GeoSys.Chem: Estimate of reservoir fluid characteristics as first step in geochemical modeling of geothermal systems

Mahendra P. Verma*

Geotermia, Instituto de Investigaciones Eléctricas, Reforma 113, Col. Palmira, Cuernavaca, Mor., C.P. 62490, México

A R T I C L E   I N F O

Article history:
Received 28 February 2012
Received in revised form
26 April 2012
Accepted 1 June 2012
Available online 12 June 2012

Keywords:
GeoSys.Chem
GeoChem
VB.NET
Geochemical modeling
Los Azufres

A B S T R A C T

A computer code GeoSys.Chem for the calculation of deep geothermal reservoir fluid characteristics from the measured physical–chemical parameters of separated water and condensed vapor samples obtained from drilled wells is presented. It was written as a dynamic link library (DLL) in Visual Basic in Visual Studio 2010 (VB.NET). Using this library a demonstration program GeoChem was developed in VB.NET, which accepts the input data file in the XML format.

A stepwise calculation of deep reservoir fluid characteristics of 11 production wells of Los Azufres geothermal system is performed. The calculated concentration of CO₂ (e.g. 1270 mmole/kg in the well AZ-09) in the vapor, discharged into the atmosphere at the weir box, from the water sample indicates some problem in the analysis of carbonic species concentrations. In the absence of good quality analysis of carbonic species it is suggested to consider the CO₂ in the vapor sample at the separator and the total dissolved carbonic species concentration in the water sample (i.e., without considering the liberation of CO₂ in the atmospheric vapor at the weir box) for the geothermal reservoir fluid composition calculations. Similarly, it presents various diagrams developed in Excel for the thermodynamic evolution of Los Azufres geothermal reservoir.

1. Introduction

Geochemical modeling of geothermal system contemplates the determination of its thermodynamic equilibrium state to enlighten the physical and chemical processes responsible for its origin and evolution (Chatterjee, 1991; Verma, 2002). According to the second law of thermodynamics, the total entropy of the system and its surrounding is maximum in the equilibrium state. For a closed system, this state is also characterized by a minimum in its Gibbs free energy, if temperature and pressure are the independent thermodynamic variables (Garrels and Christ, 1965; Smith and van Ness, 1975; Heidemann, 1978). It is further simplified in the form of relations between the equilibrium constants of chemical reactions and the activities (or molar concentrations in dilute solution) of chemical species, which exist in the system at the given temperature and pressure (Moor, 1983; Chatterjee, 1991).

The computer programs for chemical modeling of the equilibrium state of multi-component fluids are useful tools for understanding water chemistry in nature as well as in the laboratory, and tracing the reaction mechanisms and processes for water-bodies evolution (Nordstrom et al., 1979; Plummer et al., 1988; Bethke, 1992; Verma, 2002). SOLMNEQ (Kharaka and Barnes, 1973), MINEQ (Westall et al., 1976), WATEQX (van Gaans, 1989) and EQ3NR (Wolery, 1983) deal chemical speciation using input parameters as dissolved species concentration, temperature and pH; while WATEQ (Truesdell and Jones, 1974), WATCH (Arnórsson et al., 1982), CHILLER (Reed, 1982) and EQQYAC (Barragan and Nieva, 1989) may recalculate the pH using charge balance or H⁺ mass-balance. NETPATH (Plummer et al., 1991) and “The Geochemist’s Workbench” (Bethke, 1992, 1994) can also take into account mixing, dilution and evaporation processes. Nordstrom et al. (1979) reviewed over 30 chemical modeling programs and concluded that every modeling program had been developed for specific purposes with its own individual capacities and limitations. Fundamental limitations were the form of alkalinity input and non-carbonic alkalinity correction, and pH calculation. These limitations are still needed to be resolved in the revised versions of computer-programs (Verma, 2000; Verma and Truesdell, 2001).

The first step in the geochemical modeling of geothermal system is the calculation of deep reservoir fluid characteristics from the measured physical-chemical parameters of surface manifestations like spring, fumarole and drilled wells. Using the chemical geothermometers and the conservation of mass, energy and alkalinity, the chemical concentrations are converted to the reservoir conditions in order to predict the state of water-rock interaction and reservoir processes like boiling, condensation,
mixing with other fluids, mineral dissolution-precipitation, etc. (Verma, 2002). The calculation procedures with certain limitations like the calculation of pH and alkalinity are systematically documented by Henley et al. (1984). Verma (2008a) developed an algorithm to calculate the reservoir fluid pH in geothermal systems with uncertainty propagation. Similarly, the quartz geothermometry is extended to estimate deep reservoir temperature and vapor fraction with multivariate uncertainty propagation (Verma, 2008b, in press).

This article presents a computer code GeoSys.Chem, written in the object oriented programming (OOP) approach, for the first step of geochemical modeling of geothermal systems (i.e., the calculation of reservoir fluid compositions). The program is written as a dynamic link library (DLL) in Visual Basic in Visual Studio (VB.NET). Additionally, a demonstration program GeoChem is also written in VB.NET to illustrate the calculation procedure considering the Los Azufres geothermal field as an example.

2. Theoretical aspects

Fig. 1 shows the conceptual diagram of geothermal system (modified after Verma, in press). The geothermal fluid flows up in the well and is separated into vapor and liquid in the separator. The vapor sample (Vapor$_2$) is collected at the separator and the separated liquid (Water$_2$) is further flushed in the weir box to collect the water sample (Water$_1$). The first step in geochemical modeling is the calculation of composition of the vapor (Vapor$_3$) and liquid (Water$_3$) phases in the geothermal reservoir.

The algorithm contemplates the separation of total discharge fluid into vapor and liquid at a given pressure (or temperature) along the liquid-vapor saturation curve and vice versa (Henley et al., 1984; Verma, 2002). Assuming adiabatic steam separation (i.e., heat loss or gain by the fluid from its surroundings is negligible) the distribution of reservoir fluid enthalpy between the liquid and vapor phases is expressed by

$$ H_{ld} = (1 - y)H_l + yH_v $$

(1)

where $H$ is enthalpy, $y$ is the fraction of vapor by weight and sub-indices $l$, $v$ and $t$ represent the corresponding parameter for the total discharge, vapor and liquid, respectively. The similar equation for the concentration of any chemical species is written as

$$ C_{td} = (1 - y)C_l + yC_v $$

(2)

The non-volatile species like Na$^+$, Cl$^-$, etc., resides only in the liquid phase (i.e., their concentration in the vapor phase is zero). However, the gaseous species like CO$_2$, H$_2$S, NH$_3$, N$_2$, CH$_4$, etc., distribute between liquid and vapor phases. The distribution coefficient $D_{coef}$ for a gaseous species is defined as the concentration ratio of the species in the vapor and liquid phases.

$$ D_{coef} = \frac{C_v}{C_l} $$

(3)

There are three types of equations for an aqueous solution: mass balance, charge balance and proton balance. But out of the three equations two are independent and the third can be derived as an algebraic sum of the other two equations (Verma and Truesdell, 2001). Theoretically, a solution must be electrically neutral. It is well known that the electro-neutrality condition is rarely satisfied in analytical compositions of water as a consequence of the analytical errors. Thus the alkalinity approach (i.e., proton balance) is used here for the pH calculation of geothermal fluids (Verma, 2000).

A base-neutralizing capacity (BNC) or acid-neutralizing capacity (ANC) is the equivalent sum of all the acids or bases that can be titrated with a strong base or acid to a preselected equivalence point (Stumm and Morgan, 1981). The BNC and ANC are more commonly known as acidity and alkalinity, respectively. Both of

![Fig. 1. Schematic diagram of geothermal system (modified after Verma, in press). The vapor sample (Vapor$_2$) is collected at the separator and the separated liquid (Water$_2$) is further flushed in the weir box to collect the liquid sample (Water$_1$). The first step in geochemical modeling is the calculation of composition of the vapor (Vapor$_3$) and liquid (Water$_3$) phases in the geothermal reservoir.](image-url)
these terms are defined for certain pertinent equivalence points (EPs) for the system. Acidity is the negative of alkalinity for the same reference EP. In the carbonic (bi-proton) systems there are three equivalence points called the $H_2CO_3EP$, $NaHCO_3EP$ and $Na_2CO_3EP$. Alkalinity could be defined with respect to either EP. The geothermal fluids also have other weak acids and bases like $H_2SiO_4$, $B(OH)_3$, $H_2S$, $NH_3$, etc. In order to handle the calculations efficiently, the alkalinity in the geothermal fluids is defined with respect to the acid equivalence point as

$$Alk = [OH^-] - [H^+] + CF_{car}(x_{1car} + 2x_{2car}) + CF_{TS}(x_{1TS})$$

$$+ CF_{TS}(x_{1TS}) + CF_{TS}(x_{3}) + CF_{TN}(x_{3TN})$$

(4)

where the $x$’s are the ionization fractions (Stumm and Morgan, 1981) and $C_F$ is the total dissolved concentration of the subscripted constituent, i.e., carbonic acid (car), boric acid (B), silicic acid (Si), hydrogen sulfide (S) and ammonia (N), respectively. In case of ammonia the $x$’s are defined for the corresponding acid (NH$_4^+$). Thus the alkalinity defined here does not change upon dissolution or exsolution of CO$_2$ ($H_2CO_3$ and $H_2S$); but it does affect with NH$_3$ (Stumm and Morgan, 1981). Similarly, the addition or removal of bicarbonate ($HCO_3^-$), carbonate ($CO_3^{2-}$), silicic ($H_2SiO_4$), boric ($B(OH)_4^-$), sulfide ($HS^-$, $S^{2-}$), hydrosilicate ($OH^-$) minerals will increase or decrease alkalinity. The precipitation of minerals is not considered in the algorithm. The fluid may be supersaturated with respect to some minerals like quartz; and there is no sufficient time to get them precipitated during the separation of fluid into the liquid and vapor phases at the separator and weir box. Therefore, the distribution of NH$_3$ between the liquid and vapor phases is handled. Thus, the alkalinity in the vapor phase is equivalent to the concentration of NH$_3$ in the vapor phase. In other words, the alkalinity is distributed between the liquid and vapor phases according to the following equation

$$Alk_{ld} = (1-y)Alk_{l} + yAlk_{v}$$

(5)

where the alkalinity in the liquid phase ($alk_{l}$) is defined according to Eq. (4) and the alkalinity in the vapor phase ($alk_{v}$) is turned out to be its NH$_3$ concentration. The alkalinity is a conservative entity during chemical reactions in a system (Stumm and Morgan, 1981).

When the separation pressure (or temperature) is known (e.g., at the separator and weir box), the calculation of composition of the liquid and vapor phases from the total discharge fluid composition and vice versa is easy to perform at the separation conditions.

In the geothermal reservoir the total discharge composition of fluid is same as the total discharge composition of fluid at the separator; however, we do not know the reservoir pressure (or temperature) in the geothermal reservoir. Therefore, the quartz solubility geothermometers are used to estimate the reservoir temperature and vapor fraction (Verma, in press).

This algorithm is programmed in the computer code GeoSys. Chem to calculate the deep reservoir fluid composition from the vapor and liquid samples collected from a production well.

3. Program description

3.1. GeoSys

The GeoSys was written as a dynamic link library (DLL) in Visual Basic in Visual Studio 2010 (VB.NET) using the object oriented programming (OOP) approach. A namespace GeoSys was created which will be used in future to include all the programs associated with the geochemical modeling. The namespace approach is a Microsoft’s naming convention in OOP which avoids the name conflict during programming. Presently, GeoSys contains three namespaces, Chem, ThemoData and Geotherms for geochemical modeling of geothermal system, thermodynamics data and chemical geothermometers, respectively. The Geotherms namespace contains the classes associated with the quartz solubility geothermometers (Verma, in press).

3.2. GeoSys.Chem

The namespace GeoSys.Chem contains various classes as shown in Fig. 2. A class encapsulates the data and methods, and serves as blue-prints for creating objects. The functionality of a class may be extended without knowing its code (Verma, 2008a, b).

The most important class of GeoSys.Chem is “Fluid” (Fig. 2). It has nine properties (ID, Name, Htd, Press, Temp, VapPrac, Liquid, Vapor, and TD), two instance methods (TDtoFluid and FluidToTD) and four class methods (AssignFluidValues, AssignLiquidValues, AssignVaporValues, and AssignTDValues). The names of properties and methods are quite explicit and are not described here. The class methods are associated with the class and are used without creating an instance of the class (i.e., object).

The properties of built-in types are shown without their types (e.g., ID as integer, Name as string, etc.); whereas the properties of user defined types are depicted with their respect types. For example, the property, Liquid of the class Fluid is of LiquidPhase type. Similarly, the properties and methods of LiquidPhase and other classes are given in Fig. 2.

3.3. GeoSys.ThermoData

The namespace GeoSys.ThermoData contains three classes: KConst, SteamTables and DCoef for the equilibrium constant for various species, thermodynamic properties of water (Verma, 2003) and distribution coefficient of gaseous species, respectively (Fig. 3).

Fig. 4 shows the variation of the equilibrium constants for the species of class KConst with temperature. The values of equilibrium constants are taken from Henley et al. (1984). They reported the values up to 300 °C. Since the temperature in the geothermal reservoir is sometimes higher than 300 °C, the values are extrapolated up to the critical point of water with a linear tendency among the last three or more data points. The quadratic interpolation is carried out to obtain the intermediate values between the data points.

The equations for the distribution coefficients for the gaseous species are taken from Giggenbach (1980). Similarly, the equations are considered valid up to the critical point of water; although he reported the equations for the temperature range 100 to 340 °C.

3.4. GeoChem: A demo

The program GeoChem can be downloaded from the journal webpage or requested from the author. It can be installed with running the setup program and following the instructions. The default installation folder is C:\ProgramFiles\GeoSys.Chem. Fig. 5 shows its graphic user interface to calculate the deep geothermal reservoir fluid compositions. The following steps are needed to conduct these calculations:

1. Creating input data file: The program accepts the input data file in the XML format. Table 1 shows an input data file for one well. The values are written within the opening and closing tags. For example, the total discharge enthalpy (Hr = 1179 kJ/kg) is written as $\lt Hr \gt = 1179 \lt /Hr \gt$. The field wellID is for the identification of the well. It is planned to implement in future a database management system for the geochemical analyses.
An XML file may be created in any text editor, although many free XML editors are available on internet. The Visual Studio has its own XML editor. Open a new file in any text editor and copy and paste the content of Table 1 in it. The measurement units are: enthalpy in kJ/kg, pressure in MPa, aqueous species concentration in ppm, gas/steam ratio \((X_g)\) in % volume, and condensed vapor species (CO2, H2S, ...) in % volume in the dry gas.

One can write his data values within the corresponding tags (Miller and Lawrence Berkeley Laboratory Report LBL, 1979). Similarly, to add another well one has to copy the content between the tags \(<\text{WellData}\>\) and paste it within the tags \(<\text{GeoSys}\>\) and save the file with an extension .xml.

2 Reading data file: Run the program GeoChem and press the button “Read” on the tab “Input Data” (Fig. 5) and select the...
To open the same data file every time when the program starts, save the data file in the program folder with the name, WellData.xml. It is the default file name.

3 Concentration correction: It is necessary to convert the concentration in mmole/kg before conducting any calculation. Similarly, the normalization of gaseous species concentration is the default option. Unselect the option “Gas Normalization”, if you do not want to normalize gas concentrations. Press the button “Data Correction”. It will show the calculated data in the tab “Correct Data”. It also calculates the charge unbalance and alkalinity for each sample. First, it calculates all the existing species. For example, the boron concentration is reported as the total concentration. Actually, there are B(OH)3 and B(OH)4 species in the solution (sample). The proportion of their concentrations depends on the pH of the solution. So, the concentration of B(OH)4 is calculated and included in the charge unbalance calculations.

4 Reservoir fluid composition calculation: On pressing the button “Calc” on the tab “Correct Data”, it calculates the fluid compositions at various places including in the geothermal reservoir. It will be explained later in case of well AZ-09.

5 Output results: The results are shown in the DataGridView controls. One can copy and paste them in any file.

4. A case study: Los Azufres geothermal field

The geochemical data of 11 production wells from the Los Azufres geothermal field are taken from Arellano et al. (2005). These data in an XML file (WellData.xml) are also uploaded on the journal webpage. Arellano et al. (2005) presented the thermodynamic evolution of the Los Azufres geothermal reservoir using a well simulation, WELFLO (Miller, 1979). The geochemical studies also provide similar evidences on the thermodynamic evolution of Los Azufres geothermal system.

Fig. 6 shows the stepwise calculation of geothermal reservoir parameters for well AZ-09. It shows only the carbonic species due...
to space limits. It is helpful to install and run the program GeoChem with the default file, which contains the data of Los Azufres geothermal field. The calculation procedure is performed according to the following steps:

1. **Heating liquid sample up to the weir box separation temperature:**
   The water samples are analyzed at the laboratory temperature (say 25°C). First it calculates the charge unbalance to verify the analysis quality (i.e., including all the major chemical parameters). The charge unbalance for these analyses is less than 5% (see Tab “Correct Data” of the program GeoChem). It means that the analytical quality is satisfactory. The concentrations of all the carbonate species are calculated from pH and HCO$_3$ concentration, measured in the water sample. Similarly, the alkalinity at 25°C is calculated from pH and acid-base species for each sample. The well AZ-09 has the alkalinity 0.971 meq/kg and it is a conservative entity during heating the sample from 25 to 100°C (Stumm and Morgan, 1981).

   Similarly, the total concentration of carbonic species (0.939 mmole/kg) is conserved, but the distribution of carbonic species and pH change on heating the sample from 25 to 100°C. See the results on the tab “Fluid Weir” of the program.

2. **Calculation of vapor composition at the weir box:**
   The gaseous species are liberated in the vapor phase during the liquid–vapor separation at the weir box. The carbonic species are only measured in the water sample. So, the concentration of CO$_2$ in the vapor phase at the weir box is calculated using the distribution coefficient (Giggenbach, 1980). The vapor has 1270 mmole/kg of CO$_2$. It can be observed that there is tremendous difference in the carbonic species compositions of Water$_2$ and Water$_{2\text{Weir}}$. This separated water (Water$_2$) is flushed in the weir box at the atmospheric conditions. This also shows that there is no sufficient CO$_2$ in the separated water to liberate the tremendous amount of CO$_2$ (1270 mmole/kg) in the atmospheric vapor at the weir box (see step 2). The complete results are on the tab “Sep Fluid Weir”.

3. **Calculation of separated water composition from vapor phase:**
   The gaseous species are analyzed in the vapor sample (Vapor$_2$). By considering the concentration of non-volatile species and alkalinity of the separated water (Water$_{2\text{Weir}}$) one can construct the separated water compositions (Water$_2$) from Vapor$_2$. It can be observed that there is tremendous difference in the carbonic species compositions of Water$_2$ and Water$_{2\text{Weir}}$. This separated water (Water$_2$) is flushed in the weir box at the atmospheric conditions. This also shows that there is no sufficient CO$_2$ in the separated water to liberate the tremendous amount of CO$_2$ (1270 mmole/kg) in the atmospheric vapor at the weir box (see step 2). The complete results are on the tab “Sep Fluid Weir”.

4. **Calculation of geothermal reservoir fluid compositions:**
   The compositions of geothermal reservoir fluid are calculated by combining the separated water and vapor compositions at the separator. Three types of separated waters are considered: (i) Water$_r$, (ii) water which liberates the vapor only (i.e., without any gaseous species) at the weir box in forming the Water$_r$, and (iii) Water$_{2\text{Weir}}$. The calculated geothermal reservoir fluid compositions are given on the tabs “Res Fluid 1”, “Res Fluid 2”, and “Res Fluid 3”, respectively. The steps 5a and 5c are the extreme cases of the process. In the absence of good quality analysis of carbonic species, the geothermal reservoir fluid compositions are considered as obtained by the step 5b (i.e., the results on the tab “Res Fluid 2”).
4.1. Enthalpy—pressure diagram

The enthalpy—pressure diagram for water is constructed in Excel using the SteamTables class (Verma, 2003). The separation boundary between the liquid and vapor phases is formed by the critical isochor and the two phase region (Fig. 7). The conditions of the geothermal reservoir fluids for all the wells are in the two phase region and between the isotherms at 200 and 300 °C. Therefore, the geochemistry of Los Azufres provides the similar evidences as obtained by the well simulator (Arellano et al., 2005).

4.2. Cl—enthalpy mixing diagram

Henley et al. (1984) presented a Cl—enthalpy mixing model to evaluate reservoir processes in the formation of natural
manifestations. Fig. 8 shows the total discharge and liquid phase compositions of the production wells. The corresponding vapor enthalpies for all the wells are in the range 2749–2803 kJ/kg (i.e., averaged value as 2785 ± 21 kJ/kg). It is clear that the vapor enthalpies fall at the same point for a wide range of temperature and pressure. Similarly, the total discharge and the corresponding liquid phase values have no relation unless the fraction of vapor is known. In other words, it is not possible to predict the relation among wells if the fraction of vapor is unknown.

In the formation of natural manifestation the geothermal reservoir liquid is flushed at the atmospheric conditions. The values corresponding to each well are shown with cross marks (Fig. 8). The region for natural manifestations which is formed with the mixing of ground water and a component of geothermal reservoir is shown in the Fig. 8. It is clear that the Cl⁻–enthalpy mixing diagram works well if the formation of natural manifestations is controlled only by the geothermal reservoir liquid phase.

4.3. Behavior with elevation

Fig. 9 shows the behavior of enthalpy, temperature, vapor fraction and Cl⁻ concentration with the elevation of production zone for each well. The production zone elevation data are taken from Nieva et al. (1987). The wells at higher elevation have higher enthalpy (Fig. 9a) and vapor fraction (Fig. 9c); whereas the temperature (Fig. 9b) and chloride (Fig. 9d) have contrary behavior. This supports the formation of geothermal production zone as a consequence of evaporation and condensation process as proposed by Nieva et al. (1987).

5. Conclusions

The dynamic link library GeoSys.Chem, written in VB.NET, is a useful tool for the calculation of reservoir fluid characteristics during the exploration and exploitation of geothermal systems. It is programmed according to the OOP approach, so it can be incorporated and extended its functionality in any OOP language like C-sharp, VB.NET, C++, JAVA include VBA in Excel in the Windows environment.

The geochemical thermodynamic database is also implemented using the OOP approach and is applicable up to the critical point of water. The quadratic interpolation is carried out to obtain the intermediate values between the data points, since their behavior is in-between the linear and exponential tendency. A linear extrapolation is developed for calculating the thermodynamic values above 300°C, since the tail of exponential behavior dataset is close to linear tendency.

The fundamental class of GeoSys.Chem is Fluid which has main properties Liquid, Vapor and TD (total Discharge) and methods TDtoFluid and FluidToTD. The calculation procedure of geothermal reservoir parameters is to assign the values of the properties and invoke the respective method. The vast difference in the calculated concentrations of CO₂ in the secondary vapor, discharged in the atmosphere at the weir box, from the vapor sample at the separator and water sample at the weir box is a consequence of high analytical errors. Thus there is necessary to revise the analytical procedures for the determination of carbonic species concentration in the vapor and water samples (Verma, 2004).

The Los Azufres geothermal reservoir temperature is 200–300°C and dominating process in the upper part of the reservoir is the evaporation and partial condensation. The Cl⁻–enthalpy
diagram devised with considering the liquid component of geothermal reservoir fluid is useful for understanding the process of natural manifestations formation.

Acknowledgments

This paper is dedicated to a friend and colleague, Ignacio Salvador Torres Alvarado, who passed away on 15th January, 2012. He worked actively on the geochemistry and geology of geothermal systems till the last day of his life. He will always be remembered for his friendship and helping attitude. The author highly appreciates Richard Glover and the anonymous reviewer for critical reading and providing constructive comments and suggestions to improve of the manuscript.

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jageo.2012.06.001

References


