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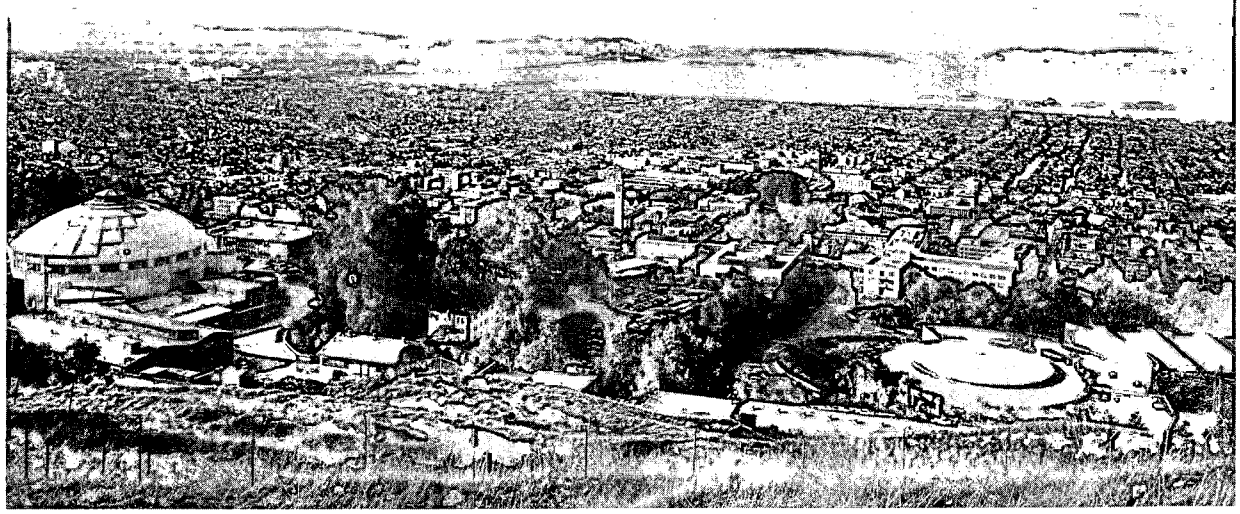

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CORRELATIONS BETWEEN STEAM SATURATION, FLUID COMPOSITION, AND WELL DECLINE IN VAPOR-DOMINATED RESERVOIRS

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Abstract

A large body of field data from Larderello and other vapor-dominated geothermal reservoirs shows striking temporal correlations between (1) decline of well flow rate, (2) produced gas/steam ratio, (3) chloride concentration, (4) degree of superheat, and (5) 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 fraction can be interpreted in terms of a "multiple source" model, as suggested by D'Amore and 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 vapor-dominated 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. Indirect evidence has also been found for the deep water table hypothesized by White, Muffler, and Truesdell (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 vapor-dominated reservoirs. It is probable that large differences in vapor saturation exist between fractures and a rock matrix of low permeability (Pruess and Narasimhan, 1982).

Recently, Giggenbach (1980) and D'Amore and 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 the "vapor fraction" in Larderello discharges. Most of our considerations specifically pertain to the Fischer-Tropsch reaction:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad (1)$$

which was selected as an example of a gas phase reaction which occurs in geothermal systems and is being used to compute the steam fraction y for several wells in this paper. Depending upon reaction kinetics and mineral buffer control, the arguments presented here could be applicable in modified form for other reactions as well. In this section, we use mass action laws

only for disucssion of trends rather than for detailed quantitative evaluations; therefore, we prefer to deal with the approximate equations written down by Giggenbach (1980), which are simpler than the more rigorous treatment of D'Amore and Celati (1983).

Giggenbach (1980) showed that under some suitable assumptions one can obtain the following equation for discharged mol fractions $x_{d,i}$ of species i:

$$\frac{x_{d,CO_2} \cdot x_{d,H_2}^4 \cdot P_t^4}{x_{d,CH_4}} = K_c'(T,y) \qquad (2)$$

(the notation used is Giggenbach's). The effective equilibrium constant K_c' involves ratios of the form $y + (1-y)/B_i$, where at a temperature of t=250°C the distribution coefficients B_i have values of 107, 418, and 526, respectively, for CO_2, CH_4, and H_2. Therefore, for $y > 0.10$ one can approximate $y+(1-y)/B_i \approx y$ to obtain the following approximation to Equation (2):

$$\frac{x_{d,CO_2} \cdot x_{d,H_2}^4}{x_{d,CH_4}} \cdot \frac{P_t^4}{P_{H_2O}^2} \simeq K_c(T) \cdot y^4 \qquad (3)$$

In this equation the dependence upon vapor fraction y is made explicit, which is convenient for discussing general trends (see below). Before applying these equations to field data, it is well to remember the (explicit or implicit) assumptions and conditions for which they were derived.

(1) The discharge sample is obtained from a single fluid source, which consists of a two-phase mixture of liquid and vapor.

(2) The fluid source is in thermodynamic and chemical equilibrium.

(3) The chemical reactions considered are in equilibrium in the gas phase.

(4) A "small" two-phase sample of discharge fluid is taken such that there is negligible change in chemical or phase composition in the source.

(5) The sample is transferred to the well head without any mass gain or loss.

(6) There is no re-equilibration of species during transport from the source to the well head (i.e., the species mol fractions $x_{d,i}$ present in a parcel of fluid maintain their values from the original source).

Applicability of Idealized Sampling Conditions.

In actual field applications, the conditions as stated above will usually be violated to some extent. The fluid source is a large volume of porous rock, in which substantial spatial variations in temperature, pressure, vapor saturation, and chemical composition of fluids may be present. Fluids sampled at well head represent a spatial and temporal average over sources of different conditions, which are continuously distributed throughout the drainage volume of the well. The two requirements that reservoir fluids be in chemical equilibrium locally, but do not re-equilibrate as they flow towards the well will in general not be compatible. If reaction kinetics are "slow", then these requirements may be compatible as long as the natural state of the reservoir, and the chemical compositions of fluids in that state, are not significantly disturbed by exploitation. However, as fluids are being produced the chemical composition of liquid and vapor phases in situ will change because of production-induced boiling, and quite likely also from release of gaseous species from minerals. If reaction kinetics were fast enough to permit re-equilibration of gaseous species in situ, then one should also expect at least partial re-equilibration to occur along the flow path towards the well. If reaction kinetics were really "fast", then all gas reactions would be in local equilibrium everywhere, and application of equations such as (2) would yield y=1 for Larderello wells, because in the vicinity of well feeds single-phase vapor conditions are present in the reservoir. The fact that observed y-values at Larderello are considerably smaller than 1, typically y=0.3, clearly shows that the Fischer-Tropsch reaction re-equilibrates only partially, or not at all, in the single-phase vapor regions. This suggests that kinetics are "slow", and that re-equilibration in response to exploitation-induced chemical composition

changes should also be expected to be partial at most. Conditions may be closer to equilibrium in reservoir regions where fluid flow velocities and phase change rates are smaller, i.e., at larger distance from wells.

Interpretation of Vapor Fraction y.

From a reservoir engineering standpoint, the most important parameter relating to fluid phase composition is in-place vapor saturation S_v, which is the volume fraction of gas phase present in the void space of the formation. This quantity is of crucial importance for estimates of fluid reserves, as the effective density of two-phase fluid is given by $\rho = S_v\rho_v + (1-S_v)\ \rho_\ell$. The vapor fraction $y = n_{v,w}/(n_{v,w}+n_{\ell,w})$, with $n_{v,w}$ and $n_{\ell,w}$ representing the mols of discharged water originating from vapor and liquid, respectively, provides a measure of the phase composition of the reservoir fluid. However, because the ideal conditions assumed in the derivation of y from gas concentrations are violated in the field to some extent, it is not clear how y can be quantitatively related to reservoir engineering quantities, such as in-place vapor saturation S_v, or flowing steam quality $Q_f = F_v/(F_\ell+F_v)$. (Here F denotes mass flow rate in the reservoir.)

We shall now consider a number of (hypothetical) idealized models and conditions, which may or may not be applicable to actual vapor-dominated reservoirs, but which will help to obtain some insight into the interpretation of y under well-defined circumstances.

(1) Let us assume we take a small two-phase sample from an equilibrated source. The vapor fraction y computed from measured mol fractions $x_{d,i}$ then represents the instantaneous flowing steam quality Q_f in the source. Assuming Darcy's law to be valid for two-phase flow, and capillary pressure effects to be negligible, we have

$$y = Q_f = \frac{F_v}{F_v + F_\ell}$$

$$= \frac{k_v \rho_v / \mu_v}{k_v \rho_v / \mu_v + k_\ell \rho_\ell / \mu_\ell} \tag{4a}$$

Here, k_v and k_ℓ denote relative permeability, μ_v and μ_ℓ denote viscosity. Thus, the observed y would permit us to evaluate the ratio of liquid and vapor relative permeabilities for the phase composition present in the source:

$$\frac{k_\ell}{k_v} = \frac{\mu_\ell \ \rho_v}{\mu_v \ \rho_\ell} \ (\frac{1}{y} - 1) \tag{4b}$$

Inserting values representative of Larderello (t = 280°C, y = 0.35) we obtain $k_\ell/k_v \approx 0.42$. If one further assumes $k_\ell + k_v \approx 1$, 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 $k_\ell/k_v = 0.42$ would correspond to an in-place vapor saturation of $S_v \approx 0.43$.

(1a) Now let us consider transport effects. If no re-equilibration or mass transfer whatsoever takes place as the fluid sample migrates from its original source in the reservoir to the sampling point at the well, even as phase change may occur, then all $x_{d,i}$ and the resulting y remain unchanged if original source fluid temperature is used in the analysis. If source temperature is unknown, and a lower temperature corresponding to conditions near the well is used in the analysis, then a larger value for y will be obtained. This can

be seen from the approximate Equation (3), noting that K_c decreases rapidly with decreasing temperature. If partial re-equilibration takes place as the fluid sample approaches the well, migrating through regions of increasing vapor saturation, then the y obtained from mol fractions at the well will be larger than the y at the original fluid source.

(2) Consider now an extreme case with no re-equilibration, and no rock/fluid interaction. As a reservoir region is being depleted, the cumulative production of each species will approach the total amount of that species originally stored in the reservoir fluids. The average mol fractions obtained from cumulative discharge then will approach the original in-place mol fractions, so that the "cumulative" vapor fraction y_c computed from average mol fractions will approach the original in-place steam quality $Q_i = M_v/(M_v + M_\ell)$. (Here M is mass in-place.) From this one can obtain the original in-place vapor saturation

$$S_v = (y_c/\rho_v)/[y_c/\rho_v + (1-y_c)/\rho_\ell]. \tag{5}$$

(3) Now let us assume that (extremely) strong mineral buffers are present, which constrain all phase compositions to remain in local equilibrium with the minerals in those reservoir regions where liquid phase is present. If no re-equilibration occurs in the single-phase vapor regions, then y as obtained from samples of well fluid will represent the (average) flowing steam quality at the vapor/two-phase boundary.

(4) Suppose now that the original fluid sample contains CO_2, released from an internal or external source, which re-equilibrates only partially with other gases. The mol fraction of "excess" (non-equilibrated) CO_2 in the vapor phase is

$$x_{v,CO_2}^{exc} = x_{x,CO_2} - x_{v,CO_2}^{eq} \tag{6}$$

where the equilibrium CO_2 mol fraction obeys the mass action law for the Fischer-Tropsch reaction:

$$x^{eq}_{v,CO_2} = K_c \frac{P^2_{H_2O}}{P^4_t} \frac{x_{v,CH_4}}{x^4_{v,H_2}} \tag{7}$$

The excess CO_2 will make x_{d,CO_2} larger, so that according to Equation (3) y will become larger than it would be without excess CO_2.

(5) Several interesting results can be derived for two-source models. The simplest case to analyze involves two sources with the same temperature and chemical composition, but different y. We have

$$x^{(1)}_{d,i} = y^{(1)} x_{v,i} + [1-y^{(1)}]x_{\ell,i} \tag{8a}$$

$$x^{(2)}_{d,i} = y^{(2)} x_{v,i} + [1-y^{(2)}]x_{\ell,i} \tag{8b}$$

Withdrawing $n^{(1)}$ mols from source 1 and $n^{(2)}$ mols from source 2, the mixture composition is

$$x_{d,i} = \frac{(y^{(1)} n^{(1)} + y^{(2)} n^{(2)}) x_{v,i} + ([1-y^{(1)}] n^{(1)} + [1-y^{(2)}] n^{(2)}) x_{\ell,i}}{n^{(1)} + n^{(2)}}$$

$$= \bar{y} x_{v,i} + (1-\bar{y}) x_{\ell,i} \tag{9}$$

where

$$\bar{y} = \frac{y^{(1)} n^{(1)} + y^{(2)} n^{(2)}}{n^{(1)} + n^{(2)}} \tag{10}$$

is the average vapor fraction in the mixture. Thus, when analyzing data from multiple sources with identical temperature and chemical composition, one obtains a y which represents an arithmetic average.

(6) Now consider two fluid sources, of which one is in two-phase conditions, the other being single-phase vapor with different gas content. An analysis similar to the foregoing shows, as expected, that mixing with single phase vapor of higher (lower) gas content will produce a sample corresponding to higher (lower) vapor fraction.

(7) Multiple sources with different chemical composition are considerably more difficult to analyze. Consider two sources with the same temperature and vapor fraction y, but different $x_{v,i}$, $x_{\ell,i}$. Discharge mol fractions are (k = 1,2)

$$x_{d,i}^{(k)} = y\, x_{v,i}^{(k)} + (1-y)\, x_{\ell,i}^{(k)}$$

$$= x_{v,i}^{(k)} \left(y + \frac{1-y}{B_i}\right) \tag{11}$$

The mixture composition is

$$x_{d,i} = x_{d,i}^{(1)} f_1 + x_{d,i}^{(2)} f_2 \tag{12}$$

where

$$f_k = \frac{n^{(k)}}{n^{(1)} + n^{(2)}} \tag{13}$$

is the fractional discharge from source k (= 1,2). Inserting Equation (12) into the approximate Equation (3) and rearranging, we obtain the mixture vapor fraction

$$\bar{y} = y \frac{\left\{ f_1 + (1-f_1) \cdot \frac{x^{(2)}_{v,CO_2}}{x^{(1)}_{v,CO_2}} \right\}^{1/4}}{\left\{ f_1 + (1-f_1) \cdot \frac{x^{(2)}_{v,CH_4}}{x^{(1)}_{v,CH_4}} \right\}} \cdot \left(f_1 + (1-f_1) \left[\frac{x^{(2)}_{v,CH_4} \cdot x^{(1)}_{v,CO_2}}{x^{(1)}_{v,CH_4} \cdot x^{(2)}_{v,CO_2}} \right]^{1/4} \right) \tag{14}$$

Note that $x^{(k)}_{v,CO_2}$, $x^{(k)}_{v,CH_4}$ $(k = 1,2)$, and f_1 can vary freely, so that in general $\bar{y} \neq y$. Thus we have the somewhat surprising result that mixing of two fluid samples with the same temperature and y, but different chemical composition, will in general produce a sample with y different from the endmembers.

Calculation of y

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

$$\log(\%H_2) = 7.75 - \frac{12776}{T} - \log\frac{Nl}{Kg} - \frac{1}{2}\log P_{O_2} + \log A_{H_2} \quad (15)$$

$$\log(\%H_2S) = 10.22 - \frac{6483.5}{T} - 0.79\log T - \log\frac{Nl}{kg} - \frac{1}{6}\log P_{O_2} + \log A_{H_2S} \quad (16)$$

$$4\log(\%H_2) - \log\frac{(\%CH_4)}{(\%CO_2)} = 20.12 - \frac{5227}{T} - 4\log\frac{Nl}{kg} + 4\log A_{H_2} + \log A_{CO_2} - \log A_{CH_4} \quad (17)$$

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

Nl/kg = gas/steam ratio expressed in liters 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/water 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.

Usually 90% of the non-condensible 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 and 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. (17) at a given temperature, will also differ, unless (% H_2) x (gas/steam) = constant, and CH_4 / CO_2 = constant. These conditions will only be fulfilled if the kinetics of the gas reactions are fast compared to the kinetics of the 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 Larderello, in the uppermost part of the reservoir, consisting of dolomites, anhydrite and calcite, one possible reaction capable of buffering CO_2 is calcite hydrolysis:

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2 \qquad (17a)$$

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

$$2Ca_2Al_3Si_3O_{12}(OH) + 2CaCO_3 + SiO_2 + 2H_2O =$$
$$3Ca_2Al_2Si_3O_{10}(OH)_2 + 2CO_2 \qquad (17b)$$

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 in °C.

$$\log P_{CO_2} = -2.81 + 1.437 \cdot 10^{-2}t - 1.4 \cdot 10^{-5}t^2 \qquad (17c)$$

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

In other words, the calculated y at Larderello 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). Moreover, Figure 1 shows that the calculated y at both Larderello and The Geysers by eq. 15-17 correlates

with the gas/steam ratio. The wells chosen at Larderello had temperatures between 250°C 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. (17), we calculated y as a function of temperature for different values of the gas/steam ratio from 1 to 50 Nl/kg (Fig. 2). Figure 3, on the other hand, was based on eq. (16), using a known function of temperature for oxygen partial pressure (see D'Amore and Gianelli, 1984):

$$\log P_{O_2} = -3.808 - 13708.3/T - 2.075.10^6/T^2 \qquad (18)$$

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 stronger the correlation between y and temperature. For example, from 240°C to 280°C, at 30 Nl/kg, y varies from 0.54 to 0.34.

In the case of H_2S (Fig. 3), 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. (15), (16) and (17) simultaneously as a function of T and y, we obtain:

$$6 \log \frac{(\%H_2S)}{(\%H_2)} + \log \frac{(\%CH_4)}{(\%CO_2)} = 25.75 - \frac{8121.8}{T} - 4.74\log T + 6\log A_{H_2S} - 6\log A_{H_2} - \log A_{CO_2} + \log A_{CH_4} \quad (19)$$

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. 1 and 2.

CORRELATION BETWEEN TEMPORAL TRENDS OF CHEMICAL SPECIES AND Y

Figures 4 to 12 show the temporal trend of the y value calculated from eq. (17), as well as the trends of the flow rate Q in tonnes/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 at 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 ratios tend 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 at 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 and Truesdell, 1979).

The temporal trends observed can be explained by the 'multiple sources' model described by D'Amore and Truesdell (1979).

Although the absolute values obtained for y are, as we have already said, probably too high, the trend is compatible with this model, which considers that the fluid comes from three main sources located in different zones of the reservoir. The increase during the early stages of production corresponds to an increase in fluid from 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 condensated 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 contributes largely to production right from the start, 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-rate 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 $\frac{m_r}{m_\ell} \frac{\phi}{1-\phi}$ (in fig. 4) 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 temporal 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 14 gives, for some wells, the initial y and Q values (circles) and the y and Q values when Q tends to stabilize (x). For comparison, this figure also includes well T22 (see Fig. 13) from the Travale field, 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. 15). Where y is around 0.02, and has remained nearly constant over 4 years, production has dropped by 0 to 15%. For wells in which y has increased from 0.02 or 0.06 to 0.10 the drop in production has been much higher - from 20 to 40%. 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 the

mineral buffer seems to have 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.

Observed Changes in Vapor Fraction and Conclusions

Generally speaking, temporal variations in vapor fraction y observed at Larderello could be caused by any of the following:

(1) Differences in liquid saturation between different reservoir regions, either in the natural state or induced by exploitation. (This possibility relates closely to the three-source model of D'Amore and Truesdell, 1979).

(2) Differences in chemical composition of fluids from different reservoir regions, which may be present in the natural state or may be induced by exploitation. Such differences may relate to systematic variations in mineral compositions between different reservoir regions. (A case of special interest in Larderello is excess - CO_2 released from minerals during exploitation, which does not re-equilibrate with other gas species. This will cause y to be overestimated; see Equation 3.)

(3) Differences in source temperatures. (If "true" y = const, and source temperatures are rising, then analysis using constant T will yield a larger y.)

(4) Differences in relative permeability behavior. (Different sources with the same in-place vapor saturation S_v will yield different y if relative permeability functions are different.)

(5) Partial re-equilibration of gaseous species along flow paths of varying length and travel time. (Fluid flow is generally from regions of lower vapor saturation towards higher vapor saturation near the well. Thus, partial re-equilibration would tend to yield an increased y.)

(6) Partial re-equilibration of gaseous species in-place, as chemical compositions of phases change because of phase transitions and release of gases from minerals.

Observed temporal variations of y in Larderello are generally moderate (less than a factor 2 over several decades). A typical pattern of change is as follows: y increases for a number of years, then remains constant for a while, and eventually declines. Given the large number of possible causes for such variation (see above), an unambiguous identification of the underlying reservoir conditions and processes is not possible. To develop plausible hypotheses for explaining the temporal variations in y, it is necessary to consider correlations with other parameters, such as flow rate decline, gas/steam ratio, chloride concentration, and degree of superheat.

However, some important conclusions can be drawn from y alone. It was pointed out above that in an extreme model with no rock/fluid interaction, and no re-equilibration in the gas phase, the "cumulative" vapor fraction y_c computed from average cumulative discharged mol fractions must approximate original in-place vapor fraction as reservoir depletion is being approached. Results for "cumulative" vapor fraction, using average mol fractions, are shown for well ALR in Figure 16. It is seen that $y_c \gtrsim 0.30$; similar values are also obtained for other wells. Inserting typical values of t = 280°C, $y_c = 0.35$ into Equation (5), we obtain $S_v = 0.92$, which is substantially

larger than the range of values compatible with total fluid extraction to date in the central zone of Larderello ($S_v < 0.75$; cf. Pruess et al., 1985). We conclude from this that 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 relased from minerals during exploitation (or both).

The fact that y is substantially smaller than 1 makes it clear that re-equilibration in the gas phase is at most partial, and possibly may not occur at all. It was shown by Pruess et al. (1985) that most of the CO_2 produced at Larderello was not originally stored in the reservoir fluids, but was released from minerals in response to exploitation-induced decline of CO_2 partial pressure. As re-equilibration of the Fischer-Tropsch reaction in the (large) single phase vapor regions surrounding the wells is at most partial, it appears quite likely that re-equilibration in situ with the CO_2 released from minerals is also at most partial. Thus, vapor fractions obtained using the Fischer-Tropsch reaction after substantial reservoir depletion has occurred reflect the following effects:

(i) the "memory" of two-phase conditions, with substantial liquid, in the (presumably) deep ultimate fluid sources (this tends to make y small);

(ii) the release of CO_2 from minerals, which never (fully) equilibrates (this excess CO_2 tends to make y large);

(iii) possibly partial re-equilibration in the gas phase, which could become more significant as travel times of fluid parcels increase with increasing reservoir depletion (this tends to yield a y closer to 1).

ACKNOWLEDGEMENT

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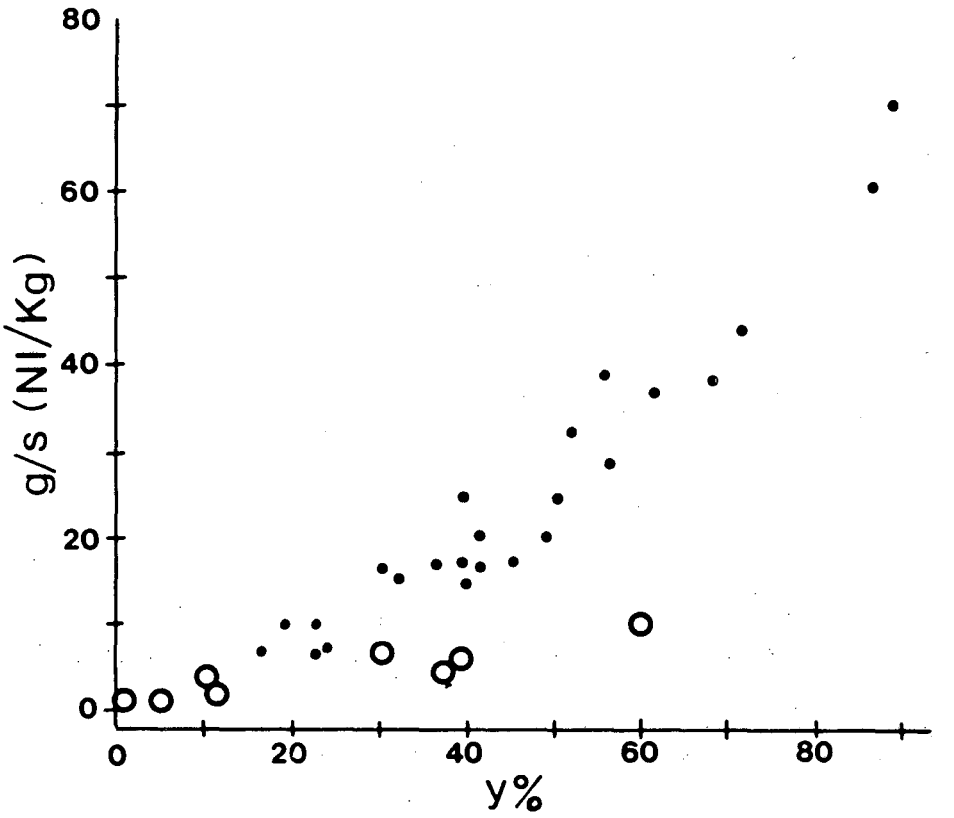
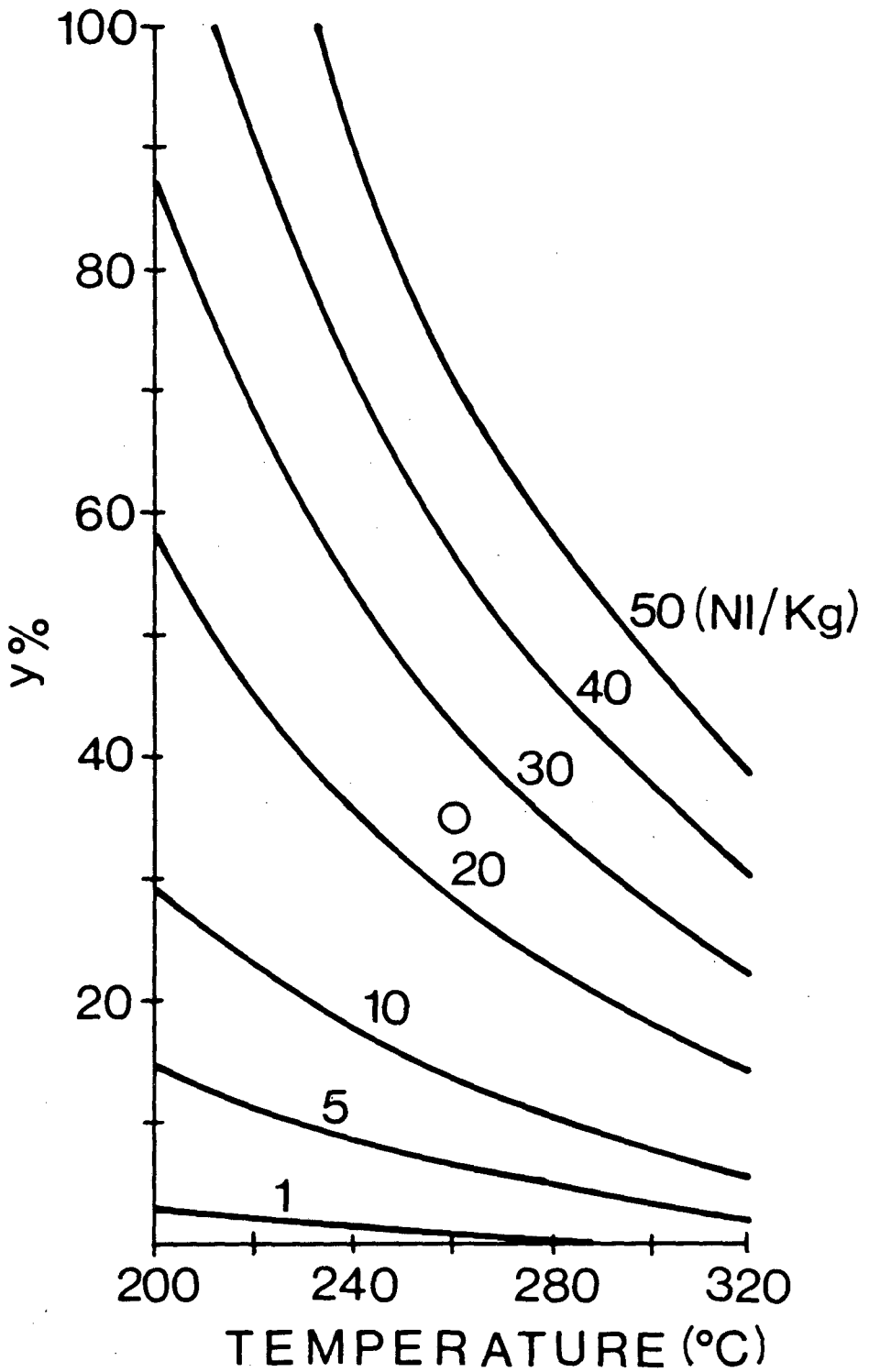


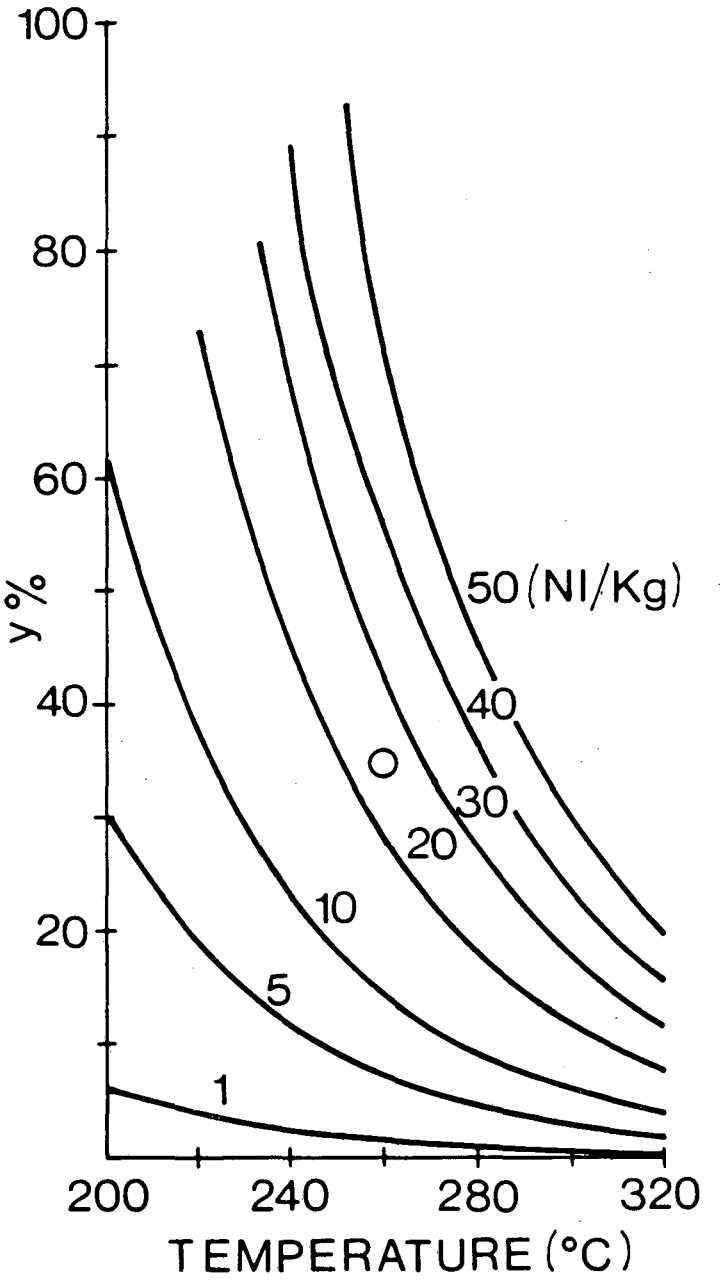
XBL 854-2207

Fig. 1: Percentage of y (calculated from eq. 17) as a function of the 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.



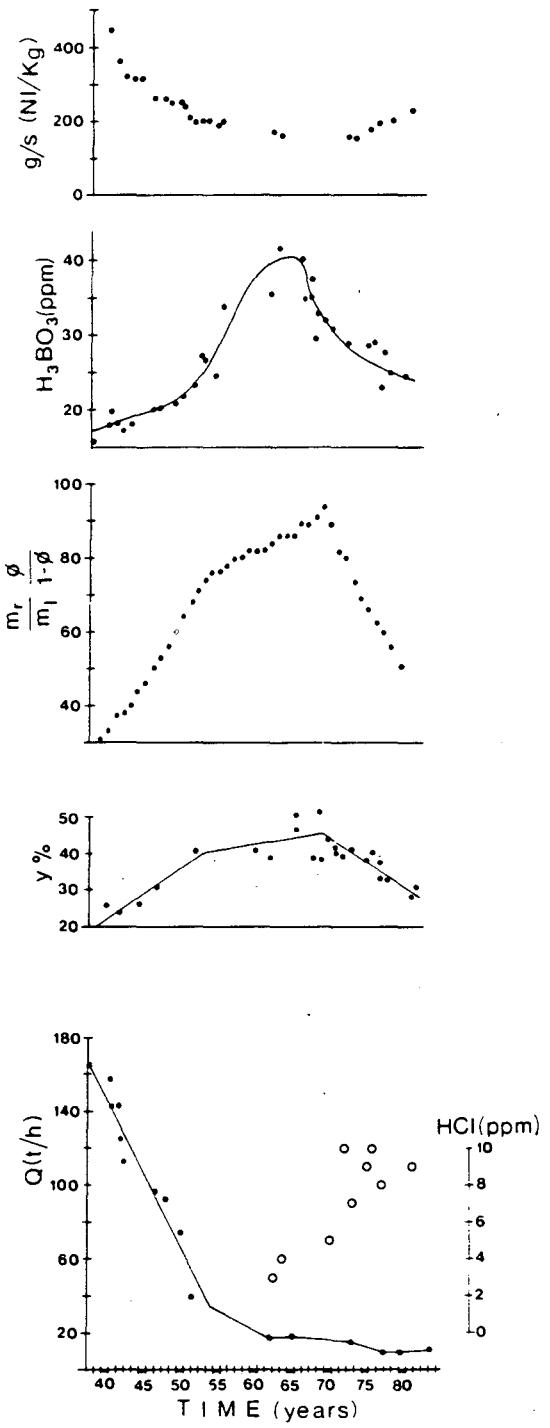
XBL 854-2212

Fig. 2: y% computed from eq. 17 at a given composition (see text) as a function of temperature at different values of the gas/steam ratio (expressed as Nl/kg).



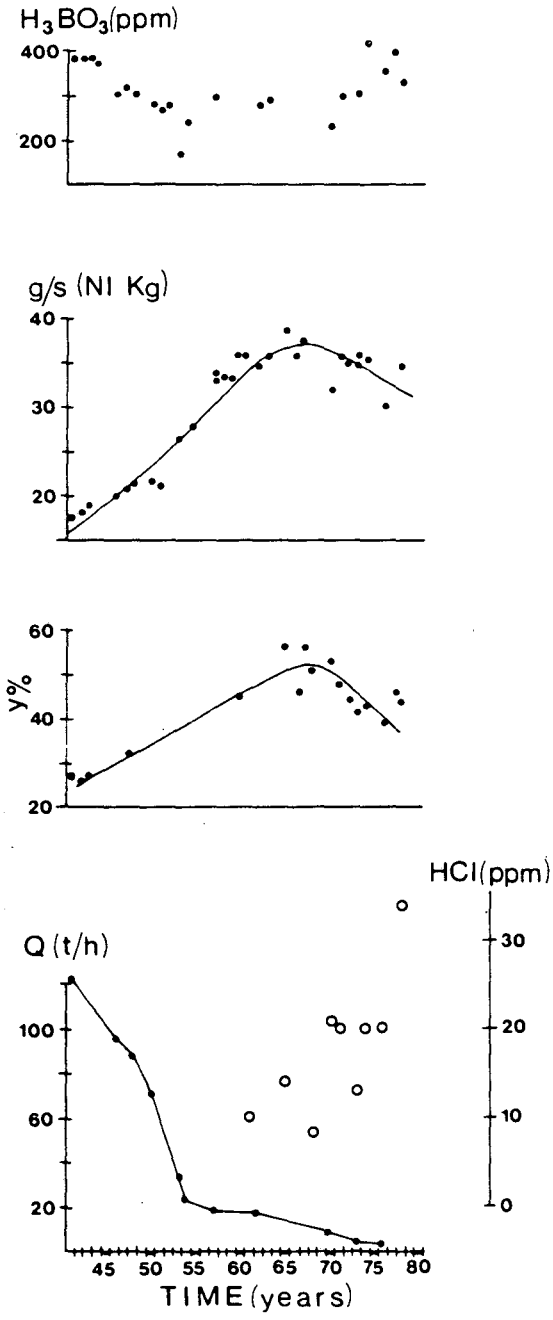
XBL 854-2198

Fig. 3: y% computed from eq. 16 at a given composition (see text) as function of temperature at different values of the gas/steam ratio expressed as Nl/kg.



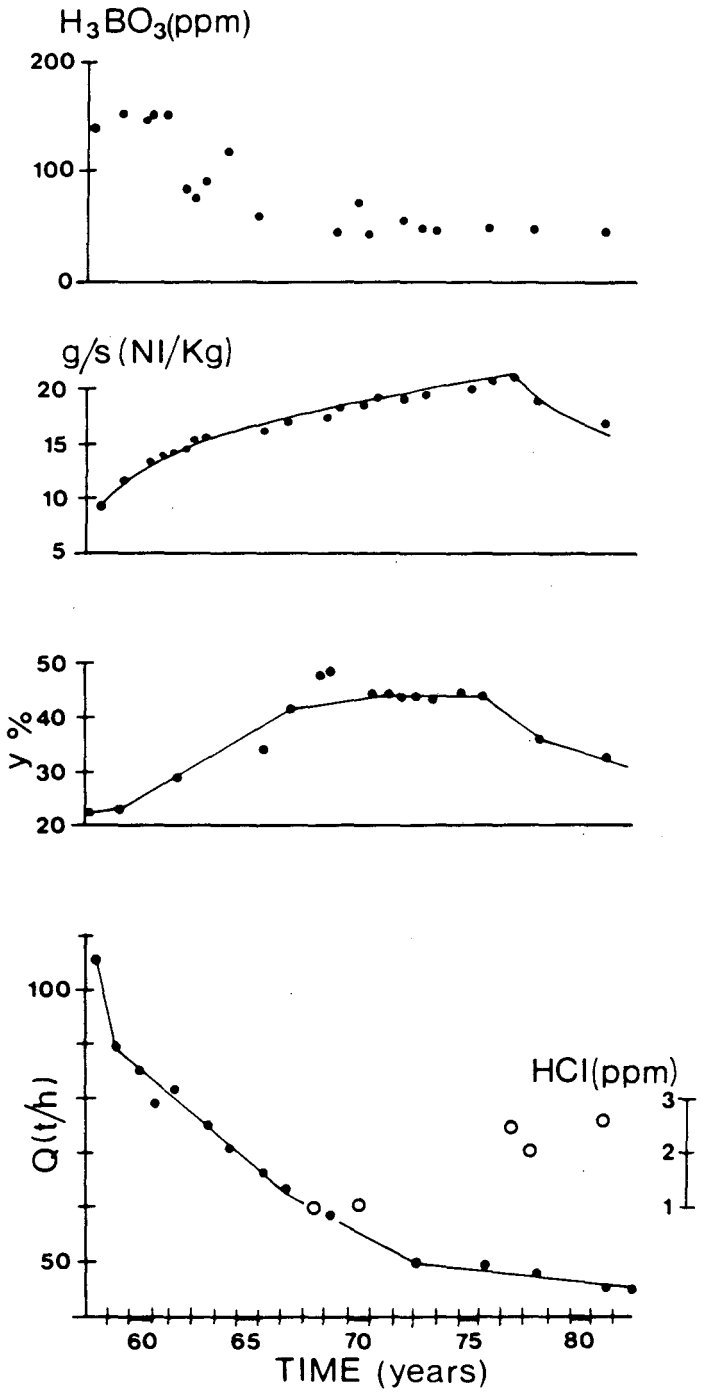
XBL 854-2200

Fig. 4: Temporal evolution for well ALR of flow-rate Q in t/h, together with HCl in ppm, y% calculated from eq. 17, parameter $m_r\phi/m_\ell(1-\phi)$ (see text), gas/steam ratio in Nℓ/kg (liters of gas at standard conditions per kg of steam), H_3BO_3 in ppm.



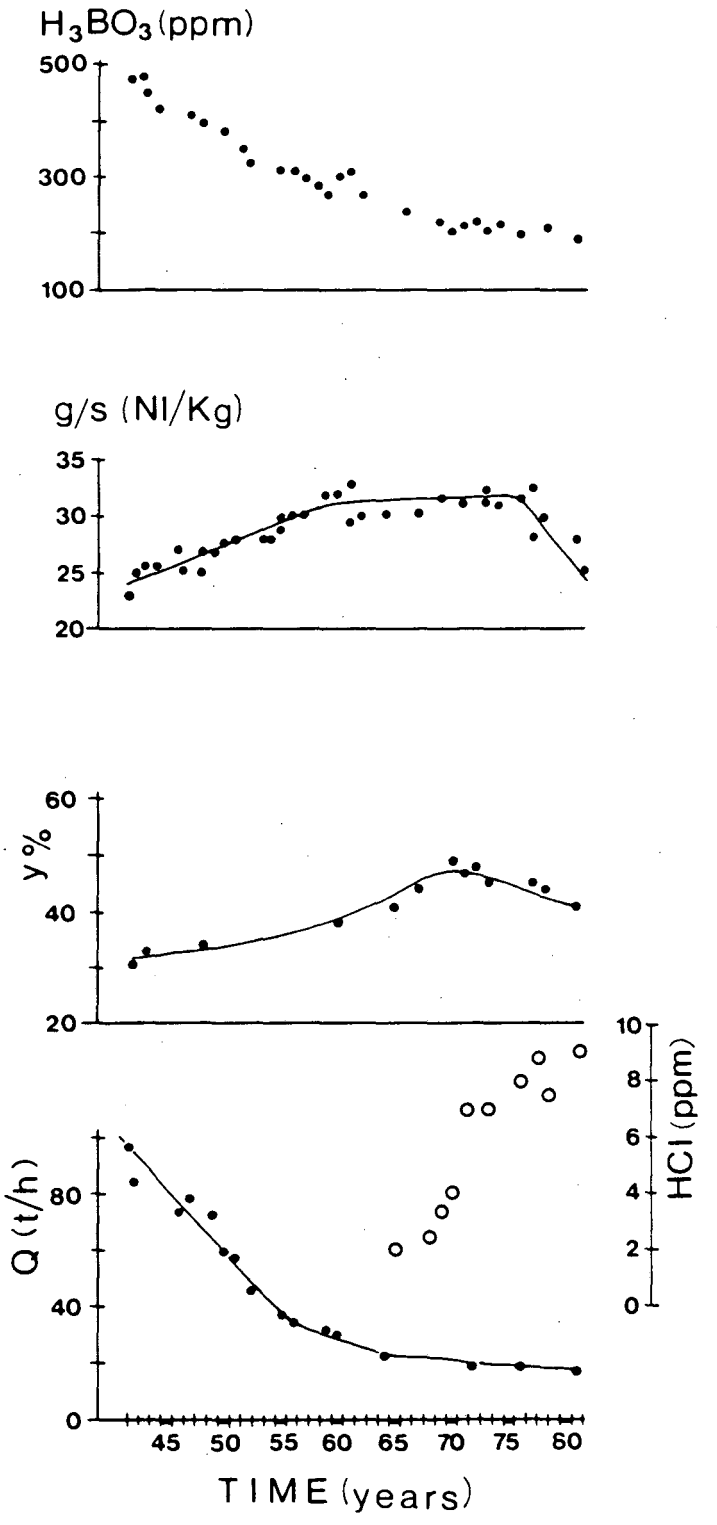
XBL 854-2208

Fig. 5: Temporal trend for well BEL. See Fig. 4 for legend.



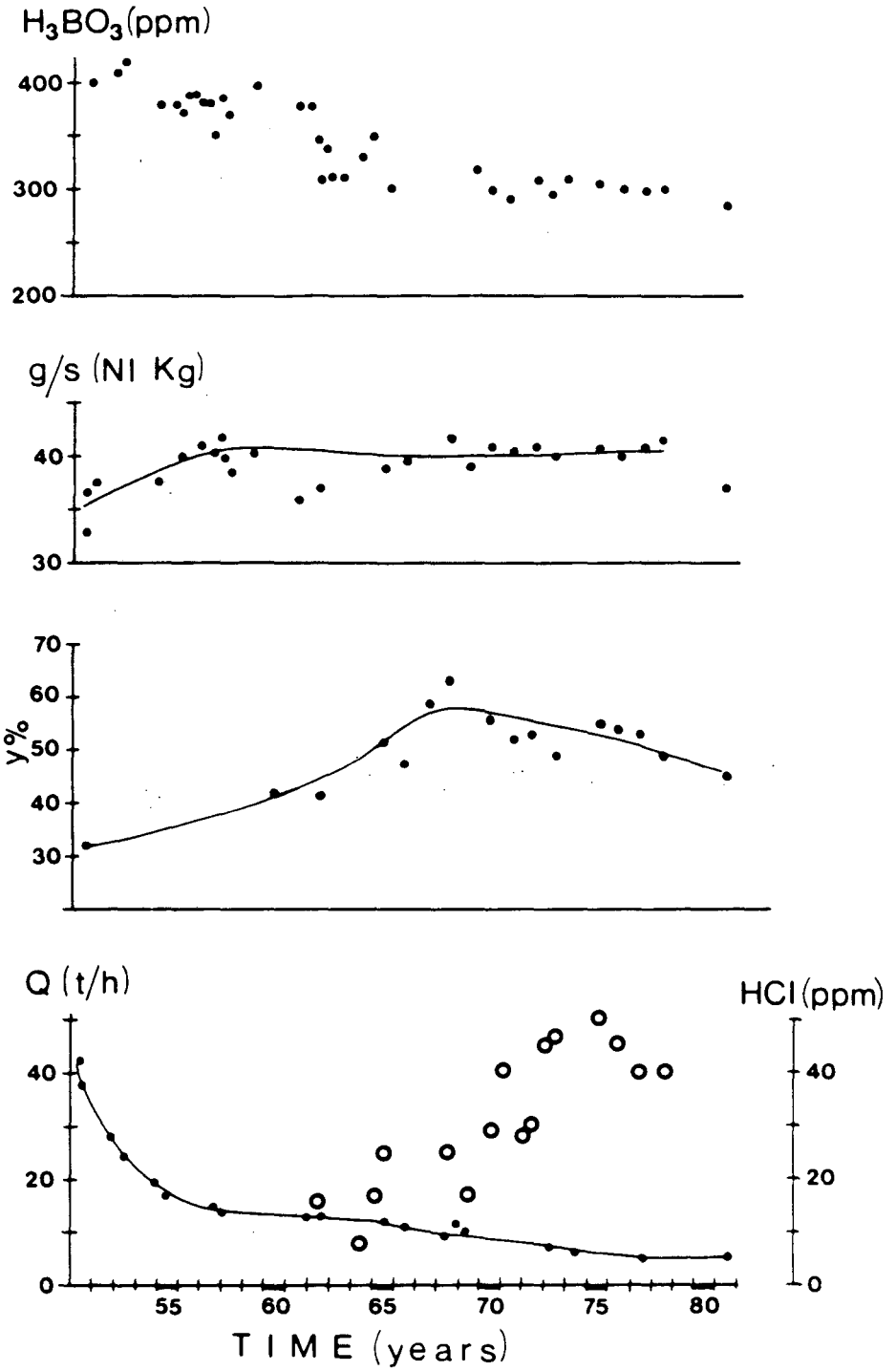
XBL 854-2206

Fig. 6: Temporal trend for well 145. See Fig. 4 for legend.



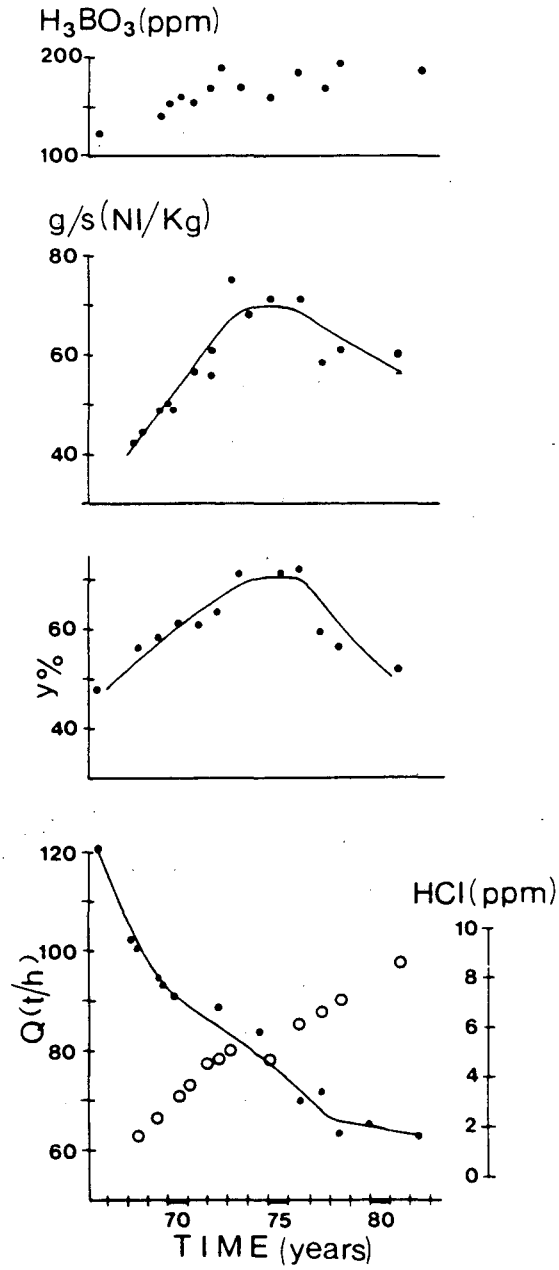
XBL 854-2209

Fig. 7: Temporal trend for well FAB. See Fig. 4 for legend.



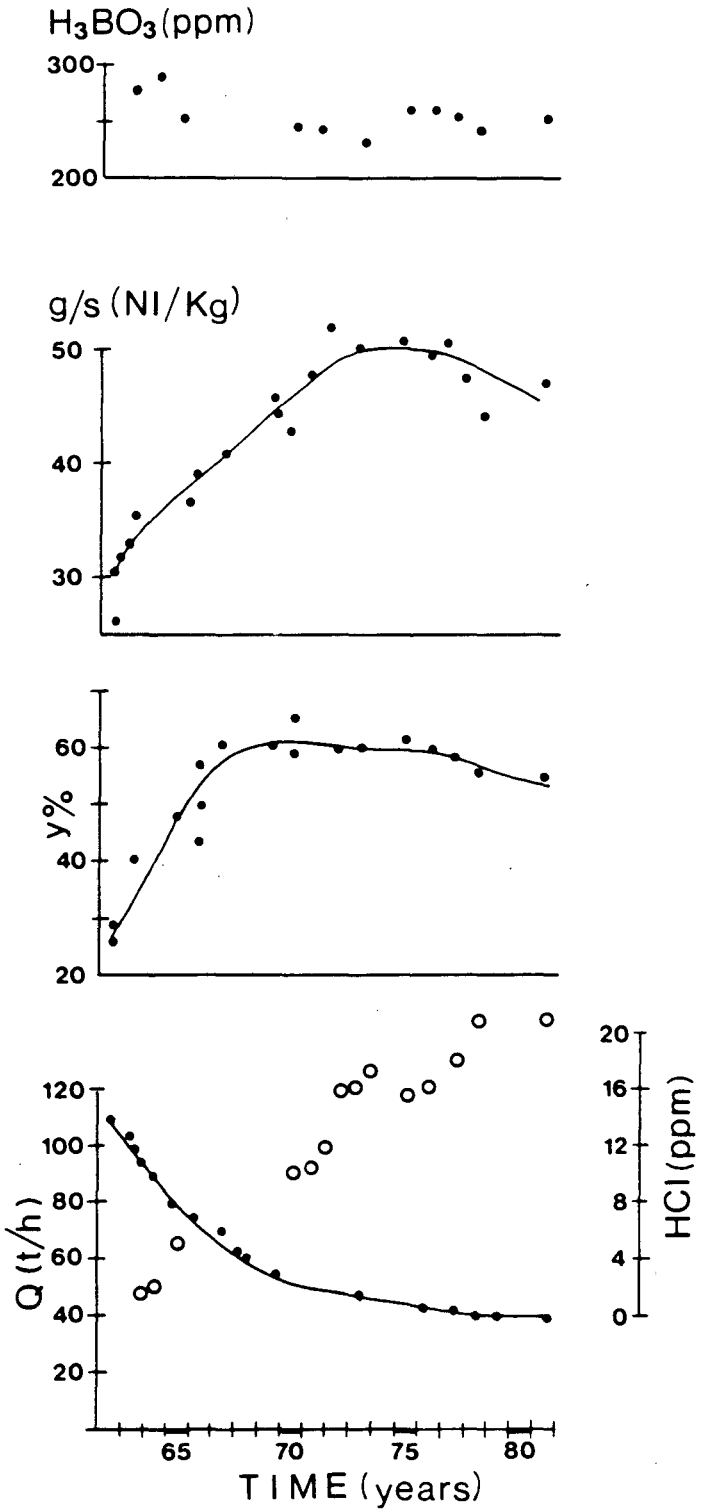
XBL 854-2201

Fig. 8: Temporal trend for well 80. See Fig. 4 for legend.



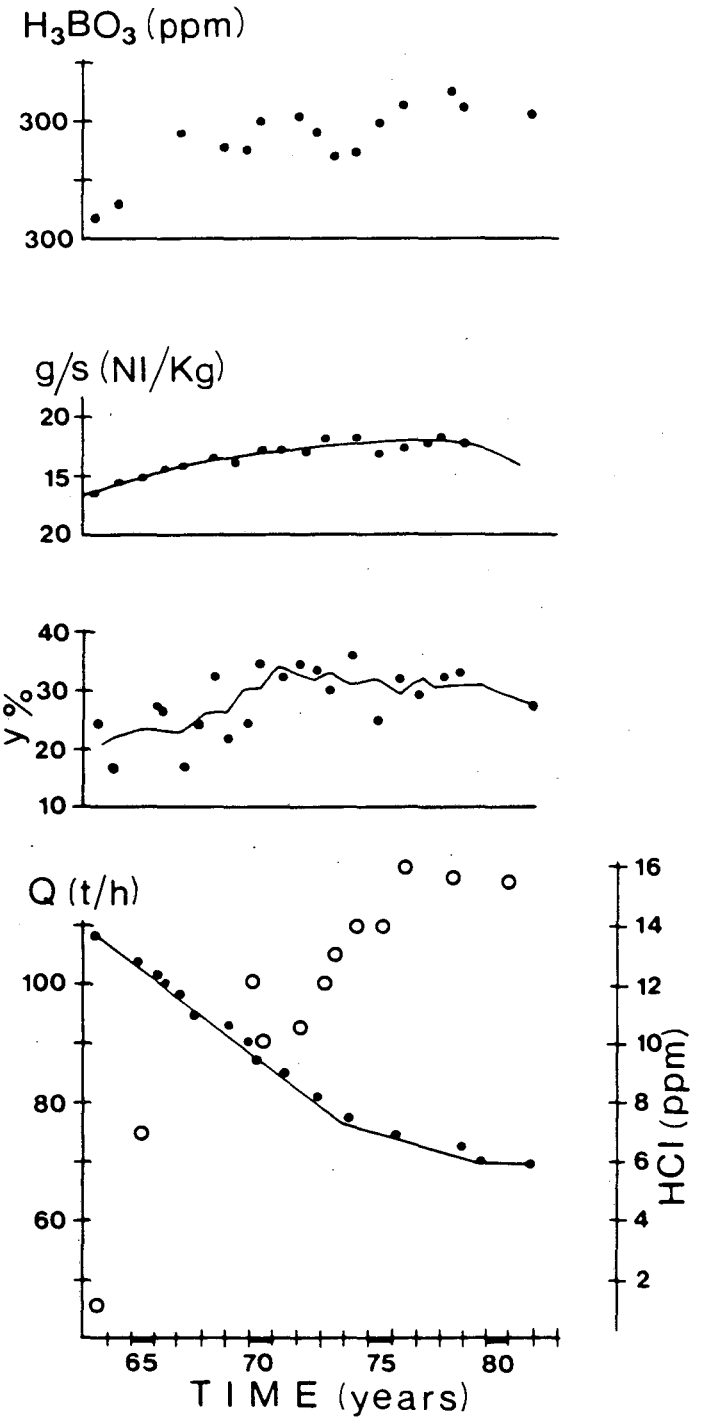
XBL 854-2199

Fig. 9: Temporal trend for well G/9. See Fig. 4 for legend.



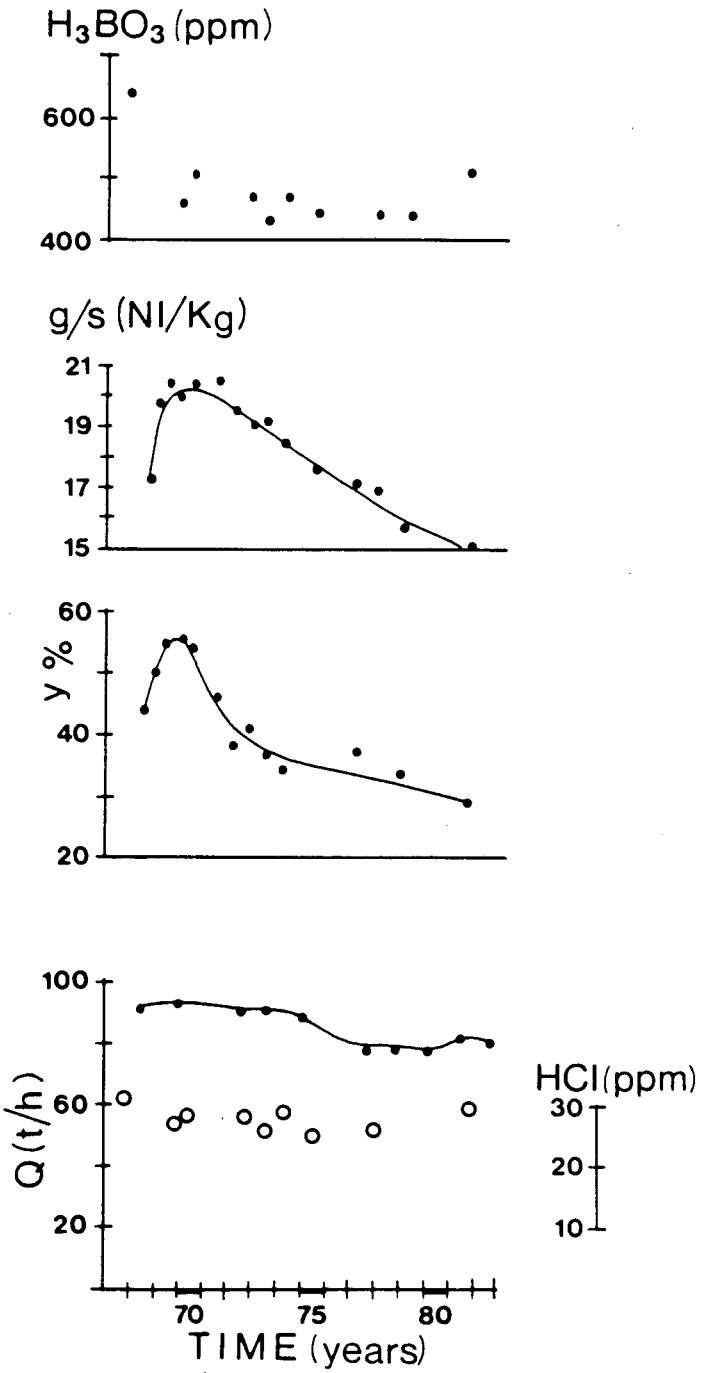
XBL 854-2210

Fig 10: Temporal trend for well G/1. See Fig. 4 for legend.



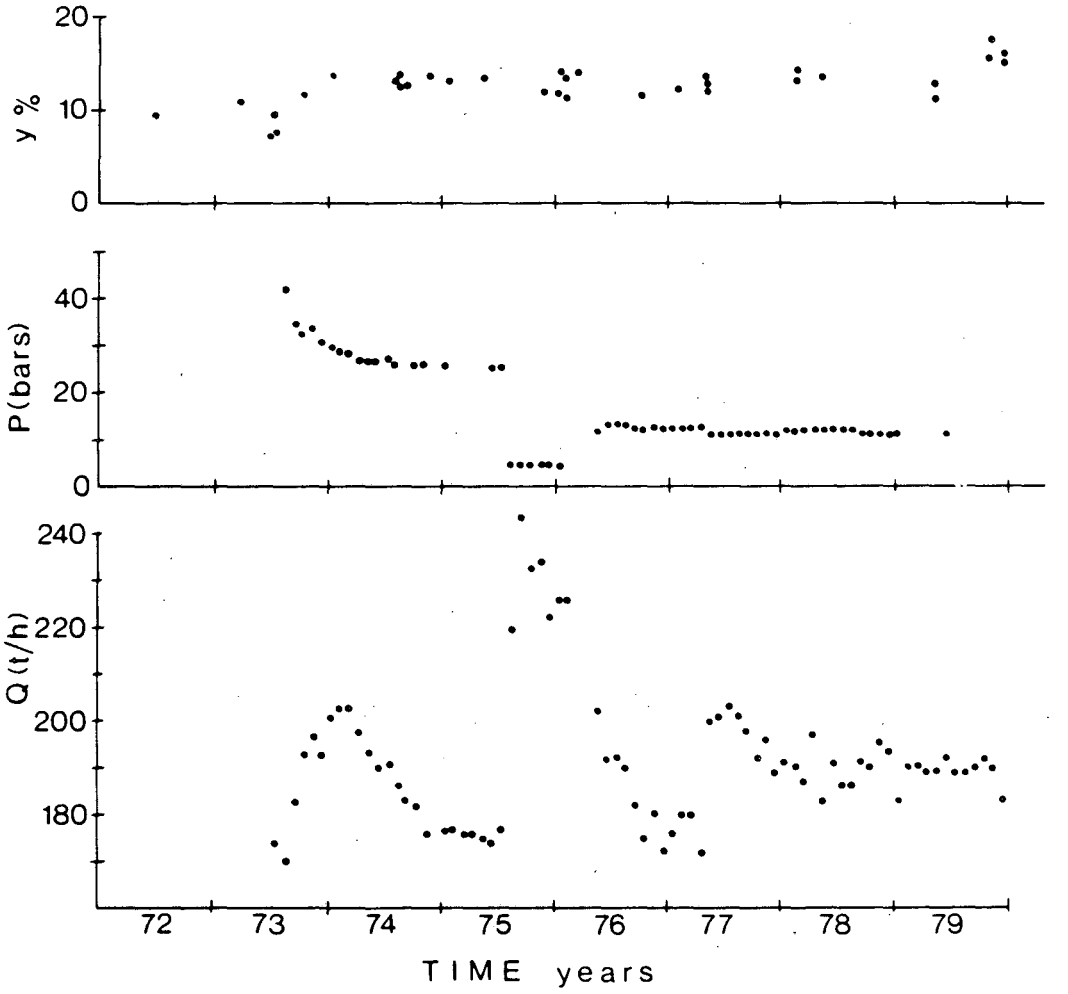
XBL 854-2204

Fig. 11. Temporal trend for well VC/10. See Fig. 4 for legend.



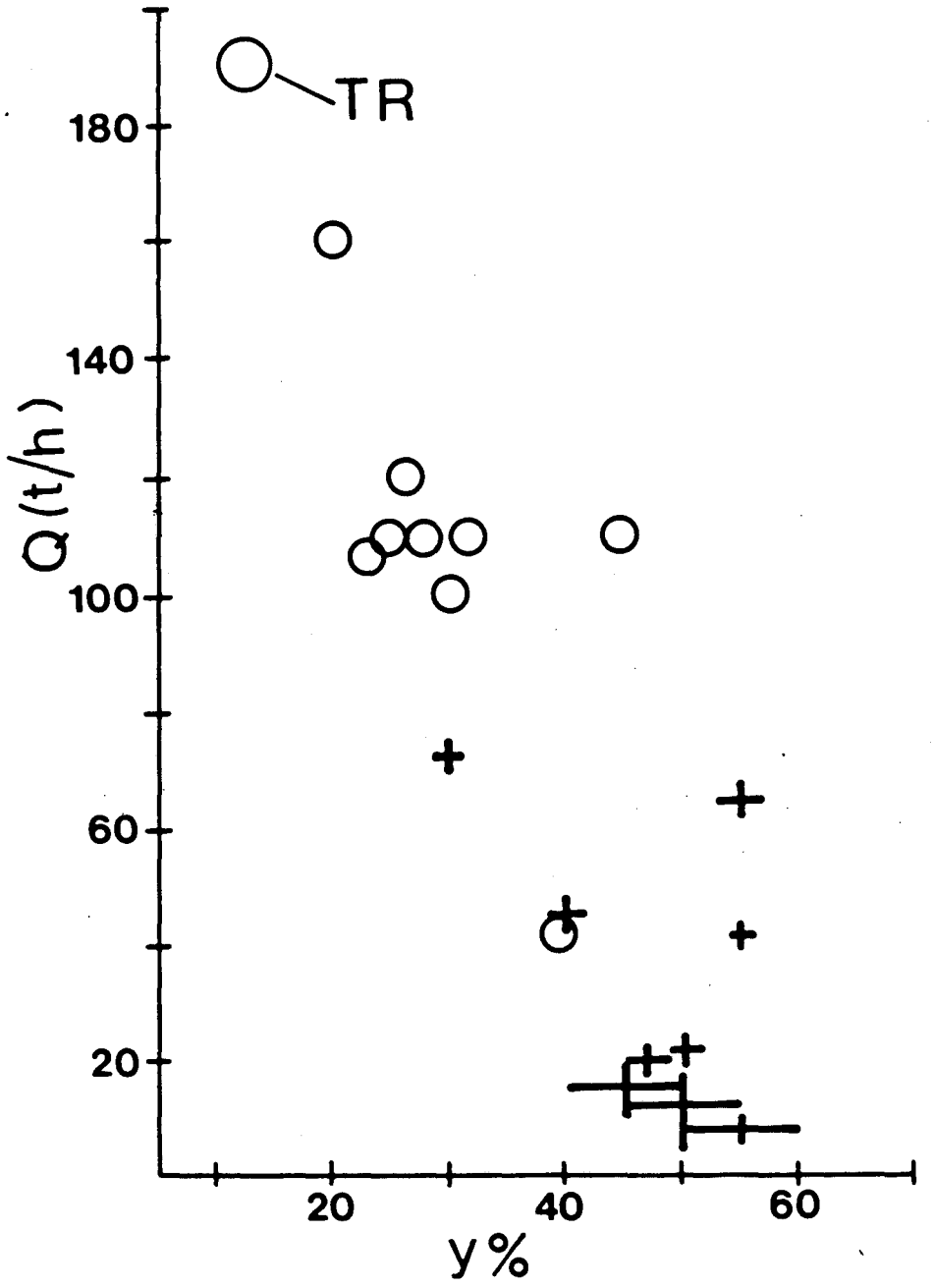
XBL 854-2211

Fig. 12: Temporal trend for well QUE. See Fig. 4 for legend.



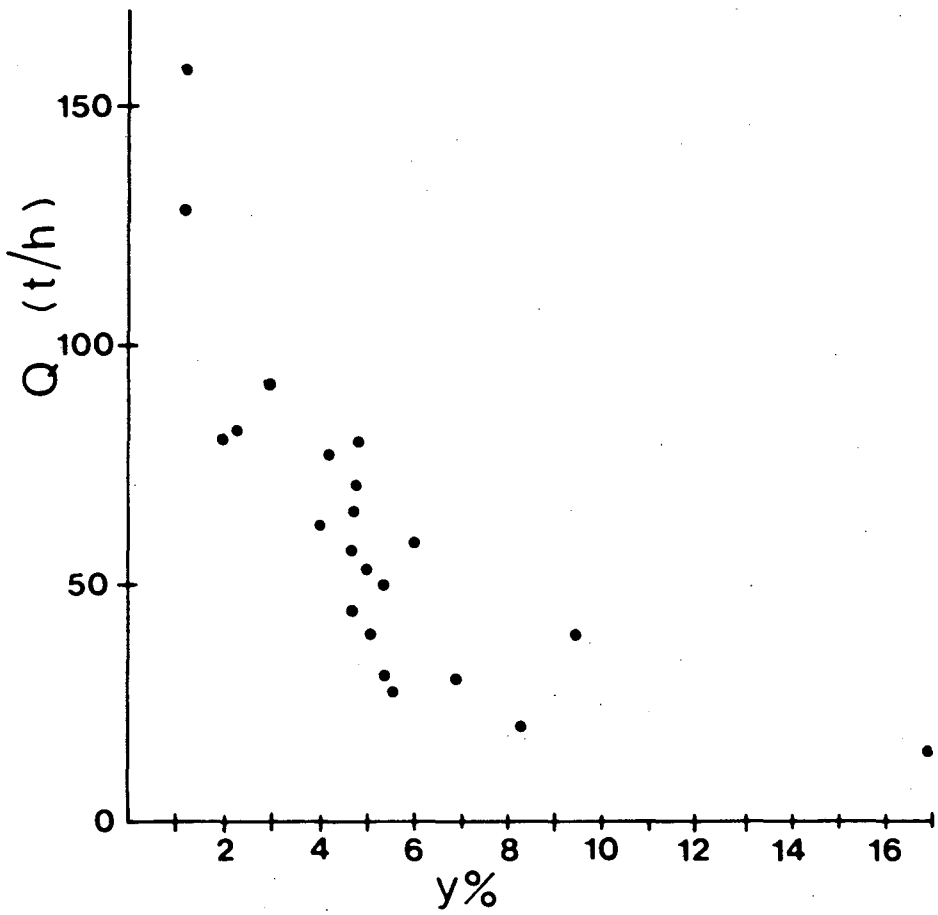
XBL 854-2205

Fig. 13: Temporal trend for well T22 of the Travale geothermal field. Flow rate Q in t/h, wellhead pressure in bars and computed y%.



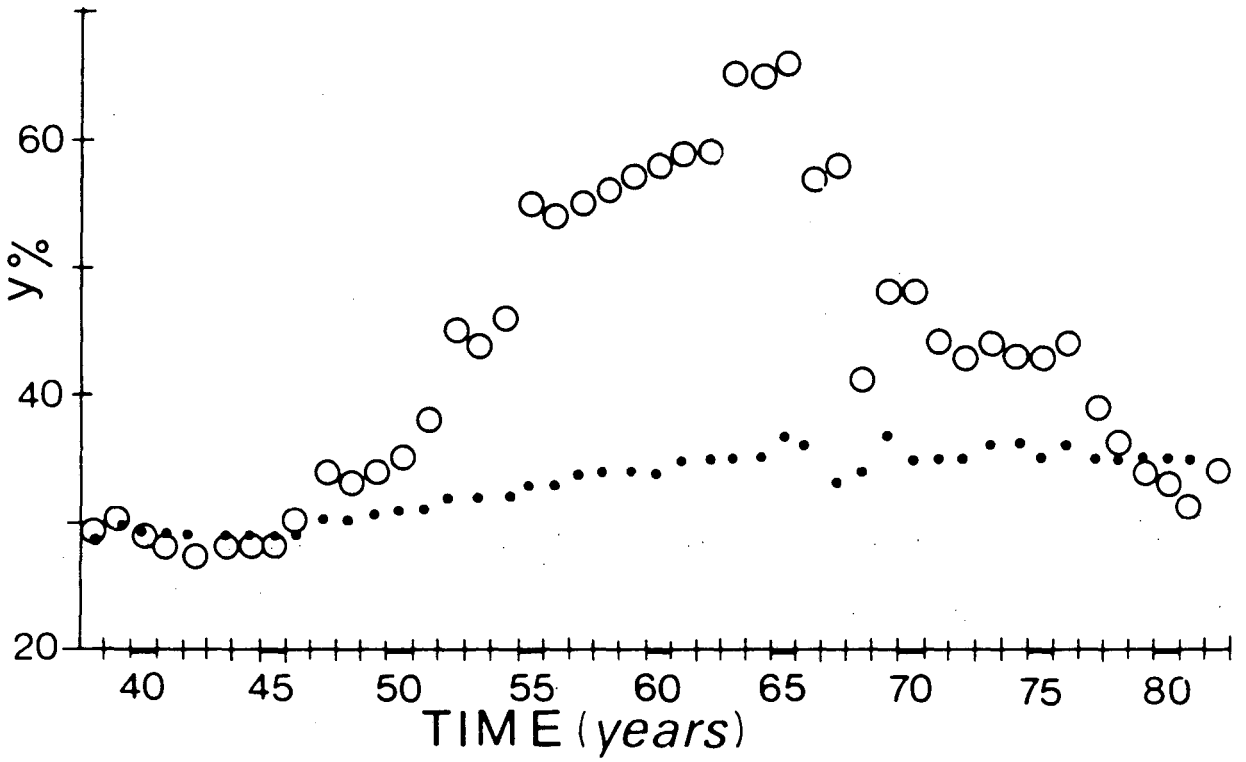
XBL 854-2203

Fig. 14: Relationship between flow rate Q in t/h and y% for some wells of the Larderello field and including well T22 of the Travale field (TR). Open circles refer to values at the start of production and crosses to values when flow rate began to stabilize.



XBL 854-2213

Fig. 15: Relationship between flow rate and y% for some wells of The Geysers field.



XBL 854-2202

Fig. 16: Temporal evolution of "instantaneous" and "cumulative" y for well ALR.

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