The Los Humeros Geothermal Field: On the Acidity of Fluids

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ABSTRACT

Evidence from Mineralogical, geochemical and fluid inclusions data have shown the occurrence of two geothermal reservoirs in the Los Humeros Geothermal Field (LHGF) as well as the formation of acid fluids that at once promoted corrosion in well casings. Analysis of production and reservoir engineering data from wells of LHGF, and pressure distribution profiles for the unperturbed system, were used as evidence for the existence of two reservoirs: one of high liquid saturation and other of low liquid saturation.

The unperturbed system did not contain a proper acid zone. No evidence of acid fluids occurring in the reservoirs have been found. The only instance of shallow acidity is the surface argillic alteration as a result of H_2SO_4 formation. Deep corrosive fluids in wells were formed after the exploitation of the field began.

1. INTRODUCTION

The LHGF has been subject to a large number of studies that have provided a great source of information about the system. At the present, the occurrence of at least two reservoirs are well understood (Arellano et al., 2003). The geochemistry of fluids, once thought to be an out of equilibrium system, is also understood to a greater degree. Different approaches have been made in order to explain the occurrence of acidity in the fluids. Izquierdo et al., (2000) gave a detailed explanation of the probable formation of acid fluids in LHGF. The present work gives more evidence that sustains and corroborates the explanation given before.

The most important species in a geothermal system that provide acidity to an hydrothermal fluid are the volatile components that emanate from the magma such as H_2O, Cl, SO_2, H_2S, H_2 and CO_2. Its interaction with geothermal fluids and the physical-chemical changes that occur in the reservoir generate a fluid of acid nature; which is modified when it moves upwards to the surface. The aqueous solution of acid nature tends to be neutralized or become alkaline due to its interaction, with the rocks that conform the reservoir. However, the chemical composition of the fluids collected in the surface may show the presence of components related to the acidity of the geothermal fluid; such is the case of excess of chloride and sulfate and, in consequence a chemical unbalance.

The main acid species commonly found in geothermal environments are HCl and H_2SO_4. Several approaches are known to explain the origin of the HCl. Some of these include its formation from acid fluids of magmatic origin, formation of NaCl from deep boiling brine or by reactions between halite, formed from that brine deep, and silicates. For H_2SO_4 different mechanisms of formation have been proposed according to the environment in which it is produced. In a magmatic-hydrothermal environment its formation has been proposed by the complex reaction between SO_2 and H_2O.

It has been considered that the main conditions for the HCl formation is pH, temperature and chloride concentration in the fluid.

The mechanism of transportation of HCl in superheated vapor introduced by Haizlip and coworkers (D'Amore, 1990) has been well accepted. On the origin of the HCl two considerations proposed by D' Amore (1990) are known. One of thoughts is its formation from neutral or acid boiling brine at high temperature, or through reactions in vapor between halite and silicates producing HCl gas that is transported in superheated vapor. Experimental data, considering that HCl in the vapor in equilibrium with brine or with halite, showed that the concentration of HCl increases as a function of temperature. In practice it has been observed that this relation is complied in high temperature geothermal reservoirs

D' Amore (1990) and Truesdell (1989) have suggested that the origin of vapor containing HCl is a product of the high temperature (> 325 °C) reaction between NaCl solid and the minerals of the rocks. The mechanism proposed by these authors considers that in the natural state of a geothermal reservoir, there should exist deep boiling brine that generates ascending vapor required for the transportation of heat and gases but not of soultes (Cl) to the top of the vapor dominant reservoir. Furthermore they propose that if this deep liquid exists, it should be concentrated brine due to the accumulation and concentration of solutes.

2. STUDY AREA

The Los Humeros geothermal field (LHGF) is located in the eastern part of the Mexican Volcanic Belt. The volcanic system has several geological structures. The main feature is the Los Humeros Caldera (LHC). This structure has a diameter of 16 km approximately and contains the Los Potreros and El Xalapasco calderas (Figure 1)

The geothermal field is located in the State of Puebla, between 19º35´- 19º45´ longitudes and 97º24´- 97º30´ latitudes. As far as geothermal electric generation in the country is concerned, LHGF is at present the third geothermal resource; 40 wells have been drilled and 7 units of 5 MWe each have been installed.
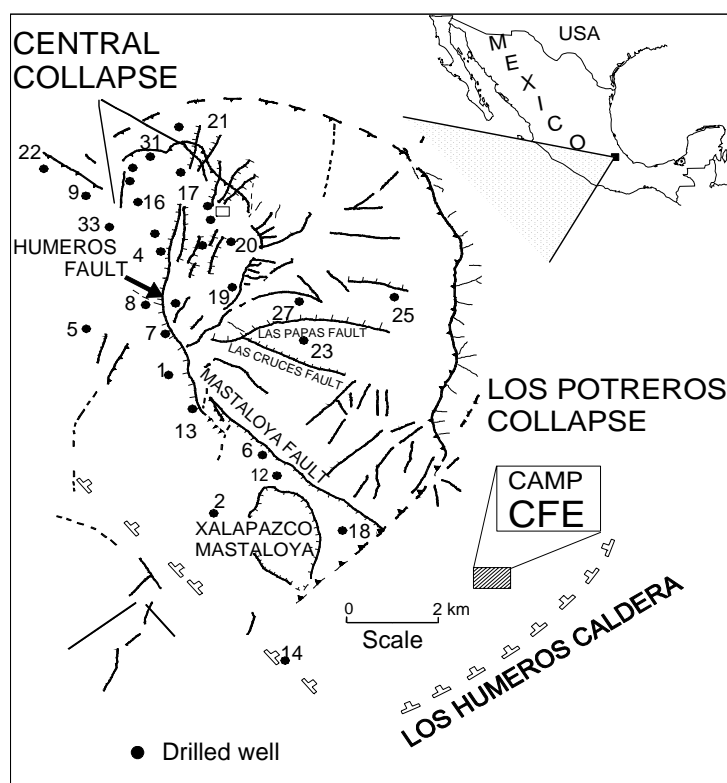
Figure 1: LHGF location of wells and main geological structures.

The local basement is formed by a Paleozoic metamorphic complex, chlorite-muscovite shales, a Mesozoic folded sedimentary sequence, lower Tertiary syenitic and granodioritic intrusions and Pliocene andesites. The subsurface geology (taken from Cedillo, 1997), is the result of the interpretation of petrological and geophysical logs that have contributed to identify hidden faults and to subdivide the four lithological units previously recognized (Viggiano and Robles, 1988 a) into nine lithological units. From surface to depth this units are Unit 1: Pumice, basalts and andesites; Unit 2: Lithic tuffs; Unit 3: Vitreous and lithic ignimbrites; Unit 4: Intercalation of andesites and ignimbrites; Unit 5: Augite andesites; Unit 6: Vitreous tuff; Unit 7: Hornblende andesite; Unit 8: Basalts; and Unit 9: Limestone, metamorphic limestone and intrusives.

3. RESULTS AND DISCUSION

3.1 Pressure distribution

From Arellano et al., (2003) Figure 2 represents an overall unperturbed pressure altitude profile of the field. A boiling point pressure for depth (BPD) curve (Grant et al., 1982) has been matched to the data and it shows high correlation between 1600 and 1025 m.a.s.l. However, below 1025 m. a.s.l., a group of wells does not follow this behavior, because the reservoir contains two-phase fluid with low liquid saturation (< 5-10 %) and hence the pressure seems to fit the shape of a vapor-dominated type reservoir (Truesdell and White, 1973).

This pressure profile may be represented by the following expression:
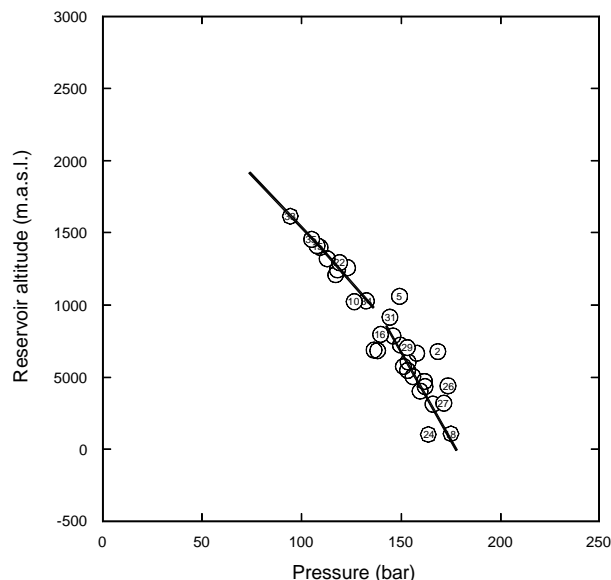
$$P = 177.5 - 0.0405Z \qquad (1)$$

Figure 2: Unperturbed pressure-altitude profile. For simplicity not all the well numbers are shown.

Where P is the pressure in bar and Z is the altitude in m.a.s.l. In Figure 2 matching of the data to the BPD model (upper line) and to equation 1 (lower line) are shown. Thus it can be concluded that for LHGF there exists at least two reservoirs. One located between 1025 and 1600 m.a.s.l. is defined as liquid dominant, with a pressure profile corresponding to a hydrostatic gradient at a temperature of 300-330 °C (temperatures were estimated by the SRF method from Ascencio et al., 1994 in Arellano et al., 2003). The deeper reservoir is located between 850 and 100 m.a.s.l. and is considered as a low liquid saturation reservoir with temperature above 300 °C. The change in the pressure

distribution slope (Figure 2) at 900 m.a.s.l. is related to the lithological unit formed by vitreous tuff of relatively low permeability. This unit is considered a barrier between the two reservoirs.

3.2 Hydrogeological model of LHGF

Regional studies of hydrology, gechemistry and structural geology (Cedillo. 2000 and Portugal et al., 2000) have lead to a hydrogeologycal model of the Los Humeros reservoirs. There are only indications of vertical and lateral recharge from meteoric water; which mixes with geothermal brine from the upper reservoir and groundwater. But no evidence of recharge of the deep reservoir has been given. Figure 3 shows the model of groundwater flow and main lithological units in LHGF (taken from Portugal et al.).

In the unperturbed system it is quite probable that the deeper reservoir did not mix at all with the upper one because the occurrence of the not very thick vitreous tuff; which has been acting as a barrier between the two reservoirs. The permeability of the vitreous tuff could be modified by the effect of hydrothermal alteration, since high temperature mineral assemblages have been found in this unit. This alteration could provoke secondary permeability by leaching, dissolution, and at the same time sealing spaces by crystallization of new minerals. It is possible that in the unperturbed system the vapor dominant reservoir was isolated by the lateral geological barriers and at depth by the metamorphosed limestone of very low primary permeability.

3.3 Hydrothermal mineralogy

In general two types of hydrothermal alteration have been recognized: a neutral alteration (neutral to basic pH) formed by sodium chloride fluids of high temperature and with almost neutral pH, and characterized by clay minerals, pyrite, calcite, quartz, zeolites, epidote, biotite etc. The other is an acid alteration formed by the contact with fluids of low pH or acid sulfate fluids; represented by Kaolinite, dickite, pyrophyllite, diaspore, andalusite, zunyite, tourmaline, lazulite, etc.

In LHGF a systematic petrography analysis of cuttings and mineralogical registers from the Comisión Federal de

Electricidad (CFE), showed in general terms a low intensity of hydrothermal alteration but also high temperature assemblages at depth. This can have two explanations: the water rock ratio is low, or LHGS is a young system. The relative highest alteration percentages are found in the litological unit formed by augite andesites. In contrast at depth in the hornblende andesite alteration is very low; however, high temperature minerals were found such as garnet, amphibole, biotite, etc. The main hydrothermal minerals found in the alteration zones of the system are: chlorite, epidote, quartz, calcite, low proportion of leucoxene and pyrite. Apart from these minerals clays, biotite and in low amount zeolites, anhydrite, anfíbol, garnet, diopside and wollastonite have been recognized. In agreement with Reyes (1990), the pH conditions in which these minerals are formed are considered neutral to alkaline environments.

For several secondary minerals three geological sections were drawn. Figure 4 shows the distribution of calcite in wells located in the Colapso Central in a NNW-SSE section. It can be seen that at depth in the unperturbed system there is no calcite at all. It was believed that acid fluid reacted neutralizing the carbonate. If acid fluids were in the reservoir inhibiting calcite deposition; at least there should be traces of hydrothermal minerals typical of acid environments interacting with rocks. Instead minerals typical of neutral to basic pH were formed. An explanation of the absence of calcite at depth is possible because of the low water: rock ratio. In general, when the amount of water increased the percentage of alteration minerals increased. The high percentage of alteration minerals coincides with the depth at which the liquid reservoir is located.

The same explanation can be done for the occurrence of epidote. Major concentration of this mineral is found in the zone of high liquid saturation (augite andesites), and even when temperature is high in the low liquid saturation reservoir epidote occurs in low proportion. Wells located close to the Colapso Central but far from the vapor reservoir show high proportion of epidote at depth; the same happens for most hydrothermal minerals.
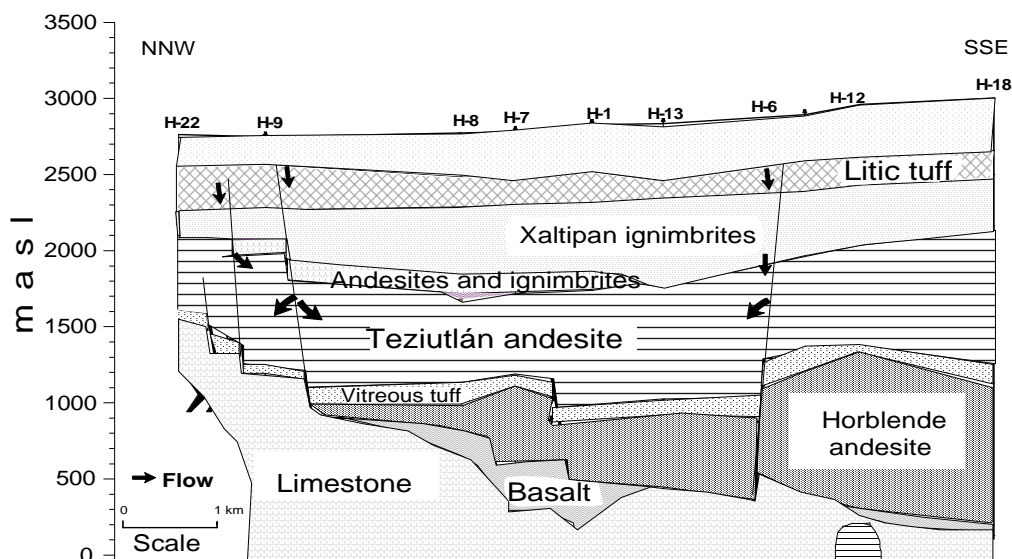

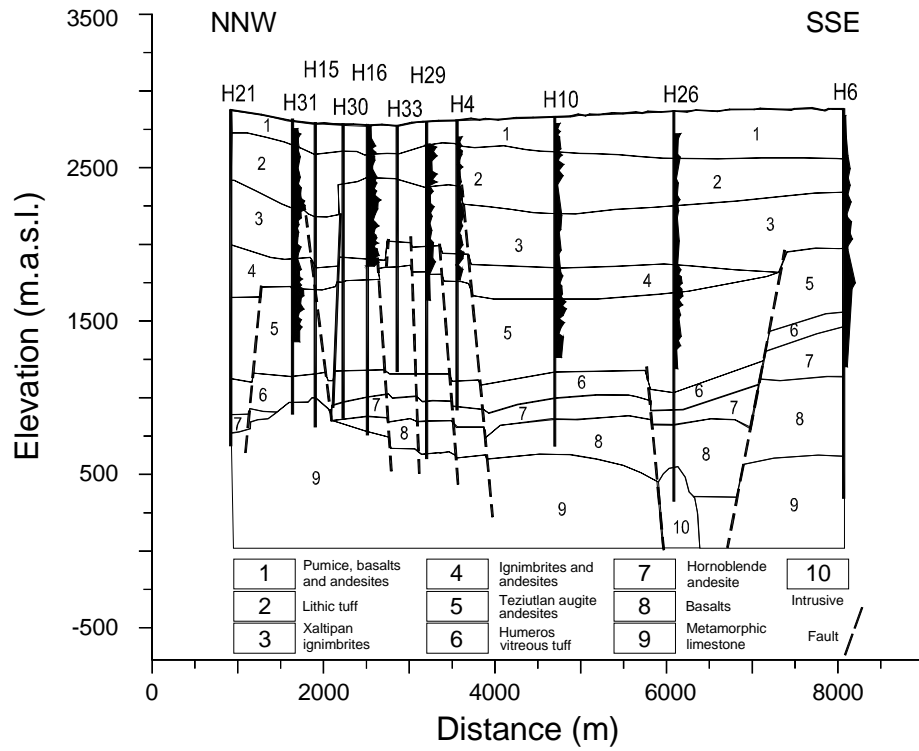**Figure 3: Groundwater flow and lithological units in LHGF.**

Figure 4: Distribution of calcite in wells located in or close the Colapso Central.
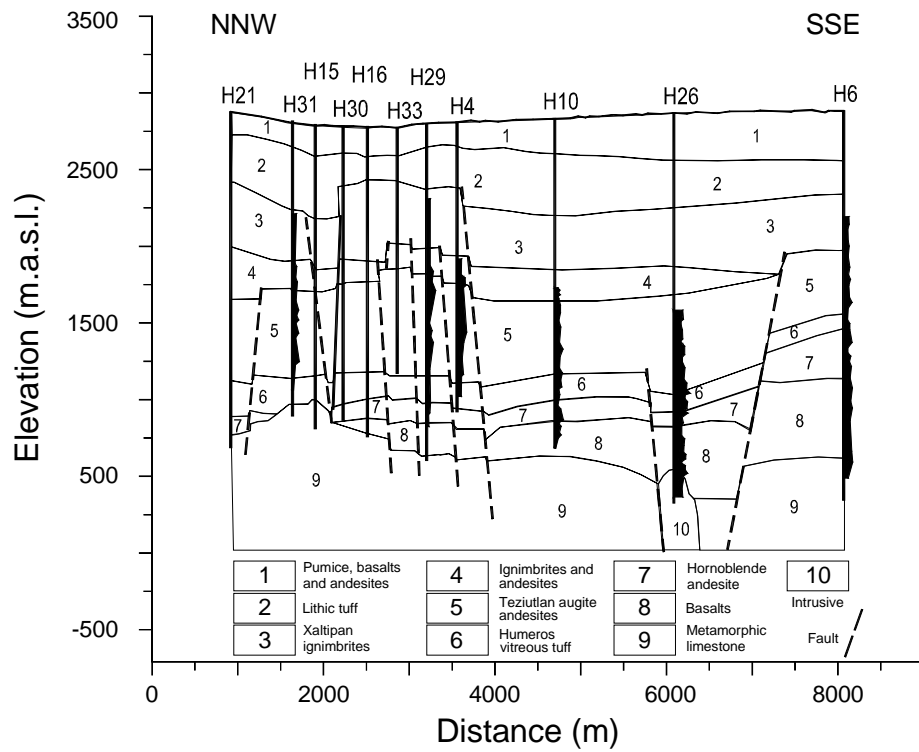

Figure 5: Distribution of epidote in wells located in or close the Colapso Central.

The distribution of the epidote, anfibol, diopside, garnet and biotite indicate zones of high temperature. In wells drilled in the Colapso Central, the distribution of these minerals clearly show ascent of hottest fluids than in surrounded zones. The hottest zone in the field is located in the Colapso Central area where the vapor dominant reservoir has been recognized.

3.4 Clay minerals

Phyllosilicates identified by X-ray diffraction in the clay fraction of cores and cuttings from wells H-14, H-15, H-16, H-17 and H-29 are those formed in a neutral to basic environments: smectite, kaolinite, illite/smectite, chlorite/smectite, scarce kaolinite/smectite, illite, biotite and chlorite, (Libreros R.E., 1991; Izquierdo M. G., 1993). There was no evidence of pyrophyllite, the only clay mineral formed at temperature in an acid environment.

From the minerals identified in the clay fraction, kaolinite is the only clay mineral whose presence can be related to the interaction of a felsic rock with an aqueous fluid of low pH, or just be product of hydrothermal alteration of a felsic rock at a temperature below 200 °C. Kaolinite is found at shallow depths where the rock is felsic discarding its formation as product of the interaction of the rock with an acid fluid.

Another evidence of the low water: rock ratio can be given by the low amount of chlorite at temperatures higher than 300 °C. Using X-ray diffraction as a tool, the composition of chlorites from the clay fraction of cuttings from well H-29 was estimated using a method proposed by Oinuma et al., 1972. The geothermometer based on the chlorites composition (Cathelineau and Nieva, 1985), state that the amount of Iron in the chemical composition of chlorites has a direct relation with temperature.

Table 1, gives the depth at which cuttings were selected to calculate composition of chlorites based on X-ray diffraction analysis of the clay fraction. It can be observed roughly that the amount of Iron has a tendency to increase with depth, except at 1470 and 1570 m. It has been seen at the top limit of the vapor dominant reservoir depth, the temperature decreases slightly. From 1670 m Iron increases again. It is worth to mention that the relative proportion of chlorites in the clay fraction is low even the temperature is high (above 300 °C).

Of course this can be considered as a semi quantitative approach, however it is a good approximation to sustain the existence of low water: rock ratio at depth.

3.5 Argillic alteration

Acidity in geothermal fluids originated by acid-sulfate water, indicates an oxidizing medium and conditions of very low pH. The occurrence of sulfuric acid in hydrothermal systems contributes to the acidity of the geothermal fluids provoking notably the alteration of the superficial rocks (advanced argillic alteration).

The analysis by X-ray diffraction of superficial samples from distinct zones of the geothermal field indicates the main crystalline components that correspond to the advanced argillic alteration such as: Alunite, kaolinite, gypsum, small amounts of jarosite, alunogen, and scarcely potash alum.

Table 1

WELL H-29

Depth (m)	Chlorite composition
310	$(Mg_{2.3} Fe_{2.7} Al) (Si_3 Al)O_{10} (OH)_8$
390	$(Mg_{4.15} Fe_{0.85} Al) (Si_3 Al)O_{10} (OH)_8$
470	$(Mg_{2.15} Fe_{2.85} Al) (Si_3 Al)O_{10} (OH)_8$
510	$(Mg_{2.05} Fe_{2.95} Al) (Si_3 Al)O_{10} (OH)_8$
550	$(Mg_{1.2} Fe_{3.8} Al) (Si_3 Al)O_{10} (OH)_8$
590	$(Mg_{1.15} Fe_{3.05} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
650	$(Mg_{1.4} Fe_{2.8} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
690	$(Mg_{0.5} Fe_{3.7} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
890	$(Mg_{1.1} Fe_{3.1} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
930	$(Mg_{1.7} Fe_{2.8} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
970	$(Mg_{2.16} Fe_{3.1} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
1030	$(Mg_{1.25} Fe_{2.9} Al_{1.85}) (Si_{2.15} Al_{1.85})O_{10} (OH)_8$
1070	$(Mg_{2.6} Fe_{2.8} Al_{0.6}) (Si_{3.4} Al_{0.6})O_{10} (OH)_8$
1110	$(Mg_{1.45} Fe_{2.7} Al_{1.85}) (Si_{2.15} Al_{1.85})O_{10} (OH)_8$
1190	$(Mg_2 Fe_3 Al) (Si_3 Al)O_{10} (OH)_8$
1470	$(Mg_{1.55} Fe_{3.45} Al) (Si_3 Al)O_{10} (OH)_8$
1590	$(Mg_{2.7} Fe_{1.45} Al_{1.85}) (Si_{2.15} Al_{1.85})O_{10} (OH)_8$
1670	$(Mg_3 Fe_{1.2} Al_{1.8}) (Si_{2.2} Al_{1.8})O_{10} (OH)_8$
1790	$(Mg_{2.2} Fe_{2.8} Al) (Si_3 Al)O_{10} (OH)_8$
1850	$(Mg_{1.15} Fe_3 Al_{1.85}) (Si_{2.15} Al_{1.85})O_{10} (OH)_8$

Argillic alteration extends on a large fringe from north to south; wells H-35, H-37, H- 33, H-29, H4, H-10, H-7 are closed to de zone of argillic alteration. H4 is a remarkable well, before production started, it was out of control because of his very high pressure and strong emission of H_2S was shut down and abandoned with his corroded casing. It is quite probable that due to the high H_2S content and the evidence of argillic alteration the casing corrosion was promoted by H_2SO_4. CFE cuttings showed high degree of alteration and minerals from high temperatures assemblages; but at depth no evidence of minerals formed in acidic environments was found.

3.6 Fluid inclusions

Fluid inclusion studies in samples from wells of LHGF has been a difficult task; since for most wells cuttings are of very small size and the amount of transparent secondary minerals, such as quartz and calcite, is reduced and the size of fluid inclusions is very small. However, samples from different wells have been studied. The salinity of trapped fluids was estimated from ice melting temperatures. All samples showed the presence of a low salinity fluid (even the deepest samples). Homogenization temperature increases progressively from the shallow levels to depth. In most of the well samples close to the vitreous tuff show a decrease in temperature in some tenths. Some time ago this fact and the occurrence of certain minerals was interpreted as cooling of the system. We believe that this decrease in temperature may be due to the presence of gases in the fluid and the presence and amount of certain minerals is due to the low water: rock ratio even the temperature is high at depth. This has been shown in deep small calcite fragments, which showed the presence of non aqueous fluid inclusions. From their behavior on heating, after cooling at –150°C, it is assumed the presence of CO_2, methane and hydrocarbons. The presence of gases in the fluid inclusions an indication of mobility of deep fluids favored by secondary permeability of the basement.

Most fluid inclusions are of the water-vapor type with varying proportions of each one of the phases; at depth single vapor phase inclusions were observed, especially in well H29 at 2150 – 2200 m depth in well H29. These

samples coming from the undistroyed system show the presence of vapor as a single phase, but not by a boiling process. Additional work has to be done on this topic to support or discard this assumption.

CONCLUSION

In previous work by Arellano et al., 2003 the existence and limits of two reservoirs in LHGF have been demonstrated, and good match with the distribution of hydrothermal minerals in several geological sections of the field was noticed as for calcite and epidote.

In the low liquid saturation reservoir a process of ascending and condensation of fluids had contributed to the alteration of the barrier made of vitreous tuff and not to the formation of acid fluids. If acid fluids were formed in this reservoir, minerals typical of acid environments would be found mainly in the vitreous tuff; as well as an anomalous high chloride concentration in production fluids.

Fluid inclusions at depth showed very low salinity brine instead of concentrate brine as the model of HCl formation from a deep boiling brine rich in NaCl, or by reaction between halite, formed from that brine and silicates. So, these mechanisms of HCl formation in LHGF are discarded.

Acidity in LHGF is produced by H_2SO_4 and HCl, the first one should be formed, as already known, by oxidation of H_2S or by reaction of SO_2 and H_2O upon decreasing temperature.

In the unperturbed system, HCl should be formed from volatile components from the magma trapped in the vapor reservoir. When some wells from the Central Colapse were drilled reaching this reservoir, volatile components move upwards mixing with the hot aqueous phase forming aqueous HCl. This aqueous form of HCl is aggressive and will corrode tube pipes of the production wells.

The mechanism considering condensation of the low liquid saturation phase containing HCl in gaseous form is less probable to occur. Where should the vapor containing HCl condensate? If it would be in the barrier formed by the vitreous tuff, then acid forming minerals would be found. Maybe part of the vapor phase containing volatiles condenses in the pipes walls provoking corrosion; but most of the acid fluids come from the reaction in the liquid reservoir, and this only happened when drilling of wells located in the Colapso Central area stared.

For drilling new wells in the Colapso Central area, where underneath is the low liquid saturation reservoir, a good indication of approaching the low liquid saturation reservoir are single vapor phase fluid inclusions.

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