

COAL MINE SALINE DRAINAGE: A STUDY ON ALKALINITY

R. Strand^A

^AGolder Associates, 147 Coronation Drive, Milton QLD 4064

ABSTRACT

Coal mining in Queensland only rarely encounters sulfides with concentration or volume to produce acidic response in worked water (ACARP 2006). In contrast, saline-alkaline worked water is common, and managing worked water in a sustainable manner is an ongoing challenge.

The source of saline-alkaline water is not usually a point source, but occurs through multiple processes: evaporation, blasting residue deposition resulting in algal blooms, detergent use, groundwater seepage and salt leaching may all play subtle roles in driving up salinity. Alkaline water may result from algal blooms, and evaporation may concentrate water - driving up salinity and exacerbating ion imbalances. Hydroxide distribution at elevated pH and ionic strength may result in alkaline water which does not respond as readily to either dilution (as a method to reduce pH) or acid dosing due to latent alkalinity (hydroxide stored as complexed species).

Speciation modelling (and specifically hydroxide species distribution) performed by the author for the purpose of calibration of a water quality model for a simple salt solution provides valuable insights in understanding how hydroxide distribution into latent species may complicate efforts to lower pH prior in saline-alkaline worked water.

An equilibration model simulates dynamic speciation over the course of a titration (pH 10.5 to 4.4) performed by the author at University of Queensland. The equilibrium model employs a unique solve methodology built by the author, the solving mechanics are based on the fundamental assumption that equilibrium between any two ions can be represented by the interaction between those two ions and their bonded counterpart.

1.0 INTRODUCTION

When the word alkalinity is used, we often think of common inorganic carbon species known to occur in water, such as bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}). For many naturally occurring waters, alkalinity is sufficiently represented by these species that the assumption that alkalinity is inorganic carbon is not far off. Alkalinity, in fact, is a measure of the *acid neutralizing capacity* (Appelo and Postma 2005). As we will see in this discussion, inorganic carbonate, at much of the pH range tested, is a considerable contributor to alkalinity, but at elevated pH, we will see a shift towards metal and cation bound hydroxide – termed latent alkalinity contributing species.

Since inorganic carbon is an effective proton acceptor, it follows that aqueous inorganic carbon is so frequently thought of as alkalinity. Worked water is an industry specific term which can broadly be defined as alkaline, saline water with a range of impurities ranging from colloidal coal particulate matter to a range of organics (Rao and Finch 1989).

Here, we explore the terms acidity and alkalinity from a speciation standpoint in context of ‘worked water’: Alkalinity is not *just* inorganic carbon. Worked water tends to have elevated pH and higher salinity, and based on speciation work completed to date, we find a selection of latent hydroxide and (bi)carbonate species contributing to alkalinity.

2.0 Approach

Historically, geochemical simulations have been performed in software utilizing the Newton Raphson method to calculate a solution to a polynomial given a starting point where the derivative of the function is not zero. The Newton Raphson method (Ypma 1995) iteratively revises an initial set of values for the unknowns and convergence (success) is when the residuals is less than some predefined tolerance:

$$r_i = - \sum_j^J \frac{df_i}{dx_j} dx_j$$

The modelling system used for this assessment finds an exact numerical solution for any positively charged ion (M_i) in solution acting against any other negatively charged ion (X_j) in solution, with $[M_i] = \alpha_i M_i$, where $\alpha_i M_i$ is the activity of cation i , and $[X_j] = \alpha_j X_j$. Activity coefficients for ions are solved explicitly but activity coefficients for charged or neutral (no charge) complexes is assumed to be unity. Oppositely charged, interacting ions variance from equilibrium is assessed using the quadratic equation which solves for the change required to return to equilibrium:

$$\partial[M_i] = \frac{-([M_i] + [X_j]) + \sqrt{([M_i] + [X_j])^2 - 4\{([M_i] * [X_j]) - K_{M_i X_j} [M_i]\}}}{2}$$

Where $\partial[M_i]$ is stoichiometrically equated with $\partial[X_j]$ (i.e. for a 1:1 salt, the values are the same), and $K_{M_i X_j}$ is the equilibrium constant for $[M_i][X_j]$ (Strand et al 2017, Tian et al. 2017). A variant of this equation is used when the complex concentration needs to be taken into account.

Iterations are needed when there is more than one influence on a single ion for example, calcium is elevated and both gypsum and calcite are exerting a controlling influence; iterations repeat until there are no further influences on the ion, the delta terms are zero, and Gibbs free energy is minimised.

The simulation platform used for the modelling is GoldSim, and the thermodynamic database employed is Thermo.dat; the model also has capability to model temperature effects on solubility and speciation between 0°C and 100°C, (Tian et al. 2017).

Here, we explore the terms acidity and alkalinity from a speciation standpoint: Alkalinity is not *just* inorganic carbon, as worked water tends to have elevated pH and higher salinity, we find an increased distribution of hydroxide and (bi)carbonate species contributing to alkalinity.

3.0 Methodology

Ten titrations were performed at the Landfill laboratory at University of Queensland (Hawkins Engineering Building). A model of the titration procedure was built in GoldSim. The model simulates the following processes:

- preparation of the solutions (i.e. weight of salt, addition of water weight),
- dosing with 1 molar NaOH (to pH 10.8)
- titrant addition (0.1 molar HCl) at regular intervals

Numerical records of the titration in terms of volume of titrant added and timestamp were transcribed into GoldSim as the driver to induce change of the solution.

Since the pH of the titration was recorded, for each step-wise addition of HCl into the titration vessel there is a corresponding pH for the total mixture of salt, water, NaOH and HCl, resulting in a large number of calibration points for the simulation.

Results of the titration simulations were assessed in terms of simulated changes to speciation in the solution as well as interrogation into latent alkalinity species contributing to buffering.

4.0 Materials

Ten solutions were mixed based on two mother liquors.

The first mother liquor solution contained 4.1045g pure NaCl salt flakes dissolved in 500 ml millipure deionized water.

The second mother liquor solution contained 9.1085 g red sea salt (RSS) flakes dissolved in 250 ml millipure deionized water.

Five solutions of decreasing concentration were mixed directly from the mother liquors (serial dilution was not used, to avoid unnecessary error magnification).

Mother liquor and dilution quantities for each of the 10 solutions are shown in Table 1.

Table 1. Titration solution composition

Solution #	Mother liquor type (NaCl or RSS)	Mother Liquor (g)	Final Solution (g)	Millipure DI water (by difference) (g)
1	NaCl	50.0073	50.0073	0
2	NaCl	25.0763	50.0126	24.9363
3	NaCl	12.5760	49.9756	37.3996
4	NaCl	5.0170	49.9515	44.9345
5	NaCl	2.5135	50.0197	47.5062

Solution #	Mother liquor type (NaCl or RSS)	Mother Liquor (g)	Final Solution (g)	Millipure DI water (by difference) (g)
6	RSS	49.9999	49.9999	0
7	RSS	25.0685	49.9942	24.9257
8	RSS	12.5142	50.0133	37.4991
9	RSS	5.0172	50.0027	44.9855
10	RSS	2.5028	49.9757	47.4729

The ten final solutions (calculated) are shown in Table 2.

Table 2. Ten titration solutions with various composition

Solution #	Na (mol/L)	K (mol/L)	Mg (mol/L)	Ca (mol/L)	NH ₄ (mol/L)	Cl (mol/L)	SO ₄ (mol/L)	NO ₃ (mol/L)
1	0.14	0	0	0	0	0.14	0	0
2	0.070	0	0	0	0	0.070	0	0
3	0.035	0	0	0	0	0.035	0	0
4	0.014	0	0	0	0	0.014	0	0
5	0.0070	0	0	0	0	0.0070	0	0
6	0.47	0.010	0.053	0.011	5.5E-07	0.55	0.027	3.5E-07
7	0.24	0.0051	0.026	0.0053	2.8E-07	0.27	0.014	1.7E-07
8	0.12	0.0025	0.013	0.0026	1.4E-07	0.14	0.007	8.7E-08
9	0.047	0.0010	0.0053	0.0011	5.5E-08	0.055	0.00	3.5E-08
10	0.024	0.00051	0.0026	0.00053	2.8E-08	0.027	0.00	1.7E-08

0.1 ml of premixed 1.0 molar NaOH standard was added to each solution to raise the pH prior to the titration.

The titrant was 0.1 molar premixed HCl standard.

The titration sequence was preset, which was not known until after the experiment. The preset titration sequence followed roughly a repeated 24 s delay of addition of titrant in 0.075 ml increments, in most cases, the final (target) pH of 4.4 was achieved after 330 seconds and the addition of ~1.05 ml of titrant.

5.0 Titration results

Titration for all ten solutions were carried out, recorded, transcribed and interrogated. For the purposes of this discussion paper, only the results of the most concentrated solution are shown, titration #6 (Figure 1).

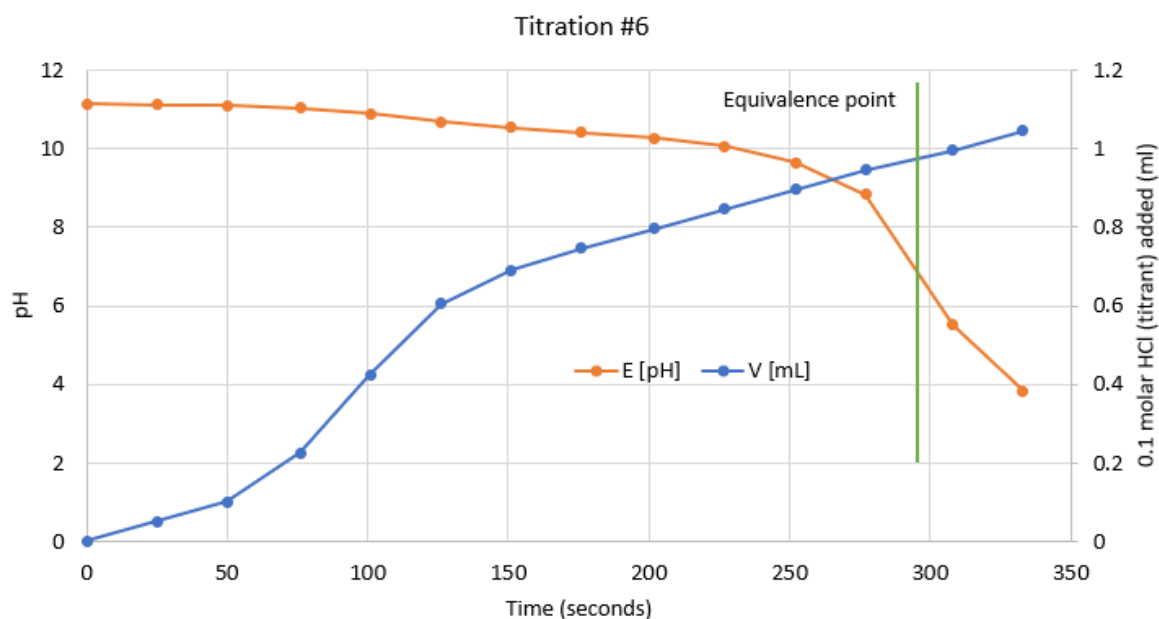


Figure 1. Titration #6 progression and equivalence point

6.0 Simulation details

Summary of details of the simulation are shown here for reproducibility:

- Container sizing
 - Surface area: 12 cm²
 - Depth: 7 cm
- Volume: ~50 ml
- Head space: 0 mL (Closed system)
- Temperature: 298K
- Air pressure: 0.9943 atm at ~50m above sea level
- Water density: (calculated) 1.03 kg/L
- Runtime: Simulation 1: 200s, Simulation 2: 10000s
- Standardisation of timing: intervals of 50s used for both simulations, allowing maximum of 49 iterations per titration step
- Closed system with respect to CO_{2(g)} exchange

Note: simulation details as listed were unchanged from simulation 1 to simulation 2.

7.0 Interrogation of titration

Speciation modelling was performed for each step of the titration, and the equilibrium species distribution are plotted for each step of the titration. As the titration progresses, various species become energetically favourable (Figure 2). Particularly those species containing hydroxide, carbonate or bicarbonate become less favourable as the pH decreases.

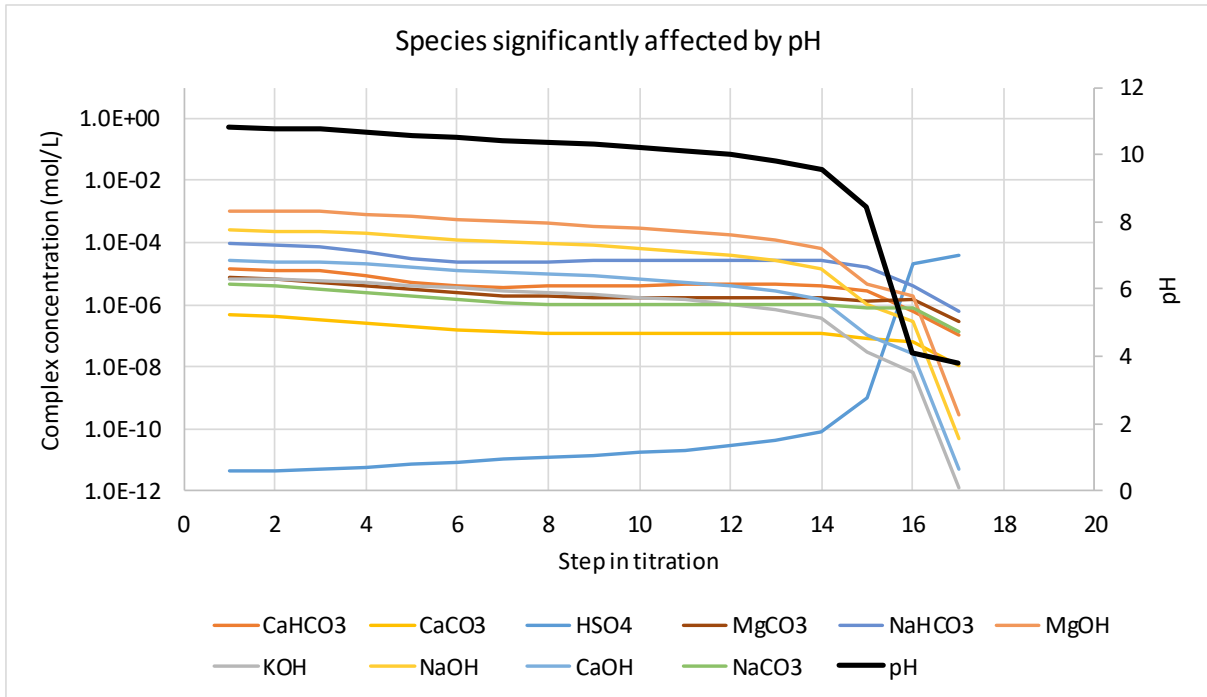


Figure 2. Energetic favorability affecting species distribution (Simulation 1)

To assess the distribution and contribution of latent alkalinity species, only those species containing bound carbonate, bicarbonate or hydroxide are plotted after accounting for stoichiometry to assess the most significant species contributing to alkalinity. As can be seen in Figure 3, MgOH is the largest contributor of latent alkalinity in the prepared solutions. Prior to seeing a significant drop in pH, the alkalinity contributing species are depleted.

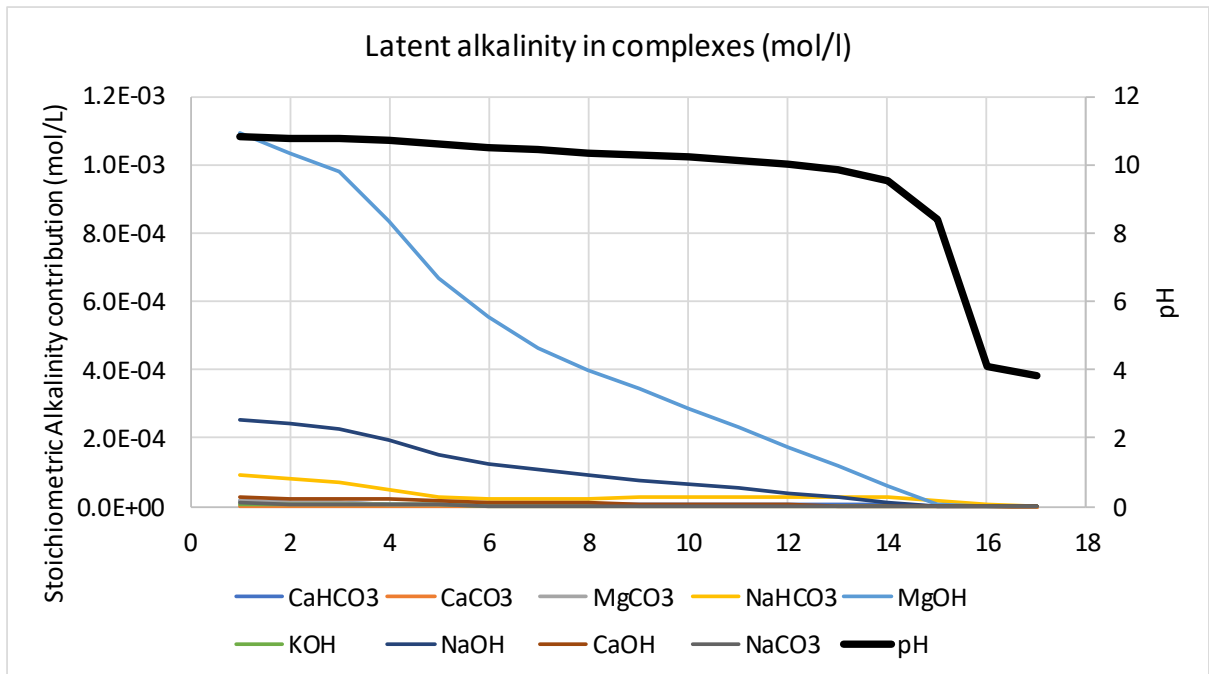


Figure 3. Latent alkalinity contributions (Simulation 1)

The materials used in the titration did not explicitly include inorganic carbonate which may explain the somewhat depressed inorganic carbonate species present in the above figures. Since the prepared solutions did not contain appreciable inorganic carbon, a second test was made to examine the effects of carbonate alkalinity.

8.0 Simulation 2

A second test (simulation) was programmed based on a groundwater sample from near a worked water storage facility. The analytical assessment provided sufficient information to develop a significantly different simulated response based on a similar titration sequence. The sample of water had chemical parameters as indicated in Table 3.

Table 3. Chemical composition from worked water sample in Central Queensland Coal Mine

pH	Na	Cl	Ca	Mg	SO ₄	K	HCO ₃	CO ₃	Ionic error
7.33	3680	5850	246	184	0.5	16	950	0.5	23%

The simulation with the actual sample was run, and some differences were immediately observed:

- The pre-titration dose of NaOH results in a less pronounced pH shift (and is rapidly affected by preliminary doses of acid)
- There is a delayed response where buffering is based on the prevalence of HCO₃
- The titration does not have the same end point
- Bicarbonate containing complexes have a different trend compared to hydroxide containing species as the titration progresses

The results from simulation 2 are shown in Figure 4 and Figure 5. General trends are similar between simulation 1 and 2 with all alkalinity contributing species being depleted prior to the pH shift, however, some residual HCO₃ containing complexes (NaHCO₃ and CaHCO₃) persist even after the titration endpoint is achieved, albeit at significantly lower concentration.

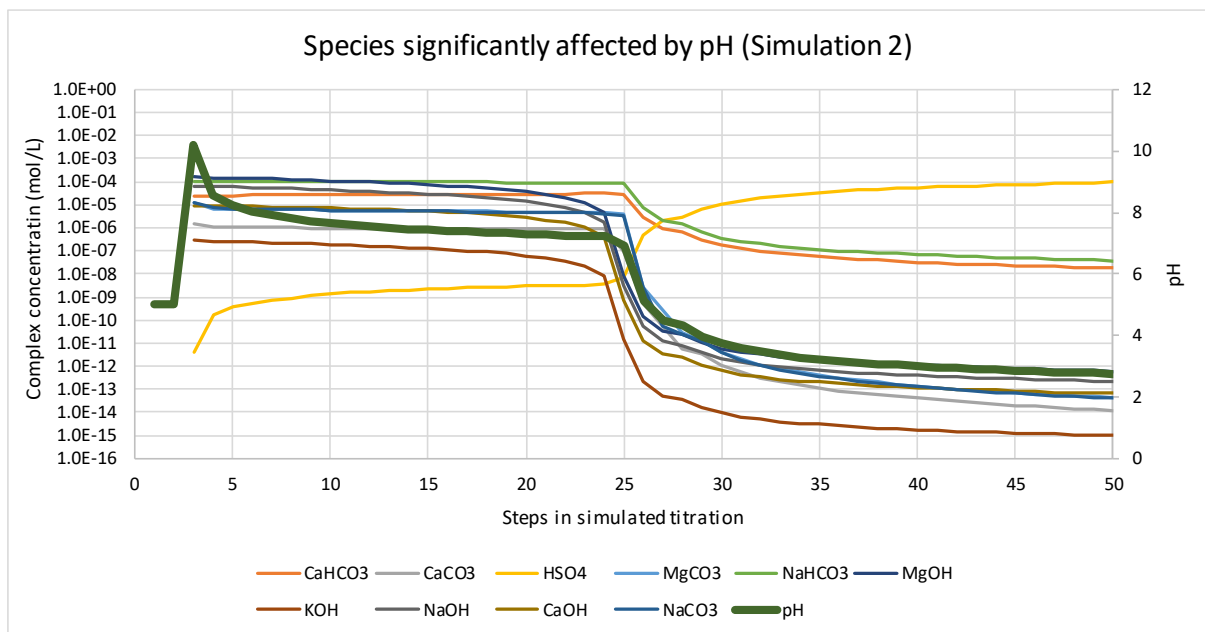


Figure 4. Energetic favorability affecting species distribution (Simulation 2)

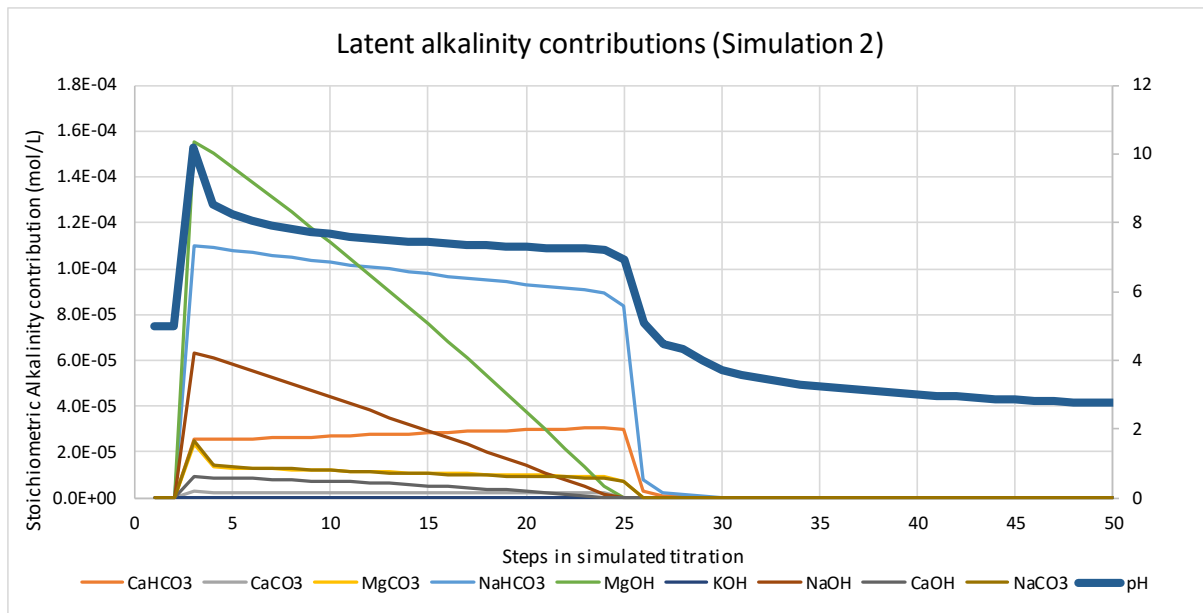


Figure 5. Latent alkalinity contributions (Simulation 2)

One result that is counterintuitive is the relatively slow increase in the CaHCO_3 complex as the titration progresses. This is unusual because we would expect HCO_3^- containing complexes to decrease as the alkalinity source is consumed in the titration. This result can be explained by considering first that the solution has very high bicarbonate and moderately elevated calcium to start with, then the pre-dose of NaOH forces a rapid shift in equilibrium to favor carbonate, which immediately causes calcite to precipitate. The titration, then is not only consuming bicarbonate but slowly consuming calcite, which maintains the pH while also protonating liberated carbonate, effectively replacing *two* bicarbonates for each mole of calcite consumed. Hence, while calcite is being depleted, bicarbonate is continually being replaced. The titration endpoint is achieved not when all bicarbonate is consumed (protonated), but when the distribution of inorganic carbon no longer retains significant buffering potential – when $\text{H}_2\text{CO}_3 \sim \text{HCO}_3^-$ which occurs near pH 6.3. Indeed, this can be observed in both Figure 4 and Figure 5.

To check this interpretation directly, plots of inorganic carbon distributions were assessed against pH directly using model outputs. As can be seen in Figure 6 there is a close match. The author notes there is a minor lag in the pH, this is likely due to a numerical artifact where the software doesn't update the reported value until immediately before the next step, resulting in a visual observation not lining up exactly, overall, however, the observation holds true.

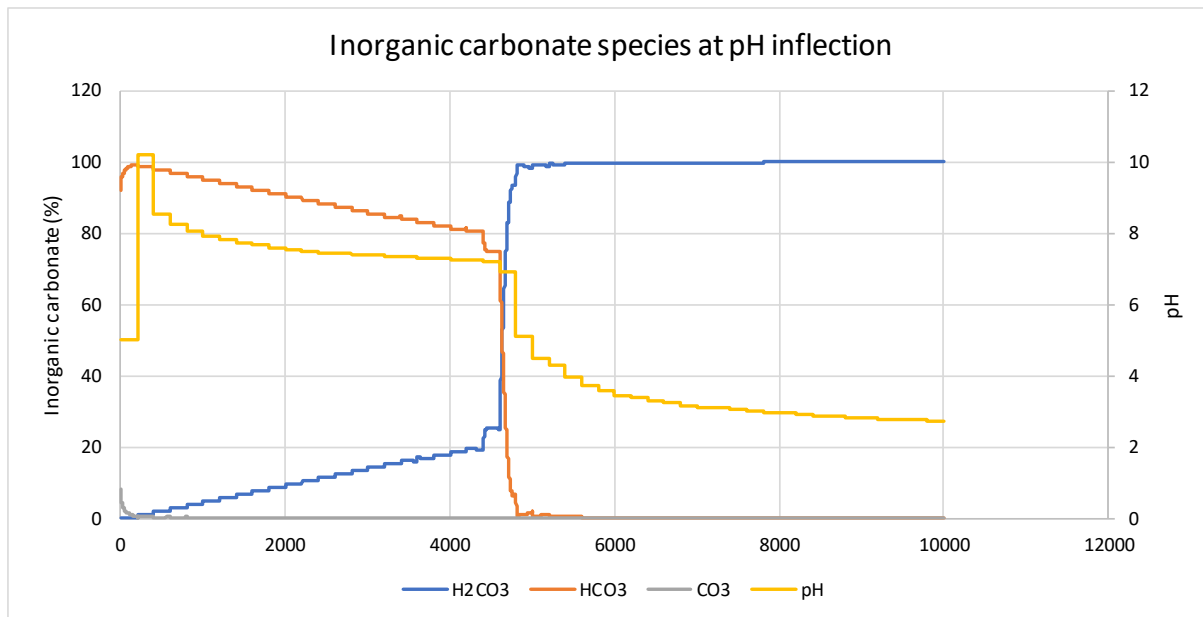


Figure 6. Inorganic carbon distribution and pH

9.0 Conclusions

Alkalinity distributions in solution, and in solutions undergoing acidification are fundamentally related to the starting concentrations and the quantity of inorganic carbon present. When bicarbonate is present as the most prevalent species of inorganic carbon, there is a strong tendency for the solution to buffer near pH 8.3. If other inorganic carbon species such as carbonate are present, then the pH will shift upwards, and downwards if carbonic acid is present. Above 10.3 pH, hydroxide species may start to contribute significantly more alkalinity than inorganic carbonate, and broadly, the influence of complexed species will mirror the free species (accounting for relative activity).

Some bicarbonate species tend to persist even near the pH inflection point, which suggests that the stability of bicarbonate complexes may not readily protonate until there is a significant abundance of protons in competition for the protonation site.

pH changes in response to acid dosing of worked water may be significantly altered by the type of alkalinity present. Changes to pH when the worked water has pH in the 8.3-10.3 range may be complicated by multiple forms of inorganic carbon (carbonate and bicarbonate), as well as a range of species which may subtly alter solution chemistry (specifically EC – since uncharged complexes do not contribute to electrical conductivity). Furthermore, as shown in the second simulation, efforts to adjust pH may be complicated substantially by the presence of previously precipitated materials – of particular concern – calcite.

Takeaway messages: ion-specific, thermodynamic speciation code in GoldSim is effective at simulating various solution stressors and simulating solution chemistry changes at a range of pH, including complex distribution based on energetic favourability and fundamental relationships involving buffering, pH balancing and protonation and hydroxylation.

10.0 References

ACARP (Australian Coal Association Research Program) 2006, Northern Bowen Basin Water and Salt Management Practices, Prepared by University of Queensland Centre for Water in the Mineral Industry.

- Appelo, CAJ and Postma, D 2005, *Geochemistry, groundwater and pollution*, A.A. Balkema Publishers, Leiden 649 pp., ISBN 0415364280.
- Rao, SR and Finch, JA, 1989, A review of water re-use in flotation, *Minerals Engineering*, 2(1), 65-85.
- Strand, R, Tuff, J, and Usher, B, 2017, Non-iterative modelling of Mine site Hydrogeochemistry, 9th Australian Acid and Metalliferous Drainage Workshop Proceedings.
- Tian, Y, Strand, R, Wang, G, Tuff, J, Usher, B, 2017, Water quality predictions under highly variable moisture and temperature: A case study on the importance of thermodynamics, 9th Australian Acid and Metalliferous Drainage Workshop Proceedings.
- Ypma, TJ, 1995, Historical Development of the Newton-Raphson Method, *SIAM Rev.*, 37(4), 531-551.