1. Introduction

Geothermal reservoirs can be considered closed systems in which fluid-rock interaction processes take place at relatively high temperatures (≥150 °C) and hence the assumption of chemical equilibrium is justified (Truesdell et al., 1987). For this reason the chemistry of fluids discharged by geothermal wells reflects important characteristics of the deep conditions, which are useful for evaluating the resource and deciding on its optimal utilization. In order to estimate the capacity of liquid and steam-dominated reservoirs to produce power the volumetric liquid saturation, which is defined in terms of temperature and in situ amount of steam in the two-phase original fluid, should be investigated (D’Amore and Pruess, 1986; D’Amore, 1992; D’Amore and Truesdell, 1995). When the liquid saturation is close to zero in a reservoir, in most cases the flow will decrease rapidly and will not support electric power generation. In two-phase reservoirs when water is produced this is taken as a good indication of relatively high liquid saturations in the reservoir. Besides, the chemical composition of water helps in estimating reservoir conditions like deep temperatures through liquid geothermometers. By contrast, in steam-dominated reservoirs the liquid remains in the rock as an immobile phase and no water is produced to give an indication of actual liquid saturation conditions at the reservoir which are needed to evaluate the resource potential. For both wet two-phase and dry geothermal wells the chemistry of steam through the modeling of mineral-gas reactions allows estimation of deep conditions in terms of reservoir temperatures and in situ two-phase conditions. Among a number of existing steam models (D’Amore and Panichi, 1992).
2. Description of the FT-HSH gas equilibrium methods (Siega et al. 1999)

For the three equilibrium models FT-HSH1, FT-HSH2 and FT-HSH3, the Fisher–Tropsch reaction (FT) which is given in Eq. (1) is considered.

\[(FT): \text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}\]  
(1)

For the FT-HSH1 method, the pyrite-magnetite (HSH1) mineral buffer is considered to be controlling the concentration of \(H_2S\) in fluids. This reaction is given in Eq. (2):

\[(HSH1) \ 2H_2 + 2H_2O + 3/2FeS_2 = 3H_2S + 1/2FeS_O\]  
(2)

While for the FT-HSH2 method, the concentration of \(H_2S\) in fluids is considered to be controlled by a mineral buffer resulting from the combined pyrite-magnetite and pyrite-hematite equilibria, according to Eq. (3):

\[(HSH2) 5/4H_2 + 1/4Fe_2O_3 + 3/2FeS_2 + 7/4H_2O = 3H_2S + FeS_O\]  
(3)

And for the FT-HSH3 method, the concentration of \(H_2S\) in fluids is considered to be controlled by a mineral buffer resulting from the combined pyrite-magnetite and pyrite-pyrrhotite equilibria, according to Eq. (4):

\[(HSH3) H_2 + FeS_2 = H_2S + FeS\]  
(4)

Thermodynamic equilibrium constants for the reactions given in Eqs. (1)–(4) expressed in molar proportion with respect to \(H_2O\) are given as follows:

\[\log K_{FT} = 4 \log P_{H_2} + \log P_{CO_2} - \log P_{CH_4} - 2 \log P_{H_2O}\]  
(5)

\[\log K_{HSH1} = 3 \log P_{H_2S} - log P_{H_2} - 2 \log P_{H_2O}\]  
(6)

\[\log K_{HSH2} = 3 \log P_{H_2S} - 5/4 \log P_{H_2} - 7/4 \log P_{H_2O}\]  
(7)

\[\log K_{HSH3} = \log P_{H_2S} - \log P_{H_2}\]  
(8)

and writing the constants in terms of the water partial pressure, according to (D’Amore, 1992):

\[\log P_i = \log \left(\frac{n_i/n_{H_2O}}{C_0}\right) - \log A_i + \log P_{H_2O}\]  
(9)

where \(\frac{n_i/n_{H_2O}}{C_0}\) is the molar ratio of \(i\) component regarding the total water. The coefficient \(A_i\) for every species “\(i\)” is defined as a function of temperature and the steam fraction “\(y\)”. In following equations \(y > 0\) refers to vapor gain while \(y < 0\) refers to vapor loss:

\[\text{If } y \geq 0: A_i = y + (1-y)/B_i\]  
(10)

\[\text{If } y < 0: A_i = 1/(B_i (1 + y-yB_i))\]  
(11)

\(B_i\) is the distribution coefficient for every gas which is a function of temperature (Giggenbach, 1980; D’Amore, 1992). For temperatures between 100 and 340 °C, \(t\) in °C:

\[\log B_{CO_2} = 4.7593 - 0.01092t\]  
(12)

\[\log B_{H_2S} = 4.0547 - 0.00981t\]  
(13)

\[\log B_{CH_4} = 6.0783 - 0.01383t\]  
(14)

\[\log B_{H_2} = 6.2283 - 0.01403t\]  
(15)

Thus, equilibrium equations for every reaction are as follows.

\[\text{For } FT = \log K_{FT} + 4 \log P_{H_2} + \log P_{CO_2} - \log P_{CH_4} - 2 \log P_{H_2O}\]  
(16)

\[\text{For } HSH1 = \log K_{HSH1} + 3 \log P_{H_2S} - \log P_{H_2}\]  
(17)

\[\text{For } HSH2 = \log K_{HSH2} + 3 \log P_{H_2S} - 5/4 \log P_{H_2}\]  
(18)

\[\text{For } HSH3 = \log K_{HSH3} + \log P_{H_2S} - \log P_{H_2}\]  
(19)

Equilibrium constants of the general form, where \(T\) is in K:

\[\log K = a + b/T + c \log(T)\]  
(20)

Table 1 gives the constants \(a, b\) and \(c\) for every reaction.

The equilibrium equations can be expressed as a molar proportion of every species with respect to \(H_2O\). The logarithm used is base 10.

\[\text{FT} = 4 \log(P_{H_2}/P_{H_2O}) + \log(P_{CO_2}/P_{H_2O}) - \log(P_{CH_4}/P_{H_2O})\]  
(21)

\[\text{HSH1} = 3\log(P_{H_2S}/P_{H_2O}) - \log(P_{H_2}/P_{H_2O})\]  
(22)

\[\text{HSH2} = 3\log(P_{H_2S}/P_{H_2O}) - 5/4 \log(P_{H_2}/P_{H_2O})\]  
(23)

\[\text{HSH3} = 3\log(P_{H_2S}/P_{H_2O}) - \log(P_{H_2}/P_{H_2O})\]  
(24)

The graphical solutions of Eqs. (16) and (17); (16) and (18) and (16) and (19) provide the theoretical grids in the coordinates (HSH1, FT), (HSH2, FT) and (HSH3, FT), given in Figs. 1–3 respectively, to be used as frame references. The parameters FT, HSH2 and HSH3 are obtained from the gas compositions according to Eqs. (21–24) where concentrations of gas species are taken in

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Coefficients (a, b) and (c) for the reactions (Siega et al., 1999).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{FT})</td>
<td>-4.330</td>
</tr>
<tr>
<td>(K_{HSH1})</td>
<td>6.449</td>
</tr>
<tr>
<td>(K_{HSH2})</td>
<td>7.609</td>
</tr>
<tr>
<td>(K_{HSH3})</td>
<td>4.940</td>
</tr>
<tr>
<td>(P_{H_2O})</td>
<td>5.510</td>
</tr>
</tbody>
</table>
the total discharge fluid.

Alternatively, (Eqs. (21) and 22), (21) and (23) and (21)–(24) can be solved numerically to provide the temperature and the steam fraction, according to methods FT-HSH1, FT-HSH2 and FT-HSH3, respectively. This is automatically performed by the EQUILGAS program. The following considerations should be taken into account when these methods are used (D’Amore, 1998):

(1) Thermodynamic equilibrium must be attained in the considered reactions.
(2) All the considered chemical species (including water) must be in both chemical and phase equilibrium.
(3) No water gain or loss is allowed after the original equilibration of the system.
(4) The fluid at wellhead generally consists of fluids coming from various sources in the reservoir with different chemical and physical characteristics. Then what it is obtained through the application of this method are integrated values of the steam fraction and temperature for all these different sources. This is important when the different sources have different gas/water ratios. When a deep hot zone of the reservoir located below the exploited reservoir, rich in reactive gas species and CO2, supplies an important fraction of the total produced gas, an overestimation of the local reservoir temperature and y values are obtained.
(5) It is assumed that there is no re-equilibration of the chemical species from the source or sources to wellhead.

Siega et al. (1999) provided the following criteria for deciding which of the FT-HSH methods is more appropriate for a specific application.

(1) FT-HSH1 method is suitable for mature, equilibrated, liquid-dominant systems, in which the steam is produced by boiling of the deep liquid.
(2) FT-HSH2 method considers more oxidizing conditions at the reservoir and is suitable for steam-dominated systems and two phase reservoirs with relatively high contents of non-condensable gases in steam. FT-HSH2 method is useful when the gas compositions show relatively high H2S but minimum H2 concentrations.
(3) FT-HSH3 method is suitable in steam-dominated reservoirs containing magmatic constituents and usually gas discharges containing relatively high contents of H2.

When the reservoir temperature and the fraction of steam in the two-phase mixture are estimated the liquid saturation at the reservoir ($S_L$) can be obtained from Eq. (25) (D’Amore and Truesdell, 1995):

$$S_L = \frac{(1-y)V_L}{(1-y)V_L + yV_V}$$

where $V_L$ and $V_V$ are the specific volumes of liquid and steam at the reservoir temperature respectively and $y$ is the fraction of steam in the two-phase fluid at the reservoir.
3. Total discharge fluid calculations

The chemical composition of the gas species in geothermal fluids is determined in steam samples collected from geothermal wells by using standard procedures (Giggenbach, 1980; Arnórsson et al., 2006). When the wells produce only steam, it is assumed that the steam, as collected, is representative of the fluid flowing from the reservoir to the wellhead through the pipe, which is usually called the total discharge fluid. However when wells produce two-phase fluids, the gas concentrations in the total discharge fluid should be calculated taking into account the amount of steam removed due to the (liquid-steam) separation process. This separation of phases occurs because of the fluid pressure-drop during the ascent from the reservoir to the wellhead.

The concentrations of gas species “$i$” ($c_i$) in the total discharge fluid are calculated according to Henley et al. (1984):

$$ (c_i)_{TD} = y_s (c_i)_s + (1 - y_s) (c_i)_l $$

where “$y_s$” represents the steam fraction removed at sampling conditions and subscripts s and l refer to steam and liquid phases.

For a specific separation temperature ($T_s$), the steam fraction removed ($y_s$) from the total fluid is calculated from an enthalpy ($H$) balance:

$$ H_{TD} = y_s (H_s)_{TD} + (1 - y_s) (H_l)_{TD} $$

where $H_{TD}$ refers to the wellhead enthalpy while $H_s$ and $H_l$ represent the enthalpies of steam and liquid phases at the given temperature and are taken from the steam tables. The steam fraction at sampling, “$y_s$”, is obtained from Eq. (28):

$$ y_s = (H_{TD} - (H_l)_{TD}) / (H_s - H_l)_{TD} $$

4. Program description

The EQUILGAS program was written in Visual Fortran for Windows (Lawrence, 2002); it was developed for calculating both the temperatures and two-phase conditions of reservoirs using FT-HSH gas equilibrium models by a numerical approach. The flowchart of EQUILGAS is given in Fig. 4.

For the FT-HSH1 method the constant parameters FT and HSH1 are obtained from the chemical composition of gas samples and referred to the total discharge fluid, (Eq. (26)) as it is the fluid that ascends to the wellhead before separation of steam due to decompression (Eq. (28)). FT and HSH1 parameters are related to the reservoir temperature ($T$) and the steam fraction ($y$) according to Eqs. (16), (17) and (21), (22). Thus, $T$ and $y$ can be obtained by solving the following system of non-linear equations:

$$ FT[ T, y ] = FT_a $$

$$ HSH1[ T, y ] = HSH1_a $$

Newton’s method is widely used to find the root $x$ of a non-linear function $f(x)$ (Weihong et al., 2009). The iterative process is given by:

$$ x_{n+1} = x_n - \left[ J(\tilde{x}_n) \right]^{-1} \tilde{F}(\tilde{x}_n) $$

where $J(\tilde{x}_n)$ is the Jacobian matrix defined by:

$$ J(\tilde{x}_n) = \begin{bmatrix} \frac{\partial F_1}{\partial x_1} & \frac{\partial F_1}{\partial x_2} \\ \frac{\partial F_2}{\partial x_1} & \frac{\partial F_2}{\partial x_2} \end{bmatrix} $$

In order to obtain the derivatives of the Jacobian matrix a central differences approach was used. A modified Powell algorithm was used to solve the nonlinear system of equations (Powell, 1970).

As an example, Table 2 shows the results from the Newton method for a specific data where $FT_a = -15$ and $HS1_a = -10$; for this example, initial values for $T_0$ and $y_0$ of 300 and 0 were taken.

![Fig. 4. Flowchart of EQUILGAS program.](image-url)
The solution is given at the 6th iteration, \( t = 169.8 \) and \( y = 0.178124 \).

The EQUILGAS program is provided through the journal website. The program can be installed on a Windows PC by using a friendly interface. Fig. 5 shows the screen displayed by EQUILGAS. Input data can be either typed when running the program or can be provided by an external file. In the same way, results are given through the screen and subsequently they can be saved.

The following steps are followed in running the program once the file is opened by clicking the menu File.

Input data should be given as follows: Sample code, separation temperature (°C), steam fraction at sampling, (gas/water) ratio in steam (‰ mol), gas concentrations in the following order CO2, H2S, H2, CH4, N2 and NH3 in (‰ mol, dry basis), reservoir temperature in K (an arbitrary value, a constant value of 573 can be used) and date, leaving a blank space between day, month and year (DD MM YY). This file should be saved in Notepad format with \[ .txt \] extension with no headlines (Fig. 6).

Then select the equilibrium model to be used by clicking the option (Fig. 7).

The option “Run” appears in active mode (in the first line), this option should be selected in order to run the program. Fig. 8 shows the results: sample code, date, FT, HSH, reservoir temperature, fraction of reservoir steam and the value of the minimized error function \( |F(X_n)| \).

5. Examples for Mexican fields

In order to illustrate the use of FT-HSH methods, examples for Mexican geothermal fields are given as follows.

The Cerro Prieto geothermal field, located in Baja California, northwestern México, is the largest liquid-dominated resource developed in the world (Truesdell et al., 2003). Cerro Prieto I (CP I) sector was the first production area in which the well discharges were representative of a 260–300 °C liquid-dominated reservoir

<table>
<thead>
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<th>Iteration</th>
<th>Iterative results.</th>
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<tr>
<td>0</td>
<td>300.000000</td>
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<tr>
<td>1</td>
<td>237.943586</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>170.453581</td>
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<tr>
<td>4</td>
<td>169.819707</td>
</tr>
<tr>
<td>5</td>
<td>169.800192</td>
</tr>
<tr>
<td>6</td>
<td>169.800192</td>
</tr>
</tbody>
</table>

Fig. 5. Screen displayed by EQUILGAS.

Fig. 6. Example of data file for well A-5 from Los Azufres geothermal field.

Fig. 7. Screen displayed by EQUILGAS to select the model to be used.

Fig. 8. Results displayed by EQUILGAS in the following order: sample code, date, FT, HSH, reservoir temperature, fraction of steam in the reservoir and the value of the function to be minimized.
Data for Los Azufres well LA-5 (2005) that produces dry steam and for the Los Humeros two-phase well LH-6 (data for 1987–1992) with a high steam fraction at separation conditions were used.

The FT-HSH3 method has been used to study the Cerro Prieto IV (CP IV) sector deep characteristics (Barragan et al., 2006; Arellano et al., 2003; 2004; 2005; 2006; 2011). CP IV is located to the NE of the Cerro Prieto field, not far from the location of the gases upflow of the field (Truesdell et al., 2003), thus the presence of magmatic species has been noticed in well discharges. The behavior of well 404 (data for 2002–2004) is discussed as an example.

Table 3 shows chemical compositions of steam samples of representative Cerro Prieto I, Los Azufres, Los Humeros and Cerro Prieto IV wells. FT: Separation temperature; ys: steam fraction at sampling; XG: nc gas/water in steam (%mol); Gas concentrations (%vol) dry basis; TC: Guess for reservoir temperature, it could be 573 K for geothermal reservoirs and H2S: measured enthalpy.

The FT-HSH3 method has been used to study the Cerro Prieto IV (CP IV) sector deep characteristics (Barragan et al., 2006; Arellano et al., 2011). CP IV is located to the NE of the Cerro Prieto geothermal field, not far from the location of the gases upflow of the field (Truesdell et al., 2003), thus the presence of magmatic species has been noticed in well discharges. The behavior of well 404 (data for 2002–2004) is discussed as an example.

Table 3 shows chemical compositions of steam samples of representative wells of Cerro Prieto I (CPI), Los Azufres (LA), Los Humeros (LH) and Cerro Prieto IV (CPIV). Depending on the measured enthalpies at wellhead, the wells listed in Table 3 have different steam fractions at separation conditions (ys) given by Eq. (28) as follows. The CPI wells 131 and 138 are characterized by relatively low total discharge enthalpies in the two-phase wells LH-6 and 404 produce ys of 0.75 and ~0.55, respectively. As shown by the data in Table 3, in all the wells the CO2 is the major component while H2S is the second in Los Azufres and Los Humeros wells but H2 is the second in the CP IV well (for 2003 and 2004 data) and for CP I wells H2S concentrations compare well with these of CH4.

Numerical results for FT, HSH, reservoir temperatures and fractions of steam provided by EQUILGAS program and the results for volumetric liquid saturations at the reservoir are given in Table 4. Graphical results on a FT-HSH1 theoretical grid for Cerro Prieto I data are given in Fig. 9, results for Los Azufres and Los Humeros data on a FT-HSH2 grid are shown in Fig. 10 while results for Cerro Prieto IV data on a FT-HSH3 grid are seen in Fig. 11.

For the well 131 from Cerro Prieto I, the FT-HSH1 method with 2005 gas data provided almost negligible reservoir steam fractions (of 0.002) indicating that it produces from an equilibrated liquid phase at a reservoir temperature of 269 °C (Table 4). From these data rather high liquid saturations (up to 0.95) for the well were estimated. In contrast, for the well 138 producing from the same aquifer than well 131, the FT-HSH1 results indicate a reservoir temperature of 266 °C and moderate liquid saturations (of 0.674) due to the presence of relatively low reservoir steam fractions (0.016) in Table 4. In order to explain the results, it is necessary to recognize what is the source or the nature of the reservoir steam. In geothermal reservoirs, the in situ reservoir steam could be originated from the production of preexisting reservoir steam or from vaporization of water in the reservoir either by near-well boiling and heat transfer from the rock, or by general boiling and preferential flow of steam to the well. In order to identify the possible sources of the reservoir steam it is useful to investigate the chemistry of fluids along with the total discharge enthalpy of the wells. Previous studies in Cerro Prieto I wells (Truesdell et al., 1987) have suggested that the reservoir steam originates from

Table 3
Chemical compositions of steam samples of representative Cerro Prieto I, Los Azufres, Los Humeros and Cerro Prieto IV wells. Tc: Separation temperature; ys: steam fraction at sampling; XG: nc gas/water in steam (%mol); Gas concentrations (%vol) dry basis; Tc: Guess for reservoir temperature, it could be 573 K for geothermal reservoirs and H2S: measured enthalpy.

Table 4
Numerical results provided by EQUILGAS in the following order: Code sample, date, FT, HSH, Tc: Reservoir temperature; ys: Fraction of reservoir steam and error. The volumetric liquid saturation at reservoir (Sv) was also included.
near-well boiling with all fluid moving to the well, being this the possible explanation for the moderate liquid saturation found in well 138. In fact the near-well boiling process has dropped the temperature of well 138 with regard to the aquifer temperature given by 2005 more representative data of well 131 (269 °C).

The results of EQUILGAS for 2005 data of the Los Azufres steam well LA-5 (1 740 m. a. s. l.) using the FT-HSH2 method in Table 4 indicate high reservoir temperatures (295–299 °C) and relatively low steam fractions at the reservoir (0.018–0.023). Currently it is accepted that in the Los Azufres reservoir gas geothermometers indicate little reservoir steam while the high enthalpy of wells are due to boiling and heat transfer (Nieva et al., 1987; Truesdell et al., 1987). By using the EQUILGAS results for well LA-5, relatively high liquid saturations for the reservoir are calculated (0.71–0.77) which compare well with these reported for the well in 1987 (Nieva et al., 1987). However, in this well two-phase fluids were produced at the beginning while after some years of exploitation boiling increased and the well became a steam producer (Arellano et al., 2005, 2015). Results of EQUILGAS for well LH-6 (340 m. a. s. l) from Los Humeros geothermal field using the FT-HSH2 method indicate very high reservoir temperatures (up to 320 °C) and very variable fractions of steam in the reservoir, (from 0.06 to 0.52) in Table 4. These large variations are due to multiple fluid entries to the well, in agreement with the conceptual model that proposes the existence of at least two reservoirs in the system (Arellano et al., 2003). According to this, a relatively shallow liquid-dominant reservoir and a deeper low-liquid-saturation reservoir with temperatures between 300 and 400 °C occur. Thus, both reservoir temperatures and steam fractions will depend on the amount of fluid that each reservoir contributes to the well discharge. In this case, the reservoir liquid saturations were also variable, from 0.05 to 0.59. According to Table 3 the well LH-6 in 1987 produced a relatively high proportion of deeper fluids since the higher steam fraction at separation conditions (ys) and a high value of non-condensable gases (XG) were found. Data for 1988–1992 indicate higher liquid saturations at reservoir which could be due to the entry of higher proportions of shallower fluids, as compared with 1987 data. Other studies have concluded that the proportion of fluids from every reservoir entering the wells depends on the production orifice.

In Table 4, the results of EQUILGAS for the well 404 from Cerro Prieto IV reservoir using the FT-HSH3 method indicate high reservoir temperatures (274–298 °C) and moderate and variable steam fractions at the reservoir (from 0.08 to 0.36). The higher liquid saturation for this well (0.41) was calculated for initial (2002) data. Soon, after production, liquid saturations decreased indicating first a poor liquid saturation in 2003 (0.041) and then in 2004 a partial recovery (0.274) due to the entry of lower temperature waters to the reservoir induced by exploitation (Arellano et al., 2011).
6. Conclusions

The chemical composition of the steam produced by geothermal wells is useful for investigating reservoir conditions by using gas equilibrium models. FT-HSH methods are based on the FT reaction combined with gas-mineral reactions that control the H₂S–H₂ concentrations of geothermal fluids. Three FT-HSH methods which allow the estimation of reservoir temperatures and the in situ amount of steam of the two-phase mixture of fluids based on different mineral buffers have been developed. However, for all of them graphical solutions are involved and hence, relatively large errors in estimations occur. To facilitate the use of the FT-HSH methods and minimize errors in estimations the program EQUILGAS was written. The program solves the three FT-HSH gas equilibria methods numerically. Some examples for Mexican fields were also provided to illustrate its use. The EQUILGAS program is available through the journal website.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.cageo.2015.12.009.

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