HLWYM HEmails

From: David Pickett
Sent: Friday, July 14, 2006 3:44 PM
To: Konstantinos Makris
Subject: RE: update

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Konstantinos,

I'm leaving today for a two-week vacation, so you won't be hearing from me for a while. I haven't put together any explicit instructions for you, but please take a look at my last few emails and think about further tests you can construct to get at the pH-controlling mechanism. Aso please try to put together the input/output files and link them to the notebook, as I've asked. (All of his depends, of course, on your availability.)

I mentioned the question of calcite precipitation. Here's a paragraph that Paul Bertetti wrote with his ideas about what may be happening in our solutions. Xihua recently found that pH was rising even in the absence of steel:

"I believe there are a couple of contributors to the pH change in the test cells. Based on our analyses of the pore waters and chemical changes in the carbon steel test cells, it appears likely that calcite precipitates form solution as the solutions age. This is accompanied by an overall depletion of CO2 in the system. Even though the solutions are open to atmosphere, my calculations suggest that the partial pressure of CO2 is quite low (relative to atmosphere -- log fugacity -4.42 for the combined solution that had been opened and mixed for at least two hours -- so inside the test cells it may have been lower). The loss of CO2 and its incorporation into calcite is consistent with a pH increase. Moreover, the addition of fresh solution to replace samples continues to calcite precipitation process as more Ca is added. The small evaporation that does occur and the addition of original solution also tends to increase the pH. I might recommend addition of deionized water, diluted solution, or nothing to replace the water lost from sampling. Finally, the loss of SO4 and increase in S should be addressed. Based on analysis of the carbon steel solution samples, not all S is in the form of SO4 as one might predict from the redox (highly oxidizing for our sorption solutions at +500 mV Eh."

Maybe we can address some of this with GWB. If you want to discuss any of this with Paul, his email address is pbertetti@swri.edu.

Take care,

David

-----Original Message-----
From: Konstantinos Makris [mailto:Konstantinos.Makris@utsa.edu]
Sent: Tuesday, July 11, 2006 2:52 PM
To: dpickett@cnwra.swri.edu
Cc: Dibyendu Sarkar
Subject: RE: update

> Dr. Pickett,
>
> Regarding the closed system, I doubt that the software uses a closed system approach. Yes, I agree with you that Eh and fO2 goes down but not much; for example, Eh goes down from 650 to 450 mV, which is still oxidized conditions.
>
> I am attaching two scripts. One showing how MnO influences the pH of the system by using no cutoff value for the other mineral components and another script that shows the combined effect of MnO and Fe2O3 on pH evolution. Their maximum cutoff values for these 2 components were chosen based on weight losses that were recorded by your staff during the experiment.

If only MnO controls the overall pH magnitude then we see that MnO dissolution results in a pH decrease, but when Fe_2O_3 starts to react by forming Fe hydroxides then pH increases which gives the relatively good fit.

Konstantinos.

-----Original Message-----
From: David Pickett [mailto:dpickett@cnwra.swri.edu]
Sent: Tuesday, July 11, 2006 10:17 AM
To: Konstantinos Makris
Subject: RE: update

Konstantinos,

I just had another thought in looking at the schoepite and uraninite outputs you sent earlier.

It appears the runs may be under a closed system. I see Log fO_2 and Eh decreasing steadily during the runs, as if the reaction is consuming oxygen. Under our experimental conditions, atmospheric oxygen is probably maintained (though carbon dioxide may not be). Could you tell me if I am correct that you are not maintaining atmospheric oxygen?

David

-----Original Message-----
From: Konstantinos Makris [mailto:Konstantinos.Makris@utsa.edu]
Sent: Friday, July 07, 2006 10:26 AM
To: dpickett@cnwra.swri.edu
Subject: RE: update

Dr. Pickett,

From the re-run simulations I came to know that O_2 fugacity has little effect on the overall pH evolution of the carbon steel dissolution. Changing O_2 fugacity from 0.02 to 0.2 or even to 2 results only in minor changes in the initial (first 4-5 days), but after this no discrete increase/decrease on the magnitude of pH.

Konstantinos.

-----Original Message-----
From: David Pickett [mailto:dpickett@cnwra.swri.edu]
Sent: Thursday, July 06, 2006 11:04 AM
To: Konstantinos Makris
Subject: RE: update

Konstantinos,

A follow-up question:

On page 8 of your notebook, you got pH to go up to about 9.2. This appears to be because you set dissolved oxygen to a low value (0.2 ppm). I'm trying to understand how, in subsequent runs, you got pH to stay high (e.g., plot on page 14). For the plot on page 19 (pH plateau at about 9.6), did you stil have the wrong O_2 fugacity (0.02), or was there some other reason pH stayed high? I'm guessing the O_2 was still not too low, because the high-pH effect of the steel can still be seen in the uranium phase runs in which you say 02 fugacity was back to 0.2. What I'm trying to get at is what factor causes the high pH in your carbon steel runs - in contrast to your first carbon steel run, whichhad decreasing pH.

David

-----Original Message-----
From: Konstantinos Makris [mailto:Konstantinos.Makris@utsa.edu]
Sent: Thursday, July 06, 2006 10:32 AM
To: dpickett@cnwra.swri.edu
Subject: RE: update

Dr. Pickett,

I hope you had a nice 4th of July break. Sorry that I delayed to answer to your e-mail.

1. Yes, you are right, in some runs (my mistake) accidentally I used 0.02 O2 fugacity instead of 0.2 (20%). However, this is only in some runs, and when I run the uranium phases I used an O2 fugacity of 0.2.

2. I believe we allow them to dissolve. When I change for example the amount of the uranium phase (schoepite) from 1 to 50 g then I see a drastic decrease in pH, suggesting solid phase dissolution.

3. I hope I have answered your questions. How should I proceed from now on? What simulations you are most interested to run?

Konstantinos.

-----Original Message-----
From: David Pickett [mailto:dpickett@cnwra.swri.edu]
Sent: Friday, June 30, 2006 3:01 PM
To: Konstantinos Makris
Subject: RE: update

Konstantinos,

Another question: I'm not quite sure from your notebook how you treated oxygen in the last set of simulations. I see that you had set O2 fugacity to 0.02 at some point (1/10 atmospheric). Did this stay the same throughout the runs involving uranium phases? I see that removing nitrate from the basis set allowed pH to go up. What was O2 like in these runs? What was it in the uranium phase runs?

Also, with the schoepite and uraninite runs: are you simulating dissolution of these, or simply allowing them to equilibrate with the solution?

David

-----Original Message-----
From: Konstantinos Makris [mailto:Konstantinos.Makris@utsa.edu]
Sent: Friday, June 23, 2006 3:33 PM
To: dpickett@cnwra.swri.edu
Subject: update

Dr. Pickett,

I hope you are doing fine. I am sorry for not contacting you earlier. Mike Simpson visit was just fine. Now, the big question is still how are we going to explain the pH increase with time of the carbon steel experiment your staff conducted? The latest simulation we got, if you remember is the one below showing a pretty good fit. This fit occurred when we remove nitrate from the basis entry list (see below). Is it possible to have denitrification that converts nitrate to ammonia gas?? The solid phases that evolve are hematite and goethite. What do you suggest?

Konstantinos.

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Konstantinos C. Makris, Ph.D
Postdoctoral Fellow
Environmental Geochemistry Laboratory
Earth and Environmental Science Department
The University of Texas at San Antonio
6900 North Loop 1604 West
San Antonio, TX 78249-0663, U.S.A.
Ph: (210) 458-5745
FAX: (210) 458-4469
http://www.utsa.edu/EGL
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