GAS GEOTHERMOMETRY BASED ON CO CONTENT--APPLICATION IN ITALIAN GEOTHERMAL FIELDS

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ABSTRACT

This paper discusses gas chemical equilibria in geothermal reservoirs involving the species \( \text{CO}_2, \text{CH}_4, \text{CO}, \text{H}_2\text{S}, \text{H}_2, \) and \( \text{H}_2\text{O}. \) A set of equations is developed correlating ratios of gas to \( \text{CO}_2 \) with temperature, steam fraction, and \( \text{CO}_2 \) partial pressure in the reservoir. A method for solving the set of nonlinear equations is proposed. These equations do not involve discharge gas/total \( \text{H}_2\text{O} \) ratios and may therefore be used for fumaroles and hot-spring fluids. Applications to fumarole and well-discharge fluid compositions in Italian geothermal fields show good correlations between temperatures calculated with this method and the temperatures measured in the reservoir (between \( 140^\circ \) to \( 330^\circ \).C).

INTRODUCTION

Several studies in recent years have demonstrated chemical equilibria among gas species in geothermal reservoirs. Gas composition has been correlated successfully with reservoir temperature, steam fraction, and redox conditions in both liquid- and vapor-dominated systems.

Except for empirical geothermometers, the application of this composition has been limited to fluid discharges for which the gas/(total water) ratio was known. In Giggenbach (1980) and D'Amore and Truesdell (1985) several gaseous species were considered (\( \text{CO}_2, \text{H}_2\text{S}, \text{H}_2, \text{CH}_4, \text{NH}_3, \text{N}_2 \)), but all the geothermometers were based on measured gas/\( \text{H}_2\text{O} \) ratios. In this paper an attempt has been made to utilize the relative concentrations of a limited number of gaseous species, including carbon monoxide, to exclude the gas/\( \text{H}_2\text{O} \) ratio. This method could be used to evaluate reservoir temperature and gas partial pressures when, for various reasons, the original gas/steam ratio is unknown, such as fumaroles, or any natural manifestations in which part of the \( \text{H}_2\text{O} \) cannot be sampled or emerges separately. The method could thus be applied in geothermal exploration. The main conditions are that (1) a precise measurement of \( \text{CO} \) concentration in the dry gas is available (sensitivity of 0.1 ppm in moles), (2) chemical equilibrium is attained at depth in the system \( \text{CO}_2+\text{H}_2=\text{CH}_4+\text{H}_2\text{S}=\text{CO}+\text{Fe}_3\text{O}_4=\text{Fe}_2\text{S}_2 \), and (3) the deep gas composition (but not necessarily the gas/steam ratio) is maintained until its emergence. Sometimes the latter condition cannot be fulfilled because of some physical phenomena affecting the fluid during transport to the sampling point, such as selective degassing of liquid, or multistep condensation of vapor, or chemical reaction such as local oxidation of some species or sulfide precipitation.

The limited amount of data on \( \text{CO} \) content that is available limits for the moment the application of the method to the gas analyses of some Italian geothermal fields: Larderello, Bagnore, and Piancastagnalo on the Monte Amiata volcano, Travale (all in Tuscany), and a fumarole in the Phlegraean Fields. The computed temperatures have been compared with the known temperature conditions existing in the reservoirs.

MODEL DEVELOPMENT

For any gas species, its partial pressure in the reservoir can be expressed as a function of the molar concentration \( n_i \) with respect to the water at its discharge point \( (d) \), the molar steam fraction, \( \gamma \), and the molar distribution coefficient between steam and liquid, \( B_i \) (D'Amore and Truesdell, 1985):

\[
\log P_i = \log (n_i/n_{i(d)}) + \log A_i + \log P(H_2O). \tag{1}
\]

In most cases (with \( \gamma > 0 \)), \( A = \gamma + (1-\gamma) / B_i \), but in gas depleted waters (with \( \gamma < 0 \)), \( A_i = 1/(B_i(1+\gamma)) \). In this case \( \gamma \) is the fraction of steam lost from the original system (Giggenbach, 1980; D'Amore and Truesdell, 1987). The vapor-liquid distribution coefficients, \( B_i \) from 100° to 374°C, are described by the equation, \( \log B_i = a + bT°C \), with constants \( a \) and \( b \) for each gas species given in Table 2 (Giggenbach, 1980; D'Amore and Truesdell, 1987).

For each species, it is possible to express its partial pressure as a function of the concentration of \( \text{CO}_2 \) by dividing equation (1) by the equation for \( \log P(\text{CO}_2) \) to eliminate \( \text{H}_2\text{O} \):

\[
\log P_i / P(\text{CO}_2) = \log (n_i/n_{i(d)}) + \log A_i + \log A_i + \log (n_{i(d)}/n_{i}) + \log P(\text{CO}_2) \tag{2}
\]

\[
\log P_i / P(\text{CO}_2) = \log A_i + \log A_i + \log (n_{i(d)}/n_{i}) + \log P(\text{CO}_2).
\]
For each chemical reaction involving gaseous species, an equilibrium expression can be written in terms of the partial pressure, \( P_i \), of each reactant and product.

The reactions considered and symbols are reported in Table 1. Rearranging the five equations of Table 1 in order to eliminate \( S_2 \) and \( O_2 \), we obtain the following 3 equations:

\[
\begin{align*}
4 \log P(H_2) + \log P(CO_2) - \log P(CH_4) &= \log K_2 + 2 \log P(H_2O) \\
3 \log P(H_2S) - \log P(H_2) &= 2 \log K_9 - 3 \log K_8 - 3/2 \log K_{MP} + 2 \log P(H_2O) \\
4 \log P(CO) - 3 \log P(CO_2) - \log P(CH_4) &= 4 \log K_8 + \log K_9 - 2 \log P(H_2O)
\end{align*}
\]

Inserting equation (2) for each \( P_i \) and using suitable expressions as a function of the absolute temperature \( T \) for the equilibrium constants (D’Amore and Truesdell, 1987), we obtain the following equations (each gaseous species is expressed in mole % of dry gas samples):

\[
\begin{align*}
4 \log (H_2/CO_2) - \log (CH_4/CO_2) &= HC = 6.69 - 1214.06/T + 4.605 \log T + 4 \log AH_2 - 3 \log ACO_2 - \log AC_{CH_4} - 4 \log PCO_2 \\
3 \log (H_2S/CO_2) - \log (H_2/CO_2) &= SHC = 17.25 - 10318.15/T - 0.412 \log T + 3 \log AH_2S - 2 \log ACO_2 - \log AH_2 - 2 \log PCO_2 \\
4 \log (CO/CO_2) - \log (CH_4/CO_2) &= COC = 4.73 - 12913.84/T + 0.719 \log T + 4 \log ACO - 3 \log AC_{CO_2} - \log AC_{CH_4}
\end{align*}
\]

The \( A_i \) term in equations (3) through (8) is a function of temperature \( T \) and steam fraction \( y \) so the following nonlinear set of equations must be solved:

\[
\begin{align*}
HC &= F_1(t) + F_1(t,y) - 4 \log PCO_2 \\
SHC &= F_2(t) + F_3(t,y) - 2 \log PCO_2 \\
COC &= F_4(t) + F_5(t,y)
\end{align*}
\]

The set of equations (6), (7) and (8) is strongly dependent on temperature but nearly independent of steam fraction when \( y \geq 0.1 \). It was not possible to write an equation that is strongly \( y \) dependent for any possible combination of chemical reactions when considering ratios with \( CO_2 \).
The approach used to solve the nonlinear equation system is based on the fact that equation (11) is independent of \( P(\text{CO}_2) \) and that the temperature and \( y \) value will be such that \( P(\text{CO}_2) \) computed by equation (9), \( P(\text{CO}_2)_{\text{HC}} \), will be equal to \( P(\text{CO}_2) \) computed by equation 10, \( P(\text{CO}_2)_{\text{SCHC}} \). Starting from an assigned low temperature (\( t_0 \)), the value of \( F_3(t,y) \) is computed by:

\[
F_3(t,y) = \text{COC} - F_1(t) \tag{12}
\]

If this computed value is positive, the \( t \) value must be increased. At a certain temperature the difference \( \text{COC} - F_1(t) \) will be negative. This will be the first temperature value, \( t_i \), for calculating the two values of \( P(\text{CO}_2) \). A value of \( y \) is obtained from \( F_3(t_i,y) \). From \( t_i \) and \( y \) it is possible to calculate \( F_1(t_i), F_3(t_i,y), \) and \( F_3(t_i,y) \). Inserting these values in equations (9) and (10) it is then possible to compute two independent values of \( P(\text{CO}_2) \).

\[
\log P(\text{CO}_2)_{\text{HC}} = \frac{1}{4} (F_1(t) + F_3(t_i,y) - \text{HC}) \tag{13}
\]

\[
\log P(\text{CO}_2)_{\text{SCHC}} = \frac{1}{2} (F_1(t) + F_3(t_i,y) - \text{SCHC}) \tag{14}
\]

If the temperature used is too low, then \( P(\text{CO}_2)_{\text{HC}} > P(\text{CO}_2)_{\text{SCHC}} \), and the \( t \) value must be increased and new values of \( y \) and \( P(\text{CO}_2) \) computed from the new value of \( F_3(t_i,y) \) (equation (12)).

The following equations can be written from reactions C, CO, and a combination of H, S and MP:

\[
\log K_C = \log P(H_2O) - \log P(\text{CO}_2) = 3 \log(H_2/H_2O) - 4 \log A_{H_2} + 2 \log A_{H_6} \tag{15}
\]

\[
\log K_H = -3/2 \log K_S - 3/4 \log K_{MP} + 3/2 \log P(H_2O) - 3/2 \log P(\text{CO}_2) = -1/2 \log(H_2/H_2O) + 1/2 \log A_{H_2} - 3/2 \log A_{H_2S} + 3/2 \log A_{CO}_2 \tag{16}
\]

\[
\log K_{CO} = \log(CO/\text{CO}_2) = \log H_2/H_2O - \log A_{CO} + \log A_{CO}_2 + 2 \log A_{H_2} \tag{17}
\]

The left side of the equations contains known factors: temperature-dependent components, \( P(\text{CO}_2) \), and the ratios \( (H_2/\text{CH}_4), (\text{H}_2S/\text{CO}_2) \) and \( (\text{CO}/\text{CO}_2) \). Using suitable thermodynamic data for the equilibrium constants (D’Amore and Truesdell, 1987), the following temperature-dependent components can be used:

\[
\log K_C = \log P(H_2O) = -9.84 - 6000.08/T + 4.635 \log T \tag{18}
\]

\[
\log K_H = 3/2 \log K_S - 3/4 \log K_{MP} + 3/2 \log P(H_2O) = 11.382 - 6183.08/T - 0.206 \log T \tag{19}
\]

\[
\log K_{CO} = 5.019 - 2240.44/T - 0.979 \log T \tag{20}
\]

Only two unknowns are present, \( y \) and the \( (H_2/H_2O) \) ratio. Using two at a time of the three possible sets of these equations it is possible to calculate \( y \) and the \( (H_2/H_2O) \) ratio, and then the \( (\text{gas}/H_2O) \) ratio from the equation:

\[
\text{gas}/H_2O = (H_2/H_2O) \times 100/(\text{HC}_2) \tag{21}
\]

Average values of the results are considered. Starting from the percentage in the dry gas of five species (\( \text{CO}_2, \text{H}_2S, \text{H}_2, \text{CH}_4, \text{CO} \)), with some restrictions, it is then theoretically possible to evaluate the following parameters for the reservoir: temperature, \( P(\text{CO}_2) \), \( y \), and gas/H_2O. The \( F_i \) of all other gases can be calculated from equation (2).

Generally this method results in convergent values of the two \( P(\text{CO}_2) \) at some temperature below 370°C, because with increasing \( t \), the computed value of \( P(\text{CO}_2)_{\text{SCHC}} \) increases much faster than \( P(\text{CO}_2)_{\text{HC}} \). A special case is when the absolute value of \( HC \) is much larger than \( \text{SCHC} \). This is generally due to \( H_2 \) contents much lower than \( H_2S \) contents (i.e., by two orders of magnitude). In this case, convergence is never obtained below 370°C, and computed values of \( P(\text{CO}_2)_{\text{SCHC}} \) are extremely high. This occurs when the gas comes from a boiled water depleted in the less soluble species as \( H_2 \). In this case, negative values of \( y \) must be used. Starting from \( t_0 \) (low temperature), \( P(\text{CO}_2)_{\text{HC}} \) and \( P(\text{CO}_2)_{\text{SCHC}} \) are computed with different values of \( y \) (from \(-0.001 \) to \(-1 \)). If there is no convergence for \( t_0 \), temperature is increased and for any new \( t \) we scan with negative values of \( y \). Of course this method will give the minimum temperature of the system (at the value of \( y \) closest to 0). Note that if \( F_1(t) > -13.310 \), \( t > 370°C \). In this case all the \( B_i \) values are set equal to 1, so that \( F_1(t,y) \) and \( F_2(t,y) \) will be equal to 0.

Sometimes at \( t_1 \), \( P(\text{CO}_2)_{\text{SCHC}} > P(\text{CO}_2)_{\text{HC}} \). This means that for some content of carbon monoxide (11) produces an overestimate of temperature. In this case, \( y \) is set arbitrarily equal to 1, and to obtain convergence the temperature must be decreased until \( P(\text{CO}_2) \) values computed from equations (20) and (21) are equal (of course \( F_1(t,y) \) and \( F_2(t,y) \) are equal to 0). This will produce a minimum calculated temperature.

**APPLICATION**

In order to calibrate the method, \( P(CO_2) \) was applied to 32 well fluids collected in different zones of the Larderello field having very different reservoir temperatures, to 3 well fluids of the Travale field, to 5 well fluids of the Monte Amiata geothermal area (Bagnore and Plancaetagnaio fields) showing wide differences in temperature and depth, and to a well-known fumarole of the Phlegraean Fields area (Bocca Grande at Pozzuoli).

Table 4 reports the chemical compositions of the gases and measured gas/H_2O molar ratios (g), together with the sources of data.

Table 5 reports the following parameters for all the wells: wellhead temperature (\( t_{WH} \)), temperature (\( t_r \)) in the upper part of the reservoir tapped by the well; estimated by in-hole physical measurements (R. Celati, pers. commun., 1978) or computed bottom-hole temperatures (Calore, 1979), and the temperature, \( P(\text{CO}_2) \), \( y \), and gas/H_2O ratio computed.
in this work. In the case of the fumarole, a temperature of 290°C was measured in an exploration well drilled in the area of the Solfatara at a depth of 1800 m (data reported in Carapezza et al., 1984). It must be noted that in the Mofette field 5 km west of the Solfatara, recently drilled wells show large gradients of temperature as function of depth. The maximum value recorded in the deep part of the reservoir (2700 m) is 347°C (Carella and Guglielmetti, 1983).

In Figure 1 the temperatures computed with the geothermometer are shown, together with those reported in Table 4. The agreement is fair (r^2 = 0.88), considering that the temperatures of the reservoir have been estimated by physical data measured before 1978 and that any possible fluid evolution has not been considered.

The computed values of the gas/H_2O ratio are absolutely not consistent with the measured gas/steam ratio. With few exceptions the computed values are much lower.

Figure 1. Estimated temperatures in the upper part of the reservoir reported versus the values of temperatures obtained from the calculations made in this paper (see Table 5).
CONCLUSIONS

If the methodology reported in D’Amore and Truesdell (1985) is used, considering molar ratios of chemical species with respect to water, high values of steam fraction \( y \) and temperatures are obtained for Larderello data. A typical example is shown in this paper using the grid FT vs. HSH where \( FT = 4 \) \( \log (H_2/H_2O) - \log (CH_4/CO_2) \) and \( HSH = 3 \log (H_2S/H_2O) - \log (H_2/H_2O) \). Taking well Gabbro 1 as an example, using data in Table 4, values of \( t = 287^\circ C \) and \( y = 0.40 \) are obtained with the method of D’Amore and Truesdell (1985). This computed temperature is quite in excess of the local 260°C reservoir temperature and, as observed in D’Amore and Pruess (1986), a value of \( y = 0.40 \) corresponds to a volume steam saturation \( S_v \) of about 0.95, which is substantially larger than the range of values compatible with total fluid extraction to date in this area of the field. Well Gabbro 1 has a flow rate exceeding 60 tons/h. With this new method that does not utilize the measured gas/steam ratio at wellhead, values of \( t = 256^\circ C \) and \( y = 0.051 \) are obtained, which are more consistent with the reservoir characteristics of this well. The computed value of gas/H_2O molar ratio in the reservoir is 3.06x10^{-3} compared value at wellhead of 32x10^{-3}. This discrepancy may be due to transport phenomena affecting H_2O species between the reservoir and well bottom. As defined in D’Amore and Truesdell (1985), one of the main limitations of the validity of equation 1 (which utilizes molar ratios of each species with respect to \( H_2O \)) is that the sample collected at wellhead should be transferred from the reservoir without any mass gain or loss. These ratios must then be representative of the relative concentrations in the reservoir. This condition cannot be fulfilled if in the decompression volume, between the bulk of the reservoir and well bottom, the steam produced from partial evaporation of the liquid moves faster than liquid phase. Most of the gas present locally in the liquid fraction is transferred in the new formed steam and this steam and gas phase contains a gas/H_2O ratio in excess of that representative of the reservoir. In the method presented in this paper ratios with respect to \( CO_2 \) instead of \( H_2O \) are used, so that this method may be considered almost independent of \( H_2O \) transport phenomena.

Let us see if gas ratio are altered by transport phenomena. Consider, in a given volume of reservoir, there are 1000 moles of water, 50 as steam and 950 as liquid corresponding to \( y = 0.05 \), as for well Gabbro 1. For this well at a computed temperature of 256°C, \( P_{H_2O} = 43.9 \) bar, \( P_{CO_2} = 2.08 \) bar, and \( P_{H_2S} = 0.031 \) bar. From these data it is possible to calculate the number of moles of \( CO_2 \) and \( H_2S \) associated with 50 moles of steam and 950 moles of liquid:

\[
\begin{align*}
\nu_l(CO_2) &= 0.38 \\
\nu_l(H_2S) &= 0.016 \\
\nu_s(CO_2) &= 2.60 \\
\nu_s(H_2S) &= 0.039
\end{align*}
\]

Then the ratio \( H_2S/CO_2 \) is 0.015 if only the vapor arrives at wellhead and 0.018 if the 950 moles of liquid are also vaporized. The difference is very small, so that ratios with respect to \( CO_2 \) used in the model are almost independent of the amount of vaporized water. Of course, the final gas/H_2O ratio will depend on the fraction \( f_v \) of vaporized liquid water which arrives at wellhead. If the total number of gas moles is 3, the final gas/H_2O ratio at WH will be 3/(50+f_v).

The proposed methodology requires testing in other active geothermal systems where \( CO \) data are available.

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GENERAL REFERENCES


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