SCIENTIFIC NOTEBOOK

767E

By

Konstantinos C. Makris

Environmental Geochemistry Laboratory, Earth and Environmental Science,
University of Texas, San Antonio, Texas

INITIAL ENTRIES

Scientific Notebook:	#767E
Issued to:	K.C. Makris
Issue Date:	January 23, 2006
Account Number:	20.06002.01.222
Title:	GWB Chemical Modeling of the Constrained Chemical Environment inside a Nuclear Waste Package
Objective:	This scientific notebook will document K.C. Makris' work on chemical modeling of fuel waste corrosion products to understand aqueous and surface chemistry.

This notebook will document activities conducted by Konstantinos Makris, Dibyendu Sarkar and Saurabh Sharma from the Univ. of Texas, San Antonio. Specifically, we will be performing chemical calculations of corrosion (degradation) of carbon steel and glass wastes in a typical Yucca Mountain groundwater chemical composition at elevated temperatures (60 and 90 C). Results will be compared with published data in the TBD07 In-Package environment Report. Finally, our modeling calculations will be fit to actual experimental data obtained by the staff of SWRI (Xixua He).

We will use GWB Standard Version 6.0 in the following sequence:

1. Calculate water chemistry and mass of solid products precipitated as the system is allowed to reach equilibrium using GWB codes.
2. Calculate effects of reaction time on pH evolution of A516 carbon steel and SRL EA glass corrosion in J-13 water at 60 and 90 C.

3. Perform comparative analyses with DOE process model results and performance assessment abstractions.

Mode of Approach to the SWRI Scope of Work

1. Get familiar with GWB software and its chemical modeling capabilities
2. Set up the objectives of the project which are the following:
   i. Calculate water chemistry and mass of solid products precipitated as the system is allowed to reach equilibrium using GWB codes.
   ii. Calculate effects of reaction time on pH evolution of A516 carbon steel and SRL EA glass corrosion in J-13 water at 60 and 90 C.
   iii. Perform comparative analyses with DOE process model results and performance assessment abstractions.

3. Get the experimental data from the SWRI staff that describes corrosion of carbon steel and glass wastes at different temperatures as a function of reaction time in a typical well-water of Yucca mountain area.
4. Get the oxide composition of the wastes from the In-Package Chemistry Abstraction report assuming an initial weight of waste used in the actual experiments (16.94 g).
5. Attempt to put degradation rate constants for the wastes as defined by their corresponding oxide content.
6. Regulate fugacity of carbon dioxide.
5. Input the well-water composition into the REACT-GWB aqueous phase set-up window. Do the same for the 2 wastes by using their respective oxide components.
6. Set up the temperature and the reaction time using REACT-GWB.
7. Run the simulations, and attempt to fit the experimental data to the simulated (pH as a function of reaction time) model.

Phase I was allotted to learning the GWB software and doing preliminary simulations with experimental data obtained from the SWRI staff. We also developed the mode of approach to the SWRI scope of work. The requested amount of money for Phase I of the project is allocated as shown below:

Phase I	$ hour^{-1}	# hours	Expected bill
Sarkar	68	20	$1,365
Makris	25	160	$4,000
Sharma	25	120	$3,000

Total amount requested			**$8,365**

January 29, 2006

The dissolution of high-level radioactive waste glass, which contains high concentrations of sodium and potassium, could generate an alkaline condition by releasing alkalis (Na^+, K^+, or Ca^{2+}) into solution:
$Glass{-}Na^+ + H^+ \rightarrow Na^+ + Glass{-}H^+$ (Eq. 3-1).
In contrast, the Carbon Steel Type A516, which contains elemental sulfur, is a strong acid generator: $Metal{-}S + H_2O + 3/2O_2 \rightarrow SO_4^{2-} + 2H^+ + Metal^+$

Metal corrosion proceeds initially by the direct oxidation of reduced constituents (iron, aluminum, chromium, etc.) to form a coating of metal hydroxides that can slow the further access of water and oxygen to the dissolving metal surface.

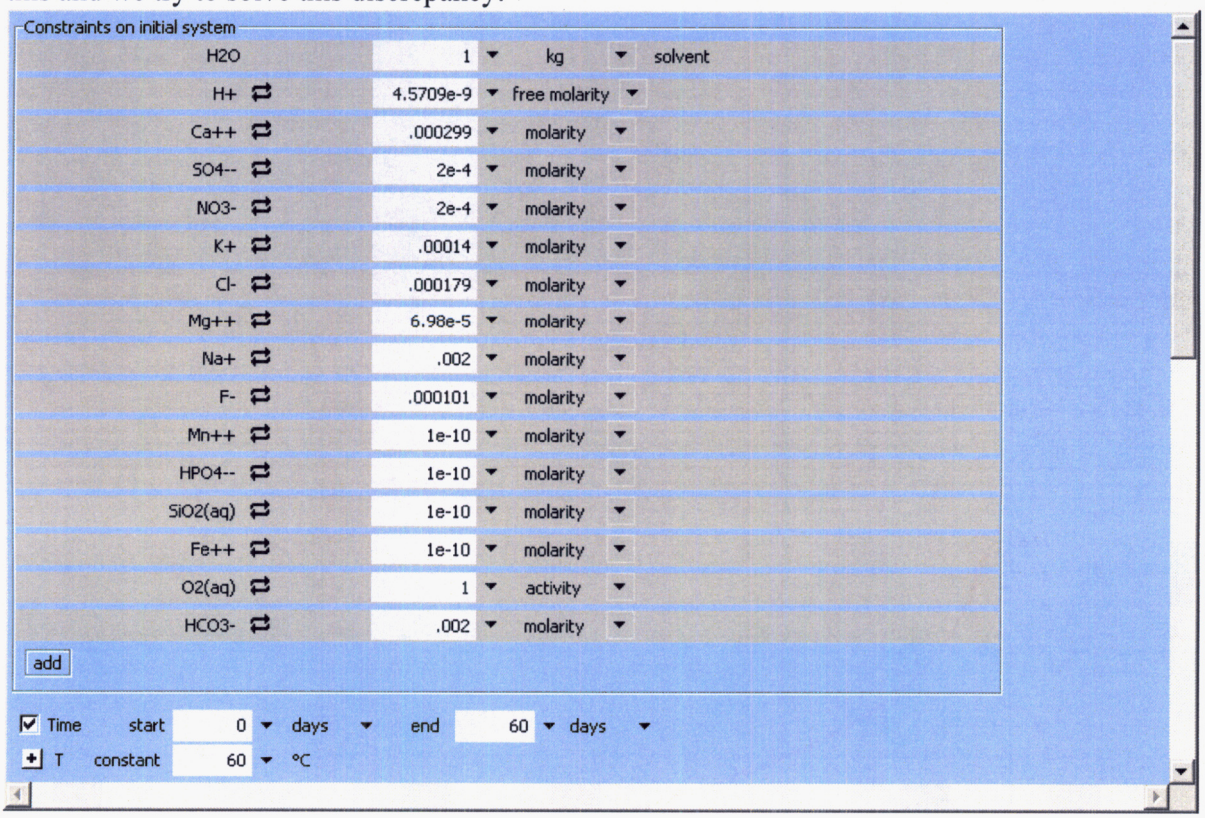
The chemical composition of the carbon steel seems invalid since the weight % composition of the waste exceeds 100 %. The correct composition was taken from In-Package Chemistry Abstraction report (July, 2003, pp. 25). Since the % composition is given on a elemental basis I had to convert them to oxide compositions to be used as inputs in the REACT subroutine of the GWB chemical modeling software. A constant weight of 17 g of A516 was used in the lab experiments done by X. Xu, and was used also for the GWB modeling.

I attempted to model the experimental data submitted to us using REACT of the GWB modeling software, but the attempt was unsuccessful because iterations did not converge. The following

windows show the inputs. (**File 1**)

I tried to re-run the above model but it was unsuccessful. We are trying to solve the problem. The problem was solved by putting a minimal molarity for the elements that we put zero concentration in the initial system. So, we put 10^{-10} M and the system converged (**File 2**).

However, the pH versus time figure (see below) does not fit the experimental data. pH seems to decrease as a function of time at 60C during corrosion of the carbon steel. We are puzzled about this and we try to solve this discrepancy.

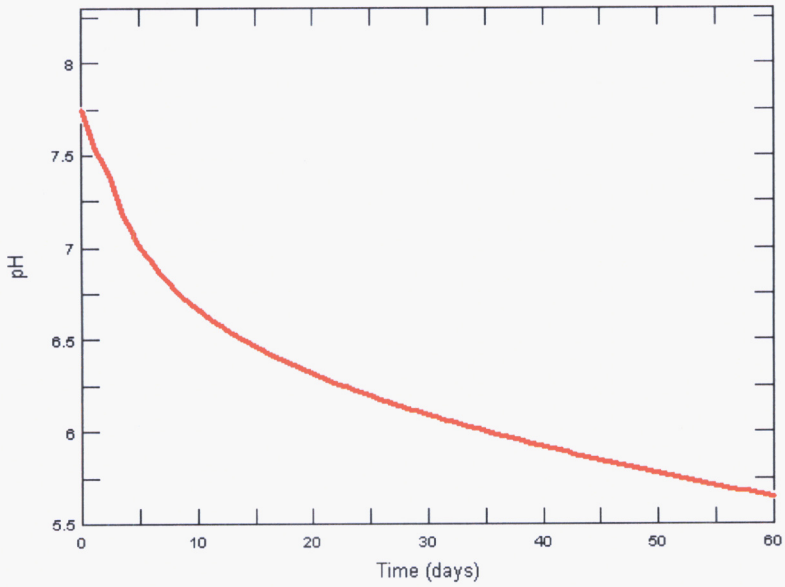


Reactants and kinetic reactions

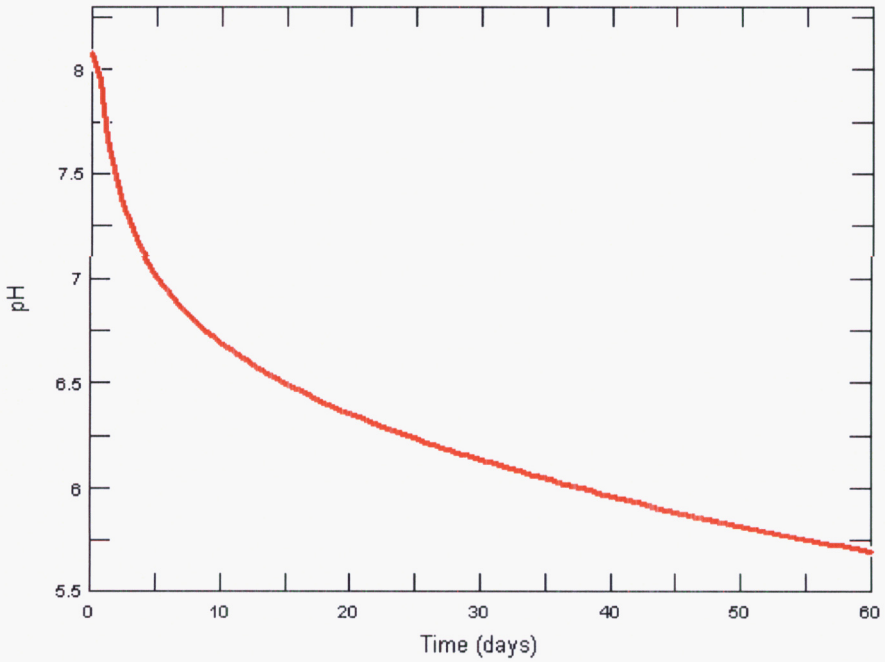
React	.228579	gram	of	MnO
React	.013579	gram	of	P2O5
React	.014808	gram	of	SO3
React	.0922	gram	of	SiO2
React	23.8276	gram	of	Fe2O3
React	.19	gram	of	CO2(g)

add

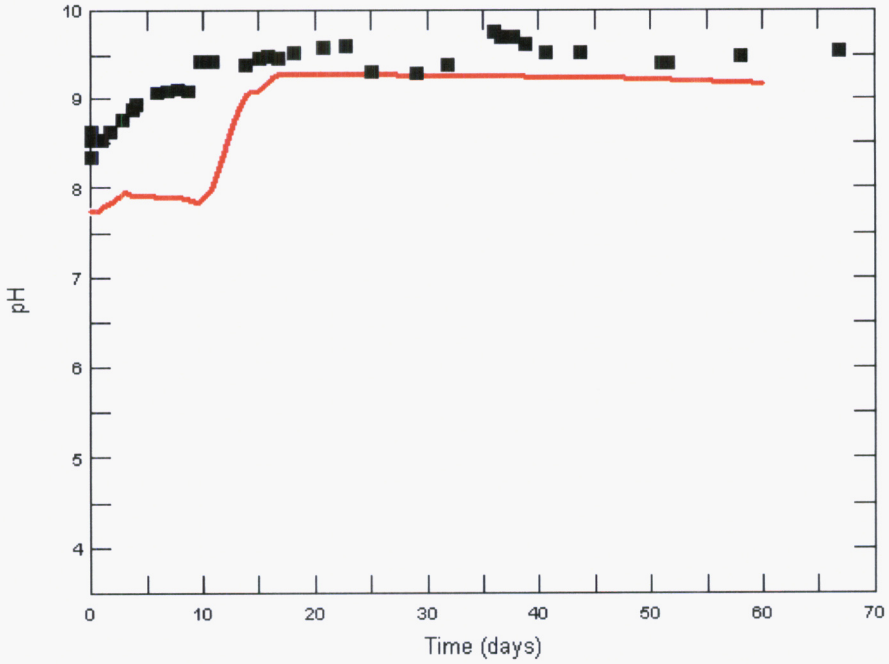
reactants times 1



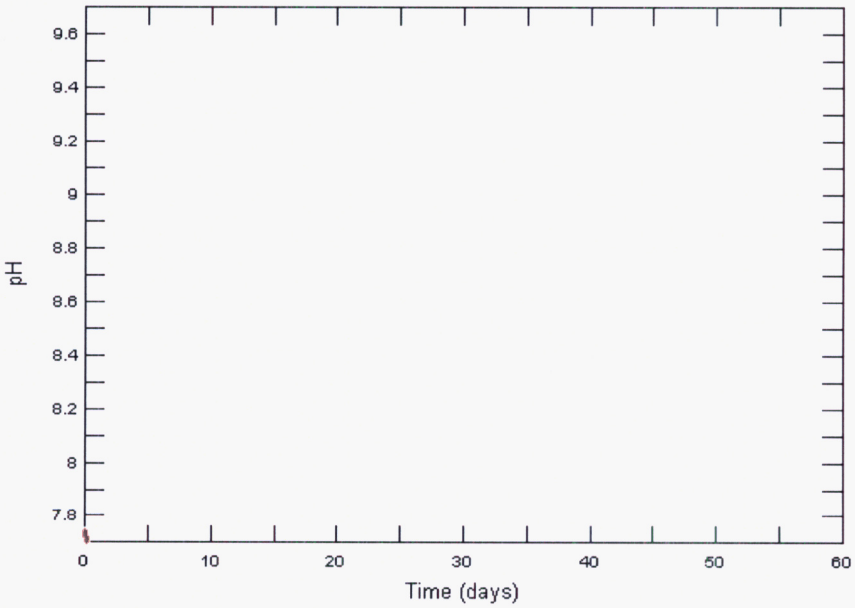
In our attempt to run the same exactly system as above, but at T=25C we got a similar graph (**File 3**):

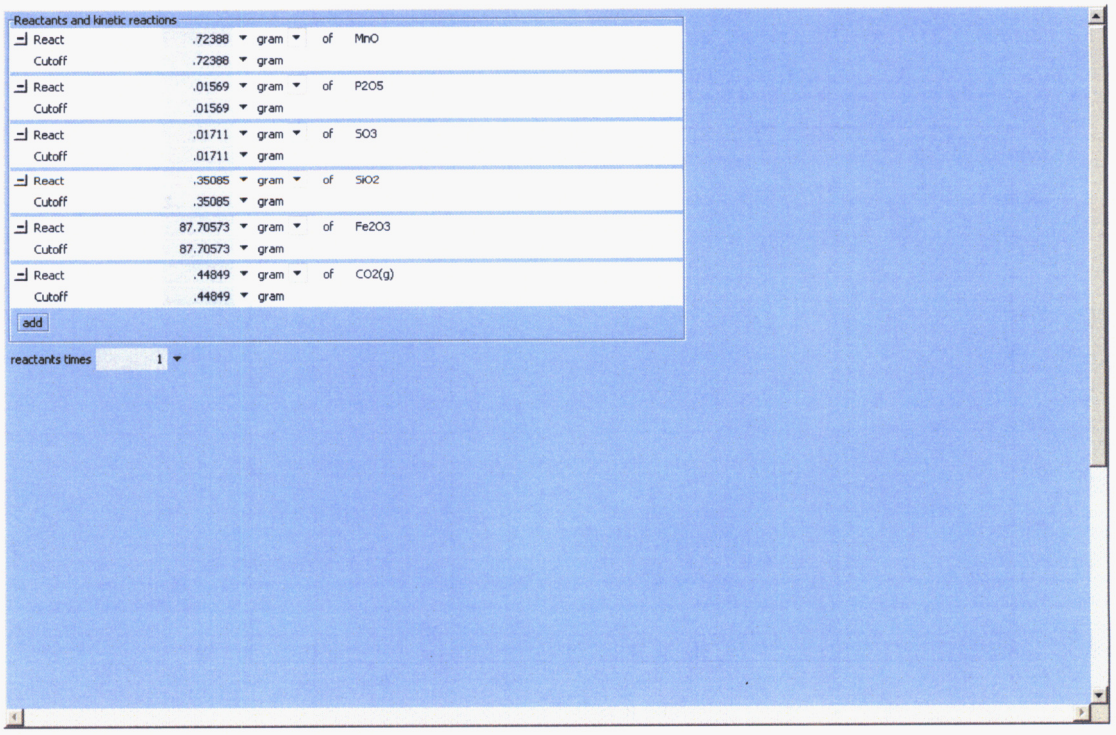


Now if we change in the solution the concentration of O_2 to a very low value e.g.0.2 ppm and that of CO_2 to 1e-8 g, then this is what I get assuming that the rest of the input factors remain the same.



Which is a reasonable fit to the experimental data provided by SWRI staff (**File 4**).


9.6
9.4
9.2
9
8.8
8.6
8.4
8.2
8
7.8
pH
0
10
20
30
40
50
60
Time (days)



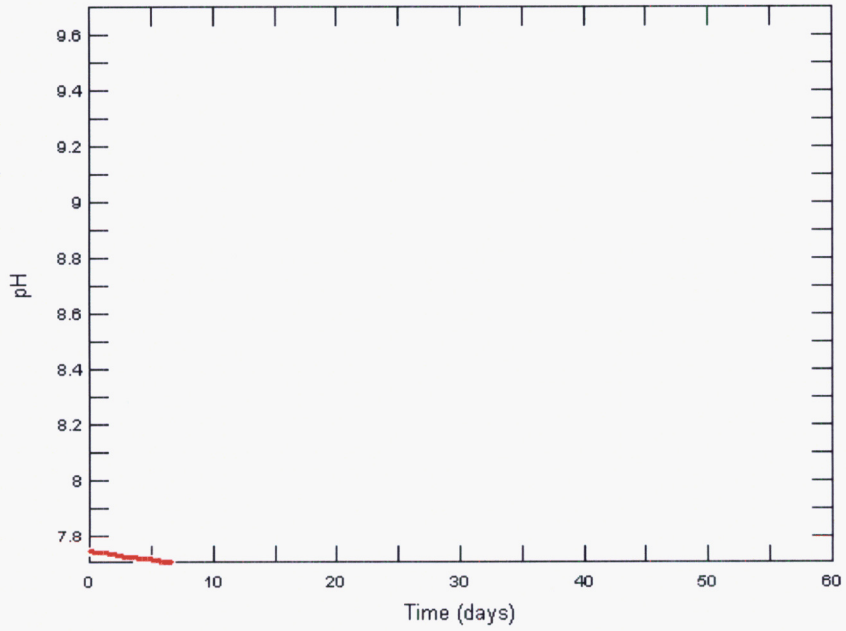
Reactants and kinetic reactions

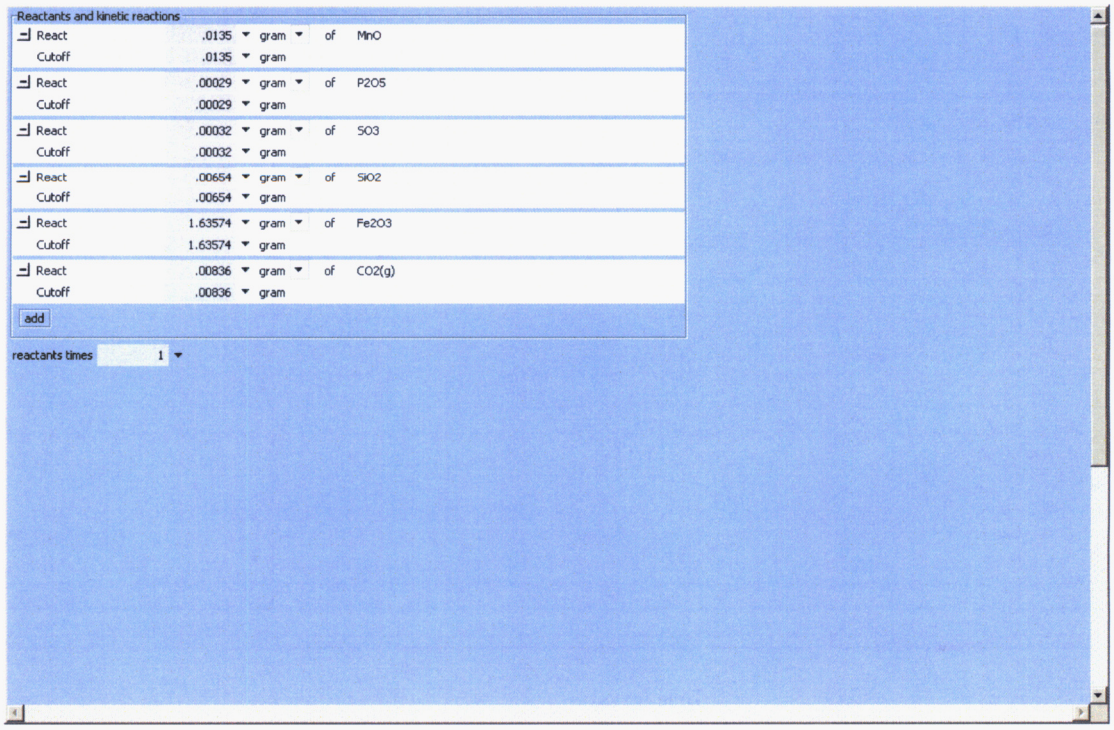
React	.72388	gram	of	MnO
Cutoff	.72388	gram		
React	.01569	gram	of	P2O5
Cutoff	.01569	gram		
React	.01711	gram	of	SO3
Cutoff	.01711	gram		
React	.35085	gram	of	SiO2
Cutoff	.35085	gram		
React	87.70573	gram	of	Fe2O3
Cutoff	87.70573	gram		
React	.44849	gram	of	CO2(g)
Cutoff	.44849	gram		

add

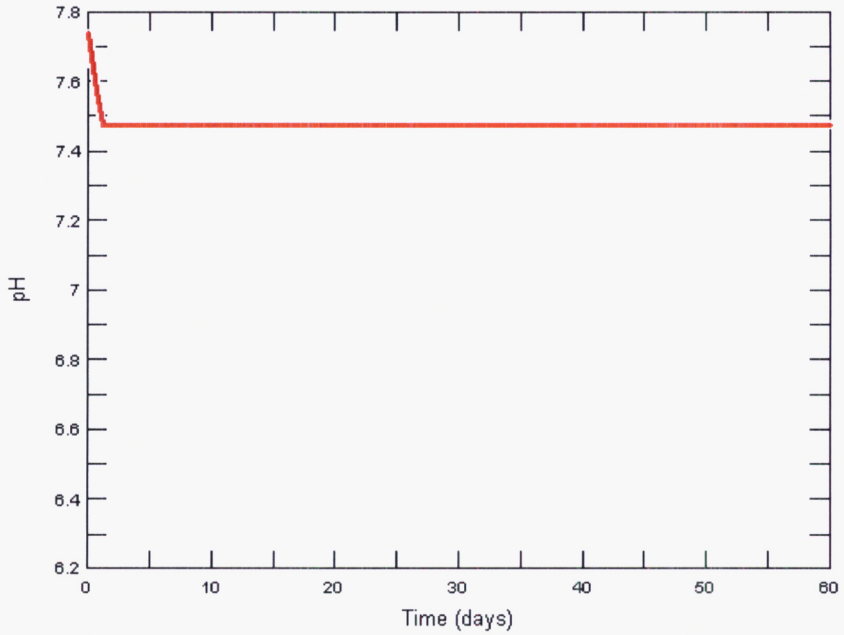
reactants times 1

Figure 1 Original values (reactant) (100 % reacted) (**File 5**).


9.6
9.4
9.2
9
8.8
8.6
8.4
8.2
8
7.8
pH
0
10
20
30
40
50
60
Time (days)



(File 6)
Figure 2 partially reacted values (reactant).


7.8
7.6
7.4
7.2
7
6.8
6.6
6.4
6.2
pH
0
10
20
30
40
50
60
Time (days)

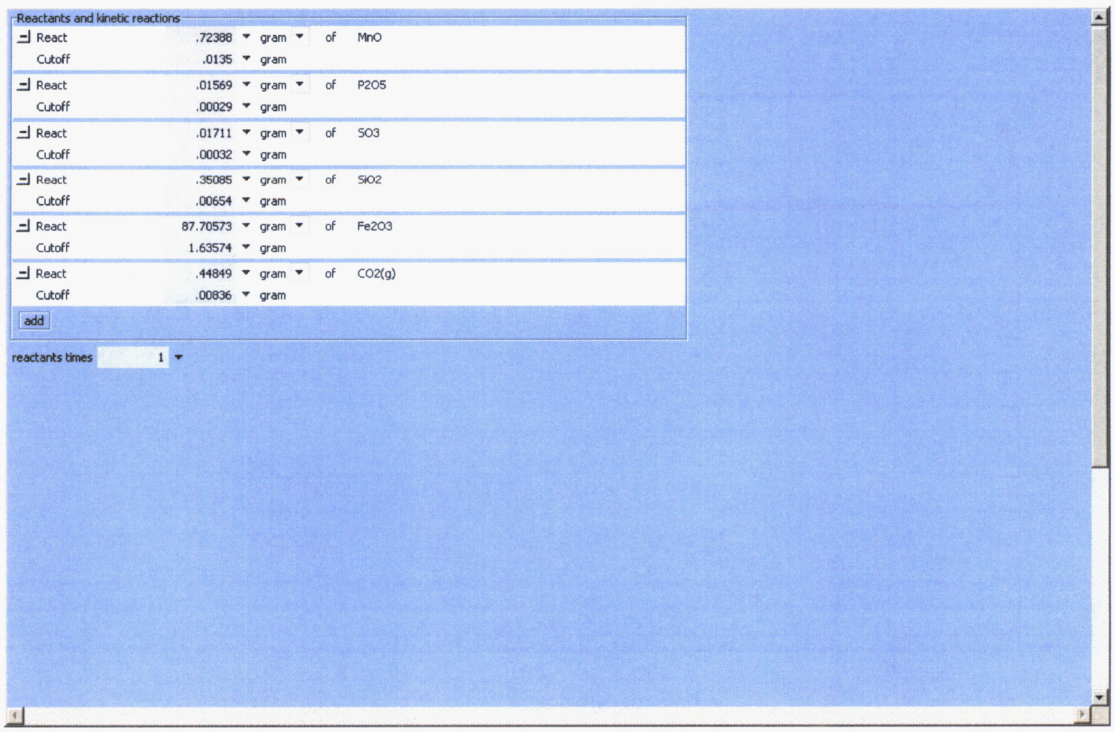
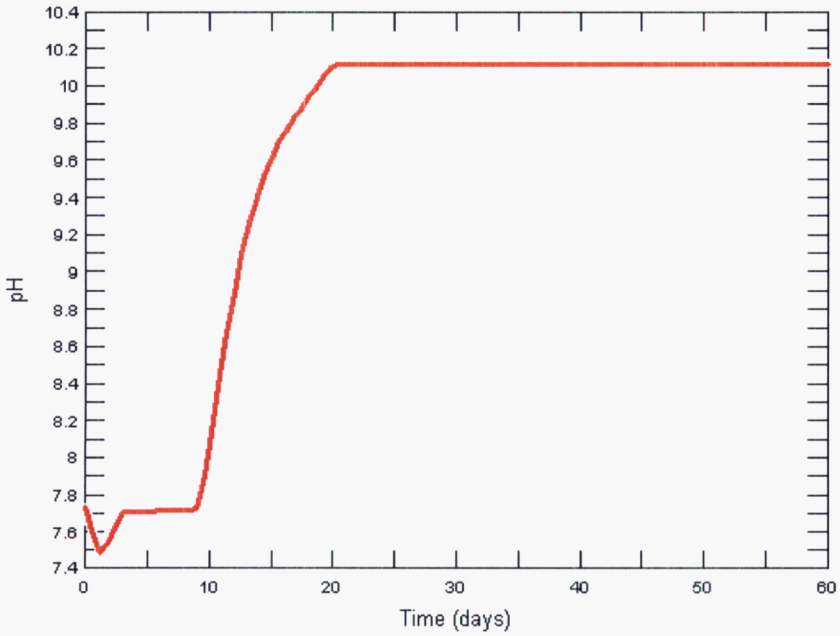


Figure 3 Original values + cut off values (reactant). This does not assume equilibrium between O2 and CO2 (**File 7**).


pH
10.4
10.2
10
9.8
9.6
9.4
9.2
9
8.8
8.6
8.4
8.2
8
7.8
7.6
7.4
0
10
20
30
40
50
60
Time (days)

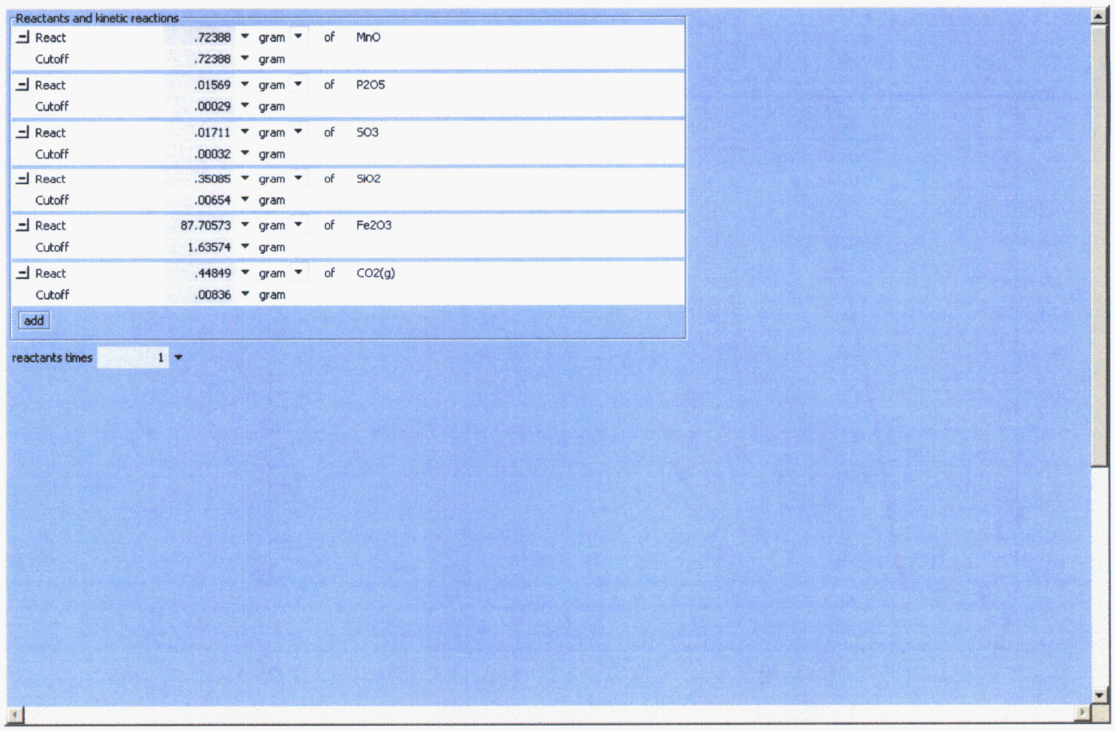


Figure 4 Original values + cut off values (MnO cut off value changed to Original values). If you do the same thing for the other reactants then there is a decrease in pH as a function of time.(**File 8)**

Now if you use the same script as this last one except that you swap HCO3 for atm. CO_2 and dissolved O_2 for gas O_2, then you get a better fit.(File 9)

Constraints on initial system

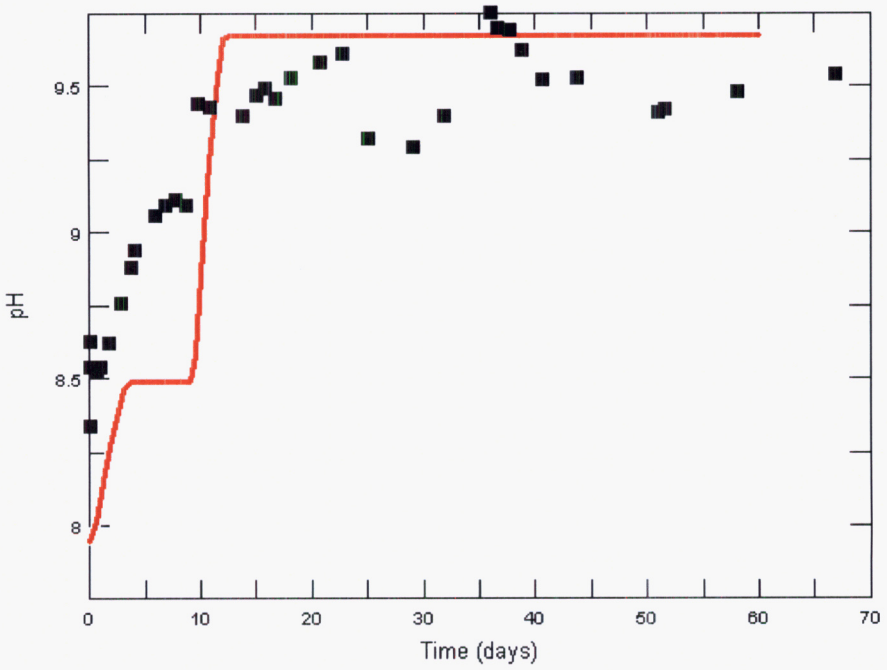
H2O		1	kg	solvent
H+		8.34	pH	
Ca++		.000299	molarity	
SO4--		2e-4	molarity	
NO3-		2e-4	molarity	
K+		.00014	molarity	
Cl-		.000179	molarity	
Mg++		6.98e-5	molarity	
Na+		.002	molarity	
F-		.000101	molarity	
Mn++		1e-10	molarity	
HPO4--		1e-10	molarity	
SiO2(aq)		1e-10	molarity	
Fe++		1e-10	molarity	
O2(g)	O2(aq)	.02	fugacity	
CO2(g)	HCO3-	-3.5	log fugacity	

Reactants and kinetic reactions

React	.7235	gram	of	MnO
Cutoff	.7235	gram		
React	.0157	gram	of	P2O5
Cutoff	0	gram		
React	.017	gram	of	SO3
Cutoff	0	gram		
React	.3	gram	of	SiO2
Cutoff	0	gram		
React	87	gram	of	Fe2O3
Cutoff	87	gram		
React	.44849	gram	of	CO2(g)
Cutoff	0	gram		

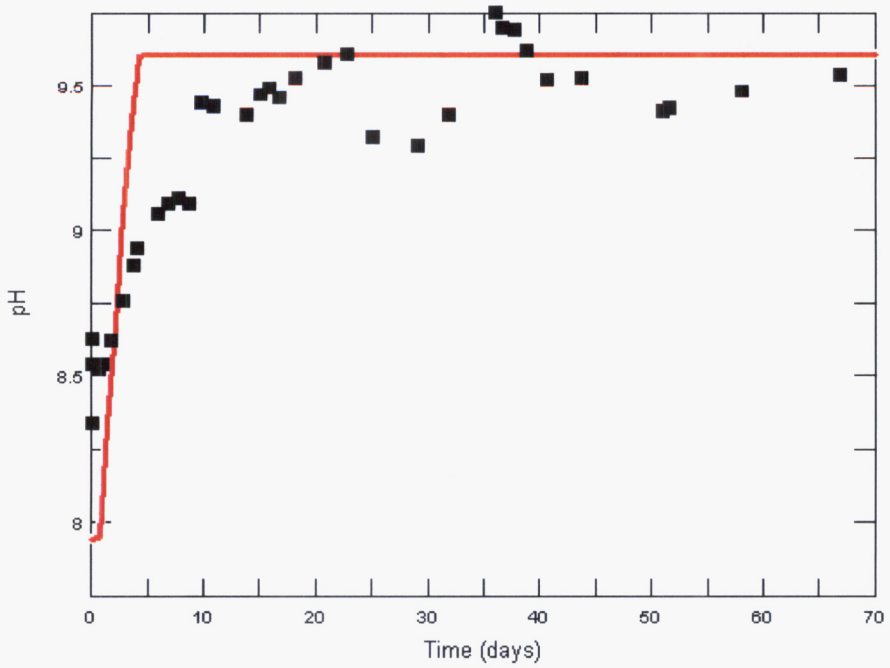
add

reactants times 1



This graph is only due to MnO contribution given that the cutoff value for the other reactants is 0 (except Fe oxide)..(File 10).

If you keep everything the same but you remove nitrate from the basis entry list, then you get even better fit. It seems that anaerobic condition may have evolved that convert nitrate to ammonia gas??

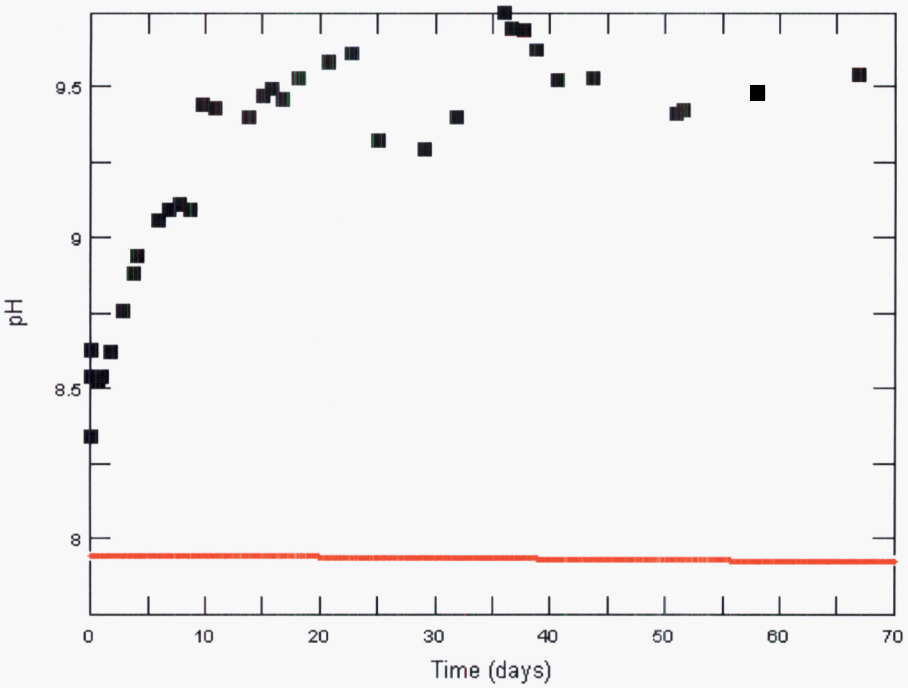

pH
9.5
9
8.5
8
0
10
20
30
40
50
60
70
Time (days)

April 27 2006. We finalized the experimental design to include some uranium solid phases that are typically introduced with the nuclear fuel.

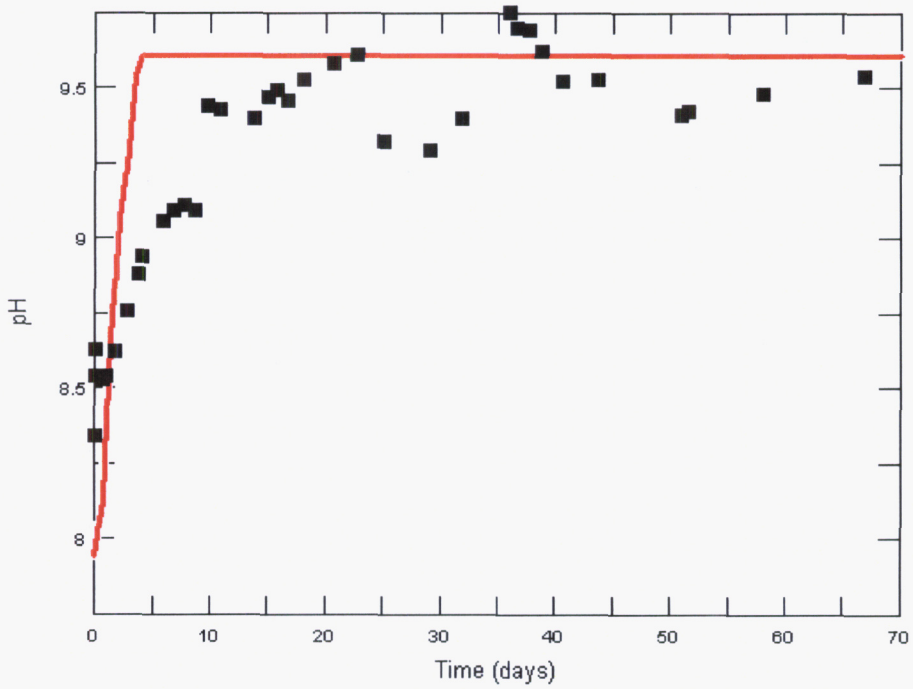
We want to run the following simulations:

i) uraninite only
ii) uraninite + steel
iii) schoepite only
iv) schoepite + steel

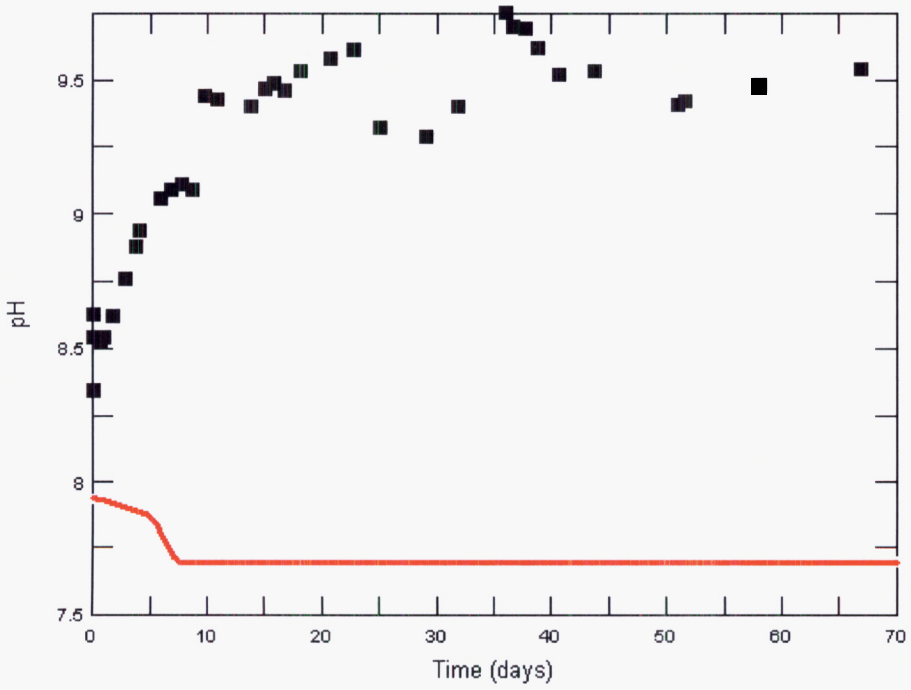
Running only uraninite (0.5 g) with the model well water solution composition we got the following graph:no change with ph. Changing the amount of uraninite to 0.01 or 1 g did not result in significant change of the graph below (File 11).



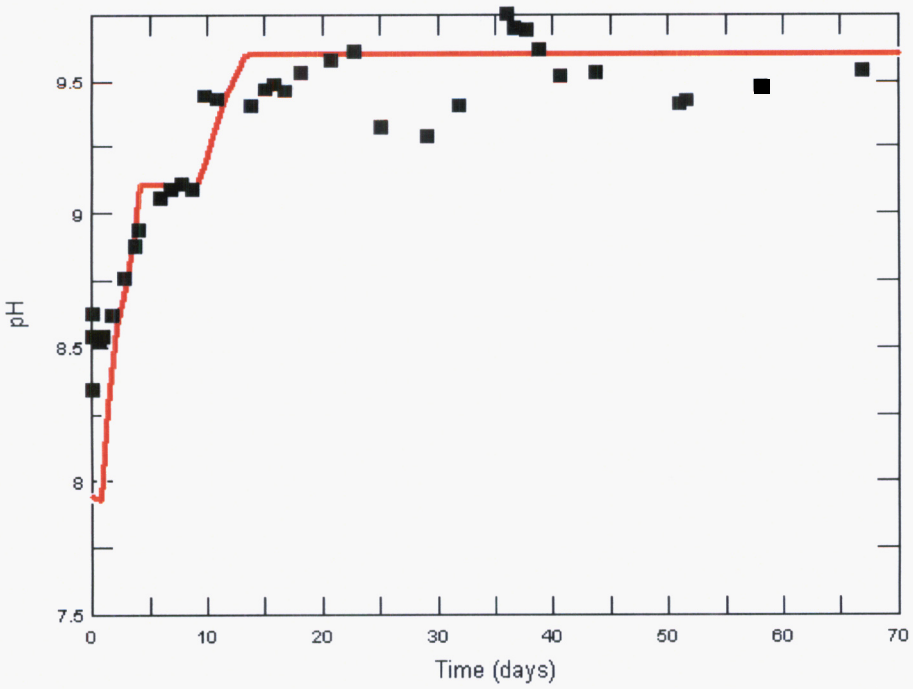
May 09, 2006. Running uraninite with contact with the common steel composition and the well water solution composition we got the following simulation graph (File 12):



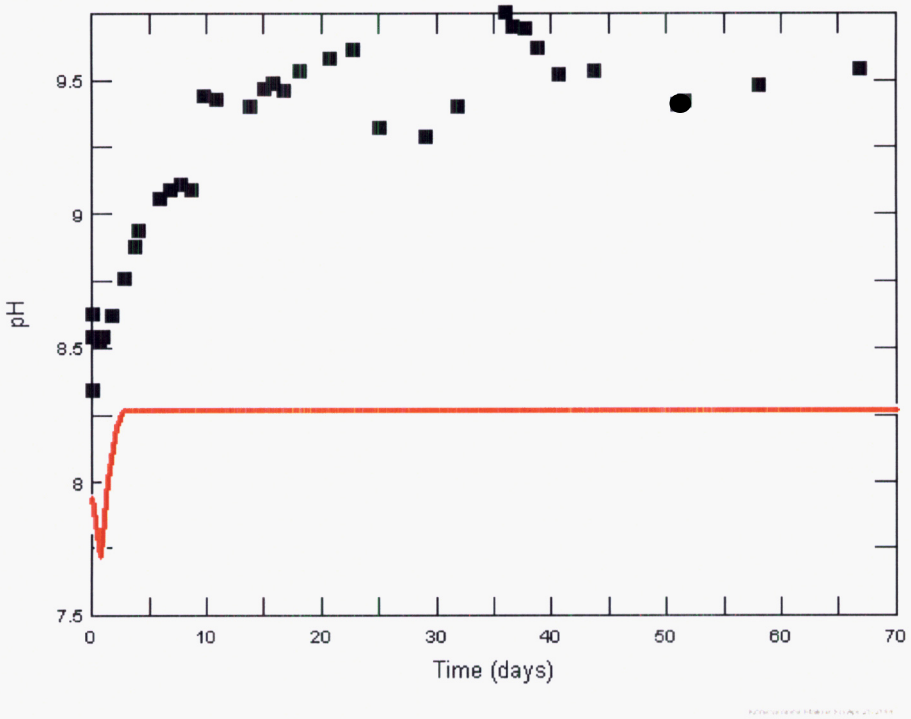
Running only schoepite (0.5 g) with the model well water solution composition we got the following slight decrease of the pH. Changing the amount of schoepite to 0.01 or 1 or 10 or 100 g did not result in significant change of the graph below. (File 13).



Running schoepite (1 g) and steel we got the following simulation graph. Excellent fit!!! (File 14).



May 23, 2006. Changing the amount of schoepite to 100 g we got this: (File 15).



File 15.

GEOSCIENCES AND ENGINEERING DIVISION

SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No.: 767 E Project Numbers: 20.06002.01.222

Accomplished

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

Any discrepancies must be resolved before notebook closeout.

==========

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

E. C. R

Manager's Signature

1/23/2007

Date

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

Form QAP-01 (10/2006)