

**Electronic Scientific Notebook
877E**

Actinide Mobility

Project # 20.06004.01.007

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7/6/07

Actinide Mobility

By Lynn Sabido LS

Objective: To model the solubility or stability of 5 actinides (Se, Tc, U, Np, and Pu) in a specific aqueous environment. Determining the dominant oxidation state at each pH-Eh conditions will give insight into that actinides mobility at those conditions. This will be done using pH vs Eh diagrams and solubility runs on two modules of Geochemists Workbench know as Act2 and React.

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

Hypothesis: Predict the oxidation state of the 5 actinides over a range of Eh and pH values to demonstrate the mobility of these species. At higher pH values above 6 and equilibrated with air CO₂, these oxidized species will form anionic carbonate complexes that are more mobile due to the decreased likelihood of adsorption to mineral surfaces.

Approach: Model each actinide in the presence of carbonate using an Air pCO₂ or higher to demonstrate what species are dominant. These runs will be done using a range of Eh values for each systems chemistry to see how the Eh affects the stability fields and saturation indexes of the species over a range of pH values. Sulfate will also be added to see if it affects the actinide speciation/stability.

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: Based around potential water chemistries and possible Eh and pH ranges for the system of interest. The initial input waters will be determined from literature and possible Eh values will be used to create separate runs over the same pH range.

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

LS

5/31/07

There are two GWB modules that can be employed to look at the stability/solubility of each species of interest Se, Tc, U, Np, and Pu. Act2 plots Eh-pH over a specified range for a given species that can be in the presence of other gases or aqueous species. The React module allows you to react in any phase into the system and then graph the pH vs Eh or any other parameter. The stability field calculated in Act2 uses the nearest equation which should allow determining the SI of phases. $SI = \log(Q/K)$, where K is given for each equation, but I'm not sure that the reported output reports the concentrations of each phase. Only the activities are reported, so if activity coefficients are =1, then the activities= concentrations.

LS

6/1/07

Not sure how to determine concentrations or mineral saturation index from the Act2 Eh-pH diagram output. The equations that employed the nearest formula to set the stability boundaries are all included. But no concentrations for solids phases are reported.

LS

6/4/07

Work on solubility of each species of interest Se, Tc, U, Np, and Pu. Where the pH and Eh are slide, using the react pane in GWB in order to access the stability of various oxidation states. However, this is not the desired method, need to specify one the general aqueous chemistry of the problem and decided a series of Eh values for the same system in order to make a comparison of the plots over a specified pH range. These data will then be graphed onto one figure. The chosen actinide concentration will dependant on keeping all phases slightly under saturated.

LS

6/5/07

A series of pH-Eh runs were done for Se, Tc, U, Np, and Pu. For all 5 species were run alone or with SO₄ of .03 activity, or a CO₂ (g) -3.5, each either suppressing or allowing solids at a concentration of 1e-6M, these runs were done also allowing solids, but with an actinide concentration of 1e-3M. Only the figures for each of the 45 runs were saved and 5, one for each species of interest, input files were saved for future use. This is because the files are so easily altered and the desired results are the graphs.

LS

6/7/07

The Majority of the previous runs were redone using the Thermo.com.v8.r6+.dat database. The default actinide concentration was changed to 1e-8M, dissolved carbonate 1e-4M, and the graphs ranges from a pH of 4 to 14 and an Eh of -.05 to 1.0.

LS

8/23/07

Given 6 water chemistries, with two Eh values, and one with two S values, I created the base files to incorporate the radionuclides (Se, Tc, U, Np, Pu). Some of these files can't

reach equilibrium alone, possibly because of the large charge imbalance. All files will be included with this notebook.

	Water 1	Water 2	Water 3	Water 4	Water 5	Water 6
pH	13.44	12.55	13.4	12.2	12.5	10.5
Na+	.101	.169	.363	.363		
K+	.303	.0057	.0039	.0039		
Mg ⁺⁺	1.3e-08	1e-07	7.43e-11	9e-10		
Ca ⁺⁺	8.43e-04	.0201	5.62e-04	8.53e-04	.02	.002
Al ⁺⁺⁺	1e-05	5e-06	1.54e-03	1.74e-04		
Cl-		.16	2.74e-02	2.47e-04		
F-	7.6e-04	1e-04				
CO ₃ ⁻⁻	2.04e-04	1e-05	4.42e-02	3.76e-05		Control by calcite, given Ca ⁺⁺
SO ₄ ⁻⁻	7.5e-04	1e-04	2.35e-04	5.56e-04	.001 and 0.02	.001
H ₂ SiO ₄ ⁻⁻	5e-05	1.6e-05	3.23e-04	2.73e-04	1e-04	.001
NO ₃ ⁻						
Eh values to model	-350 mV +80 mV	-350 mV +200 mV	-350 mV +80 mV	-350 mV +200 mV	-350 mV +200 mV	0 mV +600 mV
	PSI Bericht 02-26, Table 2, initial stage	PSI Bericht 03-06, Table 3, Stage II	Topic 1B, Table 5-5, OPC. Cl high because in equil with groundwater.	Topic 1B, Table 5-5, 75%BFS-OPC	Berner 1992 and Atkins et al. 1991. Sulfur sensitivity for BFS.	Berner 1992 and Atkins et al. 1991. Don't consider BFS.

All concentrations in mol/L

Water 1

I tried adding Se to the -350mv run, but it couldn't converge. I added 1e-8 of Se to the +80mv run and it converged, but the Se concentration was raised to 1e-4 to increase the saturation of Se species. AT the concentration the highest mineral saturation value was for CaSeO₃:2H₂O of -4.7788. Any larger concentration, the run didn't converge.

LS

8/24/07

Water 1

I tried adding Np to the -350mv run, but it couldn't converge. I added 1e-8 of Np to the +80mv run and it converged, but the Np concentration was Decreased to 1.5e-13, which gave a -.0020 SI for NpO₂, a 2.0e-13 Np concentration gave a SI of .1229. 1.507e-13 gave Np at saturation (0).

The Pu saturation limit concentration is $1.3015e-17$ for the eh +80mv. I have tried to use charge balance, and alter the options to encourage convergence of the other files. This didn't work, the error message in most cases states the maximum residual has been reached.

LS

8/27/07

I set up all the runs for the six different waters, different Eh values, and for #5 different SO4 value. I have a few questions/problems I wanted to run by you to make sure I was on track.

In general, (using REACT for more control) initially find the one closest (or most over) to saturation. Then adjust the radionuclides concentration to bring that mineral to saturation.

None of the waters with a -350mV, will converge. I know the charge imbalance is far off. The error states that the maximum residual is a high number and that the total species concentration is all residual. See excerpt below. I ran water 1, with -350mV in Minteqa2 with out any radioclides and the file did converge, but suppressed some gases and the residual amounts were very different than those of GWB. For GWB, I did try to change the options, specify charge balance to make the file converge, but with no luck.

The positive Eh runs converge fine, and report the charge imbalance on the run screen. There are some convergence errors when considering the radionuclides that still have to be worked out. I have started a spreadsheet, called saturation limits, documenting the charge imbalance, since it's not reported as output.

I have been trying to get the SI of most saturated species exactly at 0.

The setup of water 6, in which the CO3-2 is to be controlled by Calcite as defined by Ca+. The concentration of Ca is .002 mol/L, HCO3 must be swapped for calcite and I'm not sure what value to enter for calcite (.002 mol/L)?

LS

8/31/07

I continued working on the saturation limits of waters 1-5, only those with positive Eh values. For each run suppressing the minerals to find the most saturated mineral, and then controlling the radionuclide with that mineral concentration worked for most runs. A spreadsheet, saturation limits, was updated to include the results. Some runs wouldn't converge using the radionuclide as base species; some took after using a reduced or oxidized species. For water five, both S concentrations, there were many runs that would not converge after minerals were allowed due to the solution being oversaturated with respect to one or several species. However the output file reported the initial composition and calculated the moles in solution for the radionuclide of interest. These values may be a bit off and therefore not acceptable.

LS

9/4/07

Finishing up waters 5 and 6 for the runs with a positive Eh. I had many problems with solution 5 and a few with 6. The files wouldn't converge when minerals were allowed to precipitate, the output went through and evaluated the initial water, then failed to precipitate out the minerals. This may be due to creating a larger charge imbalance, however the errors ranged from supersaturated or just not being able to converge. Back to water one, the runs with a -350, which I tried to make converge. The problem states the maximum residuals are too large. Once again the residuals are the same concentrations and the input. The Eh is not allowing specific reactions to take place. The charge imbalance fix was tried using either nitrate or chloride. The chloride entered into negative values and there were problems entering nitrate as an ion to perform the charge balance.

LS

9/5/07

Looking at the Minteqa2 file that converged, the charge imbalance was entered into the GWB file as NO₃⁻ or NO₂⁻, but the run didn't know how to handle this and on occasion stated that it wasn't in the database, which it was, but maybe dealing with charge balance the equations are not retrievable. The file works with a slightly higher Eh value. So I slide the Eh from -0.1 to -0.35 and the file converged. However, when compared to the MINTEQA2 output for specie concentrations and mineral SI's, the two output files are off (see tab named compare1 in the saturation limits spreadsheet). This is because the equilibrium system is altered once in equilibrium with an Eh of -0.1. For each water with a Eh of -350mV, I tried to balance on Cl or Nitrate also incorporating the radionuclide species in oxidized form. This didn't work; the only solution was sliding the Eh.

LS

9/17/07

After reviewing the files with David Pickett, it was decided that the process that needed to occur should resemble that to which the spec8 module performs. Once the mineral closest to or most oversaturated is found, that mineral would be selected to be in equilibrium with the rest of the system, while all others are still suppressed. Previously when performed in the React module all minerals were allowed to precipitate which could affect the radionuclide's saturation/solubility limit. The react module will be used and the Eh will be slid from -350mV to +200mV in 100 step process. This allows intermediate values to be easily obtained. If the Eh can't be slid in React, the Spec8 program will be used.

LS

9/24/07

There is a separate folder for each water, which contains the output files for the various runs. Also, there is a new Saturation limits spreadsheet in the folder that has been updated. The only problems I had were making sure that the Tc runs. Many of the Tc runs, marked in yellow, will not reach the saturation limit and were in many cases checked using Spec8 and React. The last

column in the spreadsheet may contain a number, which indicates the resultant concentration pulled from Spec8 for comparison to the runs done in React where the Eh was slide. The runs checked against Spec8 are limited and are mostly done using positive Eh values. Runs for waters 6, 19, 25, 26, 27, 29, and 30 were done using Spec8 and are marked so in the last column.

LS

9/27/07

I re-ran many runs in order to see (i) uranium results with CaUO_4 and haiweeite suppressed and (ii) Tc results with KTcO_4 and Tc_3O_4 suppressed. I'm having problems with the TC run. At low -350 Eh, the next highest saturated mineral is $\text{Tc}(\text{OH})_3$ and the file will not converge if I allow that mineral to precipitate and specify it in the input window, but if I allow it to precipitate and specify Tc as a aqueous species in the input window then $\text{Tc}(\text{OH})_3$ is at equilibrium with the system. So these are the values I used. All files have been put into a subfolder marked W#-suppressed.

LS

10/2/07

Graphing of the existing data has been requested and a file that contains three columns (pH, Eh, and concentration) for Se has been modified (Se concs for 3D plot).

1. 3-D surface plot. pH on the x axis, Eh on the y axis, concentration on the vertical z axis (log).
2. 2-D contour plot of concentrations projected on pH-Eh plot.

Because the water chemistries don't necessarily vary smoothly, contouring may not work very well. But maybe some broad contour intervals will help. I have Sigmaplot installed on my computer. I believe you can import an excel spreadsheet as your source of data. I also have access to tecplot, but I think the input data needs to be formatted with headers even if its in excel.

LS

10/3/07

Yesterday I was looking at using Sigma plot and encountered a lot of issues, I then looked to tecplot and I would have to make a suitable input file for it to be read into the program. Today I had chad fix my copy of Sigma plot. As far as pulling the data for slid runs, there is a way; I'm just not sure what would work best and how to set that up, either a unix script, excel macro?

Email question/concern:

I was wondering why you were getting solubility control of Tc in some of the higher-Eh waters (e.g., 27 and 29) and then noticed that you were not fixing potassium in the runs that had KTcO_4 saturation control. This applies to other waters, as well (e.g., water 2). The K concentration needs to be fixed at the table value (or the lower value for the low-K sensitivity runs). I assume your first run of the water is showing

is showing KTcO4 to be the least under- or most over-saturated. When you then do the KTcO4 saturation run, do not fix K concentration by KTcO4. Fix it at the water composition value.

For instance, your Water 27 KTcO4 run gives 0.09544 molal K+, when in reality the water has only 3.2e-05 molal. This has the result of underpredicting the Tc concentration (think of the solubility product of KTcO4).

Also, think if there are other cases - where the solubility-limiting phase has two cations - where a similar error could have been made. I did a quick check of some U runs with CaUO4 and it appears you correctly fixed Ca at the required concentration - but please check this. The Ca-Se phases could also be affected.

RESPONSE

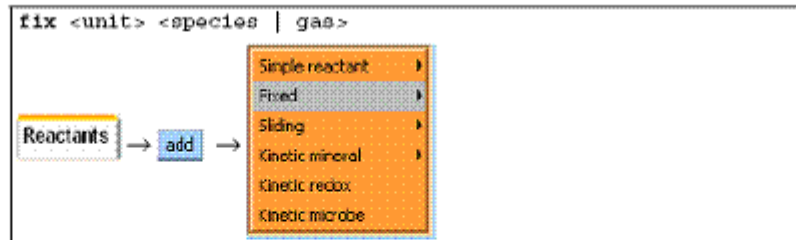
In the case of water 27, which was done with spec8, K is specified as 3.2e-5, but in order to allow KTcO4 be at equilibrium it needs to be entered in as the Tc species present and initially we said the concentration amount didn't matter. However, I just tried entering KTcO4 as 3.2e-5, then KTcO4 as 3.2e-5 and K as 1e-10, and I get the same results. For Spec8, if you don't specify the mineral in the basis pane, then it will not precipitate. I'll check tomorrow to see if this occurs to just the runs with Spec8 (waters 27+29) or within the react runs as well.

LS

10/4/07

I went through the saturation limit spreadsheet and identified all the runs where the solubility-limiting phase has two cations and checked to make sure that the second cation (k, Ca, or Na) did not exceed the concentration defined in the water composition. The ones highlighted in green have a second cation (k, Ca, or Na) that exceeds the input amount. These were checked using Spec8 and allowing the limiting phase (mineral) specified as free grams or free moles (I tried both) and neither worked. However, if the second cation concentration was increased one to three orders of magnitude, the file converged without problems. I didn't keep copies of the increased concentration runs. The ones in Blue had the second cation exceed the input concentration, but in spec8 allowing the limiting phase is entered as free grams, the problem worked correctly and the results are reported separately in the spreadsheet at the bottom. Any saved files for these corrections have the word "free" at the end of the filename, see the spreadsheet. I did go through the react runs and tried changing on several files allowing the limiting phase entered as free grams, this didn't work. The fix option in react doesn't constrain concentration, rather just activity of an ion, which doesn't work. I don't believe the fix command works for concentrations. Also For water one, the Ca-Se species at 200 and 80mv will not work properly if I specify the mineral as free mol or grams. If I increase the Ca concentration 3 orders to 0.843, then the run completes with 0.843 ca and .07920 Se. If I specify SeO3--, then as you know it becomes trial and error. I'm working my way down the list using spec8 and hopefully get some correct results using the "free" mineral concentrations.

fix



Use the "fix" command to hold the activity of a species, fugacity of a gas, or an activity ratio constant over the course of a run. The <unit> can be "activity" or "fugacity" ("a" or "f" for short), "ratio", "pH", "pe", or "Eh", or it can be omitted. Examples:

```
fix pH
fix a H+
fix f O2(g)
fix ratio Ca++/Na+^2
```

LS

10/8/07

After a suggestion I am considering a concentration of 1 M to define "no solubility limit." You could set up the water chemistry as in the table and set Se (or Tc) to 1 M. Un-suppress only the Se (or Tc) phases - maybe you can limit the list to those you've seen show up as saturated in existing runs. Solubility limitation of Se (or Tc) should happen only when the limit gets under 1M - and maybe we won't get the dumping of Ca etc into the solution and maybe Ca will stay constant.

This method can not be done using Spec8, you need to specify the one and only mineral in equilibrium with the system to get any sort of precipitation. I did get correct results as a hit or miss with Spec8, by allowing the kg of water be 1 Free Kg, which allows the system to maintain a constant 1 KG of water. There were only two instances I found this to work. I tried with several React runs, however this didn't work.

LS

10/9/07

Basically I did what was suggested suggested, allowed aqueous Se or Tc be 1M, I have tried to add it as 1 Free Molal. In many instances at higher Eh values all Se or Tc minerals are under-saturated and nothing is in equilibrium, but within the range of -250 to -350mv one mineral is at saturation. At first I wasn't sure if that's what was desired, but at certain conditions, no Tc or Se will be at saturation. I'm checking to make sure the water is 1 KG, I've seen it go as high as 1.1KG and also that Ca and K are not beyond the initial values.

For some of the Tc runs, I had to use 0.5 M to get the run to converge. However, the water mass is still at 1 and nothing is beyond the concentration of the initial input.

LS

10/10/07

Continuing work on Tc and Se modified (1M) slides.

LS

10/11/07

I separated out the recent runs and put them into a folder named React1M in my S drive folder. I also included an updated version of the spreadsheet, but leaving the older version. For many of the Se react runs, the aqueous species concentration was 0.7M instead of 1M (marked so in the spreadsheet) in order to allow convergence. I think this affected the results.

LS

10/12/07

Trying to make the 3-d and contour plots in sigma plot, the whole range of values can be graphed for the 3-d line plot and the axis can be adjusted accordingly. However, for the contour plots, when the entire range or even intervals of 6 data xyz triplets are selected and error message occurs. If the z column (Concentration) is duplicated and the graph style is changed to XY Many Z a graph will be produced, but double lines occur from the 2 columns of Z data.

LS

10/16/07

I pulled new SE data from the 1M runs and plotted a 2-D and 3-D plot using sigma plot. I had the same problems with the contour plots as before, bad XYZ triplet.

LS

1/17/08

Additional modeling needs to be done for the Solubility report. A different database will be used the GWB-format database incorporating NEA data, obtained from:

<http://migrationdb.jnc.go.jp/english.html>

It simply needs to be renamed *something*.dat in order to work, I chose NEA.Dat
To start only the Np data will be compared between modules of GWB and between the different databases. One water from each group outlined in Pickett's report "Radionuclide Solubility in Cement-Based Material Pore-Fluids" and I chose to compare waters one, two, four, six, twenty seven, and twenty nine. All compared new or old (copied) to a folder named NEA_comparison_2008 and within will be a separate folder for each water. I pulled or ran new SpecE8 run with GWB database thermo.com.v8.r6+ and the existing React data for waters one, two and four that were run using the same database. New SpecE8 and React runs were created using the NEA database to compare solubility limits. Waters 1,2, and 4 had only React files created and waters 6, 27, and 29 had SpecE8 files and React files created for each. The results are listed in a spreadsheet named comparison_NEA. The H₂SiO₄-2 had to be calculated for H₂SiO₄, which is the species listed in the NEA DB. Water six presented a problem due to the fact the Np solubility is also controlled by calcite, which is not in the NEA database. I entered Ca+2 and CO₃-2 as 0.002 molality and specified only the NpO₂ (cr-NEA notation) solid. I'm not sure this can be used for comparison.

LS

2/6/08

The waters that were used in these runs can be grouped into a few categories, according to Pickett's paper. Group 1 waters 1, 3, and 16 run an eh range of +80 to -350 and have a 13.4 ph value and similar chemistries. Group two consists of waters 4, 7, and 8 who have a eh range of +200 to -350 with a ph range of 11.9 to 12.3 and share a similar chemistry. Group 3 waters, 2, 5, and 14 has a pH of 12.5 and span a eh of 200 to -350. The four group is a bit more diverse (6, 19, 25, 26, and 30) with a variable pH (8.27-11) and the eH is of variable ranges or it allows oxygen fugacity to control eH. For each group the individual waters were run suppressing all the minerals except the top three that affect the Se solubility limit, in this case its minerals Se, CaSeO4, and CaSeO3:2H2O and calcite for group four. Se was entered as SeO3-2 with a concentration of 0.5 molar. Once run, a group comparison of SeO3-2 concentration versus Eh was made to see if the results were the same. Groups 1-3 look comparable, but group four is off. Group four was set up with defining a oxygen fugacity of 0.2 and sliding the Eh to -100mvolts. Due to the various chemistries an F(O2)=0.2 creates a different starting eh value for the various waters. This process may be changed.

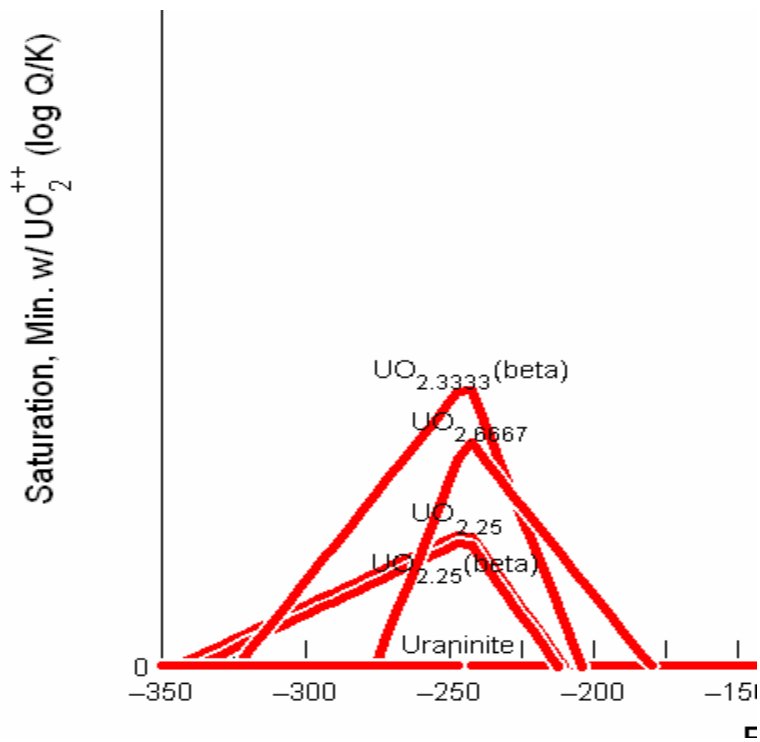
LS

2/11/08

I set up the other radionuclide runs in the same manner as I did with Se, suppressing all minerals except the top 3-6 solubility limiting minerals and allowing the aqueous radionuclide concentration equal to 0.5 molar.

Radionuclide – entered as aq species	Allowed minerals
NpO2+	NpO2, Np2O5, NpO2OH(am), Np(OH)4
PuO2+	PuO2, Pu(OH)4, Pu(OH)3, PuO2(OH)2
TcO4-	KTcO4 NaTcO4 Tc(OH)2 Tc(OH)3 Tc3O4 TcO3
UO2++	CaUO4 MgUO4 Na2U2O7 Soddyite Uraninite

In the Np and Pu runs NpO2 and PuO2 is the solubility limiting species over the entire Eh range. For Tc species at positive Eh levels all Tc species are under saturated and KTcO4, having the highest SI. At negative Eh values Tc3O4 is in equilibrium. Over the range of Eh U solubility is controlled by CaUO4, MgUO4, Na2U2O7, and Soddyite. At more increasingly negative Eh values other U (UO2.6667, UO2.25, UO2.25(beta))species become briefly supersaturated and vary depending on which water type.



However by Eh values of -350mv the species in equilibrium are Uraninite and CaUO4 and include Na2U2O7 in group one. The only problem with the files not converging are the uranium group 4.

LS

2/12/08

I worked on the group 4 of the uranium and while all the files are running; I had to alter them to do so. Originally only water 6 and 30 would run properly specifying 0.5 molar of UO2+, while 19, 25 and 26 failed. Water 19 converged when the units were altered to 0.5 mg/kg even though it's the same total moles because it's a dilute system in 1kg of water. Waters 25+26 would only run if uranium was specified as 0.5 mg/kg UO2++. There are many U species that become supersaturated (when all but the top 5 species are suppressed) when they were far under saturated.

I reran the files suppressing CaUO4 as we had done before, although the reason for doing so wouldn't apply so much to these runs. Previously the U-mineral CaUO4 was set in equilibrium with the water, in some cases the Ca concentration increased to far beyond reasonable. By suppressing CaUO4 for these runs, a certain few, the Ca concentration and U aqueous species are affected by the suppression and the files in the folder are labeled with "suppressed" at the end.

Screen print comparisons are also included in the folder.

LS

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 877E

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Remarks: (computer runs, etc.)	Media contains: Attachments