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FLUID GEOCHEMISTRY APPLICATIONS IN RESERVOIR ENGINEERING (VAPOUR-DOMINATED SYSTEMS) (+)

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ABSTRACT

During these last few years fluid geochemistry has proved to be a valid tool for analysing the processes occurring in geothermal reservoirs. Space and time variations in fluid composition have been interpreted as being due to geological setting and reservoir processes, including water recharge, steam condensation and vaporization of liquid water.

The major effort is now invested in developing conceptual and quantitative models for chemical and physical processes that could produce the observed variations in fluid composition.

These models are an effective complement to the classical methods of reservoir engineering in field development and exploitation.

The fields in which the geochemical methods seem to be most effective are:
- individuation of the main zones of steam upflow and of fluid sources in the various parts of the reservoir;
- identification of the main flow paths of the fluid in the reservoir;
- geothermometry;
- estimates of liquid saturation of the reservoir;
- analysis of the processes of natural recharge and reinjection.

Previous work in the field, as well as current development of research conducted by the authors on gas composition, are discussed and reviewed.

INTRODUCTION

It is only recently that some authors have shown that the chemical and isotopic composition of the steam in vapour-dominated geothermal systems can be related to physical and chemical processes occurring in the reservoirs. This composition can be used to develop conceptual models of the reservoirs prior to and during exploitation, and, in some cases, even to provide quantitative information (Celati et al., 1973; Panichi et al., 1974; D'Amore et al., 1977; D'Amore, 1977; Truesdell et al., 1977; Truesdell and Frye, 1977; D'Amore and Nuti, 1977; Truesdell and Nehring, 1978; Mazor, 1978; D'Amore and Truesdell, 1979; Calore et al., 1980; D'Amore et al., 1981). The chemical and isotopic composition of the fluid in vapour-dominated fields has, in fact, been seen to vary areally inside the latter and, in certain areas, undergoes conspicuous and regular temporal variations.

This paper reviews some of the chemical and physical processes that may be responsible for the observed variations and proposes some simple quantitative models.

The belated interest in the geochemistry of the vapour-dominated systems stems from the fact that the fluid produced consists merely of water and a limited number of volatile chemical species, whereas nothing is known of the composition of the liquid phase from which the steam originated. The chemical composition, moreover, can be extremely different from one point to the next within the same field, and from one field to another. In the case of The Geysers and Larderello, for example, the variation in gas/steam ratio exceeds three orders of magnitude, and two orders in the concentration of H_2, H_2S and CH_4 in the uncondensable gas. Nor is it always possible to distinguish between differences in original composition and those deriving from field exploitation, due to the frequent lack of data and to the fact that exploitation itself can produce multiple interactions between the various parts of the system and modify the original flow patterns (D'Amore et al., 1981).

The relations between the reactive gas species

(+) The results from the Larderello field form part of the ENEL-CNR research agreement.

are, moreover, greatly dependent on unknown redox conditions in the reservoir, which, in their turn, are controlled by complex chemical reactions involving oxides, silicates and iron sulphides (Giggenbach,1981).

The geochemical models considered so far are based on the main gaseous species only and are extremely simplified. Very little is known as yet on the kinetics of the chemical reactions involved in the models (Giggenbach,1982; Nehring and D'Amore,1981). A further problem related to the hypothesis of chemical equilibrium concerns fluid components such as CH_4 and CO_2, or N_2 and NH_3, which may have different origins and undergo a mixing within the system under study. We generally have no knowledge of the time required to reach equilibrium.

In the next section we will review previous work in the application of volatile components to the study of some characteristics of vapour-dominated reservoirs.

STATE-OF-THE-ART

One of the most important objectives of the exploration and exploitation phases of a geothermal field is to individuate the upflow areas in the field, characterized by the upward movement of deep high-temperature fluids. Generally these areas have a relatively high permeability down to great depths. During exploitation the fluid characteristics in these areas are:

- relative maxima of temperature, revealed by direct measurements and geothermometric computations;
- positive $\delta^{18}O$ values with respect to nearby areas, as shown at Larderello and The Geysers (Panichi et al.,1974; D'Amore and Truesdell, 1979; Truesdell et al.,1977). These positive values are probably tied to the fact that the steam produced derives from a water that has interacted with the rocks for relatively long periods in a high-temperature environment, without undergoing local condensation or mixing with recent meteoric water;
- local maxima of H_3BO_3 and HCl values, as found in the central areas of the Larderello field (D'Amore et al.,1977);
- low values of NH_3 and gas/steam ratio;
- high concentrations of H_2 and H_2S in the gas.

This composition may be related to a fluid derived from the boiling of a brine with high NaCl and H_3BO_3, and low NH_3 and gas concentrations (D'Amore and Truesdell,1979),moving through prevalently "dry" conduits.

Condensation greatly modifies the composition of the fluid with respect to some apparently non-reactive or poorly reactive species such as CO_2 , H_3BO_3, HCl, NH_3 and Ar.

In 1979 D'Amore and Truesdell proposed a condensation model in which the steam flows laterally from a central area of boiling or upward flow,and releases heat to the surface conductively. This heat loss causes a progressive partial condensation of the steam. The liquid formed is drained downwards to reach the deep liquid-dominated zone, while the residual steam continues its lateral movement towards the edges of the field. On the margins of the vapour-dominated system, where no steam condensation takes place, the temperature decreases considerably. Gravity segregation may result in accumulations of gas in the uppermost parts of the reservoir.

Because of the high gas contents, the wells at Larderello are non-commercial in zones where the fraction of condensed steam exceeds about 80%; at The Geysers, on the other hand, where the gas content is generally at least one order of magnitude lower than at Larderello, the wells are still exploitable in areas in which the condensed fraction reaches 95%.

High condensation areas show relative minima of $\delta^{18}O$ and H_3BO_3, absence of HCl, and high values of gas/steam ratio and NH_3 content. Permeability and temperature frequently decrease on approaching these field boundaries.

The spatial variations in the composition of the steam phase predicted by the condensation model should refer to a two-phase system unaffected by exploitation. During exploitation the concentrations of the different species change as the fluid produced derives partly from the original steam phase and, for the most part, from the boiling of the liquid phase. The composition of the fluid produced then depends on the relative contribution of the two original phases, as the concentrations of each individual species may be very different in these two phases. The variations induced by exploitation are smaller for the more soluble species. With regard to ^{18}O in particular, D'Amore and Truesdell (1979) have shown that the difference in isotopic composition between the steam and condensate phases remains constant in an isothermal condensation process; that is, the condensate has the same gradient as the steam. The steam produced by vaporization of the condensate will thus have the same ^{18}O gradient as the liquid, and the values will merely be about 2‰ higher(at 230°C).

Relatively negative $\delta^{18}O$ values, low gas/steam ratios, low H_3BO_3 and generally low NH_3 values, absence of HCl and presence of tritium were also noted at Larderello, near the recharge areas on the field margins. These characteristics of fluid composition have been attributed to a mixing between steam of deep origin and steam deriving from the vaporization of locally infiltrated water (Celati et al.,1973; Panichi et al.,1974; Petracco and Squarci,1975; D'Amore et al.,1977). Pressure declines within the reservoir caused by exploitation were shown to increase the contribution of recent meteoric waters to the fluid produced (Calore et al.,1982).

The geochemical and isotopic investigations have also proved particularly useful in the analysis of fluid mixing processes caused by reinjection in the central areas of Larderello. Analysis of gas, ^{18}O and D contents, in particular, have been utilized in a quantitative evaluation of the contribution of reinjected water to production (Nuti et al.,1981; Giovannoni et al.,1981; Cappetti et al.,1982).

An analysis of the long production histories of Larderello (Sestini,1970) revealed that the observed chemical variations could be related with the behaviour of certain physical variables such as well flow-rate and temperature (D'Amore and Truesdell,1979; D'Amore et al., 1981). One model capable of explaining the observed variations assumes that at least three sources of fluid contribute to production, in varying degrees, during exploitation. These three sources coincide with the three different zones of the reservoir (upper condensate, intermediate two-phase and deep brine), hypothesized by White et al.(1971) and Truesdell and White (1973). The temporal evolution of the chemical and physical parameters are interpreted as a gradual modification to the contribution from each of these sources induced by exploitation. Simple quantitative models can, with a good approximation, reproduce the trends in flow-rate, temperature, gas/steam ratio, H_3BO_3 , NH_3 and HCl observed in individual wells (D'Amore and Truesdell,1979).

These models were also used to reproduce the evolution simultaneously observed in all the wells in the Serrazzano area, assuming that the chemical and physical characteristics of the three sources vary from place to place, in accordance with a progressive condensation model (D'Amore et al.,1981).

The only geothermometers applicable to vapour-dominated systems are those based on the ratios of the gaseous components (H_2, CO_2, CH_4, H_2S)(Hulston and McCabe,1962; Truesdell and Nehring,1978; D'Amore and Truesdell,1980;D'Amore and Panichi,1980) and on the distribution of the C,H and O isotopes among the gaseous components (i.e., $\delta^{13}C(CO_2\text{-}CH_4)$, $\delta D(CH_4\text{-}H_2)$, $\delta D(H_2O\text{-}H_2)$, $\delta^{18}O(H_2O\text{-}CO_2)$(Craig,1953; Craig, 1975; Hulston and McCabe,1962; Bottinga,1969; Panichi et al.,1977; Hulston,1977; Panichi and Gonfiantini,1978; Panichi et al.,1979). Panichi et al.(1979) applied the isotopic geothermometers to the fluid of numerous wells at Larderello.

The pair CH_4-CO_2 gives, on average, temperature values of the order of 340°C at Larderello. Comparison with the estimated temperatures at the top of the reservoir suggests that the reaction $CO_2 + H_2 = CH_4 + 2H_2O$ is unable to explain the observed isotopic compositions, or, at least, that attainment of isotopic equilibrium must be such a slow process (Giggenbach, 1981) that the high temperature values can only be related to deeper zones of the reservoir far below the horizons exploited at present. It was then proposed that the synthesis reactions for methane and carbon dioxide ($C + 2H_2 = CH_4$ and $C + O_2 = CO_2$), forwarded for Larderello by D'Amore and Nuti(1977),could represent an adequate alternative for reproducing the thermal state of the field. It would,therefore, appear that CH_4 and CO_2 have a separate origin and do not reach isotopic equilibrium in the layers exploited at present. The pair CH_4-H_2 gives an average value of 312°C, and the pair H_2O-H_2 254°C.

The isotopic composition appears to give the temperatures reached by the geothermal fluid in different parts of the system. The various geothermometers equilibrate at different rates; i.e., in decreasing order,CO_2-H_2O, H_2O-H_2, CH_4-H_2, CH_4-CO_2. If the fluid cools during its rise towards the exploited horizons, then comparison of the temperatures provided by the various pairs should give an indication of the thermal history of the fluid.

With the exception of the geothermometer proposed by D'Amore and Panichi(1980), which is based on purely empirical concepts, all the other geothermometers utilizing the gaseous composition to estimate the temperatures in vapour-dominated reservoirs have two main limitations:

1) the geothermometers are based on the hypothesis that certain chemical equilibria exist in the steam phase, but the composition utilized is actually that of the fluid at wellhead, which derives in part from the vaporization of the liquid phase existing in the reservoir. The chemical equilibria in question do not effectively refer to the fluid produced, but to the steam phase in the reservoir; this phase may be much different in composition from the steam produced. Despite this drawback, a good geothermometer for the vapour-dominated systems has proved to be the $\log(H_2S/CO_2) = 8.92 - 4033.5/T - 0.79 \log T - \frac{1}{2}\log(\text{litres } CO_2 \text{ STP/kg steam})$. This geothermometer was applied by D'Amore and Truesdell (1980) to the computation of the percentage volume of liquid water in the reservoir at The Geysers and Larderello. They assumed that the difference between the geothermometric and bottomhole temperature values in a producing well reflects the cooling produced in the reservoir by vaporization of the liquid phase. Nehring and D'Amore (1981) and D'Amore and Truesdell (1980) have also developed some geothermometers based on the gaseous composition that can be applied to liquid-dominated systems. Again no account was made for the possible two-phase nature of the fluid in the reservoir. Recently Giggenbach (1980) developed and applied to the New Zealand fields a method by which temperature and saturation can be computed simultaneously;

2) with the exception of the geothermometer based on the Fisher-Tropsch equation, all the geothermometers utilize oxygen fugacities obtained from empirical equations, and sulphur fugacities based on simple geochemical models that ignore the real mineralogical composition of the reservoir rocks.

It is only by taking into account the existence of two-phase conditions in the geothermal reservoirs that reasonable solutions can be obtained for the various problems related to gas geochemistry in vapour-dominated systems.

The development of methods for determining the fractions of the two fluid phases is a prerequisite for any quantitative considerations on the composition of the fluids in these geothermal systems. Thus an estimate of liquid saturation in the reservoir is one of the main objectives of current geochemical investigations. These studies are also of considerable interest in reservoir engineering, as they can be used to estimate fluid reserves. The results of the first studies in this field were presented by Grant (1979), Celati et al.(1980), Giggenbach (1980), D'Amore and Truesdell (1980) and D'Amore and Celati (1983). Giggenbach's method, which assumes the existence of two simultaneous equilibria

$$N_2 + 3H_2 = 2NH_3$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

seems inadequate for vapour-dominated fields such as Larderello and The Geysers, as the first reaction is not in equilibrium. D'Amore and Celati (1983) developed a method for calculating the steam/liquid ratio in the reservoir utilizing only the second equation, with an assigned temperature value. The results of the latest developments in this direction are now described.

NEW RESULTS IN RESEARCH ON GASEOUS COMPOSITION

Large temporal variations in the gas/steam ratio had already been observed in the Larderello field(Sestini,1970). D'Amore and Truesdell (1979) and D'Amore et al.(1981) based their interpretation of this temporal evolution on the simple quantitative models outlined earlier in this paper. An attempt was later made to interpret the spatial and temporal variations in the gaseous composition also.

If we exclude those areas of the field in which the chemical evolution is clearly due to water recharge, then a correlation can be observed between the percentages of H_2 and H_2S in the dry gas and the gas/steam ratio. A typical example is shown in Fig.1, where the temporal

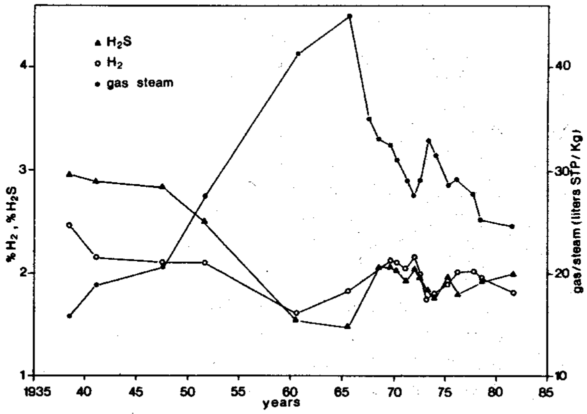

Figure 1. Example of temporal variations in the gas/steam ratio, and ($\%H_2$) and ($\%H_2S$) in the dry gas of one well at Larderello.

variation in the gas/steam ratio is accompanied by an inverse variation in the percentages of H_2 and H_2S in the dry gas.

The type of relationship existing between gas/steam ratio and H_2 and H_2S can be individuated by study of a large number of wells. Figures 2 and 3 show this relationship for wells with reservoir temperatures between 240°C and 270°C.

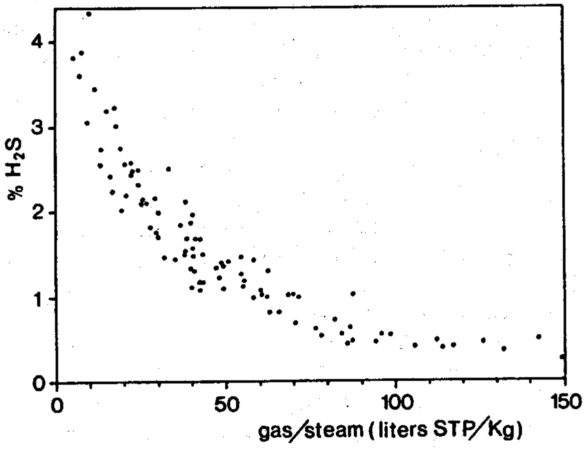

Figure 2. (%H_2S) in dry gas vs gas/steam ratio for Larderello wells with reservoir temperatures between 240° and 270°C.

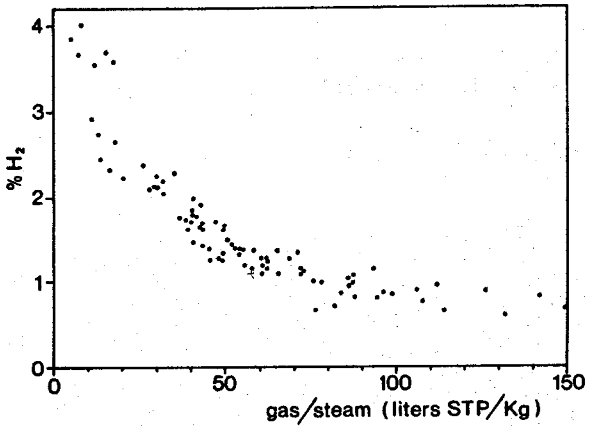

Figure 3. (%H_2) in dry gas vs gas/steam ratio for Larderello wells with reservoir temperatures between 240° and 270°C.

Note that the trend is the same for different wells and for one single well in different periods, whether the gas/steam ratio increases or decreases.

Figures 4 and 5 give the percentages of H_2S and H_2 plotted vs the gas/steam ratio for wells with reservoir temperatures between 180°C and 230°C.

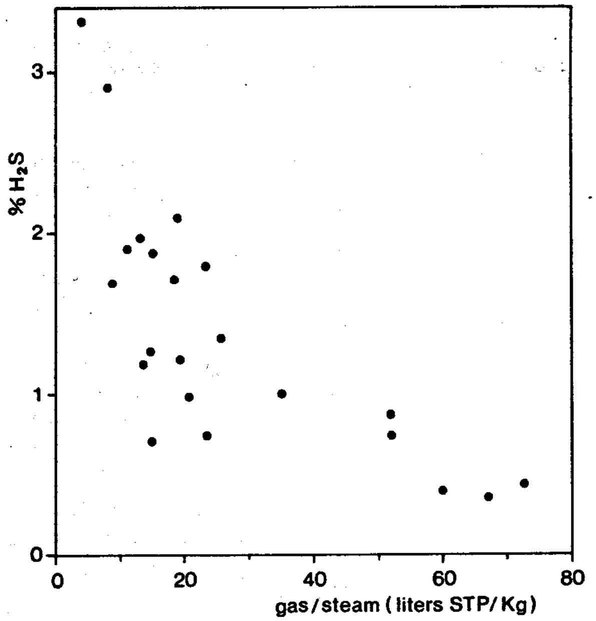

Figure 4. (%H_2S) in dry gas vs gas/steam ratio for Larderello wells with reservoir temperatures between 180°C and 230°C.

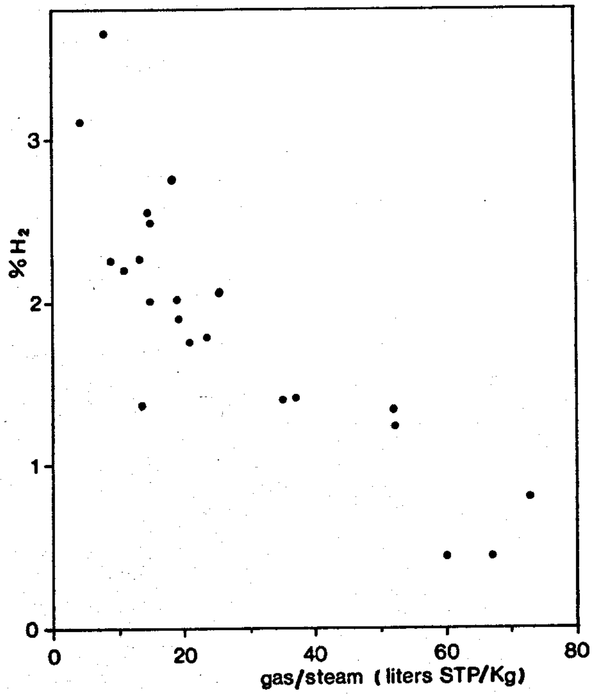

Figure 5. (%H_2) in dry gas vs gas/steam ratio for Larderello wells with reservoir temperatures between 180°C and 230°C.

The estimated reservoir temperatures are based on in-hole temperature logs and bottom-hole temperature values calculated for the productive wells (Calore,1979; Calore et al.,1979).

Note that an inverse correlation with the gas/steam ratio was also observed for the percentage of H_2 in the dry gas in the superheated fumaroles of the Lassen geothermal system (Truesdell, written comm.,1982) and for the H_2 and H_2S in the fumaroles of Chipilapa area,El Salvador (Martinez, pers.comm.,1982). The approximately hyperbolic trend suggests that the H_2/H_2O and H_2S/H_2O ratios for a given temperature value are almost constant and, therefore, that the H_2 and H_2S contents are controlled by chemical reactions involving water.

Using several data on gas composition from The Geysers it was possible to extend the observed relationship for H_2 and H_2S up to three orders of magnitude for the gas/steam ratio.

Plotting the Larderello and The Geysers data on log-log paper (Figs.6,7), a deviation from a -1 slope straight line is observed, increasing towards the low values of the gas/steam ratio. This corresponds to the fact that, at a given temperature, the H_2/H_2O and H_2S/H_2O ratios do not remain constant as the gas/steam ratio decreases, but decrease continually and with differing trends.

For hydrogen we considered the reaction of water dissociation in the steam phase:

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad (1)$$

The equilibrium constant is

$$\log K_H = 2.652 - 12776/T \qquad (2)$$

For this reaction we obtain the following equation:

$$\frac{P_{H_2}}{P_{gas}} = \frac{1}{P_{gas}/P_v} \cdot \frac{K_H}{f_{O_2}^{\frac{1}{2}}} \qquad (3)$$

where P_v is steam pressure and f_{O_2} oxygen fugacity. At first oxygen fugacity was computed from a linear function of 1/T, which is intermediate between those utilized by D'Amore and Panichi (1980) and D'Amore and Truesdell(1980):

$$\log f_{O_2} = 5.29 - 22512/T \qquad (4)$$

At 250°C, for a gas/steam ratio of 200 l/kg (STP) we obtain

$$(\%H_2) = P_{H_2}/P_{gas} \cdot 100 = 0.79$$

This point practically lies on the curve obtained for Larderello field data at that value of gas/steam ratio (Point A in Fig.7).

Assuming that at such high values of gas/steam ratio the reservoir fraction of steam by weight y is about unity, then H_2 and H_2O can be considered in equilibrium in the vapour phase, in accordance with equ.(1). From equ.(3) it then follows that

$$P_{H_2}/P_v = K_H/f_{O_2}^{\frac{1}{2}} \qquad (5)$$

that is, at a fixed temperature and for high steam quality values

$$((\%H_2)\text{in the gas}) \;.\; (\text{gas/steam}) = \text{constant}$$

Thus, if the steam phase alone exists in the reservoir, we should obtain a straight line of

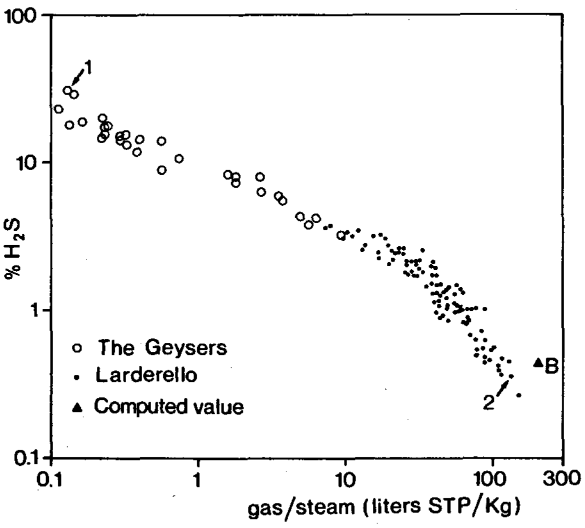

Figure 6. Log-log plot of ($\%H_2S$) in dry gas vs gas/steam ratio for wells at Larderello and The Geysers.

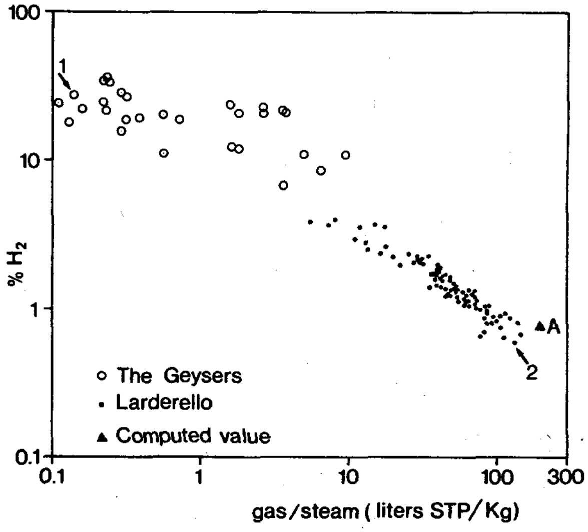

Figure 7. Log-log plot of ($\%H_2$) in dry gas vs gas/steam ratio for wells at Larderello and The Geysers.

slope -1 in the diagram in Fig.7. This is indeed almost the case, with some scattering of points, for the Larderello wells with the highest observed gas/steam ratios.

The slope of the curve in Fig.7 decreases with the decrease in gas/steam ratio until it more or less reaches constant values of ($\%H_2$) for the lowest gas/steam ratios at The Geysers. It is reasonable to assume that such low gas/steam ratios reflect high liquid saturations in the reservoir. We can, therefore, consider reaction (1) still valid for the steam phase in the reservoir, but the deviations from the straight line of slope -1 will depend on the fact that the fluid produced derives from a fluid whose steam quality y in the reservoir is less than 1. Thus, the third parameter, along with temperature and gas/steam ratio, required to explain the trend in Fig.7, is reservoir steam saturation.

Let us now consider the following equations, where n represents number of moles, subscripts v and 1 the steam and liquid phases in the reservoir, WH the fluid at wellhead, y the molar fraction of steam, and B_{H_2} the coefficient of H_2 distribution between the steam and liquid phases, which is a temperature-dependent quantity:

$$n_{H_2O,v} + n_{H_2O,1} = n_{H_2O,WH} \qquad (6)$$

$$n_{H_2,v} + n_{H_2,1} = n_{H_2,WH} \qquad (7)$$

$$(n_{H_2}/n_{H_2O})_v \,/\, (n_{H_2}/n_{H_2O})_1 = B_{H_2} \qquad (8)$$

$$n_{H_2O,v} \,/(n_{H_2O,v} + n_{H_2O,1}) = y \qquad (9)$$

From equations (6) and (9) we can obtain:

$$y\left(\frac{n_{H_2}}{n_{H_2O}}\right)_v + (1-y)\,\frac{1}{B_{H_2}}\left(\frac{n_{H_2}}{n_{H_2O}}\right)_v = \left(\frac{n_{H_2}}{n_{H_2O}}\right)_{WH} \qquad (10)$$

From equations (5) and (10) we then obtain:

$$\log(\%H_2) = 5.095 - \log(G/V) + \log\frac{K_H}{f_{O_2}^{\frac{1}{2}}} + \log\left(y + \frac{1-y}{B_{H_2}}\right) \qquad (11)$$

where the coefficient 5.095 is required if all the species are considered ideal gases and the gas/steam ratio (G/V) is expressed in STP litres/kg. Note that in this equation ($\%H_2$)is a function of the gas/steam ratio, temperature and steam quality. The percentage of hydrogen tends to increase with the decrease in the gas/steam ratio and increase in temperature and steam quality.

An equation similar to (11) can also be obtained for H_2S. We start with the following equation of equilibrium between H_2 and H_2S:

$$H_2S = H_2 + \tfrac{1}{2}S_2 \qquad (12)$$

The equilibrium constant is

$$\log K_S = -0.13 - 4394.5/T + 0.79 \log T \qquad (13)$$

The strong correlation observed between the values of H_2S and H_2 (Fig.8) in areas of the Larderello geothermal field with comparable temperatures and no local condensation or mixing phenomena supports equ.(12).

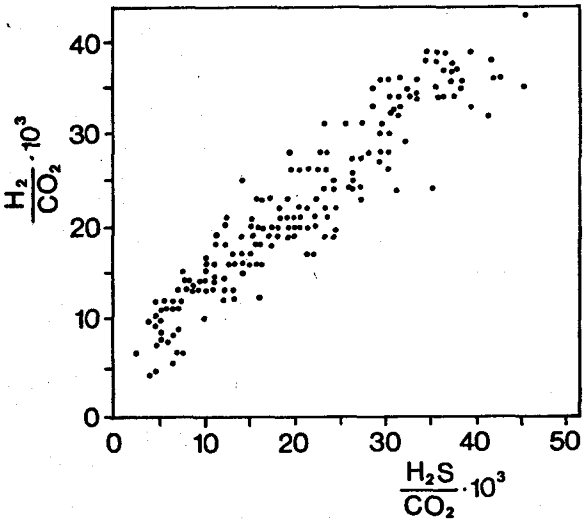

Figure 8. Relationship between H_2 and H_2S for Larderello wells (from D'Amore, 1977).

Let us now consider equations similar to those from (6) to (9) for H_2S, utilizing the distribution coefficient B_{H_2S} :

$$(n_{H_2S}/n_{H_2O})_v \,/\, (n_{H_2S}/n_{H_2O})_1 = B_{H_2S} \qquad (14)$$

We then obtain an equation similar to equ.(10):

$$y(n_{H_2S}/n_{H_2O})_v + (1-y)\,\frac{1}{B_{H_2S}}\,(n_{H_2S}/n_{H_2O})_v = (n_{H_2S}/n_{H_2O})_{WH} \qquad (15)$$

Combining equs.(12) and (1) we have:

$$P_{H_2S}/P_{H_2O} = (K_H\, f_{S_2}^{\frac{1}{2}})/(K_S f_{O_2}^{\frac{1}{2}}) \qquad (16)$$

where f_{S_2} is sulphur fugacity. From equations (15) and (16) we have:

$$\log(\%H_2S) = 5.095 - \log(G/V) + \log\frac{K_H f_{S_2}^{\frac{1}{2}}}{K_S f_{O_2}^{\frac{1}{2}}} + \log\left(y + \frac{1-y}{B_{H_2S}}\right) \qquad (17)$$

A simple equation relating the O_2 and S_2 fugacities could be obtained from the magnetite-pyrite equilibrium:

$$1/3Fe_3O_4 + S_2 = FeS_2 + 2/3O_2 \qquad (18)$$

The equilibrium constant is:

$$\log K_{MP} = -4.683 - 3796/T \qquad (19)$$

Although relatively large quantities of pyrite have been found in all the geothermal fields, including Larderello and The Geysers, magnetite shows only a sporadic occurrence. We can thus deduce that the magnetite field is occupied by iron silicates whose thermodynamic data are poorly known at the moment (Truesdell and Henley,1982). Obviously we should consider the real equilibria between iron silicates in the reservoir for oxygen fugacity also, instead of an empirical equation such as (4). However, equ.(18), which has been used by numerous other researchers in the past, could be a useful approximation at high temperatures. For example, from equ.(16), which includes $f_{S_2}^{\frac{1}{2}}$ and $f_{O_2}^{\frac{1}{2}}$, and equ.(18), we obtain:

$$(P_{H_2S} / P_{H_2O}) = \frac{K_H}{K_S\, K_{MP}^{\frac{1}{2}}} \frac{1}{f_{O_2}^{1/6}} \qquad (20)$$

so that the H_2S/H_2O ratio is dependent on $f_{O_2}^{1/6}$. Uncertainties of one order of magnitude in f_{O_2} thus lead to no serious errors in the computation of P_{H_2S}/P_{H_2O}.

Assuming y = 1 and a gas/steam ratio of 200 l/kg, ($\%H_2S$) becomes 0.46, which agrees with the field data for high gas/steam ratios observed at Larderello (point B in Fig.6). From equ.(20) we can modify equ.(17) to:

$$\log (\%H_2S) = 5.095 - \log (G/V) + \log\frac{K_H}{K_S K_{MP}^{\frac{1}{2}} f_{O_2}^{1/6}} + \log \left(y + \frac{1-y}{B_{H_2S}}\right) \qquad (21)$$

Utilizing equ.(4) for the f_{O_2} at 250°C we obtained the diagrams shown in Figs.9 and 10 for various values of y; the values observed for H_2S and H_2 are also plotted vs gas/steam ratio. In these figures the shift towards low gas/steam ratios corresponds to a regular decrease in steam saturation. Plotting all the field data on the diagram for 250°C is not entirely correct as the reservoir temperatures for the wells considered at The Geysers and Larderello run from 230° to 270°C. The saturation values attainable from the two diagrams, however, are compatible. For example, for samples 1 and 2 of The Geysers and Larderello (at extreme values of the gas/steam ratio), we obtain from the H_2 diagram y(1) = 2.2% and y(2) = 51%; from the H_2S diagram y(1) = 2.0% and y(2) = 51%.

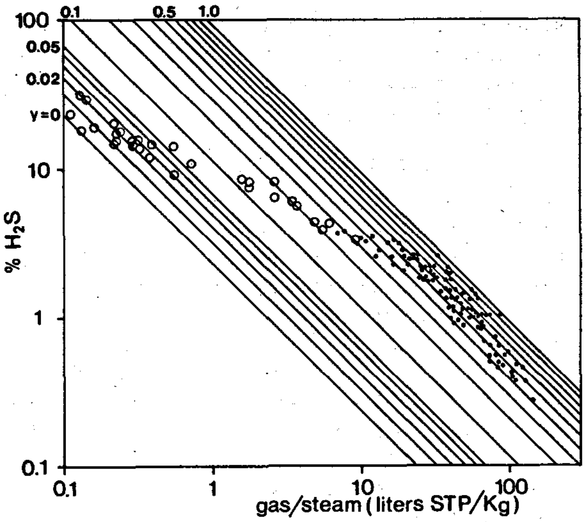

Figure 9. Relationship between ($\%H_2S$) and gas/steam ratio for different values of y at 250°C according to equ.(21), using empirical equ.(4) for f_{O_2}.

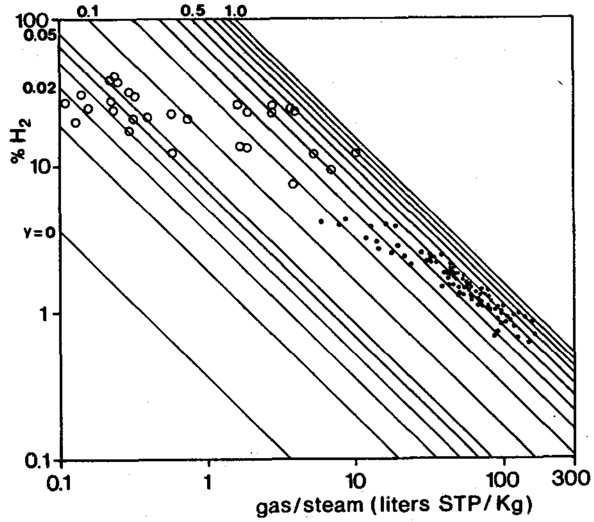

Figure 10. Relationship between ($\%H_2$) and gas/steam ratio for different values of y at 250°C according to equ.(11), using empirical equ.(4) for f_{O_2}.

Utilizing the H_2 and H_2S concentrations, simultaneous evaluations of temperature and saturation in the reservoir can now be obtained, provided that a more accurate f_{O_2} than that given by equ.(4) could be introduced in equs.(22) and (23).

$$\log (H_2/H_2O) = 2.652 - 12776/T - \tfrac{1}{2}\log f_{O_2} + \log \left(y + \frac{1-y}{B_{H_2}}\right) \qquad (22)$$

$$\log (H_2S/H_2O) = 5.124 - 6483/T - 0.79 \log T - 1/6 \log f_{O_2} + \log \left(y + \frac{1-y}{B_{H_2S}}\right) \qquad (23)$$

Equation (4) is, in fact, not accurate enough for H_2, as (H_2/H_2O) is a function of the square root of f_{O_2}. The y values obtained from H_2 concentrations using equ.(4) for f_{O_2} were generally poorly compatible with those calculated by means of the Fisher-Tropsch equation, according to D'Amore and Celati (1983):

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad (24)$$

The equilibrium constant is:

$$\log K_C = 10.76 - 9323/T \qquad (25)$$

Starting with the total composition of the fluid at wellhead, this method calculates for each temperature the molar fractions of all the gaseous components in the steam phase coexisting with the liquid phase in the reservoir. The calculated values of these concentrations, $X_{v,i}$, are functions of temperature and of the molar steam fraction, y, present in the reservoir. The gaseous species are, in fact, distributed in the two phases in the reservoir. Steam quality y is calculated from

$$(K_C f_w^2 \gamma_{CH_4} / \gamma_{CO_2} \gamma_{H_2}^4) = (X_{v,H_2}^4 X_{v,CO_2} / X_{v,CH_4}) P_t^4 \qquad (26)$$

where f_w is water fugacity, γ_i the fugacity coefficients for the various species i, and P_t total pressure in the reservoir. The left-hand side of the equation is dependent on temperature alone, but the right-hand side is also a function of y. For each temperature value there will, therefore, be one y value such that the two members of equ.(26) will be equal.

To obtain a value of f_{O_2} for each gas analysis we utilized equ.(24) with equ.(1), so that:

$$\log f_{O_2} = -\tfrac{1}{2} \log(CH_4/CO_2) + 18.014 - 23648.7/T - 4.152\log T - \tfrac{1}{2}\left[\log\left(y + \frac{1-y}{B_{CO_2}}\right) - \log\left(y + \frac{1-y}{B_{CH_4}}\right)\right] \qquad (27)$$

When calculating f_{O_2} we ignore the term in brackets containing y and the distribution coefficients. This term is in fact less than 0.1 logarithmic units for $y > 0.01$ and temperatures $< 270°C$. By introducing the approximated equ. (27) in equs.(22) and (23) we obtain:

$$\log(H_2/H_2O) = -6.355 - 951.6/T + 2.076\log T + 1/4 \log(CH_4/CO_2) + \log \left(y + \frac{1-y}{B_{H_2}}\right) \qquad (28)$$

and

$$\log(H_2S/H_2O) = 2.122 - 2542/T - 0.098 \log T + 1/12 \log(CH_4/CO_2) + \log \left(y + \frac{1-y}{B_{H_2S}}\right) \qquad (29)$$

where B_{H_2} and B_{H_2S} are known temperature-dependents:

$$\log B_{H_2} = 6.2283 - 0.01403\ t°C \qquad (30)$$

$$\log B_{H_2S} = 4.0547 - 0.00981\ t°C \qquad (31)$$

Table 1 gives the calculated steam qualities for some wells at Larderello and The Geysers, at fixed temperatures: y (FT) were obtained from the method by D'Amore and Celati (1983), $y(H_2)$ from equ.(28) and $y(H_2S)$ from equ.(29). The temperatures used for Larderello are reservoir values estimated as described above. As the reservoir temperature is not known for each well at The Geysers we assumed a value of 240°C; this leads to some inaccuracy in the calculation of y, as the temperatures may obviously vary from well to well. Figures 11 and 12 are diagrams showing the saturation values obtained by the various methods. A better fitting would be obtained by plotting a temperature of 220°-230°C for some wells at The Geysers, instead of 240°C.

Using both equs.(28) and (29) concomitantly, we can calculate both temperature and saturation, as shown in Fig.13. Plotting the data from Table 1 we can see that the temperatures of The Geysers samples are generally lower than those from Larderello, and the steam quality values much lower.

We must point out that calculation of f_{O_2} with equ.(27) gives an approximate value only, as the CH_4/CO_2 ratio is also a function of steam pressure (P_v) and the latter varies from one part of the reservoir to another.

$$P_{CH_4}/P_{CO_2} = \frac{K_H P_v^2}{K_C f_{O_2}^{1/2}} \qquad (32)$$

Instead of P_v we used saturated steam fugacity, which is a function of temperature only. The problem still remains of developing a method capable of evaluating f_{O_2} and f_{S_2} in the various fields, and zones of the same field or reservoir.

The calculated value of steam quality, y, can be used to estimate the drainage volume of each productive well. Let us assume that the steam

Locality	Temp. °C	Gas/steam lSTP/kg	$\log \frac{H_2S}{H_2O}$	$\log \frac{H_2}{H_2O}$	$\log \frac{CH_4}{CO_2}$	y(F.T.) %	$y(H_2S)$ %	$y(H_2)$ %
1) The Geysers	240	0.11	-4.71	-4.67	-0.63	1	1	1
2) The Geysers	240	0.13	-4.72	-4.72	-1.14	1	1	1
3) The Geysers	240	0.18	-4.57	-4.33	-0.39	2	2	2
4) The Geysers	240	0.22	-4.58	-4.21	-1.24	5	2	5
5) The Geysers	240	0.23	-4.55	-4.18	-1.00	5	2	4
6) The Geysers	240	0.32	-4.47	-4.17	-0.89	5	3	4
7) The Geysers	240	0.56	-4.39	-4.31	-1.14	4	4	3
8) The Geysers	240	0.72	-4.21	-3.97	-0.79	7	7	6
9) The Geysers	240	1.6	-4.14	-3.80	-0.61	10	8	8
10)The Geysers	240	1.8	-3.94	-3.51	-0.71	21	15	18
11)The Geysers	240	1.8	-3.98	-3.79	-0.70	11	13	9
12)The Geysers	240	3.8	-3.78	-3.20	-0.53	38	21	33
13)The Geysers	240	4.4	-3.74	-3.15	-0.78	49	32	42
14)The Geysers	240	5.2	-3.49	-3.04	-0.69	45	52	60
15)The Geysers	240	5.6	-3.63	-3.02	-0.48	56	31	48
16)The Geysers	240	9.8	-3.35	-2.84	-0.53	86	61	75
17)Larderello	210	3.6	-4.77	-4.40	-3.27	16	7	15
18)Larderello	240	6.1	-3.83	-3.79	-2.05	23	26	20
19)Larderello	220	8.8	-3.92	-3.80	-2.03	28	23	25
20)Larderello	260	9.5	-3.65	-3.78	-2.32	23	26	19
21)Larderello	270	14.0	-3.46	-3.37	-1.72	37	30	31
22)Larderello	270	18.0	-3.35	-3.33	-1.83	44	40	36
23)Larderello	270	19.0	-3.31	-3.26	-1.77	49	44	41
24)Larderello	260	20.0	-3.48	-3.50	-2.21	41	40	34
25)Larderello	260	20.0	-3.35	-3.14	-1.64	67	49	56
26)Larderello	270	22.0	-3.27	-3.20	-1.76	57	47	48
27)Larderello	250	25.0	-3.41	-3.41	-1.79	44	54	37
28)Larderello	240	28.0	-3.72	-3.64	-2.16	35	35	30
29)Larderello	270	28.0	-3.25	-3.18	-1.67	56	50	46
30)Larderello	260	33.0	-3.35	-3.31	-1.88	52	51	43
31)Larderello	260	44.0	-3.25	-3.24	-2.14	71	68	59
32)Larderello	250	44.0	-3.33	-3.19	-2.11	87	70	74
33)Larderello	240	135.0	-3.42	-3.21	-2.01	87	69	75

Table 1. Steam qualities for some wells at Larderello and The Geysers, at fixed temperatures.

produced by a well from the start of production derives from the total vaporization of the liquid water stored in the volume V:

$$V = \frac{m_1 v_1}{\emptyset S_1} \qquad (33)$$

where m_1 is the cumulative steam production, v_1 is the specific volume of liquid water at boiling point,$\emptyset$ is porosity, and S_1 is liquid saturation

$$S_1 = 1 + (\frac{1}{y} - 1)(v_1/v_v) \qquad (34)$$

Applying equ.(33) to some wells at Larderello, at 250°C, and assuming a porosity of 10%, we can calculate the radius r of a hypothetical spherical volume of the reservoir feeding each well. For wells that have been producing for a few tens of years r is about one kilometre. In the case of recent wells at The Geysers, on the other hand, r proves to be of the order of about 150 m. These values are reasonable if we consider that at the moment at Larderello the liquid water boils far from wellbottom.

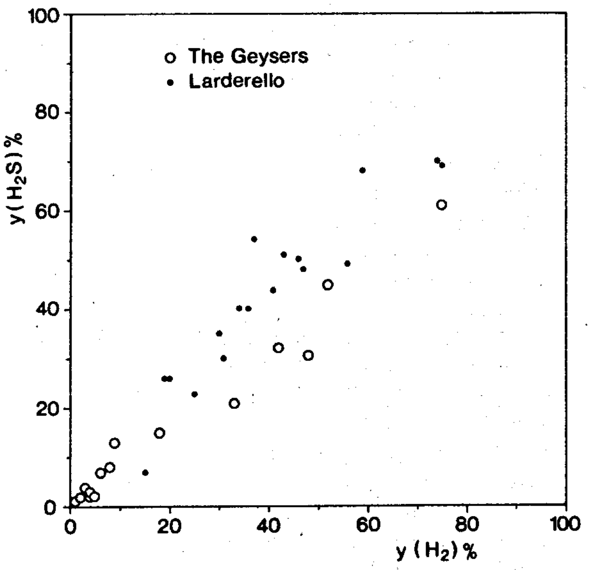

Figure 11. Comparison of y values calculated with equs.(28) and (29) from data given in Table 1, at fixed temperatures.

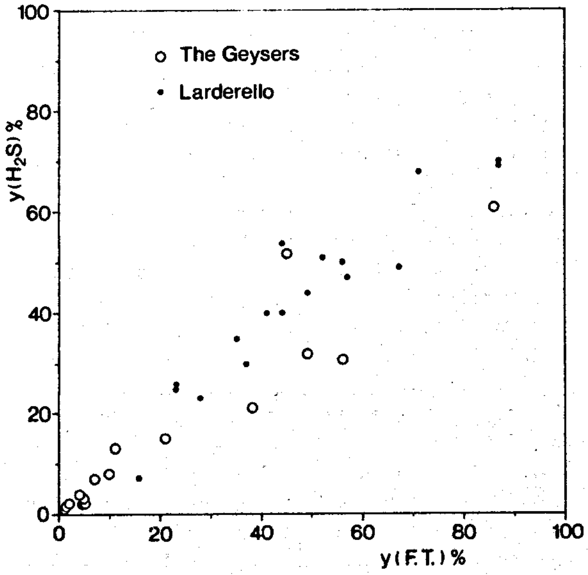

Figure 12. Comparison of y values calculated with equ.(29) and with the Fisher-Tropsch equation (24), using the method of D'Amore and Celati (1983).

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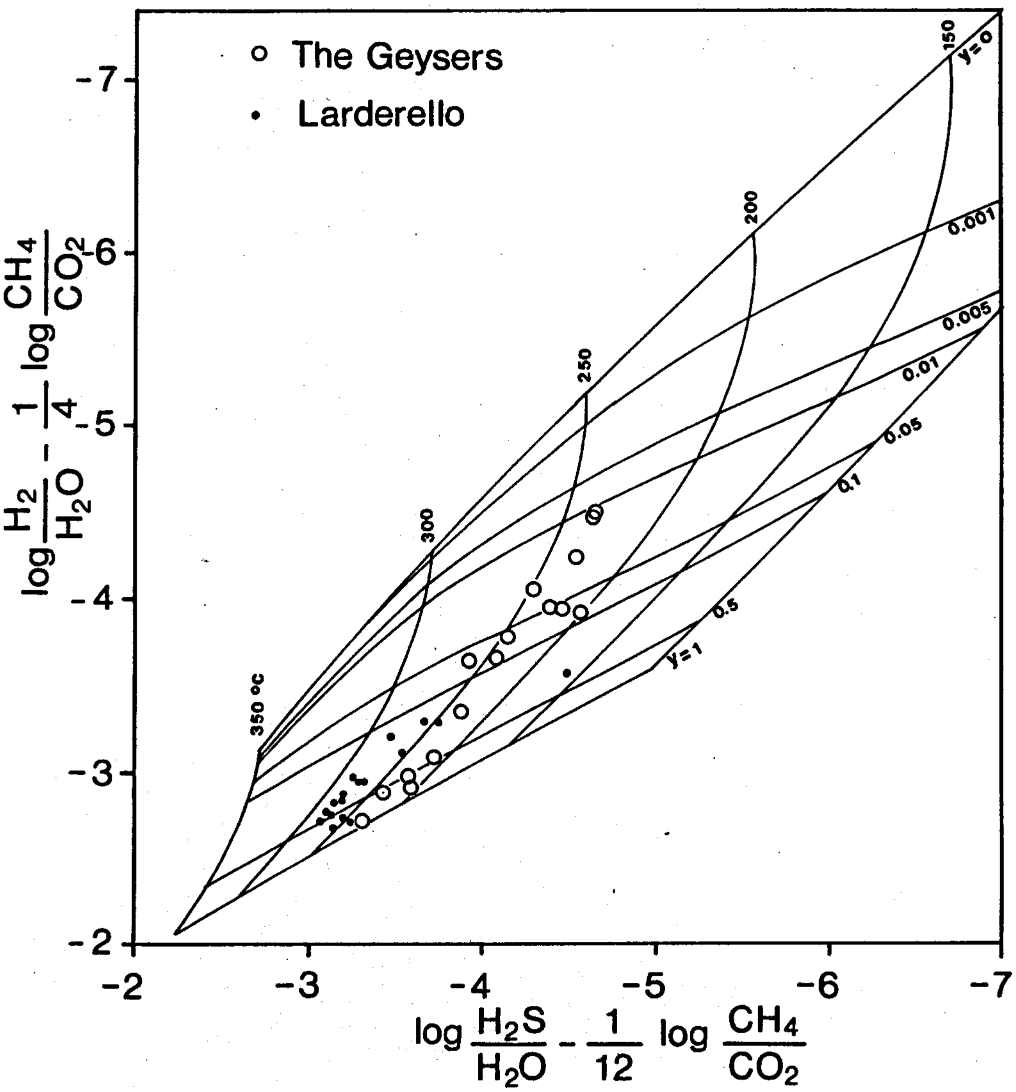

Figure 13. Application of equations (28) and (29) to the simultaneous calculation of temperature and steam quality.