

CEE 543 Autumn 2006 Final Exam

1. A well water at pH 8.4 contains 4 mg/L $TOTFe(II)$ and is thought to be in equilibrium with siderite ($FeCO_3(s)$), with which it was in contact underground (no solids are in the water collected in the well). When the water is brought to the surface, it is aerated, thereby oxidizing essentially all of the $Fe(II)$ to $Fe(III)$ and causing precipitation of ferrihydrite. The aeration also equilibrates the solution with atmospheric CO_2 . Answer the following questions, assuming that the solution is ideal (activity coefficients all equal to 1.0) and considering all $Fe(II)$ -OH and $Fe(III)$ -OH complexes listed in Table 8.2 (and *only* those complexes).

- What is the alkalinity of the untreated water?
- Write a balanced redox reaction for oxidation of Fe^{2+} by dissolved oxygen to form ferrihydrite.
- What is the alkalinity of the treated water (considering the dissolved species, but not the precipitated ferrihydrite)?
- What is the composition of the treated water (pH and all Fe and CO_3 species)?
- How much $CO_2(g)$ was exchanged between the solution and the gas bubbles during the aeration step?

Answer. (a) The alkalinity of the untreated water could have contributions from both CO_3 and $Fe(II)$ species. Therefore, to determine the alkalinity, we need to find the composition of the solution. The molar concentration of $TOTFe(II)$ is:

$$TOTFe = \frac{4 \text{ mg/L}}{56,000 \text{ mg/mol}} = 7.143 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

The pK_a 's for Fe^{2+} are 9.50, 11.07, and 10.43, respectively, so the only Fe-OH complex of significance at pH 8.4 is $FeOH^+$. Assuming that the solutes behave ideally, the molar concentrations and activities of Fe^{2+} and $FeOH^+$ are therefore:

$$(Fe^{2+}) = \frac{(H^+)}{K_a + (H^+)} TOTFe = \frac{10^{-8.40}}{10^{-9.50} + 10^{-8.40}} (7.143 \times 10^{-5}) = 6.617 \times 10^{-5}$$

$$(FeOH^+) = TOTFe - (Fe^{2+}) = 7.143 \times 10^{-5} - 6.617 \times 10^{-5} = 5.256 \times 10^{-6}$$

The molar concentrations of the CO_3 species can then be found from various equilibrium constant relationships:

$$(\text{CO}_3^{2-}) = \frac{K_{s0, \text{FeCO}_3(s)}}{(\text{Fe}^{2+})} = \frac{10^{-10.55}}{6.617 \times 10^{-5}} = 4.259 \times 10^{-7}$$

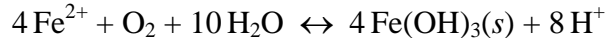
$$(\text{HCO}_3^-) = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{K_{a2}} = \frac{10^{-8.40}(4.259 \times 10^{-7})}{10^{-10.33}} = 3.625 \times 10^{-5}$$

$$(\text{H}_2\text{CO}_3) = \frac{(\text{H}^+)(\text{HCO}_3^-)}{K_{a1}} = \frac{10^{-8.40}(3.625 \times 10^{-5})}{10^{-6.35}} = 3.231 \times 10^{-7}$$

Essentially all the FeOH^+ is converted to Fe^{2+} during the alkalinity titration, so the alkalinity of the solution is:

$$\begin{aligned} \text{ALK} &= (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{FeOH}^+) \\ &= 3.625 \times 10^{-5} + 2(4.259 \times 10^{-7}) + 5.256 \times 10^{-6} = 4.236 \times 10^{-5} \end{aligned}$$

- (b) Each oxygen molecule combines with four electrons when it is reduced, whereas each Fe(II) ion releases one electron, so the stoichiometric ratio of Fe(II):O₂ is 4:1. The stoichiometry of the remaining species in the reaction can be determined by the algorithm given in the text. The balanced equation for oxidation of Fe²⁺ is:



- (c) The treated water is generated by converting all the Fe(II) in the original solution to Fe(III) and equilibrating the solution with atmospheric CO₂. The exchange of CO₂ has no effect on the alkalinity, so the only change of importance for determining the alkalinity of the treated solution is the oxidation of the Fe(II) species. Based on the calculations in part *a* and the assumption that all the Fe(III) is present as Fe(OH)₃(s), the oxidation converts 6.617 × 10⁻⁵ mol/L Fe²⁺ and 5.256 × 10⁻⁶ mol/L FeOH⁺ to 7.143 × 10⁻⁵ mol/L Fe(OH)₃(s). Based on the reaction developed in part *b*, each mole of Fe²⁺ that is converted to Fe(OH)₃(s) releases two moles of H⁺. Correspondingly, each mole of FeOH⁺ that is converted to the solid must release only one mole of H⁺. Each mole of H⁺ released reduces the alkalinity by one equivalent. Therefore, the change in alkalinity accompanying the oxidation reaction is:

$$\begin{aligned} \Delta\text{ALK} &= -2(\text{Fe}^{2+} \text{ oxidized}) - 1(\text{FeOH}^+ \text{ oxidized}) \\ &= -2(6.617 \times 10^{-5}) - (5.256 \times 10^{-6}) = -1.376 \times 10^{-4} \end{aligned}$$

The alkalinity of the treated water is therefore:

$$\begin{aligned} \text{ALK}_{\text{treated}} &= \text{ALK}_{\text{untreated}} + \Delta\text{ALK} \\ &= 4.236 \times 10^{-5} - 1.376 \times 10^{-4} = -9.524 \times 10^{-5} \end{aligned}$$

The alkalinity of the treated water is negative, meaning that *base*, not acid, is needed to titrate the solution to pH 4.7.

- (d) The result in part *c* indicates that 9.524×10^{-5} mol/L OH^- is needed to titrate the solution to pH 4.7. The pH of this solution can be determined by a charge balance. Since the solution pH is < 4.7 , we can ignore the contributions of OH^- , HCO_3^- , and CO_3^{2-} to the charge balance (CB). Also, since we are assuming that all the Fe(III) is present as ferrihydrite, dissolved Fe(III) species do not contribute significantly to the CB. Therefore, the only ions we need to consider in a CB on the treated solution are H^+ and any ions other than Fe and CO_3 species that were present in the original solution. The net charge on the unknown ions in the original solution can be determined by a CB on that solution:

$$\begin{aligned} \left(\begin{array}{l} \text{charge on known ions} \\ \text{in untreated solution} \end{array} \right) &= 2(\text{Fe}^{2+}) + 1(\text{FeOH}^+) - 1(\text{HCO}_3^-) - 2(\text{CO}_3^{2-}) \\ &= 2(6.617 \times 10^{-5}) + (5.256 \times 10^{-6}) - 1(3.625 \times 10^{-5}) - 2(4.259 \times 10^{-7}) \\ &= 1.005 \times 10^{-4} \end{aligned}$$

$$\left(\begin{array}{l} \text{charge on unknown ions} \\ \text{in untreated solution} \end{array} \right) = - \left(\begin{array}{l} \text{charge on known ions} \\ \text{in untreated solution} \end{array} \right) = -1.005 \times 10^{-4}$$

The original solution therefore contained a net charge of -1.005×10^{-4} mol/L associated with unspecified cations and anions. These species are not altered by the oxidation reaction, so the same net charge is present in the treated solution. The CB on the treated solution is therefore:

$$(\text{H}^+) + 3(\cancel{\text{Fe}^{3+}}) + 2(\cancel{\text{FeOH}^{2+}}) + \dots = (\cancel{\text{OH}^-}) + (\cancel{\text{HCO}_3^-}) + 2(\cancel{\text{CO}_3^{2-}}) + 1.005 \times 10^{-4}$$

$$(\text{H}^+) = 1.005 \times 10^{-4}$$

$$\text{pH} = 4.00$$

The composition of the solution can be determined from the pH and knowledge that the solution is in equilibrium with atmospheric CO_2 and ferrihydrite:

$$(\text{H}_2\text{CO}_3) = 10^{-4.94}$$

$$(\text{HCO}_3^-) = \frac{(\text{H}_2\text{CO}_3) K_{a1}}{(\text{H}^+)} = \frac{(10^{-4.94})(10^{-6.35})}{10^{-4.00}} = 5.129 \times 10^{-8}$$

$$(\text{CO}_3^{2-}) = \frac{(\text{HCO}_3^-)K_{a2}}{(\text{H}^+)} = \frac{(5.129 \times 10^{-8})(10^{-10.33})}{10^{-4.00}} = 2.399 \times 10^{-14}$$

$$(\text{Fe}^{3+}) = \frac{K_{s0}}{(\text{OH}^-)^3} = \frac{10^{-37.11}}{(10^{-14.0} / 10^{-4.00})^3} = 7.762 \times 10^{-8}$$

$$(\text{FeOH}^{2+}) = \frac{(\text{Fe}^{3+})K_{a1}}{(\text{H}^+)} = \frac{(7.762 \times 10^{-8})(10^{-2.19})}{10^{-4.00}} = 5.012 \times 10^{-6}$$

$$(\text{Fe}(\text{OH})_2^+) = \frac{(\text{FeOH}^{2+})K_{a2}}{(\text{H}^+)} = \frac{(5.012 \times 10^{-6})(10^{-3.48})}{10^{-4.00}} = 1.660 \times 10^{-5}$$

$$(\text{Fe}(\text{OH})_3^0) = \frac{(\text{Fe}(\text{OH})_2^+)K_{a3}}{(\text{H}^+)} = \frac{(1.660 \times 10^{-5})(10^{-7.93})}{10^{-4.00}} = 1.950 \times 10^{-9}$$

$$(\text{Fe}(\text{OH})_4^-) = \frac{(\text{Fe}(\text{OH})_3^0)K_{a4}}{(\text{H}^+)} = \frac{(1.950 \times 10^{-9})(10^{-8.00})}{10^{-4.00}} = 1.950 \times 10^{-13}$$

As it turns out, the charge on Fe(III) species accounts for ~30% of the total cationic charge in the treated solution, so the assumption that these species could be ignored in the CB was not quite valid. Carrying out an iterative solution for the CB in which the charge on dissolved Fe(III) species is accounted for (not required as part of the problem) indicates that the equilibrium pH would actually be 4.09.

- (e) The amount of CO_2 exchanged during the aeration step can be computed as the difference in $TOT\text{CO}_3$ between the untreated and treated solutions. Based on the calculations in parts *a* and *d*, these values of $TOT\text{CO}_3$ are 3.700×10^{-5} mol/L and 1.152×10^{-5} mol/L, respectively, so the treatment led to a loss of 2.548×10^{-5} mol/L CO_2 from the solution.

2. The reported composition of a groundwater in the Midwest of the U.S. is as follows.

<i>TOTCa</i>	467 mg/L as CaCO_3
<i>TOTMg</i>	257 mg/L as CaCO_3
<i>TOTSO₄</i>	502 mg/L
Alk	337 mg/L as CaCO_3 (presumed to be from CO_3 species)

pH 7.7

The only other ion expected to be present at a significant concentration is Na^+ .

- (a) Determine whether the solution is undersaturated, saturated, or supersaturated with respect to calcite, aragonite, and gypsum (K_{s0} 's in Table 8.7). Estimate activity coefficients using the Davies Equation. Which solid(s), if any, would you expect to be present if the solution reached equilibrium?
- (b) The water must be treated to reduce the concentrations of all the ions listed. Consultants have recommended adding BaCl_2 to remove the SO_4^{2-} from solution by precipitation of $\text{BaSO}_4(s)$ ($K_{s0} = 10^{-9.98}$), and then using conventional softening to reduce the Ca^{2+} and Mg^{2+} concentrations. However, $\text{BaCO}_3(s)$ is quite insoluble ($K_{s0} = 10^{-8.57}$) and might consume much of the Ba^{2+} that is added. Because BaCl_2 is relatively expensive, such a situation would be undesirable. Determine how much, if any, $\text{BaSO}_4(s)$ can be precipitated without precipitating any $\text{BaCO}_3(s)$. Although the BaCl_2 addition would change the ionic composition of the solution, assume that the ionic strength remains approximately the same as in part *a*. Also assume that any solids that were supersaturated in the initial solution remain supersaturated, so that Ba-containing solids are the only ones that form.

Answer. (a) We first need to determine the composition of the solution in greater detail. The concentrations of *TOTCa* and *TOTMg* are given in mg/L as CaCO_3 . For *TOTCa*, this means a solution with the specified concentration (467 mg/L) of CaCO_3 would contain the same concentration of *TOTCa* as the actual solution does. The MW of CaCO_3 is 100, so the actual molar concentration of *TOTCa* in the solution is:

$$\text{TOTCa} = \left(467 \frac{\text{mg as CaCO}_3}{\text{L}} \right) \left(\frac{1 \text{ mol TOTCa}}{100,000 \text{ mg CaCO}_3} \right) = 4.67 \times 10^{-3} \frac{\text{mol TOTCa}}{\text{L}}$$

For *TOTMg*, the situation is almost the same, except that in this case, we have to recognize that one mole of *TOTCa* is *equivalent* to one mole of *TOTMg* (they both have the same charge, and they both have roughly identical effects on water quality). The corresponding calculation for *TOTMg* is therefore:

$$\begin{aligned} \text{TOTMg} &= \left(257 \frac{\text{mg as CaCO}_3}{\text{L}} \right) \left(\frac{1 \text{ mol TOTCa}}{100,000 \text{ mg CaCO}_3} \right) \left(\frac{1 \text{ mol TOTMg}}{1 \text{ mol TOTCa}} \right) \\ &= 2.57 \times 10^{-3} \frac{\text{mol TOTMg}}{\text{L}} \end{aligned}$$

The concentration of *TOTSO₄* is expressed directly in terms of the mass of SO_4^{2-} , so its molar concentration can be calculated as follows:

$$TOTSO_4 = \left(502 \frac{\text{mg } TOTSO_4}{\text{L}} \right) \left(\frac{1 \text{ mol } TOTSO_4}{96,000 \text{ mg } TOTSO_4} \right) = 5.23 \times 10^{-3} \frac{\text{mol } TOTSO_4}{\text{L}}$$

The alkalinity can be converted to units of equiv/L Alk by noting that 1 equiv of CaCO₃ is 50 g of CaCO₃. Thus:

$$ALK = \left(337 \frac{\text{mg as CaCO}_3}{\text{L}} \right) \left(\frac{1 \text{ equiv ALK}}{50,000 \text{ mg CaCO}_3} \right) = 6.74 \times 10^{-3} \frac{\text{equiv ALK}}{\text{L}}$$

The pH is 7.7 and is the activity (not the concentration) of H⁺ in solution. Thus, we know that {H⁺} = 10^{-7.7} and {OH⁻} = 10^{-6.3}, but at this point we do not know the concentrations of H⁺ and OH⁻. Nevertheless, we can be confident that those species do not contribute significantly to the total charge balance or the ionic strength of the solution, given the much larger concentrations of the other solutes.

Although we don't know the concentration of HCO₃⁻ at this point, we can assume that at pH 7.7, that concentration in mol/L equals the value of ALK in equiv/L. Therefore, we can estimate [HCO₃⁻] = 6.74 × 10⁻³. Also, given the pH, we can assume that essentially all the TOTCa and TOTMg are present as Ca²⁺ and Mg²⁺, respectively, and that CO₃²⁻ contributes negligibly to the charge balance or ionic strength. Based on all the above information, we can prepare the following table:

<i>Ion</i>	<i>Concentration, c_i</i> (mol/L)	<i>Charge, z_i</i>	<i>c_i z_i</i>	<i>(c_i z_i²)/2</i>
Ca ²⁺	4.67 × 10 ⁻³	+2	9.34 × 10 ⁻³	9.34 × 10 ⁻³
Mg ²⁺	2.57 × 10 ⁻³	+2	5.14 × 10 ⁻³	5.14 × 10 ⁻³
SO ₄ ²⁻	5.23 × 10 ⁻³	-2	-1.05 × 10 ⁻²	1.05 × 10 ⁻²
HCO ₃ ⁻	6.74 × 10 ⁻³	-1	-6.74 × 10 ⁻³	3.37 × 10 ⁻³
SUM			-2.72 × 10⁻³	
Na ⁺	2.72 × 10 ⁻³	+1	2.72 × 10 ⁻³	1.36 × 10 ⁻³
SUM				2.97 × 10⁻²

The calculation of the Na⁺ concentration is based on a charge balance, the idea being that the positive charge on that ion must balance the net negative charge on the ions whose concentrations are known.

The bottom entry in the final column indicates the ionic strength of the solution. Using this ionic strength in conjunction with the Davies Equation, we can find the activity coefficients of ions with charges of ±1 and ±2 as:

$$\begin{aligned} \log \gamma_1 &= -0.51 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \\ &= -0.51(1)^2 \left(\frac{\sqrt{2.97 \times 10^{-2}}}{1 + \sqrt{2.97 \times 10^{-2}}} - 0.2(2.97 \times 10^{-2}) \right) \\ &= -0.0719 \\ \gamma_1 &= 0.847 \end{aligned}$$

A similar calculation yields $\gamma_2 = 0.516$. We can use these to calculate the activities of Ca^{2+} , SO_4^{2-} , and HCO_3^- :

Species	Concentration, c_i (mol/L)	γ_i	a_i
Ca^{2+}	4.67×10^{-3}	0.516	2.41×10^{-3}
SO_4^{2-}	5.23×10^{-3}	0.516	2.70×10^{-3}
HCO_3^-	6.74×10^{-3}	0.847	5.71×10^{-3}

We can then use the K_a expressions to calculate the activities of CO_3^{2-} :

$$\{\text{CO}_3^{2-}\} = \frac{\{\text{HCO}_3^-\} K_{a2}}{\{\text{H}^+\}} = \frac{(5.71 \times 10^{-3}) 10^{-10.33}}{10^{-7.7}} = 1.34 \times 10^{-5} = 10^{-4.87}$$

Finally, we can test for supersaturation of the solids:

$$\{\text{Ca}^{2+}\} \{\text{CO}_3^{2-}\} = (2.41 \times 10^{-3})(1.34 \times 10^{-5}) = 3.22 \times 10^{-8} = 10^{-7.49}$$

$$\{\text{Ca}^{2+}\} \{\text{SO}_4^{2-}\} = (2.41 \times 10^{-3})(2.70 \times 10^{-3}) = 6.49 \times 10^{-6} = 10^{-5.19}$$

The solubilities of both calcite ($K_{s0} = 3.31 \times 10^{-9}$) and aragonite ($K_{s0} = 4.37 \times 10^{-9}$) are exceeded, but that of gypsum is not. Therefore, gypsum will not precipitate. Since calcite and aragonite have identical stoichiometries but different K_{s0} values, the solution cannot be in equilibrium with both of them. The less soluble solid will control the solution composition, so at equilibrium, calcite will be present and aragonite will not.

(b) $\text{BaCO}_3(s)$ will first precipitate when its solubility product is exceeded. The CO_3^{2-} activity in the solution was determined in part a, so the Ba^{2+} activity and concentration for incipient precipitation of $\text{BaCO}_3(s)$ are:

$$\{\text{Ba}^{2+}\} = \frac{K_{s0, \text{BaCO}_3(s)}}{\{\text{CO}_3^{2-}\}} = \frac{10^{-8.57}}{10^{-4.87}} = 10^{-3.70}$$

$$[\text{Ba}^{2+}] = \frac{\{\text{Ba}^{2+}\}}{\gamma_2} = \frac{10^{-3.70}}{0.516} = 10^{-3.41}$$

At this Ba^{2+} activity, the activity and concentration of dissolved SO_4^{2-} are:

$$\{\text{SO}_4^{2-}\} = \frac{K_{s0, \text{BaSO}_4(s)}}{\{\text{Ba}^{2+}\}} = \frac{10^{-9.98}}{10^{-3.70}} = 10^{-6.28}$$

$$[\text{SO}_4^{2-}] = \frac{\{\text{SO}_4^{2-}\}}{\gamma_2} = \frac{10^{-6.28}}{0.516} = 10^{-6.00}$$

The amount of $\text{BaSO}_4(s)$ that has precipitated when this much SO_4^{2-} remains in solution is:

$$[\text{BaSO}(s)] = T\text{OTSO}_4 - [\text{SO}_4^{2-}] = 5.23 \times 10^{-3} - 10^{-6.00} = 5.23 \times 10^{-3}$$

Thus, essentially all the SO_4 precipitates before any $\text{BaCO}_3(s)$ forms.