Application of SOLVEQ in Evaluating the Dosing-rate of NaOH and H₂SO₄
Treatment of Geothermal fluids

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ABSTRACT
A method was developed using SOLVEQ geochemical program in evaluating the amount of base (NaOH) and acid (H₂SO₄) added to thermal fluids. In this method, pH is modified, as the charge balance is re-adjusted to compensate for the given pH. The adjustment of the charge balance, using a pre-selected ion, makes this method useful in computing the required dosage of base (such as NaOH) or acid (such as HCl or H₂SO₄) to thermal fluids to attain a desired pH.

For addition of base, Na ion (assuming addition as NaOH = Na⁺ + OH⁻) is added as the charge balancer while for acid addition, Cl⁻ is added as the balancer (assuming addition as HCl = H⁺ + Cl⁻). For acid like H₂SO₄, one can also use Cl⁻ ion as the balancer, provided its adjusted mole is divided by two by the concept neutralization-equivalent-weight or simply the equivalent of H₂SO₄ to HCl: there are two equivalents per mle of H₂SO₄ per mle of HCl.

Based from the results and comparison with actual field trials, differences highlighted the intricacy of the chemical equilibria involved in the procedure. Although measurements of pH’s at laboratory condition remain the only method of choice in evaluating the required dosages, the method shows the following sensitivity of the treatment: for NaOH, fluxes in condensate flow and the role of Eh are essential parameters to monitor effectiveness of the treatment, while for H₂SO₄, the line-temperature dictates the strength of acidity, hence the amount of dosage.

1. INTRODUCTION
Development of pH modification system for geothermal waste fluids from fluid-collection-disposal-system has become a valuable industrial procedure in altering the fluid’s chemical properties to attain a desired effect, such as corrosion control or prevent silica precipitation. Adjusting the pH of steam condensate by base addition (such as NaOH) to 8.00 (Lichti et al.1998; Villa et al., 2003), acid corrosion is minimized, while lowering the pH of the brine by acid injection (such as H₂SO₄) to 5.50 (Garcia et al., 1996), prevents deposition of amorphous silica. Although these procedures may look like simple mixing of fluids, its application to industrial scale was proven to be a not so easy task.

The critical step in its implementation is the evaluation of the optimum dosing rate to attain a desired pH of acid or base given the chemistry and flow rate of the fluids. The dosing-rate alone dictates the scale and the cost of the procedure. To-date, its evaluation is determined by laboratory titration of the collected fluid and series of field trials for the right pH. These methods were proven useful in designing and optimizing the procedure. However, these steps were at times laborious and costly.

This paper presents a method using SOLVEQ, a computer-assisted calculation of amount acid or base to be injected to the fluids to attain a desired pH. Its inception came when there was a need to have a fast and reliable tool to determine the cost of the procedure for different types of power plants at PNOC-EDC’s new projects. In absence of actual power plants and on-line fluids to conduct field trial, the method is considered as a cheap and reliable alternative.

2. THEORY
Arnorsson et al., (1995) identified three chemical processes that affect pH of geothermal fluids. They include rock dissolution, the supply of acids to the water and precipitation of some secondary minerals from the water. The first process tends to increase the water pH whereas the other two processes tend to decrease it. For this paper, only the supply of acid or base will be discussed by changing the pH using SOLVEQ. Effect of dissolution or precipitation were demonstrated from other works using pH modification, such as silica prevention by Garcia et al., (1996) and corrosion control of Villa, et al., (2003) and Sanchez, et al., (2001).

SOLVEQ is a FORTRAN computer program for computing homogeneous chemical equilibria in aqueous systems developed by Spycher and Reed (1990). It is used primarily as a work horse for processing water analyses of all types, but it is also useful for certain types of geochemical process modeling. For a given temperature, pH, and total composition of a homogeneous aqueous solution, SOLVEQ computes the activities of all aqueous species and the saturation indices of solids and gases’ fugacity. It is the SOLVEQ’s special ability to compute the homogeneous chemistry at various pH’s that make this tool ideal in evaluating addition of acid or base to a particular solution.

The pH can be changed interactively when running SOLVEQ, just as for temperature. If pH is changed, the total molar amount of hydrogen ion is re-computed, and the charge balance is re-adjusted to compensate for the given pH. It is the adjustment of the charge balance, using a pre-selected ion that makes this program useful in computing amount of a particular base (such as NaOH) or acid (such as HCl).

For a base addition, Na ion (assuming addition as NaOH = Na⁺ + OH⁻) is added as the charge balancer while for acid addition, Cl⁻ is added as the balancer (assuming addition as Cl⁻ = H⁺ + Cl⁻).
HCl = H⁺ + Cl⁻). For acid like H₂SO₄, one can also use Cl⁻ as the balancer, provided its adjusted mole is divided by two. This is invoking the concept neutralization-equivalent-weight or simply the equivalent of H₂SO₄ to HCl: there are two equivalents per mole of H₂SO₄ per mole of HCl. Direct use of SO₄²⁻ (from H₂SO₄) as a charge balancer is not possible because this will interfere with the computation of redox potential. Since the system is essentially in a reducing environment, SOLVEQ assumes a redox reaction of HS⁻ + H₂O = 9H⁺ + SO₄²⁻ + 2e⁻ in its calculation.

For this study, the following assumptions are invoked:

- Line conditions, such as temperature, fluid flow, pressure, and volume, are constant
- The given fluid chemistry represents the present fluids
- Injection temperature of NaOH or H₂SO₄, usually at ambient condition, does not significantly change the initial temperatures and volume of the fluids
- Complete dissociation of NaOH and H₂SO₄, (such as NaOH = Na⁺ + OH⁻ and H₂SO₄ = SO₄²⁻ + 2H⁺) is attained
- Complete mixing of acid or base into the fluid

It is envisaged that the differences between actual and computed values are attributed to the violations of these assumptions. If there were similarities, these assumptions were then attained.

3. METHODOLOGY

Two sets of data were used for this demonstration. These are the representative steam condensate and brine chemistry from Leyte geothermal project as shown in Table 1 and 2, respectively. Below are the SOLVEQ methodology of NaOH and H₂SO₄ treatment in pH modification of geothermal fluids:

3.1 Method for NaOH treatment to attain pH 8.00

Step 1: Get representative complete fluids chemistry as analyzed

As much as possible the data to be used has ion balance difference less than or equal to 5%. Samples with difference higher than 5% are not recommended for this type of calculations.

Step 2: Using PHREEQC or Watchworks or SOLVEQ run data at desired line temperature (as data2)

This step is called ‘data polishing’. Polishing includes correcting the ion difference to zero at line temperature. This was done by running the sample at line temperature using any reliable geochemical simulation codes (such as PHREEQC, Watchworks, or SOLVEQ). For Leyte sample, the condensate temperature is set at 45°C.

Step 3: Using SOLVEQ, run data2 at desired line temperature but vary pH to 8.00

With a polished data, we are now ready to adjust the pH to 8.00 using Na ion as the charge balancer. Refer to SOLVEQ manual (Spycher and Reed, 1990) to interactively select Na as the balancer.

Step 4: Run SOLVEQ at pH 8.00 using Na as charge-balancer simulating dissociation of NaOH

Step 5: Compute moles of NaOH (as Na⁺) added per kg condensate

To compute the amount of NaOH added per kg of sample, get the amount of Na ion added or changed from the SOLVEQ’s output file. This can be computed as illustrated below:

Sample calculation:

Find: Dosing rate of 12.5 N (50% w/v) NaOH needed per kg condensate to attain pH 8.00:

Given: From step 2 as data2, it needed 0.446e⁻³ NaOH (as Na⁺) equivalent per kg condensate at line condition to adjust pH to 8.00; Flow rate of condensate = 290 kg/s

Solution:

Volume of 12.5N NaOH/kg sample = 0.446e⁻³ equivalent / 12.5 N = 3.57e⁻⁵ liter/kg-condensate At given flow-rate , compute dosing rate:

Dosing rate = 290 kg-condensate/sec x 3.57e⁻⁵ liter/kg-condensate x 3600 sec/hr =37 l/hr

3.2 For H₂SO₄ treatment to attain pH 5.50

Step 1: Get representative complete fluids chemistry as analyzed

Step 2: Using SOLVEQ run data at desired line temperature (as data2)

Similar to NaOH treatment, initial data has to be polished before any pH adjustment. For Leyte sample, the brine temperature is set at 160°C.

Step 3: Using SOLVEQ, run data2 at desired line temperature but vary pH to 5.50

With a polished data, we are now ready to adjust the pH to 5.50 using Cl⁻ ion as the charge balancer. Again refer to SOLVEQ’s manual to interactively select Cl⁻ as the balancer.

Step 4: Run SOLVEQ at pH 5.50 using Cl⁻ as charge-balancer simulating dissociation of HCl

Step 5: Compute moles of H₂SO₄ (as Cl⁻/2) added per kg condensate

From the SOLVEQ output file, get the moles of Cl⁻ ion from the SOLVEQ’s output file, and divide it by two. This can be computed as illustrated below:

Sample calculation

Find: Dosing rate of 36 N H₂SO₄ needed per kg condensate to attain pH 5.50
Table 1: Condensate chemistry and comparison between computed and field dosing rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Field dosing rate</th>
<th>Computed dosing rate</th>
<th>Percent difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-17-2003</td>
<td>28</td>
<td>38</td>
<td>36</td>
</tr>
<tr>
<td>9-15-2003</td>
<td>42</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Average</td>
<td>40±3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Brine chemistry and comparison between computed and field data

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow, kg/s</th>
<th>Temp, °C</th>
<th>Date</th>
<th>pH</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Sr</th>
<th>SO4</th>
<th>HCO3</th>
<th>B</th>
<th>NH4</th>
<th>SiO2</th>
<th>H2S</th>
<th>TCO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB Brine</td>
<td>0.18-0.22 (Pilot Test)</td>
<td>160</td>
<td>2003-06-16</td>
<td>6.93</td>
<td>5564</td>
<td>1151</td>
<td>236</td>
<td>0.21</td>
<td>0.36</td>
<td>10699</td>
<td>20.50</td>
<td>7.96</td>
<td>209</td>
<td>3.11</td>
<td>773</td>
<td>5.02</td>
<td>23.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2004-07-11</td>
<td>7.02</td>
<td>5419</td>
<td>1429</td>
<td>250</td>
<td>0.31</td>
<td>0.38</td>
<td>10699</td>
<td>22.20</td>
<td>6.77</td>
<td>209</td>
<td>3.18</td>
<td>773</td>
<td>5.02</td>
<td>23.98</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2005-08-11</td>
<td>7.08</td>
<td>5949</td>
<td>1289</td>
<td>269</td>
<td>0.31</td>
<td>0.37</td>
<td>10699</td>
<td>20.20</td>
<td>7.78</td>
<td>209</td>
<td>3.30</td>
<td>503</td>
<td>3.82</td>
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<td></td>
<td>2006-09-11</td>
<td>7.01</td>
<td>5669</td>
<td>1225</td>
<td>254</td>
<td>0.37</td>
<td>0.42</td>
<td>10642</td>
<td>23.43</td>
<td>7.03</td>
<td>209</td>
<td>3.27</td>
<td>734</td>
<td>5.10</td>
<td>18.50</td>
</tr>
<tr>
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<td>7.01</td>
<td>5669</td>
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<td>254</td>
<td>0.37</td>
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<td>209</td>
<td>3.27</td>
<td>734</td>
<td>5.10</td>
<td>18.50</td>
</tr>
</tbody>
</table>

Table 3: Comparative analysis between computed and field data in NaOH treatment
Table 4: Comparative analysis between computed and field data in H₂SO₄ treatment

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Brine flow kg/s</th>
<th>Injection temperature °C</th>
<th>pH before- H₂SO₄ injection</th>
<th>pH after H₂SO₄ injection</th>
<th>Dosing rate (ml/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB lab pH</td>
<td>0.10</td>
<td>25</td>
<td>6.90 measured at 25°C</td>
<td>5.60 measured at 25°C</td>
<td>4.80</td>
</tr>
<tr>
<td>based from lab titration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MB pH-MOD pilot test trials</td>
<td>0.18 to 0.22</td>
<td>160</td>
<td>6.97 to 7.04 measured at 25°C</td>
<td>5.20 to 5.60 measured at 25°C</td>
<td>8.93</td>
</tr>
<tr>
<td>(actual)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>0.18 to 0.22</td>
<td>160</td>
<td>6.44 computed at 160°C</td>
<td>5.50 computed at 160°C</td>
<td>97 to 118</td>
</tr>
</tbody>
</table>

Table 5: Re-computation of H₂SO₄ treatment of brine at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>See Table 2A, use average brine chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent of H₂SO₄ per kg brine at 25°C</td>
<td>1.852e⁻⁰ equivalents</td>
</tr>
<tr>
<td>Volume of 36N H₂SO₄ per kg brine at 25°C</td>
<td>5.165e⁻⁶ liter</td>
</tr>
<tr>
<td>Computed dosing rate at 0.18 kg/s brine flow</td>
<td>0.00333 li/hr or 3.33 ml/hr</td>
</tr>
<tr>
<td>Computed dosing rate at 0.22 kg/s brine flow</td>
<td>0.00409 li/hr or 4.09 ml/hr</td>
</tr>
</tbody>
</table>

Table 6: Log K of HSO₄⁻ at 25 and 160°C

| Log K of HSO₄⁻ at 25°C | -1.96 |
| Log K of HSO₄⁻ at 160°C | -3.84 |

**Given:** From SOLVEQ output file, it needed 0.1077e⁻¹ / 2 H₂SO₄ equivalent (as HCl) per kg brine to adjust line pH to 5.50 at line condition; Flow rate of brine = 0.18 kg/s

**Solution:**
Volume of 36 N H₂SO₄/kg sample = 5.385e⁻³ equivalent / 36 N = 1.496e⁻⁴ liter/kg-brine At given flow-rate, compute dosing rate:

Dosing rate = 0.18 kg-brine / sec x 1.49e⁻⁴ liter/kg-brine x 3600 sec/hr = 0.097 li/hr

4. **RESULTS AND DISCUSSION**

The computed data from NaOH and H₂SO₄ methods are presented in Table 1 and 2, respectively. Both tables show the critical differences between the computed and the actual results.

4.1 About NaOH treatment

Table 1 shows the difference in dosing rate of the 50% (w/v) NaOH between computed and field data from two samples. Although there are significant differences of 36 to 52% between the computed and field dosing rates, the difference between resultant chemistry (except for Eh) is generally small. Example, the difference in increase in Na (from NaOH injection) between the computed and analysis varies by 1.0 to 3.0 mg/kg only, which for practical purposes, is essentially the same. The only major analytical difference is the Eh or the redox potential. Theoretically, Eh and pH are interdependent: as Eh decreases (or increase its negative value) pH increases. Since the analytical value remained unchanged, there must a possible error in its measurements, and consequently, its pH. In this case, the computed data are more reliable than the analytical values.

The disparity in Eh and pH may indicate that there must be something wrong with the on-line pH meter, hence NaOH dosage was suspect. It is also possible that condensate flow is actually larger and varies significantly than previously measured. In this case, it was recommended that a re-evaluation of the fluctuation in the condensate flow be established and check the on-line pH/Eh meter.

4.2 About H₂SO₄ treatment

The results of Table 2 were compared from the actual pH-modification system in Malitbog (MB) at Leyte (Alcober, 2003) as presented in Table 4.

The difference between the computed and field dosing rates is calculated to be more than 10x or one log unit. The disparity is caused by the difference in temperature when the pH is computed. This hypothesis is tested by re-computing the dosing rate given the sample’s average chemistry both at 25°C, and employing similar SOLVEQ methodology. If the
computed dosing rate coincided or near the measured rate, then it is likely that the higher temperature (at 160°C) caused the difference. Table 5 shows the results of this recomputation.

The computed results, 3.33 to 4.08 ml/hr assuming dosing at 25°C, is now closer to the laboratory titration data. This is understandable since the simulation does not include the actual injection temperature of 160°C. Based from this recomputation, temperature difference affects the acid treatment of the brine.

Another factor is in one of our assumptions: the complete dissociation of H₂SO₄ as SO₄²⁻ and H⁺. At 160°C, its second dissociation as HSO₄⁻, is weaker by 1.88 log unit than at 25°C. Table 6 shows the log K of HSO₄⁻ at 25 and 160°C based from Sillen and Martell (1964). Since H₂SO₄ acid (as HSO₄⁻) had actually gone weaker at line temperature, brine needs higher dosage to attain pH 5.50. At 25°C where its acidity is stronger, then lesser dosage is needed.

5. CONCLUSION

Using SOLVEQ, two sets of data from Leyte were used to demonstrate it’s special capability to compute the homogeneous chemistry at various pH’s. The pH can be changed interactively when running SOLVEQ. If pH is changed, the total molar amount of hydrogen ion is re-computed, and the charge balance is re-adjusted to compensate for the given pH. It is the adjustment of the charge balance, using a pre-selected ion that makes this program useful in computing dosage of a particular base (such as NaOH) or acid (such as HCl or H₂SO₄) into the fluids to attain a desired pH.

For base addition, Na ion (assuming addition as NaOH = Na⁺ + OH⁻) is added as the charge balancer while for acid addition, Cl⁻ is added as the balancer (assuming addition as HCl = H⁺ + Cl⁻). For acid like H₂SO₄, one can also use Cl ion as the balancer, provided its adjusted mole is divided by two. This is invoking the concept neutralization-equivalent-weight or simply the equivalent of H₂SO₄ to HCl.

Based from the results, the method can evaluate not only the needed dosage of acid or base treatment, but also the intricacy of the chemical equilibria involved in the procedure. Although measurements of pH’s at laboratory condition remain the only method of choice in evaluating required dosages, evaluation through simulation strengthen our understanding of the real conditions that affect the treatment. For NaOH, fluxes in condensate flow and the role of Eh are essential parameters to monitor effectiveness of the treatment, while for H₂SO₄, the line-temperature dictates the strength of acidity, hence the amount of dosage.

REFERENCES


