

## Estimates of geothermal reservoir fluid characteristics: GeoSys.Chem and WATCH

**Ignacio Salvador Torres-Alvarado<sup>1</sup>, Mahendra P. Verma<sup>2\*</sup>, Kizito Opondo<sup>3</sup>,  
David Nieva<sup>4</sup>, Füsün Tut Haklıdır<sup>5</sup>, Edgar Santoyo<sup>1</sup>,  
Rosa María Barragán<sup>2</sup>, and Víctor Arellano<sup>2</sup>**

<sup>1</sup> Centro de Investigación en Energía, Universidad Nacional Autónoma de México,  
Priv. Xochicalco s/n, Centro, A.P. 34, 62580 Temixco, Morelos, México.

<sup>2</sup> Geotermia, Instituto de Investigaciones Eléctricas, Reforma 113, Col. Palmira,  
62490 Cuernavaca, Morelos, México.

<sup>3</sup> Geochemistry Laboratory, Olkaria Geothermal Project, Moi South Lake Road,  
P.O. Box 785, 20117 Naivasha, Kenya.

<sup>4</sup> Dirección Ejecutiva, Instituto de Investigaciones Eléctricas, Reforma 113, Col. Palmira,  
62490 Cuernavaca, Morelos, México.

<sup>5</sup> Zorlu Energy Group, Zorlu plaza, Avcılar-Istanbul, Turkey.

\*Mahendra@iie.org.mx

### ABSTRACT

*A comparative study of the reservoir fluid characteristics calculation of ten production wells of Los Azufres, Los Humeros and Cerro Prieto geothermal fields using two computer codes GeoChem (GeoSys.Chem) and WATCH is presented. GeoSys.Chem estimates the reservoir temperature and vapor fraction through quartz geothermometry and assuming enthalpy conservation, while the average temperature of quartz and Na/K geothermometers is employed in WATCH and vapor fraction is also calculated through enthalpy conservation. Both programs use the conservation of alkalinity (i.e., proton balance) for pH calculations. The difference in temperature (pressure) causes considerable effects on the calculated geothermal reservoir fluid characteristics of high enthalpy wells and negative (or near to zero) vapor fraction for low enthalpy wells. The calculated high concentration of CO<sub>2</sub> in the secondary vapor discharged in the atmosphere at the weir box (up to 11,719 mmole/kg) suggests that the analysis of carbonic species in the geothermal waters is crucial. In the absence of good quality analysis of carbonic species it is suggested to consider the CO<sub>2</sub> 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 CO<sub>2</sub> in the atmospheric vapor at the weir box) for the calculation of geothermal reservoir fluid composition.*

*Key words: GeoSys.Chem, GeoChem, WATCH, geochemical modeling, geothermal system.*

### RESUMEN

*Se presenta un estudio comparativo del cálculo de las características del fluido de yacimiento de diez pozos productores de los campos geotérmicos Los Azufres, Los Humeros y Cerro Prieto, utilizando dos programas de cómputo, GeoChem (GeoSys.Chem) y WATCH. GeoSys.Chem calcula la temperatura y la fracción de vapor del yacimiento a través de la geotermometría de cuarzo y asumiendo conservación de la entalpía, mientras que la temperatura promedio de geotermómetros de cuarzo y Na/K se emplea en WATCH. WATCH también calcula la fracción de vapor mediante la conservación de la entalpía. Ambos*

*programas utilizan la conservación de alcalinidad (es decir, el balance de protones) para los cálculos de pH. La diferencia en temperatura (presión) provoca efectos considerables en las características del fluido de yacimiento geotérmico calculadas para pozos de alta entalpía, así como fracción de vapor negativa (o cercana a cero) para pozos de baja entalpía. La alta concentración calculada de CO<sub>2</sub> en el vapor secundario liberado en la atmósfera en el vertedero (hasta 11.719 mmol/kg) sugiere que el análisis de las especies carbónicas en las aguas termales es crucial. En la ausencia de análisis de buena calidad de las especies carbónicas, se sugiere tener en cuenta el CO<sub>2</sub> de la muestra de vapor en el separador y la concentración total de las especies carbónicas disueltas en la muestra de agua (es decir, sin tener en cuenta la liberación de CO<sub>2</sub> en la atmósfera de vapor en el vertedero) para los cálculos de las composiciones de fluidos en los yacimientos geotérmicos.*

*Palabras clave: GeoSys.Chem, GeoChem, WATCH, modelado geoquímico, sistema geotérmico.*

## INTRODUCTION

First step in geochemical modeling of geothermal systems is the calculation of deep geothermal reservoir fluid characteristics from the measured physical-chemical parameters of surface manifestations like springs, fumaroles and drilled wells. Various computer programs have been written 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). 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. SOLMNEQ (Kharaka and Barnes, 1973), MINEQ (Westall *et al.*, 1976), WATEQX (van Gaans, 1989) and EQ3NR (Wolery, 1983) deal with chemical speciation using input parameters such as dissolved species concentration, temperature and pH; while WATEQ (Truesdell and Jones, 1974), WATCH (Arnorsson *et al.*, 1982), CHILLER (Reed, 1982), EQQYAC (Barragan and Nieva, 1989) and GeoSys.Chem (Verma, 2012a) may recalculate the pH using charge balance or H<sup>+</sup> 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. Torres-Alvarado (2002) determined the evolution of chemical equilibrium state of Los Azufres geothermal field using the Geochemist’s Workbench.

This article presents a comparative study of the calculation of geothermal reservoir fluid characteristics of ten production wells of Los Azufres, Los Humeros and Cerro Prieto geothermal fields using the computer codes GeoSys.Chem (Verma, 2012a) and WATCH (Arnorsson *et al.*, 1982).

### Procedure for the calculation of geothermal reservoir fluid composition

The conceptual diagram of a geothermal system with sampling points of condensed vapor and liquid samples is

shown in Figure 1 (after Verma, 2012a). The first step in the geochemical modeling of geothermal systems is the reconstruction of reservoir fluid characteristics [*i.e.*, pressure ( $P$ ), temperature ( $T$ ), fraction of liquid ( $y_l$ ) and vapor ( $y_v$ ), and concentration of each chemical species in the liquid (Water<sub>3</sub>) and vapor (Vapor<sub>3</sub>) phases] from the vapor sample (Vapor<sub>2</sub>) collected at the separator and water sample (Water<sub>1</sub>) collected in the weir box at atmospheric conditions. There may be  $n$ -separations of geothermal reservoir fluids (Verma 2008), however, the last separator is the weir box in order to liberate the separated water at the atmospheric conditions. Figure 1 shows the separation scheme of the studied wells, which was used during the sampling of separated water and condensed vapor. Table 1 presents the analytical datasets of ten wells from Los Azufres, Los Humeros and Cerro Prieto geothermal fields, taken from Henley *et al.* (1984), Arellano *et al.* (2003, 2005) and Tello (2005).

### Geosys.Chem

Verma (2012a) wrote a demonstration computer program GeoChem using the dynamic link library GeoSys.Chem in Visual Basic in Visual Studio 2010 (VB.NET). The main class is “Fluid”, which has three principal properties, Liquid, Vapor, and TD (total discharge) and two methods, TDToFluid and FluidToTD. For the geochemical calculations, the program considers 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. At the separator and weir box, the separation pressure (or temperature) is known. In the geothermal reservoir the total discharge composition of the fluid is the same as the total discharge composition of the fluid at the separator. The reservoir temperature and vapor fraction are estimated by means of quartz solubility geothermometry and conservation of enthalpy (Verma, 2012b).

### Algorithm

The distribution of chemical species, alkalinity and enthalpy is expressed as

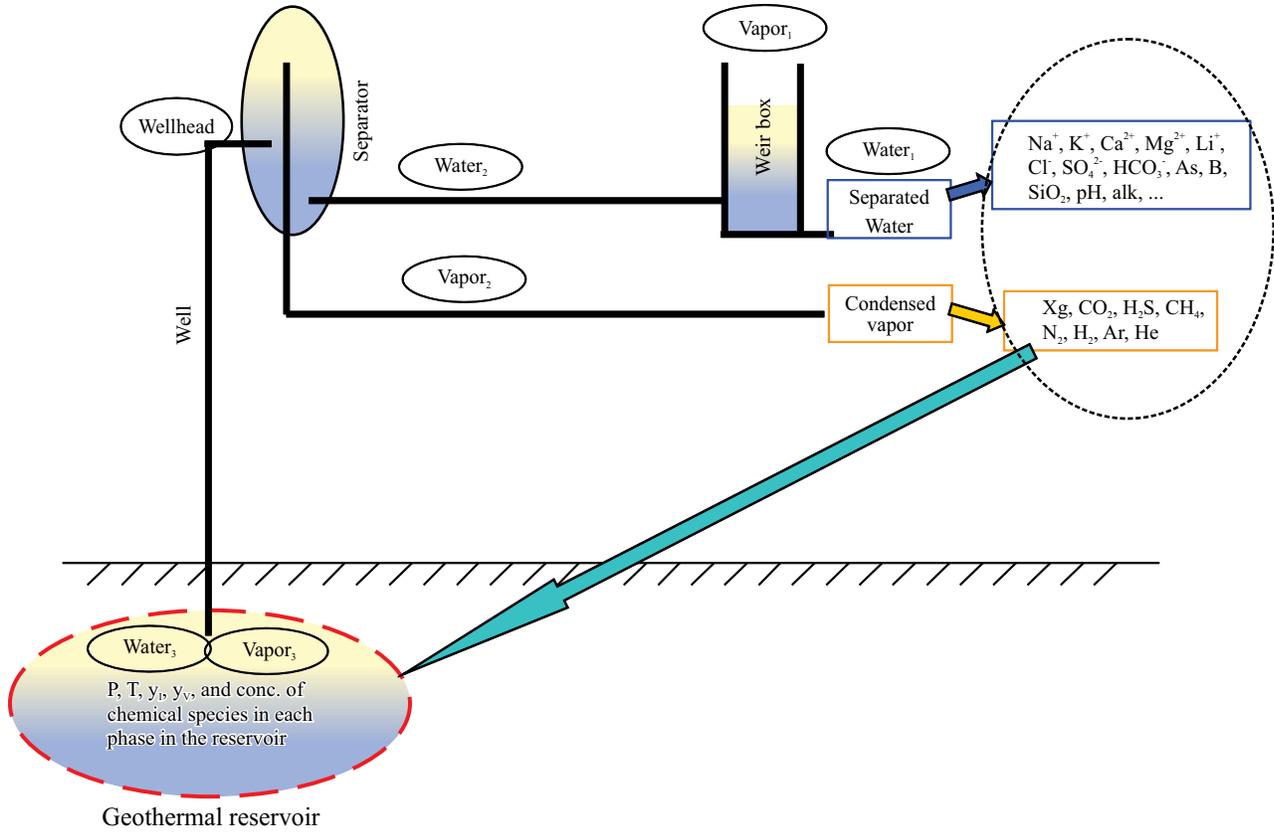


Figure 1. Schematic diagram of a geothermal system (after Verma, 2012a). The geothermal fluid (Water<sub>3</sub> and Vapor<sub>3</sub>) flows up in the well and is separated into vapor and liquid in the separator. The vapor sample (Vapor<sub>2</sub>) is collected at the separator and the separated liquid (Water<sub>2</sub>) is further flushed in the weir box. The liquid sample (Water<sub>1</sub>) is collected at the weir box. The first step in geochemical modeling is the calculation of the composition of the vapor (Vapor<sub>3</sub>) and liquid (Water<sub>3</sub>) phases in the reservoir from water and vapor samples.

$$A_{td} = (1 - y)A_l + yA_v \quad (1)$$

where  $A$  represents chemical species ( $C$ ), alkalinity ( $alk$ ) and enthalpy ( $H$ ),  $y$  is the fraction of vapor by weight and sub-indices  $td$ ,  $v$  and  $l$  represent the corresponding parameter in the total discharge, vapor and liquid, respectively.

The alkalinity in the liquid phase ( $alk_l$ ) is defined according to the following equation

$$\begin{aligned} Alk_l = & [OH^-] - [H^+] + C_{Tcar}(\alpha_{1car} + 2\alpha_{2car}) \\ & + C_{TB}(\alpha_{1B}) + C_{TSi}(\alpha_{1Si}) \\ & + C_{TS}(\alpha_{1S}) + C_{TN}(\alpha_{1N}) \end{aligned} \quad (2)$$

where the  $\alpha$ 's are the ionization fractions and  $C_T$  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 ( $N$ ). In case of ammonia, the  $\alpha$ 's are defined for the corresponding acid ( $NH_4^+$ ). A full discussion on alkalinity is in the book of Stumm and Morgan (1981). The alkalinity in a carbonic system (*i.e.*, bi-proton system) is defined with respect to one of the three equivalence points (EP) (*i.e.*,  $H_2CO_3EP$ ,  $HCO_3^-EP$ ,  $CO_3^{2-}EP$  which are represented as  $H_2CO_3EP$ ,  $NaHCO_3EP$ ,  $Na_2CO_3EP$ , respectively, in order to keep the charge balance in the chemical system). If

we define the alkalinity with respect to  $H_2CO_3EP$  as defined in Equation (2), it will decrease with the precipitation of  $CaCO_3$  or  $Ca(HCO_3)_2$ , while it will remain unchanged on the dissolution or removal of  $CO_2$ . Similarly, it will not be altered on the removal or addition of  $H_2S$ . In the same way, if precipitation or dissolution of  $NH_4Cl$  occur, the alkalinity will not change. However, the removal of  $NH_3$  will alter the alkalinity. In all the above processes, the pH of the solution will always change. Thus, the alkalinity is a conservative entity in chemical reactions, but not the pH.

The alkalinity is the acid neutralizing capacity of the solution and is defined with respect to an equivalence point like the definition of gravitational potential. The alkalinity is turned out to be the sum of the concentrations of weak acid-base species in the solution as expressed in Equation (2). The  $CO_2$  (or  $H_2CO_3$ ) concentration is not considered in the equation, and thus the alkalinity will not change on adding or removing  $CO_2$ . However, the concentration of  $NH_3$  [*i.e.*,  $C_{TN}(\alpha_{1N})$ ] in the liquid phase is included in the Equation 2, indicating that the alkalinity is affected by the removal of  $NH_3$ . During the separation of the geothermal reservoir fluid into vapor and liquid at lower pressure,  $NH_3$  distributes between the liquid and vapor phases. So, the vapor phase has alkalinity that is equivalent to the concentration of  $NH_3$

Table 1. Analytical data of separated water and condensed vapor of ten geothermal wells from Cerro Prieto, Los Azufres and Los Humeros (taken from Henley et al., 1984; Arellano et al., 2003, 2005; Tello, 2005). Analyses are considered to have been performed in the laboratory at temperature of 25 °C.

Parameter	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	Well 8	Well 9	Well 10
H <sub>r</sub> (kJ/kg)	1179	1203	2716	1532	1761	1840	1981	2142	2305	2557
P <sub>sep</sub> (MPa)	0.98	0.755	0.79	0.49	0.489	0.482	0.96	0.831	0.763	1.174
P <sub>atm</sub> (MPa)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
<i>Water samples collected in the weir box (concentration in ppm)</i>										
pH	8.3	7.27	7.4	7.5	6.9	7.0	8.1	8.0	6.5	7.5
Na <sup>+</sup>	267	7370	1860	1661	1752	2234	243	269	108	1684
K <sup>+</sup>	45	1660	464	379	570	662	48	45.7	20.0	347
Ca <sup>2+</sup>	2.0	438	19.1	26.1	10.8	7.7	2.0	0.6	0.3	43.9
Mg <sup>2+</sup>	0.11	0.35	0.01	0.04	0.01	0.05	0.22	0.030	0.05	0.08
Li <sup>+</sup>	0.47		25.7	19.9		33.1	0.30	0.60	0.30	21.5
Cl <sup>-</sup>	90	13800	3544	3053	3453	4030	76	120	74	3000
SO <sub>4</sub> <sup>-</sup>	233	18	19	28	46.1	17.7	213	94.8	17.2	27.3
HCO <sub>3</sub> <sup>-</sup>	161	52	104	64	5.7	46.6	139	294	196	65.2
B	218	14.4	277	210	292	341	453	452	942	392
SiO <sub>2</sub>	1005	808	900	773	1124	887	1120	967	600	660
Alk (meq/kg)*	5.30	0.91	2.14	1.47	0.24	0.97	5.55	7.43	3.38	1.79
% Charge unbalance*	0.99	-0.72	-2.54	-1.18	-3.83	1.81	-0.69	0.78	-5.00	0.26
<i>Condensed vapor samples collected at the separator (concentration in % volume in dry gas)</i>										
X <sub>g</sub> (gas/steam ratio, %vol)	1.77	0.588	0.912	1.552	0.338	0.285	1.74	1.326	2.309	1.282
CO <sub>2</sub>	98.20	82.20	97.48	96.28	97.23	93.44	94.7	94.6	91.38	97.36
H <sub>2</sub> S	1.09	7.91	1.36	1.25	1.64	4.52	3.69	4.12	5.635	1.013
NH <sub>3</sub>	0.20	2.31	0.00	0.00	0.5298	0.8335	0.21	0.2431	0.3425	0.1379
H <sub>2</sub>	0.12	2.86	0.275	0.417	0.2948	0.7403	0.37	0.9316	1.8789	0.2663
CH <sub>4</sub>	0.16	3.98	0.149	0.092	0.0405	0.0902	0.44	0.0457	0.5961	0.1239

\* Alkalinity (Alk) and charge unbalance were calculated by GeoChem (GeoSys.Chem). H<sub>r</sub>: geothermal reservoir enthalpy, P<sub>sep</sub>: pressure at the separator, P<sub>atm</sub>: atmospheric pressure.

in the vapor phase (Verma, 2012a). Likewise, on the precipitation of CaCO<sub>3</sub> the alkalinity goes in the solid phase. If we define the alkalinity with respect to Na<sub>2</sub>CO<sub>3</sub>EP, the addition of removal of CaCO<sub>3</sub> will not alter the alkalinity. We have to keep the track of alkalinity of the system during the chemical calculations (e.g., pH calculation).

In summary, the alkalinity (i.e., acid neutralizing capacity) is the sum of the concentrations of weak acid-base species in the solution. Its definition with different equivalence points helps to solve a specific problem. For example, if we are dealing with the dissolution and removal of CO<sub>2</sub>, it is better to define the alkalinity with respect to the CO<sub>2</sub> equivalence point. Indeed, any definition of alkalinity will do the same, but there will be less calculation and less chances of error if we use the right definition. Actually, the concentration of NH<sub>3</sub> is very low in geothermal systems, so it can be ignored without causing significant error in the geochemical modeling of a geothermal system. However, we have programmed it, so that the program can be used for other systems too.

The pH calculation is performed with the alkalinity conservation approach (i.e., proton balance).

The non-volatile species like Na<sup>+</sup>, Cl<sup>-</sup>, etc., reside only in the liquid phase (i.e., their concentration in the vapor

phase is zero); however, the gaseous species like CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, N<sub>2</sub>, CH<sub>4</sub>, etc., distribute between the liquid and vapor phases. The distribution coefficient  $D_{Coef}$  of a gaseous species is defined as the concentration ratio of the species in the vapor and liquid phases (Giggenbach, 1980).

$$D_{Coef} = \frac{C_v}{C_l} \quad (3)$$

At high temperature, partition of HCl and B between-vapor and liquid phases occur (Arnórsson and Andrésdóttir, 1995; Giroud, 2008; Bernard et al. 2011). The partition also depends on pH. Giroud (2008) presented experimental data for the distribution of B in vapor and liquid phases. The data are preliminary and limited to define the equation of the distribution coefficient of B, and consequently it is presently not feasible to deal with the distribution of B in the computer code. Additionally, our analytical data set do not have experimental values of B in the vapor phase. Thus the concentrations of HCl and B in the vapor phase are not considered in the present computer codes.

### Calculation procedure

Figure 2 shows the stepwise calculation of geothermal reservoir parameters for well 9. Only the carbonic species

are shown because of space limits. The calculation procedure is performed according to the following five steps:

**Heating the liquid sample up to the weir box separation temperature.** The water samples are analyzed at laboratory temperature (say 25°C). The charge unbalance is calculated to verify the analytical data quality. All the major ionic species including  $\text{H}_3\text{SiO}_4^-$  and  $\text{B}(\text{OH})_4^-$  are considered in the charge unbalance calculations. Actually, all ionic chemical species should be considered in the charge unbalance calculation; however, the concentration of trace species does not affect significantly the results. In the present study, the concentration of  $\text{SiO}_2$  and  $\text{B}(\text{OH})_3$  is high in some water samples, therefore, the ionic species  $\text{H}_3\text{SiO}_4^-$  and  $\text{B}(\text{OH})_4^-$  contribute significantly to the charge unbalance calculation at high pH. The charge unbalance for all the samples is less than 5% (Table 1).

The alkalinity of water samples at 25°C is calculated from pH and acid-base species for each sample (Table 1).

The alkalinity (3.380 meq/kg for well 9) is a conservative entity when the sample is heated from 25 to 100°C (Stumm and Morgan, 1981). Heating is conducted in a closed system (*i.e.*, without evaporation and steam loss). Similarly, the total concentration of carbonic species (5.540 mmole/kg for well 9) is conserved, but the distribution of carbonic species and pH change in the process of heating.

**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 samples. So, the concentration of  $\text{CO}_2$  in the vapor phase at the weir box is calculated using the distribution coefficient (Giggenbach, 1980). The vapor has 11,719 mmole/kg of  $\text{CO}_2$  in well 9. The  $\text{CO}_2$  concentration range for all wells is 393 to 11,719 mmole/kg with an average of 1901 mmole/kg.

Verma (2012a) stated the causes for such a high concentration of  $\text{CO}_2$  in the vapor phase at the weir box as

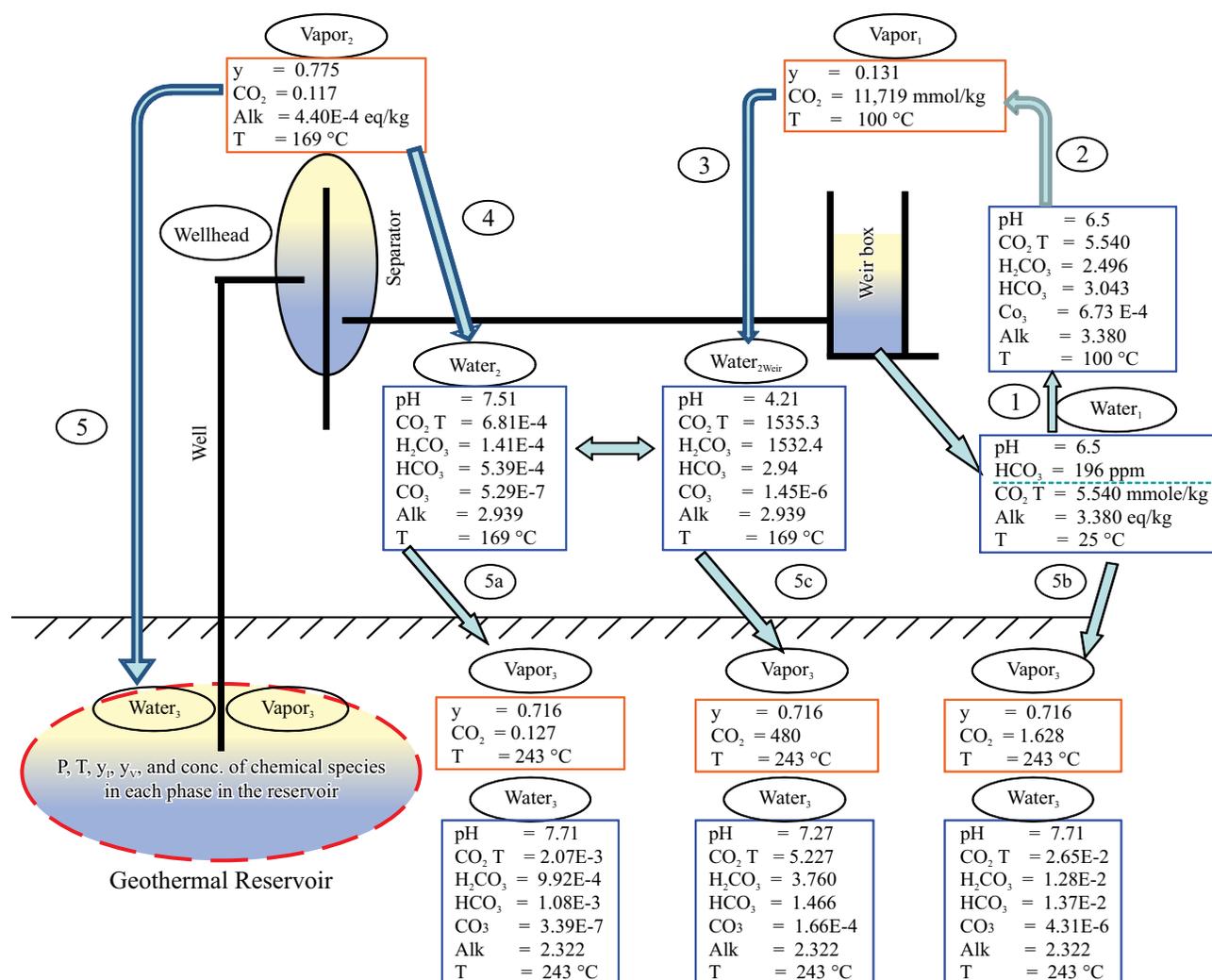


Figure 2. Illustration of the geochemical calculations for well 9, performed in five steps with Geosys.Chem, showing mainly the carbonic species. The concentrations are in mmole/kg unless specified. The calculations are explained in the text.

uncertainty in the analytical method for the measurement of  $\text{HCO}_3^-$ , non-existence of liquid-vapor equilibrium at the weir box, and uncertainty in the distribution equation for  $\text{CO}_2$ . However, the incorrect measurement of  $\text{HCO}_3^-$  is the prime factor (Verma, 2004).

**Integration of vapor-liquid to calculate the separated water composition at the separator.** The chemical composition of separated water ( $\text{Water}_{2\text{Weir}}$ ) at the separator is calculated by combining the chemical characteristics of water sample ( $\text{Water}_1$ ) and secondary vapor ( $\text{Vapor}_1$ ) at the weir box.

**Calculation of separated water composition from vapor phase.** The gaseous species are analyzed in the vapor sample ( $\text{Vapor}_2$ ). By considering the concentration of non-volatile species and alkalinity of the separated water ( $\text{Water}_{2\text{Weir}}$ ) one can construct the separated water compositions ( $\text{Water}_2$ ) from  $\text{Vapor}_2$ . There is enormous difference in the carbonic species concentrations of  $\text{Water}_2$  and  $\text{Water}_{2\text{Weir}}$ . The separated water ( $\text{Water}_2$ ) is flushed in the weir box at atmospheric conditions. This also suggests that there is not sufficient  $\text{CO}_2$  in the separated water to liberate such a large amount of  $\text{CO}_2$  (11,719 mmole/kg) in the atmospheric vapor at the weir box (see step 2). In other words, there are analytical problems in the measurement of carbonic species and/or non-existence of vapor-liquid equilibrium at the separator and weir box.

**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)  $\text{Water}_2$ , (ii)  $\text{Water}_1$  that results from the separation, at weir box, of water (*i.e.*, liquid sample) and vapor (without any gaseous species) liberated into the atmosphere, and (iii)  $\text{Water}_{2\text{Weir}}$ . The steps 5a and 5c (Figure 2) 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 in the step 5b. The results are given in Table 2.

### WATCH Computer code

The first step in using the computer code WATCH is the preparation of input data file in a text editor or through an interactive program, WAIN. The chemical speciation in the geothermal reservoir is performed by defining a reference temperature (*i.e.*, the reservoir temperature). The reference temperature may be a fixed temperature value provided by the user or calculated by the program through chemical geothermometers. The average temperature of quartz and Na/K geothermometers is most commonly used for the geochemical calculations. The calculation of the vapor fraction (excess steam) is based on the phase segregation

model (open system) proposed by Arnórsson and Stefansson (2005). In the program, it is further assumed that the phase segregation takes place between 180 °C and the initial geothermal reservoir temperature.

The reservoir parameter calculation procedure of WATCH is quite similar to that described for GeoSys.Chem: the chemical composition of secondary steam discharged in the atmosphere at the weir box is calculated from the chemical and physical parameters of the water sample ( $\text{Water}_1$ ). The characteristics of water ( $\text{Water}_2$ ) at the separator are calculated from the water sample ( $\text{Water}_1$ ) and the secondary vapor parameters ( $\text{Vapor}_1$ ). The total discharge fluid characteristics of the well are calculated by combining the properties of the separated water ( $\text{Water}_2$ ) and the vapor sample ( $\text{Vapor}_2$ ). The geothermal fluid characteristics ( $\text{Water}_3$  and  $\text{Vapor}_3$ ) are calculated from the total discharged fluid at the separator according to the procedure as described above. The results are given in Table 3.

## DISCUSSION

Table 4 presents the comparison of the calculation procedures of geothermal reservoir fluid characteristics of the computer programs GeoSys.Chem and WATCH. Most of the parameters are calculated in a similar manner by both programs. WATCH does not provide the values at the intermediate points (*e.g.*, the chemical composition of secondary vapor discharged in the atmosphere at the weir box). Thus it is not feasible to present a detailed comparison of both approaches.

### Geothermal reservoir temperature and vapor fraction

Figure 3a shows the geothermal reservoir temperatures of the wells. GeoSys.Chem uses the quartz solubility geothermometer, while the average value of quartz and Na/K geothermometers is considered in WATCH.

Initially, the quartz geothermometer was employed by considering only the liquid phase in the reservoir (Henley *et al.*, 1984). This procedure provides geothermal reservoir temperatures lower than 100°C for wells, 3 and 10, which is clearly unrealistic. Similarly, Verma (2012b) showed that there was no enthalpy balance in this approach.

Both programs, GeoSys.Chem and WATCH estimate the geothermal reservoir temperature using the quartz solubility geothermometer and assuming enthalpy conservation. GeoSys.Chem uses the linear quartz solubility equation (Verma, 2003), while WATCH uses the quartz solubility as a polynomial of absolute temperature including logarithmic terms (Gunnarsson and Arnórsson, 2000). However, both the quartz temperatures are close to each other for wells with temperature lower than 300°C. The Na/K temperature is mostly on the extreme side either lower or upper side. Thus, the Na/K temperature departs from the temperature

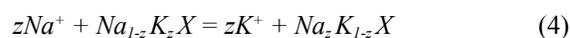
Table 2. Calculated characteristics of geothermal reservoir fluids (GeoSys.Chem). The results are presented up to 3 decimal places for comparison.

Parameter	Well 1*	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	Well 8	Well 9	Well 10
P (MPa)	7.487	5.673	3.344	5.287	8.538	6.260	8.715	7.129	3.526	3.956
T (°C)	290.420	271.950	239.950	267.450	299.590	278.370	301.050	287.070	242.980	249.710
Vapor fraction	-0.077	0.005	0.951	0.222	0.297	0.394	0.451	0.580	0.716	0.858
<i>Liquid Phase (mmole/kg liquid)</i>										
pH		7.716	7.812	7.842	7.089	7.586	8.380	8.484	7.708	7.738
Na		213.170	35.980	48.280	45.740	62.180	6.441	7.384	3.228	48.780
K		28.230	5.278	6.478	8.751	10.840	0.748	0.738	0.351	5.911
Ca		7.267	0.212	0.435	0.162	0.123	0.030	0.009	0.005	0.729
Mg		0.010	0.000	0.001	0.000	0.001	0.006	0.001	0.001	0.002
Li			1.647	1.916		3.052	0.026	0.055	0.030	2.063
Cl		258.830	44.460	57.550	58.460	72.740	1.306	2.136	1.434	56.350
SO <sub>4</sub>		0.125	0.088	0.195	0.288	0.118	1.351	0.623	0.123	0.189
<i>Carbonic species</i>										
H <sub>2</sub> CO <sub>3</sub>		0.350	0.001	0.037	0.006	0.017	0.057	0.053	0.013	0.002
HCO <sub>3</sub>		0.188	0.001	0.030	3.90E-4	0.006	0.069	0.114	0.014	0.002
CO <sub>3</sub>		2.79E-5	4.30E-7	6.68E-6	6.24E-9	5.43E-7	2.13E-5	6.52E-5	4.31E-6	5.10E-7
CO <sub>2</sub> total		0.538	0.002	0.067	0.007	0.023	0.126	0.167	0.027	0.004
<i>Boric species</i>										
B(OH) <sub>3</sub>		0.865	10.920	12.550	16.150	19.860	23.680	23.670	57.950	23.380
B(OH) <sub>4</sub>		0.021	0.475	0.429	0.062	0.327	1.860	2.722	1.924	0.773
B total		0.886	11.400	12.980	16.210	20.190	25.540	26.390	59.870	24.150
<i>Silicic species</i>										
H <sub>4</sub> SiO <sub>4</sub>		8.562	6.196	8.089	11.160	9.172	9.924	8.322	6.487	6.911
H <sub>3</sub> SiO <sub>4</sub>		0.393	0.475	0.521	0.083	0.289	1.451	1.850	0.384	0.415
SiO <sub>2</sub> total		8.955	6.671	8.610	11.250	9.461	11.370	10.170	6.871	7.326
<i>Hydrogen sulfide species</i>										
H <sub>2</sub> S		3.46E-4	1.41E-5	6.19E-5	3.54E-5	4.47E-5	3.53E-4	1.80E-4	1.65E-4	1.86E-5
HS		2.91E-4	2.82E-5	7.60E-5	3.91E-6	2.43E-5	6.47E-4	6.45E-4	2.44E-4	2.57E-5
H <sub>2</sub> STotal		6.37E-4	4.24E-5	1.38E-4	3.94E-5	6.90E-5	9.50E-4	8.25E-4	4.09E-4	4.43E-5
<i>Ammonium species</i>										
NH <sub>3</sub>		2.50E-4			3.57E-5	3.82E-5	6.44E-5	5.04E-5	9.10E-5	2.10E-5
NH <sub>4</sub>		3.84E-7			1.20E-7	6.75E-8	1.03E-8	9.12E-9	3.04E-7	5.47E-8
NH <sub>3</sub> Total		2.50E-4			3.59E-5	3.82E-5	6.44E-5	5.04E-5	9.13E-5	2.10E-5
H <sub>2</sub>		9.99E-5	1.98E-7	2.31E-6	9.19E-7	8.05E-7	4.73E-6	5.12E-6	3.96E-6	3.73E-7
CH <sub>4</sub>		1.12E-4	2.50E-7	2.88E-6	1.13E-6	9.99E-7	5.80E-6	6.33E-6	5.01E-6	4.70E-7
Alk		0.603	0.951	0.981	0.145	0.621	3.380	4.688	2.322	1.190
<i>Vapor Phase (mmole/kg vapor)</i>										
CO <sub>2</sub>		21.560	0.094	2.564	0.188	0.911	1.700	2.227	1.628	0.198
H <sub>2</sub> S		8.44E-3	7.10E-4	1.67E-3	4.63E-4	9.43E-4	3.82E-03	3.12E-3	7.72E-3	7.49E-4
NH <sub>3</sub>		1.04E-3			1.23E-4	1.51E-4	2.20E-04	1.89E-4	4.58E-4	1.01E-4
H <sub>2</sub>		2.59E-2	1.44E-4	6.92E-4	9.74E-5	1.69E-4	4.78E-4	8.13E-4	2.61E-3	1.98E-4
CH <sub>4</sub>		4.14E-2	7.80E-5	1.45E-4	1.10E-5	1.93E-5	5.69E-4	3.96E-4	8.28E-4	9.21E-5
Alk		1.04E-3			1.23E-4	1.51E-4	2.20E-4	1.89E-4	4.58E-4	1.01E-4

\*GeoSys.Chem does not work for negative vapor fractions. Therefore, the concentrations for well 1 were not calculated.

used in GeoSys.Chem and WATCH (Figure 3a).

Verma (2012c) pointed out the limitations of the Na/K cation exchange geothermometer, which is based on the following type of cation exchange reaction



where the capital  $X$  represents an anion and  $z$  denotes the stoichiometric coefficient. The limitations are the unidirectionality of the cation-exchange reaction, the undefined activity of mixed minerals,  $Na^+ = K^+$  on substituting  $z=0.5$  in Equation (4), the violation of electro-neutrality of the solution, and others.

Table 3. Calculated characteristics of geothermal reservoir fluid (WATCH). The results are presented up to 3 decimal places for comparison.

Parameter	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	Well 8	Well 9	Well 10
P (MPa)	6.850	8.190	7.677	6.609	12.479	9.155	8.380	6.545	4.296	5.346
T (°C)	274.000	285.000	291.000	280.000	327.000	304.000	298.000	281.000	254.000	268.000
Vapor fraction	0.000	0.263	0.233	0.414	0.216	0.343	0.456	0.585	0.708	0.885
<i>Liquid Phase (mmole/kg liquid)</i>										
pH	6.465	5.071	7.530	6.482	6.314	6.798	7.793	7.908	7.046	7.348
Na	7.680	203.517	80.906	46.580	41.214	60.309	6.509	6.679	3.168	48.174
K	0.761	26.954	11.868	6.250	7.884	10.058	0.756	0.751	0.345	5.837
Ca	0.033	6.938	0.651	0.420	0.146	0.114	0.031	0.009	0.005	0.721
Mg	0.003	0.009	0.002	0.001	2.06E-4	0.001	0.006	0.001	0.001	0.002
Li										
Cl	1.651	334.059	99.963	55.519	52.673	67.525	1.320	2.175	1.407	55.652
SO <sub>4</sub>	1.604	0.161	0.198	0.188	0.260	0.285	1.365	0.634	0.121	0.187
<i>Carbonic species</i>										
H <sub>2</sub> CO <sub>3</sub>	100.415	0.687	1.593	20.108	12.509	8.381	3.636	2.670	4.130	0.581
HCO <sub>3</sub>	4.183	0.506	0.601	0.918	0.107	0.433	1.654	2.531	1.036	0.268
CO <sub>3</sub>			1.67E-4		<		3.33E-4	1.00E-3	1.67E-4	
CO <sub>2</sub> total	104.599	1.193	2.195	21.026	12.616	8.814	5.290	5.203	5.167	0.848
<i>Boric species</i>										
B(OH) <sub>3</sub>	13.302	1.135	24.680	12.484	14.582	18.621	24.665	25.183	58.181	23.254
B(OH) <sub>4</sub>	0.026	1.27E-4	0.728	0.031	0.019	0.090	0.879	1.296	0.449	0.458
B total	13.328	1.135	25.408	12.515	14.602	18.711	25.544	26.479	58.630	23.712
<i>Silicic species</i>										
H <sub>4</sub> SiO <sub>4</sub>	11.046	11.321	14.530	8.275	10.118	8.739	11.169	9.834	6.671	7.027
H <sub>3</sub> SiO <sub>4</sub>	0.022	0.107	0.309	0.019	0.006	0.027	0.292	0.473	0.066	0.147
SiO <sub>2</sub> total	11.068	11.428	14.839	8.294	10.124	8.766	11.462	10.306	6.737	7.174
<i>Hydrogen sulfide species</i>										
H <sub>2</sub> S	0.157	0.006		0.593	0.455	0.067	0.190	0.139	0.129	0.000
HS	0.011	0.002		0.047	0.006	0.006	0.144	0.229	0.057	0.012
H <sub>2</sub> S total	0.169	0.008		0.640	0.461	0.073	0.333	0.369	0.186	0.012
<i>Ammonium species</i>										
NH <sub>3</sub>	0.062				0.774	0.738	0.097	0.089	0.103	0.019
NH <sub>4</sub>	0.001				0.002	0.002			0.001	
NH <sub>3</sub> total	0.063				0.777	0.739	0.097	0.089	0.104	0.019
H <sub>2</sub>										
CH <sub>4</sub>										
Alk										
<i>Vapor Phase (mmole/kg vapor)</i>										
CO <sub>2</sub>		627.305	0.000	1615.263	350.836	393.452	195.251	209.734	594.512	61.030
H <sub>2</sub> S		1.878	0.000	14.471	3.817	0.945	3.072	3.329	5.715	0.378
NH <sub>3</sub>					0.400	0.901	0.141	0.187	0.331	0.050
H <sub>2</sub>		0.695	0.000	5.660	0.943	1.399	0.347	1.196	1.935	0.099
CH <sub>4</sub>		0.966	0.000	1.252	0.132	0.171	0.412	0.029	0.612	0.047
Alk										

Figure 3b shows the results of the recalculation of the total discharge (reservoir) enthalpy from the reservoir temperature (pressure) and vapor fraction. The quartz geothermometer, by considering only liquid in the reservoir, provides lower, equal or higher values of enthalpy than the measured enthalpy for wells with positive, zero or negative values of vapor fraction, respectively.

The enthalpy recalculation results are, in general, consistent for both programs GeoSys.Chem and WATCH.

In case of WATCH, the wells 2 and 4 have higher enthalpy, while the well 3 has lower enthalpy than the corresponding measured enthalpy. Additionally, WATCH provides the reservoir conditions (*i.e.*, pressure and temperature) in the compressed liquid region for wells 1 and 2; however, the vapor fraction value for well 2 is positive, which is unlikely. The enthalpy is calculated by considering the conditions along the saturation curve, thus the vapor fraction value for well 2 is questionable.

Table 4. A comparison of the calculation procedures for geothermal reservoir parameters programmed in the different computer codes .

Parameter	GeoSysChem	WATCH
Temperature	QrtzGeotherm	Geotherm
Vapor fraction	QrtzGeotherm	Geotherm
Negative vapor fraction	No	No
Programming approach	OOP	Procedural
Programming language	VB.NET	FORTRAN
pH calculation	Alkalinity conservation	Alkalinity (conserved sum of weak acids)
Vapor alkalinity	Yes	No
Mineral precipitation	No	No
Two phases: vapor and liquid	Yes	Yes
Analysis quality	Ionic charge balance	Ionic charge balance
Analyst	Mahendra P. Verma	Kizito Opondo

QrtzGeotherm: Quartz geothermometry (Verma, 2012b); Geotherm: Average temperature of quartz and Na/K geothermometers (Arnorsson 2000a).

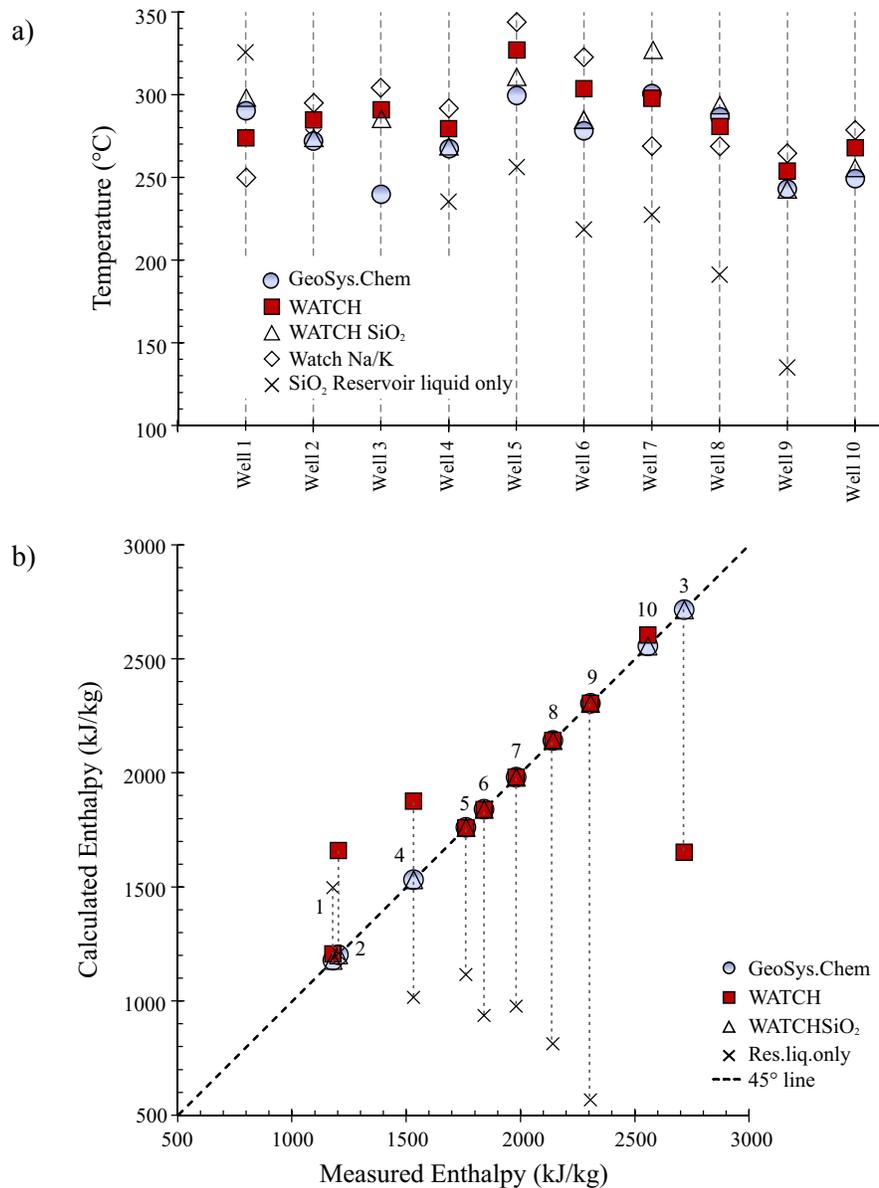


Figure 3. Comparison of (a) calculated geothermal reservoir temperature, and (b) calculated and measured enthalpy for all the wells.

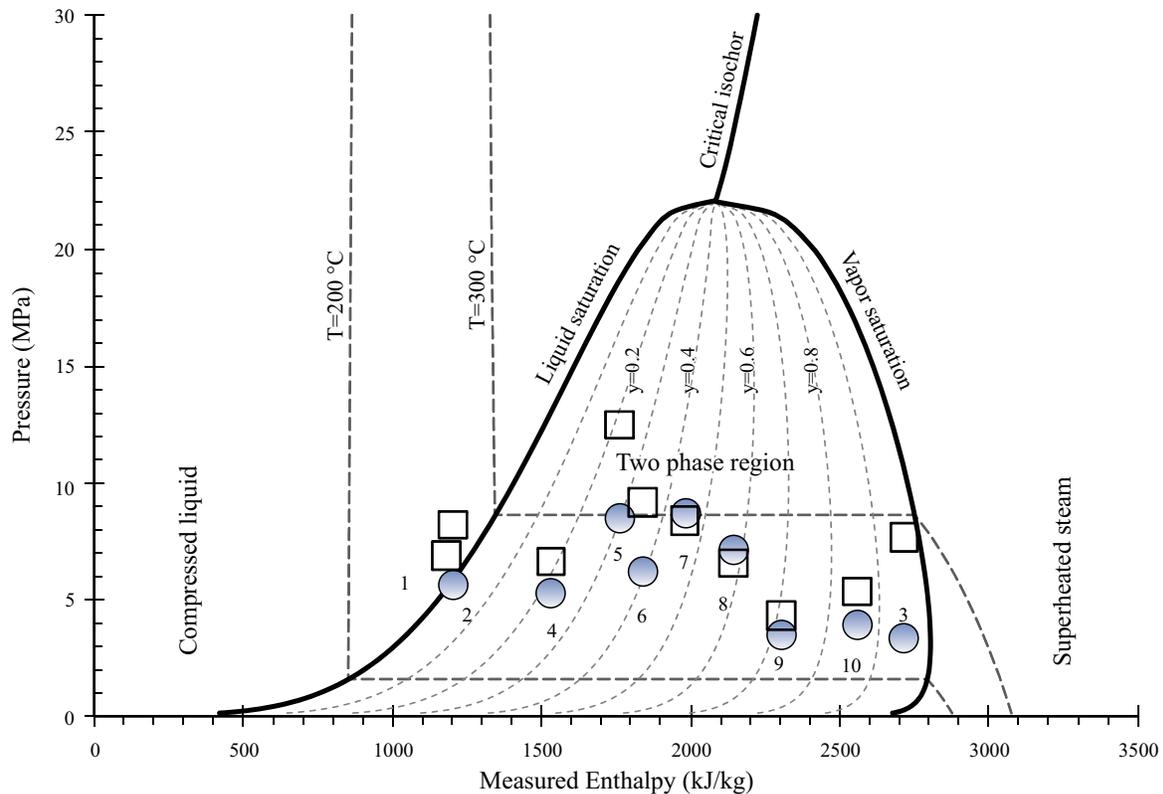


Figure 4. Enthalpy versus pressure diagram, showing the results for the ten wells obtained with GeoSys.Chem (circles) and WATCH (squares).

### Enthalpy-pressure diagram

The enthalpy versus pressure diagram (Figure 4) serves as a mechanism for understanding the evolution of a geothermal reservoir during exploitation (Arellano *et al.*, 2005). The separation boundary between the liquid and vapor phases is formed by the critical isochor and the two-phase region. Most of the wells are in the two-phase region, between the isotherms at 200 and 300 °C. The locations of the well data from GeoSys.Chem and WATCH are close except for wells 3, 5 and 6., which may be a consequence of the different geothermal reservoir temperatures used in the programs.

### Behavior of chemical species

The first check on the chemical composition of geothermal reservoir fluids is the ratio of non-volatile species like Na/K. The Na/K ratio calculated by both programs for the geothermal reservoir fluids is the same as that reported for analyzed water samples.

Figure 5a shows the variation of the concentration of CO<sub>2</sub> in the vapor phase in the geothermal reservoir. The values of the CO<sub>2</sub> concentration in the vapor phase of the reservoir fluid in well 2 are 4062 and 627 mmole/kg, for GeoSys.Chem and WATCH, respectively. However, the well has a very small fraction of vapor (<1%). So, a small

difference in the algorithm and other parameters like pH may produce significant differences in the value of CO<sub>2</sub>.

As discussed earlier, GeoSys.Chem conducts the calculation of geothermal reservoir fluid characteristics by considering three possibilities: (i) Water<sub>2</sub>, (ii) water that liberates vapor only (*i.e.*, without any gaseous species) at the weir box in forming Water<sub>1</sub>, and (iii) Water<sub>2Weir</sub>. These cases are identified here as GeoSys.Chem 1, GeoSys.Chem 2, and GeoSys.Chem 3, respectively. In the case GeoSys.Chem 3 there is a maximum concentration of CO<sub>2</sub>, since the CO<sub>2</sub> concentration of vapor liberated in the atmosphere at the weir box is considered.

The total concentration of CO<sub>2</sub> in the geothermal reservoir is shown in Figure 5b, where it can be observed that CO<sub>2</sub> concentrations are higher in the case of WATCH than in the case of maximum CO<sub>2</sub> of GeoSys.Chem (GeoSys.Chem 3). This suggests that CO<sub>2</sub> concentrations in the secondary vapor liberated at the weir box are even higher in the case of WATCH. It is well known that the geothermal systems have very little environmental impact and cannot liberate such a large amount of CO<sub>2</sub> (11,719 mmole/kg). We consider that this is an artifact due to analytical errors in the measurement of carbonic species. Thus there is a need to revise the measurement of carbonic species in the vapor and liquid phase of geothermal fluid samples.

Figure 5c shows the comparison of pH values obtained from both the programs. The differences in the values are the consequence of carbonic species concentration. The pH

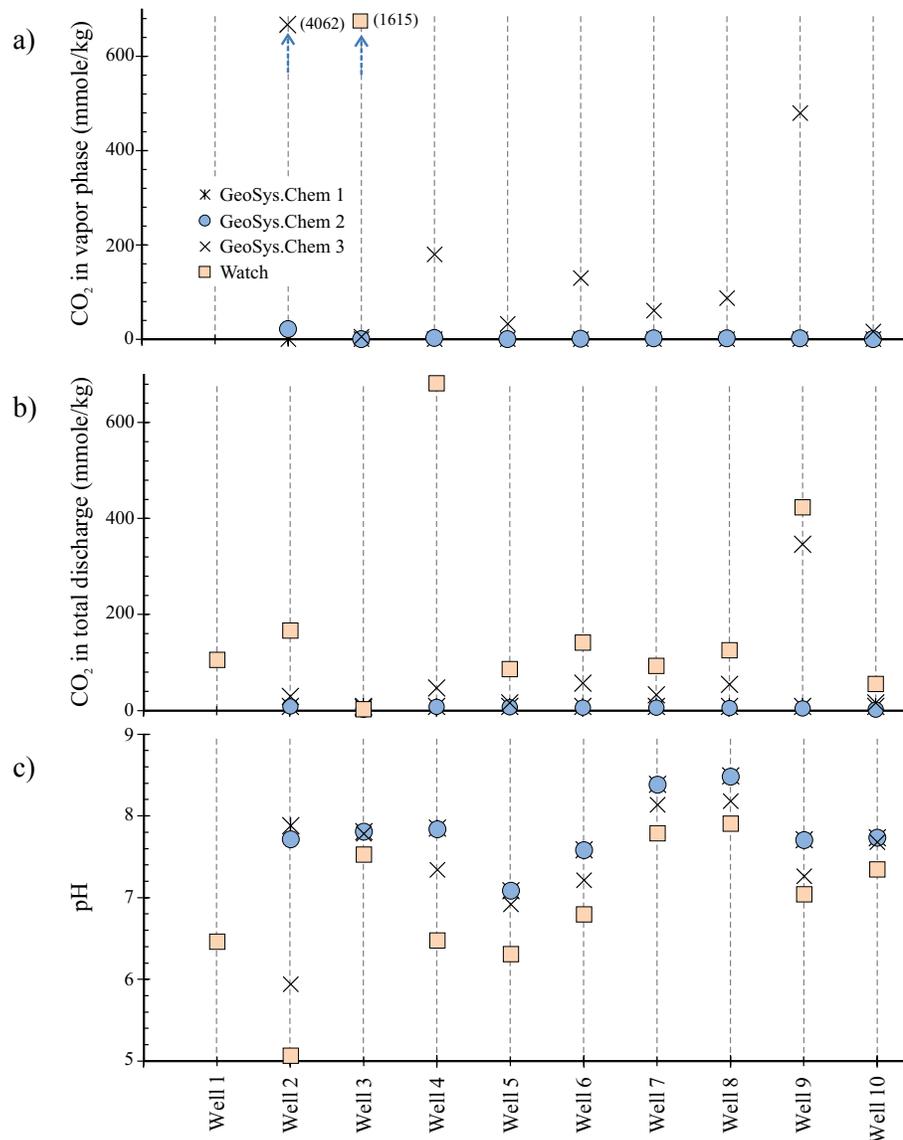


Figure 5. Behavior of chemical species in the geothermal reservoir: (a) CO<sub>2</sub> in the vapor phase, (b) CO<sub>2</sub> in the total discharge, and (c) pH in the liquid phase.

is a master variable in geothermal chemical modeling of any aquatic system, including geothermal systems (Stumm and Morgan, 1981). Thus the analytical quality of carbonic species is of prime importance.

## CONCLUSIONS

The conclusions of this study on the calculation of deep reservoir fluid characteristics from surface samples of liquid and vapor phases as the first step in geochemical modeling of geothermal systems may be summarized as follows:

Both the programs, GeoSys.Chem and WATCH have similar procedure for the calculation of pH and vapor fraction in the geothermal reservoir fluid.

The assignation of average temperature of SiO<sub>2</sub> and

Na/K of geothermometers causes substantial differences in the calculated reservoir fluid properties of high enthalpy and low vapor fraction wells. Additionally, there are conceptual limitations of cation exchange geothermometers (Verma, 2012c). Thus it is recommended to use only SiO<sub>2</sub> geothermometry, although there is high uncertainty in the calculated temperature (Verma, 2012b).

In the absence of good quality analysis of carbonic species it is suggested to consider the CO<sub>2</sub> 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 CO<sub>2</sub> in the atmospheric vapor at the weir box) for the geothermal reservoir fluid composition calculations.

The concentration of CO<sub>2</sub> highly influences the geothermal reservoir fluid pH, and pH is a master variable in geochemical modeling (Stumm and Morgan, 1981). Thus

it is of prime importance to revise the analytical procedures for the measurement of carbonic species concentration in the vapor and liquid samples.

## ACKNOWLEDGMENTS

This work is dedicated in the memory of a friend and colleague, Ignacio Salvador Torres Alvarado. He was working on this project since November, 2011. He wrote us on Friday night, January 13, 2012, "... *I have been working on it and I will surely send you my results before 31 Jan., 2012. ...*". Unfortunately, he passed away due to a sudden illness in the morning of January 15, 2012. Authors appreciate the reviewers, Yuri Taran and Héctor Panarello for their constructive comments to improve the content of the manuscript.

## REFERENCES

- Arellano, V.M., García, A., Barragán, R.M., Izquierdo, G., Aragón, A., Nieva, D., 2003, An updated conceptual model of the Los Hornos geothermal reservoir (Mexico): *Journal Volcanology and Geothermal Research*, 124, 67-88.
- Arellano, V.M., Barragan, R.M., Torres, M.A., 2005, Thermodynamic evolution of the Los Azufres, Mexico, geothermal reservoir from 1982 to 2002: *Geothermics* 34, 592-616.
- Arnórsson, S., Andrésdóttir, A., 1995, Processes controlling the distribution of boron and chlorine in natural waters in Iceland: *Geochimica et Cosmochimica Acta*, 59, 4125-4146.
- Arnórsson, S., Stefánsson, A., 2005, Wet steam well discharges. I. Sampling and calculation of total discharge compositions: Antalya, Turkey, *Proceedings of the World Geothermal Congress 2005*, 8 pp.
- Arnórsson, S., Sigurdsson, S., Svavarsson, H., 1982, The chemistry of geothermal water in Iceland. I. Calculation of aqueous speciation from 0° to 370°C: *Geochimica et Cosmochimica Acta*, 4, 1513-1532.
- Barragan, R.M., Nieva, D., 1989, EQYAC: Program for determining geothermal reservoir chemical equilibrium: *Computers & Geosciences*, 15, 1221-1240.
- Bernard, R., Taran Y., Pennisi, M., Tello, E., Ramirez, A., 2011, Chloride and Boron behavior in fluids of Los Hornos geothermal field (Mexico): A model based on the existence of deep acid brine: *Applied Geochemistry*, 26, 2064-2073.
- Bethke, C.M., 1992, The question of uniqueness in geochemical modeling: *Geochimica et Cosmochimica Acta*, 56, 4315-4320.
- Bethke, C.M., 1994, *The Geochemist's Workbench, Version 2.0, a User's Guide to Rxn, Act2, Tact, and Gtplot*: USA, University of Illinois, Department of Geology, Hydrology Program, 174 pp.
- Giggenbach, W.F., 1980, Geothermal gas equilibria: *Geochimica et Cosmochimica Acta*, 44, 2021-2032.
- Giroud, N., 2008, A chemical study of arsenic, boron and gases in high-temperature geothermal fluids in Iceland: Iceland, University of Iceland, Faculty of Science, Ph.D. Thesis, 110 pp.
- Gunnarsson, I., Arsnórsson, S., 2000, Amorphous silica solubility and the thermodynamic properties of  $\text{H}_2\text{SiO}_4^0$  in the range 0° to 350°C at  $P_{\text{sat}}$ : *Geochimica et Cosmochimica Acta*, 64, 2295-2307.
- Henley, R.W., Truesdell, A.H., Barton, P.B., Whitney, J.A., 1984, Fluid-mineral equilibria in hydrothermal systems: El Paso, TX, Society of Economic Geologists, *Reviews in Economic Geology*, v. 1, 267 pp.
- Kharaka, Y.K., Barnes, I., 1973, SOLMNEQ: Solution-Mineral Equilibrium Computations: NTIS Technical Report PB-214-899, 82 pp.
- Nordstrom, D.K., Plummer, L.N., Wigley, T.M.L., Wolery, T.L., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, B., Hoffman, M., Holdren, G.R., Lafon, G.M., Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.M., Sposito, G., Thraillkill, J., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, *in* Jenne, E.A. (ed.), *Chemical Modeling of Aqueous systems*: American Chemical Society, Symposium Series 93, 857-892.
- Plummer, L.N., Parkhurst, D.L., Fleming, G.W., Dunkle, S.A., 1988. PHRQPITZ- a Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines: United States Geological Survey, Water-Resources Investigations, Report 88-4153, 310 pp.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991, An Interactive Code (NETPATH) for Modeling NET Geochemical Reactions along a Flow PATH: United States Geological Survey, report 91-4078, 227 pp.
- Reed, M.H., 1982, Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases and an aqueous phase: *Geochimica et Cosmochimica Acta* 46, 513-528.
- Stumm, W., Morgan, J.J., 1981, *Aquatic Chemistry: an Introduction Emphasizing Chemical Equilibria in Natural Waters*: New York, Wiley, 780 pp.
- Tello, E., 2005, Estado de equilibrio soluto-mineral y saturación de minerales de alteración en fluidos geotérmicos de alta temperatura de México: Universidad Nacional Autónoma de México, Facultad de Ingeniería, Ph.D. Thesis, 271 pp.
- Torres-Alvarado, I.S., 2002, Chemical equilibrium in hydrothermal systems: the case of Los Azufres geothermal field, Mexico: *International Geology Review*, 44, 639-652.
- Truesdell, A.H., Jones, B.F., 1974, WATEQ a Computer Program for Calculating Chemical Equilibria of Natural Waters: United States Geological Survey Journal of Research, 2, 233-248.
- van Gaans, P.F.M., 1989, WATEQX: a restructured, generalized, and extended FORTRAN 77 computer code and database format for the WATEQ aqueous chemical model for element speciation and mineral saturation, for use on personal computers and mainframes: *Computers & Geosciences* 15, 843-887.
- Verma, M.P., 2003, QrtzGeotherm: a computer program for the quartz solubility geothermometer in moderately saline brines up to 270°C: *Transactions – Geothermal Research Council*, 341-346.
- Verma, M.P., 2004, A revised analytical method for  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  determinations in geothermal waters: An assessment of IAGC and IAEA interlaboratory comparisons. *Geostandards and Geoanalytical Research*, 28, 1-19.
- Verma, M.P., 2008, QrtzGeotherm: an AcitveX component for the quartz solubility geothermometer: *Computers & Geosciences*, 34, 1918-1925.
- Verma M.P., 2012a, GeoSys.Chem: Estimate of reservoir fluid characteristics as first step in geochemical modeling of geothermal systems: *Computers & Geosciences*, 49, 29-37.
- Verma, M.P., 2012b, QrtzGeotherm: A revised algorithm for quartz solubility geothermometry to estimate geothermal reservoir temperature and vapor fraction with multivariate analytical uncertainty propagation: *Computers & Geosciences*, 48, 316-322.
- Verma, M.P. 2012c, Cation exchange geothermometry: a critique: *Geothermia*, 25, 53-56.
- Westall, J.C., Zachary, J.L., Morel, F.M.M., 1976, MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems: Cambridge, M.A., Massachusetts Institute of Technology, Department of Civil Engineering, Technical Note No. 18, 91 pp.
- Wolery, T.J. 1983, EQ3NR a computer program for geochemical aqueous speciation-solubility calculations: user's guide and documentation: Livermore, CA, University of California, Lawrence Livermore Laboratory, Report UCRL 53414, 191 pp.

Manuscript received: April 10, 2012

Corrected manuscript received: August 8, 2012

Manuscript accepted: August 10, 2012