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Thermodynamic Modeling of Hanford Waste Tank 241-AN-107

AR Felmy

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Letter Report

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September 7, 2005

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Pacific Northwest National Laboratory
Richland, WA 99352

Introduction.

The high level waste storage double-shell tanks at the Hanford site are highly basic. The high basicity is a key factor in controlling the chemical behavior of different components of the waste and in influencing the corrosion rate of the carbon steel primary tanks. However, the introduction of atmospheric CO_2 can reduce the pH of the tank wastes over time and possibly alter the corrosion rate of the carbon steel tanks. In order to at least partially address this issue for waste tank 241-AN-107, thermodynamic modeling calculations were performed to predict the changes in pH and carbonate concentration that could occur as CO_2 is absorbed from the atmosphere. The calculations were extended to complete equilibrium with the partial pressure of CO_2 in the atmosphere (i.e. $pCO_2 = 10^{-3.5}$ atm).

Simulations were performed for both the "upper" segments of tank 241-AN-107, which have been influenced by the introduction of high concentrations of NaOH to the supernatant, and for the "lower" segments where the salt cake/interstitial liquid have not been substantially altered by the introduction of base concentration.

Thermodynamic Modeling

Two different thermodynamic models were used in the simulations, the Environmental Simulation program ESP model (OLI Systems Inc) which uses the Bromley-Zematis equations for the activity coefficients, and the GMIN thermodynamic model(1) which is equivalent to the Pitzer Version of ESP(2). The thermodynamic database supporting the use of the Pitzer equations has been extensively tested and validated (3-12) including highly concentrated carbonate solutions. Examples of the accuracy of the model for carbonate containing systems are given in Figures 1-3. Figure 1 shows an extensive comparison of the model predictions with experimental mineral solubilities for binary (two electrolyte) systems containing carbonate and bicarbonate system. Figure 2 shows comparisons of the model predictions with the more complex ternary (three electrolyte) systems and Figure 3 of the complex reciprocal $Na\text{-}K\text{-}HCO_3\text{-}CO_3\text{-}H_2O$ system. In particular the agreement of the model with the solubility data for trona shown in Figure 1c, Figure 2c,d and Figure 3 are noteworthy since as we will show, trona is a potentially important mineral phase that can form in Tank 241-AN-107.

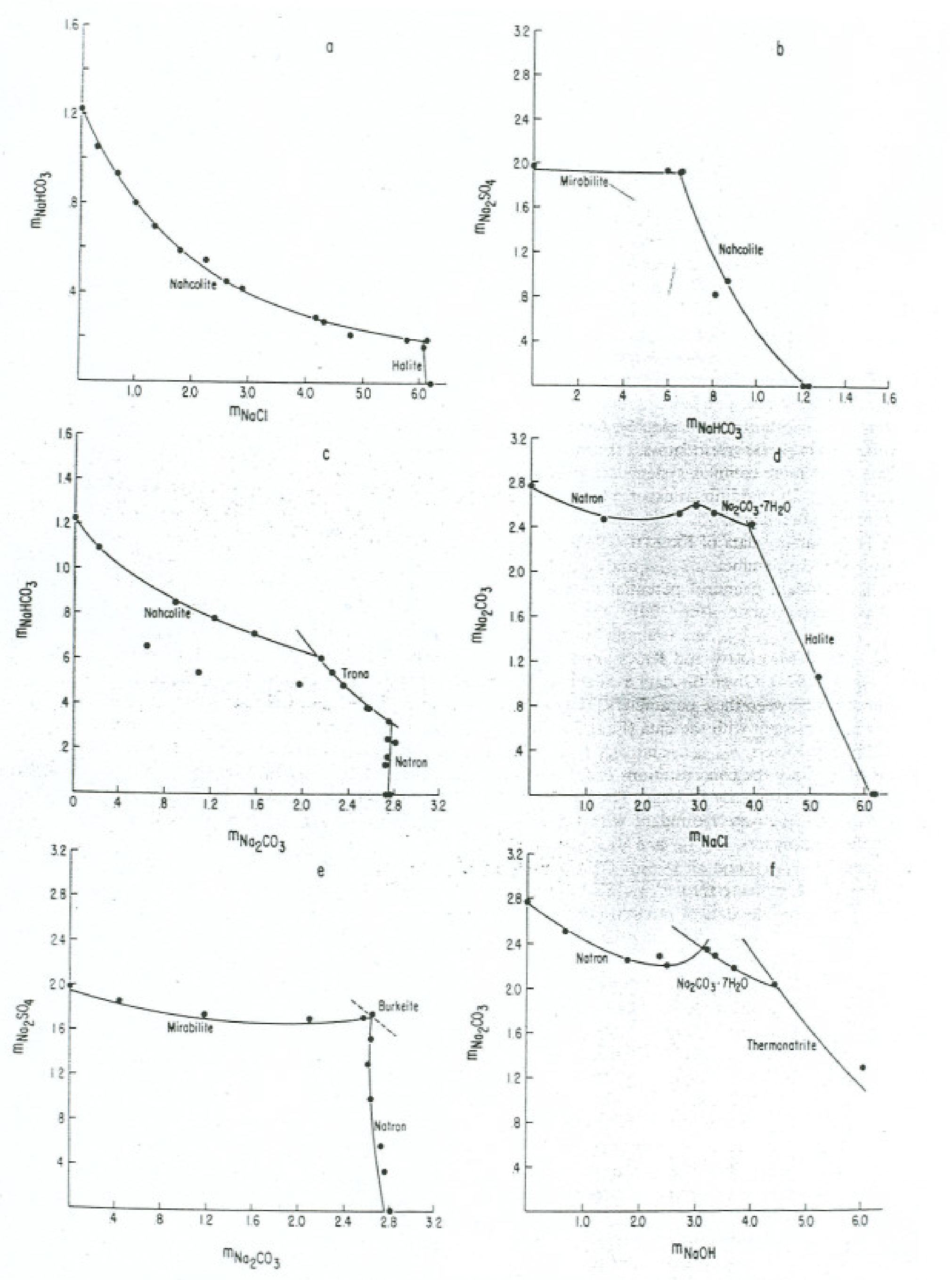

Figure 1. Mineral solubilities in the Na-Cl-SO_4-HCO_3-CO_3-OH-H_2O system (from Harvie et al. 1984).

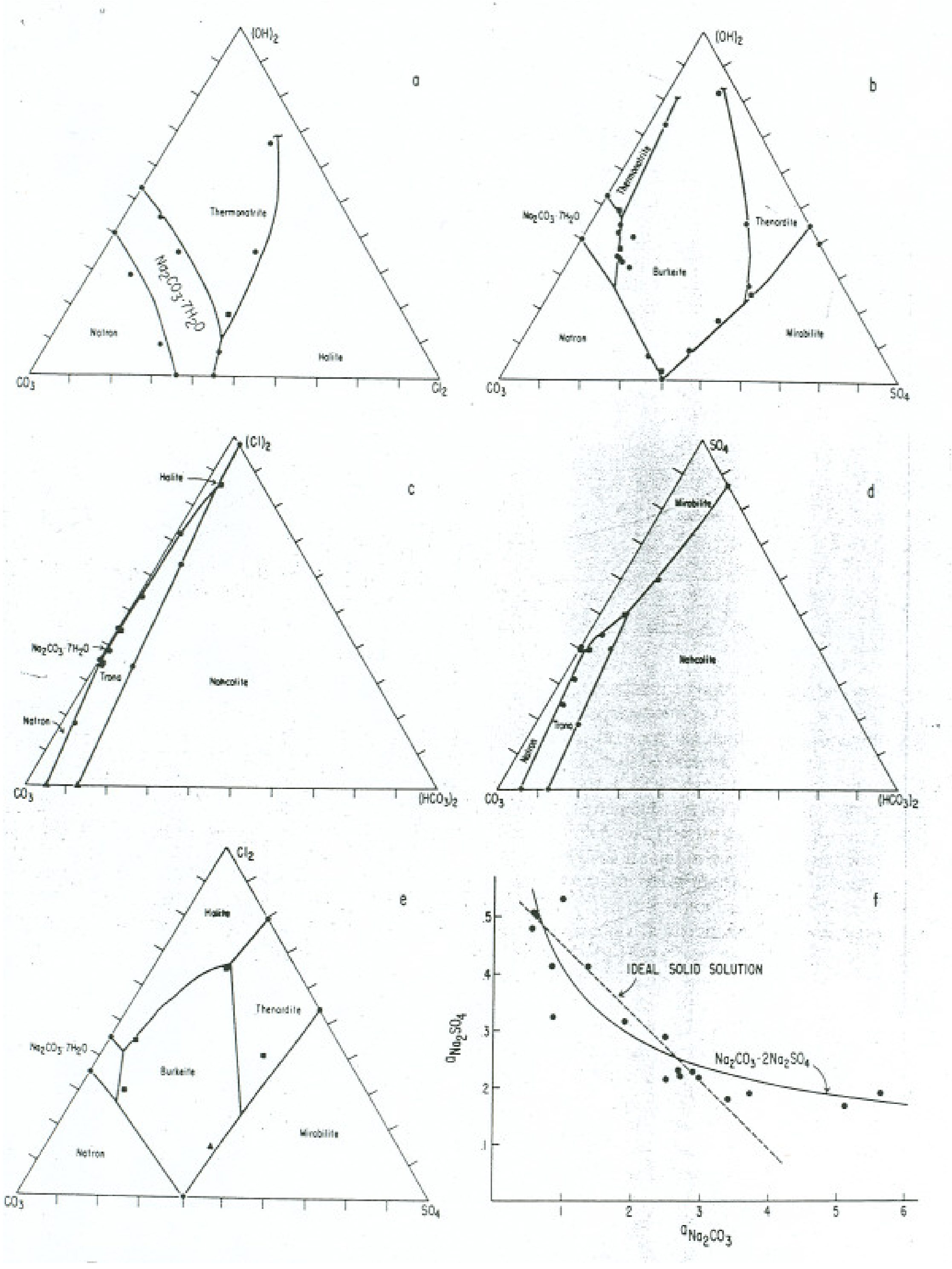

Figure 2. Jänecke projections of minerals solubilities for ternary systems in the Na-Cl-SO_4-HCO_3-CO_3-OH-H_2O system (from Harvie et al. 1984).

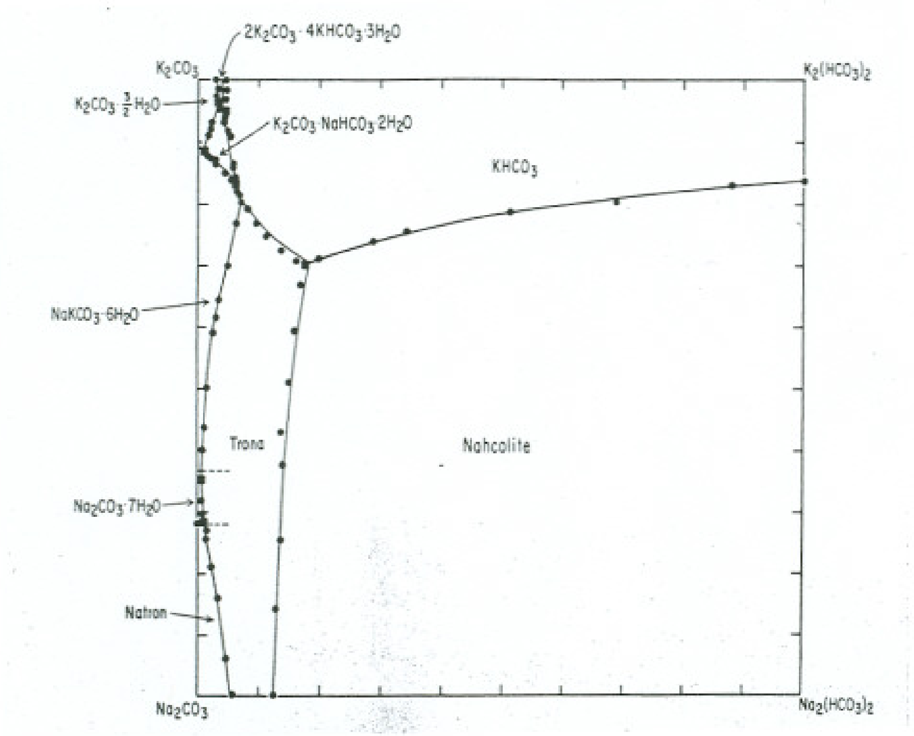

Figure 3. Mineral solubilities in the reciprocal Na-K-HCO_3-CO_3 system (from Harvie et al. 1984).

The simulations for tank 241-AN-107 were initially done with the Pitzer model because of its accuracy, ease of use in fixing partial pressures, and its availability. The ESP model was then used to check the final model predictions. Both models predict similar final pH values and precipitated solids.

241-AN-107 Solution Compositions

The waste tank chemical compositions used in the simulations were taken from the updated tank 241-AN-107 core sample analytical results(13). In the case of the upper segments, the analytical results for supernatant segments 1, 9, and 16 were averaged. For the lower segments the salt cake interstitial liquid data for segment 20 were used since this segment had the lowest pH, 11.0, and was considered most likely to be influenced by the introduction of any acidic components. The analytical results in mg/l were converted to units of molality (moles/Kg H_2O) for use in the model simulations (see Table 1). In the case of the upper segments it was necessary to adjust the reported Na concentrations to achieve charge balance (i.e., 9.9m analytical to 10.3m). For the lower segment, there was an analytical excess of cations over anions. Hence, the unreactive component Cl was increased to achieve the correct ionic strength and obtain charge balance. Besides the constituents shown in Table 1, tank 241-AN-107 also contains significant concentrations of organic chelates (total concentration ~0.5m). The majority of the organic carbon is present as low molecular weight organics, formate and glycolate. Formate and glycolate are not included in the thermodynamic data base for the Pitzer model. However, formate and glycolate do not undergo acid/base reactions above pH 4 (pKa values range from 3.8 to 3.9 depending upon ionic strength). Hence these organics will not participate in the acid/base reactions important to this study.

Table 1. Input chemical compositions of upper and lower segments of tank 241-AN-107. All concentrations are reported in units of molality. The notation (CB) indicates the concentration of the component was adjusted to achieve charge balance.

Component	Concentration (upper segment)	Concentration (lower segment)
Na	10.3 (CB)	8.24
NO_3	4.04	3.11
NO_2	1.44	1.34
$Al(OH)_4$	0.046	0.0043
SO_4	0.023	0.074
PO_4	0.023	0.019
Cl	0.046	0.53 (CB)
CO_3	1.51	1.51
OH	1.58	~0.001 (pH 11)

Results and Discussion

Two sets of simulations were performed. The first set of simulations were performed by incrementally adding increasing masses of $CO_2(g)$ to the solution compositions shown in Table 1 until equilibrium with atmospheric $CO_2(g)$ was achieved (i.e., $pCO_2 = 10^{-3.5}$ atm). These simulations provide information on the overall evolution of the supernatants as atmospheric gases infiltrate the tank The second set of simulations were performed by incrementally adding increasing concentrations of HNO_3 to the upper segment concentrations shown in Table 1. These simulations provide information on the overall acid buffering capacity of the supernatants.

The changes in carbonate concentration as a function of added CO_2 are shown in Figure 4. The results follow the expected trends. In the upper segments, the introduction of atmospheric CO_2 results in a net neutralization of the excess NaOH and the formation of aqueous Na_2CO_3, i.e. reaction (1),

(1) $CO_2(g) + 2NaOH = Na_2CO_3(aq) + H_2O$.

The aqueous carbonate concentration increases in solution almost, but not quite, to equilibrium with natron ($Na_2CO_3 \cdot 10H_2O$). At this point the aluminum and some carbonate precipitates as dawsonite ($NaAlCO_3(OH)_2$). Continued introduction of CO_2 results in the precipitation of trona via reaction (2),

(2) $CO_2(g) + NaOH + Na_2CO_3 + 2H_2O = Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (trona)

Trona then continues to precipitate until equilibrium is reached with atmospheric CO_2. The final predicted solid phases are trona and dawsonite.

In the case of the lower segment, the initial solutions are predicted to be in equilibrium with dawsonite. Introduction of CO_2 then precipitates a small amount of trona before equilibrating with the atmosphere.

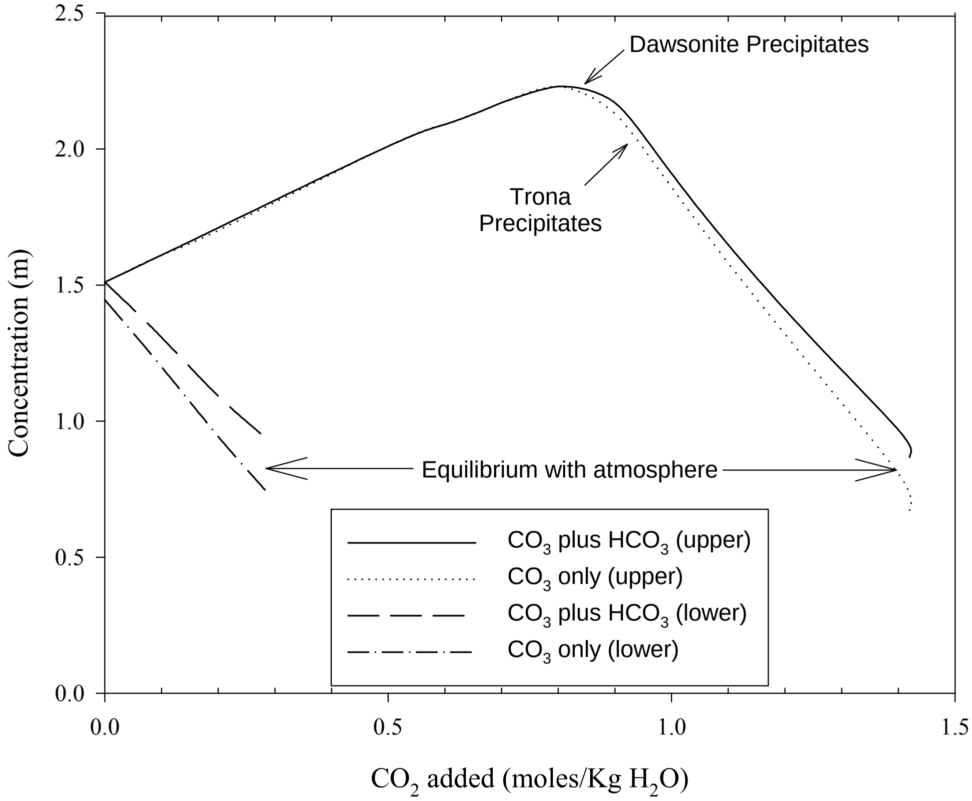

Figure 4. Calculated changes in aqueous carbonate concentration in both the upper and lower segments of tank 241-AN-107 using the Pitzer model.

The calculated changes in pH values as a result of CO_2 additions, Figure 5, reflect the changes in predicted hydroxide and carbonate concentration. In the upper segments, the introduction of CO_2 results in a gradual decrease in the pH as the excess NaOH is neutralized. Once most of the NaOH is neutralized the pH decreases rapidly owing to the lack of buffering capacity until the aqueous solution begins to form significant concentrations of bicarbonate (HCO_3^-) which, along with the formation of trona, buffers the changes in pH. In the lower segment there is little excess NaOH and the changes in pH are initially buffered by the formation of bicarbonate and trona.

The final calculated pH values using the Pitzer model are 10.26 for the upper segment and 10.24 for the lower segment. The standard ESP model gives similar results except for the mass of CO_2 required for neutralization. For the upper segment the ESP model predicts the formation of the same solid phases as the Pitzer model (dawsonite and trona) and a similar final pH (10.08). However, the ESP model predicts that the neutralization of the upper segment will require only 1.1 moles CO_2/Kg H_2O while the Pitzer model predicts 1.4 moles CO_2/Kg H_2O. Since less CO_2 is required to achieve equilibrium, the ESP model also predicts less trona formation and hence a higher carbonate concentration in solution. The results are similar for the lower segment. The ESP model predicts a similar final pH (10.03) to the Pitzer model (10.24) but less introduced CO_2 to achieve equilibrium (0.11moles/Kg H_2O versus 0.28 moles/Kg H_2O). ESP predicts final equilibrium with dawsonite, but not trona in the lower segment.

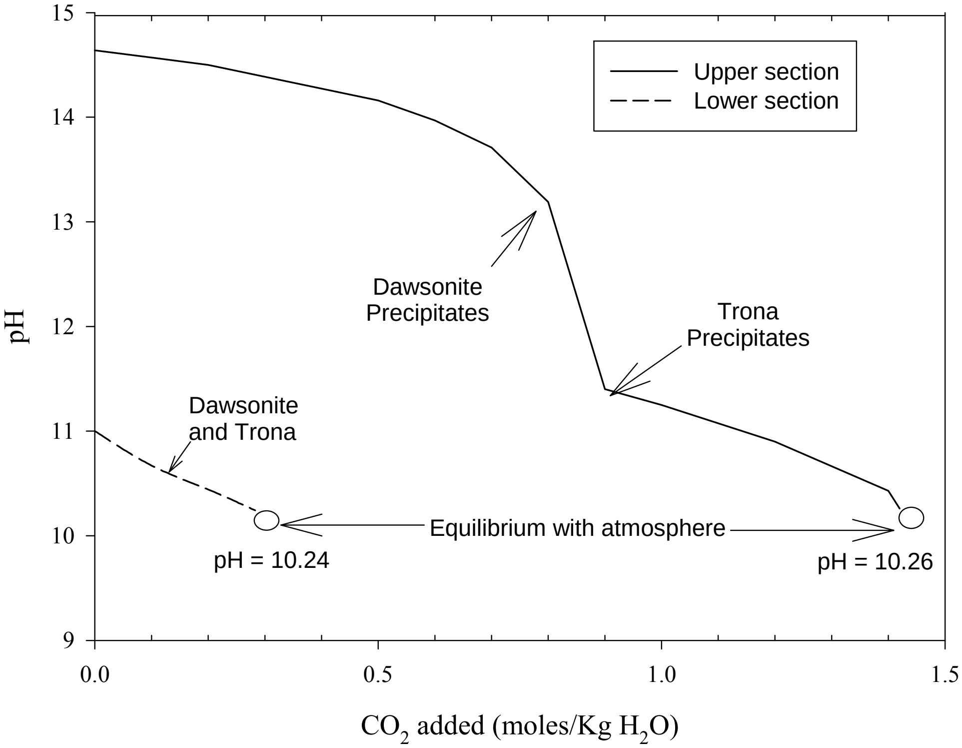

Figure 5. Calculated pH values for the upper and lower segments of tank 241-AN-107 using the Pitzer model.

The calculations shown above yield information on the expected changes in pH that could occur as CO_2 infiltrates the supernatants. However these calculations do not yield direct information on the stability of these pH values due to acid additions from organic degradation reactions or other processes. In this regard, the calculated pH values for the upper section of tank 241-AN-107 are shown in Figure 6 as a function of added nitric acid. The pH is initially high owing to the high NaOH concentration. As more and more acid is added to the system the pH gradually decreases until the free OH is effectively consumed. The pH then drops rapidly until trona precipitates and the solution equilibrates with the atmosphere (pH 10.25). Further additions of acid cause CO_2 to outgas (pCO_2 maintained at $10^{-3.5}$ atm), trona to dissolve, and the pH to remain essentially constant. The reason for the high buffering capacity can be seen from the dissolution reaction for trona in equilibrium with CO_2 (g), reaction (3),

(3) $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (trona) + $3H^+ = 3Na^+ + 2CO_2(g) + 4H_2O$.

At fixed pCO_2, the pH is dependent only upon the concentration of Na+ which remains relatively constant. Reaction (3) then buffers the pH until essentially all of the carbonate is removed from solution. The pH then drops rapidly owing to the loss of buffering capacity.

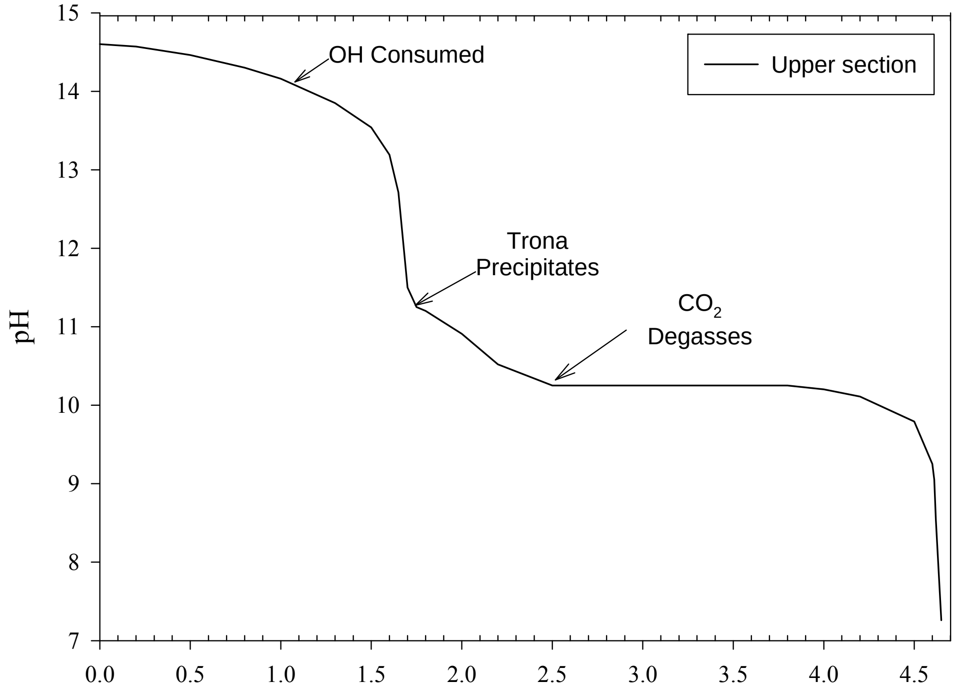

Figure 6. Predicted changes in pH as the result of acid additions to the upper segments of tank 241-AN-107 using the Pitzer model.

Summary

Thermodynamic modeling simulations of the neutralization of the supernatants in tank 241-AN-107 by atmospheric CO_2 predict the initial formation of $Na_2CO_3(aq)$ in the upper supernatant segments followed by the precipitation of dawsonite and trona which buffer the final pH values. In the lower salt cake segment the interstitial liquid solution is initially much closer to equilibrium with the atmosphere and buffered by the carbonate/bicarbonate equilibrium. The final calculated pH values are similar for the both the upper and lower segments and similar between the Pitzer and ESP models (i.e. upper segment 10.26 (Pitzer), 10.08 (ESP); lower segment 10.24 (Pitzer), 10.03 (ESP)), overall 10.1 ± 0.2. The differences between the models appear to be related to different equilibrium constants for trona formation ($\Delta \log K \sim 0.05$) and differences in activity coefficients. The final calculated pH values are expected to be extremely stable with respect to possible acid additions since they are buffered by the high carbonate concentration and the presence of the solid phase trona.

Finally it should be noted that measurement of pH in concentrated brines is complicated by liquid junction potentials, unknown single ion activities, and different calibration procedures[14]. Hence measurement of pH within the estimated modeling accuracy reported here (±0.2 units) could be quite challenging for these concentrated electrolytes.

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