

**Electronic Scientific Notebook
874E**

**Modeling Np(V) Sorption to Calcite based on
Batched Sorption experiments and Surface
Complexation Modeling performed by Zarvin
et. al, 2004**

Project # 20.06002.01.212

Lynn Sabido

Notebook Number 874E
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4/27/07

Modeling Np(V) Sorption to Calcite based on Batched Sorption experiments and Surface Complexation Modeling performed by Zarvin et. al, 2004

By Lynn Sabido LS

Objective: To model the results of the Surface Complexation Model used in Zarvin et al, (2004) using speciation constants and surface species reactions reported in said paper. This will be implemented in the PHREEQC, version 2.12.5 modeling program.

Training: In order to perform said mentioned work one needs to be familiar with the Phreeqc computer program and have a basic understanding of carbonate aqueous systems and sorption processes. I personally read the instruction manual and became acquainted with the program by performing examples from the books.

Hypothesis: Sorption log k values of Np(V) to calcite were derived from lab experiment data that was fitted to a constant capacitance surface complexation model within a pH range of 7.5 to 10. Although the authors of the paper did not fit the results to a unique solution, they show Np(V) sorption is controlled by pH and CO₂ fugacity. They do not specify the specific surface coordination, rather the reaction stoichiometry. Using the Phreeqc model, we hope to duplicate the results from the Zarvin et. al, 2004 paper.

Approach: Set up a PHREEQC input file that mimics the steps followed to create the lab experiments and use the calculated sorption data to achieve similar results to those reported in the article. While the Np sorption is not reported for a specific surface coordination, the values were applied to surface site CaOH₂⁺, as the author attributes sorption to a >Ca⁺ site. However, as unclear, separate runs will be created specifying one surface at a time, and then with both types of surface sites and switching Np(V) sorption from one site to another. This may indicate the predominate surface for Np(V) sorption based on the aqueous chemistry and pH.

Mathematical and other model assumptions: The user is referred to the instruction manuals that accompany the program to determine theory and assumptions employed by the program.

Input Files: The input files will be generated based on the processes used to perform the lab experiments.

File Location: D:\Sorption, however at the conclusion of this project all files will be transferred to a cd that will accompany this notebook.

LS

4/27/07

Sometime has gone into figuring out how to set up the PHREEQC input file. Incorporating the Np +4 and specific aqueous reactions, the surface sites and their protonation/deprotonation reactions along with the Np sorption reactions to calcite surface sites. Initially both calcite surface sites were to be specified, however due to errors, one site to CaOH₂⁺, was chosen to start with, based on the authors assumptions of sorption to a >Ca⁺ site. Once a working file was created, it was continually tuned up to mimic the article results and steps used in the lab experiments. Some file specifics, because the experiment used only 40ml, all specified data was multiplied by 25 to achieve a solution of 1L.

SPECIFICS

	Experiment	Phreeqc File
Calcite surface area	.262 m ² /g	6.55m ² /g
Mass of Calcite	.5g	12.5g
V water	40ml	1L
# surface sites	5e-9/m ²	2.5e-008/m ²
CO ₂ (g)	.03%	-3.5 for SI = log(.03/100)
Ionic Strength	0.1	0.1
NpO ₂ ⁺ reacted	1e-7 mol/L	1e-7 mol/L

Initially for the CaOH₂⁺ sites I used the following reactions and correlated them to the reported log K values



**note took the following reaction from

Validating Mechanistic Sorption Model Parameters and Processes for Reactive Transport in Alluvium

M. Zavarin, S.K. Roberts, T.P. Rose, and D.L. Phinney May 2, 2002 UCRL-ID-149728 Lawrence Livermore National Laboratory

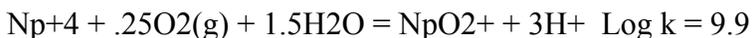


Table 1. Predominant aqueous species and their reaction constants.

Reaction	log K (298 K, I = 0)	Reference
$\text{NpO}_2^+ + \text{H}_2\text{O} = \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	-11.30	3
$\text{NpO}_2^+ + \text{HCO}_3^- = \text{NpO}_2\text{CO}_3^- + \text{H}^+$	-5.37	3

$\text{NpO}_2^+ + 2\text{HCO}_3^- = \text{NpO}_2(\text{CO}_3)_2^{3-} + 2\text{H}^+$	-14.12	3
$\text{NpO}_2^+ + 3\text{HCO}_3^- = \text{NpO}_2(\text{CO}_3)_3^{5-} + 3\text{H}^+$	-25.49	4
$\text{HCO}_3^- + \text{H}^+ = \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	7.81	4
$\text{HCO}_3^- + \text{H}^+ = \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$	6.34	4
$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-10.33	4

3: Lemire et al. [18];
4: Johnson and Lundeen [15];

Table 2. Surface complexation model for calcite based on data from Pokrovsky and Schott [1].

Surface reaction	$\log K$ (298 K, $I = 0$)
$>\text{CO}_3\text{H} = >\text{CO}_3^- + \text{H}^+$	-5.1
$>\text{CO}_3\text{H} + \text{Ca}^{2+} = >\text{CO}_3\text{Ca}^+ + \text{H}^+$	-1.7
$>\text{CaOH} = >\text{CaO}^- + \text{H}^+$	-12.0
$>\text{CaOH} + \text{H}^+ = >\text{CaOH}_2^+$	11.85
$>\text{CaOH} + \text{HCO}_3^- + \text{H}^+ = >\text{CaHCO}_3 + \text{H}_2\text{O}$	13.17
$>\text{CaOH} + \text{HCO}_3^{2-} = >\text{CaCO}_3^- + \text{H}_2\text{O}$	6.77

Table 3. Best fit parameters for modeling sorption to calcite.

Reaction ^b	$\log K$ (298 K, $I = 0$)	Data Set
$>\text{Ca}^+ + \text{NpO}_2^+ + \text{HCO}_3^- = >\text{CaCO}_3\text{NpO}_2^0 + \text{H}^+$	4.36	0.03% $\text{CO}_2(\text{g})$
$>\text{Ca}^+ + \text{NpO}_2^+ + 2\text{HCO}_3^- = >\text{CaCO}_3\text{NpO}_2\text{CO}_3^{2-} + 2\text{H}^+$	-1.54 ^a	24 h

a: If only the $>\text{CaCO}_3\text{NpO}_2\text{CO}_3^{2-}$ species is included in the fit, $\log K = -1.14$ and the overall fit to the data is still reasonably good;

b: These reactions only imply a reactions stoichiometry and do not imply a reaction mechanism. All reactions were written in terms of the primary species of our database ($>\text{Ca}^+$, Eu^{3+} , HCO_3^- , Sm^{3+} , NpO_2^+ , PuO_2^+ , and Pu^{4+} , H_2O , and H^+).

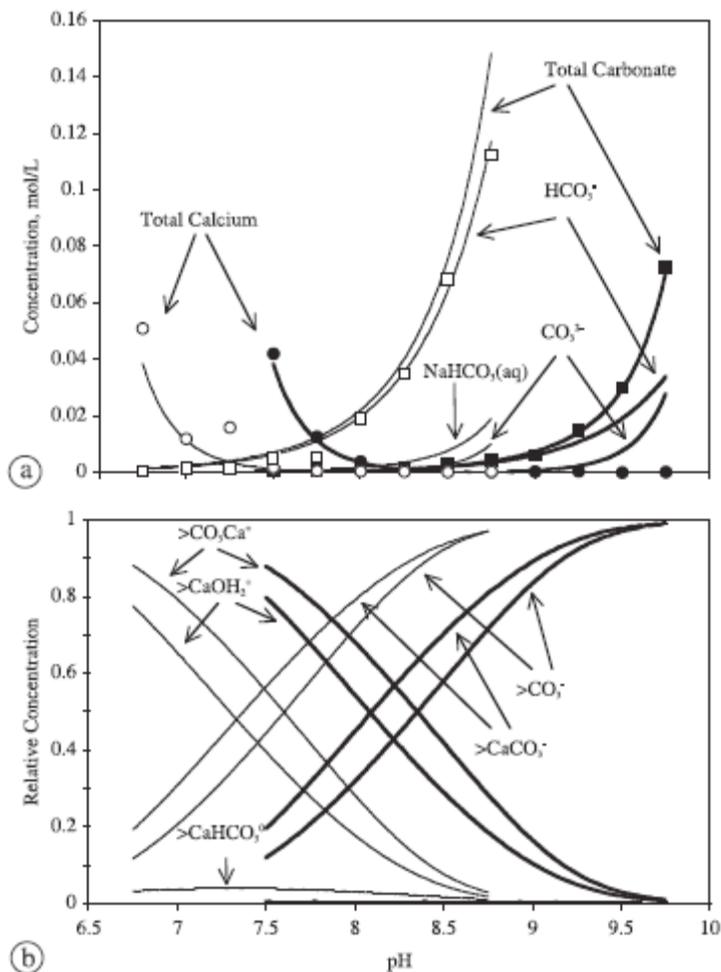


Fig. 1. Predominant (a) aqueous and (b) surface species at calcite saturation conditions. $I = 0.1$ and 0.03% $\text{CO}_2(\text{g})$ (thick lines) or 1% $\text{CO}_2(\text{g})$ (thin lines). \circ and \square represent typical batch solution total calcium and carbonate alkalinity results, respectively (0.03% $\text{CO}_2(\text{g})$ = filled symbols, 1% $\text{CO}_2(\text{g})$ = open symbols).

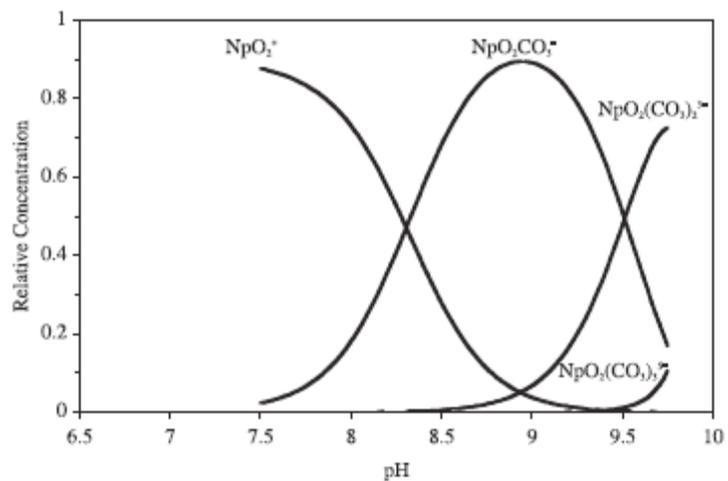


Fig. 3. Speciation of Np(V) at 0.03% $\text{CO}_2(\text{g})$, $I = 0.1$, and calcite saturation conditions.

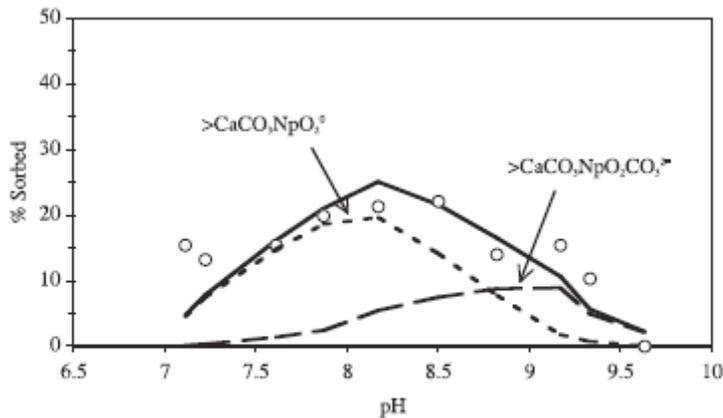


Fig. 10. Np sorption to calcite at 0.03% CO₂(g) at 24 hours (O). Lines present total and individual species SC model fits.

Many variations of the input file were created with various alterations/corrections for the initial 1 surface site run CaOH₂⁺. Many of the results are recorded in an excel file named Npsorp1, many of the actual test files are in the folder labeled Sorption, as files are refined some versions may be saved and put into the folder labeled extras within the sorption folder. Below is a brief summary of the process followed thus far, please see the excel file for specific results.

Sorption 1 used original Ca sorption table 2 from Zarvin and log k Np species started with Calc_cOH₂⁺ and values 4.36 -1.54. I was unsure what .03% CO₂ (g) referred to, I assumed mass, so initially it was entered as CO₂ (g) -3.5= SI, 0.0003=moles. Np⁺⁴ was reacted. The trends were off.

Sorp 2 Changed Eq 6 Ca-SCM to that of Pokrovsky who specified HCO₃⁻ as its components. I'm not sure if table 2 eq 6 has a typo (zarvin), the HCO₃⁻ is specified as HCO₃⁻². Np⁺⁴ was reacted. The results were the same.

Np SORP3 Corrected ionic strength to 0.1 NpO₂⁺ reacted instead of ion solution and defined as a "phase". Very little Change, Trends were there for all so far, just off

Sorp 4 corrected CO₂g -3.5 and Sorp 4 corrected CO₂g -3. However, I'm not sure what I had initially entered, Then end result that lead into the next file specified moles were changed to 10, because .03% meant the SI, but at first I thought just -3, but it really is log (.03/100) = SI. I also Changed the chemistry of the initial file -Change chemistry Na-.06, Cl .03 and Ca .04 as their salts and added Np and equilibrated the same time. These results were not much better.

Sorp 5 0.1 M NaCl 1e-7 NpO₂⁺, and 10 moles of CO₂ gas. Adjusting the molar concentration of CO₂ gas adjusted the trends of the aq Np complexes in solution; however, the total concentration of the species was closer to 50% of the initial. The carbonate and calcite species were still incorrect, the total Ca was far less than it should be, and the surface species concentrations (only have two dominate ~ because used only one initial surface) was also off. Calcite remained constant.

Second part I separated out the equilibration of calcite with solution and the Np reaction. This improved the results.

Sorp 6 Separate out Np reaction try diff chemistries to make I=.1, however, somehow the file was corrupted. When making changes and rerunning to get a new selected out file, the file was not updated correctly, when comparing the output to the selected output file. Discarded and started over.

Sorp 7 file Npsurface1 react and equilibrate CO2 same time and file Npsurface1-sep2 equilibration with calcite and reaction of Np separated. Both .1 NaCl. Trends for both were the same and relative concentration of Np species improved because NpO₂⁺ wasn't consumed in the equilibration process. The carbonate aq species and amounts of surface sites still off. The file Npsurface1-sep2 was rerun with allowing Na₂CO₃ to equilibrate pH, no significant change.

No Np – File SurfaceCaSCM

The file was run without reacting Np to look at the chemistry and site concentrations. m_Calc_xCaCO₃⁻ and m_Calc_xCaOH₂⁺ site concentrations exhibit the correct trends. However the carbonate chemistry is off. I changed the file to NaCl as initial solution, even after equilibration, this didn't help the calcite concentration. And the carbonate species were still off.

I then started working on another file Ca(SCM) were the solution was off initially (NaCl = .1), but I stopped equilibrating the solution with calcite at each step and separate out the solution with equilibration completely. The initial solution was not pH calibrated to 7.5 it was specified, then allowed to change as it came into equilibrium with calcite. This is an improvement; calcite is supersaturated and should be pulling Ca out of solution. Changing the initial chemistry to

Na	0.03
Cl	0.02
Ca	0.04

The Ca doesn't show being consumed. First I'll add the second surface site first. Later when the Np is reacted, the order of solution, surface and reaction may be more important. The second surface site was added, the run had no errors, and however the site concentrations are off. > CO₃Ca⁺ remains constant at its initial value where at higher pHs it should shift to >CO₃⁻ sites, it doesn't.

NOTE** if the salt used to bring the system to a specific pH is changed, no noticeable change is observed. Also if Np⁺⁴ or NpO₂⁺ are reacted there is no difference as long as the proper phase is specified.

LS

5/3/07

The second surface was added and the site moles were divided in half. The site concentrations are further off from the article than when only one site was defined. Several runs were completed switching around where the surface and phases were defined, along with the site concentrations. I wasn't sure if the paper meant there were 5um of each site or total for both. In order to get the calcite and aragonite to precipitate both solid solution AND the phase keywords need to be filled out. Changing around the keyword order obviously has an affect on how the reactions are followed through. Minerals are precipitating, but the Ca value isn't decreasing. The execution of reactions needs to follow a particular order and once set up properly should mimic the article results.

LS

5/4/07

I used the file CaSCM2surfC, in this file the solution and equilibrium of CO₂, calcite, and pH calibration was separated from the surface and solid solution with the save and use keywords. Each specified pH was all defined in 1 simulation. This in effect brings the surface to equilibrium without altering the solution, both aq and site concentrations were off. I began using the PUNCH

keyword to pull data to the selected output file. In file CaSCM2surfD I eliminated the save/use keys between the surface and solid solution key. The file separated solution and surface/solid solution with an end keyword. In CaSCM2surfD3 the solution was pH equilibrated with the surface present and the solid solution/mineral phase were separated with the end key. The results were the same for both and gave good results for the surface site concentrations and total calcium, the total Carb was also ok, but all specified as HCO₃. In these runs the output was specified incorrectly and may be noted in the Npsorp1 spreadsheet. CaSCM2surfD4, I changed the species used to correct for pH from NaOH to HCL (failed to execute) and Na₂CO₃. There was no significant change in site concentrations. The total carbonate is too high so in CaSCM2surfD5 I changed the initial solution to add more Ca and make Na 0, and added the 3 HCO₃ equations from table 1 of Zarvin, this did not help. CaSCM2surfD6, the initial surface site moles were changed to 1.25e-8, no improvement on the carbonate speciation.

**note the logK values for Calcite and aragonite are from MINTEQA2

LS

4/7/07

The total alkalinity in D1-4 is .79, in D5 +D6, it is .76, and this is probably due to the log k changes made to carbonate species. CaSCM2surfF I used D6 and reentered the log K for carbonate species (except for gas CO₂ + H₂O = HCO₃⁻). The author didn't mention NaCO₃, so I will try to suppress or decrease the Na concentration. I noticed my aqueous carbonate species look ok up til 9.5, I ran the simulation to 10, where as the data from the article looks to run up to 9.75, once I changed the last fixed pH to 7.5, the results are in much better agreement. However, NaCO₃ is present and CO₃ end concentration is lower than it should be (CaSCM2surfF2). In CaSCM2surfF3, I first made NaCO₃ log k = 0, this decreased the concentration of both NaCO₃ and NaHCO₃ and slightly increased carbonate. I then changed NaCO₃ log k = -1.27 (normally 1.27) this decreased total carbonate at 9.5 to 5.7e-002, it should be about 7.5e-2. I tried combinations of NaCO₃ log k greater than one and below 1.27, while altering NaHCO₃'s log K (which had little effect). If the log K of NaCO₃⁻ is 1.1 (instead of 1.27) this fixes the total carbonate and CO₃⁻ concentration is more accurate. For CaSCM2surfF4, I still specified the carbonate log K's according to table 1, but I changed the CO₂ partial pressure and SI, if its specified as -3.55 at pH 9.75, the results are better, but the CO₂ concentration slightly lower than reported. I reset the CO₂ back to -3.5, and tried to alter the database changing the CO₂ gas to aq log K, or adding the equation in table 1 that specifies CO₂gas to HCO₃, this didn't work. So far the best results were obtained by altering the NaCO₃ log K.

LS

4/8/07

Going back to F3 and F4, not all the solution species have the two equations from table 1 in the SOLUTION_SPECIES

CO₃-2 + H⁺ = HCO₃⁻

log_k 10.33

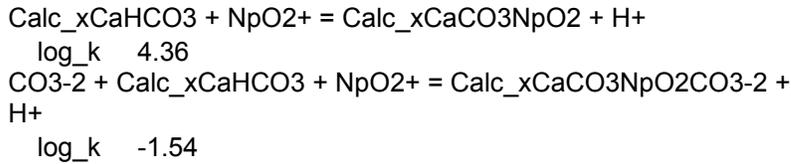
CO₂ + H₂O = HCO₃⁻ + H⁺

log_k -6.34

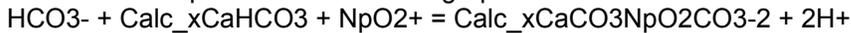
These were added by using the paste and cut method in the text pane on the right of the input screen, and for some reason it is not updating the actual keyword. So I had to go into the keyword and manually add one or both of the above equations. Then once the run has completed and then look at the input file, it bumps out either equation, for reasons I do not know. Using the file CaSCM2surfF3 and changing the name to CaSCM2surfNp and CaSCM2surfNp2, I reacted 1e-7 moles of Np⁺⁴, with both site concentrations 1.25e-8 or 2.5e-8, the intersection of Np(V) species indicates that 1.25e-8 moles per site is the better choice (at relative concentration of .45 rather than .38 as with 2.5e-8 concentration per site). However, because the way the Np(V) species were entered, the two predominate surface sites are CO₃Ca until 8.25 it's a 50/50 concentration with CO₃⁻ surface site who steadily increases until it reaches dominance above pH 8.5. CaSCM2surfNp3- set the mol sites for each to 2.5e-8 and Added >CO₃Ca+ reactions with NpO₂⁺, I then reduced the log K for all four Np(V) reactions by 2. Neither method worked.

CaSCM2surfNp4 I only entered Np surface speciation with >CaO- and deleted all others. Obviously the >CO3H surface site concentrations were unaffected, however >CaOH2+ was 0, and >CaCO3 started to increase much later than expected. The surface site concentrations were set at 2.5e-8, this didn't affect anything.

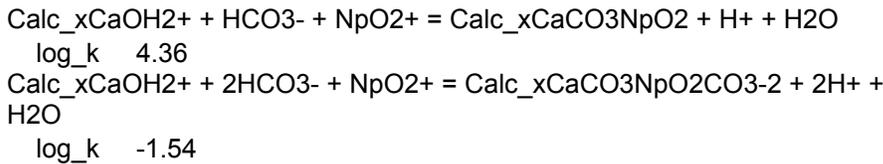
File 4 used these equations.



The second equation was revised, which made the results worse off and the percent sorbed looks more like the aqueous concentration graph.



The second surface is added, and without reacting Np and adjusting the NaCO3- log k value I get many of the same graphs as in the paper. However, due to the way the Np sorption equations were added the site concentrations are off when Np is reacted. Initially I had altered the equations using the >CaOH2+,



++However, >CaOH2 to >CaCO3- is not defined. I've also tried using the >CO3Ca+, this made matters worse.

I pulled the following equation from one of the Inl papers; I could just specify NpO2+ as just that without Np+4 to Np+5

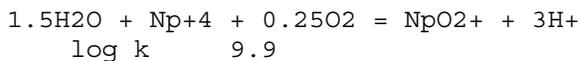
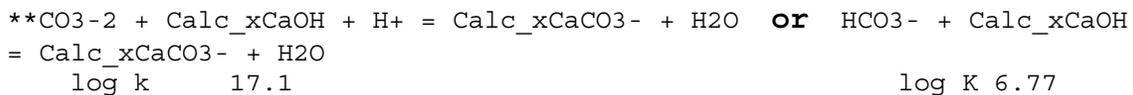


Table 3

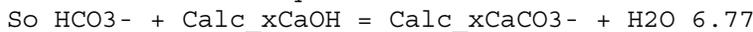
$>\text{Ca}^+ + \text{NpO}_2^+ + \text{HCO}_3^- = >\text{CaCO}_3\text{NpO}_2^0 + \text{H}^+$	4.36	0.03% CO ₂ (g)
$>\text{Ca}^+ + \text{NpO}_2^+ + 2\text{HCO}_3^- = >\text{CaCO}_3\text{NpO}_2\text{CO}_3^{2-} + 2\text{H}^+$	-1.54 ^a	24h



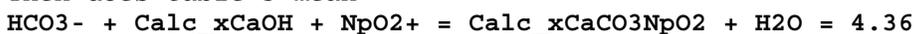
**Currently I have it as seen on the left because initially I didn't specify the log Ks from table 1 for HCO3- association, I will switch this.

For Calc_xCaCO3NpO2

So I assume that the site must have a Ca+ attached to the actual surface- that's why the valance is +1



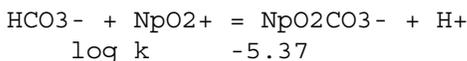
Then does table 3 mean



As opposed to $\text{Calc_xCaCO}_3^- + \text{NpO}_2^+ = \text{Calc_xCaCO}_3\text{NpO}_2 \log k \ 4.36$

For the $\text{Calc_xCaCO}_3\text{NpO}_2\text{CO}_3^-2$

Table 1 states



So I'd assume that $2\text{HCO}_3^- + \text{Calc_xCaOH} + \text{NpO}_2^+ = \text{Calc_xCaCO}_3\text{NpO}_2\text{CO}_3^-2 + \text{H}_2\text{O} + \text{H}^+ \log k \ -1.54$

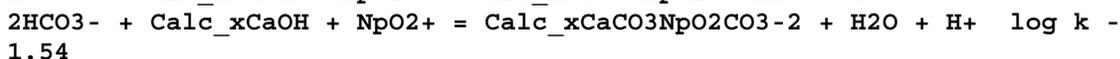
As opposed to $\text{Calc_xCaCO}_3^- + \text{NpO}_2\text{CO}_3^- = \text{Calc_xCaCO}_3\text{NpO}_2\text{CO}_3^-2 \log k \ -1.54$ OR

Or $\text{Calc_xCaCO}_3^- \text{NpO}_2^+ + \text{HCO}_3^- = \text{Calc_xCaCO}_3\text{NpO}_2\text{CO}_3^-2 + \text{H}$ or any other combination.

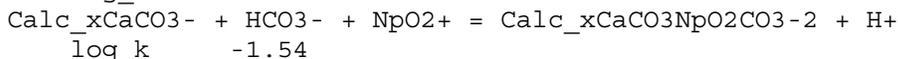
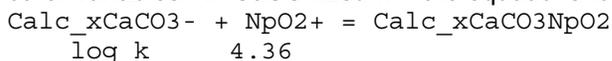
LS

5/9/07

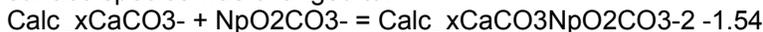
Start CaSCM2surfF 5 with above, the equations for Np sorption were changed to



All the tables were right on except for % Np(V) sorbed was off (Mols of surface site concentration/ $1e-7 * 100$). Looking closely at the values of the Np(V) aq species, you can see the numbers are slightly higher than in the article. The site concentration was set at $1.25e-8$. The values printed from the user punch keyword are incorrect. The % or relative concentrations and many other calculations can be specified in user punch, However if not properly added, it computes incorrect values. For CaSCM2surfF6 the site concentrations were changed to $2.5e-8$ moles, this improve the Np sorbed concentrations ever so slightly and didn't really effect all the other variables. In CaSCM2surfF7 the equations for Np surface sites were modified to

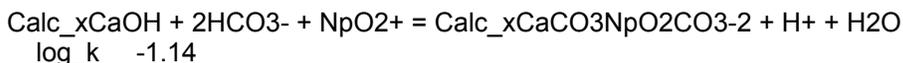
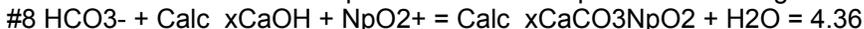


The only thing this changed was the concentration of Np(V) sorption sites (increase in concentration-not enough), no other numbers were changed. In the same file the equation for surface species was changed to:



This didn't work and actually decreased the % Np sorbed.

For file CaSCM2surfF8 an equation for surface species was changed to:



This messed up the CaSCM2surfF9 graph entirely. I may try to only use just the

$\text{Calc_xCaCO}_3\text{NpO}_2\text{CO}_3^-2$ site. I may look for an equation that links $>\text{CaOH}$ sites in table 2 to $>\text{Ca}^+$ sites.

LS

5/10/07

SPECIFICS

	Experiment	Phreeqc File
Calcite surface area	.262 m ² /g	6.55m ² /g remains .262m ² /g
Mass of Calcite	50mg	1.25g
V water	40ml	1L
# surface sites	5sites/nm ²	????
CO ₂ (g)	.03%	-3.5 for SI = log(.03/100)
Ionic Strength	0.1	0.1
NpO ₂ ⁺ reacted	1e-7 mol/L	1e-7 mol/L

I noticed today that my specific surface area was wrong; there is a factor of 25 (.04L *25 = 1L). I had 12.5, instead of the correct 1.25. This made matters worse, so I know what I had entered as the site values were wrong, that's why the total % Np sorbed was off. However, I don't really know why I used the # of sites in moles I did, and when I try to convert or figure out what the paper really meant by 5sites/nm², the value corrupts the run. I had entered the sites as a fixed value.

There are 2 ways for this problem to specify amount of sites

- 1) fixed = Total number of sites for this binding site, in moles. Doesn't account for precipitation or dissolution.
- 2) In equilibrium with a phase (calcite) = Sites_per_mole -- Moles of this surface sites per mole of phase, unitless (mol/mol).

The manual states

If the total number of sites is proportional to the moles of a pure phase, if the phase dissolves the number of surface sites decreases.

The number of sites was correctly calculated, I previously was multiplying the specific surface area * the factor of 25, this is incorrect.

T sites = Site density (sites/nm²) * 10e18 nm²/m² * mass/L (1.25g/L) * specific surf area (.262 m²/g) all divided by 6.023e23 sites/mole

Sites in moles = 2.719e-6

After a few runs with changing the site moles, Np reacted (changed back to 1e-7) the chemistry was changed back to moles of, Na-0.03, Cl-0.02, Ca-0.04. The graphs indicate that the manner in which the Np surface sites are defined are incorrect. It was suggested that log K and reactions specific to the actual original surface sites from table 2 and 3 be combined.

LS

5/17/07

Constant Capacitance layer of constant charge that separates the surface from the bulk solution. $I^{1/2}/m^2$ (f/m²).

M₂ = specific surface area .262 m²/g * weight 1.25g = 0.3275m²

CC = $.1^{1/2} / 0.3275 = .10356$ but paper uses $.1^{1/2} / .006 = .001897$, The Capacitance must not be specific to the total surface area being modeled.

In the Phreeqc modeling program, under surface, I assumed that the no diffuse layer would calculate the CC, however I don't believe it does. The other two options are the non-electrostatic model and the diffuse layer. I tried to take CaSCM2surfF9 using the

correct site moles and setting the surface to non-electrostatic. This made little changes, and according to Turner 95, the diffuse double layer would be an efficient modeling tool that uses the least number of parameters.

From Turner 1995

For the sorption of contaminants such as radionuclides, sorption reactions can be developed by analogy to aqueous speciation. For example, for the sorption of a cation CZ⁺, the formation of a surface complex can be written as

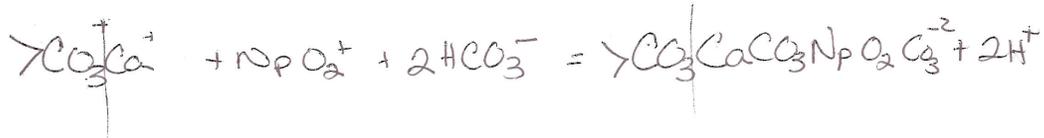
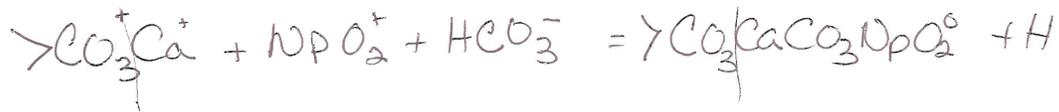


The corresponding equilibrium constant for this reaction, K_c, is commonly called a sorption or binding constant, and contains corrections for the effects of the electrostatic double layer at the mineral-water interface.

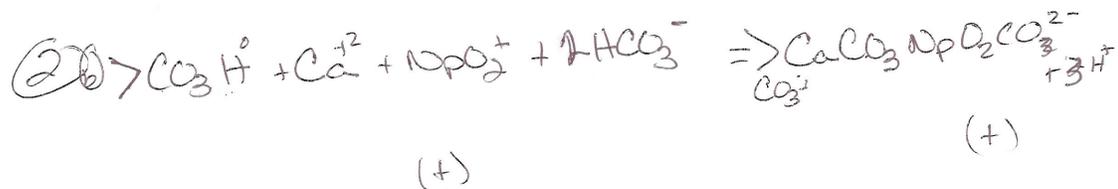
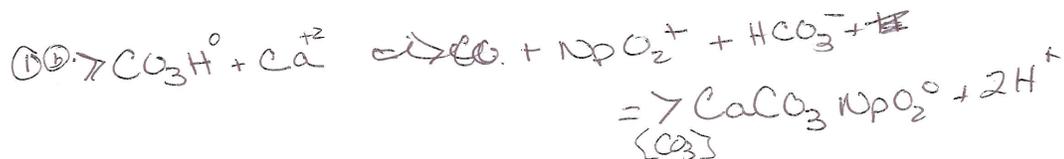
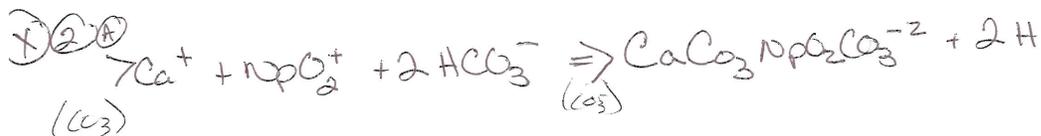
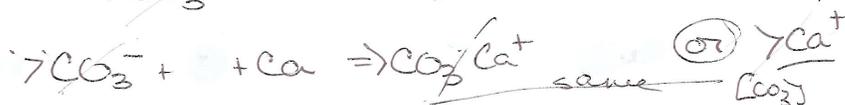
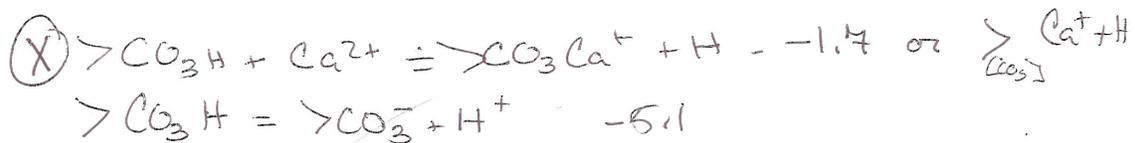
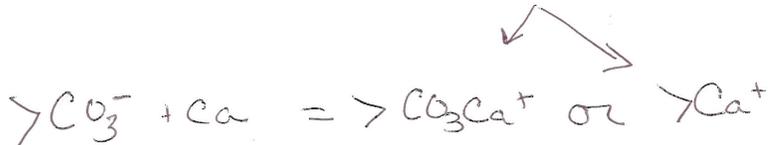
So does the article Zarvin et. al, 2005, imply that the equations seen in table 3 refer to the complexation reaction (see insert below 1b and 2b have log K of 2.66 and -3.24 respectively) or just the sorption to an intermediate surface site (equation 1a and 2a).

The paper states:

*Over the range of conditions examined here, the relative abundance of the >CO₃⁻ and >CaCO₃⁻ and the >CaOH₂⁺ and >CO₃Ca⁺ surface species as a function of pH are similar (Fig. 1). This is not altogether unreasonable since, upon sorption of Ca²⁺ to a >CO₃⁻ site, **the resulting surface site can be described as either >Ca⁺ or >CO₃Ca⁺ depending on where one defines the surface boundary.** This interpretation of the surface was proposed to explain the unusually high capacitance of the calcite surface. In fact, a surface species such as >CaCO₃EuCO₃⁰ should not be distinguished from >CO₃EuCO₃⁰ in our SC model. Furthermore, mechanistically, our SC model can be interpreted to suggest that sorption occurs when Ca²⁺ at a >CO₃Ca⁺ site is exchanged by EuCO₃⁺ or Eu(CO₃)₂⁻, similar to what has been suggested in [30]. **For simplicity, we rely solely on the >Ca⁺ surface terminations for sorption modeling.***



Surface site terminated different locations



Equations 1b and 2b were entered as surface species and run using the general SCM file (CaSCM2surfNpDL). The results of the Ca sorption sites were similar to those found in CaSCM2surfF9, the relative concentrations are almost horizontal lines around 50%. The Np species however are nearly depleted, while the Np sorbed to the surface sites are around 88% total.

LS

5/18/07

The same setup was run using the diffuse layer, with the default thickness. The solution had to be balanced; I chose to balance it using Cl (CaSCM2surfNpDL2). This had no effect on the results.

The surface species were then changed to equations 1a and 2a, no charge balance, and the General DL. The output was exactly the same. I re-evaluated the surface parameters; however as above the specific SA remains the same .262, the mass is 1.25g, and the sites moles 2.719×10^{-6} . If the SSA is incorrect, so would the site moles, changes to these two didn't help the run. Also the solid solution, or getting calcite and/or aragonite to precipitate out will affect surface sorption. If the solid solution is used, moles of calcite and aragonite are reported, however if they are specified in the equilibrium key as 0 SI and O initial moles, this means they are only allowed to precipitate. The output shows no precipitation, however the data for all other parameters are not much different. There may be a problem with how the problem is set up, if the equil key is used to precipitate solids.

LS

5/21/07

Due to the fact that Phreeqc doesn't incorporate the constant capacitance model, I was trying to find log K values for a general or DDL model to from the Lawrence Livermore papers. Also The CCM parameters will be used in MINTEQA2 for comparison. However, The general site distribution (without Np) can be modeled in the windows version, because its easier to navigate. The Np sorption will need to be modeled in the dos version that has had a modified database for CNWRA purposes. Although the windows database may be modified to include the Np aqueous species. The Np surface sorption equations were modified, hopefully correctly, using CaCO_3^- and CO_3^- as the binding sites for Np (5) species.

LS

5/22/07

In Minteqa2 for windows, the pH was entered as a sweep and in equilibrium with calcite and precipitation allowed. The trends are off and I tried to enter the problem several times into the dos version by creating multiple problems at each pH rather than a sweep. Upon running the file, a error was reported stating the file had a conversion error. The general site distribution in Phreeqc and Minteqa2 are incorrect (using .262m²/g, 1.25 g/L, 2.719×10^{-6} moles of sites), they are being distributed at a constant 50/50 percent. I was wondering if there was a typo in the Zarvin paper for the number of sites (5nm vs 5um) which would change the site concentration and order of 6 magnitudes to 2.719×10^{-12} . This gives a proper distribution. However, there may be an overall conversion problem (ionic strength?) when increasing from .04L to 1L. The problem will be entered as is set up in the paper to see if the distribution is correct.

LS

5/29/07

In Phreeqc I allow the ionic strength to be ~0.1 before it comes in contact with the surface, however after contact the IS varies. I thought that if the IS remained constant, that the site speciation would improve. The initial solutions were altered (inputs as mg/L) to allow the IS to equilibrate to .1 after contact with the calcite surface species. This did not improve the output. In Minteqa2 the IS can be calculated or made constant over the pH range chosen. Neither made much difference, however the placement of Calcite as an equilibrium species did. If specified as in equilibrium with solution, the calcite (even though allowed) doesn't precipitate. If not specified the initial speciation at 7.5 looks ok, but because it's a sweep rather than separate problems, the calcite doesn't react with the system and no further calcite precipitate, which throws the site

speciation off. Starting over, with calcite in equilibrium separate problems were run for each pH, in turn this is resultant chemistry is to be put back into the program with the sorption surface while allowing minerals to precipitate, this didn't work either. The trend in the sweep starts off ok, but as soon as all the calcite precipitates the site modalities remain a straight line (2 sites cross at 7.5, rather than 8.25).

LS

5/30/07

Whether the solution is in equilibrium or not, whether the IS is held at .1 or not, whether the initial .04L or 1L problem was set up the site modalities didn't work out. I added calcite as a finite solid, rather than have it in equilibrium, this didn't work. All the mentioned files worked when the site molality was reduced to e-12 rather than e-6. Once again, I'm not sure if that is the solution, but I don't see what is tripping up the system other than that parameter (however, doesn't appear to be a typo, which is a common unit to report site molalities in).

LS

6/18/07

Re-evaluating the data, I showed the calcite surface site evolution from the former file CASCM2surfNp6 that used 2.5e-8 mole site, 6.55 for specific SA, and 12.5g for mass calcite, all were incorrect. Changing one parameter at a time to 2.7e-6 mole sites, .262 specific surface area, and 1.25g of calcite you can see that the result is a 50 50 split between sites (NpSorp1 spreadsheet tab 6/18) but when the site moles were changed to 2.7e-12, the results were similar to those of the Zarvin paper. The point being, there must be a conversion error somewhere. These problems exist before the Np species are even entered into the problem. This same problem occurred in the Minteqa2 example also.

LS

6/29/07

I initially was working out the equations to come up with one general site, however when one general site is used the effect of pH is lost because you can't account for protonation and deprotonation.

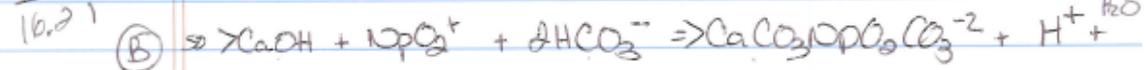
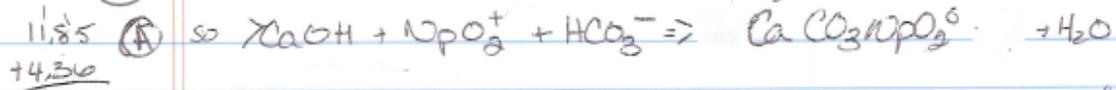
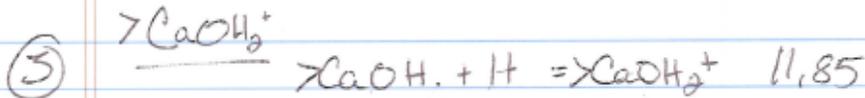
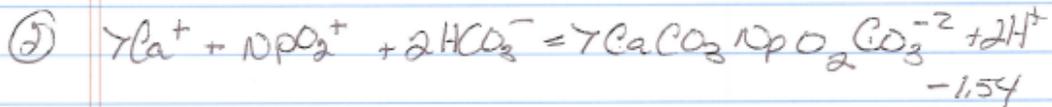
LS

7/2/07

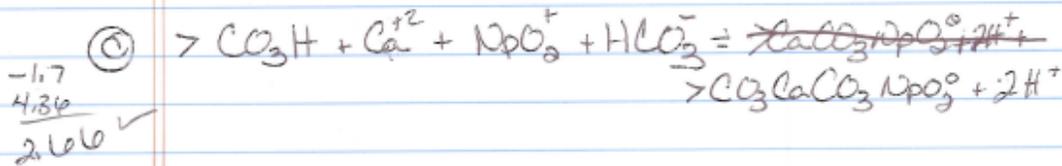
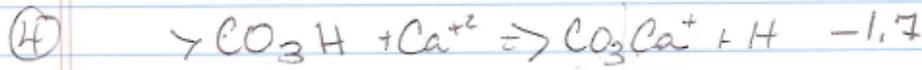
Since the Np sorption in the tables of Zarvin et al 2005 are general, I tried to consume two surface sites for one reaction and by making each site 2.719e-6 moles. However this is incorrect and doesn't achieve the desired affects. See the equations below, I entered the a-d into the file and had to balance the solution based on CL. The file ran, however there was much too much sorption. After the fact I noticed I used an old file that was based on the original volume of water, so the mass of water was changed. I also will run the file using the protonated surface sites see equations e-h. There are errors in the file that have accumulated so I will go back through the sections to make sure all the input matches (too much cutting and pasting).

γCaOH_2^+ can be written as $\gamma \text{OH}_2\text{Ca}^+$

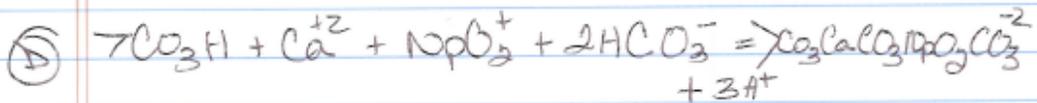
$\gamma \text{CO}_3\text{Ca}^+$ can be written as γCaCO_3^+



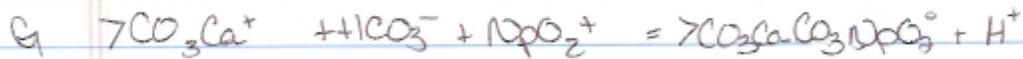
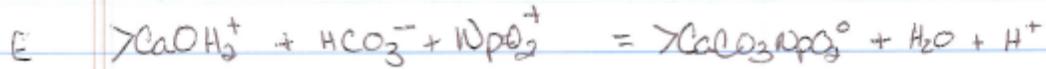
11,85
-1,54
10,31



-1,7
4,36
2,66 ✓



-1,7
-1,54
-3,24 ✓



LS

7/5/07

The results whether using equations a-d or e-h, above, for Np surface sorption are the same. When using the Non-electrostatic model in PHREEQC with all the proper inputs, the surface site concentrations worked out along with the major element concentrations, but the Np sorption and Np aqueous speciation are incorrect (from 49-95% of Np sorbed). If the Np surface reactions were removed the Np aq speciation was corrected. Either the equations e-H are wrong, or it's that the lack of correction for surface charge. Using Minteqa2, the Langmuir adsorption model was the only sorption model that accurately predicted the surface site concentrations. The Langmuir sorption model used in MINTEQA2 uses the activities rather than concentrations. However, the windows version would need to have the database altered to accommodate Np speciation and sorption.

LS

7/9/07

Using the non-electrostatic model, I increased the Np concentration to 1e-4, this corrected the relative concentration of the aqueous Np species and the % adsorbed was around 3%. I also increased the Np concentration in Phreeqc using the diffuse layer and No diffuse layer (default) sorption methods. This maintained the Np aqueous concentration distribution and also predicted 3% of Np sorbed, however on both Diffuse and no diffuse methods the site concentrations were off. Looking at the results, using the same log K's for both surface sites doesn't make sense. I changed the log K values of equations E-H (above) to the values of equations A-D. I tried this in all three Phreeqc sorption models with Np as 1e-7 and 1e-4M. The lower Np concentration returned better results. Still both predicted 100% of Np sorption and the Non-electrostatic predicted the site concentrations accurately; where as the other two did not.

LS

7/10/07

Looking at the results from yesterday the diffuse layer predicts almost a 50/50 of 60/40 relative concentration of the surface sites before the Np is reacted, this is incorrect. Should be about a 90/10 down to 50/50 back to 10/90 for the protonated vs deprotonated. So far the NEM works correctly, however when the Np surface sites are added the % sorption is off, therefore the equations and Log Ks are still wrong. Checked and altered solution species to make sure the HCO3- equations from the paper were included. I increased the amount of Np reacted because 100 % was sorbed which altered the aqueous distribution. I also went back to single sites for the Np surface species equations, using different log K values. Below is a chart of some of the results.

LS

7/11/07

Updated chart

File Name	Model	Np eqs CaOH or CO3H or both	Prot/Deprot	logK	site concen	Site Concentration predicted	%Np Sorption Predicted
CaScm2surfNp9_7-10	NEM	CaCO3-	Deprot	4.36/-1.54	2.72E-06	Ok	0.1-1.5
CaSCM4basesites7-2CaCO3	GDL	CaOH	base	16.21/10.31	2.72E-06	50/50	80's
CaSCM4basesites7-2CO3Ca	GDL	CO3H	base	2.66/-3.24	1.35E-06	50/50	80's
CaSCM4protsites7-9	GDL	both	prot	16.21/10.31/2.66/-3.24	1.35E-06	50/50	80's
CaSCM4protsitesCO3Ca	GDL	CO3Ca	prot	4.36/-1.54	1.35E-06	50/50	80's
CaSCM4protsitesNEM	NEM	both	prot	4.36/-1.54/4.36/-1.54	1.35E-06	ok	100
CaSCM4protsitesNEM_CO3Ca	NEM	CO3Ca	prot	4.36/-1.54	1.35E-06	ok	100
CaSCM4protsitesNEM_logkadd	NEM	both	prot	16.21/10.31/2.66/-3.24	1.35E-06	Ok	100
CaSCM4protsitesNEM_logkadd1e-6	NEM	both	prot	16.21/10.31/2.66/-3.24	1.35E-06	Conc off ex CaCO3- is .3 (.9-should be)	100
CaSCM4protsitesNEM_NpO21e-4logkadd	NEM	both	prot	16.21/10.31/2.66/-3.24	1.35E-06	off by at least 2 orders of magnitude	2.6

LS8/14/07

Based on the chart above, the CaSCM4protsites7-9 file was adjusted to increase the amount of surface sites and order of magnitude. This improved the results. The Specific surface area was modified, but ultimately changed back to a value of .262. The Np sorption and aqueous are still off from the reported values. A new file was created, altering how the Np aqueous master solution species is entered. Initially this file only performs the calculations at 7.5 and 9.75 to access the accuracy of the file. The set up was changed in order to make alterations much easier, below is a copy of the file set up. The Np calculations may be inaccurate, so modifications will be made.

File 8-14b

```

SELECTED_OUTPUT
  -file                8-14b.txt
  -molalities          CO3-2  HCO3-  NaHCO3  NaCO3-
USER_PUNCH
-headings TotCa TotCarb Sicalcite MolCalc MolArag NpO2(CO3)2-3
NpO2(CO3)3-5 NpO2+ NpO2CO3- xCaOH2+ yCO3- yCO3Ca+ xCaCO3- yCO3CaNpO2
yCO3CaNpO2CO3-2 xCaCO3NpO2 xCaCO3NpO2CO3-2 %np(0) %np(-2)
-start
10 PUNCH TOT("Ca")
20 PUNCH MOL("HCO3-")+MOL("NaCO3-")+MOL("CO3-2")
30 PUNCH SI("Calcite")
40 PUNCH EQUI("Calcite")
50 PUNCH EQUI("Aragonite")
60 PUNCH(MOL("NpO2(CO3)2-3")/1e-7)
70 PUNCH(MOL("NpO2(CO3)3-5")/1e-7)
80 PUNCH(MOL("NpO2+")/1e-7)
90 PUNCH(MOL("NpO2CO3-")/1e-7)
100 PUNCH(MOL("Calc_xCaOH2+")/1.35e-6)
110 PUNCH(MOL("Calc_yCO3-")/1.35e-6)
120 PUNCH(MOL("Calc_yCO3Ca+")/1.35e-6)
130 PUNCH(MOL("Calc_xCaCO3-")/1.35e-6)
140 PUNCH MOL("Calc_yCO3CaCO3NpO2")
150 PUNCH MOL("Calc_yCO3CaCO3NpO2CO3-2")
160 PUNCH MOL("Calc_xCaCO3NpO2")
170 PUNCH MOL("Calc_xCaCO3NpO2CO3-2")
180 PUNCH((MOL("Calc_xCaCO3NpO2")+MOL("Calc_yCO3CaCO3NpO2"))/2.7e-005)*100
190 PUNCH((MOL("Calc_xCaCO3NpO2CO3-2")+MOL("Calc_yCO3CaCO3NpO2CO3-2"))/2.7e-005)*100
-end
SOLUTION 1
  temp      25
  pH        7.5
  pe         4
  redox     pe
  units     mol/kgw
  density   1
  Cl        0.02
  Ca        0.04
  Na        0.02
  C(4)     0.02
  -water    1 # kg
SOLUTION_MASTER_SPECIES
  Np        NpO2+          0      269      269
SOLUTION_SPECIES
NpO2+ = NpO2+
  log_k     0
H2O + NpO2+ = NpO2OH + H+
  log_k     -11.3
HCO3- + NpO2+ = NpO2CO3- + H+
  log_k     -5.37
CO2 + H2O = HCO3- + H+
  log_k     -6.34
2HCO3- + NpO2+ = NpO2(CO3)2-3 + 2H+
  log_k     -14.12

```

```

3HCO3- + NpO2+ = NpO2(CO3)3-5 + 3H+
  log_k      -25.49
SAVE solution 1
END
SURFACE_SPECIES
Calc_xCaOH = Calc_xCaOH
  log_k      0
Calc_xCaOH = Calc_xCaO- + H+
  log_k      -12
Calc_xCaOH + H+ = Calc_xCaOH2+
  log_k      11.85
Calc_xCaOH + H+ + HCO3- = Calc_xCaHCO3 + H2O
  log_k      13.17
Calc_xCaOH + HCO3- = Calc_xCaCO3- + H2O
  log_k      6.77
Ca+2 + Calc_yCO3H + HCO3- + NpO2+ = Calc_yCO3CaCO3NpO2 + 2H+
  log_k      2.66
Calc_yCO3H = Calc_yCO3H
  log_k      0
Ca+2 + Calc_yCO3H = Calc_yCO3Ca+ + H+
  log_k      -1.7
Ca+2 + Calc_yCO3H + 2HCO3- + NpO2+ = Calc_yCO3CaCO3NpO2CO3-2 + 3H+
  log_k      -3.24
Calc_yCO3H = Calc_yCO3- + H+
  log_k      -5.1
Calc_xCaOH + 2HCO3- + NpO2+ = Calc_xCaCO3NpO2CO3-2 + H+ + H2O
  log_k      10.31
Calc_xCaOH + HCO3- + NpO2+ = Calc_xCaCO3NpO2 + H2O
  log_k      16.21
SURFACE_MASTER_SPECIES
  Calc_x      Calc_xCaOH
  Calc_y      Calc_yCO3H
SURFACE 1 1.35e-6 for both sites
  Calc_xCaOH 1.35e-005 0.262 1.25
  Calc_yCO3H 1.35e-005
  -no_edl
SAVE surface 1
END
PHASES
Fix_H+
  H+ = H+
  log_k      0
EQUILIBRIUM_PHASES 1
  Calcite    0 10
  CO2(g)     -3.5 10
  Fix_H+     -7.5 Na2CO3 10
REACTION 1
  NpO2+      1
  1e-007 moles in 1 steps
USE solution 1
USE surface 1
END
EQUILIBRIUM_PHASES 1
  Calcite    0 10
  CO2(g)     -3.5 10
  Fix_H+     -9.75 Na2CO3 10
PHASES

```

```

Fix_H+
  H+ = H+
  log_k      0
REACTION 1
  NpO2+      1
  1e-007 moles in 1 steps
USE solution 1
USE surface 1
END

```

LS

8/15/07

The new file was further altered due to the fact that Np aqueous speciation and percent sorbed was mis-calculated. The relative concentration should be divided by the total aqueous Np concentration not the total in the system (even though the relative concentration adds up to only .9 -90%)

```

Relative concentration
(MOL("NpO2(CO3)2-3")/1e-7)
(MOL("NpO2(CO3)3-5")/1e-7)
(MOL("NpO2+")/1e-7)
(MOL("NpO2CO3-")/1e-7)
CORRECTED
(MOL("NpO2(CO3)2-3")/TOT("Np"))
(MOL("NpO2(CO3)3-5")/TOT("Np"))
(MOL("NpO2+")/TOT("Np"))
(MOL("NpO2CO3-")/TOT("Np"))

```

Initially I thought the % Np sorbed was the % of total sites bound to Np, not Np sorbed or % Np Sorbed

```

MOL("Calc_xCaCO3NpO2")+MOL("Calc_yCO3CaCO3NpO2")/2.7e-005)*100
MOL("Calc_xCaCO3NpO2CO3-2")+MOL("Calc_yCO3CaCO3NpO2CO3-2")/2.7e-005)*100

```

Corrected

```

MOL("Calc_xCaCO3NpO2")+MOL("Calc_yCO3CaCO3NpO2")/1e-7)*100
MOL("Calc_xCaCO3NpO2CO3-2")+MOL("Calc_yCO3CaCO3NpO2CO3-2")/1e-7)*100

```

Which gives

%np(0)	%np(-2)
9.8919e+001	6.1216e-001
5.0946e-001	9.9316e+001

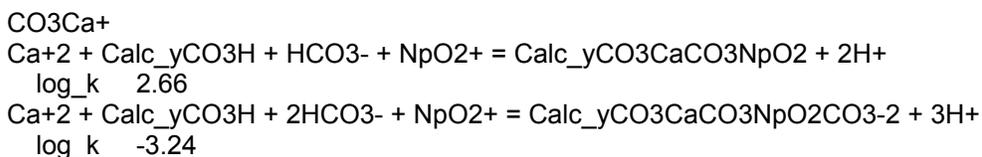
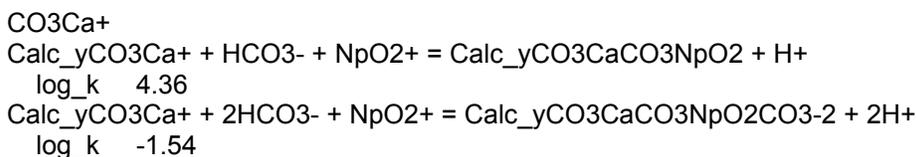
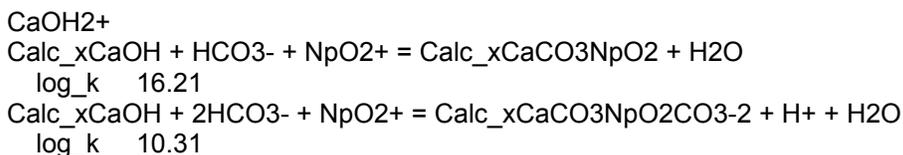
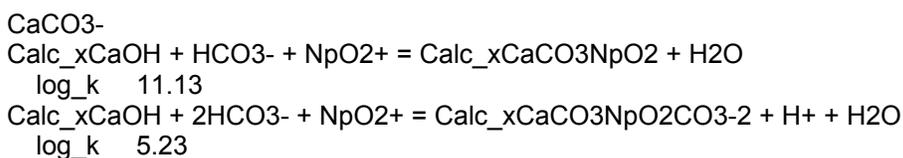
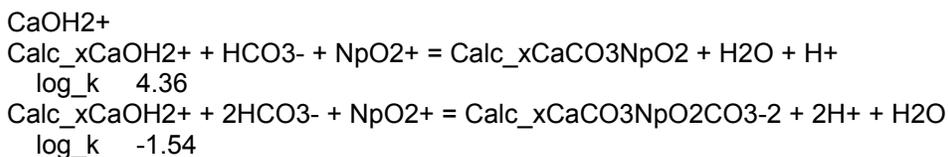
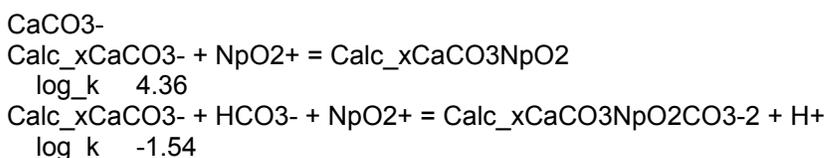
OR

```

(MOL("Calc_xCaCO3NpO2")/1.e-7)*100
(MOL("Calc_xCaCO3NpO2CO3-2")/1.e-7)*100
%Canp0      %canp-2
4.9091e+001  3.0380e-001
2.0429e-001  3.9825e+001

```

The site concentrations were bumped up to 2.79e-6 for each site, which had little or no effect Np% sorbed. In the text it mentions that the sorption data fit well with a single SC reaction fit to the data. Here I am weeding through the various interpretations of Table 3. The reasonable possibilities for the actual sorption equations are on the "possible equations" tab of the Npsorp1.xls spreadsheet. While all of the graphs match well with the exception of the %Np is still off. I believe the interpretation of Table 3 is the key to correcting this problem. Through a process of elimination, the best fit Np sorption equations will be sought out.

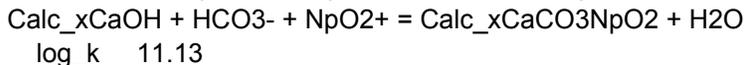


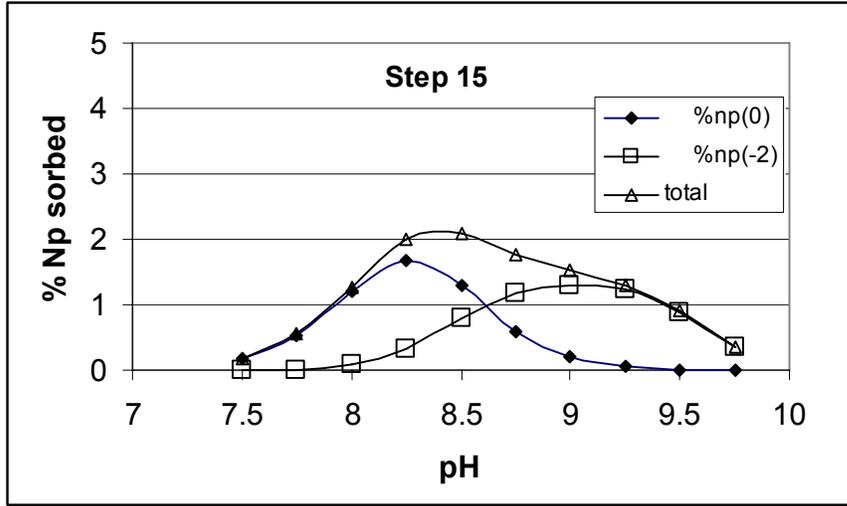
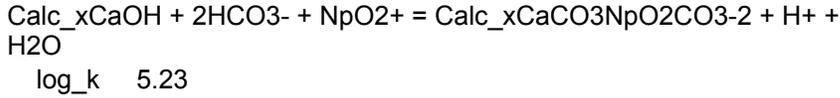
Step 1, use the base CaOH only equations- results NP sorbed up to 99% wrong trends on graph
 Step 2 Change site concentrations to 2.719e-6 each- result still 99% wrong trends on graph

LS

8/16/07

Steps 3-17 are recorded in the Npsorp1.xls spreadsheet on the worksheet labeled 8-15. Various combinations of sorption equations were looked at: one or both surface sites, entered as base, protonated, de-protonated sites, and equations for three surface sites were used CO3Ca+, CaOH2+, and CaCO3- (which the equations seem least likely to be accurate. However, the results indicate that Calc_xCaOH equations alone yield the best Np% sorbed trends, but the actual % is still off. The results of trial 6 and 15 are compared and graphically represented on the bottom of the possible equations table in the npsorb1.xls. See below





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8-17-07

Using the step 15 setup, the concentration of the surface sites was altered to determine if more sites increased the amount of Np sorption that takes place. When increasing the site mole concentration, an order of magnitude the % sorbed increased, but not to the % expected, two order of magnitude increase sorption too much. In between 2.7×10^{-4} and 2.7×10^{-5} worked best and altering the actual number of moles to 4.4×10^{-5} , which is just a random number between 2.7×10^{-4} and 2.7×10^{-5} . However the system is very sensitive to the site mole concentration and 4.4×10^{-5} give the best fit according to the data in Figure 10. If at a pH of 7.5 the 14 % is sorbed (1.4×10^{-8} moles/L) then the amount in solution at that pH is 8.6×10^{-8} and so on. See table below. If 4.4×10^{-5} moles sites are the best fit, however the % sorbed at pH 8.5 is higher than at pH 8.25, which is the opposite of the Zarvin paper.

According to Figure 10 Zarvin et al 2005

pH	% sorbed- Figure10	Sorbed Conc $1 \times 10^{-7} \%$	Percent Aq Tot Np- Sorbed
7.5	14	1.40×10^{-8}	8.60×10^{-8}
8.25	25	2.50×10^{-8}	7.50×10^{-8}
8.5	22	2.20×10^{-8}	7.80×10^{-8}
9.75	2	2.00×10^{-9}	9.80×10^{-8}

0.000044 site moles	pH	CaCO ₃ NpO ₂	CaCO ₃ NpO ₂ CO ₃ -2	total	In solution	Aq Np conc based % paper
	7.5	2.96×10^0		1.83×10^{-2}	2.98	9.70×10^{-8}
	7.75	8.01×10^0		1.57×10^{-1}	8.17	9.18×10^{-8}
						8.60×10^{-8}

8	1.62E+01	1.00E+00	17.23	8.28E-08	
8.25	2.08E+01	4.07E+00	24.90	7.51E-08	7.50E-08
8.5	1.58E+01	9.76E+00	25.54	7.44E-08	7.80E-08
8.75	7.63E+00	1.49E+01	22.54	7.74E-08	
9	2.78E+00	1.72E+01	19.99	8.00E-08	
9.25	8.52E-01	1.67E+01	17.51	8.25E-08	
9.5	2.05E-01	1.26E+01	12.84	8.72E-08	
9.75	2.80E-02	5.47E+00	5.50	9.45E-08	9.80E-08

The Ionic strength doesn't remain at 0.1 once in equilibrium with calcite and CO₂(g).
The file was restructured to try to preserve the 0.1 ionic strength, this returned the same results as the 8-15 file.

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2/6/08

Work on this project has halted; the notebook will be closed and handed in to QA. If the project is to be resumed in the future a new notebook will be created.

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ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 874E

Document Date:	04/27/2001
Availability:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, Texas 78228
Contact:	Southwest Research Institute® Center for Nuclear Waste Regulatory Analyses 6220 Culebra Road San Antonio, TX 78228-5166 Attn.: Director of Administration 210.522.5054
Data Sensitivity:	<input checked="" type="checkbox"/> "Non-Sensitive" <input type="checkbox"/> Sensitive <input type="checkbox"/> "Non-Sensitive - Copyright" <input type="checkbox"/> Sensitive - Copyright
Date Generated:	10/01/2006
Operating System: (including version number)	Windows XP
Application Used: (including version number)	PHREEQC, V 2.12.5 & MINTEQ for Windows V.15.
Media Type: (CDs, 3 1/2, 5 1/4 disks, etc.)	1 CD
File Types: (.exe, .bat, .zip, etc.)	.mtq, .out, pdf, and doc
Remarks: (computer runs, etc.)	Media contains: Attachments and notebook