

PRODUCTION OF HCl BY MINERAL REACTIONS IN HIGH-TEMPERATURE GEOTHERMAL SYSTEMS

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ABSTRACT

Thermodynamic data for reactions involving halite (NaCl) and silicates (\pm calcite) have been used to calculate the HCl gas concentration in vapor at high temperatures in the presence of a hypersaline brine. Mineral reactions produce as much as 700 ppm HCl in vapor at 350 °C. Agreement with earlier calculations by Haizlip and coworkers involving hypersaline brine alone (without halite) is very good. High temperatures favor HCl gas and equilibrium concentrations at 250 °C are negligible. The correlation of HCl with high temperature is clear at Larderello and (with less data) at The Geysers. HCl is expected to become a problem in all geothermal systems with temperatures > 300 °C that produce superheated steam as a result of drying.

INTRODUCTION

The appearance of HCl gas in superheated steam from many wells of Larderello, Italy, and The Geysers, USA, and from some wells elsewhere has caused accelerated corrosion and has prevented the utilization of part of the geothermal resource. Understanding of the origin and transport of HCl gas in steam is necessary for reservoir management involving mitigation and possible prevention. The problem was first identified at The Geysers by Haizlip and Truesdell (1988), although Cl was known to be related to corrosion at Larderello (Allegrini and Benvenuti, 1970)

and identified as HCl (D'Amore et al., 1977) much earlier. The limitation of HCl transport to superheated steam moving along dry (condensate-free) pathways, introduced by Haizlip and coworkers (e.g. Haizlip and Truesdell, 1988; Truesdell et al., 1989), is now established, but the origin of HCl from boiling neutral brine suggested by these authors has been questioned on the grounds that the amount would be small (Andersen, 1989) or that generation from reaction of solid NaCl (halite) with silicates was more probable and supported by higher temperature experimental data (Fournier, 1983, and pers. commun., 1986-89). The relationship of HCl gas with high-temperature zones in the Larderello and The Geysers reservoirs, although required by both brine and halite genetic mechanisms has not been explicitly indicated.

It is the purpose of this paper to examine in detail the genesis of HCl gas from both boiling brine and mineral-halite reactions and to give examples based on field data. The mineral-halite reactions have been studied using published thermodynamic data (e.g. Helgeson et al., 1978; Fritz, 1981; Arnorsson et al., 1982) rather than new experimental work. As in calculations of HCl from boiling brine, high temperatures are necessary for formation of HCl by mineral reactions. Therefore the existence and genesis of high-temperature zones is discussed as a major control on the formation of HCl in geothermal systems.

MINERAL - HALITE (NaCl) REACTIONS

Formation of volcanic HCl gas from silicate-halite reactions has commonly been suggested (Ellis, 1957; Guggenbach, 1975 and 1979) and the hydrolysis of salts at 600 °C with or without silicates was indicated by Fournier (1983 and 1986) to be a source of acidic brines. It is well known that $MgCl_2 \cdot n H_2O$ evolves HCl when heated to dryness in air or vacuum (Cotton and Wilkinson, 1972). Thus mineral-halide (NaCl, KCl, $MgCl_2$, etc.) reactions are a reasonable alternative to the boiling brine offered by Haizlip and coworkers as the generative mechanism for HCl gas in geothermal steam. In order to test this idea we have calculated the concentration of HCl in vapor in equilibrium with halite (the major halide mineral) and mineral assemblages observed (or reasonably assumed) to occur in (or beneath) the reservoirs of Larderello and The Geysers.

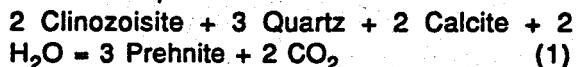
Prolonged boiling of deep liquid beneath the vapor-dominated reservoir must result in the formation of a brine. Not only does the "heat pipe" process (White et al., 1971) cause solubles materials contained in the upper reservoir to be leached and moved downward, but the loss of steam through surface venting results in solute accumulation and evaporative concentration. Evaporation in the natural state could have produced halite crystallization. In addition, accelerated boiling due to exploitation would lower the level of the liquid surface and leave pockets and surface films of brine which would evaporate to high concentration and eventual dryness to precipitate halite. Hypersaline NaCl-saturated brine has been found in fluid inclusions from Larderello (Belkin et al., 1985; Marignac et al., 1987; Cathelineau et al., 1989). Inclusion homogenization temperatures are consistently higher than those measured

in drill-holes, suggesting that both temperatures and salinity probably do not reflect exploitation-produced boiling.

The hydrothermal minerals found in the normal reservoir (close to 250 °C) and in zones of high temperature (> 300 °C) are shown in Table 1. Reactions involving halite and HCl may be grouped by temperature reactions with minerals stable for $t < 300$ °C and higher temperature reactions for $t > 300$ °C. Mineral reactions involving calcite and dependent on CO_2 pressure are also considered.

Case A: $t \leq 300$ °C, calcite present, $P(CO_2)$ involved.

Cavarretta et al. (1982) showed that the CO_2 partial pressures at Larderello are close to equilibrium for the reaction:

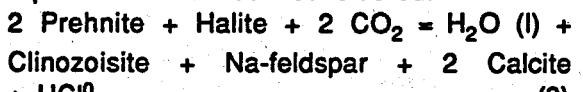


The temperature dependence of $P(CO_2)$ at equilibrium was then expressed by an empirical fit of data from reaction (1) valid from 200 to 300 °C (Cavarretta et al., 1982) :

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

Depending on the amount of Fe^{3+} in clinozoisite, we may assume a variability in the computed $P(CO_2)$ from equation (2) of about two bars. This equation is considering to produce minimum values of $P(CO_2)$ in Larderello. It must be noted that not all CO_2 may be in chemical equilibrium with minerals in some areas of Larderello (Calore et al., 1985).

Inserting halite in the system following equilibrium has been considered:



HCl^0 in equation (3) is in solution as the

unionized weak acid. This is related to the HCl concentration in vapor by the distribution coefficient B (HCl) :

$$B(\text{HCl}) = C_v(\text{HCl}) / C_l(\text{HCl}^0) \quad (4)$$

In the calculation of the equilibrium constant for reaction (3) activities of minerals are assumed to be close to unity (values lower than one for clinzoisite would increase the computed HCl concentration). The values for B (HCl) have been taken from Haizlip and Truesdell (1988). Table 2 shows lists of computed values for the equilibrium constant and concentrations of HCl (ppm in produced steam) at selected temperatures and CO_2 partial pressures.

If we assume that steam at the well head consists of a mixture of steam from the vapor-dominated upper layer and steam from the boiling brine, we can assume that the content of HCl in steam at the wellhead must be lower than that produced by the brine, because no HCl is contributed by the two-phase upper layer at about 250 °C.

As an example consider Querciola 2 a typical high-temperature well of Larderello. In 1981 this well had the following steam composition :

gas/steam	CO_2	H_2S	H_2	CH_4	N_2	HCl
(molar ratio)						ppm
12.3×10^{-3}	90.11	3.68	3.69	1.81	0.71	74

For a temperature of 300 °C (computed using the grid method of D'Amore and Truesdell, 1985), $P(\text{CO}_2)$ can be computed using two methods:

a) from equation (2) with $P(\text{CO}_2) = 1.7$ bar (a minimum value).

b) from the following equation (D'Amore and Truesdell, 1985):

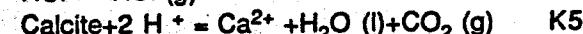
$$\log P(\text{CO}_2) = \log (\text{CO}_2 / \text{H}_2\text{O}) - \log (y + (1-y) / B(\text{CO}_2)) + \log P(\text{H}_2\text{O}) \quad (5)$$

where y is the effective steam fraction computed from gas composition (in this case $y = 0.2$). This gives a value of $P(\text{CO}_2) = 4.2$ bar.

From these two values of $P(\text{CO}_2)$, computed values of HCl in the steam are 33 and 190 ppm. These values are in agreement with the order of magnitude of the HCl concentrations measured for this well. At The Geysers, gas contents vary widely from south-east to north-west. Maximum values of $P(\text{CO}_2)$, computed using steam analyses from Truesdell et al. (1987) are in the order of 4 bar in the NW zone where temperatures and y values are high, and of 0.2 bar in the SE zone where temperatures and y values are lower.

If we know the order of magnitude of HCl content, for a given value of temperature and $P(\text{CO}_2)$ we can calculate the pH and salt concentration in the brine.

The following equilibria have been considered:



Most of the Cl⁻ ion is electrically balanced by Na, K and Ca ions:

$$m(\text{Cl}^-) = m(\text{Na}^+) + m(\text{K}^+) + 2m(\text{Ca}^{2+}) \quad (6)$$

The extended Debye-Hückel expression can be used to compute activity coefficient values, γ_i for all ionic species. In this calculation the ionic strength I can be considered equal to the Cl⁻ concentration.

In the case of well Querciola 2, with 74 ppm of HCl in the steam, at 300 °C and $P(\text{CO}_2) = 4.2$ bar, a pH value of 4.9 is obtained for a ionic strength I using the following equation:

$$\begin{aligned}
 & K_3 m(HCl)_g / K_4 a(H^+) \gamma(Cl^-) \\
 & = K_2 K_4 a(H^+) / K_3 m(HCl)_g \gamma(Na^+) \\
 & + K_2 K_4 a(H^+) / K_1 K_3 m(HCl)_g \gamma(K^+) \\
 & + 2 K_5 a^2(H^+) / P(CO_2) \gamma(Ca^{2+}) \quad (7)
 \end{aligned}$$

From these equations the following concentrations in the brine have been computed:

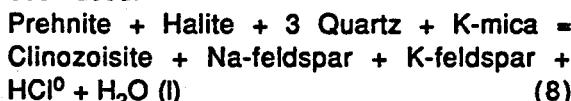
$$\begin{aligned}
 m(Cl^-) & = 5.0, m(Na^+) = 3.7, m(K^+) = 0.52, \\
 m(Ca^{2+}) & = 0.42
 \end{aligned}$$

Thus the high measured HCl concentration in steam from this well may be explained as due to the resulting from a high salinity brine boiling at about 300 °C, with a pH close to 4.9. It seems likely that chemical reactions similar to those shown in case A may explain the correlation of high gas content with high HCl concentration in the steam in some areas of The Geysers (Haizlip and Truesdell, 1989).

The reaction given in equation (3) involves calcite and therefore the computed concentration of HCl in vapor depends on the CO₂ pressure as well as on temperature. This may be unrealistic for parts of Larderello and The Geysers with temperatures above 300 °C where calcite is not present (G. Gianelli, pers. commun; 1989, Sternfeld, 1989, and table 1). For these conditions alternative reactions may be written in which silicates take the place of calcite and CO₂ does not appear. With these reactions the concentration of HCl in vapor is entirely a function of temperature.

Case B: no calcite involved, t ≤ 300 °C

The following chemical equilibrium has been used:

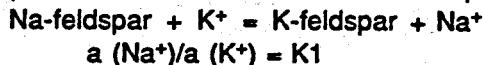


Using thermodynamical data presented by Helgeson et al. (1978) and Fritz (1981),

computed values of equilibrium constants and ppm of HCl in the steam for selected temperatures are presented in Table 3.

The chemical composition of the brine may be computed for this case using the following assumptions:

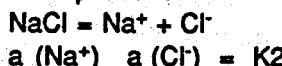
a) equilibrium between Na and K-feldspars



b) charge balance (with Ca content disregarded in absence of calcite)

$$m(\text{Na}^+) + m(K^+) = m(Cl^-)$$

c) halite present

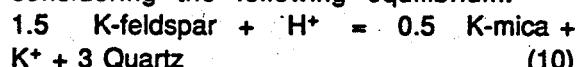


Then:

$$\begin{aligned}
 m(Cl^-) & = \left(\frac{K_2}{\gamma_{\text{Na}} \gamma_{\text{Cl}}} \right) / \\
 (1 - & \frac{1}{1 + K_1 \gamma_K / \gamma_{\text{Na}}})^{1/2} \quad (9)
 \end{aligned}$$

At 300 °C the following concentrations have been computed: m(Cl⁻) = 4.6, m(Na⁺) = 4.0, m(K⁺) = 0.6.

The pH at 300 °C can be calculated considering the following equilibrium:



which yields a pH of 4.6, using the computed value of a(K⁺).

Case C: no calcite involved, t > 300 °C.

Muscovite is not stable at temperatures exceeding 300 °C (and it has not been found at Larderello and The Geysers above 300 °C, as shown in Table 1).

The following chemical reaction involving amphiboles (tremolite) and pyroxenes (diopside) has been considered:

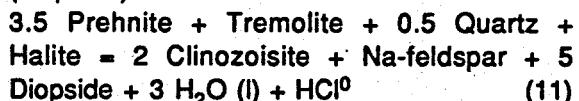


Table 3 lists values of the equilibrium

constant and the computed concentrations of HCl in the vapor at selected temperatures.

Figure 1 summarizes the results of HCl concentrations in the vapor obtained from the different chemical reactions (cases and lines A, B and C) and HCl concentrations computed by Haizlip and Truesdell (1988) (line D) and Andersen (1989) (line E) at pH = 5 and 100,000 ppm of Cl in solution. Except for Andersen (1989) at high temperature our calculations using mineral assemblages with halite are in agreement with those involving a hypersaline brine alone. Computed HCl concentrations in the steam at 250 are negligible. With increasing temperature a trend is evident, with production of HCl in the order of 10 ppm at 275 °C, 100 ppm at 300-325 °C, and close to 1000 ppm at 350-375 °C.

CORRELATION OF HIGH TEMPERATURES AND HCl

Calculations of HCl in vapor in equilibrium with brine or halite show that HCl concentrations increase with temperature. Therefore a correlation between HCl and high-temperature geothermal reservoirs is expected and indeed found. The correlation is concealed by the necessity that steam containing HCl does not contact liquid at moderate or low temperatures (< 275 °C) where HCl would be scrubbed (Haizlip and Truesdell, 1988). This effectively limits produced HCl to superheated steam from relatively dry reservoir zones. High-temperature reservoirs at The Geysers have been discovered only recently (Drenick, 1986; Walters et al., 1988) and their extent, temperature and relation to the normal reservoir are poorly known. The correlation of high-temperature zones at The Geysers with high total gas and high Cl (actually HCl) in steam up to 200 ppm at

340 °C was discussed briefly in Walters et al. (1988). They suggest that steam partially results from boiling of a fossil high temperature liquid-dominated system underlying the "typical" reservoir and containing some connate water. In contrast, deep high-temperature reservoirs at Larderello have been studied since the late 1960s for their possible energy resources and are well described in the literature (e.g. Cappetti et al., 1985) although many aspects remain unclear. Since the location and concentration of HCl in Larderello steam is also known (e.g. D'Amore and Truesdell, 1979, Calore et al., 1980, D'Amore et al., 1981), it is possible in theory to correlate reservoir temperature and HCl in steam. Unfortunately, deep drill holes are few and temperatures above 300 °C are known only in a general way, so the temperatures at the top of the reservoirs which are known in detail and show the same general pattern as deep temperatures, have been used instead. The correlation of HCl concentration with reservoir top temperatures is nearly exact (figures 2 and 3, along selected transects A-B-C). Temperature data in this figure are largely unpublished (R. Celati, pers. comm. 1988) although temperatures are shown in less detail in Cappetti et al. (1985) and Calore et al. (1988). A generalized geological section and isotherms from 150 to 400 °C are shown in figure 4, based on geological sections in Cappetti et al. (1985) (points corresponding to transects A-B-C are also shown).

HCl concentrations and (to a lesser extent) temperatures are affected by recharge from S and SE (shown by arrows in figure 2) and by condensation (N of Larderello, NW of Serrazzano), which cool the reservoir and maintain liquid saturation to scrub HCl from steam. If this scrubbing did not take place, the pattern of HCl concentrations would be similar to that of H_3BO_3 which is

also a volatile acid but remains unionized to much lower temperature and higher pH. Similar patterns of Cl and B concentrations were found by D'Amore and Truesdell (1979) for central Larderello and also exist along the western section of figures 2 and 3 (from Calore et al., 1980, and D'Amore et al., 1981). The main difference is that minimum concentrations are higher for H_3BO_3 than for HCl.

The correlations of HCl with reservoir temperatures (figures 2,3) do not prove any genetic connection but show that HCl (along with heat and H_3BO_3) rises in zones of upflow and is absent in zones of condensation and recharge (where heat and H_3BO_3 are also lower). The heavy exploitation of these areas, which coincide with high-points of the reservoir and were therefore exploited early, could have produced conditions of superheat which allow a temperature increase and chemical transfer of HCl and H_3BO_3 . It is possible, therefore, that the patterns are related to transport rather than genesis and HCl may be produced over a much broader zone similar to the 350 °C isotherm shown in figure 4.

THE ORIGIN OF DEEP HIGH TEMPERATURES AND HCl

The origin of deep high temperature reservoir fluid has a considerable influence on our choice of mechanism for the genesis of HCl and incidentally on the size of the deep energy resource at Larderello and The Geysers. Drenick (1986), D'Amore and Pruess (1986) and others before them have speculated about the deep parts of vapor-dominated systems. It seems clear that in the natural state a deep boiling brine must have existed to provide the upflow of steam necessary for the "heat pipe" mechanism which carried heat and gases but no

solutes (Cl) to the top of the vapor-dominated reservoir (White et al., 1971). The few observed temperature gradients below the bottom of the vapor-dominated reservoir indicate a boiling-point-to-depth consistent with the putative deep liquid. If this deep liquid exists, it must (for the reasons mentioned earlier) have become a very saline brine through continued accumulation and concentration of solutes. It is possible that superheated steam from extended production (at Larderello) or relatively dry conditions (northern The Geysers) allowed HCl in steam boiled from this brine to reach production wells without being scrubbed. This supposes that pressure reduction from exploitation has not produced accelerated boiling in the brine itself. If permeabilities are much lower in the brine zone than in the overlying reservoir (Pruess et al., 1987) this may be possible. Under this hypothesis the calculations by Haizlip and Truesdell (1988) of HCl concentration in steam boiling from brine are most important, and the fluid resource consisting of high-temperature brine could be large. The lower HCl contents indicated by Andersen (1989) are not consistent with observed concentrations and if true would rule out brine as the source of HCl.

A more likely consequence of exploitation is that pressure decrease produced accelerated boiling of the deep brine and a decrease of its level. The boiling reduced rock temperatures in the brine zone by an amount related to porosity, but if these remained near the original boiling-point-to-depth 316 °C would be reached 1000 m below the original liquid level (Calculation by Drenick, 1986).

CONCLUSION

HCl in superheated steam has been produced from wells at Larderello, The

Geysers and elsewhere. The genesis of this HCl is clearly related to high-temperature reactions involving chloride brine and/or minerals.

Fluid-inclusion data and observed counterflow of vapor and condensate at Larderello and The Geysers suggest that boiling hypersaline brine, and probably halite, occur in deep zones of vapor-dominated geothermal systems. Earlier studies showed that HCl gas could be generated by boiling of hypersaline brine. Here we show that equilibrium of halite with silicate and carbonate minerals found in the Larderello and Geysers reservoirs could also generate HCl gas in quantities similar to those found.

These minerals are considered as medium ($< 300^{\circ}\text{C}$) and high ($> 300^{\circ}\text{C}$) temperature assemblages and lead to a series of possible reactions for medium and high temperatures with and (at $t > 300^{\circ}\text{C}$) without calcite. The resulting HCl concentrations are similar to those calculated earlier for boiling brine by Haizlip and Truesdell (1988) as shown in Fig. 1, and do not agree with those calculated by Andersen (1989). The correlation of high-temperature areas of the Larderello and Geysers reservoirs with HCl in steam emphasizes the strong relation of HCl concentrations to temperature shown by present and past calculations. The production of hypersaline brines and superheated steam through extreme boiling and drying of a reservoir originally containing a more or less concentrated brine is not limited to deep parts of vapor-dominated systems but can occur in liquid-dominated reservoirs as well. High-temperature ($> 300^{\circ}\text{C}$) systems such as Krafla (Iceland) and Los Humeros (Mexico) have encountered HCl corrosion. Others such as Cerro Prieto (Mexico) and the Salton Sea (USA) could also produce HCl. Injection of cooler water can prevent the transport and ultimately the generation of HCl. Reservoir management of high-temperature geothermal systems should aim at limiting

boiling in the reservoir and preventing production of superheated steam. In most cases these objectives can only be achieved by injection of cooler liquid.

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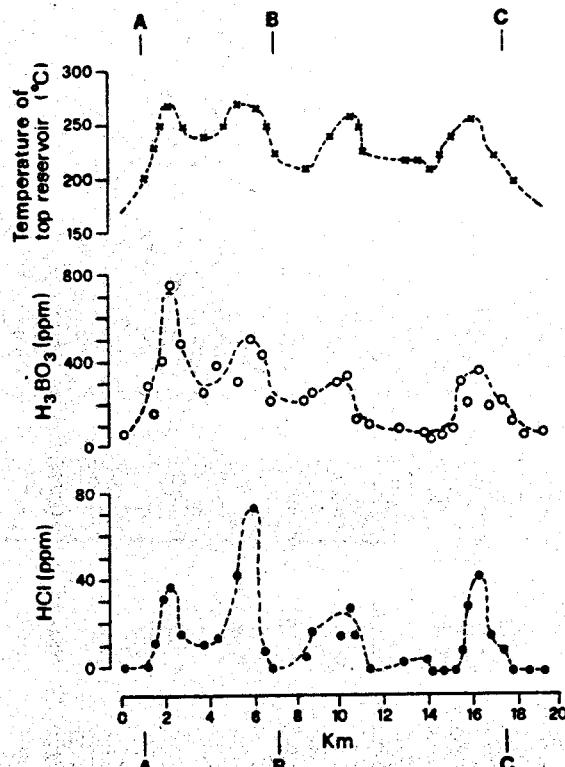


Figure 3. Observed concentration profiles of HCl and H_3BO_3 in steam and of temperatures of the top of the reservoir along the line A-B-C of figure 2 through the Larderello field.

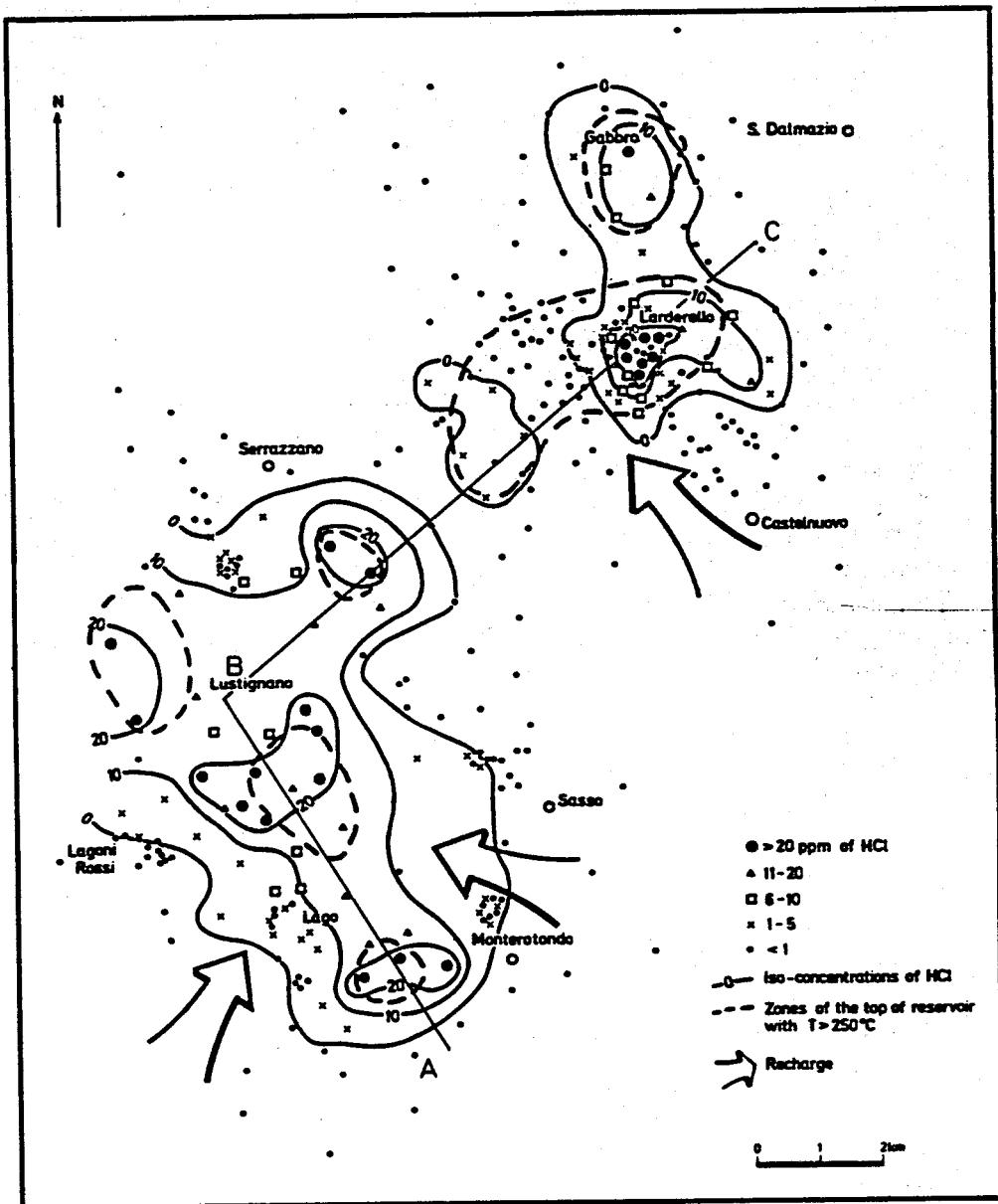


Figure 2. Patterns of HCl concentration in Larderello steam and temperatures of the top of the reservoir. The line A-B-C of the profiles in figures 3 and 4 is shown.

Table 1. List of selected hydrothermal minerals at Larderello and The Geysers in the normal reservoir (temperature < 300 °C) and in zone of high temperature (> 300 °C). Abbreviations: Qz = quartz, Cc = calcite, Ch = Chlorite, Ep = epidote and/or clinzozoisite, Ac = tremolite or actinolite, Pl = sodic plagioclase, Px = diopside and/or hedenbergite, Pr = prehnite, Mu = K-mica and/or illite, Ab = Na-feldspar, Bi = biotite, Ks = K-feldspar.

Larderello (Cavarretta et al., 1982; Bertini et al., 1985; Belkin et al., 1985; Cathelineau et al., 1989):

< 300 °C Qz, Cc, Ch, Mu, Ep, (Ac), Ks, (Pl), (Px), (Pr)
> 300 °C Qz, Ch, Ep, Ac, Ks, (Pl), Px, Ab, Pr

The Geysers (Walters et al., 1988; Sternfeld, 1989):

< 300 °C Qz, Pr, (Cc), (Ch), Mu, Ks, (Ab), Ac, (Ep)
> 300 °C Qz, Pr, Ks, Bi, Px, Ac, (Ep)

Table 2. HCl (in ppm) in the steam at selected temperatures and $P(\text{CO}_2)$. Values of equilibrium constant for reactions (3) and of HCl distribution coefficient are also reported.

t °C	$P(\text{CO}_2)$	0.1	0.5	1.0	5.0	10	log K	B(HCl)
225		0.001	0.02	0.07	(1.7)	(6.7)	-7.4	45
250		0.01	0.2	0.5	(10)	(42)	-6.3	25
275		0.02	0.6	2.2	55	(220)	-5.4	16
300		0.1	2.6	10	250	(1000)	-4.6	12

Table 3. Values of equilibrium constants and computed concentrations of HCl in the vapour for Case B (reaction 8) and Case C (reaction 11).

t °C	log K(eq. 8)	HCl(ppm)	logK(eq.11)	HCl(ppm)	B(HCl)
250	-5.9	1			25
275	-4.6	15			16
300	-3.3	220	-4.6	11	12
325	-2.0	(2900)	-3.5	92	8
350			-2.4	730	5
375			-1.6	920	1

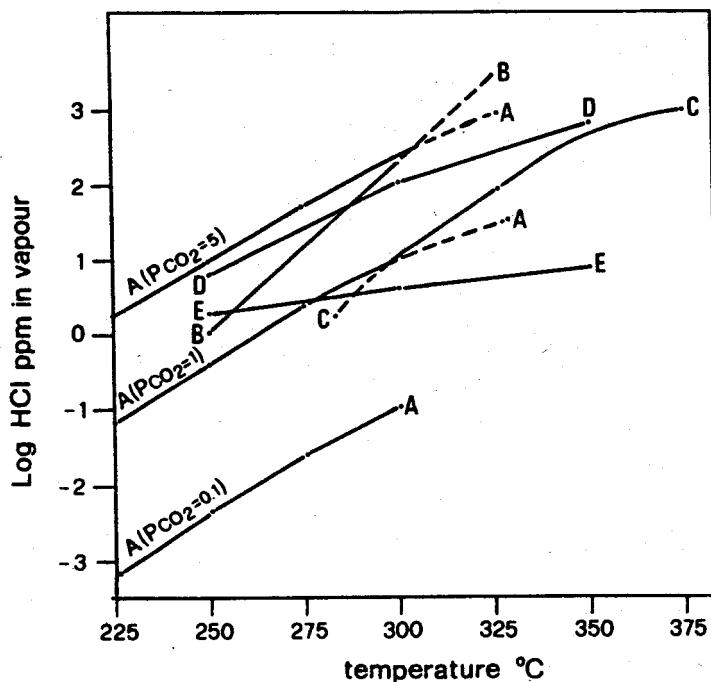


Figure 1. Computed HCl concentration in reservoir vapor vs. temperature. A: from reaction (3) at different $P(CO_2)$ values, valid for $t < 300$ °C; B: from reaction (8), valid for $t < 300$ °C; C: from reaction (11), valid for $t > 300$ °C; D: from Haizlip and Truesdell (1988) and E: from Andersen (1989), both for pH 5 and 100,000 ppm of Cl in reservoir liquid.

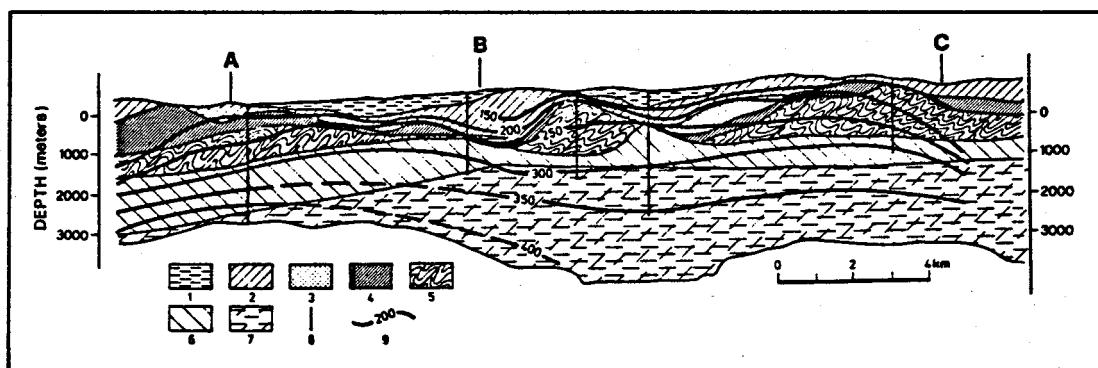


Figure 4. Geological cross section through the Larderello field (line A-B-C of figure 2). 1. Neogene sediments; 2. Flysch nappes (shaly-marly formation, Cretaceous - Eocene); 3. Sandstone (Cretaceous); 4. Limestone, dolomite, anhydrite (Upper Triassic-Lower Cretaceous); 5. Quartzite, phyllite, anhydrite, dolomite (Upper Triassic); 6. Phyllite and quartzite (Ordovician-Silurian); 7. Mica schist, gneiss and amphibolite (Lower Paleozoic); 8. Deep well; 9. Isotherm.