PROCEEDINGS, Tenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 22-24, 1985
SGP-TR-84

CORRELATIONS BETWEEN VAPOR SATURATION, FLUID COMPOSITION AND WELL DECLINE IN LARDERELLO

Franco D'Amore° and Karsten Pruess+

° Istituto Internazionale per le Ricerche Geotermiche, CNR, Via del Buongusto 1, 56100 Pisa, Italy, and + Lawrence Berkeley Laboratory, Berkeley, CA94720, USA

ABSTRACT

A large body of field data from Larderello shows striking temporal correlations between decline of well flow-rate, produced gas/steam ratio, chloride concentration and produced vapor fraction. The latter is inferred from measured concentrations of non-condensible gases in samples of well fluid, using chemical phase equilibrium principles. Observed temporal changes in the vapor fractions can be interpreted in term of a 'multiple source' model, as suggested by D'Amore 6 Truesdell (1979). This provides clues to the dynamics of reservoir depletion, and to the evaluation of well productivity and longevity.

INTRODUCTION

A long-standing problem in the evaluation of vapordominated reservoirs is the estimation of fluid reserves. It is now generally agreed that most of the mass extracted from reservoirs such as Larderello, Italy, and The Geysers, California, had been stored in place as liquid, even though no direct evidence has been found for the deep water table hypothesized by White et al.(1971). The most important reservoir parameter relating to fluid reserves is in-place vapor saturation S_v, which is the volume fraction of gas phase present in the void space of the formation. Unfortunately there is no direct method available by which S_v could be measured in the field. The situation is further complicated by the fractured nature of vapordominated reservoirs. It is probable that large differences in vapor saturation exist between fractures and rock matrix (Pruess 6 Narasimhan, 1982).

Recently, Giggenbach (1980) and D'Amore 6 Celati (1983) developed methods by which information on phase composition in boiling reservoirs can be obtained from concentrations of non-condensible gases observed in geothermal fluids. These methods have a potential for providing estimates of spatial distribution as well as average values of in-place vapor saturation.

In the present paper we utilize several gas phase reactions to estimate vapor fractions in Larderello discharges. Observed temporal variations in the vapor fractions at a number of wells are found to strongly correlate with other parameters, including gas/steam ratio, chloride and boron concentrations, and flow-rate decline. The temporal trends are consistent with the 'multiple source' model of D'Amore & Truest dell (1979). We also discuss possibilities and limitations for identifying reservoir parameters and processes from observed vapor fractions.

CALCULATION OF VAPOR FRACTION

From D'Amore et al.(1982) it is possible to obtain, for the volatile species H_2S, H_2, CH_4 and CO_2, three equations that correlate the concentrations at wellhead of these species (in moles percent in the dry gas) to some physical-chemical parameters of the reservoir:

$$\log(\%H_2) = 7.75 - \frac{12776}{T} - \log\frac{N1}{kg} - \tfrac{1}{3}\log P_{O_2} + \log A_{H_2} \quad (1)$$

$$\log(\%H_2S) = 10.22 - \frac{6483.5}{T} - 0.79 \log T - \log\frac{N1}{kg} - 1/6 \log P_{O_2} + \log A_{H_2S} \quad (2)$$

$$4\log(\%H_2) - \log\frac{(\%CH_4)}{(\%CO_2)} = 20.12 - \frac{5227}{T} - 4\log\frac{N1}{kg} + 4\log A_{H_2} + \log A_{CO_2} - \log A_{CH_4} \quad (3)$$

where P_{O_2} = oxygen partial pressure (redox condition in reservoir)

$A_i = y + (1 - y)/B_i$

y = molar fraction of steam with respect to total water present in the reservoir, both as vapor and liquid

B_i = distribution coefficient of the species i between vapor and liquid, as a function of temperature

$N1/kg$ = gas/steam ratio expressed in litres of gas in standard conditions per kg of steam

From these equations we note that the gas percentages observed at wellhead are governed by the gas/steam ratio, as well as other parameters. In the paper by D'Amore et al. (1982), the gas/(vapor + liquid) ratio was considered uniform in the reservoir, and identical to the gas/steam ratio at wellhead. Moreover, CO_2 was considered in total equilibrium with the gas species, although eventual water-rock interactions and their effects on the CO_2 partial pressure were neglected.

LARDERELLO DATA

Figures 1 to 9 show the temporal trend of the y value calculated from eq.(3), as well as the trends of flow-rate Q in t/h, of the gas/steam ratio (practically CO_2) expressed in Nl/kg, of HCl and of H_3BO_3(in ppm) for some typical wells at Larderello. The calculated y value is of particular significance, as it is probably the average of the y values from the different parts of the reservoir contributing to fluid production.

The wells chosen in various parts of the Larderello field have shown varying contents of HCl in the condensate over a certain production period. The trend generally observed is as follows:

a) flow-rate initially decreases rather rapidly during the early years of production, and then stabilizes on values between 5 and 70 t/h, showing a very slow decrease from then on;

b) although the HCl content varies greatly from one well to another, depending on the position of the well within the field, it tends to increase strongly whenever flow-rate starts to stabilize;

c) the gas/steam ratio tends to increase to a maximum value that is usually quite close to the point at which the flow-rates stop decreasing, and then they stabilize. During the final stage, coinciding with the maximum observed HCl values, the gas/steam ratio tends to decrease;

d) H_3BO_3 generally decreases until it levels out at the same time as the flow-rates begin to stabilize. In wells ALR and BEL there is an increase in correspondence to the period when HCl reached a maximum. In wells VC/10 and G/9, on the other hand, the H_3BO_3 tends to increase before stabilizing on near-constant values;

e) the calculated y values usually increase until flow-rate stabilizes and the gas/steam ratio reaches its maximum. In many cases they tend to decrease with the increase in HCl or a decrease in the gas/steam ratio;

f) wellhead temperature generally increases rapidly from less than 200°C to stabilize eventually around 230' - 260°C. This temperature increase usually coincides with the maximum decrease in flow-rate. At times the temperatures also tend to decrease during the last stages of production when the HCl contents are highest (D'Amore & Truesdell, 1979).

The temporal trends observed can be explained by the 'multiple sources' model described by D'Amore & Truesdell (1979).
Although the absolute values obtained for y are, as we will see later, ptobably too high, the trend is perfectly compatible with this model, which considers that the fluid comes from three main sources located in three) different zones of the reservoir. The increase during the early stages of production corresponds to an increase in fluid fsom a part of the reservoir with less liquid water and a higher gas content. The superheated fraction increases with the decrease in the contribution of fluid from the shallower source, which contains a high percentage of wndensated liquid water. The relative increase in the gas/steam ratio is governed by the contribution from the deepest source, consisting essentially of an NaCl-enriched brine. In well VC/10, which is the deepest of the wells chosen for our study, this 'brine' probably contributed to production right from the stprt, so that there is only a small increase ,in its gas/steam ratio. This well also has a temperature of about 260°C from the beginning, and shows no dramatic decrease in flow-raite as observed in the other wells. Its H_3BO_3 content also tends to increase, and is clearly affected by the increase in the contribution of the 'brine' to production with respect to the two-phase zone of the reservoir.
The value of the parameter $\frac{m_r}{m_l}\,\frac{\phi}{1-\phi}$ (in Fig.1) calculated for well ALR gives roughly the same information as y, but exaggerating the temporal trend. During the first period of production, when the contribution from the two-phase zone increases, the liquid mass tends to decrease with respect to the rock mass; on the other hand, when the contribution of 'brine' tends to increase significantly, the m_r/m_l ratio also shows a strong decrease since the 'brine' is probably liquid water for the most part.

Well QER shows an atypical trend, with a decrease in gas/steam ratio and a high constant HCl value; the trend of y is also constant at the beginning and then decreases strongly. The main source right from the start of production is, in this case, probably the brine.

To conclude, the temporary trend of y confirms that several sources, that is several zones of the reservoir having differing chemical and physical characteristics, may contribute to production.

In the case of a shallow well, such as ALR and BEL, at least three sources are the main suppliers over a certain period. Since the third source, the 'brine', is quite distant, flow-rate will, according to Darcy's law, be very small, albeit nearly constant.

Generally the faster the increase in y the faster is the decrease in flow-rate.

A correlation was also observed between flow-rate Q and y. Figure 10 gives, for some wells, the initial y and Q values (circles) and the y and Q values when Q tends to stabilize (x), but before the decrease in y. For comparison this Figure also includes well T22 (TR) from the Travale geothermal field, Tuscany, whose flow-rate and y are nearly constant with time (very high flow-rate and relatively small y). A certain correlation between Q and y was also noted at The Geysers (Fig.11). Local permeability is obviously another parameter capable of influencing the different flow-rates. (For The Geysers field we considered the average values of 4 years of production in the southern zone of the field). At low Q any mineral buffer for C02 has a stronger effect (excess CO_2 then higher y). Q is low because the boiling source (where the buffer acts) is far from the wells (in the new unit considered at The Geysers the source is closer and thus y is smaller), and the volumetric rate of boiling is small.

INTERPRETATION OF VAPOR FRACTION

It was shown above that there is a strong correlation between vapor fraction y and other parameters of well discharge. While this observation gives general support to a multiple source model, the quantitative significance of y for reservoir parameters and processes is less clear. It has usually been assumed in the literature that the various gaseous species involved in the determination of y are in chemical equilibrium in the 'ultimate' fluid source in the reservoir, but do not re-equilibrate as the fluid flows towards the well, even though phase change may occur. If these assumptions are correct, then the vapor fraction y as computed from mol fractions of non-condensible gases in well discharges represents an instantaneous flowing steam quality in the source. This then would permit an estimate of the ratio of liquid and vapor relativq permeabilities in the source:

$$\frac{k_l}{k_v} = \frac{\mu_l \rho_v}{\mu_v \rho_l} \left(\frac{1}{y} - 1 \right) \qquad (4)$$

Inserting values representative of Larderello ($t = 280°C$, $y = 0.35$) we obtain $k_l/k_v = 0.42$.

If one further assumes $k_l + k_v \approx 1$, as is usually done for fractured reservoirs (Pruess et al., 1983), one could obtain absolute values for k_l and k_v. However, estimates of in-place vapor saturation can only be made if the functional form of saturation dependence of k_l and k_v is known. No relative permeability functions have yet been determined for Larderello reservoir. If the relative permeabilities used by Pruess et al. (1984) for the fractured two-phase reservoir at Krafla, Iceland, were applicable to Larderello, then $k_l/k_v = 0.42$ would correspond to an in-glace vapor saturation of $S_v \simeq 0.43$.

It is difficult to ascertain to what extent the above-stated assumptions regarding chemical equilibrium are correct. Clearly, if any re-equilibration during flow to the wells were to occur it could at most be partial, because the well feeds in Larderello are surrounded by extensive regions of single-phase vapor, so that we would observe y = 1 if complete re-equilibration were taking place, The fact that y is substantially smaller than 1 suggests that the kinetics of the gas phase reactions used to obtain vapor fractions are 'slow'. Consequently one should expect in-place re-equilibration in response to exploitation-induced changes in phase and chemical composition also to be partial at most. It appears, therefore, that the two assumptions of perfect chemical equilibrium in-place, and no re-equilibration during flow to the well, are incompatible in a reservoir which has undergone significant discharge.

Let us know consider a hypothetical model with no re-equilibration whatsoever and no rock-fluid interaction. As a reservoir region is being depleted, the cumulative production of each chemical species will then approach the total amount of that species originally stored, in the reservoir fluids. Therefore, the average mol fractions obtained from the cumulative discharge will approach the original in-place mol fractions, so that the "cumulative" vapor

fraction y_{cum} computed from average mol fractions will approach the original in-place steam quality $Q_i = M_v/(M_v + M_l)$. (Here M is mass in place). From this one can obtain the in-place liquid saturation

$$S_l = \frac{(1 - y_{cum})/\varrho_l}{y_{cum}/\varrho_v + (1 - y_{cum})/\varrho_l} \qquad (5)$$

Results for "cumulative" vapor fraction, using average mol fractions, are shown for well ALR in Fig.12. It is seen that $y_{cum} \gtrsim 0.30$; similar values are also obtained for other wells. Inserting typical values of t = 280°C, $y_{cum} = 0.35$ into Equation(5), we obtain $S_l = 0.08$, which is substantially smaller than the range of values compatible with total fluid extraction to date in the central zone of Larderello ($S_l \geq 0.25$; cf.Pruess et al., 1985). This discrepancy indicates that the assumptions made in our hypothetical model are wrong. We conclude from this tha either there is partial re-equilibration in the single-phase vapor zones near the wells, or there is non-equilibrated "excess" CO_2 present in the produced fluids, which is released from minerals during exploitation (or both). The latter possibility seems quite realistic, as reservoir engineering studies have demonstrated that only a small fraction of the CO_2 produced in Larderello could have been originally stored in the reservoir fluids (Pruess et al., 1985).

Usually 90% of the main gas is CO_2, especially in the vapor-dominated geothermal field at Larderello. In the present paper we assume that the CO_2 concentration, and hence the gas/steam ratio, may be controlled by local mineral buffers. As early as 1979, D'Amore & Truesdell hypothesized that the fluid at wellhead may have originated from various sources with different physical and chemical characteristics, sited at differing depths within the reservoir. Now, different buffers could exist or act with different kinetics in the various parts of the reservoir. Imagine two different parts of the reservoir which have identical phase compositions (in-place as well as flowing), but different mineral buffers. The gas/steam ratios will, therefore, be different and the resulting y values, determined for instance by eq.(3) at a given temperature, will also differ, unless ($\%H_2$) X (gas/steam) = constant, and CH_4/CO_2 = constant. These conditions will onfy be fulfilled if the kinetics of the gas reactions are fast compared to the kinetics of the mineral buffer. If, on the other hand, the mineral buffer is faster, then different y values will be obtained, even though all phase compositions may be identical.

In the uppermost part of the reservoir, consisting of dolomites, anhydrite and calcite, one possible reaction capable of buffering CO_2 is calcite hydrolysis:

$$CaCO_3 + 2\,H^+ = Ca^{2+} + H_2O + CO_2 \qquad (6)$$

Analysing the last thirty years of production at Larderello, we calculated that the total CO_2 produced by this reaction has led to the destruction of less than 1 meter of limestone throughout the 200 km^2 of this field. This is effectively a very small quantity.

In the deepest part of the reservoir, consisting of quartzitic phyllites, the following reaction is likely to occur between epidote, calcite, quartz and prehnite:

$$2Ca_2Al_3Si_3O_{12}(OH) + 2CaCO_3 + SiO_2 + 2H_2O = 3Ca_2Al_2Si_3O_{10}(OH)_2 + 2CO_2 \qquad (7)$$

Utilizing clinozoisite activity, with a pistacite molar fraction of 0.275 (average at Larderello), we obtain the following equation correlating the CO_2 partial pressure to temperature t °C:

$$\log P_{CO_2} = -2.81 + 1.437 \times 10^{-2} t - 1.4 \times 10^{-5} t^2 \qquad (8)$$

At 260°C, $P_{CO_2} \simeq 1$ bar, which is compatible with the CO_2 pressure measured in the central part of the field.

In other words, the calculated y at Larderella may be affected by an excess of CO_2. This conclusion derives from the observation that the calculated y values are generally very high (from 0.2 to 0.8), and liquid saturation, i.e. the fraction of volume occupied by the liquid in the reservoir, is far too small compared to the cumulative production of many wells, since most of the fluid produced must come from evaporation of the liquid fraction (usually less than 5 % at Larderello).

Figure 13 shows that the calculated y% at both Larderello and The Geysers is closely correlated with the gaslsteam ratio.
The wells chosen at Larderello had temperature between 250° and 270°C. At The Geysers y was calculated at 240°C. This could indicate a mixing between fluids from differing parts of the reservoir containing different percentages of CO_2.

We considered an average composition typical of the central area of the Larderello field: CO_2 = 90%; H_2 = 1.9%; H_2S = 1.6%; CH_4 = 1.5%.

Using eq.(3) we calculated y as a function of temperature for different values of the gas/steam ratio, from 1 to 50 Nl/kg (Fig.14). Figure 15, on the other hand, was based on eq.(2), using a known function of temperature for oxygen partial pressure (see D'Amore & Gianelli, 1984):

$$\log P_{O_2} = -3.808 - 13708.3/T - 2.075 \times io^6/T^2 \quad (9)$$

Note first of all the strong variation in y with gas/steam ratio. For example, at 260°C from 20 to 30 Nl/kg, y varies from 0.3 to 0.43. Moreover, the higher the gas/steam ratios, the closer the correlation between y and temperature. Thus, from 240' to 280°C, at 30 Nl/kg, y varies from 0.54 to 0.34.

In the case of H_2S (Fig.15), the dependence of y on temperature is even more remarkable. The point shown in the two figures represents the average gas/steam ratio (25 Nl/kg) and average temperature (260°C) of the central part of the field. The two methods give roughly the same value of y, i.e. 0.35.

Solving eqs. (1),(2) and (3) simultaneously as a function of T and y, we obtain:

$$6 \log \frac{(\% H_2S)}{(\% H_2)} + \log \frac{(\% CH_4)}{(\% CO_2)} = 25.72 - \frac{8121.8}{T} - 4.74 \log T + 6 \log A_{H_2S} - 6 \log A_{H_2} - \log A_{CO_2} + \log A_{CH_4} \quad (10)$$

This equation is of limited use for calculating y where the latter has high values or temperature is low.

For example, at 260°C for various values of y, the right-hand side of the equation gives the following values (F):

Y	F
0	3.13
0.01	0.35
0.1	-1.89
0.25	-2.24
0.50	-2.37
1	-2.44

Using the same field data we used earlier, we merely obtain 0.25 < y (0.50. However, this is compatible with the results obtained from Figs. 14 and 15.

CONCLUSIONS

In a qualitative sense, the temporal variations in vapor fraction for many wells are strongly correlated with changes in gas/steam ratio, chloride and boron concentrations, and flow-rate decline. This striking correlation supports the multiple source model of D'Amore & Truesdell (1979).

For the above discussion it is also apparent, however, that the quantitative significance of y-values obtained at Larderello remains uncertain at the present time. Observed vapor fractions reflect several reservoir conditions and processes, including (1) tht 'memory' of two-phase conditions with substantial liquid in the (presumably) deep ultimate fluid sources; (2) the release of CO_2 from minerals, which equilibrates only in part or not at all with other gaseous species; and (3) possibly partial re-equilibration of non-condensible gases in the single-phase vapor regions surrounding the wells.

REFERENCES

D'Amore,F. and Truesdell, A.H. (1979), 'Models for Steam Chemistry at Larderello and The Geysers' , Proc. Fifth Wotkshop Geothermal Reservoir Engineering, Stanford, CA., pp.283-297.

D'Amore, F. and Celati, R. (1983) 'Methodology for Calculating Steam Quality in Geothermal Reservoirs', Geothermics, v.12, 2/3, pp.129-140.

Giggenbach, W.F. (1980),'Geothermal Gas Equilibria', Geochim.Cosmochim.Acta, v.44, pp.2021-2032.

Pruess,K. and Narasimhan, T.N. (1982),'On Fluid Reserves and the Production of Superheated Steam from Fractured, Vapor-Dominated Geothermal Reservoirs', J.Geophys. Res.,v.87, no. 811, pp.9329-9339.

Pruess,K., Bodvarsson,G.S. and Stefansson,V. (1983), 'Analysis of Production Data from the Krafla Geothermal Field, Iceland', Proc. Ninth Workshop Geoth. Reser. Engng., Stanford, CA., pp. 345-350.

Pruess,K., Bodvarsson, G.S., Stefansson,V. and Eliasson,E.T.(1984),'The Krafla Geothermal Field, Iceland, 4, History Match and Prediction of Individual Well Performance', Water Res. Res., v.20, no.11, pp.1561-1584.

Pruess,K., Celati, R.,Calore,C. and D'Amore, F.(1985),'CO_2 Trends in the Depletion of the Larderello Vapor-Dominated Reservoir', presented at Tenth Workshop Geothermal Reservoir Engineering, Stanford University, California.

White, D.E., Muffler,L.J.P. and Truesdell,A. H. (1971), 'Vapor-Dominated Hydrothermal Systems Compared with Hot-Water Systems', Econ. Geol.,v.66, no.1, pp.75-97.

D'Amore,F., Celati, R. and Calore,C. (1982), 'Fluid Geochemistry Applications in Reservoir Engineering (Vapor-Dominated Systems)', presented at Eighth Workshop Geothermal Reservoir Engng., Stanford University, Stanford, CA.

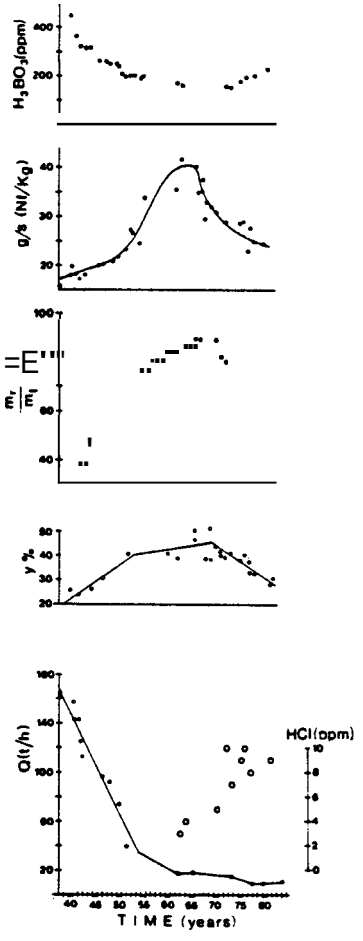

Figure 1. Temporal trend for well ALR of flow-rate Q in t/h, as well as HCl in ppm, y% calculated from eq.(7), parameter $m_r \phi m_l(1-\phi)$ (see text), gas/steam ratio in Nl/kg (liters of gas at standard conditions per kg of steam, H_3BO_3 in ppm.

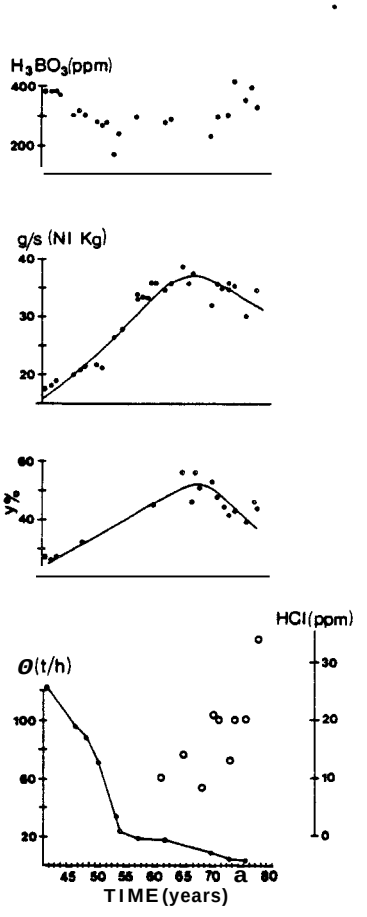

Figure 2. Temporal trend for well BEL. See Fig.1 for legend.

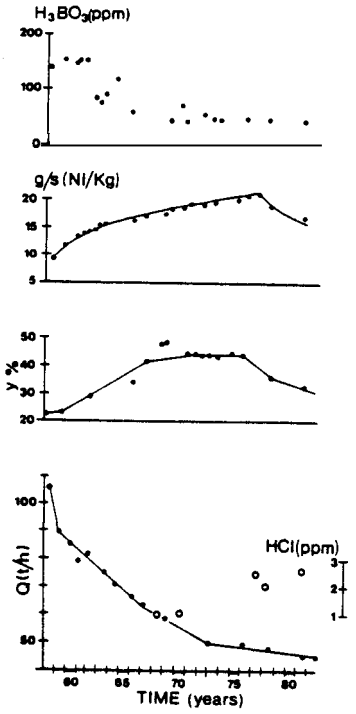

Figure 3. Temporal trend for well 145. See Fig.1 for legend.

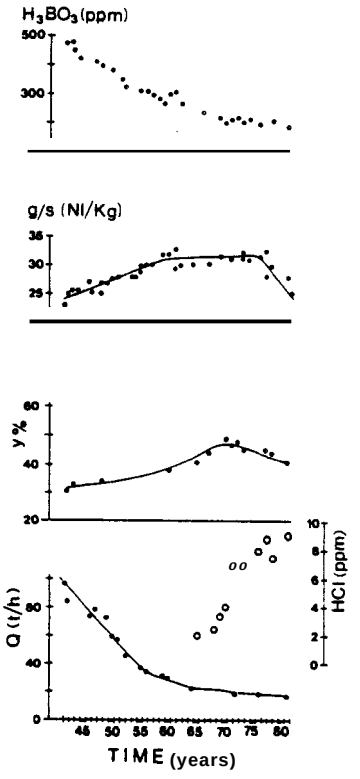

Figure 4. Temporal trend for well FAB. See Fig.1 for legend.

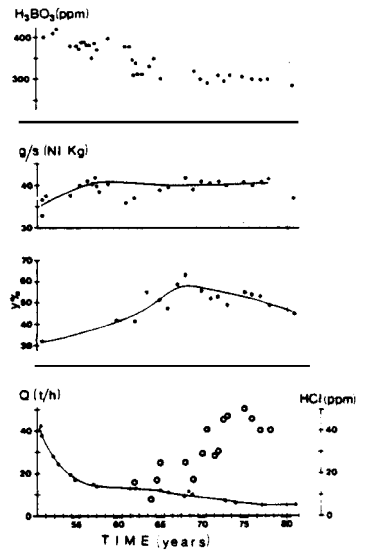

Figure 5. Temporal trend for well 80. See Fig.1 for legend.

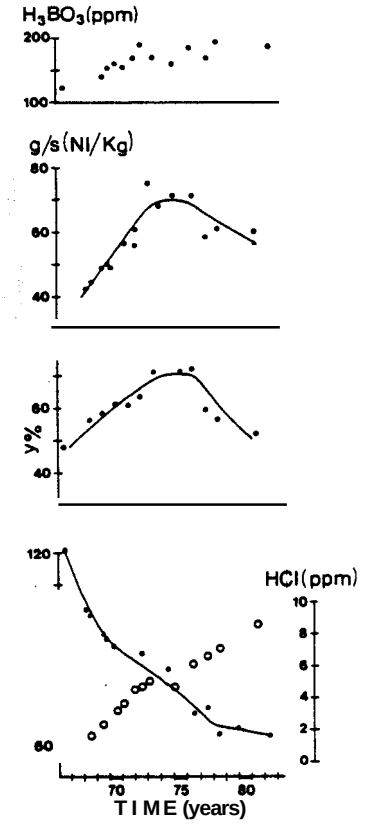

Figure 6. Temporal trend for well G/9. See Fig.1 for legend.

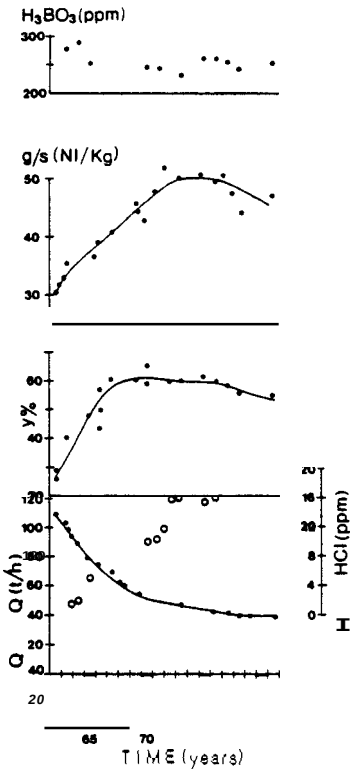

Figure 7. Temporal trend for well G/1. See Fig.1 for legend.

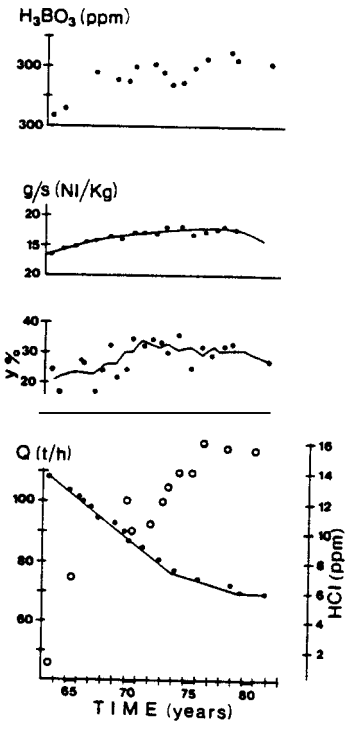

Figure 8. Temporal trend for well VC/10. See Fig.1 for legend.

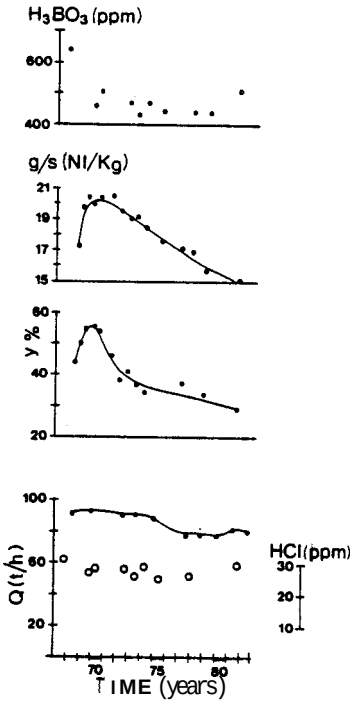

Figure 9. Temporal trend for well QUE. See Fig.1 for legend.

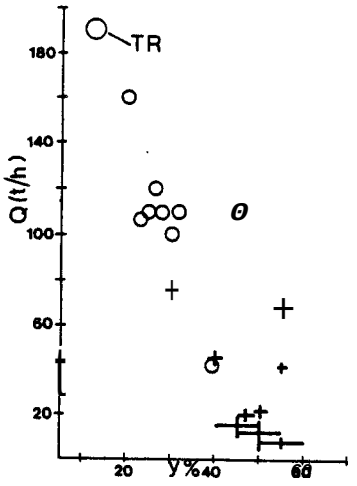

Figure 10. Relationship between flow-rate Q in t/h and y% for some wells of the Larderello field and including well T22 of Travale field (TR). Open circles refer to values at start of production and crosses to values when flow-rate began to stabilize.

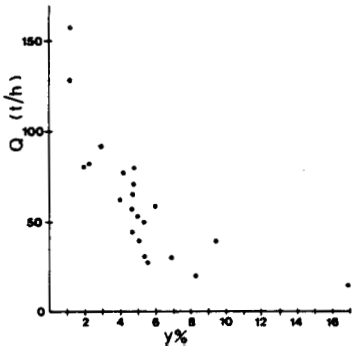

Figure 11. Relationship between flow-rate and y% for some wells in The Geysers field.

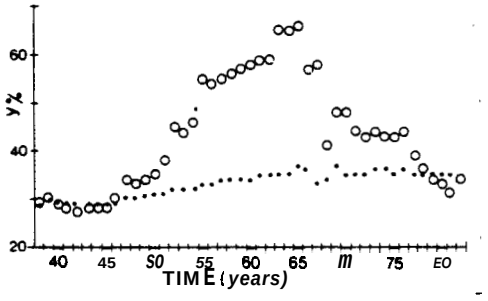

Figure 12. Vapor fractions computed for well ALR vs time. Circles: y computed from eq.(3); dots: cumulative y (see text).

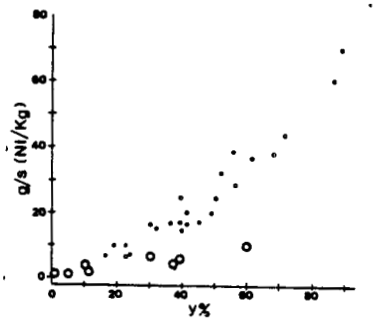

Figure 13. Percentage of y (calculated from eq.(7)) as a function of gas/steam ratio expressed in Nl/kg (liters of gas at standard conditions per kg of steam). Dots refer to Larderello and open circles to The Geysers.

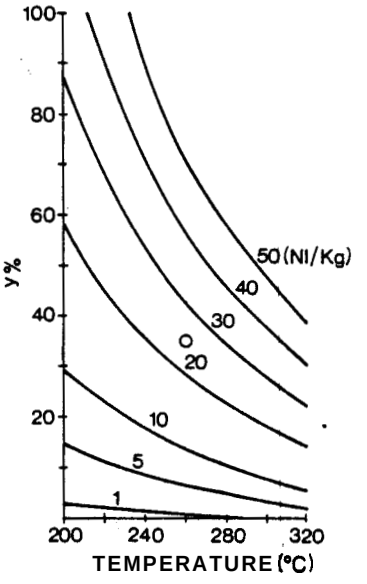

Figure 14. y% computed from eq.(3) at a given composition (see text) as a function of temperature at different values of the gas/steam ratio (expressed as Nl/kg).

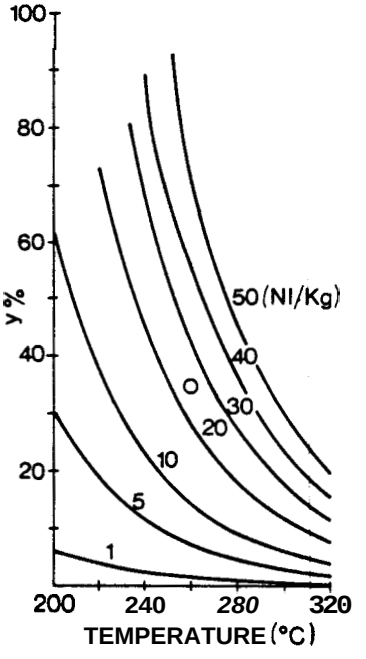

Figure 15. y% computed from eqs(2) and (9) at a given composition (see text) as a function of temperature at different values of the gas/steam ratio (expressed as Nl/kg).