Commercialization of Acidic Geothermal Wells by pH Buffering

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Abstract: A potential pH buffering method for commercializing high-enthalpy acidic geothermal wells was explored in this study to raise the pH of the geofluids to greater than 3.5, a level considered by geothermal reservoir engineers to be non-corrosive to low-carbon steel. The pH buffering was modeled using a statistical software with five design factors (pH geofluid, pH buffer, volume buffer, concentration buffer and temperature of solution), and one response factor (pH of resulting solution). The buffer used was β-chloropropionic acid-Sodium β-chloropropionate (BCPH-NaBCP). Laboratory results based on two experimental designs showed that BCPH-NaBCP could raise the pH to > 3.5 for the first design and equal or greater than 4 for the second design. In both designs, the temperature of the solution did not show any significant effect on the buffered pH. It was also found out that for a closer range of concentration, there was no significant change in the buffered pH. The best combination of factors in the first design was then used in a bench-scale set-up to investigate the possibility of applying pH buffering at high velocity. Results showed that BCPH-NaBCP was useful for fast buffering and could be used to commercialize acidic wells.

Keywords: Acidic Geothermal Wells, pH Buffering, BCPH-NaBCP Buffer, Geofluid, Corrosive.
Introduction

Geothermal energy is virtually inexhaustible since it draws heat from the earth and its emission of greenhouse gases is minimal compared to fossil fuels. Its potential negative environmental effects are negligible due to the removal of hydrogen sulfide from high-temperature steam and the injection of spent geothermal fluids into the ground. Since the Philippines is part of the “Pacific Ring of Fire”, it is abundant in geothermal energy. It ranks second to the United States in terms of installed capacity and third behind Mexico in power generation [14]. The country has six geothermal power plants: Mak-Ban, Tiwi, Tongonan, Palimpinon, Bac-Man, and Mt. Apo with a generating capacity of 1909.23 MWe in year 2000. With the implementation of the 1996-2025 Philippine Energy Plan, geothermal power has supplied 22.6% of the country’s power generation. In spite of the huge available geothermal resource in the country, many of the geothermal wells drilled have produced acidic geofluid. These wells have high energy content but cannot be commercialized because their geofluid is corrosive to the casing and pipelines of geothermal plants. Of the more than 600 geothermal wells drilled, 27 wells produced acidic geofluid with high enthalpy and high wellhead pressure [4]. With the current practice of plugging and abandoning acidic wells, the geothermal industry incurs a huge financial loss [5]. Therefore, it becomes imperative to research and develop methods/techniques to be able to use these wells for power generation. Thus, if acidic wells are commercialized, drilling and other costs can be recovered, and correspondingly, an increase in energy production can be obtained.

Based on the main acid compound controlling its acidity, acid geothermal fluids are classified into hydrochloric acid type [(Cl)⁻ type] which includes Larderello, The Geysers, Kakkonda and Onikobe and the sulfuric acid type [(SO₄)²⁻ type] which includes Palimpinon, Bacman, Mt. Apo and Sumikawa [12,16, 19]. The hydrochloric type is due to the presence of Cl⁻ as HCl in superheated steam [9,3,2,6,18] whereas the sulfuric acid type could be formed by oxidation of H₂S, hydrolysis of SO₂ or hydrolysis of S (native sulfur) [12].

Though the corrosive properties of these acidic fluids limit their utilization for power generation, recent successes about new methods of treating them by raising their pH to a non-corrosive level may bring them back to power lines. At the Onikobe Geothermal Power Plant in Japan, for underground facilities, the internal surface of the acidic wells were coated with PbS; the production casing from the well mouth to a depth of 200 meters was made of CR-25 stainless steel; ceramic plasma was sprayed on the coupling section to provide insulation between different metals to prevent galvanic corrosion; and a third stage casing was inserted for depths from 350 m to 600 m so that if damage occurred on the production casing, the double or triple casing would still be present to extend the well life [1]. At the Coldwater Creek Steam Field and the Aidlin Geothermal Project of the Geysers in California which produced acidic chloride condensate in the well casings and steam lines of certain fields, a complete treatment was installed utilizing caustic/water injection and steam washing as part of an over-all corrosion mitigation system [13]. At the Miravalles Geothermal Field in Costa Rica, 50% by weight sodium hydroxide was injected at 950-m depth to neutralize the acid fluid. The developed neutralization system raised the surface pH values from 2.5 to 6.5 and maintained the pH range stable over the test period of 28 days [15].
In the Philippines, PNOC had performed a mitigation process for the Mahanagdong Acidic Well at Tongonan, Leyte in 1998 which consisted of injecting NaOH solution into the wellbore to neutralize the acidity of the well [17,20]. At Tiwi Geothermal Field in Tiwi, Albay, NaOH injection was performed at its Bariis 8 well. The well was then connected to the Tiwi steam gathering system for three months after which it was stopped because the well flow decreased slightly. Efforts to pull the injection assembly out of the well have been unsuccessful to date and the commercial mitigation operation had to be stopped for safety considerations [8].

Neutralization using NaOH is expensive and at the same time poses a potential health hazard during the handling of the concentrated solution. It also entails wasted cost due to the neutralization of the CO2 and H2S even if these two compounds are present in gaseous form. NaOH absorbs CO2 according to the reaction:

$$2\text{NaOH}(l) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(l) + \text{H}_2\text{O}(l)$$

The resulting Na2CO3 is partially ionized to form (HCO3)−. Since (HCO3)− is a natural buffer, the solution has a pH of 8-10. However, if an excess amount of NaOH is injected, the pH could be higher than 10 and silica scale will precipitate. Similarly, H2S is absorbed in NaOH solution according to the reaction:

$$2\text{NaOH}(l) + \text{H}_2\text{S}(g) \rightarrow \text{Na}_2\text{S}(l) + 2\text{H}_2\text{O}(l)$$

The two acid forming gases, CO2 and H2S, are responsible for the acidity of the brine. Thus, the removal of these gases is an added cost that is not essential. For non-corrosive geofluid, these gases are bled off and partly go with the steam sent to the power plant. Aside from this loss in income, the two reactions induce also side reactions. For example, the basicity of the brine increases the solubility of the CO2. The higher the concentration, the more CaCO3 is precipitated, thus, inducing scaling problem. If the brine is basic due to the addition of NaOH (pH > 10), the following reactions will occur:

$$\text{Ca}^{++} + 2\text{OH}^- \rightarrow \text{Ca(OH)}_2(s)$$

$$\text{Ca}^{++} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(s)$$

These reactions create scaling which is a detrimental problem. In the presence of a high concentration of electrolyte in a basic solution, such as in the case of geothermal brine with excess NaOH, these two precipitates, Ca(OH)2 and CaCO3, are insoluble. Thus, neutralization with NaOH introduces more problem than just protecting the casing and the steam gathering system from corrosion. These side effects will not likely to occur if the concentration of the Ca++ in the brine is below its saturation point. Unfortunately, acidic wells are normally high in Ca++ (>200ppm). Another technique is the injection of CO2 or re-injection of NCG. This method utilizes the natural buffering effect of CO2. An excessive amount of CO2 in the brine solution forms HCO3− instead of the CO3− as illustrated in the equations below.
The HCO$_3^-$ has an equilibrium pH of 8-10. This method had been overlooked from a theoretical standpoint. It is true that the injection of CO$_2$ or the re-injection of NCG adjusts the geofluid to a more stable non-corrosive pH of 8.35. However, when the geofluid is allowed to flow out of the well, the pressure drops, and the temperature remains high, resulting in a substantial decrease in the solubility of CO$_2$. As the concentration of dissolved CO$_2$ drops, the natural buffering effect of CO$_2$ is affected; as a result, the natural acidity of the geofluid makes this technique futile for adjusting the pH. This method had been tried in the Philippines but was eventually rejected.

The technique of commercializing acidic wells through the use of acid resistant materials of construction for the steam gathering system and well casing would entail high initial fixed cost that is not feasible in third world countries, like the Philippines. This would likewise result in a high cost of power conversion of geothermal energy making it less favorable compared to other sources of energy.

**Materials and Methodologies**

**Buffer and Buffer Capacity**

A buffer, composed of a weak acid and its strong salt with a strong base or a weak base and its strong salt with a weak acid, has the ability to maintain the pH of a solution between narrow limits [11]. Therefore, a buffered solution will have no appreciable change in its pH upon dilution or addition of slight to moderate amounts of a strong acid or base. Buffer capacity is a measure of the ability of the buffer system to neutralize added strong acid or base without a significant change in pH. The resistance to change in pH of a solution is greatest when [acid] / [salt] = 1. Therefore, buffer capacity is a maximum for buffer solutions containing equivalent amounts of a weak acid and its salt. As the ratio [acid]/[salt] changes from unity, either by decreasing or increasing the acid concentration or the salt concentration, the buffer capacity changes. A solution is generally considered to have a useful buffer capacity if the [acid] to [salt] ratio is within the range from 0.1 to 10; hence, effective within the range pK$_a$ ± 1 [11].

**New Buffering Solution**

The new buffer used in this investigation is β - chloropropionic acid- sodium - β-chloropropionate (BCPH- NaBCP) with a pK$_a$ = 4.11 [10] and a boiling point of 205 °C [7]. It has a high decomposition point in water (>200) via hydrolysis (Merck Index, 1989). This buffer system was chosen because the designed pH is within 4.11 ± 1 which is the effective buffer range [11] and will not react with geofluid components.

For more than three years now, an extensive study of applying pH buffering to solve corrosion and silica-scaling problems encountered in geothermal systems [21] has been conducted. Cabigon had successfully tested this method in the laboratory for silica dissolution without affecting low carbon steel casing.
Methodology

Laboratory Tests

Using the response surface method with emphasis on central composite design, five factors were included in each of the two experimental designs as shown in the table above. The factors were held at specified levels, classified as controllable, while the temperature of the resulting solution was allowed to vary in design I but not in design II. The response variable employed was the resulting pH of solution. After entering all the factors to be considered and the response to be obtained by experimentation, a tabular form with a total of 50 experiments at different combinations of factors was generated for each design. The response (pH of solution) was experimentally determined for each combination of factors.

Since all the acidic wells are plugged / cemented and abandoned, the geofluid used was obtained from a geothermal well at the MakBan Geothermal Field. It was used to maintain the original chemical composition of the geofluid and was acidified with HCl to simulate acidic geofluid.

For the laboratory experiments done at room temperature, 750 ml of geofluid was placed in a one-liter Erlenmeyer flask and into it were added the required pH, concentration and volume of the BCPH-NaBCP buffer according to the experimental design. The pH of the resulting solution was measured with a pH meter. However, for the temperature greater than the room temperature, the 750 ml geofluid was placed in a three-necked flask in a reflux setup and was added with the required combination of pH, concentration and volume of the BCPH-NaBCP buffer. In the reflux setup, a thermometer was inserted in the first neck; the second with an ordinary condenser and the third neck is where the sampling was done. Since the pH meter has a temperature probe, the actual reading in the pH meter was recorded.

The tests for the thermal stability of the buffering strengths of BCPH-NaBCP solutions were done by heating the solutions for one hour in sealed glass bulblets at 100°C, 120°C, 140°C, 160°C, 180°C and 200°C. Also, in this study, the buffer capacity to an added H2SO4 and the beta factor of the BCPH-NaBCP solution were determined.
Experiments Using the Bench Scale set-up
For the bench-scale set-up as shown in Figure 1, the buffering effectiveness of the BCPH-NaBCP solutions was evaluated. Geothermal brine (geofluid) from the brine tank is pumped to the mixing tank where the geofluid is heated with steam coming from the boiler. Then, the heated geothermal brine passes through the bottom of the 25-ft long, 1.5” diameter column and mixes with BCPH-NaBCP solution pumped from the solution tank. After two minutes, samples of the mixed geothermal brine and BCPH-NaBCP solutions are collected at the five ports starting at the bottom of the column and at 5-ft intervals up to the top of the column. The same procedure was done using this time the 25-ft long, 2.0” diameter column.

Discussion of Results

Laboratory Tests
In this research, the laboratory data were processed and the significant factors were determined using the statistical analysis software for the two designs of experiments (DOE). The data was analyzed through graphs and model adequacy testing and then validation of the model using confirmation runs. Table 1 shows the significant factors and the interactions for DOE I and for DOE II in Table 2. For both designs, the temperature is not a significant factor. This finding is very important because this implies that the buffered pH is stable at elevated temperatures. This means that hot acidic geofluid can be buffered and this could lead to its commercialization. Furthermore, it was found out in Table 2 that for a concentration range of 0.2 to 0.5, the concentration is not a significant factor. This implies that a small amount of buffer is needed, thus, making the buffering technique inexpensive and could be commercially viable.
Results showed that based on a completely randomized blocking experiments, the equation for the pH of solution as obtained from the software used for the experimental design I is:

\[
\text{pH Solution} = -6.94715 + 7.08047 \times \text{pH Geo} - 0.12811 \times \text{pH BCPH-NaBCP} - 0.00993464 \times \text{BCPH-NaBCP} - 5.82739 \times \text{conc BCPH-NaBCP} - 1.18407 \times \text{pH Geo}^2 - 7.9500E-03 \times \text{pH Geo} \times \text{BCPH-NaBCP} + 0.008222 \times \text{BCPH-NaBCP} \times \text{BCPH-NaBCP} + 1.61020 \times \text{pH BCPH-NaBCP} \times \text{BCPH-NaBCP} + 0.013648 \times \text{BCPH-NaBCP} \times \text{conc BCPH-NaBCP}
\]

| Table 2 Experimental Design I Analysis of Variance |
|-----------------|--------|--------|
| SOURCE          | F VALUE| PROB > F |
| Model           | 52.87  | < 0.0001 |
| A - pH Geo      | 246.82 | < 0.0001 |
| B - pH YODIN    | 63.33  | < 0.0001 |
| C - vol YODIN   | 18.45  | 0.0001  |
| D - conc YODIN  | 28.43  | < 0.0001 |
| A^2             | 29.95  | < 0.0001 |
| AC              | 6.35   | 0.0158  |
| BC              | 6.80   | 0.0127  |
| BD              | 39.12  | < 0.0001 |
| CD              | 4.50   | 0.0412  |

| Std. Dev        | 0.18   | R-Squared | 0.9222 |
| Mean            | 2.96   | Adj. R-Squared | 0.9047 |
| C.V.            | 0.03   | Pred. R-Squared | 0.8717 |
| PRESS           | 2.10   | Adeq. Precision | 28.213 |

| Table 3 Experimental Design II Analysis of Variance |
|-----------------|--------|--------|
| SOURCE          | F VALUE| PROB > F |
| Model           | 91.525 | < 0.0001 |
| A               | 313.963 | < 0.0001 |
| B               | 31.963  | < 0.0001 |
| D               | 79.170  | < 0.0001 |
| A^2             | 88.433  | < 0.0001 |
| AD              | 31.050  | < 0.0001 |
| BD              | 4.573   | 0.0382  |

| Std. Dev        | 0.2714 | R-Squared | 0.9274 |
| Mean            | 3.371  | Adj. R-Squared | 0.9773 |
| C.V.            | 8.1329 | Pred. R-Squared | 0.8946 |
| PRESS           | 4.5991 | Adeq. Precision | 26.821 |
Figure 2 shows the actual value vs the predicted value of the pH of the solution using the model equation for the pH of the solution. The graph shows the closeness in the actual and predicted values of the pH of the solution.

For the experimental design II, the pH of solution is:

\[
\text{pH}_{\text{solution}} = -2.38331 + 7.72522 \times \text{pH Geo} + 0.53962 \times \text{pH BCPH-NaBCP} - 0.026366 \times \text{vol BCPH-NaBCP} - 1.37556 \times \text{pH Geo}^2 + 0.017832 \times \text{pH Geo} \times \text{vol BCPH-NaBCP} + 0.020319 \times \text{pH BCPH-NaBCP} \times \text{vol BCPH-NaBCP}
\]

Experiments on the capacity of BCPH-NaBCP to a change in pH from 4.0 to 3.0 and from 4.5 to 3.5 by the addition of a strong acid showed that the greater is the concentration of BCPH-NaBCP, the greater is the capacity of the buffer solution. Likewise, experiments on the Beta factor or Beta value of BCPH-NaBCP for a change in pH from 4.0 to 5.0 and a pH from 4.5 to 5.5 showed that the Beta factor increases with the concentration of the buffer system for the same pH.

**Results using the Bench Scale Set-up**

Predicting the best pH of solution using the different combinations of parameters through the statistical analysis software was also done in this study to find out the best combination of factors to be used in the bench-scale set-up. Due to the high costs of chemicals needed, this procedure was considered necessary so that lesser number of trials could be performed, but still with the best results. So, the best combination of factors which were used for the bench-scale set-up were the following: pH geofluid = 3.0, pH buffer = 4.0 and concentration buffer = 0.25M.

The pH of solution at the different ports, e.g., from the bottom to the top of the column which are 5 ft from each other, has values greater than 3.5 (Table 4, Table 5). Hence, the results showed that the buffer system can effectively buffer the geofluid.
Conclusions

Laboratory Tests
The results of the laboratory tests showed that the pH buffering technique using BCPH-NaBCP solutions raised the geofluid pH to as high as 4.086 for the first experimental design and for the second, to 4.369. The laboratory tests showed that the initial pH of the geofluid, the pH concentration and volume of BCPH-NaBCP solutions significantly influenced the pH of the final solution. Results showed that the pH adjustment could be made using the model equation for the two experimental designs. It was also proven that the buffer works at elevated temperatures and that smaller amounts of buffer will bring the desired pH.

Bench-Scale Set-up
The results of the 1.5-inch diameter column (Table 4) and the 2.0 inch diameter column (Table 5) showed that BCPH-NaBCP buffer system raised the geofluid pH to a value greater than 3.5 in all the five ports in each column with an interval of 5 ft. Based on the pH of the resulting solution, the diameter of the column is immaterial in the buffering of the acidic geothermal brine because the range of values for the 1.5-inch column and the 2.0-inch column are almost the same which is equal or greater than a pH of 3.5

Recommendations
Since this particular research has not been tested in an actual acidic geothermal well, it is recommended that the most advisable strategy is to introduce the BCPH-NaBCP buffer solution at high concentration to the reservoir and then to shut-in the well for a day or two to allow the well to heat up and to build up pressure, after which BCPH-NaBCP solution is introduced using an acid string set at the production well. The acid string is inserted through the hole at the top of the geothermal well assembly to reach a certain level where acidic waters enter the geothermal well. Let the geofluid flow out of the well while simultaneously injecting a regulated amount of BCPH-NaBCP.
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