PROCEEDINGS, Twenty-Fifth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 24-26, 2000
SGP-TR-165

pH CALCULATION THROUGH THE USE OF ALKALINITY IN GEOCHEMICAL MODELING OF HYDROTHERMAL SYSTEMS

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ABSTRACT

An algorithm based on the alkalinity conservation is presented in order to calculate the natural water pH with incorporating the effects of heating, boiling, dilution and mixing of different types of fluids. Alkalinity with respect to the equivalence point of H_2CO_3 is defined as

$$\boldsymbol{alk} = \left[OH^-\right] + \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[H_3SiO_4^-\right] + \left[HS^-\right] - \left[H^+\right] - \left[NH_4^+\right]$$

Dissolution of gases (CO_2, H_2S, NH_3) does not alter the alkalinity. Therefore it permits us to recalculate the deep reservoir liquid pH including the effect of separated vapor.

The back calculation procedure using conservation of energy and mass is implemented to compute the geothermal reservoir fluid physical-chemical parameters from the parameters measured at the surface in the geothermal fluid (vapor and liquid). The scheme is simplified with considering a steady state homogeneous two-phase flow and neglecting fractional pressure drop in comparison of gravitational and acceleration pressure drops in the well. The application of this method is demonstrated in calculating the pH together with other parameters of deep reservoir fluid in case of well M-19A at Cerro Prieto.

INTRODUCTION

Chemical modeling of the equilibrium states of multi-component fluids is an integral part of geochemistry to interpret water chemistry in nature as well as in the laboratory, and to trace the reaction mechanisms and processes for water-bodies evolution (Nordstrom et al., 1979; Plummer et al., 1988; Bethke, 1992). Some of the existing software like SOLMNEQ (Kharaka and Barnes, 1973), MINEQ (Westall et al., 1976), WATEQX (van Gaans, 1989), EQ3NR (Wolery, 1983), deal chemical speciation using input parameters as dissolved species concentration, temperature and pH; while others WATEQ (Truesdell and Jones, 1974), WATCH (Arnorsson, 1982), CHILLER (Reed, 1982), EQQYAC (Barragan and Nieva, 1989) may recalculate the pH using charge balance or H^+ mass-balance. NETPATH (Plummer, 1991) and “The Geochemsit’s Workbench” (Bethke, 1992, 1994) can also take into account mixing, dilution and evaporation processes. Norstrom et al. (1979) reviewed over 30 computerized chemical modeling softwares. Every modeling program had been developed for specific purposes; therefore it had its own capacities and limitations. Fundamental limitations were the form of alkalinity input and non-carbonic alkalinity correction, and pH calculation. These limitations are still not resolved completely in the improved versions of these commercial computer-softwares.

Chemical modeling of a geothermal system is basically evaluation of reservoir fluid-mineral equilibrium-state from the surface natural manifestation and well discharge chemistry. We measure the dissolved species including pH in separated water at weirbox and the non-condensable gaseous species in vapor phase at separator. The chemical composition of reservoir fluid is reconstructed as a mixture of separated water and vapor. The reservoir temperature is unknown but higher than the separated water pH-measuring and chemical composition analyzing temperature (generally 25ºC). Thus it requires first the calculation of temperature, pH and chemical composition of both vapor and liquid phases in the reservoir in order to deal chemical speciation (modeling) of geothermal systems. The concentration calculation of the total discharge dissolved species (like Na^+, K^+, Cl^-,...) are calculated using mass and enthalpy balance equations (Henley et al., 1984). The reservoir temperature and vapor-fraction are estimated through chemical and gas geothermometers and the distribution of gaseous species (Giggenbach, 1980). Verma (1997) presented a two-phase flow approach to calculate the concentration of the dissolved species in the liquid phase in the reservoir except pH. The reservoir fluid pH is a fundamental parameter; unfortunately, the methods used so far for its calculation are still questionable.

Reed and Spycher (1984) pointed out that the previous methods for calculating pH at high temperature from the analyses at low temperature, without the use of equilibrium among minerals (Truesdell and Jones, 1974; Merino, 1979; Arnosson et al., 1982) were based on the estimate of "total ionizable hydrogen"; but they referred an ill-defined quantity to the abundance of hydrogen ion. Reed and Spycher (1984) used the total moles H^+ as conservative quantity in order to calculate pH with temperature change. They adjusted the concentration of Cl^- in their data sets though charge balance. This requires to justify that the chloride analyses were only incorrect. Bethke (1992) applied the measured pH value or fixed pH by setting the fluid's CO_2 fugacity. Henley et al (1984) had demonstrated that the various alternative procedures: *based on the first dissociation constant of carbonic acid, solubility of calcium carbonate and charge balance equation* provided inconsistent values for the reservoir pH.

Alkalinity is a conservative quantity in chemical reactions and is independent of change in pressure and temperature (Stumm and Morgan, 1981). For example, if two waters are mixed together, their alkalinity will be an arithmetic sum of the individual water alkalinity, but it may not necessarily be true for pH. Similarly, if we heat or cool a solution, the change in the dissociation constant values for the week acid-base may produce or consume H^+ or OH^- ions. Thus the pH of the solution will change generally with temperature, but not the alkalinity. In other words the conservation of proton in aqueous solution modeling used in the computer softwares is not a valid hypothesis. In this article a systematic approach to calculate pH using alkalinity during various processes like heating, boiling, dilution and mixing of two or more fluids is presented. The methodology will be discussed for the pH calculation of geothermal reservoir fluid using data from CP-M-19A well at Cerro Prieto as an example.

LIMITATIONS IN RESERVOIR TEMPERATURE AND VAPOR FRACTION CALCULATION

Verma (2000) elucidated that the correction of total discharge silica content from a well for the vapor fraction in the geothermal reservoir is a fundamental limitation in applying the silica (quartz) solubility regression equation in order to estimate the reservoir temperature. For knowing the vapor fraction there is indirectly need of knowing the reservoir temperature. Thus the silica solubility equation can not be used as a chemical geothermometer for the geothermal reservoir temperature estimation.

Similarly there is no valid fundamental concept beyond the development of above cation-exchange geothermometers which are commonly used in dealing the chemistry of geothermal fluids. For example, a cation-exchange reaction between Na^+ and K^+ can be written in general as following

$$xNa^+ + Na_{1-x}K_xX = xK^+ + Na_xK_{1-x}X$$

Where the capital X represents an anion. The activity of solid phases is taken as unity in developing the geothermometers. The minerals like $Na_xK_{1-x}X$ are not pure phases, so their activity cannot be considered as unity. To avoid the situation it is considered the end members of the mixed minerals. It means that we are indirectly considering the solubility of NaX and KX. Then the Na/K ratio will not only depend on temperature, but also on the type and concentration of anion X^-. Additionally, to reach the solubility equilibrium, the concentration of Na^+ and K^+ will be very high as can be observed in seas and oceans.

The mathematics presented for the Fischer-Tropsch methane-breakdown reaction (Giggenbach (1980) and D´Amore and Truesdell (1984) and others) in order to estimate the geothermal reservoir vapor fraction is incorrect. The following is the reaction of Fischer-Tropsch

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

In order to know the state of equilibrium of this reaction in either vapor or liquid phase in the geothermal reservoir, it requires knowing the vapor fraction as well as temperature in the reservoir (which are unknown) and the value of the break-down equilibrium constant at the condition of temperature. Then one can use the distribution coefficient for CH_4 and H_2 to partition the total discharge concentration in both the phases in the reservoir. But it is also needed to know pH for CO_2 distribution, because CO_2 in solution presents in the form of carbonic species. The distribution of carbonic species depends on pH, too. Therefore the two-phase flow approach of Verma (1997) will be extended here in order to calculate the deep reservoir fluid pH.

TWO PHASE FLOW APPORACH TO CALCULATE RESERVOIR PARAMTERS

As the geothermal fluid flows up in a well, it flashes within wells and in the separator. The separated water is flashed further in the weirbox at atmospheric pressure or passed through a cooling coil attached to the separator to collect the sample. Samples of water from the weirbox and steam from the separator are, generally, collected to analyze for geochemical constituents. Verma (1997) presented the calculation procedure for reservoir physicochemical parameters except for pH with considering total energy as conservative entity, and gravitational and accelerational pressure drop. It was assumed that the flow in the well and separator was so fast which didn't allow the precipitation of mineral during flow. Steady state flow and no heat loss by conduction in the well are assumed in this approach, too.

At the well separator

The separated liquid is flashed in the weirbox at atmospheric pressure and the water sample is collected after the weirbox. Some fraction of vapor with non-condensable gases is lost in the atmosphere. The chemical composition of separated water can be calculated back from the analyzed composition of the water sample after weirbox using the following procedure.

The fraction of vapor lost at the weirbox will be

$$y_{atm} = \frac{H_{l,sep} - H_{l,atm}}{H_{v,atm} - H_{l,atm}}$$

The chemical composition of the dissolved species (Na^+, K^+, …) in the separated water could be expressed as

$$C_{l,sep} = C_{l,atm} \cdot \left(1 - y_{atm}\right)$$

The non-condensable species such as CO_2, H_2S, CH_4, etc are only measured in vapor phase. In order to calculate the concentration of these species in liquid phase we use the experimental distribution coefficient for the species at the separation pressure

$$B = \frac{C_v}{C_l}$$

The liquid flow rate at the separated will be

$$Q_{l,sep} = \frac{Q_{l,atm}}{1 - y_{l,atm}}$$

The calculation of pH is not so simple like for the dissolved chemical species, because the dissociation constants of water and the acid-base change with changing pressure and/or temperature. Similarly the dissolution or removal of gases like CO_2 also change the pH of the solution.

Therefore, we work on the approach based on the knowledge of alkalinity. Alkalinity is a conservative entity during chemical reactions in a solution and in mixing of two solutions (Stumm and Morgan, 1981). The alkalinity with respect to the equivalence point of $H_2CO_3^*$ can be written as

$$\begin{aligned} \boldsymbol{alk} &= \left[OH^-\right] + \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[H_3SiO_4^-\right] \\ &\quad + \left[HS^-\right] - \left[H^+\right] - \left[NH_4^+\right] \\ &= \left[OH^-\right] + C_{Tcar}\left(\alpha_1 + 2\alpha_2\right) + C_{TB}\left(\alpha_{1B}\right) + C_{TSi}\left(\alpha_{1Si}\right) \\ &\quad + C_{TS}\left(\alpha_{1S}\right) - \left[H^+\right] - C_{TN}\left(\alpha_{N1}\right) \end{aligned}$$

The ionization fraction (α) may be written as

$$\alpha_{\boldsymbol{i}} = \frac{\left(\dfrac{\prod_{j=0}^{i} K_j}{\left[H^+\right]^i}\right)}{\sum_{i=0}^{N}\left(\dfrac{\prod_{j=0}^{i} K_j}{\left[H^+\right]^i}\right)}$$

Where K_0 is equal to 1 and C_T is the total dissolved concentration. The subscripts Car, B, Si, S, and N represent the total dissolved concentration carbonic acid, boric acid, silicic acid, hydrogen sulfide and ammonia, respectively. The alkalinity is generally included in the analytical data set, but sometimes it is implicitly expressed as concentration of HCO_3^-. With knowing pH, alk and total dissolved concentrations for the species included in the expression of alkalinity, one can calculate chemical speciation.

The alkalinity is independent of pressure and temperature. According to the definition the alkalinity with respect to the equivalence point of $H_2CO_3^*$ should not change with dissolution or removal of CO_2 ($H_2CO_3^*$). It is interesting to note that the alkalinity defined in the above expression will also not change with dissolution or removal of $B(OH)_3$, H_4SiO_4, H_2S, NH_3. This fundamental aspect has not been paid any attention in discussing the chemical thermodynamics of aqueous solution. However, it is helpful in dealing pH calculation of geothermal fluids. Therefore, the alkalinity of separated water in the separator will be equal to

$$\boldsymbol{alk}_{l,sep} = \boldsymbol{alk}_{l,atm} \cdot \left(1 - y_{atm}\right)$$

The non-condensable gases like CO_2, H_2S, NH_3, CH_4, etc. are lost from water samples during the sampling to analysis time. The concentration of these non-condensable gases is measured with much care the vapor phase. Therefore, the concentration of these gases in liquid phase is calculated from their distribution constants. Here a decision is needed to make on the total concentration of carbonic species, because the concentration of dissolved CO_2 can be calculated from the analysis of both liquid and vapor phases. This will be explained in the next section.

At the wellhead

Now the concentrations of both the phases at the wellhead are calculated using mass- and energy-balance equations.

$$m_{l,hd} + m_{v,hd} = m_{l,sp} + m_{v,sp}$$

$$\begin{aligned} &\tfrac{1}{2} m_{l,hd} u_{l,hd}^2 + \tfrac{1}{2} m_{v,hd} u_{v,hd}^2 + m_{l,hd} H_{l,hd} + m_{v,hd} H_{v,hd} = \\ &\qquad \tfrac{1}{2} m_{l,sp} u_{l,sp}^2 + \tfrac{1}{2} m_{v,sp} u_{v,sp}^2 + m_{l,sp} H_{l,sp} + m_{v,sp} H_{v,sp} \end{aligned}$$

The procedure used for the concentration, alkalinity and pH calculation is same as mentioned above. It also requires keeping constant the total concentration of gaseous species between liquid and vapor phase.

Within the well

As the liquid (geothermal fluid) flows up the well, pressure drops due to gravitational, frictional, and accelerational effects. The gravitational pressure drop is dominant, and friction accounts for only a few percent of the total pressure drop in the well. The frictional pressure drop will be neglected in order to simplify the calculation. The back calculation procedure will be applied.

Table 1: Physical-chemical parameters of geothermal fluid at various positions in the well M-19A at Cerro Prieto. The values are reported up to 3 decimal point just sake of comparison. The actual accuracy depends on the analytical error.

Parameter	Weirbox		Separator	Corrected data	Wellhead	Reservoir
	(25ºC)*	(100ºC)**	***	at Separator		
Pressure (Bar)	1	1	7.55	7.55	35.00	46.90
Temperature (ºC)	25	100.00	168.06	168.06	242.30	259.72
Q_{liq} (ton/hr)	97.8	112.33	112.33	112.33	135.31	139.90
Q_{vap} (ton/hr)			63.20	63.20	40.22	35.63
Vapor Fraction				0.36	0.23	0.20
			Liquid Phase(mmol/kg water)			
Na^+	320.577	279.106	279.106	279.106	231.702	224.108
K^+	42.457	36.965	36.965	36.965	30.685	29.681
Ca^{2+}	10.928	9.514	9.514	9.514	7.898	7.640
Mg^{2+}	0.016	0.014	0.014	0.014	0.012	0.012
Li^+	28.814	25.087	25.087	25.087	20.826	20.143
NH_{3T}				1.002	1.771	1.987
NH_4^+				0.094	0.044	3.55E-2
NH_3				0.908	1.726	1.951
H_2S_T				5.38E-3	0.945	1.414
H_2S				1.83E-3	0.788	1.258
HS^-				3.55E-3	0.157	0.157
B_T	1.332	1.160	1.160	1.160	0.963	0.931
$B(OH)_3$	1.318	1.146	1.141	1.139	0.958	0.928
$B(OH)_4^-$	0.014	.014	0.018	0.020	0.004	0.003
SiO_{2T}	13.448	11.708	11.708	11.708	9.720	9.401
H_4SiO_4	13.410	11.607	11.469	11.443	9.644	9.345
$H_3SiO_4^-$	0.038	0.101	0.239	0.265	0.047	0.056
$C_{T(carbonic)}$	0.958	0.834	0.058	0.948	3.646	5.916
H_2CO_3*	0.105	0.161	0.302	0.321	3.183	5.456
HCO_3^-	0.852	0.672	0.531	0.638	0.462	0.460
CO_3^{2-}	7.42E-4	5.11E-4	2.39E-4	1.150E-4	1.950E-5	1.10E-5
As	0.067	0.058	0.058	0.058	0.048	0.047
Cl^-	389.248	338.892	338.892	338.892	281.334	272.114
SO_4^{2-}	0.187	0.163	0.163	0.163	0.135	0.131
pH	7.27	7.041	7.174	7.221	6.832	6.865
Alkalinity	0.906	0.789	0.789	0.789	0.655	0.655
CO_2			0.321α			
H_2S			1.83E-3			
CH_4			4.133E-5			
H_2			2.272E-5			
N_2			2.260E-6			
NH_3			0.908			
			Vapor phase (mmol/mol steam)			
CO_2			4.845ϕ	4.845	7.438	8.228
H_2S			0.466	0.466	0.675	0.727
CH_4			0.136	0.136	0.366	0.411
H_2			0.235	0.235	0.264	0.296
N_2			0.169	0.169	0.047	0.053
NH_3			0.030	0.030	0.375	0.158

* Analytical data for liquid phase

ϕ Analytical data for vapor phase

α Concentration obtained through gas distribution (in mmol gas/kg water)

** Just before flashing in the weirbox at the atmospheric conditions

*** Just after vapor separation, the liquid phase concentration were calculated from the separated water.

The void fraction is the fraction of cross section area occupied by vapor phase and is defined as

$$\alpha_{hd} = \frac{V_{v,hd} m_{v,hd}}{V_{v,hd} m_{v,hd} + V_{l,hd} m_{l,hd}}$$

The mass flow rates for vapor and liquid phase at the well head can be expressed as

$$m_{v,hd} = \frac{u_{v,hd} \alpha_{hd} A_{hd}}{V_{v,hd}}$$

$$m_{l,hd} = \frac{u_{l,hd} (1 - \alpha_{hd}) A_{hd}}{V_{l,hd}}$$

The parameters $m_{l,hd}$, $m_{v,hd}$, α_{hd}, $u_{l,hd}$ and $u_{v,hd}$ are calculated using the above equations and mass- and energy-balance equations. The procedure can be repeated dividing the well height in small segments, until the liquid saturation conditions are reached. After this saturation point, the pressure of the liquid increases and one has to use compress-water steam table data. The equation for concentration calculations is the same as discussed earlier with slight modification. The steam fraction must be calculated as

$$y_{sp} = \frac{m_{v,sp}}{m_{v,sp} + m_{l,sp}}$$

With knowing the fraction of vapor and specific volumes of vapor and liquid in the reservoir one can calculate the specific volume of the fluid (i.e. combined specific volume of vapor and liquid) as

$$V_R = y_R V_{v,R} + (1 - y_R) V_{l,R}$$

Here it is supposed that the vapor and liquid do not have preferential flow to the well in the reservoir. Thus the flow rates are proportional to the quantity of vapor and liquid in the reservoir. Similarly, all the cavity space in the reservoir is either filled with liquid or vapor. The homogeneous flow method is simple and provides reasonably good precision (Griffith, 1985).

In these calculation the fluid parameters are at the bottom of the well in the well flowing conditions. Thus, to obtain the reservoir fluid parameters it requires to consider the fluid-flow through the reservoir rock around the well. The work is still under developing.

RESERVOIR PARAMETER CALCULATION FOT WELL CP-M-A9A

A computer program in Visual Basic has been written to perform the calculation of reservoir parameters including pH and alkalinity. The algorithm of the program and important subroutines of the program have been described by Verma (1997). Similarly, Verma (1997) has also presented a comparative study of different methods for the reservoir parameter calculation. Therefore, the emphasis of this work is on the calculation of pH through the conservation of alkalinity.

A data set for geochemical analysis of the geothermal well M-19A in Cerro Prieto is taken from Henley et al. (1984) and Verma (1997). The reservoir enthalpy, calculated from the flow rate of water and vapor at the separator, is somewhat higher than the reported one. Here the calculated enthalpy is used. The values of equilibrium constants for all the reactions considered during the fluid flow in the well are taken from the compiled data of Henley et al. (1984).

Table 1 shows the analytical data as well as the calculated values of all the geothermal fluid parameters at the weirbox, well separator, wellhead and reservoir for the well M-19A at Cerro Prieto. The value of alkalinity of the separated water is calculated from the analytical data at 25ºC. The temperature is changed to 100ºC in order to know the chemical composition of separated water in the weirbox just after the flashing to atmospheric conditions. Then the fluid is diluted with the lost vapor in the atmosphere. The alkalinity and total dissolved concentration of all the species were corrected for the atmospheric vapor (data shown in Table 1). Changing of temperature changes to the equilibrium constants of the reactions, therefore the pH and concentration of species were recalculated. Here the concentration of volatile species was not corrected for the loss of gas with steam during flashing in weirbox. Now the water is heated up to the separator temperature. The calculated values of all the species is given in the Table 1.

The gas analysis of condensed vapor at separator is converted in mmol/mol steam. Using gas distribution coefficient (Giggenbach, 1980) the concentration of the gaseous species in liquid phase is calculated. The concentration of dissolved CO_2 is calculated from both liquid and vapor analysis. It can be observed in the Table 1 that the concentration of dissolved CO_2 calculated from vapor phase is higher than that calculated from liquid phase. It is due to that the separated water concentrations were not corrected for the gaseous species lost in the weirbox. Similarly, the concentrations of gaseous species were not measured in the separated water. Therefore, the concentrations in liquid phase at the separator were corrected for the concentration in vapor phase. These data were used for further calculations.

Now, the gaseous species were redistributed between the liquid and vapor phase. The concentration of all the species in both the phases at the wellhead and in the reservoir are given in the Table 1. The reservoir concentrations are at the bottom of the well. Still, we are working to consider the fluid flow within the reservoir.

CONCLUSIONS

The two-phase flow approach is based on the simplified assumptions of homogenous steady state flow, conservation of energy and mass, and pressure drop due to gravitation and acceleration. The alkalinity is a fundamental parameter in order to calculate the pH of the reservoir fluid. The chemical geothermometers are still very empirical.

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