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 CO_2, CH_4, CO, H_2S, H_2, and H_2O. A set of equations is developed correlating ratios of gas to CO_2 with temperature, steam fraction, and 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 H_2O 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° to 330°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.[1]

Except for empirical geothermometers, the application of gas 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 (CO_2, H_2S, H_2, CH_4, NH_3, N_2), but all the geothermometers were based on measured gas/H_2O 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/H_2O 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 H_2O 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 CO con-

centration in the dry gas is available (sensitivity of 0.1 ppm in moles), (2) chemical equilibrium is attained at depth in the system CO_2-H_2-CH_4-H_2S-CO-Fe_3O_4-FeS_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 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 Piancastagnaio 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, y, and the molar distribution coefficient between steam and liquid, B_i (D'Amore and Truesdell, 1985):

$$\log P_i = \log (n_i/n_{H_2O})d - \log A_i + \log P(H_2O). \quad (1)$$

In most cases (with y>0), $A = y + (1-y) / B_i$, but in gas depleted waters (with y<0), $A_i = 1/(B_i(1+y-yB_i))$. In this case y 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 CO_2, dividing equation (1) by the equation for log $P(CO_2)$ to eliminate H_2O:

$$\log P_i = \log (n_i/n_{CO_2})d - \log A_i + \log A_{CO_2} + \log P(CO_2). \quad (2)$$

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[1] A selection of general references to geothermal gas studies is given in the bibliography.

Table 1. Chemical reactions considered in the present work.

Symbol	Reaction	Equilibrium Expression
H	$H_2O = H_2 + 1/2\ O_2$	$\log K_H = \log P(H_2) + 1/2 \log P(O_2) - \log P(H_2O)$
S	$H_2S = H_2 + 1/2\ S_2$	$\log K_S = \log P(H_2) + 1/2 \log P(S_2) - \log P(H_2S)$
C	$CH_4 + 2 H_2O =$ $4 H_2 + CO_2$	$\log K_C = 4 \log P(H_2) + \log P(CO_2) - \log P(CH_4)$ $- 2 \log P(H_2O)$
CO	$CO_2 + H_2 = CO + H_2O$	$\log K_{CO} = \log P(CO) + \log P(H_2O) - \log P(CO_2)$ $- \log P(H_2)$
MP	$1/3\ Fe_3O_4 + S_2 =$ $FeS_2 + 2/3\ O_2$	$\log K_{MP} = 2/3 \log P(O_2) - \log P(S_2)$

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:

$$4 \log P(H_2) + \log P(CO_2) - \log P(CH_4)$$
$$= \log K_C + 2 \log P(H_2O) \qquad (3)$$

$$3 \log P(H_2S) - \log P(H_2) = 2 \log K_H - 3 \log K_S$$
$$- 3/2 \log K_{MP} + 2 \log P(H_2O) \qquad (4)$$

$$4 \log P(CO) - 3 \log P(CO_2) - \log P(CH_4)$$
$$= 4 \log K_{CO} + \log K_C - 2 \log P(H_2O) \qquad (5)$$

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):

$$4 \log (H_2/CO_2) - \log (CH_4/CO_2) = HC = 6.69$$
$$- 12144.08/T + 4.635 \log T + 4 \log A_{H2}$$
$$- 3 \log A_{CO2} - \log A_{CH4} - 4 \log P(CO_2) \qquad (6)$$

$$3 \log (H_2S/CO_2) - \log (H_2/CO_2) = SHC = 17.25$$
$$- 10318.15/T - 0.412 \log T + 3 \log A_{H2S}$$
$$- 2 \log A_{CO2} - \log A_{H2} - 2 \log P(CO_2) \qquad (7)$$

$$4 \log (CO/CO_2) - \log (CH_4/CO_2) = COC = 4.73$$
$$- 12913.84/T + 0.719 \log T + 4 \log A_{CO}$$
$$- 3 \log A_{CO2} - \log A_{CH4} \qquad (8)$$

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:

$$HC = F_1(t) + F_1(t,y) - 4 \log P(CO_2) \qquad (9)$$

$$SHC = F_2(t) + F_2(t,y) - 2 \log P(CO_2) \qquad (10)$$

$$COC = F_3(t) + F_3(t,y) \qquad (11)$$

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.

Table 2. Distribution coefficients, B_i, as a function of temperature.

Species	a	b	R²	Validity range t°C
CO$_2$	5.0358	-0.013292	0.9995	20 - 99
	4.8951	-0.011754	0.9998	100 - 149
	4.7695	-0.010961	0.99996	150 - 320
	5.3934	-0.012947	0.997	321 - 350
	13.1739	-0.035211	1.0	351 - 374
H$_2$S	4.6005	-0.014363	0.9990	20 - 99
	4.3774	-0.012025	0.9996	100 - 149
	4.0442	-0.009798	0.99992	150 - 330
	7.9880	-0.02133	0.997	331 - 374
H$_2$	6.8689	-0.021121	0.9986	20 - 99
	6.4325	-0.016323	0.9994	100 - 149
	5.9681	-0.013301	0.9994	150 - 320
	8.4225	-0.02105	0.996	321 - 350
	16.3152	-0.043542	0.991	351 - 374
CH$_4$	6.5971	-0.017338	0.9998	20 - 99
	6.4000	-0.015902	0.9996	100 - 149
	6.0809	-0.0138746	0.9998	150 - 340
	12.6492	-0.033150	0.993	341 - 359
	16.8590	-0.045012	0.995	360 - 374
CO	6.6890	-0.017588	0.998	20 - 99
	6.4490	-0.014850	0.99998	100 - 140
	6.2865	-0.013729	0.99995	141 - 320
	6.8316	-0.015464	0.9995	321 - 350
	21.9307	-0.058616	1.0	351 - 374

Between 100° and 350°C the terms $F_1(t)$, $F_2(t)$ and $F_3(t)$ vary by about 14, 11, and 14 orders of magnitude, respectively. Each of equations 9, 10 and 11 can then be considered as a potentially effective geothermometer. The term $F_3(t)$ alone was used by Bertrami et al. (1985) to calculate reservoir temperatures for several wells of the Larderello geothermal field. The three terms F(t,y) have small values and change little with temperature for $y \geq 0.1$, but their contribution cannot be neglected when solving the set of equations, especially in the case of high temperatures or small y values (see Table 3). It can be shown that the solution of the set of equations may not give reliable values of the computed y.

PROPOSED SOLUTION OF THE SYSTEM

After determining equilibrium temperature and $P(CO_2)$, we can use the following method to calculate both the order of magnitude of the steam fraction y and the gas/H_2O ratio. A computer program has been developed for these calculations.

Table 3. Values of $F_1(t,y)$, $F_2(t,y)$ and $F_3(t,y)$ at selected temperatures in °C and y values.

t°C	y: -0.1	-0.01	-0.001	0	0.001	0.01	0.1	0.5
				$F_1(t,y)$				
100	-6.47	-6.45	-6.27	-3.24	-0.21	-0.02	0.00	0.00
150	-5.02	-4.95	-4.44	-2.59	-0.60	-0.08	-0.01	0.00
200	-4.36	-4.14	-3.22	-2.13	-1.15	-0.24	-0.02	0.00
250	-3.66	-3.14	-2.22	-1.85	-1.50	-0.58	-0.08	-0.01
300	-2.89	-2.12	-1.64	-1.52	-1.43	-0.97	-0.22	-0.03
350	-0.80	-0.58	-0.54	-0.53	-0.53	-0.49	-0.27	-0.05
				$F_2(t,y)$				
100	5.43	5.37	4.92	2.72	0.51	0.07	0.01	0.00
150	4.98	4.77	3.84	2.50	1.16	0.24	0.02	0.00
200	4.36	3.87	2.83	2.21	1.60	0.56	0.07	0.01
250	3.66	2.87	2.12	1.93	1.73	0.99	0.19	0.01
300	2.76	1.95	1.64	1.59	1.54	1.23	0.42	0.06
350	1.67	1.28	1.22	1.21	1.21	1.15	0.76	0.20
				$F_3(t,y)$				
100	-7.79	-7.77	-7.57	-3.89	-0.22	-0.02	0.00	0.00
150	-7.02	-6.94	-6.37	-3.53	-0.67	-0.09	-0.01	0.00
200	-6.22	-5.97	-4.83	-3.12	-1.42	-0.28	-0.03	0.00
250	-5.34	-4.71	-3.37	-2.72	-2.06	-0.72	-0.09	-0.01
300	-4.35	-3.29	-2.48	-2.32	-2.15	-1.35	-0.28	-0.04
350	-3.27	-2.30	-2.06	-2.03	-2.00	-1.76	-0.79	-0.14

The approach used to solve the nonlinear equation system is based on the fact that equation 11 is independent of $P(CO_2)$ and that the temperature and y value will be such that $P(CO_2)$ computed by equation 9, $P(CO_2)HC$, will be equal to $P(CO_2)$ computed by equation 10, $P(CO_2)SHC$. Starting from an assigned low temperature (t_o), the value of $F_3(t,y)$ is computed by:

$$F_3(t,y) = COC - F_3(t) \qquad (12)$$

If this computed value is positive, the t value must be increased. At a certain temperature the difference $(COC - F_3(t))$ will be negative. This will be the first temperature value, t_1, for calculating the two values of $P(CO_2)$. A value of y is obtained from $F_3(t,y)$. From t_1 and y it is possible to calculate $F_1(t)$, $F_2(t)$, $F_1(t,y)$ and $F_2(t,y)$. Inserting these values in equations (9) and (10) it is then possible to compute two independent values of $P(CO_2)$.

$$\log P(CO_2)HC = 1/4 \ (F_1(t) + F_1(t,y) - HC) \quad (13)$$

$$\log P(CO_2)SHC = 1/2 \ (F_2(t) + F_2(t,y) - SHC) \quad (14)$$

If the temperature used is too low, then $P(CO_2)HC > P(CO_2)SHC$, and the t_1 must be increased and new values of y and $P(CO_2)$ computed from the new value of $F_3(t,y)$ (equation 12).

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

$$\log K_C - \log P(H_2O) - \log P(CO_2)$$
$$- \log (H_2/CH_4) = 3 \log (H_2/H_2O)$$
$$- 4 \log A_{H2} + \log A_{CH4} \qquad (15)$$

$$\log K_H - 3/2 \log K_S - 3/4 \log K_{MP} + 3/2 \log P(H_2O) - 3/2 \log P(CO_2) - 3/2 \log (H_2S/CO_2)$$
$$= -1/2 \log (H_2/H_2O) + 1/2 \log A_{H2} - 3/2 \log A_{H2S} + 3/2 \log A_{CO2} \qquad (16)$$

$$\log K_{CO} - \log (CO/CO_2) = - \log (H_2/H_2O)$$
$$- \log A_{CO} + \log A_{CO2} + \log A_{H2} \qquad (17)$$

The left side of the equations contains known factors: temperature-dependent components, $P(CO_2)$, and the ratios (H_2/CH_4), (H_2S/CO_2) and (CO/CO_2). Using suitable thermodynamic data for the equilibrium constants (D'Amore and Truesdell, 1987), the following temperature-dependent components can be used:

$$\log K_C - \log P(H_2O) = -9.84 - 6000.08/T$$
$$+ 4.635 \log T \qquad (18)$$

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

$$\log K_{CO} = 5.019 - 2240.44/T - 0.979 \log T \quad (20)$$

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 (gas/H_2O) ratio from the equation:

$$gas/H_2O = (H_2/H_2O) \ 100/(\%H_2). \qquad (21)$$

Average values of the results are considered. Starting from the percentage in the dry gas of five species (CO_2, H_2S, H_2, CH_4, CO), with some restrictions, it is then theoretically

possible to evaluate the following parameters for the reservoir: temperature, $P(CO_2)$, y, and gas/H_2O. The P_i of all other gases can be calculated from equation (2).

Generally this method results in convergent values of the two $P(CO_2)$ at some temperature below 370°C, because with increasing t, the computed value of $P(CO_2)SHC$ increases much faster than $P(CO_2)HC$. A special case is when the absolute value of HC is much larger than SHC. 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 $P(CO_2)HC$ 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_o (low temperature), $P(CO_2)HC$ and $P(CO_2)SHC$ are computed with different values of negative y (from -0.001 to -0.1). If there is no convergence for t_o, 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 when $F_3(t) > -13.330$, t > 370°C. In this case all the B_i values are set equal to 1, so that $F_3(t,y)$, $F_2(t,y)$ and $F_1(t,y)$ will be equal to 0.

Sometimes at t_1, $P(CO_2)SHC > P(CO_2)HC$. This means that for some reason the 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 $P(CO_2)$ 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, it 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 Piancastagnaio 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, $P(CO_2)$, y, and gas/H_2O ratio computed

Table 4. Gas compositions used in this work (mole % in dry gas). [g = molar gas/H2O ratio. The first 32 wells are located in the Larderello field; (T) = Travale; (A) = Monte Amiata field]

No.	Well	g·10³ (a)	H2	H2S	CH4	CO2	CO·10⁴ (b)	N2
1	Alloro (c)	21.9	0.74	1.99	1.84	92.95	6.8	2.37
2	Camorsi 1 (c)	16.5	1.96	2.22	1.72	91.80	3.8	2.00
3	Capannoli (c)	6.24	6.03	4.14	1.74	87.29	23.6	0.53
4	Gabbro 1	32.4	1.54	1.49	0.80	95.70	9.5	0.47
5	Gabbro 6 (c)	56.2	1.21	1.09	1.18	94.50	12.2	0.74
6	Gabbro 7	138	0.67	0.33	1.26	96.75	14.4	0.99
7	Guiducci	2.96	1.14	0.53	0.14	97.71	1.7	0.37
8	Lago 7 (c)	7.46	6.03	3.70	0.71	89.90	4.8	1.16
9	Lago 8 (c)	1.5	4.31	8.06	2.35	84.00	10.6	0.11
10	LRA (c)	16.6	2.88	1.68	1.17	93.11	4.9	0.92
11	Lustignano 5	25.5	3.29	2.93	2.24	90.98	23.1	0.65
12	Monterotondo 11 (c)	4.32	6.06	2.85	4.03	85.70	2.7	1.20
13	Monterotondo 21 (c)	4.02	4.14	1.94	5.13	87.58	13.3	1.27
14	Puntone 1 (c)	12.3	5.55	3.18	1.84	88.55	17.5	0.54
15	S. Martino 3 (c)	3.92	4.96	4.39	3.13	85.59	13.5	1.69
16	S. Silvestro (c)	13.5	1.85	2.10	1.62	93.28	2.2	0.48
17	Sasso 9 (c)	9.59	3.12	2.60	1.59	92.07	3.3	0.58
18	S. Vincenzo 1	44.9	0.46	0.35	0.27	98.72	2.9	0.21
19	S. Vincenzo 2	41.4	1.16	1.45	1.23	95.47	6.6	0.64
20	S. Vincenzo 5	42.9	0.95	0.99	0.79	96.92	4.7	0.32
21	S. Vincenzo 9 (c)	108.5	0.37	0.21	1.11	97.05	9.6	0.73
22	Scarzai 1 (c)	10.1	1.81	1.12	0.55	96.58	1.1	0.16
23	VC 10	12.2	3.70	2.73	1.31	90.97	17	1.25
24	Zuccantine	5.94	2.48	2.29	0.74	93.72	2.6	1.00
25	77	21.5	2.08	1.92	1.63	93.62	16	0.75
26	89	9.37	2.32	2.34	1.43	92.91	8.8	1.00
27	113	12.2	1.39	0.90	0.05	97.61	6.0	0.05
28	128 (c)	13.4	0.51	1.08	0.23	95.95	2.9	1.99
29	141 (c)	8.67	1.01	2.48	0.64	94.93	7.2	0.88
30	145 (c)	12.5	1.08	3.02	0.87	94.07	7.4	0.94
31	152	26.1	1.77	1.83	1.17	94.40	14	0.83
32	157 (c)	91.4	0.72	0.91	0.47	96.87	7.9	0.35
33	(A) Bagnore 18 (d)	86.6	0.44	0.031	9.71	85.97	1.1	2.60
34	(A) PC 7 (c)	80.3	0.37	0.52	3.05	95.69	4.2	0.40
35	(A) PC 8 (c)	--	0.52	0.60	3.86	94.30	3.3	0.61
36	(A) PC 26 (c)	--	0.92	2.46	1.05	95.10	12.9	0.45
37	(A) PC 30 (c)	--	0.70	2.19	1.62	95.60	26.2	0.29
38	(T) R 6 (c)	39.1	0.70	1.24	0.54	96.80	2.8	0.72
39	(T) R 9 (c)	29.3	0.54	1.07	1.91	95.52	12.2	0.79
40	(T) R 15 (c)	35.6	0.19	0.69	3.07	95.07	3.6	1.28
41	Fumarole (e)	189	0.124	1.924	0.0104	97.79	1.6	0.142

(a) g data for wells are from ENEL (1984); (b) and (c) data from Istituto di Geocronologia e Geochimica Isotopica, CNR, Pisa, Italy (1984).
(d) 1978 chemical analyses from ENEL (except for CO).
(e) Data for the Bocca Grande Fumarole, February 2, 1984, are from Sabroux et al. (written commun., 1985).

Table 5. With the same order of Table 4, average wellhead temperature during 1984 for each well (t_WH); estimated temperature (±5°C) in the upper part of the reservoir (t_r); results obtained from the calculations made in this paper: temperature t_c, P(CO2) in bars, steam fraction y, gas/H2O molar ratio g.

No.	t_WH	t_r	t_c	P(CO2)	y	g·10³
1	229	260	261	3.62	0.004	1.34
2	192	235	227	0.68	0.007	0.33
3	250	270	273	1.05	0.95	19.9
4	242	260	256	2.08	0.051	3.06
5	241	260	261	3.39	0.070	6.16
6	189	230	233	3.14	0.617	68.63
7	185	200	197	0.34	0.570	13.97
8	217	240	232	0.265	0.083	0.916
9	191	260	268	0.90	0.011	0.51
10	184	230	228	0.57	0.050	1.25
11	229	270	280	2.37	0.136	6.26
12	172	220	204	0.15	0.011	0.148
13	235	270	249	1.06	0.327	10.37
14	249	280	255	0.73	0.732	14.00
15	265	270	261	0.93	0.041	1.21
16	180	240	212	0.42	0.04	0.167
17	184	220	219	0.36	0.009	0.234
18	198	220	222	2.11	0.032	3.28
19	226	240	246	1.98	0.014	1.27
20	198	230	234	1.68	0.015	1.21
21	230	240	244	7.63	0.531	116.9
22	157	200	190	0.20	0.007	0.15
23	259	280	270	1.53	0.315	9.86
24	186	220	217	0.36	0.009	0.22
25	250	260	269	2.61	0.079	4.81
26	255	270	251	1.29	0.026	1.24
27	190	240	209	0.32	0.226	4.08
28	227	230	237	2.04	0.006	0.83
29	234	270	264	2.66	0.008	1.20
30	236	260	267	2.65	0.006	1.09
31	229	270	268	2.69	0.067	4.07
32	204	240	256	3.75	0.030	3.62
33	127	140	122	0.11	0.048	2.97
34	189	225	230	4.11	0.004	1.52
35	204	225	219	2.26	0.004	0.83
36	188	320	284	5.39	0.013	2.85
37	---	330	311	14.78	0.019	9.46
38	183	230	229	1.43	0.004	0.54
39	235	270	272	8.39	0.012	4.42
40	186	255	250	8.85	0.001	2.36
41	158	290	287	7.6	-0.002	2.79

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 Mofete field about 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 Guglielminetti, 1983).

In Figure 1 the temperatures computed with the geothermometer are compared 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/H2O ratio are absolutely not consistent with the measured gas/steam ratio. With few exceptions the computed values are much lower.
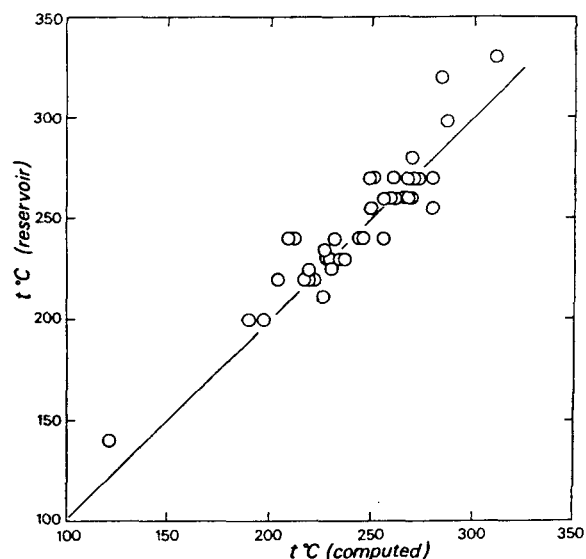

Figure 1. Estimated temperatures in the upper part of the reservoir reported versus the values of temperatures obtained from the calculations made in this paper (see Table 5).

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°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 Sv 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°C and y = 0.051 are found, which are more consistent with the reservoir characteristics of this well. The computed value of gas/H_2O molar ratio in the reservoir is 3.06×10^{-3} compared to the measured value at wellhead of 32×10^{-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. Those 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_{H2O} = 43.9 bar, P_{CO2} = 2.08 bar, and P_{H2S} = 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:

$n_l(CO_2)$ = 0.38 $n_l(H_2S)$ = 0.016
$n_v(CO_2)$ = 2.60 $n_v(H_2S)$ = 0.039

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 fv 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+fv).

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

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