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Application of SOLVEQ in Evaluating the Dosing-rate of NaOH and H_2SO_4 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 (H_2SO_4) 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 H_2SO_4) 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 H_2SO_4, 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 H_2SO_4 to HCl: there are two equivalents per mole of H_2SO_4 per mole 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 H_2SO_4, 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 H_2SO_4) 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 (assumimg addition as

HCl = H^+ + Cl^-). For acid like H_2SO_4, 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 H_2SO_4 to HCl: there are two equivalents per mole of H_2SO_4 per mole of HCl. Direct use of SO_4= (from H_2SO_4) 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^- + H_2O = $9H^+$ + $SO_4^=$ + $2e^-$ 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 H_2SO_4, usually at ambient condition, does not significantly change the initial temperatures and volume of the fluids
- Complete dissociation of NaOH and H_2SO_4, (such as NaOH = Na^+ + OH^- and H_2SO_4 = $SO_4^=$ + $2H^+$) 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 H_2SO_4 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^{o}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 condensateTo 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-condensateAt given flow-rate , compute dosing rate:

Dosing rate = 290 kg-condensate / sec x 3.57e^{-5} liter/kg-condensate x 3600 sec/hr =37 li/hr

3.2 For H_2SO_4 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 treament, initial data has to be polished before any pH adjustment. For Leyte sample, the brine temperature is set at 160^{o}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 H_2SO_4 (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 H_2SO_4 needed per kg condensate to attain pH 5.50

Table 1: Condensate chemistry and comparison between computed and field dosing rates

TABLE 1: RESULTS AND COMPARISON OF COMPUTATION OF PH AND CHEMISTRY ADJUSTMENT OF UM BASIN CONDENSATE USING COMPUTER GEOCHEMICAL PROGRAMS															
CHEMISTRY IN MG/KG EXCEPT PH AND Eh															
SAMPLE 1: UM CONDENSATE COLLECTED AT BASIN DTD 2003-8-17															
FLOW RATE:	*290 KG/S*														
INITIAL CHEMISTRY OF UM CONDENSATE FROM BASIN															
DATE	PH/25C	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
8/17/03	6.98	0.00	2.23	0.61	0.34	0.02	0.03	2.02	8.73	45.6	8.3	14.1	0.39	0.49	47.2
COMPUTED CHEMISTRY AFTER DOSING 12.5 N (50%W/V) NAOH TO ATTAIN PH 8.0 AT LINE CONDITION															
DATE	PH/45C	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
8/17/03	8.00	38.00	12.73	0.61	0.34	0.02	0.03	2.02	11.23	45.6	8.3	14.1	0.39	0.49	47.2
ANALYZED CHEMISTRY AFTER DOSING 12.5 N (50%W/V) NAOH TO ATTAIN PH 8.0 AT LINE CONDITION															
DATE	PH/25C	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
8/17/03	8.37	28.00	14.7	0.47	0.32	0.04	0.47	1.02	8.78	72.1	6.99	11.9	0.33	0.2	53.1
SAMPLE 2: UM CONDENSATE COLLECTED AT BASIN DTD 2003-9-15															
FLOW RATE:	*290 KG/S*														
INITIAL CHEMISTRY OF UM CONDENSATE FROM BASIN BEFORE DOSING															
DATE	PH/25C	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
9/15/03	6.85	0.00	1.72	0.15	0.28	0.03	0.03	1.09	8.9	38.2	8.3	14.3	0.69	1.99	44.7
COMPUTED CHEMISTRY AFTER DOSING 12.5 N (50%W/V) NAOH TO ATTAIN PH 8.0 AT LINE CONDITION															
DATE	PH/45C	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
9/15/03	8.00	42.43	13.4	0.15	0.28	0.03	0.03	1.09	15.15	38.2	8.3	14.3	0.69	1.99	44.7
ANALYZED CHEMISTRY AFTER DOSING 12.5 N (50%W/V) NAOH TO ATTAIN PH 8.0 AT LINE CONDITION															
DATE	PH	DOSAGE LI/HR	NA	K	CA	MG	FE	CL	SO4	HCO3	B	NH3	SIO2	H2S	TCO2
9/15/03	8.18	28.00	16.8	0.47	0.28	0.03	0.03	1.01	7.18	70.9	9.66	14.8	0.68	2.42	52.2

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

TABLE 2A: REPRESENTATIVE CHEMISTRY (AS AVERAGE) OF MB BRINE FOR PH ADJUSTMENT TO 5.50 AT LINE CONDITION USING 36N H2SO4

Source	Treatment	Flow, kg/s	Temp, °C	Date	pH	Na	K	Ca	Mg	Fe	Cl	SO_4	HCO_3	B	NH_3	SiO_2	H_2S	TCO_2
MB Brine	H_2SO_4, 36N (18M)	0.18-0.22 (Pilot Test)	160	2003-06-19	6.97	5564	1157	238	0.21	0.39	10691	20.50	7.96	209	3.11	773	5.02	23.90
				2003-07-11	7.01	5553	1089	264	0.60	0.53	10574	27.00	6.42	213	2.68	713	5.36	18.40
				2003-08-11	7.04	5949	1428	259	0.31	0.35	10660	22.80	6.72	206	1.32	776	4.91	13.20
				AVERAGE	**7.01**	**5689**	**1225**	**254**	**0.37**	**0.42**	**10642**	**23.43**	**7.03**	**209**	**2.37**	**754**	**5.10**	**18.50**

TABLE 2B: COMPUTATION OF DOSING RATE OF 36N H2SO4 TO ADJUST PH 5.5 AT LINE CONDITION FROM SOLVEQ/PHREEQC PROGRAMS USING AVERAGE BRINE CHEMISTRY

GIVEN THE AVERAGE BRINE CHEMISTRY IN TABLE 1 AND BRINE-LINE PH OF 6.44 AT 160C

1) COMPUTED MOLES OF CL (AS HCL) TO ADJUST LINE PH TO 5.50 PER KG BRINE = **0.00177 MOLES**
2) VOLUME OF 36N H2SO4 TO ATTAIN PH 5.50 IN LITERS= (0.00177 / 2) / 36 N = **0.000150 LITERS**
3) DOSING RATE OF 36N H2SO4 (LITERS/HR) AT BRINE FLOW OF 0.18 KG/S = **0.097 LITERS/HR**
3) DOSING RATE OF 36N H2SO4 (LITERS/HR) AT BRINE FLOW OF 0.22 KG/S = **0.118 LITERS /HR**

BASED FROM THESE COMPUTATION, TO ADJUST THE BRINE- LINE PH FROM 6.44 TO 5.50:

THE DOSING RATE OF 36N H2SO4 RANGES FROM **97 ML/HR TO 118 ML/HR** OR AN ***AVERAGE DOSING*** OF **108 ML/HR**

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

Sample	Field dosing rate li/ hr (Villa et al., 2003)	Computed dosing rate li/hr	Percent difference (computed – field)/field x 100
8-17-2003	28	38	36
9-15-2003	28	42	52
Average		40±3	

Table 4: Comparative analysis between computed and field data in H_2SO_4 treatment

Comparison	Brine flow kg/s	Injection temperature ^oC	pH before-H_2SO_4 injection	pH after H_2SO_4 injection	Dosing rate (ml/hr)
MB lab pH based from lab titration	0.10	25	6.90 measured at 25^{o}C	5.60 measured at 25^{o}C	4.80
MB pH-MOD pilot test trials (actual)	0.18 to 0.22	160	6.97 to 7.04 measured at 25^{o}C	5.20 to 5.60 measured at 25^{o}C	8.93
This study	0.18 to 0.22	160	6.44 computed at 160^{o}C	5.50 computed at 160^{o}C	97 to 118

Table 5: Re-computation of H_2SO_4 treatment of brine at 25^{o}C

Sample	See Table 2A, use average brine chemistry
Equivalent of H_2SO_4 per kg brine at 25^{o}C	1.852e^{-4} equivalents
Volume of 36N H_2SO_4 per kg brine at 25^{o}C	5.165e^{-6} liter
Computed dosing rate at 0.18 kg/s brine flow	0.00333 li/hr or 3.33 ml/hr
Computed dosing rate at 0.22 kg/s brine flow	0.00409 li/hr or 4.09 ml/hr

Table 6: Log K of HSO_4^- at 25 and 160^{o}C

Log K of HSO_4- at 25^{o}C	-1.96
Log K of HSO_4- at 160^{o}C	-3.84

Given: From SOLVEQ output file, it needed 0.1077e^{-1} / 2 H_2SO_4 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 H_2SO_4 /kg sample = 5.385e^{-3} equivalent / 36 N = 1.496e^{-4} liter/kg-brineAt 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 H_2SO_4 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 H_2SO_4 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^{o}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 re-computation**.**

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 re-computation, temperature difference affects the acid treatment of the brine.

Another factor is in one of our assumptions: the complete dissociation of H_2SO_4 as $SO_4^{=}$ and H^+. At 160°C, its second dissociation as HSO_4^-, is weaker by 1.88 log unit than at 25°C. Table 6 shows the log K of HSO_4^- at 25 and 160°C based from Sillen and Martell (1964). Since H_2SO_4 acid (as HSO_4^-) 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 H_2SO_4) 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 (assumimg addition as HCl = $H^+ + Cl^-$). For acid like H_2SO_4, 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 H_2SO_4 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 H_2SO_4, the line-temperature dictates the strength of acidity, hence the amount of dosage.

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