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Managing Process Chemistry with Acid-Base pH Buffers

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ABSTRACT

In geothermal process engineering there is an increasing need for reliable and stable pH control, for managing scaling and corrosion. Acid-base pH buffer solutions, such as those based on acetic acid and acetate, provide a simpler route to achieving this, compared to the use of strong acids and bases (e.g. sulphuric acid and sodium hydroxide). While pH buffering is a central part of fluid-mineral equilibrium studies, there has been little practical application in steamfield process chemistry. Recent papers by the author and colleagues have covered acetic acid dosing for silica scale avoidance. This work is updated and other potential applications described including:

- Maintaining stable pH in binary plants, to avoid both stibnite and silica scaling.
- Delaying neutralisation in the formation of acid-dosed injectate.
- Neutralising corrosive acidity in production wells.

1. INTRODUCTION

Acid-base equilibria and the properties of pH buffer solution are a core part of under-graduate chemistry. A pH buffer solution contains an acid (HA) and its conjugate base (A-), both moderately weak. They have the property of buffering pH, i.e.: addition of acid or base causes a relatively small change in pH - compared to unbuffered solutions. This paper considers the buffer system based on acetic acid (CH_3COOH) and acetate (CH_3COO^-). Other common weak acid-base pairs that have buffering properties are citric acid/citrate and ammonium/ammonia (NH_4^+/NH_3). The term 'weak acid' does not refer to the concentration but to the degree of dissociation of the acid. Unlike a strong acid, a weak acid does not completely dissociate, so significant concentrations of acid and base can lie each side of the following equilibrium:

$$\underset{\text{acid}}{CH_3COOH} \leftrightarrow \underset{\text{base}}{CH_3COO^-} + H^+ \qquad -(1)$$

The acid dissociation constant (K_a) is:

$$K_a = [CH_3COO^-][H^+] / [CH_3COOH] \qquad -(2)$$

$$= 1.75 \times 10^{-5} \quad \text{(at 25°C)} \qquad -(3)$$

For similar concentrations of acid and base ($CH_3COO^-/CH_3COOH \sim 1$),

$$Ka = [H^+]$$

$$pH = -\log(H^+) = -\log(K_a)$$

$$= 4.7$$

For geothermal brine, a pH of 4.7 is ideal for avoiding both scaling (silica and calcite at least) and corrosion. Adding this buffer to geothermal brine will see the pH shift towards 4.7. It also has the property of stabilising pH because the reservoir of acid and base absorbs any added acid and alkali - so long as they don't exceed the concentration of the buffer. Adding acid to an excess of acetic acid-acetate buffer will see the acid consumed by the base (CH_3COO^-):

$$CH_3COO^- + H^+ = CH_3COOH,$$

while added base will be consumed by the acid (CH_3COOH):

$$CH_3COOH + OH^- = CH_3COO- + H_2O$$

The buffer will be depleted when the added acid or base exceeds the concentration of the buffer. As a result, increasing the concentration of the buffer makes it last longer, i.e.: it takes more acid or base to deplete the buffer.

As an example of the buffering effect of the acetic acid/acetate; addition of 20 ppm sulphuric acid to a 100 ppm buffer solution (100 ppm of acetic acid + 100 ppm of acetate) would see the pH drop from 4.7 to 4.5. Addition of 20 ppm sulphuric acid to pure water would produce a pH of 3.4.

An acetic acid buffer can be prepared by mixing the acid (CH_3COOH) with the base, e.g. sodium acetate (CH_3COONa) or by adding sodium hydroxide to the acetic acid (converting half the acid to base). However, experiments have shown that good control over pH can also be achieved by dosing with pure acetic acid. This is because acetic acid reacts with alkalinity in the brine (mainly HCO_3^-) to produce pH buffering conditions:

$$CH_3COOH + HCO_3^- = CH_3COO- + CO_2 + H_2O \qquad - (4)$$

Dosing with acetic acid alone greatly simplifies practical applications and cost. Figure 1 shows the titration curves for geothermal brine, titrated with (1) a pH 4.8 buffer, (2) acetic acid and (3) sulphuric acid. All have the same H^+ concentration. Sulphuric acid has a very steep curve around pH 5. At this pH the brine is highly unbuffered and a very small change in acid dose rate will cause a large change in pH. In contrast the acetic acid and the pH 4.8 buffer have much gentler titration curves which level out above pH 4. This plot highlights the key difference between strong acids and weak acids.

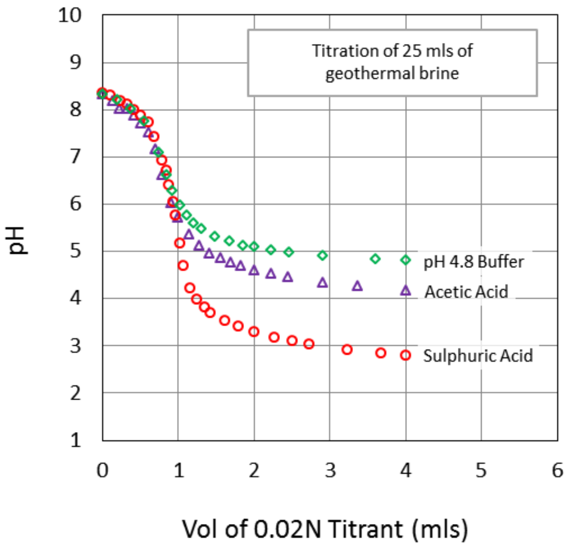

Figure 1. pH titration curves for sulphuric acid, acetic acid-acetate buffer and acetic acid. The brine is weirbox water from a Wairakei well (Lovelock, 2015).

The required dose rate (and cost) for acidising geothermal water (e.g. for silica scale control) is determined primarily by the bicarbonate (HCO_3^-) concentration; the higher the bicarbonate the more acid that is required to lower the pH to 5.0. To lower the pH bicarbonate is converted to CO_2:

$$CH_3COOH + HCO_3^- = CH_3COO^- + CO_2 + H_2O \qquad - (5)$$

2. ACETIC ACID PROPERTIES

Properties of acetic acid and concentrated sulphuric acid are presented below. Pure 100% acetic acid (called glacial acetic acid) is a clear liquid with a boiling point of 118°C. It is combustible; when heated to 40°C it can be ignited with a flame. Glacial acetic acid has a much lower density than sulphuric acid but on a weight basis has a similar number of moles of H^+ (15.9 moles per kg versus 19.6 for H_2SO_4) so dose rates on a weight basis are similar (acids are generally sold on a weight basis). Acetic acid is at least twice the price of sulphuric acid (US$0.90/kg in 2017).

Glacial acetic acid has low viscosity of 1.2 cP at 20°C (c.f. 1.0 cP for water). In comparison, concentrated sulphuric acid is viscous (27 cP) and together with its high density limits its ability to mix quickly in the pipeline. In New Zealand sulphuric acid is pre-diluted to provide good mixing and better dose rate control.

Table 1 Properties of Acids

Acid	Formula	Mol. Weight g/mole	Density kg/litre	Concentrations			
				'Percent'	mole/L	moles/kg	moles H^+ / kg
Sulphuric Acid ~98%	H_2SO_4	98.08	1.83	~98	~18	9.8	19.6
Glacial Acetic Acid	CH_3COOH	60.05	1.05	100	16.7	15.9	15.9

The dissociation constant for acetic acid (equation 2 above) is shown below for the temperature range 25-200°C. Also shown is the pH of a 50 ppm acetic acid solution. The pH rises slightly with increasing temperature. The pH of hot dosed brine will generally be measured cold, after withdrawing the brine through a cooler. If acetic acid and sulphuric acid are dosed to give the same cold sample pH (say pH 5) the pH at the pipeline temperature may be slightly different in each case. This should be considered when optimising dose rate, generally done by monitoring silica polymerisation and corrosion/deposition coupons.

Table 2 Acetic Acid Dissociation Constants: $CH_3COOH = CH_3COO^- + H^+$ (Schoonen and Barnes, 1997)

Temperature (°C)	25	50	100	150	200
logK	-4.74	-4.79	-4.98	-5.23	-5.51
pH of a 100 ppm Solution	3.76	3.78	3.88	4.00	4.14

3. ACETIC ACID DOSING TO AVOID SILICA SCALING

Acid-dosing of geothermal brine, to avoid silica scaling, is carried out at several geothermal plants around the world, including three in New Zealand. Acid dosing delays polymerisation of silica – the precursor to scaling – and allows brine to be flashed to a lower pressure and a high amorphous silica saturation indices (SSI), thus maximizing steam production. Sulphuric acid is the preferred acid for dosing because of its low cost. However, the use of sulphuric acid is challenging because of the steep pH-versus-dose curve (Figure 1) where slight changes in dose rate or acid demand (e.g. from changing field conditions) can cause large changes in pH and a risk of over-dosing or under-dosing (e.g. Addison *et al*. 2015). Consequently, there is a need for complex process control to maintain an optimum pH (typically pH 4.5–5.0). Additionally, there is a need for hot pre-dilution of the acid to over-come the high viscosity of sulphuric acid and provide better dose control.

The author has investigated the use of weak-acid buffers as an alternative to sulphuric acid. The development work is summarised in Lovelock (2015) and Lovelock et al. (2017). The latter includes the implementation of acetic acid dosing on a brine injection line at the San Jacinto geothermal field (Lovelock et al. 2017). This is still ongoing.

Acetic acid is at least twice the price of sulphuric acid, so it is likely to be favoured where acid demand (and cost) is moderate but silica scale or corrosion avoidance is critical, for example:

- High-enthalpy fields where the separated brine flow is low, but silica scale avoidance is a critical requirement.
- Dosing of high-silica wells on isolated well pads to avoid scaling until lower-silica brine from other pads is mixed in.
- Trimming pH on double or triple-flash plant where the primary dose is with sulphuric acid.

4. BINARY PLANT OPTIMISATION

Over the past ten years there has been increasing interest in installing binary bottoming plants on existing brine injection lines, with acid dosing to avoid silica scale and to optimise heat recovery. Acidising of binary plant brine presents special challenges:

- The power plant is exposed to corrosion risk, rather than just pipelines.
- There is increased risk of stibnite (antimony sulphide) scaling which is strongly dependent on both temperature and pH (Brown, 2011).

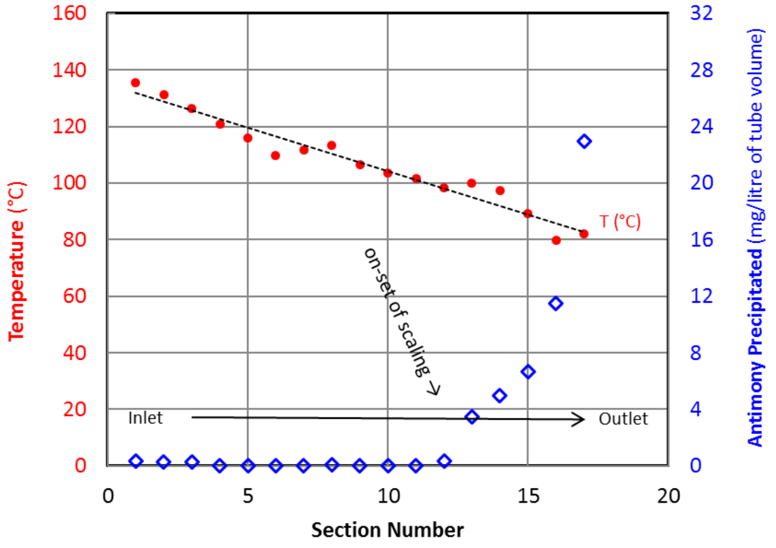

Figure 2. Plot showing on-set on stibnite scaling with brine cooling. Brine dosed to ~ pH 5 with acetic acid.

The developer may aim for operating conditions where generation is maximised, but with both silica and stibnite scaling avoided. In this case acid dosing will aim for a pH low enough to avoid silica scaling but not so low that stibnite scaling occurs. As a result, the plant may operate with a narrow pH target range and pH stability will be essential. In this case acetic acid dosing may be particularly applicable.

Testing may be required to optimise the operating conditions. Figure 2 shows the results of a simulated binary plant scaling test where 140°C feed brine with an SSI of 1.3 was dosed with acetic acid to pH 5, to avoid silica scaling. The test rig simulated binary plant cooling of the brine from 140 to 80°C along the test train. At a temperature of about 100°C, stibnite scaling starts to occur with an exponential rise in scaling rate as temperature falls between 100 and 80°C. For such testing, maintaining a constant pH is essential for achieving a convincing temperature trend - a small change in pH would have produced a change in the location of the stibnite scaling and would have obscured the temperature effect.

5. OTHER POTENTIAL APPLICATIONS

Other practical applications of acid-base buffers are presented below. These have been tested in the laboratory by not in the field.

5.1 Delaying Neutralisation of Acidified Injection Brine.

Dosing highly silica-supersaturated brines with sulphuric acid has been largely successful at preventing scaling in injection systems. However, declines in injectivity have still been seen at Kawerau in New Zealand. The brine in this field is acid-dosed to avoid silica scaling and it has been suggested that silica scaling may have occurred in the formation because of neutralisation of the brine by calcite in the formation (Addison et al. 2015). The brine chemistry is conducive to this happening since although the brine is acidified (to ~pH 5), it is highly unbuffered. As suggested by the steep titration curve (Figure 1) very little neutralisation is required to significantly raise the pH. Since the brine is highly supersaturated, polymerisation and the on-set of scaling could be fast with neutralisation.

If it emerges that neutralisation in the formation is the primary cause of injectivity decline, then a possible solution is to buffer the brine pH with a top-up dose of acetic acid-acetate buffer, prepared in the target pH range (pH 4.5-5.0). The addition of the buffer would not change the pH, merely increase the buffering capacity at the target pH. So, it would require a lot more water-rock reaction in the formation to shift the pH and thus more time to move the unpolymerised brine away from the wellbore. It would have the added benefit of smoothing out any variability in the pH resulting from imprecision in the sulphuric acid dosing. Only a rudimentary dosing system would be required with no special material requirements.

5.2 Neutralisation of Acidity

Acidity in production wells is a major constraint to production. In some cases, acidity can be neutralised with dosing through downhole tubing, but if a strong base is used (e.g. NaOH) there is a risk of over-dosing causing carbonate scaling, especially if dissolved CO_2 is converted to carbonate ion:

$$2NaOH + Ca^{2+} + CO_2 \quad = \quad 2Na^+ + CaCO_3\downarrow + H_2O$$

A solution of sodium acetate (CH_3COONa), the conjugate base of acetic acid, may be a better option because it avoids the risk of very high pHs. Excess acetate ion reacts with acid to produce the acetic acid-acetate buffer pair thus stabilizing pH, e.g.:

$$HCl + CH_3COO^-Na^+ \quad = \quad CH_3COOH + Na^+ + Cl^-$$

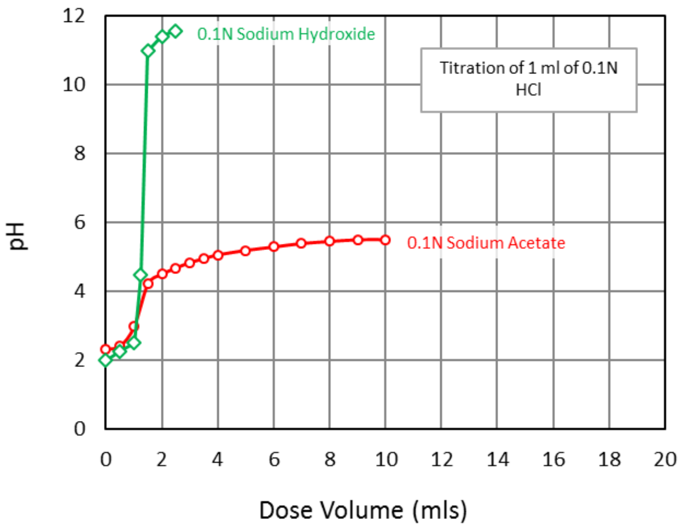

Figure 3. Plot showing pH stabilisation of pH with sodium acetate.

Figure 3 shows a simple bench-top titration where hydrochloric acid is titrated with (1) sodium hydroxide and (2) sodium acetate. For the strong base the pH-dose trend is essentially the reverse for the sulphuric acid dose trend, i.e. with a very steep pH versus dose trend and levelling out at very high pHs (>pH 10). In contrast, the sodium acetate has the effect of levelling out the pH at 5-6.

6. FURTHER WORK

The research and field testing summarised in this paper show that there is good scope for extending the use of pH buffers in the management of brine chemistry. More testing is required to establish practical applications and to identify risks and limitations. Following are some areas where further work is required:

- To date, acetic acid dosing has only been carried out only in single-phase, liquid conditions. Acid-dosed plants are generally double or triple flash with dosing into the first-flashed brine, before the SSI exceeds 1.0. The acidified brine is then flashed to lower pressures and it is essential that no acid is lost to the steam side. Acetic acid has a boiling point of 118°C and there is a possibility that some acetic acid may pass into the steam phase. This would raise the pH of the remaining brine and could increase the corrosion risk on the steam side of the plant. This has not been tested.
- Further work is required to understand the mechanism for injectivity decline acid-dosed wells. If it is found that fluid-rock neutralisation close to the wellbore is the reason, then buffers provide a potential solution.

7. CONCLUSIONS

Weak acid pH buffers can adjust and stabilise pH more effectively than strong acids and bases and have the potential to provide a range of brine treatment applications that can protect critical plant from scaling and corrosion, including:

- Acid dosing to avoid silica scaling.
- Delaying neutralisation of acid-dosed injectate in the well formation
- Ensuring pH stability in acid-dosed binary plants.
- Neutralisation of acid production fluids.

It is hoped that this paper will encourage developers to test these applications.

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