0.106	-0.13	-22.6415	-0.116	
Gypsum	0	0	0	0.014	
55					
Anhydrite	-0.027	-0.089	-229.63	-0.082	
Gypsum	0	0	0	0.007	
65					
Anhydrite	0	0	0	-0.05	100
Gypsum	-0.066	0.05	175.7576	0	100
75					
Anhydrite	0	0	0	-0.02	100
Gypsum	-0.17	0.014	108.2353	-0.007	95.88235

4/11/06

updated = logK  
Enthalpy in  
Gypsum Section  
logK = 4.500 Enth = 4560  
Results worse

Salido

4/10/07

Modified Database

12/23/05 JS

2006 LS 4/7/06

As of yet 1/6/2005 the MinteqA2 H Windows Ver 1.5 has not modified its database to include the radionuclide thermodynamic data needed to perform various tests concerning the Yucca Mountain site

(NPL) Speciation (file name Np\_mint2 has been put on hold

(U(VI) Speciation - also on hold  
(file U-mint3)  
(file U-mint2)

11/7/06 JS

15 Salido

Salido  
1/7/06

4/1/06 This problem was ~~run~~ run as two separate files, one with gypsum (as Equilibrium) for the various Temp. and one with Anhydrite. The original problem switched from gypsum to Anhydrite at 60°, I can't do that in MinteqA2 for Windows. There seems to be good agreement between the two versions for the Anhydrite and gypsum Saturation indexes up to 60°, then when the second file (Anhydrite) based over 60° the results vary more. JS

4/18/06 I changed (for this problem only) the logK + Enthalpy for Anhydrite + Gypsum (2nd Set of data). This did not make a improvement. JS

1/30/2006 Ran Valid67B - Gypsum and anhydrite as Equilibrium Solid phases not as Finite Solids. Results are not any better. Also ran as Equ. Solid with Corrected thermo dynamic logK values. Results - not much better - worse

LS  
3-5-07



1/31/06 Valid 67a -  
Fixed pH at 7 - got same exact results as 4.02  
Gypsum/Anhydrite are still finite Solids

Valid 67b

ran problem with fixed pH Gypsum (25-55) Anhydrite (60-75)  
as Solids at Equilibrium - no difference when I ran it without  
fixing the pH.

ran problem with fixed pH Gyp (25-55) Anhy (60-75) as  
finite Solids - no diff when I ran without fixing the pH.

Running it as a finite gives comparable results w/ Phreeqc  
until 60°, but original problem (run 4.02) ran it as a  
Equilibrium solid

2/1/06 Tried running same H data sets for 67B  
Gypsum (25-55) as finite, but allowed precipitation. no  
change - typical the results are not supersat.  
Same thing when allowed to precip (and Gyp - as Equil solid)  
no change b/c nothing in solution is supersaturated

Anhydrite (60-75) finite - precipitation allowed  
There was <sup>8.5-18-06</sup> no improvement / however not close to run 4.02  
Phreeqc results. Equilibrium Solids w/ precipitation allowed  
SI - values stay supersaturated.

SS

15  
3/31/07

2/25/06 Still cannot get the same trends seen in the  
MinteqA2 <sup>8.5-18-06</sup> from previous runs. Plan on changing  
the MinteqA2 4 windows database to match that  
of Phreeqc 2.12.5. Have to pull out log K and  
delta H values for all species present in the  
67a and 67B output files. These numbers then  
need to be converted to the correct units for  
MinteqA2, then the problems can be rerun

alib  
2/25/06

Species	Phreeqc		Minteqa2		Put in MINTEQA2	
	log K	delta H (k cal)	log K	delta H (kJ/mol)	log K	convert to KJ/mol
HSO4-	1.988	3.85	1.99	22	1.988	16.1084 -
CaSO4	2.3	1.65	2.36	7.1	2.3	6.9036 -
OH-	-14	13.362	-13.997	55.81	-14	55.906608 -
CaOH+	-12.78	14.535	-12.697	64.11	-12.78	60.81444 -
Gypsum	-4.58	-0.109	4.61	-1	4.58	-0.456056 -
Anhydrite	-4.36	-1.71	4.36	7.2	4.36	7.15464 -
PORTLANDIT	22.675	-30.69	-22.804	128.62	-22.675	128.40696 -
Lime	32.797	-46.265	-32.6993	193.91	-32.797	193.57276 -

(1 kcal/mol = 4.184 kJ/mol)

- Above data shows comparison of what was  
in each database and the third column  
shows what was put into MinteqA2 to  
update the database

- The above changes to the MinteqA2 did not  
significantly change the results (see next  
page). The original 67B was run with  
Gypsum + Anhydrite as Equilibrium species  
I tried both with Gypsum/Anhydrite as  
finite solid or Equilibrium solids.

SS

- MinteqA2 doesn't contain CaHSO4, Phreeqc does,  
however should not make a big difference



2/26/06 Tables of Results from previous page 88

67a

COMPARISON OF MINT 4 WIN and 4.02 and Phreeqc

Table 3-9. Comparison of Saturation Indexes (SI) Calculated by MINTEQA2 FOR WINDOWS, Version 1.5 and MINTEQA2, Version 4.02 for Anhydrite and Gypsum as a Function of Temperature.

T(°C)	MINTEQA2 FOR WINDOWS			MINTEQA2, Version 4.02			PHREEQC, Version 2.4.2		
	pH	SI(Anhy)	SI(Gyp)	pH	SI(Anhy)	SI(Gyp)	pH	SI(Anhy)	SI(Gyp)
25	7.08	-0.175	0.000	7.08	-0.175	0	7.07	-0.220	0
30	7.01	-0.153	0.000	7.01	-0.153	0	7	-0.200	0
35	6.95	-0.131	0.000	6.94	-0.126	0	6.94	-0.171	0
40	6.89	-0.111	0.000	6.88	-0.096	0	6.88	-0.141	0
45	6.83	-0.091	0.000	6.82	-0.061	0	6.82	-0.106	0
50	6.77	-0.071	0.000	6.76	-0.023	0	6.77	-0.068	0
55	6.72	-0.053	0.000	6.7	0	-0.019	6.72	-0.026	0
60	6.67	-0.034	0.000	6.65	0	-0.064	6.67	0	-0.019
65	6.63	-0.017	0.000	6.59	0	-0.112	6.62	0	-0.067
70	6.59	0.000	0.000	6.54	0	-0.162	6.57	0	-0.117
75	6.54	0.000	-0.017	6.49	0	-0.216	6.53	0	-0.170

67b

as finite

Temperature	SI(anh)	SI(gyp) MIN 4	SI(anh) MIN 4.02	SI(gyp) MIN 4.02	SI(anh) Phreeqc	SI(gyp) Phreeqc
	MIN 4 WIN	WIN	MIN 4.02	4.02	Phreeqc	Phreeqc
25	-0.190	0.000	-0.220	0.000	-0.220	0.000
30	-0.168	0.000	-0.198	0.000	-0.200	0.000
35	-0.147	0.000	-0.172	0.000	-0.171	0.000
40	-0.126	0.000	-0.141	0.000	-0.141	0.000
45	-0.106	0.000	-0.106	0.000	-0.106	0.000
50	-0.087	0.000	-0.068	0.000	-0.068	0.000
55	-0.068	0.000	-0.027	0.000	-0.026	0.000
60	0.000	0.050	0.000	-0.018	0.000	-0.019
65	0.000	0.320	0.000	-0.066	0.000	-0.067
70	0.000	0.015	0.000	-0.117	0.000	-0.117
75	0.000	-0.002	0.000	-0.170	0.000	-0.170

67b

as equilibrium

Temperature	SI(anh)	SI(gyp) MIN 4	SI(anh) MIN 4.02	SI(gyp) MIN 4.02	SI(anh) Phreeqc	SI(gyp) Phreeqc
	MIN 4 WIN	WIN	MIN 4.02	4.02	Phreeqc	Phreeqc
25	-0.220	0.000	-0.220	0.000	-0.220	0.000
30	-0.198	0.000	-0.198	0.000	-0.200	0.000
35	-0.177	0.000	-0.172	0.000	-0.171	0.000
40	-0.156	0.000	-0.141	0.000	-0.141	0.000
45	-0.136	0.000	-0.106	0.000	-0.106	0.000
50	-0.117	0.000	-0.068	0.000	-0.068	0.000
55	-0.098	0.000	-0.027	0.000	-0.026	0.000
60	0.000	0.080	0.000	-0.018	0.000	-0.019
65	0.000	0.062	0.000	-0.066	0.000	-0.067
70	0.000	0.045	0.000	-0.117	0.000	-0.117
75	0.000	0.029	0.000	-0.170	0.000	-0.170

3/20/06 May have to further change Min 4 Windows to make Temperature problem work. Will calculate Anhydrite and Gypsums Log K values using Polynomial found in Phreeqc's program using the constants found in phreeqc's database then entering these values into MinteqA2 4 window somehow A<sub>1</sub>-A<sub>5</sub> in Phreeqc database

$$\log K = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log T + \frac{A_5}{T^2}$$

7/2/06

C°	Temperature		Log K	
	C°	K°	Gypsum	Anhydrite
25	298.15		-4.58091	-4.36081
30	303.15		-4.58372	-4.3856
35	308.15		-4.58936	-4.41771
40	313.15		-4.59763	-4.45664
45	318.15		-4.60837	-4.50197
50	323.15		-4.62143	-4.55327
55	328.15		-4.63666	-4.61015
60	333.15		-4.65391	-4.67226
65	338.15		-4.67308	-4.73927
70	343.15		-4.69403	-4.81086
75	348.15		-4.71665	-4.88674

	Gyp	Anhy
1	68.2401	197.52
2	0	0
3	-3221.51	-8669.8
4	-25.0627	-69.835

J. Salgado  
4/1/06

Neither Anhydrite or Gypsum had a 5<sup>th</sup> term \* Deviation from test plan code will be compared to Phreeqc instead of older MinteqA2 version.

J.S.

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4/10/06 (page 19) ran 67a. using calculated  $\log K$  @ 25, but with current  $\Delta H$ , for temp range 25-75. Shows Gypsum slightly undersat low temp and undersat high. Anhydrite undersat low and slightly undersat high temp. This occurs even if specify to precip all saturated solids.

Try to run 67a at individual temperatures changing  $\log K$ 's (insubty below p. 19), entering zero for  $\Delta H$  (anhydrite) results for gyp - ~~undersat~~ undersat (not at equilibrium), Anhydrite same value as table p. 18.

ran changing  $\log K$  - using Edit thermo button results poor

then ran using Sensitivity Analysis, but can change only 1 solids thermo value.

Gypsum SI values at high temp improved

onto 67B.

just to show that trends are working - specify the  $\log K$  for T 25-55, but can only specify 1 temp (25) Gypsum goes from supersat to undersat Anhydrite remains under saturated

then change to Anhydrite - change  $\log K$  for (60-75) but only specify 1 temp (55).

Anhydrite increasing more undersat  
at 25 SI = .001 to -.527  
at 75 SI = .001 to -.527

Change  $\log K$  individual temps.

at 25 gyp Ded - better when changes  
at 30 gyp Ded - results improved however Anhydrite SI improve the SI of Gypsum undersat instead of 0

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zh

4/10/06 <sup>cont</sup> 67a - as change Gypsum ~~log K~~ <sup>LS</sup>  $\log K$  5-18-06, Anhydrite SI improves

67B - run gyp to 55 Anhydrite 75 step by step changing  $\log K$  doesn't work. If you run Gyp - 25-75 (Eq with solid) improved, but off

4/11/06 - notice  $\Delta H$  for Gypsum had - sign, Made change should be positive, Made change, data not improved

4/12/06 Started with ~~newly~~ <sup>8/5-18-06</sup> newly installed programs. From the Phreeqc database I deleted the polynomial constants. In Minteqa I updated the database with the species (except Anhydrite + Gypsum) listed in the table on page 17.

Part B - For Both programs I ran 2 parts to Part B Gypsum 25-55 and Anhydrite 60-75.

There was one warning for the Minteqa 2 program stating that gypsum was added to the excluded species so to avoid a phase rule violation -

Other than that the SI were comparable for Anhydrite. Gyp/Anhy  $\log K$   $\Delta H$  values changed in the run.  
\* things to do go back change Anh/Gyp right in Mint database  
\* check to see if Phreeqc properly uses Van't Hoff

Part A - Phreeqc - when both Anhydrite / Gypsum are in Equilibrium w/o the polynomial values the program calculates Gypsum in Eq or the entire temp range and Anhydrite as undersaturated. Using 1 mol/L in Minteqa resulted in values that are off, altering the concentration to  $9.7e^{-2}$ , resulted in similar SI values w/ Phreeqc, but SI Gypsum is oversaturated - density of H<sub>2</sub>O  
\* warning regarding Activity of Water -  $\uparrow$  cone in System

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4/14/06 In Minteqa  $\Delta H$ ,  $\log K$  for Anhydrite / Gypsum changed in Run

4/13/06

4/14/06

✓ ~~run~~ MinteqA2 database

- Change  $\log K$  and  $\Delta H$  of Gypsum and Anhydrite and rerun the problem, didn't make any drastic changes, SE improved slightly, closer to Phreeqc values

- Ran Phreeqc using Minteq.v4.dat which is the same data as in MinteqA2 4win it resulted in same out put (#'s off bit) as the Altered Phreeqc database.

Also did run using Minteq.dat, same trend, #'s off and equilibrium switch over occurred at a diff temperature than the original ex2 problem using Phreeqc.dat

MinteqA2 → To Compare Ran Part A (w/ <sup>Concentration 88 4/14/06</sup> 1 mol/L + 1 mg/L) for Part B as usual using 2 Runs.  
1) Original database      2) Altered database

Phreeqc problem ran using Minteq.v4.dat and phreeqc.dat and altered phreeqc.dat with the analytic constants removed.

4/14/06 The results of Part A, <sup>88-18-06</sup> ~~run~~ All the runs show the same trends, the values were off due to the the different values in the database, only 1 Run varied from the trend, which was the Phreeqc run that used the original database with the analytic expressions for Gypsum / Anhydrite, All other runs used the Van't Hoff equation. Original Phreeqc database not considered further

4/14/06

88-18-06

There is also a warning in ~~phase~~ MinteqA2 for Part A, where 1 mol Gyp + Anh are entered as finite solids. The error states that Computed Activity of water may be in error. Because Anh / Gyp are finite considered in equation  $a_{H_2O}$  the  $a_{H_2O}$  in MinteqA = .949 in Phreeqc  $a_{H_2O} = 1$   
Also, we no longer considering original Phreeqc-Analytic database - so the fact MinteqA doesn't contain CaHSO<sub>4</sub> and Phreeqc does is irrelevant.

The results for Part B; 25-55 were taken from just having Gypsum specified (in MinteqA as finite) and 60-75 were taken from ~~having~~ <sup>having 88-18-06</sup> Anhydrite being the only species. The results from the 2 programs are comparable, same trends, % difference less than 2% in part B for MinteqA2 the  $a_{H_2O} = 1$ , because Gypsum and Anhydrite were specified as infinite.

There is also a warning for Part B in MinteqA2 stating that to avoid a phase rule violation, Gypsum was put on the excluded solids list (so it can't precipitate). This is why the SE values at 91 temps are a positive value rather than a negative. This must also be the case for Phreeqc. Only message - Charge balance adjusted to redox equilibrium

+ At high temp Gyp SE is positive? See MinteqA2 error message above

88

3/5/07  
25

5/8-06

Make table  $\log k$  vs  $k$  using  $\text{ran}^2$  diff + Polynomial (19)  
ran't diff

$$\ln k_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad T = \text{temp in K}$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\Delta H_r^\circ = \text{cal/mol or J/mol}$$

$$-\log k_2 = -\log k_1 + \frac{\Delta H_r^\circ}{4.576} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

↓  
2.303R

Gypsum  $\Delta H$  0.456 KJ/mol      1 Kcal = 4.184 KJ

Anhydrite  $\Delta H$  7.155 KJ/mol      1 Kcal = 10<sup>3</sup> cal

1 KJ = 10<sup>3</sup> J  
gg

All Results (Final) can be seen in the MinteqA2 Validation folder.

These files are used to create the MinteqA2 for windows validation report.

gg

11/13/06 Figured out how to properly modify code for Problem 64, by emailing Cream and Jerry Allison. The process lacks documentation, but is simple. ANALYT.DBS needs to be updated with a text editor. The Constants for the polynomial needed to be \*by(-1) because MinteqA2 solid phase reactions ( $\log k$ ) are written as formation reactions, where Phreeqc's solid phases are written as solubility reactions. The Files format is written in the validation report. Once the changes were made, the files were changed to calculate pH, instead of fixed pH, the results were the same (log in the thousands place - rounding errors.)

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Phreeqc CI Version 2.12.5 Software Validation

test plan  
by Lynn Sabido gg

2/5/06

Objective: To perform a Software Change Report (SCR) for the updated Phreeqc version from the former version 2.8

Training/Qualifications: Familiarity with Phreeqc programs, computers, and a basic understanding of various aqueous systems.

Hypothesis: With the new release of version 2.12.5, updates which include mostly bug fixes, shouldn't affect the overall performance of the program. No major updates, as far as functionality were performed and should therefore yield similar results, however some differences may arise due to rounding techniques.

Approach: The same set of example files that accompany the program will be used as an installation check. The results of these 18 files will be compared between the old and newer version of Phreeqc. Secondly, the same set of validation problems used in the validation process for Phreeqc V2.6 and MinteqA2 will be used here again. The output for these validation files will be compared to the output of these same files that were run through the older version of Phreeqc. Any discrepancies will be evaluated and accounted for.

Program description - Same mathematical theories, assumptions, and algorithms are used in version 2.12.5 as in former versions 2.8 and 2.6 please see the Validation Report and Proposal for Phreeqc Version 2.6 for specifics. See Manual for details

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Status This code, Phreegc 2.12.5, is under review for compliance with TOP-018 and all the tests performed will be done on a PC computer. The code will be located in C:\Program Files\Phreegc

input files The installation, IS files, input files are described in detail at the end of the Phreegc Manual in an appendix. The validation files are described in detail including data sources in the validation test plan for Phreegc 2.12.5.

Program location C:\Program Files\OSGS\Phreegc\Interactive 2.12.5

Files storage - a folder named Phreegc, installation tests are in a 2-12 configuration folder. Examples as received are old version files, installation tests - has the output from the new 2.12.5 version. Both sets of files were compared (folder install-comparison files). The validation files are set up in the same manner under folder 2-12 validation. 5-18-06

3/19/07 - note - All file location have been moved to Cd 5-18-06

2/6/06 Ran installation test - Most all output files on target. 2 problems files #14 and 15 couldn't get correct databases to run. So I just <sup>incorporated</sup> ~~incorporated~~ databases into file. Not proper procedure. All files either exact or much less than factor 2. File #12 had the most variance in concentration values. 5/18/06

2/7/06 Figured that in Phreegc you don't hit options to select the proper database, you right click on the specific file (input file that's opened in program) and select properties in order to change the database file. Installation check complete - All OK 5/18/06

Running Validation problems - files for two runs - Barite dissolution in pure water and NaCl solution. Predict the same conc of Ba + SO4 in solution, however diff. eg. Phases - old version has Ba(OH)2 · 8 H2O. New version - BaSO4 still in solution, not totally ~~dissociated~~ dissociated and new version has NaOH + NaSO4 as complexes in solution whereas the old version does not. 5-18-06

Problem 8. The Distribution of species were off - meaning the old version had more Zn(OH) species than the newer version - same with Zn(NO3) species, why Zn and H2O wasn't and H2O-SO4 5-18-06 values (moleality) are a bit off for the two versions 5/18-06

hangover 97 Values are off a bit 2.5 x 10^-6 2.6 x 10^-6 or less severe not due to different speciation complexes, however SI repeat in old version includes Portlandite and Lime, new version always include SI for that why? 5/18-06



2/17/06 cont

Redox example there are more various S species in the newer version than the old. That's why in Redox 2 the concentrations  $H_2S^-$  are off, but closer to the MinteqA2 version 1.05 for Windows.

\* Files Valid62.phrg, NP.phrg2, U.phrg2, U.phrg3 can't be run properly at this time because the database is not updated with the C.N.W.R.A. data. Example 1 same as Valid62

\* Stumm 96. speciate seawater from Stumm + Morgan error could not find species  $H_2CO_3$  why. (S)

2/8/06 small problems with old database Phreeze 2-42 only need to look 5 above problem - but run all Barite - #1 same <sup>pe 6.15-0.3</sup> very comparable  $ba^{2+}SO_4^{2-}$  concentrations #2 diff " " (S)

\* Ex 1 - could be run using 2-42 database, results comparable  $Bo^{+}$  off due to 2 diff database (slightly diff log K values, diff species). Seems in 2.42 dat there are more  $U-OH$  species  $\therefore$  SI of many more species + minerals

Ex 2 ok looking SI, Anhyd / Gypsum which is good, pH off a bit

Ex 8 Double Diffuse layer Numbers (concentration carbonate species) comparable off by 1.0341 vs 1.0364

Redox 1 - ok however both predict same values,  $I^{st}$  value is off from that found in MinteqA2 (Stumm + Morgan 96 ix 8.2A) defined  $Fe^{+2}/Fe^{+3}$  pH 7 (S)

2/8 cont Redox 2 - results were better with original database / the  $M-HS^{2-}$  actually became more with phreeze 2-42.dat why more S species in 2.42  $S_5^{2-}, S_4^{2-}, S_6^{2-}, HS^-, S^{2-}, H_2S, S_3^{2-}, S_2^{2-}$ , old model - only  $HS^+$

Seawater - Very Comparable  $Fe(2)$  off bit (new version more  $Fe^{2+}$  species at concentrations  $10^{-24}$ )  $Mn(2)$   $MnSO_4$  - in new version - more free  $Mn^{2+}$  off

\* Stumm 96 - another seawater very comparable Ca-species off less than a factor of 2 because rounding?

\* U.phrg2 and U.phrg3 output same as old version

\* NP.phrg2 output same as old version

\* Valid62 output same as old version (S)

2/15/06 Using the Comparison function of Microsoft Word, I ran all the ~~old~~ validation files comparing them to the original output files from the 2.16 Phreeze validation. When the comparison is complete all changes are in red, if there is a line through the text (x ~~red~~), it means the word was deleted from the former file where it appeared and is absent in the new file. If a word or text is underlined with a line beneath (red), it means that this is new text that didn't exist in the old file. However, the program sometimes get "hipped up" by spaces or symbols no longer used in the new  $\rightarrow$

2/15/06 Phreeqct version 2.12.5. This is seen when the comparison of .sel and .123 files are ran. In the old version headings began with "word" threw off file (spacing + all) file repeats itself - New version (with out quotes) some info same, but marked as different. Also if Ag. Species show up out of order in sections I → III mark them as incorrect. (88)

2/16/06 Had to rerun validation files using Phreeqct database 2-6 and 2-6a for Redox 1 and Redox 2. Then compare these files to the files for Phreeqct v 2.6 validation test that also used database 2-6 and 2-6a. I also ran installation files for comparison. (88)

2/17/06 The only major differences in the validation files are the Ion Activity Product and Log<sub>K</sub>T are off for many phases, off by more than just a little bit. (K<sub>T</sub> for CH<sub>4</sub>(g) in ex 14 is =43.93 old version / =2.86 New) However, the Saturation Index is the correct value SI = IAP/K

#2 Example files 12, 13a, 13b, and 13c are the only files showing major differences. I had to do with the print option. If you look at the old files get the word print there a warning in each file, followed by what info is to be printed. In the New files on 2.12.5 the last section is missing. I originally ran the example files from the folder I received from Jim (examples as received), if you look at the →

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(88)

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2/17/06 Continued

- Input files, the print options vary, when compared to the example (12, 13a-c) files that come with the program.
- 1) I ran the original Program (2.12.5) example files - results the same, section following "print" keyword still absent
  - 2) I cut the missing options from 2.12.5 input files and pasting into (example as received) my input files results same as #1 above. (88)

2/20/06 Had wrong folder sent to me "Examples as received" with correct folder I ran Installation tests, ran comparison came out ok. (88)

5-18-06

Jaub

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PROJECT

LS  
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3/5/06  
Intro-

Using Phreegc v.2.12.5 to evaporate potential Pore Waters found at the proposed Nuclear Waste Repository Site at Yucca Mountain  
by Lynn Sabido

Objective: Use Phreegc to evaporate some of the initial Yucca Mtn Pore Waters to replicate previous results that mapped potential evaporite compositions. If results are successfully replicated, try to broaden the range of initial waters, evaporate them using Phreegc, to see if they fall within the range (11 bin waters) of previous thought (calculated) evaporite compositions.

Training/Qualifications - Familiarity with Phreegc programs, Computers, and a basic understanding of various aqueous systems (evaporite).

Hypothesis - That Phreegc can replicate previous work that demonstrated future in-drift evaporite compositions and further determine if alternative initial pore waters, once evaporated, fall into those previous determined ranges, or if other in-drift evaporite compositions need to be considered.

Approach - Take some (small) of the initial pore water compositions and replicate the original process (evaporate water down to an activity of .65) at a specified temperature to see if Phreegc can produce similar evaporite concentrations. If so, then use additional initial pore waters (to be determined - from literature) and use the same evaporate process to see if these new waters fall within the 11 evaporite bins already determined or if they fall outside these ranges.

JS  
3/5/07

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Status Phreeqc.I. Version 2.12.5 under review for compliance with TOP-018 and all the tests will be performed on a work computer at CROWRA, a PC computer,

The code will be located <sup>3/5-18-06</sup> D:\Programs\USGS\Phreeqc Interactive 2.12.5

Input files The initial input files will be from the Technical Basis document 5 (from the OCRWM website)  $\Delta$ n-Drift chemical environment pg 3-8. The outcomes, the 11 bin waters are in the same document - Appendix E page E-9

Program description - Please see manual or Phreeqc test plan.

Location program - Name as before

Document - Location D:\Mydocuments\Phreeqc\test MF.

<sup>5-18-06</sup> 3/19/06 <sup>3/17/06</sup> Files will be moved to Cd, no dis-regard file locations, 3/20/07 - Please see note on page 39

LS  
3/7/07

Ⓢ

3/18/06  
3/5-18-06

Setup problem using HD-Perm water Wb. First had to convert CO<sub>2</sub> pphv to moles. Then entered water into Stp Program as a solution, -Set up Equilibrium keyword to enter in CO<sub>2</sub> concentration and saturation index. Ran with high temperatures to see what activity of water w'd get (want .65). Activity only .09

3 ways to evaporate water in Phreeqc - 3 keywords  
1.) use Mix keyword. Mix in a neg. Amount of pure water  
2.) use Equilibrium keyword - System in equilib w/ neg Amount Pure H<sub>2</sub>O  
3.) use Reaction keyword - React system w/ neg Amount Pure H<sub>2</sub>O

Can't get any method to work, ~~using~~ Activity doesn't get below .98 Ⓢ <sup>3/5-18-06</sup>

<sup>3/5-18-06</sup> 3/3/06

Using 3 methods above, changing input parameters on 3 keywords reacting, mixing, various amounts of water - get error messages / and activities close to 1 Ⓢ

<sup>3/5-18-06</sup> 4/3/06

Retyped input file and used reaction keyword, instead of using reaction in steps. Use one reactive amount of water. Got results close to (Q<sub>w</sub> = .65), kept going back to input file and changing 1. value of pure water to react, adjust it to reached desired Q<sub>w</sub>. It was entering the sweep into Phreeqc as incremental - pure water in steps of .55 moles, then .1 moles then .01 moles. Phreeqc Not incremental steps should read -55, -55.1 -55.15 so on. Achieved desired results, now must find temperature to or temperature range to run problemat. Ⓢ

4/14/06 - haven't figured out what I did wrong w/evaporation  
Using Mix and Equilibrium keywords. Looking for  
process used to create 11 bins. Going to use Reaction keyword  
§§

4/16/06 Took 3 initial pore waters Found what amount of pore  
water needed to be evaporated in order to get an activity  
of water at .65 at 25°C.  
For water W<sub>0</sub> (HD perm) - 55.473 moles water 25°C  
W<sub>5</sub> - 55.479 moles water 25°C  
W<sub>4</sub> - 55.466 moles water 25°C

Then ran these 3 problems, taking out the correct moles of water  
(see above) with a temperature range of 25-140°  
to see at what temp .65 activity of water is maintained  
for W<sub>0</sub> .65 at 50°C - 125  
W<sub>5</sub> .65 upto ~~25-140~~ <sup>25-140</sup>  
W<sub>4</sub> .65 at 25°C - 105°C

adjust.  
-55.4795

I don't believe this is the process followed in original  
organization of bins. Will re-check process.  
§§

5/8/06 Initial entries.  
Units are Molality =  $\frac{\text{moles of Solute}}{\text{kg Solvent}}$   
density H<sub>2</sub>O at 25° = .9970479 g/mL or kg/L 1 kg/L  
So at 25° molality = molarity or multiply by .9970479  
§§  
 $\frac{\text{mol}}{\text{kg}} \times \frac{\text{kg}}{\text{kg}}$

5/8/2006 cont. Non-isothermal conditions are  
specified in the Meta file - keyword Equilibration  
Temperature is specified at depth (meters) with a temperature  
gradient used to calculate Temp of each grid block [°C/m]  
But Make sure your lower boundary condition (Blon)  
specifies the end Temperature §§

3/20/07  
This project has been put on hold/discontinued and the  
files were discarded. If the work should be continued in the future,  
New files will be created because work could continue using an  
alternative code. HS  
§§

5-8-06  
§§

Intro to 1-D Modeling with MultiFlo 2.0.01

Using MultiFlo to Model 1-D, 2-D examples of (scenarios) pore water evolution through simple systems such as pure Qtz or toff to more complex systems such as the rock layers above the proposed Yucca Mountain disposal site.

- by Lynn Abido (LS)

Objective: to model pore water chemistry and its effects to (precipitation, dissolution, porosity changes, corrosion) the surrounding area of concern, the potential nuclear ~~waste~~ waste drift. Specifically Ca-Cl concentrated waters to <sup>Model</sup> ~~see~~ potential corrosion. <sup>88-5-18-16</sup> <sup>88-5-18-06</sup>

Training - to become <sup>88-5-18-06</sup> familiar with MultiFlo and the driving processes behind the system being modeled.

Approach - To create, through various input files, a simulation that resembles and closely describes the proposed chemistry near and drift at <sup>Yucca</sup> ~~the~~ Mountain. Just starting with a 1-D approach of the system close to the drift (Bons with specified pore water chemistry) using Qtz and toff as the surrounding rocks <sup>then</sup> eventually model the changes to pore water as it passes through the units that lie above the proposed drift and leading to the exaporation of these new chemistries to observe precipitation, porosity, and chemistry changes. Specifically looking for corrosive chemistries that could reach the drift.

Status - Currently under TOP-18 Compliance

SS  
5/18/06

Locations Program D:\multifil\ MF102.01 / Files same one more folder <sup>FF</sup> Acceptance book

\* more files - D:\multifil\ meta.

program A numerical model describing two-phase description non isothermal flow and multicomponent reactive transport in variably saturated porous media. It consists of two submodules Meta (Mass + Energy Transport) and Gem (General Electrochemical Migration). A Fortran code ran on a Dos prompt. Used a pc with windows XP

input files

The input files will be created by altering existing files to resemble the chemistry and surrounding rock found around and above the potential drift. For the 1-D test 3 water chemistries will be provided. 1. Neutral 2. Ca-Cl 3. Alkaline These waters will be run through Pore Qtz - then separately through toff (Rock chem will come from Johnston et al). \* Changed to 2-D, 5-18-06

Next Existing well borehole samples that plot high on the pipes diagram of Yang et al (1996) and <sup>5-18-06</sup> Yang et al (1998) (By high, it means high Ca+Mg plus high  $SdFAtk + Cl^-$  concentrations) will be used as starting pore water compositions. The initial water will be run through the rock units that lie between where the sample was taken and the potential drift. This will be determined by the well hole lithology, to determine which units the water should be modeled to flow through. After the model calculates water-rock interactions the resulting water chemistry will be evaporated to see if corrosive waters form.

Shortly changed to a 2-D approach - For all examples.

\*\* 3/19/07 Any file locations should be disregarded because all files will be corrected to a cd that will accompany this book

1-D portion Minerals Qtz or Toff 3 system chemistries neutral / Ca-cl / alkaline

4/19/06 Take one of the Gem input files (from Acceptance test directory) and start modifications to fit 1-D Qtz / 1-D Toff problem

4/20/06 Continue to alter <sup>5-18-06</sup> ~~the~~ parameters - few questions <sup>88</sup>

4/24 AQCX - List of aqueous secondary species

MNIR - Kinetic reaction data for minerals

MNRL - List of Minerals

Created 6 files in Phreegc (Minteqa - didn't work <sup>too much</sup> <sub>involves</sub>) of the 3 waters (Alkaline, Ca-Cl, and neutral) for both the Qtz + toff runs. Tried to enter a add Cristobalite through Phreegc input file & it ended up opening the Minteq.v4.dat Copying Cristobalite info and pasting it to the Phreegc.dat database. This was done to fulfill the AQCX keyword.

Hope to get MNIR - From tough react input file and compile the list (MNRL)

Will start over with fresh input file change the chemistry only step by step to make sure changes don't corrupt file - then add kinetic changes - lastly, change <sup>5-18-06</sup> ~~base~~ parameters to match Meta file compiled by Chandrika

4/25/06 New Gem input file  
entered initial concentrations for alkaline-  
(Qtz) run - got error

- started over changed mineral assemblages - Error  
Add Qtz, Cristobalite,

\* Do not open input file and have the box checked  
saying "Always open as". I did this opening up the  
gem file as a WordPad Doc - When you try  
to then run it with MultiFlow, doesn't recognize  
the documents

Made a <sup>8/5-10/6</sup> separate folder for these trial runs  
Can't get program to run, even using ~~different~~ <sup>8/5-18-06</sup>  
same, original, input files from Acceptance test XP  
Copied all files including Couple file to new folder  
program ran fine.

Renamed my input file (Additionally more initial  
aqueous species) to DCM1, like the one that comes  
with the program - error inconsistent BL blocks  
in meta and gem  
n blk bc meta = 4    n blk bc gem = 2

Changed I-type of H, K to get 2 diff types input  
components  
Get same error

8) Then changed spacing of . character, there was  
an extra . in between boundary Faces Chemistry  
listings.

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4/26/06 file ran from 4:30pm on 4/25 till 7:26am on 4/26  
To make run shorter - want to change time steps  
and will have to also change printout time steps

- Also change Database used - use Revision 6

Took only seconds to run Model for 15 days  
at 5hrs, 10h, 15, 24hrs, 5days, 10 D, 15 D

Next - Add the secondary species

(Save files to compare 1 - time change 2. Add 2<sup>nd</sup> species)

2) After adding 2nd species from list created by the  
phreeqc runs (see 4/24), ran the program and  
received error. More 2nd species than equations.  
So I didn't specify the secondary species. Works here  
because the time frame is so short (Qtz - 15 days) ~~and~~  
did not have any computing errors  
This runs as 2.

\* will go back sometime and change file to specify  
secondary minerals

3) Change rock type from SiO<sub>2</sub>(am) to Quartz  
worked ok

88

85  
3/5/07

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4/27/06 Put Back the AOCX data Block, begin to add 1 Secondary Species at a time, checking the database to see exactly how its written  
 $CaSO_4(aq)$  /  $CaCl$  +  $1/3-CO_2(aq)$  +  $NaSO_4$

\* When I added 2 species stated # of reactions not equal to # of secondary species. So I deleted one  
Got the same message again - Closed input file, retry - worked

Tried to add a 3rd again chose  $MgOH$  + worked!  
4th  $MgSO_4$  - Error same as above deleted try to add  $NaSO_4$  - Did not work - have to change # reactions or scale secondary species or eliminate secondary species altogether.

Tried again with the 4th being  $NaSO_4^-$ , same error saved DEMI file - input + output as # 4 in saved files folder

\* Looking at DEMI.out. Program counts  $CO_2(g)$  automatically as a secondary species.

§ - Something with how comes up w/ reaction ~~250~~ <sup>5-18-06</sup> Equations

4/28/06 Add Minerals one at a time  
Added gypsum w/ guess of its rate constant - program hung up / then resumed  
runtime - over 45 min - Stopped run

§ Added few other minerals to see if I get an error message.

4/28/06 Went back to add few minerals that fit the beginning chemistry had Calcite + Gypsum ~~8-18-06~~ +  $OH^-$   
Added - Tridymite, cristobalite,  $SiO_2(am)$ , Sepiolite, halite, sylvite

#5 Error Message - "Warning: possibly skip reaction, 9 nam(i) = 3 na +  
SAVE AS #5

#6 Next - Back to Secondary Species delete repeats. Add another species delete repeat add  $MgSO_4$  ⇒ Error SAME AS before  
took out species altogether then the Matrix dimensions  
~~8-18-06~~ Equations reduce to 7 from 8

Doesn't matter if  $CO_3^{2-}$  is in 2nd list or not (Duplicate primary)  
Added  $SO_4$  to the Secondary - states n reactions ≠ n Secondary species  
8 ≠ 9

<sup>5-18-06</sup> Then ~~deleted~~ deleted halite 'Na' mineral  
Then it gives an error of "Warning possibly skip reaction i nam(i) = 3 K"  
So delete sylvite - Run started - working  
Manually Stop run after 1hr - SAVE #6 run

#7 - Next - take  $OH^-$  out of secondary and add to primary list - Ben OK  
and expand secondary list, added  $NaSO_4^-$  error -  
May be a bug - emailed to Scott, After he noticed some odd items in output file see DEMI-7.out

§

- Put  $OH^-$  back as secondary Can't add  $NaSO_4^-$ ,  $MgSO_4$  - not in proper section of the database, there is a reaction for both in the database - but not considered core species

4/28/06

To file #7, also add back halite

Make H a #8 (solution pH) positive #

Check to make sure  $CO_3^{2-}$  not top of database  
not primary?

Element  
A  
B  
C  
D

Reactions  
A+B=AB

all secondary, but at  
reaction portion of database

- $CO_2(aq)$
- $OH^-$
- $CaCO_3(aq)$
- $CaSO_4(aq)$
- $CaCl$

keep getting errors -  $MgOH$   
when add as 2ndary but -  $NaSO_4$

Scott sending another file to alter.

New File Fi.inp

more like the problem with trying to enter

5/1/06

Started with untouched DCM1 file, used  
§ Primary + Secondary species, and Mineral sections from  
Fi.inp file (deleted glass as an mineral).

Made a few adjustments - Mineral section - to match  
1x1x80 cells of the current problem. + Time Section

#1 This file is in above folder under /d2 Gtz saved as DCM1

Tried to copy primary block from altered DCM1(.dot) file  
Error

#2 From working file 1 add additional primary species missing  
and got an error # reactions ≠ secondary species

Try to alter secondary species same error  
SPECIES 385-1806

5/1/06

opened file #1 add to secondary species w/out adding to primary  
add secondary  $NaSO_4$  worked.

Try to add primary  $1b41$  - first changing the concentration to  
that of the alkaline water - OK

Added  $Mg+2$  OK

Added  $CO_3^{2-}$  Error "missing species" delete from 2ndary. OK

Added  $NO_3^-$  OK

Add Secondary Species

$MgOH^+$  OK

$MgSO_4(aq)$  OK

$H_2SiO_4$  - OK  
5-18-06

Go back add  $K^+$  as primary OK

then make  $SiO_2(aq)$  dependent on  $Gtz$  OK

\* All runs about 10-20 seconds.

Add Minerals 5/5/06

- Gypsum - OK - increase in run time - seems to  
get stuck at cycle iterations of the Bcon.

Maximum of # of tries exceeded

- Delete gypsum add Halite. OK - but run time  
increased - CTRL + T Del to stop

- Add Septolite - OK - stuck, then OK -

- Add Sylvite - OK

\* Making time step = 1 day total - no faster process

Add Gypsum - goes but Maximum #tries exceeded

SS



5/1/06 Change Max iterations to 200

Gypsum Rate =  $1.1 \times 10^{-4} \text{ mmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$   $1.1 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$   
paper

#3 Run with Gypsum still not working, but without its OK  
Saved as number 5

#4 Change all mineral settings (initial) to 0  
except gypsum  
letting it run overnight (took 35 min)  
put the regular 15 day (8 time steps in) to see how  
long the run would take #4  
5/5/06

5/2/06 change the volume/surface area again  
0 for all but Qtz 100% of Matrix + Fractures (link h6)  
and a surface area of 100  
change time to 2 steps at .2 days

change mineral SFA + Volume for all to 0, except  
gypsum - Run. at 5/8/06

Changed time to 2 steps .0001 and .001  
Added gypsum back. Completed in 3 seconds

#5 with gypsum

#6 Set up 3 folders for Qtz problem  
Start set up 3 folders for topt problem

5/3  
2006 Change surface area Qtz,  
Given  $300 \frac{\text{cm}^2}{\text{g}} \times 2.65 \frac{\text{g}}{\text{cm}^3} = 795 \frac{1}{\text{cm}}$   
fig. From Jim density

Set up togh input file - outline -

Changed system parameters -  
1.) D-T Step changed to days run  
2.) System Grid radial run  
3.) DCM XYZ Grid unskip DCM para key run  
4.) Change grid to XYZ - what it should be

Flow pg 95 Johnson et al 1998  $\Delta$  in meta not gem  
Fluid  $24 \frac{\text{mL}}{\text{day}} \frac{365 \text{d}}{1 \text{ yr}} \frac{10^3 \text{L}}{\text{ML}} = 1.56 \frac{\text{L}}{\text{y}}$

Changed DXYZ to .01 in Z direction

Changed ISYS porosity (V20) to ~~1.56~~ 2.5  
885-1806

pressure 32.9 bars =  $3.29 \times 10^6 \text{ pa}$

changed Courant # in Cpts keyword to 29.5

Time step  
min  $6.94 \times 10^{-4}$   $1 \times 10^{-3}$  max  $1.7 \times 10^{-2}$

figure out correct time step

#6 saved

#7

5/4/06 Adding additional minerals + clays to input files

Need K-feldspar reaction rate -

used Microcline - B reaction - for Max Microcline in  $M_{0.1}H_{0.6}$

Error - possible skip reaction -  $i(\text{amci}) = 3 \text{ cal}^{-1}$

Add AL as primary dependent on mineral anorthite/albite

Another error  $\text{Fe}^{+3}$ ,  $\text{Fe}^{+2}$  dependent on smectite

# 7

Saved

IF you delete all Al bearing minerals that error gone,

Start file #7, delete smectite +  $\text{Fe}^{+3}$ ,  $\text{Fe}^{+2}$ , none of the other starter minerals contain Fe, nor is it (Fe) part of the initial pore water chemistry.

Problem ran w/ no problems (AL - error message doesn't apply after smectite deleted). No Tridimite errors either ran in 6 seconds.

Changed time steps to 3 steps

$10^{-4}$   $10^{-2}$ , 0.5 days to see how long the run takes to get to 1 day - about 1.5 minutes to 5 days. another minute, 10 yrs about 30 minutes total run  $\Rightarrow$  51 minutes

When to file dem1-A - Qtz - Alkaline, which is same as #5, Alkaline composition, then made changes so it would match file #6 porosity, surface area etc. pg 51. Changed time steps to match file #7.  $\rightarrow$

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2006

Ran file with only 5 time printouts lead up to 1 day took 14.5 minutes

First to this file had to add  $\text{K}^+$  as dependant on Sylvite and also added to DEM1-CC.

DEM1-CC 4 min

DEM1-N 7 seconds

- Add correct secondary species to All Qtz + Tuff files  
OK Qtz + all 3 files ran. excluding  $\text{NO}_2^-$  species

- Updating Tuff files - error before secondary species updated  
Maximum CGstab Restart Exceeded, Stopping  
Watsoir - check problem formulation - for DEM1-IA

- After updating - DEM1-TN worked - still have Add some more secondary files, also DEM1-TCC works OK -

- ~~#7~~ DEM1-TN + DEM1-TCC work after 2nd species added.

To fix DEM1-IA, I copied DEM1-TCC and just changed the chemistry, works OK, possible another corrupt character?

Change out pot time to 40 days Qtz

88

5/5/06 Alkaline tuff file for 40 days run in 48.5 min  
CaCl - ran 14 min  
Nuehal ran - 1.5 hrs

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5/5/06 Also use  $300 \frac{\text{cm}^2}{g}$  as Surface Area total - 1

§ Cristobalite  $44.49\%$  of  $300 = 133.47 \frac{\text{cm}^2}{g} \cdot 2.27 \frac{\text{g}}{\text{cm}^3} = 302.98$

Quartz  $15.07\%$  of  $300 = 45.21 \frac{\text{cm}^2}{g} \cdot 2.65 \frac{\text{g}}{\text{cm}^3} = 119.81 \frac{\text{cm}^2}{\text{cm}^3}$

K-Feldspar  $22.94\%$  of  $300 = 68.82 \frac{\text{cm}^2}{g} \cdot 2.56 \frac{\text{g}}{\text{cm}^3} = 176.18 \frac{\text{cm}^2}{\text{cm}^3}$

Albite -  $16.94\%$  of  $300 = 50.82 \frac{\text{cm}^2}{g} \cdot 2.62 \frac{\text{g}}{\text{cm}^3} = 133.15$

Anorthite -  $0.57$  of  $300 = 1.71 \frac{\text{cm}^2}{g} \cdot 2.73 \frac{\text{g}}{\text{cm}^3} = 4.67$

\* most of densities are from webmineral.com

Add above to toff problems

- Find tortuosity values to add to files

- Fix input file. Gt stopped at time step fire

\* Back to all files start with Dem1\_7, #7, try to add BRKP datablock, decrease output 5 points 1 day being longest. - wait for printout info.

- don't see benefit of this keyword.

leave tortuosity way it is, for now

5/8/06 PA 38-39

initial entry in Molality  $\frac{\text{moles of solute}}{\text{Kg Solvent}}$   
 H<sub>2</sub>O density @ 25° 997.0479

Molality ≠ density

5/8/06 Try to Make a single Continuum Run.

Non-isothermal conditions are specified in the Equilibration keyword of the meta file. Temperature is specified at depth (in meters) include a temp gradient [°C/m].  
 Make sure Bcon specifies the same temp sequence.

Make sure grid geometry in both gem + meta files ungem. delete double species entries

§ Try to Add BRKP + Make single Continuum - error Messages  
 Changed Grid XYZ, deleted lower boundary - still problems Gem file.

5/8/06 Start over with new file #7, Add BRKP Keyword - runs

Even though the keyword BRKP didn't create proper output file saved run as #8 - file error - even when I copy working #7 and change the name to #8 in the folder marked 1-D202, created a file error as corrupted file.

— Copied over old file and will begin there -

To Make Single Continuum Meta/Gem Files

- Change Grid keyword both files to XYZ
- Skip DEM Parameters both files
- Meta delete 2nd set of boundary conditions
- Gem delete 2nd set of Ag species 3 times, Careful leaving two periods after first set.

§ Run single Continuum with new MultiFlo.exe works - NO problem

5/11/06 Tried to put keyword BRKP in different locations in input file to see if it would produce the proper output - Using updated windows version of MultiFlo Scott Painter Sent. Did not work

5/12 use cztz-cact file to alter to match Meta file.

- Changed all pertinent parameters / keywords
- Grid
- option - isurf and fact = 1, ACounr to 5000
- iplot + whatever you want for output
- BRKP -
- isystem - coupled program reads porosity etc from Meta
- DXYZ cell block sizes
- Comp IJK parameters 1, 12 1, 124
- Bcon ifact to #3top, temp #25 to match Meta
- Bcon upper + lower boundaries
- Time to match Meta

\* 5/13/06 Change Mineral boundaries (lines) to match  
\* keeps getting hung up on DXYZ time -  
made change tried to make all x+z cells 1 size  
tried inputting . for spacers, tried using

Converted 6 (cztz-tuff) files to single continuum  
No problems.

5/15/06 Matching .IMP file w/ Chandrikes Meta Sand file  
- start over - With fresh file, made changes (as seen pg 56) with the exception of BRKP. To get nodes specified in IET1.dat, use position #

BRKP  
6/1/06 also moved Pxyz data block - (simplified)  
6/1/06 to a little later in the input file.  
6/1/2006 Still getting error  
6/1/24/06

Also changed time keyword to match that of the example in the Manual -  
Stopped giving DXYZ error - now just states 9 errors in input file. I think its with the time - NO

Changed time parameters (low time entries) Got same Error message "9 errors in input data"

\* Error in Mineral Boundary Conditions - fixed it.

hanfiles message "Singular Matrix [had comp] press enter to continue" had to keep pressing enter. til there is an error -  
Geom output file is very odd - Now taking up most lines in file.

Try again when Code eroked  $\Rightarrow h = -nan$  and  
\* ionic strength negative 40 -1.6 1124  
\* excessive iterations in ionic strength loop"

Try to replace DXYZ with correct cell sizes, instead of Copy/Pasting entire Block just lines X,Z - run the problem - DXYZ Block not problem ↑ continues error mentioned above.

5/15/06 Tried with another saved file IETemp. Once the mineral boundaries are corrected (?), the file then becomes corrupt (negative strength).

Changed xyz parameters on the 9 minerals, still got the same error message

Changed back I print (under Grid) to 1  
K<sup>+</sup> initial value 1e-6 or 1e-10

Porosity in Metra changed to .2  
So, Rock Abundance 1-.2 = .8

Changed tact (opts) back to 0

5/16/06 ran Ca-Cl gtz single continuum w/ Chandruka's Metra file  
over night - Program calculated correctly for the

first 2 of 15 time points - at #2, received iteration error  
mex iter i half delt 1238 .200 0 0.9122e<sup>+4</sup>

line repeats with different values until program  
crashed -

The metra output file doesn't list an error it just  
quit - this process froze my computer up.

ran program with Alkaline file

After 40 minutes had to abort run - wanted to test the  
Neutral file. After 40 min, the Alkaline run had gotten to

step 9 - output time step. Will run overnight to see if  
file corrupts - or calculation error occurs.

5/15/06 Neutral  
Ran ~~Neutral~~ file DCML10, After 3 minutes file produced output  
up to time step number 5.

Still haven't changed file names to reflect single continuum

5/16/06 ~~After 3 min~~ Convert tough react mineral reaction rates  
from mol/m<sup>2</sup>sec to mol/cm<sup>2</sup>sec by multiplying by 1e-4 to put in MultiFlo

Put the Cournt option (under OPTS) back to 500 000

After these changes I ran 3

Neutral file - no errors in less than 1 minute

Alkaline file - no errors in about 4 minutes

Ca-Cl file - no errors in less than 2 minutes

Checked input details, X15 for correct porosity

Q<sub>g</sub> = saturated moisture content, = porosity - insaturated zones

Sand .43 so Quartz Abundance = .57

May change in the input files

8

5/17/06 change in all input files <sup>to 5/17</sup> to show SiO<sub>2</sub>(aq) as  
#7 I4yoc, with a very small concentration

Change (metra - correct Dxyz) All cells .05 x .05 meters  
change porosity in metra to .43.

then make changes in my chem file Qtz abundance .57  
these changes should allow % of Qtz to change as it  
dissolves / precipitates

NOTE: Dxyz should look the same in Metra + Chem

All files seem to run - will let them run to  
completion soon - to look for errors.

5/17/06

most create Pure file, no species in solution except water. Works fine - 4 secondary minerals, Qtz, SiO<sub>2</sub> am, Tridymite, and Cristobacite.

5/18/06 ran the pure water test once allowing all secondary minerals to precipitate, once prohibiting all secondary minerals. The results were the same.

Preparing tuff input files to run with Meta input file. (Meta needs changes also - Thermal prop and Porosity) as is, so will use the 12.24 grid and the current porosity. Making many of the changes on pages 58-59. Allowing all secondary minerals to precipitate.

-Change to All same values for the thermal and PCKR as the Ptn 25 tough cl took from Multiflo XP acceptance test

Get error maximum <sup>85-18</sup> number of tries exceeded. Some parameters are rusty off.

For any Primary species with a zero change type to 7, and concentration to 1e-10.

Tuff alkaline - error exceeds iterations, neutral and the Ca-Cl tuff seem to run, but take a while - will let me over night to see what happens.

Qtz files run 3 types with mineral precip on and off to see if there are any changes

2

5/19/06

Ran Tuff CC (Ca-Cl) allowing all solids to precipitate. Run goes to completion in 20 minutes. Running same file with ~~not~~ letting anything precipitate.

Ran Qtz alkaline file 2 times, allowing and prohibiting precipitation in both files porosity changes match and so do the volume changes. The <sup>85-19</sup> aqueous species changes are the same in both files, the numbers may be slightly different when you look at the ten-thousands place.

Re-ran the other 2 files (Qtz-neutral / Ca-Cl).

See change porosity and Qtz volume in alkaline and Ca-Cl files only - there is no change in the neutral file. However, in the neutral file the amount of ~~SiO<sub>2</sub> am~~ <sup>85-19</sup> SiO<sub>2</sub> am increases, and the SiO<sub>2</sub> dependent secondary species increase (actually show same value for both).

Ran Qtz alkaline as ambient (no heat source) at 20°C and 90°C to look at differences porosity etc

8

5/22/06 Running All Qtz files Pure, Neutral, alkaline, Ca-Cl at 20 and 90 degrees - All in separate folders under D:\Multiflo\Metal\ambient. For all these files the heat source was included by skipping the section in the Meta file. Created excess spreadsheet named Ambient porosity that pull information on porosity, Qtz volume, SiO<sub>2</sub> concentration for all water types at the 2 ambient temperatures.



5/22/06 took results from 5/19 (page 61) and put them into table form, excel file porosity  
 under D:\Multifid\Meta\Qtz  
 3 excel Files 1 for Volume Qtz, Porosity,  $SiO_2$  Concentration in D:\Multifid\Meta\Tuff.

5/23/06 Ran Qtz Runs without vapor pressure lowering. All three files had the same relative humidity values (=1) with and without vapor pressure lowering

Note: excel can't find way to plot depth on the y-axis.

Back to Tuff Single Continuum. Changed various parameters - no luck running it. So I took Ca-Cl file saved as another name and copied in the alkaline chemistry. This did not work.

6/22/06 Trying to create a pore file for Tuff, by skipping the water chemistry, which would indicate a pure water system. The Secondary, Gases, and unneeded minerals from the MNR and MWIR list should be skipped. This leaves the 5 mineral that are to comprise the Tuff Cristobalite, quartz, anorthite, k-span, and albite-low. Moving keyword skip around (before + after headers), keep getting error message

possibly skip reaction inam(i)=2h+

Continued on -- page 63

toughreact 6/2

6/22/06 worked on getting Tuff-alkaline Single Continuum to work. Made changes, restarted w/ original file, couldn't get file to converge - it quits after 17 iterations. Changing the max iterations only made ~~it~~ it take longer to fail.

6/23/06 started with the Qtz pore file and added the proper minerals - Albite-low, Anorthite, and K-span. However, got the error message inam(i)=2h+, so I had to enter a pH of 7. Kept ~~it~~ getting same error for different elements so I had to add insignificant amounts of  $K^+$ ,  $Ca^{+2}$ ,  $Na^+$ ,  $Al^{+3}$  to the initial input file. It failed after the 7<sup>th</sup> time step, computer began to run physical dump - may be because I had other files and programs open.

Try to create Ambient Qtz - run w/ a pH of 7 at 25°  
 could not get file to recreate the results that Sim Meyers got using toughreact. Went over file and changed the rate, didn't work, divided rate by 12 (x=12 cells) like you have to with toughreact, didn't work, sat down with Sim looking at various parameters couldn't get it to work - noticed the INIT (initial input) was wrong.

The file IETI.int gives the program the initial conditions Temp, gas saturation - so you can either change that file or have INIT be read from the input meta file.

6/28/06 I changed the Meta file to allow the initial conditions to be read directly from the file. Even with this change I didn't get the same results as <sup>5/6/06</sup> with toughreact. The trend improved. Saturating gas started at .99, liquid at .01, and the liquid saturation increased way beyond Toughreact results. I changed various parameters, rate, sweat-keyword, and checked the file against Chandrika's initial input excel spreadsheet, all parameters entered were OK, and the results of varying the numbers (of the various parameters) made no further improvement.

§  
7/6/06

Fixed INIT file in the Tuft Pore water file, but computer still began physical dump. Also fixed some inconsistencies with input file, but still failed

TO Fix INIT problem so keyword is read from the meta file not separate INIT file

1) put % in front of first line of INIT IET1

2) Remove % from the next line of INIT

3) Make sure there is no % in front of the information lines.

§

§ 7/6/06

~~Toughreact~~ § 6/2/06

Example problem #4 6/2/06 §

7/17/06

Jim Myers sent a spreadsheet with the input parameters for the Ambient Gtz problem, I entered the same parameters into the spreadsheet used in the IET1.dat file and there are a few discrepancies. Most notably was the residual moisture content in Chandrika's input Details.xls <sup>7/17/06</sup> In the IET1.dat the <sup>7/17/06</sup> residual moisture was entered as .045, however it may be  $.045 / .43$  where .43 is the Saturated Moisture Content = porosity

§

7/24/06 Jim gave me a new GBC value =  $1.93e^{-5}$  §

7/28/06 Tried running all ambient runs at 25 and 90 degrees for the 4 water types with the initial Quartz problem (Alkaline, Pore, Neutral, and Ca-Cl). I changed the proper parameters (GBC, residual moisture) and began runs. Having problem with runs freezing up. §

§ 7/31/06

7/31/06 -

Continue to run updated Quartz ambient files, had to manually turn off computer a few times because it was going through a physical dump. Most files completed successfully.

§



8/11/06 Finished running last of the Quartz ambient files successfully with few problems (errors and shutdowns)  
LS

8/11/06

Copied the files Tim Myers used to create the ambient quartz run in toughreact and copied them onto my computer (D: toughreact\quartz). I modified the chemistry to create the various water compositions mentioned (7/28/06). However, because CO<sub>3</sub><sup>2-</sup> isn't a primary species, it couldn't be added to the initial composition, so it had to be recalculated as HCO<sub>3</sub><sup>-</sup> and added to the existing concentration of that species. A few minor changes to the chemical files and the runs were completed and ready for comparison.  
LS

8/10/06 - Multiflo files -

8/10/06

Changing the four input files (for chemistry) to reflect that the water is passing through toff rock. First changed the chemical input file, keep getting error messages like Na<sup>+</sup> is not in the database (ther\_ymprNa.dat) even though I also tried to use the thermK1.01.dat and will have to set up the problem differently.  
LS

8/13/06 Multiflo files -

Changing the Flow file for Toff rocks -

Looking up various parameters. At this point I'm not sure what to use other than the (Someg) and LS

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8/13/06 the values from the Multiflo run I had set up previously. Also, try to switch database and double check input files for initial species. Still getting error messages, it has to do with initial species not being complete, meaning there's no a<sub>l</sub>O<sub>2</sub><sup>-</sup>, but an initial was specified, so very dilute concentration need to be added to the initial Primary Species.  
LS

8/30/06

At toff = 42.5% porosity, these are the surface area calculations  
300 cm<sup>2</sup> as surface area total or as listed below.

* Cristobalite	25.58% of 300	= 76.74 cm <sup>2</sup>	• 2.27 g/cm <sup>3</sup>	= 174.2	1 cm
	542	8		314.72	
* Quartz	8.66% of 300	= 25.98 cm <sup>2</sup>	• 2.65 g/cm <sup>3</sup>	= 68.85	1 cm
	542	8		124.38	
* K-Feldspar	13.19% of 300	= 39.57 cm <sup>2</sup>	• 2.56 g/cm <sup>3</sup>	= 101.3	1 cm
	1086	8		366.703	
* Albite	9.14% of 300	= 27.42 cm <sup>2</sup>	• 2.62 g/cm <sup>3</sup>	= 76.56	1 cm
	795	8		202.87	
* Anorthite	0.33% of 300	= 0.99 cm <sup>2</sup>	• 2.73 g/cm <sup>3</sup>	= 2.703	1 cm
	950	8		8.56	

\* - surface area from Johnson et al. 1998  
% add up to 57.5

8/31/06

Using the information from input\_toff folder and quartz data from Chandrika to put together a list of parameters for the toff runs.  
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8/31/06 cont. Multiflo Runs -

Try to run the pore water TUFF example @ 25°C, however a kind of the way through the file encountered an error and disrupted the run. Some parameters will be changed in order to make the file run properly. The error message only states that the maximum number of tries was exceeded.

§§

9/1/06 Multiflo Runs

fixed the SA of minerals in the 25°C pore toff example and changed some parameters according to the list that was compiled - The problem was run again, and also failed due to the same error.

§§

9/5/06 Multiflo<sup>5500</sup> Runs

I changed the file back manually, changing each parameter to what it had been previously, one by one - while rerunning the file to see where the error was coming from. However the file kept receiving errors when it was run. May have to recreate New Pore water - toff file.

§§

9/6/06 Multiflo - Runs

Started with original Meta file and updated the file to reflect desired input file. I had various errors occur, so I then copied the Quartz pore water file, and I know that file works, so I updated it for the toff run.

§§

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9/7/06 Multiflo Runs

Ran the neutral and Ca-Cl toff problems, with little to no problems after the files were updated with the proper toff parameters I wanted to use. The alkaline file appeared to be corrupted, so I took the Quartz-alkaline file and updated it with the toff information. The file appears to run, however it may need to be run overnight because after 20 minutes it still had not produced the first set of output data. The pore and alkaline files need to be run overnight, and then we'll see if they can go to completion.

§§

- Tough react runs

I had been taking the Quartz Chemical.inp file and altering the file with the data for the toff run. However I will use the toff-input files Jim Myers gave me, however they can't be used as seed files - the information needs to be copied and pasted to the proper files to preserve the mesh that was created by Chandrea.

§§

9/8/06

Tough react runs

- Changed pH value in the pore water Quartz run to a pH=7. Also fixed the Solute and Flow.inp files to include the cell blocks of interest (6, 66, 138, 282), I cut and paste portions of the three inp files from the Johnson et al 98 example into the files I created for the TUFF examples. For some reason the files run but quit within a short time. I also updated the Solute and Flow files in the same manner as I did with the Quartz files, however the files do not run to completion, through trial + error I found it's the Flow.inp file, it has something to do with the rock →

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9/8/06 continued

keyword and the fact it changed it, However, I'm not sure how to fix the problem.

SS

LS 9/11/06

9/11/06 9/11/06

Unsuccessfully I tried to alter the toff flow files to make the run go properly. I also am having problems with the quartz files running to completion. It may be more a computer related problem.

SS

9/12/06

Took the original Quartz <sup>[Toughreact]</sup> files <sup>File 9/12/06</sup> given to me by Jim Meyers and reran it on my own computer and another computer (Lisa Kannel's) and the output was different. I did several runs and my computer exited the program (most likely crashed). However when only the Flow.inp file is changed (a update key is added to the Param keyword) the file or run quits at the same point (see Gasobs.dat) when run on both computers.

SS

9/13/06 For the MULTIFLO toff ambient files, I changed the Minerals and Mineral list section to reflect that of the Johnson et al 98 example given to me by Jim Meyers. I ran all these files on an alternative computer, in which the files ran to completion. However the liquid saturation looks off.

I ran some of the same toughreact files on two separate computers, just to see if the results were the same. My computer couldn't even make it through most of the runs and when it did it quit before the other computer shut off.

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9/14/06 I reran the Multiflow toff files using the mineral assemblage that I had originally used from the header tests. The saturation was also off.

SS

9/18/06

<sup>15</sup> 9/15/06 I used the Multiflo toff files with the Johnson et al 98 mineral ~~assemblage~~ <sup>LS 9/15/06</sup> assemblage and changed a few of the permeability and gas saturations to match those of Toughreact. (permeability in xyz directions). Started new problem and set up the run on an alternative computer.

I also began fixing the toughreact toff files by changing each parameter one by one to match the Johnson et al 98 toff output file.

SS

9/18/06

Continued to rerun the Multiflow toff files changing the permeability and porosity. The files have improved, however the column 2/3rd of the way down still isn't correct, it has to do with the jet.inp file.

I also got the toughreact toff file (alkaline) to run to 100 years however when I add the update keyword to the flow file, this Gasobs file didn't complete to 100 years. I started to update the other files.

SS

9/19/06

For the multiflo runs, however using the other ~~header~~ <sup>LS 9/19/06</sup> mineral assemblage (header test) and also starting altering the permeability and gas saturations to match <sup>SS 9/19/06</sup> those of toughreact. Continue next page

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9/19/06

I continued to alter on redo the tough react toff files, getting them to match Johnson et al 98.

9/20/06

All the tough react runs (hoff) ran till 100 yrs. However their liquid saturation is off of that reported by Multiflow. And yet at this time Multiflow's saturations can't be used with confidence due to the inconsistencies within each column.

9/21/06

Even though Multiflow toff ambient files are not completed to the finished product, I'm trying to alter the initial saturation (gas). After several runs either increasing or decreasing the saturation, I couldn't get similar results to the Multiflow runs.

9/22/06

The Multiflow toff files were altered by running Metra only to allow steady state equilibrium, this information was then cut and pasted into the Metra's int file to see if this fixed the saturation inconsistencies. It did not but should allow the problem to solve quicker.

9/25/06

All files were rerun w/ exception of 1, that took a few days, the files did not improve, the saturation is still off. The next thing is to see if minerals have been precipitating 2/3 of the way down.

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9/26/06

At the zone that's about 2/3, the mineral precip/dissolve is vastly different for certain minerals. The input file needs to be adjusted so there is no false precip/dissolution zones appearing.

10/25/06

Can't figure out why the run has a glitch with the saturation 2/3 of the way down (vertically). The run tips up before a year of calculations is complete so resetting the precip/dissolve patterns of the minerals is not a help. The run must be getting tripped up on a time step limitation or some other specified parameter that is too far off from where it needs to be.

11/21/06

Toughreact files - looking at the saturation after 100 yrs actually is accurately modeled in Toughreact. It is Multiflow (just toff problems) that has an error, error 1 - have incorrect  $\alpha$  RC rate needs to have infiltration rate of  $1.93e^{-5}$ , also the glitch in the bottom 1/3 of MF was due to the heat source not being skipped. The heat was creating a dry out zone, it had nothing to do with precipitation.

LS

11/22/06

All the MF Ambient toff files were rerun with the above ~~corrections~~ corrections and are comparable to those predicted by Toughreact.

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11/22/06

Now that the Ambient runs at 25° for each the Toff and Quartz are comparable between the two codes ~~11-22-06~~ ~~11-22-06~~ though react and Multifio, it is time to add a heat source. I graphed ~~11-22-06~~ ~~11-22-06~~ though react's mesh as is, that is if it is not changed in the future to match an updated MF file. There are 2 cells in MF ~~11-22-06~~ ~~11-22-06~~ X-5 ~~11-22-06~~ ~~11-22-06~~ 2-12 and X-6 2-12 that contain the heat source, in though these cells correspond to 0038 and 0039. Two blocks of data would need to be added to the Gener file for each cell (though folder). The blocks would contain the same info as the MF heat source data block. However, the mesh of MF may change in the near future to more accurately depict adrift. Changes will be made accordingly.  
LS

11/24/06

I took the heat blocks from the Gener file for TP problem #4 and pasted them into the Gener file of the heated Quartz file. I then changed the time step and heat rate info to that found in the MF file from Chandrika. The number of steps/heat terms were changed to reflect the 15 that Chandrika picked. The Gener term was then deleted from the Flow.in file. When run the saturation didn't change at all from the ambient case, for any example run of any water type. The heat term must have been added or the format is wrong or disturbed.  
LS

~~3/19/07~~

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11/27/06

Instead of changing the separate Gener file, I added the heat term to the Flow.in file because the heat really is constant instead of time stepped. This didn't work. I then changed the Flow.in parameter NCP19 to #2 instead of #0 so the file could be run with Treact\_eos4 that allows for vapor pressure lowering. Also blank records needed to be inserted after the Gener and INCON keywords. File still didn't run. So vapor pressure lowering was suppressed, the file did run but didn't show heat variance.  
LS

11/28/06

The results of the test w/ Treact\_eos4 and no vapor pressure lowering ran to completion, however the results were off. Again I cut + pasted data blocks from problem #4 to the actual Gener file. I only changed the heat source data and the file ran but shortly quit before reaching the end time step (this was with heat\_eos3). There was a temperature change, the cell with the heat source got up to 100-500, this I believe is incorrect and a direct result of the fact the heat source was entered as 250 J/s for each cell - gives a combined area an energy level of 500 J/s, not necessarily the level of the overall temperature in the region.  
LS

~~3/5/07~~

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11/29/06

Using treat-eos4, I tried switching some of the options and input variable to allow the run to work with vapor pressure lowering. I didn't have any luck, I also used treat-eos3 to see if various alterations would make the file run with the heat data entered directly into the Flowinp, (Adding 6.0 in places reserved for <sup>LS 11-29-06</sup> unused parameters) this did not work and corrupted the files, so even a run wouldn't complete to the last time step.

LS

11/30/06

I recopied the toughreact files into the heated quartz and toff files. I believe I was naming the heat term incorrect because I added it to the flowinp file with the name HETO1 and the generation rate of 2505/s. The files worked better and showed a more proper heat distribution with the Treat-eos4 model. However, the files didn't complete because not sure what needs to be changed in order to run them with vapor pressure lowering.

For the Multiflo runs the files were failing to converge, so the are options to change the time step parameters. I changed halmx to 20 and <sup>LS 11/30/06</sup> and stepdt = 2. This didn't make the files converge, but there may be a combination of option parameters that will allow convergence. The output file for Gem shows where the program is tripping up. I'll have to do with the mcyt, iter, thalr, and delt parameters. see page 132 (Acrobat) of the manual.

LS

12/1/06

For the toughreact files I changed the System Liquid Sat to reflect that of the results of the ambient runs, and some of the Param options. In treat-eos3 it seems to read the heat generation term as temperature because cell 138 read 300-over 400 degrees, whereas in MF the temperature reached above 100. For various runs the temperature in cell 138 was low as 6°, so something or some parameter is turned on and affecting how the heat term is read, however the files are not completing, except the pure water file and the saturations are off in the outputs.

The Multiflo files were further changed (opts-parameter) including the DtcotF being changed from .5 to .8, while keeping the previous changes. I'm not sure of the results until completion. When the file is manually ended the output file is not properly updated. These runs are taking <sup>12-1-06</sup> a bit of time to run, or fail - exceed the limit of time step changes.

LS

12/4/06

Toose Files

The heater term was renamed correctly, and this took care of the low temperatures that showed up. I realize the temp in the drift will exceed 100, so the previous files were OK going up to 100°, however they are still failing after a short period of time. I had changed the pressure under the Param keyword and then adjusted the boundary pressure under the Incon keyword. Apparently the value used in the Incon was too out of range and prevented the vapor pressure lowering function, also that was changed YPL was able to be used.



11/06/06

Convergence is the real problem. I changed some of the time-step related parameters, this didn't help. I assume the time steps would need to be reduced. This created more iterations to get to the same failure point in the files.

LS

12/11/06

I can not get the heated integrated runs to converge. I believe it's the rocks thermal properties that are causing a problem. The last thing I tried was to copy the rock properties of just the tuff and copy it into the quartz file, basically the results reached were similar to the ones reached in the tuff problem (SI of 000 achieved). However, I'm not sure if the saturation of the other cells is correct, it seems off. I started out by trying to change the rock grain density, formation heat, rock grain specific heat, formation of heat conductivity, and tortuosity of both files then a combination of these parameters (getting qtz to match the tuff). None of these parameters or combination solved the problem. On lines 3 and 4 the IRP 2 (relative permeability functions, and ICP 2 capillary pressure functions had the most effects when altered. If the IRP2 value is 0, the run completes, however, the temperature doesn't rise above 101 and the porosity remains 0.1045-at the lowest value. If the ICP2 is altered at the same time, to a lower #, the saturations lower limit is equal to ICP2 and the temperature reaches above 100, but the file fails quickly. However if an 0 is entered for ICP2 and IRP2 saturation reaches 0 and the file fails before completion. I thought the IRP2 was liq sat times lambda (.63), not sure about the value of ICP. The permeability difference between rocks is affecting the results. There must be some combination of changes, (getting all the above parameters to the correct ones), that will allow convergence. As a note some of the rock properties for tuff were left blank because no value was found in the Johnson 98 materials (formation heat, rock grain specific heat, formation of heat conductivity).

LS 12-11-06

LS

12/12/06

I tried a few more combinations of changes to the thermal properties in the Flow.inp file. This improved the Saturation predictions however the file still failed early in the run.

LS

12/13/06

I basically tried the same method, but with the MultiFlo files, however I ran the tuff pore water with heat and didn't make time step or thermal (rock) properties changes. After 24 hours, the file completed 35 yrs, so I'll leave it another night to finish. I had made changes to the parameters in the timestep and tolerance sections of the Meta file. However due to the long run times it is hard to determine the outcome, especially when the run is manually stopped by hitting Control C.

LS

12/14/06

For the tough react heated runs the solution is hopefully the Rock keyword. On the third and fourth lines, there are various inputs, that I'm not entirely sure what their purpose is, however I altered their values to see the effects. When IRP3 was reduced either 1 or 2 orders of magnitude and the file completed however the temperature did not reach above 100, if the IRP3 is made to be larger the file fails, however the temperature at the point of failure reached 328°. Changing some of the other parameters had little or no effect.

LS



12/14/06

For the multiflo files, we have made changes to some of the tolerances and timesteps so much that the file doesn't even converge at all barely on. Looking at the Dos window you see the time step continually being cut. Possibly we're not changing it enough or in the proper direction.

Also, when we changed some of the time step values, we did so in the gem file, but I believe when doing a fuel model the time step info is read from the meta file. The files will be re-copied from the ambient folder and then fix the heat term in order to re-try some of the runs.

LS

12/15/06

For the Multiflo files I changed the istepdt back to 3 and changed the dtcutf to 0.3 to allow better convergence - All previous option changes did not help.

LS

12/18/06

The toff file by Monday had made it to 64 years, however the Qtz file was <sup>LS 12/18/06</sup> ~~stuck~~ stuck early on. Both files were stopped and the Qtz file had Elypsom and Calcite's reaction constants decreased to  $10^{-10}$  and the dtcutf was reduced to .2. For the toff file the boehmite reaction rate was reduced to  $10^{-10}$ . Both files were started again.

LS

12/15/06  
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12/19/06

MF Files - in less than 24 hours the alkaline toff file has reached 63 years - so I'll let it run. The Alkaline Qtz file caught up before it configures the initial system. I changed the method from 2 to 1 and the concentration maximum change <sup>LS 12/19/06</sup> per step to 5. This did not work.  
LS

12/20/06

MF Files. I changed the method and the iops parameters to various combinations, while set on 1 and 2 for method, and with each iops 0, 1, and 2, none of the runs took off. I changed the method to 3 and the run initiated, however seems to be at a standstill and we'll leave it run overnight.

In order to get the tough react Qtz file to run, I took a look at the problem 4 from the users manual. I extended the run by extending the Param to 9999, I kept the short run time 2.7 years. Inflation was not added and the run completed indicating total dryout in the drift as in the near vicinity, other runs were completed and other areas of the drift were observed.

The rock properties (thermal) of a cell that reached dryout were put into the tough alkaline file and run with one change at a time (for lines 3+4), while the file hasn't completed it did get further along.  
LS

12/21/06

Another run of problem 4 was started with results from cells 1931, 1928, 2189 and 2186 being reported.  
LS -

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12/21/06 toughreact files  
 After the thermal properties for Mwin2 (Rock out) of the example 4 problem were added to the alkaline Qtz wheat, each of the Cap Pressure, CP and relative permeability RP, were changed back to what they were in the original file one by one. The file completed, but never reached Dryout or temps above 125 when CP and RP were changed back to .1045 just how it had with the CP + RP being .1900. Once the CP + RP were changed to .027, the file failed. CP#4 was changed back to 0, and similarly the file completed, but didn't reach high Temp or dry out. When CP#3 changed back, the run fails early on. CP#3 was changed to be an order of magnitude smaller than in Example #4, the problem is still running.

For the Multiflo files - the toff alkaline with heat is still properly running. The heated quartz file was run with a few more variations on the Method, iops, and other OPTS parameters, all with no positive results.

LS

12/21/06

Problem 4 was rerun with different cells to see what are the thermal properties of other cells that experience dryout. It appears that the cells have the same thermal properties, however there are some that came close to dryout and those properties, while different were used in the tough Qtz files. The files can be made to complete. However dryout doesn't occur and temperatures don't go much beyond 100 which seems not plausible. The files in the Multiflo tough folder were able to begin their runs once method 2, opt 1, dtcutf=.5, and change max concentration was increased to 5.

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12/22/06

~~12/23~~

12/26/06

Toughreacts quartz files were tried to run with a trial and error by altering the properties added from problem 4. The files also added the original thermal properties back one at a time, once again the file can complete the 100yr run but it doesn't seem to make sense.

LS

12/27/06

The MF Tuff runs started on the 22 Completed and look plausible. Once again the MF Qtz files failed + were changed with the same trial + error procedure, however because it takes much longer to run and eventually fail its hard to tell what if anything is wrong with a particular run. Different combinations of Methods and optims were used to try to get the file converge.

LS

12/28/06

For the toughreact runs the CP3 was slowly changed looking for the point between completion (temp around 100) and failure (high temps up to 300). When another parameter is adjusted it throws the file off - think its too sensitive to CP values so another parameter must be altered

LS

12/29/06

I went through the tough 2. manual to try and calculate the proper CD + RH parameters and use  $\Delta T_{25-0}^{1.5}$  them in the files. Not sure about equation solutions.

LS

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1/2/07

I incrementally changed CP back to original as reduced RP, the <sup>temp</sup> ~~temp~~ increased, but the file failed and the saturation was higher than expected. I then changed the cwet gPHT and the results were OK. Even using values Problem 4

LS

1/3/07

I went through and compared the inputs for the MF and TR files. MF heated toff worked why so many other failures. I made a chart of the basic input parameters. There are few differences but may be significant (operating systems, thermal properties)

LS

1/4/07

Taking a further look at the rock properties of the two programs input files <sup>1/4/07</sup> I noticed that for MF the Gtz file needed SiO<sub>2</sub>(am) Fkin changed to 1 (to allow precipitation) and MF tough file needs the RK of boehmite changed to .1213e<sup>-11</sup>, and Fkin values of Quartz and Cristobalite changed to 1e<sup>20</sup> as to not allow precipitation. Tough react doesn't list Activation Energies for each mineral but MF does.

LS

1/5/07

The Multiflo files were changed and all Gtz and I toff file were started for the weekend

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1/5/07

For the tough react files, starting with the quantity I thought there was a conversion factor (between <sup>LS 1/5/07</sup> MF units  $\frac{J}{kg \cdot K}$  and tough react  $\frac{J}{m^3 \cdot K}$ ) (between MF thermal properties  $\frac{W}{m \cdot C}$  and tough react  $\frac{W}{m \cdot K}$ ). I went ahead and did a conversion and it turns <sup>LS 1/5/07</sup> out that there is no difference between the two. However, I did a bunch of combinations changing the CP2, CP3, Rock specific heat (CPR) and the thermal conductivities. I did notice if the dry thermal conductivity was increased there is a point where the file completes and the temps up to 340° and had heat transfer. With very low dry conductivity - there was no heat transfer

LS

~~1/8/07~~

1/8/07

All files for MF had either corrupted or slowly progressing, I believe the virtual memory was overloaded. I began to slip minerals in the MF tough file to see where the error occurred.

LS

1/11/07

Yesterday I restarted the <sup>pure 1/11/07</sup> heated Gtz and alkaline runs. Overnight the pure run completed, while the alkaline run failed. I altered the method + opt parameters and decided after viewing the runs to allow it to continue with method 2 option 2. However the run had to be stopped because it was affecting my computer's performance

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1/12/07  
 Looking at the <sup>IS 1/12/07</sup> ~~output~~ input files the activation energies in the original Johnson Tuff file are different from what's in MF, and yet even different from the Johnson et al 98 paper, and the toughreact manual.  
 IS

1/15/07  
 The toughreact toff (heated) files were altered according to table 3 of the Johnson et al 1998 paper, among the values used for the following short list (Paragonite, Pyrophyllite, Gibbsite, Diaspore, Beehmite) and the rest from page 115, Table 8.7.3 from the toughreact manual for the list quartz, Cristobalite, k-spar, albite, Anorthite, Kaolinite, Muscovite and Silica (Am).  
 IS

Back to the Rock Specific Heat and Thermal Conductivities (wet + Dry). I found a few web pages that reported similar values Johnson used in the Quartz sand experiment ([www.Hukseflux.com/thermal%20conductivity/thermal.htm](http://www.Hukseflux.com/thermal%20conductivity/thermal.htm)). I also found values for the toff rocks which according to Johnson should be unit  $TS_{wz} = TPTD = \text{Topopah Springs phenocryst poor Seritified toff}$ .  $TS_{wz}$  has average of 2.23 per is wet conductivity (w/m) found in a Sandia report (San D 95-1955). The mean dry conductivity in this paper is 1.50 (<math>2/100^\circ\text{C}</math>) and 1.59 (>math>100^\circ\text{C}</math>). The rock specific heat capacity is about 900-930 J/kg-k. The files will be updated accordingly.  
 IS

3/5/07  
 SS

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1/16/07 toughreact  
 After the files were started, I noticed the second line in the Rock properties (of Flow file) didn't line up properly. However, all but the pore completed, so I went back in the Flow.inp files and adjusted line 2 (tortuosity) so it properly lined up and was read correctly. These files were run and they took much longer, but there was a exhibited heat transfer. Only the pore Tuff file failed.  $CP2 = 0$  and  $CP3 = 1.58e^{-4}$  and  $CP4 = 1.e^{-7}$ . The pore file was further adjusted and  $RH5$  was changed to 1,  $CP2$  remained 0 and  $CP3$  was changed to  $545e^{-4}$ , this ~~file~~ also failed. The other files reached a temperature of a little more than 100. More modification is needed. Also for the toughreact tough files I noticed that Johnson's input Flow file had  $NAD=1$ , under the rock parameter and lines 3H were absent, I made a separate folder and copied the files to alter them to look more like Johnson. These files failed immediately because setting  $NAD=1$ , tells the program to ignore the defaults for the rock parameter and to read a separate file, I do not see one included in Johnson's folder.  
 IS

1/18/07 Multifo  
 I made changes to the chemistry of the heated Gtz files, all elements added in minor amounts (due to possibility that minerals w/ those elements may dissolve - future runs) were changed to a type 7 instead of type 3.  
 SS

3/5/07  
 SS

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1/30/07

I took the  $Q_{Tz}(SiO_2(AM))$  rk value at  $25^\circ$  from tough react problem #4, but had to decrease it an order of magnitude for the pure water run. The run completed, but actually nothing really occurred because the reaction rate was so small. At Scott's suggestion, the Source output for the heat may be set too high and interfering with the ability of the runs to complete. So I ran all four water types starting with low WATTS and increased the value until a temperature of around  $150^\circ$  was reached near the source to achieve some dryout. This method worked and allowed the Pore file to complete. The CC-file also is working. RK set to original  
LS-value 1/30-07

1/31/07

I continued to use the above method, some of the chemistries used less heat source (value) to achieve dryout of some sort. The runs are really quick.  
JS

2/1/07

\*\*\*

There is a slightly different file set up due to the experimental apparatus. The new  $x = .5m, y = 1.7m$  and the  $dx = .01$ , the heat source is in the center of the apparatus, and there are various probes placed around that are defined in a file named sensor locations, the thermal and chemical properties are in a file named input details. These will all be included with the final report. The sides of the bench top will be lined with heaters  
JS

2/1/07

The Upper Boundary Condition should be a 5 (mix air and water), the lower a 6 (Free drainage) the ~~side~~<sup>LS 2/1/07</sup> sides should be a 1 (Dirichlet (constant field variables)) because the sides should remain a constant temperature to reflect the heaters on the sides of the benchmark model. Not sure if PBC should be 0 or atmospheric, I tried both ways and the one with PBC=0 is extremely slow. I ran both ways as ambient cases so I can cut and paste the initial condition information into the IETL.Int file to allow the run to complete faster. I copied all the files to do a run polling information from the left and right sides to see if a constant temperature was maintained. JS

2/2/07

The file that specified a PBC had the temperature set to  $25^\circ$  and the heat source was used. The sides of the Cell Block varied greatly in temperature ~~JS~~<sup>2/2/07</sup> so the temperature of the left + right sides was increased to 60, leaving Top + Bottom at  $25^\circ$  with the heat source on. Well however I'm entering the information is incorrect the sides started at  $25^\circ$  at the top and increased downwards. The temperature of the whole system were ~~was~~<sup>LS 2/1/07</sup> set to 60 as ambient, run, to cut + paste the initial conditions, this file will run over the weekend. The file that specified PBC=0 is incredibly slow despite cutting and pasting the initial values. This run was set to run on UNIX because UNIX is faster. However Texas is down and I'm not properly set up in Cypote to access SPainter's Spock folder. A run was set and ~~run~~<sup>to LS 2/2</sup> all weekend, one with the heat source recording various cells throughout the mesh, and a side test, one that polls data for the sides only. (The temperature was set to  $25^\circ$  and the heat source was ~~was~~<sup>LS 2/2-07</sup> used.)  
JS



2/5/07

The run PBC=atm completed however showed temperature variance 60-70°, However does this mean that there is heat loss or that the sides are affected by the heat source or is the whole system losing heat out the sides? A few more various trials were run with no success (various temperature scenarios). The PBC=0 runs didn't get past 1 year (the small weekend); the files were stopped and also showed temperature variance at the sides. The system temp was altered in the same fashion as for PBC=Atm, this didn't improve the results. Not sure what PBC=0 exactly does?

KS

2/6/07

PBC=0 means heat may conduct, but liquid can't diffuse. PBC=0 didn't work, PBC=-1 gave the desired results. We now need to decide on a PBC value, and heat capacity. Basically what we want to achieve. Also lowered Gas Sat .5, Lig Sat .5. I began altering the pore water gem file. Questions to look into. core tortuosity-different in the 2 input files. What to use Ag diff Coefficient and the Lg and gas Flow velocities. The gem file is running without a heat source, however the porosity looks off.

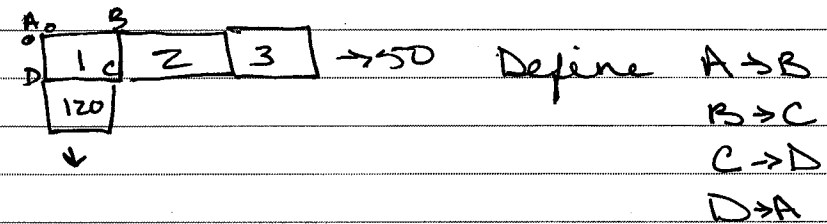
KS

2/7/07

I made a few more changes to gem; under Solv - detail changed to 1 and Method 2 opt 2 was selected. KS → continue next page

2/7/07

The gem file is running and I tried to check the results with the Mathematica Notebooks, however the Segment file needs to be formatted to this particular structured mesh (notebook → unstructured). I started an excel spreadsheet 2/6/07 and its formatted as 4 vectors and in in the order 1-600, so the four nodes at each corner must be specified in a sequential order all in the same order.



First 4 columns are the 4 vectors for the two nodes, 5th column 0.0 (null), 6th cell #, 7th 0 (null). Note if a cell is defined in excel as \$A\$# + formula# you can not drag the formula and have the sequence continue. However once the Segment file was completed it still didn't work because the headers in the gem file are not formatted for Mathematica's Notebooks (created by Spainter). They are formatted to tecplot.

KS

2/8/07

I checked the volume fraction, (Qtz) using 300cm<sup>3</sup>/g = 79.5 %cm. The ? is, VF is it 1 (Qtz only mineral and VF's add to 1 usually) or .57 (porosity .43). Continue Next page

KS

2/8/07 cont'

When 1 is used for VF, the vol of Qtz = 1, and porosity is  $1e^{-3}$ . If .57 is used for the VF the vol of Qtz is .57 and porosity = .43. This makes more sense, but by definition  $VF \phi_{Qtz} = 1$ , but in my old files it also used .57. I created a separate heat source for gem, but decided to just run it as a coupled run with completed Meta file (Ambient)

\* Note: The # of cells defined in BC of Meta + Gem must match

- Initially the  $\phi_{BC}$  was distributed over 2 cells in this version I changed the  $\phi_{BC}$  to distribute across the top, by changing Area to .5 in the input details (hydro sheet) in excel. The coupled run completed without error - but the Qtz totally dissolved + Porosity = 1. I made several runs with minor changes nothing worked except the last change - which is a mistake.

- 1) Changed VF  $SiO_2$  (am) to .001 to seed precipitation
  - 2) Speed up  $SiO_2$  (am) reaction constant (rk) value 1 order mag
  - 3) Changed my  $\phi_{BC}$  to distribute over 3 cells (24-26)
  - 4) Ran coupled run with heat <sup>speed up</sup> ~~speed~~ reactions
  - 5) Reduced Rk of Qtz several orders of mag (3) all w/ heat
  - 6) A liquid velocity - noticed effects, but not fixed
  - 7) increased  $\Delta Conc. dt$  of Qtz to 5
  - 8) increased All  $SiO_2$  mineral rk an order of magnitude
  - 9) Decreased the  $\phi_{BC}$  2-orders of mag
  - \* 10) ran Mineral section of Gem I noticed I didn't change the IJK values to 50 1120.
- This run worked - show full range Qtz - Change All Rk back  
 \* - Work continued in notebook 797 863E LS

3/19/07

\* Note:

Project was to be continued in notebook

797, However due to possible continuation and Activity of other projects in Notebook 797, the integrated Multiflo project will be continued in the Electronic Format in 863E. Any Entries that were made in 797 were scanned and made part of 863E.

LS



## ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 762

<b>Document Date:</b>	12/23/2005
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<b>Data Sensitivity:</b>	<input checked="" type="checkbox"/> "Non-Sensitive" <input type="checkbox"/> Sensitive <input type="checkbox"/> "Non-Sensitive - Copyright" <input type="checkbox"/> Sensitive - Copyright
<b>Date Generated:</b>	06/02/1998
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<b>File Types:</b> (.exe, .bat, .zip, etc.)	Various
<b>Remarks:</b> (computer runs, etc.)	Media contains: Data run outputs and validations



# GEOSCIENCES AND ENGINEERING DIVISION

## SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No. 762 Project Numbers: 20. 06002. 01. 212

### Accomplished

- 1. Initial entries per QAP-001
- 2. Dating of entries
- 3. Corrections (crossed out, one line through w/initials/date)
- 4. No White out used
- 5. Page number visible on copy or original notebook
- 6. In process entries per QAP-001
- 7. Figure information present
- 8. Text readable
- N/A 9. Copyrighted material is identified
- 10. Permanent ink or type only
- 11. Signing of entries (not required on each page)
- 12. Electronic media in the scientific notebook properly labeled
- 13. NRC Supplementary Scientific Notebook Questions are addressed.
- 14. The independent, two person verification required by AP-019, Section 5.2.1.2(b) is complete

Any discrepancies must be resolved before notebook closeout.

I have reviewed this scientific notebook and find it in agreement with QAP-001.

E.C. [Signature]  
Manager's Signature

7/2/2007  
Date

Attach this completed form to the last page of the notebook.