

ACIDIC GEOTHERMAL FLUIDS CONTAINING HYDROCHLORIC ACID : A REVIEW

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ABSTRACT

The occurrence of HCl as the main acid compound in geothermal fluids is found in two environments. In geothermal fields related to andesitic volcanism it occurs as a relict of partially neutralized magmatic fluid that has not reacted with rock minerals sufficiently to have all HCl converted to NaCl dissolved in geothermal fluid. It also occurs where high-temperature brine with or without halite is vaporized to superheated steam which follows a dry (without liquid water) pathway to producing wells. These origins have been discussed extensively in the literature which is reviewed here.

1.0 INTRODUCTION

The appearance of HCl gas in superheated steam ~~from~~ many wells of Larderello, Italy, and The Geysers, California, and ~~from~~ some wells elsewhere as Krafla (Iceland) and Tatun (Taiwan) has caused accelerated corrosion and has prevented the utilization of part of the geothermal resources ~~as at~~ The Geysers.

Understanding the origin and transport of HCl gas in ~~steam~~ is necessary for reservoir management involving mitigation and possible prevention. The problem was identified at The Geysers by Haizlip and Truesdell (1988), although Cl was known to be related to corrosion at Larderello since 1970 (Allegrini and Benvenuti), identified as HCl by D'Amore et al. (1977) and related to other chemical parameters and time by D'Amore and Truesdell (1979) and D'Amore and Pruess (1986). The limitation of HCl transport to superheated steam moving along dry (condensate ~~free~~) pathways, introduced by Hazily and Truesdell (1988) and Truesdell et al. (1989a and b), 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 high temperature experimental data (Fournier, 1989 pers. comm.)

2.0 THE MAGMATIC - GEOTHERMAL TRANSITION

Geothermal fields with the ~~most~~ acute problems with acidic waters are related to andesitic volcanism, particularly around the Pacific "Ring of Fire". This volcanism results from the subduction of wedges of sediments containing large amounts of seawater with carbon, ~~sulfur~~ and of course chlorine, dissolved in andesitic magma at great depth ~~as~~ H₂O, CO₂, SO₂, H₂S and HCl. ~~When~~ these fluids ~~are~~ released ~~from~~ the cooling magma under supercritical conditions (temperature >374°C and pressure <220 bars), these gaseous compounds are not ionized and do not react with rock minerals. However they do react ~~as~~ gases, for example H₂S and SO₂ react independent of the temperature to produce a ratio close to one:

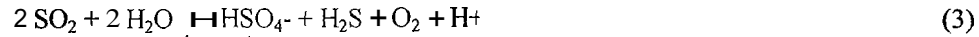


However, when the supercritical fluid enters a fractured rock at relatively shallow depth and is cooled by mixture with descending meteoric waters, the gas mixture becomes subcritical. The water condenses to liquid

augmented by the meteoric contribution and the other gases dissolve to form an acidic saline fluid with pH dependant in part on the ratio between the magmatic and meteoric fluids. In the balance to form the original pH the values of $P(\text{CO}_2)$, $P(\text{SO}_2)$, $P(\text{H}_2\text{S})$ and $P(\text{HCl})$ enter as main parameters. A vapor phase can still be present containing CO_2 , H_2S , HCl and H_2 formed by the dissociation of water:



The solution is strongly oxidized and the amount of H_2 formed is small relative to H_2S . The gases dissolve partially (as H_2S and CO_2) or totally (as SO_2 and HCl) to form ions in solution according to the following reactions for the main species:



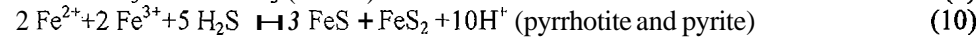
Note that SO_2 cannot exist in aqueous solution or in a two phase condition and it is the first species to be removed after the critical point when liquid water is formed.

As indicated, the product of all these dissociation reactions is a large formation of hydrogen ion, to form a strongly acidic solution. Moreover the solution is oxidising due to the formation of oxygen gas and thus poor in H_2 . This solution is then highly reactive and interacts with the minerals of the host rock schematically as follows:

$(\text{Na}^+, \text{K}^+, \text{Ca}^{2+})$ feldspars + $\text{H}^+ \rightleftharpoons (\text{Na}^+, \text{K}^+, \text{Ca}^{2+})$ in solution + clay + kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) and smectites ($\text{Ca}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$, $\text{Mg}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$, $\text{Na}_{.33}\text{Al}_{2.33}\text{Si}_{3.77}\text{O}_{10}(\text{OH})_2$ and $\text{K}_{.33}\text{Al}_{2.33}\text{Si}_{3.77}\text{O}_{10}(\text{OH})_2$)

"Calciumferromagnesian" silicate minerals of the host rock + $\text{H}^+ \rightleftharpoons \text{Fe}^{2+}$, Fe^{3+} , Ca^{2+} , Mg^{2+} + clay minerals as before, and formation of pyrrhotite, pyrite and Mg-Fe chlorite ($\text{Mg}_5\text{-Fe}_3\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$). The sulfides are formed because of the H_2S present in solution.

The products of these dissolution reactions are partially removed by the reactions of the following type with precipitation of the products:



Through these dissociation, neutralisation and precipitation reactions, the oxidised original magmatic gas, high in acid forming constituents has been changed to a reduced Na^+ , K^+ , Cl^- solution with moderate amounts of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} . The history of the geothermal fluid is not yet terminated. All the previous shown reactions are not at equilibrium. New alteration minerals are formed from the solution as a function of the amount of the local meteoric recharge water, which neutralises more of the system, and as a function of the final temperature. The amount of the recharge water arriving at depth depends on local vertical permeability, and this recharge can enter the system during the first phases of reaction. Alteration minerals such as laumontite, wairakite, prehnite, clinozoisite, epidote, Na-K feldspar, chlorites, amphiboles, garnet, pyroxenes can be formed now at equilibrium as a function of temperature. The water composition changes as new minerals are formed. We have now a true geothermal water. The final acidity is a function of the partial pressure of the acidic gases and of the balance of the original supercritical inflow from depth and the amount of the deep recharge water mixing with the deep system. This mixing lowers fluid temperature to allow ionization and reaction with rock minerals. A lack of inflow of a sufficient amount of recharge water in a long span of time will leave the deep solution relatively acidic, the possible formation of a steam layer very rich in HCl and H_2S with respect to H_2 . To model such conditions is very difficult because we do not know "a priori" the pH of the deep brine after the reaction of the magmatic species and new equilibration.

3.0 REGENERATION OF HCl

HCl is a normal constituent of deep sulphate acidic brine. Due to its volatility at high temperatures it may be carried as a gas in superheated steam into geothermal wells where it produces corrosion when steam condenses. It is probably possible to form HCl in any hot ($>300^{\circ}\text{C}$) geothermal brine which boils to dryness or in systems where conduits of superheated steam (dry pipes) are present from the deep brine to the surface. The mechanism of its formation is controversial. HCl could possibly be formed from originally high chloride brines due to the local accumulation of Cl, which is a mobile species. HCl concentration dissolved in hot NaCl brines can differ of orders of magnitude and no comprehensive experimental studies have been made on the pressure of HCl over silicates-halite mineral assemblages in high temperature brine (most of results are based on thermodynamic calculations). However, thermodynamic calculations do suggest that solid reactions of halite could form the observed amount of hundreds of ppm of HCl in steam at temperatures exceeding 300°C as function of temperature, chlorinity and pH.

Many geothermal fields in the world located close to andesitic volcanoes produce fluids with particular characteristics along with acidity that limits exploitation. Although HCl can be a constituent of steam boiled from these fluids, it is not the primary source of the acidity. For example in the Philippine fields of Manahagdong in Leyte island and Alto Peak also in Leyte most of the wells show fluids with: very low values of pH in the separated brine between 2 and 5; generally a relatively high enthalpy between 1200 and 1600 J/g; relatively low Cl/SO₄ ratios down to 5 in some cases; very high values of H₂S/H₂ ratio up to 70; and relatively low values of CO₂/H₂S down to about 8. Moreover, the ratio Ca/Mg is very low in general between 2 and 3 and Mg >10 ppm, the ratio Na/K is very low generally between 3 and 5, and the silica content is in general high, exceeding 1000 ppm. This chemistry can be due only to extreme acidic conditions in the reservoir, quite different from reservoir fluids at Larderello and The Geysers. It is evident that magmatic fluid is not locally buffered by the recharge water and HCl and SO₂ below the critical point interact strongly with the minerals of andesites probably without reaching chemical equilibrium, except with minerals like smectites and pyrophyllite. The relatively high observed values of SO₄ can be due to SO₂ dissolution and formation of high contents of H₂S. The CO₂/H₂S ratio depends on the temperature and the local partial pressure of CO₂.

So called "criptoacidic" systems are also common. They occur for example in some wells of Mahanagdong and in the field of Los Humeros (Mexico). At Los Humeros computed gas temperatures increased over 15 years from 220 to 330°C in two upflow zones and during the same time solute geothermometer temperatures for the liquid increased moderately for most wells. The separated brine remained neutral. The conceptual model of this andesitic system consists of a deep very high-temperature zone with an aggressive brine occurring naturally or by downflow and evaporation of relatively dilute waters. This brine has large amounts of H₂S and relatively little H₂ and NH₃ because of local oxidizing conditions. The high-enthalpy fluid crosses a large two-phase zone at about $280\text{--}300^{\circ}\text{C}$ where most of HCl is scrubbed and removed by rock reactions. In the upper part of the reservoir another liquid layer is present with temperatures lower than 230°C . With production, the top layer becomes thinner and in some areas dry heat pipes are formed and some deep fluid reaches the well bottoms and causes corrosion.

Waters very rich in CO₂ and H₂S can also exist in the borders of the fields. When cold water mixes with such waters and boiling does not occur, the mixture become moderately acidic because of solution of CO₂. The reason is that the dissociation of the acidic gases increases strongly with decreasing temperature (e.g. below 200°C). Acidic waters high in CO₂ are likely to be far removed from equilibrium with rock minerals (as limestone) and become quite reactive. The protons added to the water through the mixing process with cold waters stimulate dissolution of many alteration minerals with the result that the relative concentrations of the major cations can change drastically from the original equilibrium with normal secondary minerals. The distribution of cations is then approaching that dictated by stoichiometric dissolution of the matrix rock. The result is that in andesitic systems the apparent Na-K geothermometry temperature increases strongly and the Na-K-Ca and K-Mg geothermometers produce very low temperatures.

4.0 THERMODYNAMICS OF HCl

4.1 Features of HCl

HCl is a gas at temperature above -85°C and is moderately soluble in water (0.4 moles/mole H₂O at 0°C compared with 0.11 moles/mole for H₂S). Its solubility is close to that of Ar. With increasing temperature its

solubility is between that of NH_3 and H_2S . The apparent high solubility of HCl in liquid water at ordinary temperatures is due to strong dissociation into H^+ and Cl^- . The dissociation constant decreases greatly with increasing temperature. That is at high temperatures HCl is a weak acid similar to acetic acid. In the absence of liquid water, HCl in vapor remains associated as an inert gas and is not reactive.

HCl is a near universal constituent of volcanic fumarolic gases, existing at concentrations of 0.5 to 1 mole% of total gas (e.g. Ellis, 1957; White and Waring, 1963; Ozawa et al., 1973; Giggenbach, 1975; Giggenbach and Le Guern, 1976). The existence of hydrogen chloride in high temperature (more than 400°C) volcanic gases and in acidic hot spring waters closely associated with volcanoes has been reported many times. For example in the fumaroles of Vulcano island in Sicily (Italy) (with rhyolitic magma), where fumaroles exceeded a temperature of 600°C, values of HCl exceeding 800 ppm in the steam have been monitored during the 90s.

The formation of HCl in magmatic systems is favoured at high temperatures and low pressures. It forms in the magma by reaction of NaCl, water and silica to form Na_2SiO_3 and HCl. Similarly, Ca, Fe (and probably Mg) chlorides are more reactive than NaCl producing HCl at lower temperatures, so that fumaroles related to basalts have higher HCl than those related to silicic lavas (Ellis, 1957).

The concentration of HCl in vapor in equilibrium with an aqueous solution increases as the temperature and chlorinity of the solution increase and as the solution pH decreases. Natural occurrences of HCl suggest that these factors are similarly effective in generating HCl-bearing steam over a wide range of conditions. Hypersaline subsurface brines with Cl concentrations of more than 100,000 ppm are not uncommon (e.g., The Salton Sea geothermal brine in California and the Asal area in Djibouti). These brines are of 1.5 to 3 orders of magnitude higher in Cl than the normal geothermal waters (1000-5000 ppm Cl). HCl is not generally found in low temperature (less than 160°C) fumaroles associated with geothermal systems (e.g. in a 150°C fumarole in Pozzuoli, Flegrean field, Italy). But it can be found in volcanic fumaroles at relatively low temperatures together with SO_2 . The preservation of HCl in steam from wells is more likely than from fumaroles because well casings isolate the steam from local low temperature waters. For example, the Tatun field in Taiwan is a drilled volcano-related geothermal system with HCl containing water and steam discharges. This system produced high HCl in steam and brine because it had high temperatures, low reservoir pH (about 1.5), and high Cl contents in the brine. The low pH in the water remained unneutralized because there the reservoir was a pure quartz sandstone containing no feldspars or other minerals that could neutralize acid.

Chloride as HCl has appeared in dry to superheated steam from Larderello, The Geysers, and Krafla geothermal fields. In the case of Krafla, most water is nearly neutral, but well K-12 produced superheated steam with significant concentrations of HCl. These occurrences may have distinct geologic origins, but the presence of HCl in steam depends on certain chemical and physical reservoir conditions in which the HCl is transferred from the deep brine along a dry path to wells close to the surface.

The chemical and physical reservoir conditions which produce HCl-bearing steam will be examined by evaluation of geothermal systems known to produce HCl-bearing steam and by calculations based on experimental data. These investigations were initiated because of accelerated corrosion due to the presence of HCl in steam at The Geysers, Larderello and Krafla. At Tatun, the field was abandoned due to excessive corrosion of well casings. Corrosion of well casings and the surface pipes has been a problem at Larderello for many years. Since reinjection began, however, concentrations of HCl (and thus corrosiveness) at Larderello steam have strongly declined. At The Geysers, HCl is associated with drying of the reservoir and the exploitation of hotter areas, and is expected to become more widespread as these processes continue. Increased reinjection at The Geysers will have a similar Cl-reducing effect as at Larderello, but the amount of available water is limited. Additionally, methods have been developed to mitigate surface corrosion by spraying NaOH solutions into the pipes. A reduction of superheat in Krafla well K-12, possibly due to production from another diluted fluid source, terminated in the 90s the production of HCl-bearing steam.

Boiling in high temperature geothermal reservoirs such as Reykjanes, Iceland, Cerro Prieto, Mexico and Salton Sea, California, could theoretically produce reservoir vapor containing HCl. However transport of HCl to the surface does not occur in these systems because HCl redissolves in the liquid water, in upper layers, as temperature decreases in a similar way that Los Humeros.

4.2 HCl in Vapor Boiling from High-Temperature Brine

Calculations presented below show that significant concentrations in HCl in *steam* are generated from boiling moderate-to-high salinity brines of near neutral pH values (4-6) at temperatures greater than 300°C. Calculations based on water-rock interaction show similar results when NaCl solid as halite is considered present in the system. Calculations of the chemistry and temperature of brine in equilibrium with vapor containing various HCl concentrations were made by Haizlip and Truesdell (1988). These calculations, which involved the association of H⁺ and Cl⁻ in liquid to form HCl and the volatility of HCl, are summarised below.

The concentration of associated HCl in aqueous solution is determined by the dissociation reaction to H⁺ and Cl⁻, where K_d is the dissociation constant for the aqueous species



$$K_d = a_{\text{H}^+} a_{\text{Cl}^-} / a_{\text{HCl}_1} \quad (12)$$

$$\log K_d = 13.415 - 0.026 T \quad T \text{ in Kelvin} \quad (13)$$

The logarithm of the concentration of HCl⁰ (= HCl₁) dissolved in the liquid phase is thus:

$$\log m_{\text{HCl}_1} = \log m_{\text{Cl}^-} + \log \gamma_{\text{Cl}^-} - \text{pH} - \log K_d - \log \gamma_{\text{HCl}_1} \quad (14)$$

where, m is molal (moles/kg in solution); and γ is the activity coefficient. The concentration of HCl in the vapor phase in equilibrium with the liquid phase is determined by the distribution coefficient B_{HCl}, with:

$$B_{\text{HCl}} = m_{\text{HCl}_1} / m_{\text{HCl}_1}, \text{ where } m \text{ is moles/kg in each phase.} \quad (15a)$$

For a given Concentration of chlorides in solution, at a given temperature, the values of the activity coefficients can be computed, considering a salinity corresponding to NaCl. log K_d and log B_{HCl} are known functions of temperature.

$$\log m_{\text{HCl}_1} = \log m_{\text{Cl}^-} - \log B_{\text{HCl}} - \log \gamma_{\text{HCl}^-} + \log \gamma_{\text{HCl}_1} + \text{pH} + \log K_d \quad (15b)$$

Then we obtain an equation where the concentration of HCl in the *steam* is function of temperature, pH, and chlorinity.

The available database for HCl distribution coefficient were extrapolated at high temperatures, assuming that the value for log B_{HCl} approaches one at 374°C (true for all gases), lies between those of H₂S and NH₃, and like these gases is a straight line as a function of temperature in °C. The result is the equation,

$$\log B_{\text{HCl}} = 3.65 - 0.0081 t^{\circ}\text{C} \quad (16a)$$

The values of log K_d and log B_{HCl} indicate that the HCl₁ at temperatures exceeding 300°C is a weak acid with a high volatility. If, during its ascent in vapor, HCl₁ encounters a liquid phase at lower temperature, it is rapidly removed from the rising fluid because of solution and dissociation in the liquid. In addition, HCl will not accumulate to an equilibrium concentration in the lower-temperature liquid because of neutralization by rock minerals.

Evidence for HCl in *steam* and the reservoir conditions which generated HCl-bearing *steam* will be discussed for the different areas. In particular many data are available for Larderello and The Geysers because of their early production, and a large number of paper were dedicated to these fields.

4.3 Effects of chlorinity on HCl formation

The distribution coefficient for HCl and the dissociation constant of HCl₁ are used to calculate the concentration of Cl in the brine in equilibrium with the observed high HCl concentrations in the *steam*. If K_d and

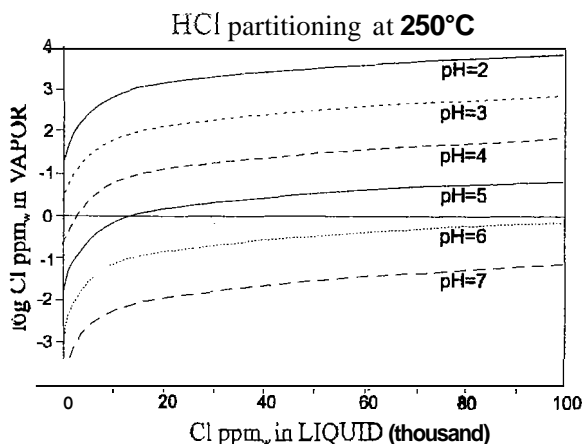


Figure 1. Cl content in reservoir vapor in logppmw vs Cl in reservoir liquid in thousand of ppmw at selected values of pH, computed at 250°C. (From Haizlip and Truesdell, 1988).

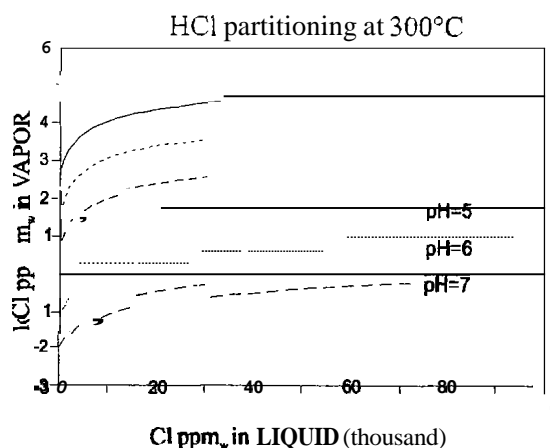


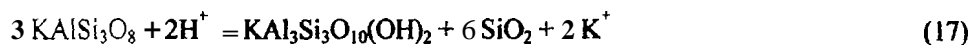
Figure 2. Cl as in Fig. 1, computed at 300°C.

B_{HCl} are known at a given temperature, and γ_{Cl^-} and the γ_{HCl} are estimated using the Debye-Huckel method. then m_{Cl} , representing the reservoir liquid chloride composition, can be calculated from equation 15b

$$\log m_{Cl} = \log m_{HCl,v} - \log B_{HCl} - \log \gamma_{Cl^-} + \log \gamma_{HCl} + \log K_d + pH \quad (16b)$$

The concentration of total Cl in the brine is then only a function of temperature, pH and HCl found in the steam. The problems are due to the possible pH of the solution and the fact that the HCl, measured at well-head can be affected by mixing with lower temperature steam which does not contain HCl. Figures 1.2 and 3 show the Cl contents in the reservoir versus Cl contents in the vapor in ppm at 250, 300 and 350°C for selected values of pH, calculated using B_{HCl} extrapolated from experimental data and K_d of Ruaya and Seward (1987).

The pH can be estimated by considering some mineral-water buffer reactions. Potassium mica and potassium feldspar are often present in geothermal fields (e.g., The Geysers, Walters et al., 1988), then in the presence of quartz:



and the activity ratio of K^+/H^+ is a function of temperature.

At selected temperatures, using this computed ratio, the Na/K ratio from the geothermometer of Truesdell (1976) and the electrical neutrality, a relation between chlorinity and pH can be derived at various temperatures. The results are shown in Figure 4.

Despite the uncertainty of the buffer reaction used, the low pH required at 250°C to generate significant HCl in the steam cannot exist in the reservoir. From the figures 1, 2 and 3 it can be seen that if Cl concentrations in the reservoir liquid are between 10,000 and 60,000 ppm, and the temperature is 300°C or 350°C at a pH of 6, steam with HCl concentrations between 10 and 200 ppm could be generated. It is interesting to note that the shape of the figures are asymptotic. Lower pH and/or higher Cl content in solution will generate more HCl in the steam.

Steam with negligible HCl is normally generated by boiling from parts of The Geysers reservoir at less than 250°C, and originally high HCl superheated fluid which has lost HCl by scrubbing as it passed through zones of high liquid saturation. Thus, steam and steam condensate at typical Geysers reservoir temperatures (220-250°C) contain negligible HCl. Because steam condenses in a two phase system, liquid is nearly ubiquitous and HCl would be solubilized and dissociated in the liquid before reaching the well. The values of HCl in the steam are thus quite

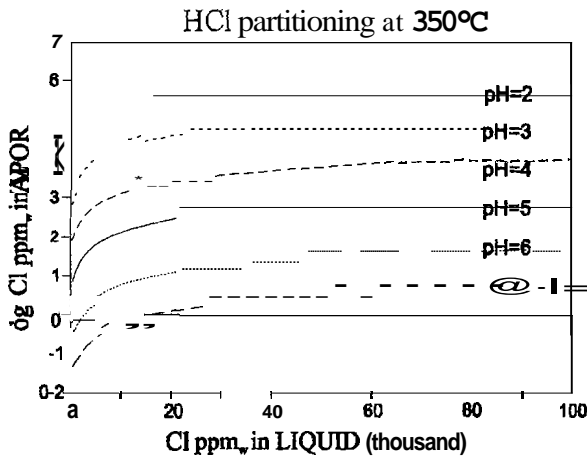


Figure 3. Cl as in Fig. 1, computed at 350°C.

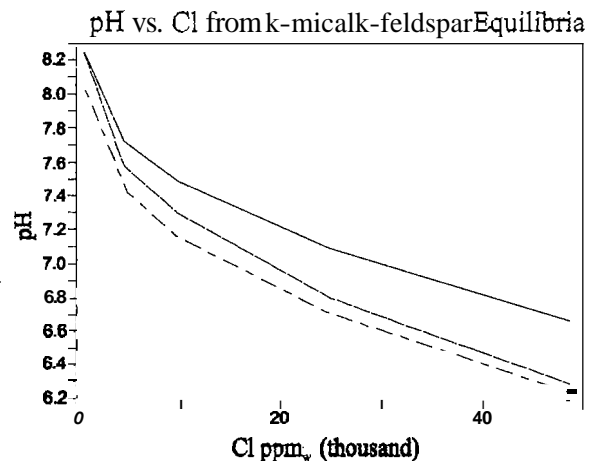


Figure 4. pH vs Cl concentration of the brine in ppmw, computed from K-mica/K-feldspar equilibrium at selected temperatures (from Haizlip and Truesdell, 1988)

dependent on the flow path of the rising fluid. Waters at very high acidity (let say with a pH=1) would alter the aluminosilicate minerals to kaolinite and clay according to temperature. Since feldspars and mica are found in The Geysers reservoir with other alteration minerals **existing** only in almost neutral solutions (Sternfeld, 1989; Walters et al., 1988), it is unlikely that such acidic waters exist.

Where mineral-liquid equilibrium for the reaction of potassium mica and potassium feldspar (or similar reactions) occur, pH values for reservoir waters with high Cl concentrations should be nearly neutral (pH=5.5 at 350°C). Therefore steam that contains significant (greater than 10 ppm) HCl must have generated at temperatures above typical reservoir temperatures and must have followed a *dry*, high-temperature path to the wellbottom. Specifically, at 350°C, **steam** with greater than 100 ppm of HCl can be generated (boiled) from liquid at pH=5 with greater than 10,000 ppm of Cl, and at pH=6, from liquid with greater than 60,000 ppm of Cl.

In andesitic systems the reservoir pH can locally be lower, but a large quantity of HCl is intercepted by scrubbing in the liquid-dominated upper level. At 300°C, liquid with pH<5 and Cl greater than 60,000 ppm is required to generate steam with 100 ppm of HCl. High-temperature (350°C) steam with 200 ppm of HCl is suggested by Walters et al. (1988) to exist in the high temperature reservoir of the Northwest Geysers, in equilibrium with a liquid containing a Cl concentration greater than 25,000 ppm. The existence of such a deep boiling brine is proposed by many models of The Geysers (e.g. White et al., 1971, Pruess, 1985), but without direct evidence.

Evidence presented by Drenick (1986) and Walters et al. (1988) suggests that Cl-bearing steam is produced from higher temperature reservoirs at The Geysers and that some wells produce mixed steam from both the high-temperature and typical reservoir lowering the observed value of HCl. They suggested mixing must occurred in the well or else the conduit through the typical lower temperature reservoir must be dry. In wells, like in Larderello that have produced for a long time, the shallower typical reservoir may have become at least in some parts dry due to production allowing the formation of dry conduits from the brine to the well. This should be true in particular in high vertical permeability zones (upflow zones).

Our results are in agreement with observations of corrosion from HCl-bearing super-heated steam at well K-12 of the Krafla, Iceland, field and with the occurrence of acidic, high-Cl condensate from steam at Tatun, Taiwan (Ellis and Mahon, 1977), although liquids in these systems may be much more acidic than those in The Geysers or Larderello. The appearance of HCl in Larderello steam in 1960s (D'Amore and Truesdell, 1979) probably resulted from the drying out of the about 240°C upper condensate level which allowed HCl to travel from the deep high temperature brine to the surface in the upflow zones.

4.4 Mineral-halite reactions

Formation of volcanic HCl gas from silicate-halite reactions has been suggested (Ellis, 1957; Giggenbach 1975) 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 MgCl₂ evolves HCl when heated to dryness. (Cotton and Wilkinson, 1982). Thus mineral-halides (NaCl, KCl, MgCl₂, etc.) reactions are a reasonable alternative to fix the Cl content into the boiling brine offered by Hazlip and coworkers as the generative mechanism for HCl gas in geothermal steam (D'Amore et al., 1990). Practically the mineral-halide acts at a given temperature as buffer for the Cl content in the brine. In order to test this idea we have calculated the concentration of HCl in vapor in equilibrium with halite and the mineral assemblages occurring in Larderello and The Geysers fields.

Prolonged boiling of deep liquid beneath the vapor dominated reservoir, must result in the formation of a brine. Evaporation in the natural state could have produced halite crystallisation. In addition, accelerated boiling due to exploitation would lower the level of the liquid surface and leave pockets and surface films of brine which evaporate to high Cl concentration and eventual dryness to precipitate halite. Hypersaline NaCl-saturated brines have been found in fluid inclusions from Larderello (Belkin et al., 1985; Marignac et al., 1987; Cathelineau et al., 1989). Inclusion homogenisation temperatures are constantly higher (>300°C) than those measured in normal producing wells in Larderello (200-275°C) at well bottom, suggesting that both temperature and salinity probably do not reflect the exploitation conditions. Then halite can be present also as fossil product, when the reservoir was much hotter. Despite that, it is present now and can act as buffer for the water in the brine.

The hydrothermal minerals found in the normal reservoir (close to 250°C and in zones at high temperature (>300°C) for Larderello and The Geysers are shown in Table 1. Reactions with minerals involving halite and HCl may be grouped by reactions with minerals stable at t < 300°C and higher temperature reactions for t > 300°C. Mineral reactions involving calcite and CO₂ pressure dependent have also been considered.

Hydrothermal minerals at Larderello, and The Geysers are given in the following list for both the normal reservoir (temperature < 300°C) and in zone of inferred high temperature (temperature > 300°C). Abbreviations are: Qz, quartz; Cc, calcite; Ch, chlorite; Ep, epidote and/or clinozoisite; Ac, tremolite or actinolite; Pl, sodic plagioclase; Px, diopside and/or hedenbergite; Pr, prehnite; Mu, muscovite; Ab, Na-feldspar; Bi, biotite; and Hs, K-feldspar.

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

temperature < 300°C	Qz, Cc, Ch, Mu, Ep, Ks, and in less amount Ac, Pl, Px, Pr.
temperature > 300°C	Qz, Ch, Ep, Ac, Ks, Px, Ab, Pr and in less amount Pl.

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

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

As an example in Larderello we can consider Querciola 2, a typical high-temperature well (well-head temperature is about 260°C) of Larderello, located in the northwest upflow zone of the field. In 1981 this well had the following composition (before reinjection) with gas composition in volume %:

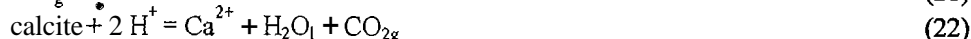
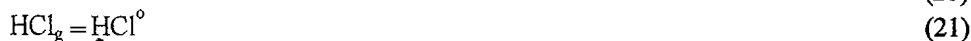
gas/steam	CO ₂	H ₂ S	H ₂	CH ₄	N ₂	HCl
molar ratio	volume%					ppmw
12.3 x 10 ⁻³	90.11	3.68	3.69	1.81	0.71	74

It is very probable that the observed Concentration of HCl is lower in respect to the vaporized amount from the brine because of dilution from the dry upper zone. It is difficult to evaluate this mixing effect. One way should be to consider the steam fraction computed at a reasonable temperature using for example the grids diagram of D'Amore and Truesdell (1985). From the diagram we obtain a value of steam fraction in the two-phase reservoir y = 0.30 at 250°C. If most of the steam would be produced from the vaporization of the two-phase at 250°C mixing with the deep steam containing the HCl, the original content of HCl in the steam would exceed 200 ppm.

The following cases can be considered:

CASE A, calcite present, $P(\text{CO}_2)$ involved.

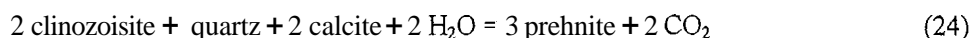
Consider the following system of equations:



Most of Cl^- is electrically balanced by Na^+ , K^+ and Ca^{2+} ions:

$$m(\text{Cl}^-) = m(\text{Na}^+) + m(\text{K}^+) + 2m(\text{Ca}^{2+}) \quad (23)$$

The extended Debye-Huckel expression can be used to compute activity coefficients γ for all ionic species. In first approximation the ionic strength is taken equal to the molar concentration of Cl^- . Cavarretta et al. (1982) showed that the CO_2 partial pressures at Larderello are close to equilibrium for the reaction:



The temperature dependence of $P(\text{CO}_2)$ at equilibrium was expressed by an empirical fit of data from reaction (1) valid from 200 to 300°C:

$$\log P(\text{CO}_2) = -2.81 + 1.437 \times 10^{-2} t - 1.4 \times 10^{-5} t^2 \quad (25)$$

$P(\text{CO}_2)$ can be computed also from the following equation (D'Amore and Truesdell, 1985) when the steam fraction in the reservoir is positive:

$$\log P(\text{CO}_2) = \log(\text{CO}_2/\text{H}_2\text{O}) - \log(y + (1-y)/B_{\text{CO}_2}) + \log P_{\text{H}_2\text{O}} \quad (26)$$

where y is the effective steam fraction computed from gas composition (0.3 for well Querciola 2).

Depending on the content of Fe^{3+} in the clinozoisite (epidote), we may assume a variability in the computed $P(\text{CO}_2)$ from equation (12) of the order of 2 bars. This equation, without any correction for clinozoisite produces the minimum values for $P(\text{CO}_2)$ in Larderello. If the value of the chlorinity of the brine is imposed, it is possible to calculate the HCl content in the produced steam and the value of the pH at equilibrium. For well Querciola 2 a pH of about 5 is obtained at 300°C.

Computed HCl concentrations in the **steam** as function of temperature are shown in Figure 5 at selected values of $P(\text{CO}_2)$.

CASE B, no calcite involved. $t < 325^\circ\text{C}$

The equations given in the **first** model involves calcite and therefore the computed concentration of HCl in the vapor depends on the CO_2 partial pressure as well as temperature. This may be unrealistic for parts of the Larderello field and The Geysers with temperatures above 300°C where calcite is not present (Gianelli G. pers.

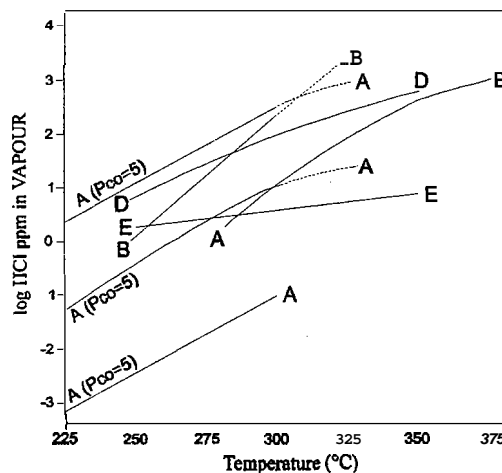
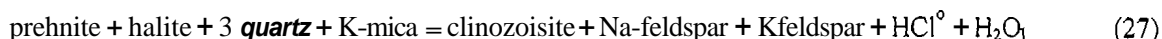


Figure 5. Computed HCl concentrations in reservoir vapor vs. temperature from the different methods in the text. Line D is from Haizlip and Truesdell (1988) at pH=5 and 40,000 ppm of Cl. Line E is from Andersen (1989).

comm., 1989, Sternfeld, 1989). For these conditions alternative reactions can be written in which silicates take the place of calcite. Using these reactions, the HCl concentrations in the steam are only function of the temperature:

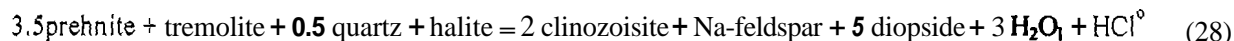


t°C	logK	HCl (ppm in vapor)
250	-5.9	0.05
275	-4.6	0.9
300	-3.3	18
325	-2.0	360
350	-1.8	571
375	-1.6	904

The computed pH is close to **5** at 300°C.

CASE C, calcite not involved, t > 300°C

Muscovite is not generally stable above 300°C and is not found at Larderello and The Geysers above 325°C. The following chemical reaction involving amphiboles (tremolite) and pyroxenes (diopside) have been considered:



In this particular case the concentrations of HCl^o are only a function of temperature.

t°C	logK	HCl (ppm in vapor)
300	-4.6	11
325	-3.5	92
350	-2.4	506
375	-1.6	920

Figure 5 summarises the results of HCl concentrations in the steam obtained from the three different chemical models (lines A, B, and C). In the case A 0.1, 1 and 5 bar for CO₂ have been considered. At high temperatures the calculations using mineral assemblages with halite are in agreement with line D involving a hypersaline brine alone (Truesdell and Haizlip, 1988); line D in Figure 5 is for pH 5 and 40,000 ppm Cl. Computed HCl values in the steam are negligible at 250°C with all models. With increasing temperature a trend is evident with production of HCl in the order of 10-20 ppm at 275°C, 100-200 ppm at 300-325°C, and 500-1000 ppm at 350-375°C. Line E is from Andersen (1989). It agrees neither with our results nor with the concentrations of HCl found in high temperature geothermal steam.

5.0 CONCLUSIONS

HCl in superheated steam has been produced from wells at Larderello, The Geysers and elsewhere. HCl is clearly generated in the steam from a brine as function of the pH, Cl concentration and temperature during reservoir boiling. The lower the pH of the brine, the lower the Cl concentration and temperature required to generate an equivalent concentration of HCl in steam. Because of dissociation HCl partitions from steam into any liquid water in which it is more soluble, and can easily be scrubbed into shallower liquid at lower temperature or high pH. Therefore HCl-bearing steam cannot pass through a normal 200-250°C vapor-dominated reservoir with descending condensate. To be present it must remain superheated by following a dry (possibly high temperature and low pressure) flow path to the well.

The necessary pH, temperature and chlorinity could be generated in several ways. At Tatun, the influx of HCl in volcanic gas and the lack of neutralizing minerals probably causes the extremely low reservoir liquid pH,

allowing HCl to volatilize. At Krafla, HCl is confined to specific wells. A combination of high temperature and local superheating of a portion of the reservoir, along with evaporation to **dryness** or near dryness of the chloride reservoir water allowed HCl production. The HCl production ceased when the enthalpy declined, probably as a result of an influx of liquid. At Larderello, drying out **of** shallow portions of the reservoir that normally scrubbed **HCl from** steam produced **from** deeper, hotter and saline zones may have allowed the transport of HCl to producing wells. However, reinjection has partially restored the liquid and scrubbed HCl. At The Geysers, production **from** hotter, deeper zones on the edge of previous production and drying of some older producing areas are producing the physical and chemical conditions in the reservoir for generating HCl-bearing steam.

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. This could be true also in liquid-dominated systems. Here we show that equilibrium of halite with silicates and calcite found in these fields could also generate a neutral pH HCl gas in quantities similar to those found. The correlation of high-temperature areas with HCl in the steam emphasizes the strong relation of HCl concentrations to temperature. Neutral solution **can** then also produce large amounts of HCl at high temperature.

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