

**Electronic Scientific Notebook
860E**

**GWB Modeling of the Evolution of Fluid Chemistry
inside a Waste Package Due to Carbon Steel and
Simulated High-Level Waste Glass Corrosion based on
Lab Results Attained from He et. al, 2007**

Project # 20.06002.01.222

Lynn Sabido

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GWB Modeling of the Evolution of Fluid Chemistry inside a Waste Package Due to Carbon Steel and Simulated High-Level Waste Glass Corrosion based on Lab Results Attained from He et. al, 2007

By Lynn Sabido LS

Objective: To model the results of Carbon Steel and Simulated High-Level Waste Glass Corrosion using GWB, version 6.0, and compare the results to those attained from Lab experiments from He et. al, 2007.

Training: In order to perform said mentioned work one needs to be familiar with the GWB computer program and have a basic understanding of aqueous systems and corrosion processes.

Hypothesis: Corrosion modeling of waste packages and waste glass can be achieved by using the GWB program. With the initial water composition, mass of waste, mass of resultant waste and composition of waste products, the chemical composition, pH, and redox potential of the fluid inside a waste package with corroding A516 carbon steel can be determined. This should show important information (pH control) for corrosion rates and Speciation and sorption processes. Using the data from the lab experiments and the GWB program the chemistry results from the lab experiments should be attainable.

Approach: Set up a GWB input file that mimics the steps followed to create the lab experiments and using the reported waste and glass waste oxides, initial chemical composition (j-13 water), and the reported corrosion mass.

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:\My Documents\Corrosion, however at the conclusion of this project all files will be transferred to a cd that will accompany this notebook.

LS

4/30/07

I was given a cd of files that contained previous work done by a group at UTSA. I initially tried to go through SCIENTIFIC NOTEBOOK 767E by Konstantinos C. Makris to figure out the thought process used to derive at the results they attained and submitted to CNWRA. I first took their file with corrosion oxide calculations, renamed it to oxidecalculations. I updated this file and made corrections to the mathematical equations and separate pages for initial grams/L of oxides in solution and the grams/L of corrosion products. The solution specifics at 60 and 90 degrees are specified in a file named Summary that accompanied the disk and has information from notebook 706. I initially I was exporting a graph of pH vs time, but as an EPS file which can be opened with Adobe Photoshop Elements, CorelDRAW, IrfanView32, Microsoft Digital Imaging Pro, or Microsoft Vision.

Trials 1-22, were not all saved, a select few were, however the Eps image of the pH vs Time was saved for other runs (see folder that accompanies disk – folder trials), which is currently in directory: (D:\My Documents\Corrosion\Trials). A summary of the various parameters changed are listed below. Some were meant to duplicate steps indicated in the UTSA notebook. In all, the resultant file they had was never achieved, possibly because the g/L of corrosion oxides were off, these values were close. Up until this point, I kept the Nitrate species present (except for 1 individual run) in the initial j-13 solution composition, whereas UTSA removed the nitrogen species. After the first few runs I didn't swap HCO₃ for CO₂ (g), but added O₂ (g) as some minor amount to achieve similar results. However, this process is not adequate or reflective of the lab experiments that state the first test was altered from the addition of SiO₂ from the test glass cell.

Trial #	Changes Made	pH curve result
1	Initial file with initial chemistry, O ₂ as .2, CO ₃ as -3.5, with the reaction amounts of the oxides as the total corroded quantities	pH decrease line stayed flat
2	The full oxide amounts were added, and specifying a cutoff as the amount reported as corroded.	pH decrease line stayed flat
3	Altered O ₂ (g) to .1 and .3	pH decrease line stayed flat
4	altered CO ₂ (g) to .1 and 1e-6	pH decrease line stayed flat
5	Used .2 O ₂ (g), not specify CO ₂ (g) of initial solution for the rest of the runs not specified either.	Did not get desired curve
6	Same as 2, But MnO cutoff is not limited (set as full oxide available)	Similar to UTSA curve/lab results
7	All but CO ₂ (g) allowed to react	ok trend-20 days to increase pH - similar to lab data
8	Remove Nitrate	Results not improved * note UTSA notebook shows level pH reached in 5 days, the same input on my computer shows different graph reaching same point in 10+ days.
9	Nitrate back, all oxides min set 0, MnO set to reactant amount	pH decrease line stayed flat
10	all allowed to react, except MnO cut	plummet pH
11	Based on UTSA notebook- Ran only Mn, Si, and Fe oxides O ₂ = 1.7e-4	similar to UTSA curve/lab results-
12	Same as above, but add other oxides one at a time	Results not improved
13	Take out Fe ₂ O ₃	Little effect on curve within 1st 10 days
14	Leave in Fe ₂ O ₃ take out SiO ₂ oxide in reactant pane	Same shape curve as trials 11+12, pH high as 10
15	All reactants at cutoff except SiO ₂ MnO allow to react all that's available, CO ₂ (g) increased slightly	Decent curve up to 25 days reach pH of 9.5 * more CO ₂ added in reactant the more the pH starts off lower initially.

16	All reactants at cutoff except SiO ₂ MnO allow to react all that's available add back other oxides	ok trend-25 days to increase pH - similar to lab data
17	all others are set at cutoff, MnO decreased to .626 or .726. If CO ₂ (g) not specified O ₂ = .2 Mn=2.7 to get a pH of 9.78	Curve ok slow to level out pH
18	If O ₂ = .1, then Mn lower	adjusting O ₂ and Mn keep same curve shape
19	if O ₂ = log fug (-10 or lower) less MnO = .09	keep similar curve
20	Take out H ₂ O to account for evaporation	Not much different
21	O ₂ -30, HCO ₃ specified all reacted to cutoff, except MnO to .09	similar to desired
22	Same as above, but MnO set back to cutoff	pH decrease line stayed flat

The following outline will be followed starting with Test 2.

Test 1

Run at 60 and 90 C. Exposed to air (so CO₂(g) = -3.5 and O₂ = .2 fugacity).

This runs pH is altered by the addition of SiO₂ from the test cell equipment.

Test 2 New Test Teflon vessels. At 60 C only, Equilibrated with air (so CO₂(g) = -3.5 and O₂ = .2 fugacity). However run only 20 days due to evaporation.

Test 3 Same as above, but tight lid to keep out air as much as possible to decrease evaporation. Then at 27 days add waste glass.

Step 1 is to accomplish part 2 exposing to air (so CO₂(g) = -3.5 and O₂ = .2 fugacity) and obtain a similar resultant curve to lab tests.

Step 2 Then use it for part 1 and add the chemistry from the glass beaker in the solution gap between test beakers reported in Table 4-3 of He et al, 2007 to see if that results in the proper hike in pH seen in test 1 of the lab experiments.

Step 3 is to take create a similar file to test three, limit exposure to O₂ and CO₂ gases, as experiment was done in a closed vessel. Run the file for 27 days, take those results and enter them into a new file and react the waste glass.

Starting part 2 I used the last file from the trial tests. I set the run for 20 days and since the experiment was partially exposed to air, I allowed CO₂ and O₂ to be at atm conditions. With this the MnO concentration still needs to be increased, and whether or not NO₃ is included makes no difference. CO₂ has an initial hike then levels out at -3, O₂ plummets to -14. Not sure if MnO is more reactive than the other oxides, because if the Fe oxide is increased many times over, it doesn't have the same results. The log K of the Fe₂O₃ was altered to reflect that of Minteqa2 (-1.4 at 25C), this did not alter the results and produce the desired precipitates. If the CO₂ isn't specified, but HCO₃ is, the pH still dips and then increases according to the amount of MnO reacted. Within the experiment they report that for part 3, magnetite and matteccite. In GWB matteccite is not included. The precipitates ranged from dolomite, fluorapatite, pyrolusite, and hematite maintained the initial concentration. Calcite was under saturated.

LS

5/1/07

For part 2 I also added Al₂O₃ oxide, but couldn't add the Cr oxide, because it was not a listed reactant. However, this had no affect on the system. The Si total concentration spikes at 3 and levels out at 2.5 mg/kg, where as in part 2, the lab experiment reported below detection limits. The total iron and sulfur concentrations agree. I fixed the pH (part 2 should be 7.16 where as in part 1 pH was set to 8.34), this had little affect on the overall pH, but dolomite no longer precipitates.

The lab experiment in part 2 (partially closed) or 3 (closed) shows no initial dip in pH, therefore the system probably is not in equilibrium with the atmosphere. Degassing of CO₂ would cause calcite to precipitate, however we will say there is none here and keep CO₂ constant. If the O₂ gas is reduced to log f = -10, there is a constant increase in pH without the initial dip. For part 2, I tried 4 combinations

Name	Log f O ₂ g	log f CO ₂ g	MnO reacted mol	Tot Si mg/kg	ph Dip down	Max pH	calc precip	CO ₂ fugacity over 20 days
part2eqilbair0.2co2	-6.99E-01	-3.5	0.06	3 +remained steady	yes	7.5	no	(-3.5 spike to -2 steady -3.1)
part2eqilbair2	-10	as HCO ₃ concentration	0.06	spike to 3 steady 1.25	no	8.5	yes	(-1.8 to -3.5)
part2eqilbair3	-6.99E-01	as HCO ₃ concentration	0.09	3 +remained steady	yes	7.2	no	(-1.9 spike to -1.65 down -1.87 but increasing)
part2eqilbair	-10	-3.5	0.03	spike to 2.3 steady 0	no	8.5	no	(-3.5 to -5.25)

LS

5/2/07

The MnO increased reactant amount allows Si concentration to decrease with very little precipitation of Si minerals, but there is precipitation of other Mn minerals to compensate for extra Mn in solution, which were not found in the corrosion products of the lab results.

Name	Log f O2 g	log f CO2 g	MnO reacted mol	Tot Si mg/kg	ph Dip down	Max pH	calc precip	CO2 fugacity over 20 days	Sulfur mg/kg	react
part2sealed2 7days1	-10	as HCO3 concentration	0.05	spike to 3 steady 2.5	no	8.2 decreases	yes increasing	(-1.9 spike to 1.87)	agrees	
part2sealed2 7days2	-10	-3.5	0.03	spike to 2.3 steady 0	no	9.1 increasing	no	(-3.5 to -6.1)	6.5 to 5	.008-CO2g and -.0015m O2
part2sealed2 7days3	-10	-3.5	0.03	spike to 2.3 steady 0	no	8.6 steady	no	(-3.5 to -5.3)	agrees	nothing
part2sealed2 7days4	-6.99 E-01	-3.5	0.05	3 +remained steady	yes	6.9	no	(-3.5 to -2)	agrees	nothing

Basically, the system isn't in equilibrium to start with and is partially closed so that the O2 is consumed. The pH isn't working out with the exact cutoff values either MnO needs to be increased to precipitate out small amounts of Si solids and also Mn solids, or Si reacted needs to be reduced. The right combination of starting CO2 and O2 gases with a combination of depleting O2 gas hasn't been found. Not sure of the reaction that is depleting O2, without reacting and precipitating more solids than reported in the article.

I tried various combinations of initial and removing O2 and add CO2 in the reaction pane to get the desired results for parts 2 and 3. However, there is some parameter that is off from the report lab experiments even if all others fit. Part 2 will have higher CO2 and O2 values than part 3, because it was partially exposed.

LS

5/3/07

The problem is that over the 20 or 27 days the solution initially contained atmospheric CO2 and O2, however in partially closed and as the O2 is consumed it is not replenished except when the containers are open to perform samplings. The GWB program uses this solution, I believe, and continually through the duration keeps the solution exposed to Atm conditions. This is why the pH was acidic initially and needed the MnO hiked up. In

reality, the solution may have atm gas conditions, but the fugacity of O2 will decrease considerably, while CO2's activity will decrease on a smaller scale, even with periodic or partial exposure to atm conditions. Since the GWB system can't be controlled there are three ways to go about this 1) decrease the initial O2 activity while removing a small molar amount in the react pane (This gives a correct pH and total Si, S, and Fe reported, but the curve is more steep) 2) start out with atm conditions and remove larger amounts of O2 and add minimal CO2 (this corrects the pH gradient, however it throws the Si, S, and Fe trends off) 3) react the system and corrosion amounts step by step (would have to figure the reaction rate per day and react the system to each sample time (fewer points) then reenter the resultant system, react the proper oxide quantities and adjust the reactant amounts of CO2 and O2 gases to account for exposure. Below are some of the results of part 2 and 3 using the first two methods stated here. Many runs were performed adjusting initial and reactant amounts of CO2 and O2 gas, only a select few were saved. While the MnO concentration and all other oxides were set at their cutoff values, a slight increase in MnO could take care of the early Si spiking that is due to how the file is entered in methods 1 and 2. Also the pH trend initially dips in the modeled results where as the lab tests showed an increasing only trend. This is due to a higher initial gas amounts. All results from subtracting O2 in the react pane and a slightly decreasing CO2 fugacity (rather than level as in part 1), allows for the precipitation of calcite. If this was present in the lab experiments, which was reported for the samples prepared for the sorption testing, it was under detection limits. This was achieved by reacting smaller quantities of O2, but still attained a desirable pH. The initial and corroded g/L of parts 2 and 3 were not previously calculated and the values for part 1 were used. These will be adjusted, however, they are not that different (see oxidecalculations spreadsheet).

Name	Log f O2 g	log f CO2 g	MnO reacted mol	Tot Si mg/kg	ph Dip down	Max pH	calc precip	CO2 fugacity over 20 days	Sulfur mg/kg	react
part2eqilbair0.2co2sub	-6.99E-01	-3.5	0.0135	spike to 4.5 steady 2	yes	8.8	yes	(-3.5 spike to -2 steady -4.75)	6.6 to 0	o2 -.002m + .001g Co2
part2sealed27days5	-2	-3.5	0.0135	spike to 4.5 decrease irreg to .05	yes	9.2	yes	(-3.5 spike to -2.25 steady -5.25)	6.6 to 0	o2 -.001m + .005g Co2
part2sealed27days6	-6.99E-01	-3	0.0135	spike to 3 decrease irreg to .0	yes	9.25	yes	(-3.5 spike to -2 steady -5.75)	6.6 to 0	o2 -.001m + 1e-5m Co2
part2sealed27days7	-6	-3.5	0.0135	spike to 3 decrease irreg to .5	yes	9	yes only 1-3mg after 22days	(-3.5 spike to -2 steady -5.75)	6.6 to 4	o2 -.0004 m + .0001g Co2

LS

5/11/07

I recalculated the part 2 and 3 (sealed for 27 days then addition of waste glass) oxide concentrations and put the runs into their respective folders (parts 1 2 and 3). The files for part 3 were initially misnamed as part2 sealed27days, but put into the part 3 folders. I tried to find a rate that would allow the proper amount of CO₂ to be added at testing intervals, and the proper amount of O₂ depletion. Not much success, very similar results as the above spreadsheet cutouts seen above. I could run the program in steps, stopping and restarting at each sampling interval to achieve the proper exposure to the atmosphere while continuing the O₂ depletion due to corrosion. However, the quick exposure time may not significantly affect the atm gas levels. Mol/day or slide fugacity.

LS

5/14/07

Using the sliding method for the log fugacity creates the closest results. CO₂ (g) and O₂ (g) are slide from atm conditions to -60 and -20 respectively. While doing this the log f (O₂) is higher than that of CO₂ for just the first two days. However it creates the desired results for pH and Sulfur, iron. The total elemental silicon is off within the first few days because the run isn't consuming the products as fast as in the lab experiment. When reacting negative amounts of CO₂ and O₂ gas, the fugacity trends are much harder to mimic those of the slide run. P2slide.rxn and P2atmgasadjustment.rxn were created for the slide and reactant amounts of gases. Subtracting O₂ and CO₂, its hard to get a smooth reduction of log fugacity in moles as opposed to sliding to the log fugacity you want to achieve. However, both methods begin with ATM conditions and show no initial dip in pH.

LS

5/23/07

For part two, the slide and subtracting gas methods, the elemental composition is off. I only allowed magnetite and a few other minerals to precipitate (under 1mg/kg) that were under the detection limit, but made an impact on the composition. In the paper they state only Magnetite and Mattecuite were found, however, I find fluorapatite, pyrolusite, antigorite, tephroite and smectite precipitate in small amounts. The slide method returns a more desirable result, however if the removing of gas/day could more accurately reflect the actual situation. For part three, once the oxide chemistry was changed, the former files (all named part2sealed27days) reported different output and needed to be adjusted. When subtracting the gases per day I can't get a good comparison to the lab experiments, also the slide method seems off.

LS

5/24/07

A few files for part three (first 27 days were created), a few slide the gases log fugacity while others subtract moles of CO₂ and O₂. The files also then were used while suppressing all species except a select few, see above. One of the files was then selected (P3-27slidesupp2) to use the resultant chemistry to enter as the continuation of part three for the next 47 days which had the waste glass disks added. Weather to start out with atm conditions or enter the file where part 3 first 27 days left off makes a difference. While the container was opened to add the glass waste, how long was it opened and exposed to the atmosphere? The best results were from file p3w-glass2, where the input included CO₂ and O₂ as atm (-3.5 and -.69) and they were slid to -5 and -20 respectively. I want to try to calculate a corrosion rate in units of g/day from the corrosion rates reported in

He et al, 2007. If entered into part 3 the results may improve and improve the results for the second half of this problem.

LS

5/25/07

Using the equations from the corrosion Dr. website (<http://www.corrosion-doctors.org/Principles/Conversion.htm>) I calculated that the mass loss rate is .252 g m⁻² day⁻¹. If I can figure out the gram loss per day, I can divide that among the oxides using the weight percents in order to react them as grams per day. I tried to convert this number to grams per day, however I'm not getting consistent answers, especially when I calculate the mass loss rate from the data reported in lab notebook 706 and the paper. Surface area is 3.62 cm² or 3.62e-4 m², over 74 days .056565 grams of steel corroded in .05L of solution. So 1.1313 g/L corroded over 74 days, so I multiplied the amount of corrosion per day times the oxide %. These values are different than those calculated from figuring out the oxide weight % which calculates more corrosion product than actually corroded (see oxidecalculations spreadsheet).

I thought I converted from penetration rates to mass loss incorrectly; however, I get the same answer when using both the mpy and mm/yr. I assume then the m² in the rate refers to the SA of the corrosion product not the initial steel volume. The numbers calculated for g/L-day will be entered into part 3 to see if that improves the run. While the amount of oxides is reported for the elemental values than for the oxides, it's the % of each that is important.

LS

6/15/07

Here are the corrosion rate calculations.

Corrosion rate

$$11.7 \mu\text{m/yr} [0.461 \text{ mil/yr}]$$

$$11.7 \mu\text{m/yr} \frac{10^{-3} \text{ mm}}{1 \mu\text{m}} = 11.7 \times 10^{-3} \frac{\text{mm}}{\text{yr}}$$

$$\text{Conversion Factor} = \frac{\text{rate}}{\text{Factor}} \quad \text{Factor} = 0.365/d \quad d = 7.87 \text{ g/cm}^3$$

$$\frac{11.7 \times 10^{-3} \text{ mm/yr}}{\text{Factor} = 0.04637} = 0.2522 \text{ g/m}^2 \text{ day}$$

$$0.461 \text{ mil/yr}$$

$$\text{Conversion factor} = \frac{\text{rate}}{\text{Factor}} \quad \text{Factor} = 14.4/d \quad d = 7.87 \text{ g/cm}^3$$

$$\frac{0.461 \text{ mil/yr}}{\text{Factor} = 1.829} = 0.252 \text{ g/m}^2 \text{ day}$$

Part 3 Try to back calculate to Corrosion rate
 $\approx 252 \text{ g/m}^2 \text{ day}$

Calculated g/L For each oxide \rightarrow just ~~corrosion~~ corroded metal

Corrosion 1.1313 g however when calculated it From oxides the total corrosion 1.6216 g/L that's a difference of -0.495 g/L which isn't much considering we are now dealing with 1 liter rather than .05 liters.

$$\left(\frac{1.1313 \text{ g}}{\text{L}} \right) \text{ total over 74 days} = .01528 \text{ g/L day}$$

$$1.6216 \frac{\text{g}}{\text{L}} \text{ total over 74 days} = .0219 \text{ g/L day}$$

If rate = $\approx 252 \frac{\text{g}}{\text{m}^2 \text{ day}}$ Area \rightarrow Surface Area $3.62 \times 10^{-4} \text{ m}^2$

Mass loss $9.12 \times 10^{-5} \text{ g/day}$ 74 days

$$\frac{\text{Steel}}{\text{Glass}} = .9 \quad \text{to initial g} = .0565 \text{ g} \quad \frac{1.1313 \cdot .0565}{3.62 \times 10^{-4} \cdot 74} = 2.109$$

$$\frac{x}{4} = .9 \cdot 3.6 \quad \frac{1.13}{3.62 \cdot 74} = 42.18$$

$$\text{SA} \% .05 \text{ L} = 7.24 \times 10^{-3}$$

$$\text{Rate} \left(\frac{.252 \cdot .05 \text{ L}}{\text{m}^2 \text{ day}} \right) \cdot 3.62 \times 10^{-4} \text{ m}^2 = 1.824 \times 10^{-3} \frac{\text{g}}{\text{L day}}$$

$$\text{Rate} \left(\frac{.252 \text{ g}}{\text{m}^2 \cdot \text{day}} \right) \cdot 7.24 \times 10^{-3} \frac{\text{m}^2}{\text{L}} = 1.82 \times 10^{-3} \frac{\text{g}}{\text{day L}} \leftarrow$$

Surface Area $3.62 \times 10^{-4} \text{ m}^2$ 74 days

$$> \frac{0.252 \text{ g}}{\text{m}^2 \text{ day}} \times 3.62 \times 10^{-4} \text{ m}^2 \times \frac{1}{0.05 \text{ h}} = 1.824 \times 10^{-3} \text{ g/day/Liter}$$

$$1.824 \times 10^{-3} \frac{\text{g}}{\text{L} \cdot \text{day}} \cdot 74 \text{ day} = 0.134976 \frac{\text{g}}{\text{L}}$$

But From data $0.0565 / 74 = 0.0007657 \text{ g/day}$
 $0.0007657 \frac{\text{g}}{\text{day}} \cdot 0.05 \text{ L} = \underline{1.13 \text{ total grams corroded}}$
 $\frac{0.05 \text{ Liter}}{0.05 \text{ Liter}} = \underline{0.015314 \frac{\text{g}}{\text{L} \cdot \text{day}}}$

used to divide between Oxide %'s

$$0.0007657 \text{ g/day} \% \text{ SA} = 2.109 \frac{\text{g}}{\text{m}^2 \text{ day}}$$

this is way off -

NOT sure what mass loss refers to

$$3.62 \times 10^{-4} \text{ m}^2 = \text{SA} \quad 0.0565 \text{ g out of } 2.37683 \text{ g} = 237\% \\ 2.37\% \text{ of SA} = 8.57 \times 10^{-5} \text{ m}^2$$

Plug into Formula $\text{g/day} \% \text{ SA} = 8.98 / \text{m}^2 \text{ day}$

part 3

$$\text{rate should} = \frac{.252g}{m^2 \text{ day}}$$

$$1.1313 \text{ g/L over 74 days} = .01528 \text{ g/L day} \text{ or } \cancel{7.64e^{-4}} \text{ g/day}$$

$$\frac{7.64e^{-4} \text{ g}}{\text{day}} \quad \% \text{ SA } (8.57e^{-5} \text{ m}^2) \\ \downarrow \\ \% \text{ SA of covered material}$$

$$\text{SA} = 3.62e^{-4} \text{ m}^2, 2.34\% \text{ of SA} = \text{products} = 8.57e^{-6} \text{ m}^2$$

$$\text{Working 1 liter } 8.57e^{-6} \text{ m}^2 \% .05 \text{ L} = 1.7e^{-4}$$

$$.252 \frac{\text{g}}{\text{m}^2 \text{ day}} * 1.7e^{-4} \text{ SA of covered in 1 liter} = 4.284e^{-5} \text{ g/day} \\ \text{or } \text{From } 7.64e^{-4} \text{ g/day}$$

$$\frac{\text{total g}}{\text{m}^2 \text{ day}} = \frac{.056g}{1.7e^{-4} \text{ m}^2 \cdot 74 \text{ day}} = \frac{\text{g}}{\text{m}^2 \text{ day}}$$

$$\frac{1.1313g}{\text{SA} \cdot 74} = .252$$

$$\text{or } \text{SA} = 8.57e^{-5} \% .05 = 1.7e^{-3} \\ \text{SA} = 3.62e^{-4} \% .05 = 7.24e^{-3}$$

$$\frac{.01528 \text{ g}}{\text{L day}} \quad \% \text{ SA}$$

or by factor 10 or 1 unit fact

NOT SURE what Rate implies / problem

Somewhere with conversion From .05L to 1L

Not sure what the rate implies (area of what) so it can't be used in GWB setup. Also, implies that corrosion is steady, but not true for all oxides involved.

LS

6/25/07

Altering the part 1 file to slide the O2 as in part 2+3, I then added the components from He et al, 2007 page 4-12. This shows the chemistry of the solution gap between the liner and the glass cell, although for a different experiment, it should be comparable to the seepage seen in part 1. Since part 1 was exposed to air, sliding the pH didn't achieve the starting pH curve, and the additions of the components released from the liner did drive the pH lower, which is what should happen. The slide needs to be slightly adjusted; however the exact numbers are just a guess.

LS

6/26/07

Part 1, I tried to come up with the proper slide combination for O2 and CO2, however this didn't work. The slides were removed and O2 and CO2 were adjusted by reacting negative amounts. I tried to incorporate the amount of components added to solution from the liner slowly as they were not released immediately. However when released continuously, the correct curve is not created. Two files will need to be created, one with the initial conditions to attain the initial dip in pH and the maximum value, a second to introduce the liner components into the experimental solution.

LS

7/16/07

For part 1 I took the file without the liner chemistry included and O2 and CO2 were adjusted by reacting negative amounts. I added in the chemistry contribution from the liner one species at a time to check out the effects. CO2 was then no longer removed from the system in the react pane. The curve looks ok; however the S, Si, and Fe concentrations do not reflect those of the report. The liner slowly added to solution over the experiment. The Si and Fe concentrations were elevated fairly early on, however the Sulfur concentration remained constant. The rates at which these reactions took place are not captured correctly. Parts 2 and 3 used the slide method.

LS

7/19/07

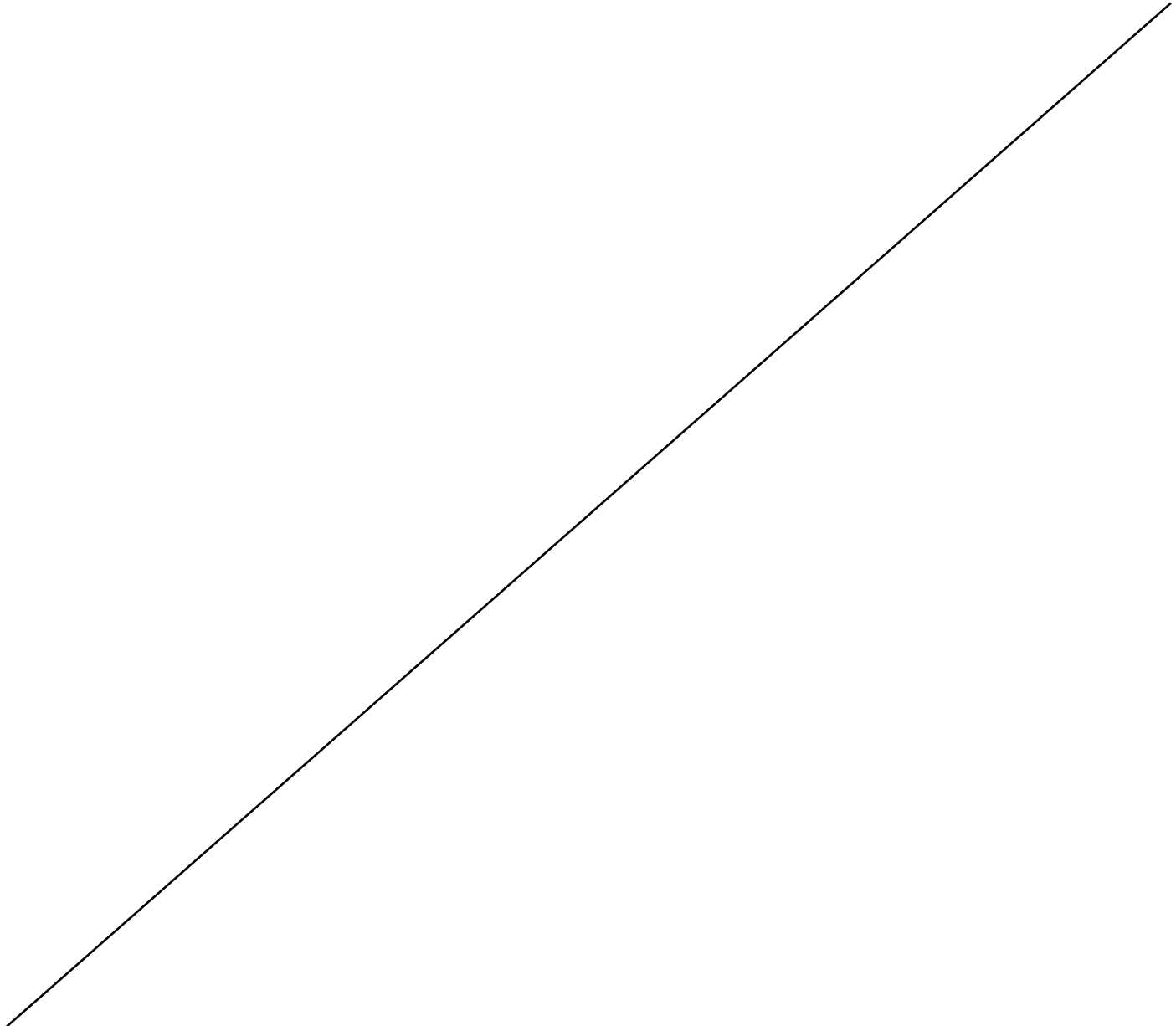
For Part 2, there are two comparable files. Both slide O2 and CO2, one suppresses no minerals and the other allows calcite aragonite, magnetite, anhydrite, pyrolusite. When using the thermo.com.v8.r6+ database the mineral suppressed file (P2slidesuppressed) more accurately predicted the pH curve and overall elemental composition. However, when hematite is allowed, the pH curve is off.

For Part 1, the thermo.com.v8.r6+ database file used threw off the pH curve. When using the same files the pH was too high and the element composition was off, especially in the suppressed file (fe was much too high). Allowing Anhydrite, Aragonite, Calcite, Fluorapatite, hematite, magnetite, and pyrolusite precipitate in all three files improved the results.

LS

7/20/09

Part 1, allowing Anhydrite, Aragonite, Calcite, Fluorapatite, hematite, magnetite, and pyrolusite precipitate while not reacting negative amounts of CO_{2g} and not adding in CO_{2aq}, the pH curve improved, but the elemental composition of Fe, S, Si are still off. Allowing Glauberite (Na₂Ca(SO₄)₂) and Kieserite (MgSO₄·(H₂O)) to precipitate (two SO minerals because Matteucitte (NaHSO₄(H₂O)) is not in the database; this had no improvement. Properly recalculating the silicon from the solution gap (table 4.3) between liners for SiO₂ (.0356g rather than .0166g) increased the Si In solution to 21 which is more comparable with the results. When the amount of CO_{2aq} added from the corrosion products was decreased to 0, this improved the curve. However it states in part 2 that only Matteucitte and Magnetite were found. Allowing only Magnetite to precipitate, as opposed to magnetite and hematite the pH curve dipped lower and stayed low for a longer period of time and reacting positive amounts of CO_{2aq} only worsened this. All Part 1 files are precipitating small amounts of Calcite.



Part 1 File Name	React O ₂ /CO ₂ gas moles/day	All Minerals suppressed except for	Minerals precipitated	CO ₂ aq reacted (g)	Aq elemental composition	pH curve
part1_startadd	slide log f to -10/-60	Anyhydrite, Aragonite, Calcite, Fluorapatite, Hematite, Magnetite, Pyrolysite	Calcite/Hematite/Fluorapatite	0.00769	Si OK, Fe=0, S=OK	no dip, too high, too fast
part1_withglasschem	*-1e-4 and 0	Anyhydrite, Aragonite, Calcite, Fluorapatite, Hematite, Magnetite, Pyrolysite	Calcite/Fluorapatite/Pyrolysite/hematite 0-20 days, then magnetite	0.00769	Si OK, Fe=0, S=OK	dip to 7 increase gradual, but up to 10
part1_withglasschem2	*-1e-4 and 1	Anyhydrite, Aragonite, Calcite, Fluorapatite, Hematite, Magnetite, Pyrolysite	Calcite/Fluorapatite/Pyrolysite/hematite 0-20 days, then magnetite	0.00769	Si OK, Fe=0, S=OK	dip to 7 increase gradual, but up to 10
part1_withglasschem3 hem and mag	*-1e-4 and 1	Glauberite, Kieserite, Anyhydrite, Aragonite, Calcite, Fluorapatite, Magnetite, Pyrolysite	Calcite/Fluorapatite/Pyrolysite/hematite 0-20 days, then magnetite		Si OK, Fe=0, S=OK	slight dip to 8.1 then curve match trend but reaches up to 10
part1_withglasschem3 mag **Hematite not allowed to precipitate	*-1e-4 and 0	Glauberite, Kieserite, Anyhydrite, Aragonite, Calcite, Fluorapatite, Magnetite, Pyrolysite	Calcite//Fluorapatite/Pyrolysite/hematite/magnetite		Si OK, Fe=0, S=OK	dip too low, too long, slow to increase
All have log f (CO ₂) = -3.5 and an fO ₂ = 0.2 and SiO ₂ reacted .0356 grams						

Part 3 the first 27 days was straightforward, after updating the database and suppressing Hematite, the results are comparable to those from the lab study. However, modeling the addition of glass using the updated

database, better results are seen when all solids are allowed to precipitate. If hematite is suppressed the elemental composition is changed.

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7/23/07

The second portion of Part 3 needs to be altered in two ways. One using the new results from Part 3 the first 27 days and two, the correct mass of oxides to be added that were contributed by the waste glass discs. There is no weight or density of the glass disc within the paper. The density of glass was estimated from sources on the web to be 2.5 g/cm³ from <http://hypertextbook.com/facts/2004/ShayeStorm.shtml>. The volume was calculated (see oxidecalculations spreadsheet) and a mass of .304g for the glass discs was estimated. However, not all of this was released in the experiment. After the addition of the glass chemistry the Si concentration was adjusted (.0095g/day) to achieve similar results to those of those in the lab experiment. Suppressing specific minerals helped the fluid elemental composition little. The file currently doesn't represent the experiment; further information will need to be retained.

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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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