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FLUID ACIDITY AND HYDROTHERMAL ALTERATION AT THE LOS HUMEROS GEOTHERMAL RESERVOIR PUEBLA, MEXICO.

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ABSTRACT

The presence of HCl in fluids in the Los Humeros geothermal reservoir has resulted in accelerated corrosion of wells in the area known as Colapso Central and along the east direction of the field side. The main objective of this work is to recognize the origin of the fluid acidity, on the basis of the evaluation of available chemical and mineralogical information.

Considering the expected alteration due to HCl in other geothermal systems, no relation to the available information from Los Humeros was found. It is possible that acidity in the geothermal fluids is recent, and generated when the deep low liquid saturation reservoir was reached by drilling. On the other hand, the occurrence of H_2SO_4 is evident due to the advanced argillic alteration of surface and subsurface rocks in some areas of the field. From the paper of D'Amore et al., 1990 we made the hypothesis that in the natural state in Los Humeros a high salinity brine could exist bellow the two known reservoirs. This high salinity brine favored the formation of the HCl gas; which moved to the low liquid saturation zone when exploitation began. HCl gas was carried by the vapor phase toward the upper reservoir (high liquid saturation) forming aqueous HCl.

1. INTRODUCTION

The most important species in a geothermal system that provide acidity to a hydrothermal fluid are the volatile components that emanate from the magma such as HCl, SO_2, H_2S and CO_2. Their interaction with geothermal fluids and the physico-chemical changes that occur in the reservoir can generate a fluid of acid nature; which is modified when it moves upwards to the surface. An acidic aqueous solution tends to be neutralized or become alkaline due to its interaction, over a long time, with the rocks. However, the chemical composition of the fluids collected at 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 producing the obvious sign of an acidic fluid at the surface (low pH).

The main acid species commonly found in geothermal environments are HCl and H_2SO_4. To explain the origin of the HCl several approaches are known. Among them are: formation from acid fluids of magmatic origin; formation of NaCl from a deep boiling brine or by reactions between halite 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.

1.1 Origin of HCl and H_2SO_4 in hydrothermal systems

Origin of HCl. The occurrence of hydrochloric acid in geothermal systems and its destructive effects in pipe lines has been the focus of experimental and theoretical studies on the origin and transportation of HCl in the geothermal vapor (Truesdell et al., 1989; D'Amore et al., 1990). It has been suggested that the main factors in HCl formation are pH, temperature and chloride concentration in the fluid. The mechanism of transport of HCl in superheated vapor introduced by Haizlip and coworkers (D'Amore et al., 1990) has been adequately described. On the origin of the HCl two considerations proposed by D' Amore et al., (1990) are known: One of them is its formation from a neutral or acid boiling brine at high temperature, the other through reactions in vapor with halite and silicates producing HCl gas. Experimental data on vapor in equilibrium with the brine or with halite, show that the HCl concentrations increase as a function of temperature. In practice it has been observed that this relation is attained in high temperature geothermal reservoirs. D' Amore et al., (1990) and Truesdell et al., (1989) have suggested that the origin of vapor containing HCl is the product of high temperature (> 325 °C) reactions between NaCl solid and the minerals in the rocks. The mechanism proposed by these authors postulates that in the natural state of a geothermal reservoir, a deep boiling brine generates ascending vapor required for the transportation of heat and gases but not solutes (Cl) to the top of the vapor reservoir. Furthermore they propose that if this deep liquid exists, it should be a concentrated brine due to the accumulation and concentration of solutes.

Origin of H_2SO_4. Acid-sulfate alteration is a special case of advanced argillic alteration in which it is common to find the association: alunite + kaolinite + quartz + pyrite. Invariably geothermal vapor is accompanied by diverse proportions of CO_2 and H_2S; the latter is easily oxidized to H_2SO_4 by oxygen brought to the subsurface by meteoric water, producing an acid fluid that immediately attacks the surrounding rocks (Browne, 1991). It has been proposed (Rye et al., 1991) that the formation of H_2SO_4 in magmatic hydrothermal systems is carried out by the reaction between SO_2 and H_2O at decreasing temperatures. This it is the reason why the argillic alteration is evident toward the surface of hydrothermal systems. The volcanic host rocks are altered, producing a mineralogical assemblage which includes alunite (or natroalunite), hematite, jarosite, kaolinite and pyrite.

According to Reyes (1990), the mineralogical evidence of ascending acid fluids of probable magmatic origin is the formation of minerals such as: Topaz, lazulite, andalusite and zunyite; sometimes found associated with diaspore, pyrophyllite, quartz, alunite, anhydrite, pyrite and occasionally native sulfur. On the other hand, the acid alteration caused by descending acid waters heated by vapor promotes the formation of: kaolinite, dickite, pyrophyllite, pyrophyllite + illite, diaspore, quartz, opal, cristobalite, trydimite, natroalunite, alunite, anhydrite, pyrite and native sulfur.

2. STUDY AREA. THE LOS HUMEROS GEOTHERMAL FIELD

At present the Los Humeros geothermal field is the third geothermal energy resource under exploitation within the Republic of Mexico. It is located in the eastern portion of the Mexican Volcanic Belt (19° 40' latitude N, 97° 25' longitude W), between Puebla and Veracruz states (Figure 1).

In 1990 the commercial exploitation of the resource began with the installation of the first 5 MWe unit. To date 40 wells have been drilled, of which 20 are producers (Figure 2) and seven 5 MWe plants have been installed (Quijano and Torres, 1995).

2.1 Geological setting

The local basement is formed by a Paleozoic metamorphic complex, chlorite-muscovite shales, a Mezozoic folded sedimentary sequence, a lower Tertiary syenitic and granodioritic intrusions and Pliocenic andesites. The two productive reservoirs are located in the upper and lower 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. Table 1.1 summarizes the subsurface geology.

3. RESULTS AND DISCUSSION

3.1 Hydrothermal mineralogy

In hydrothermal systems two main types of hydrothermal alteration have been recognized: One: neutral alteration (neutral to basic pH) formed by sodium chloride fluids of high temperature and with almost neutral pH; characterized by: clay minerals, pyrite, calcite, quartz, zeolites, epidote, biotite etc. The other: 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.

Considering that the hydrothermal minerals are indicative of the temperature, permeability, pressure, fluid composition and initial composition of the host rocks; an evaluation of the available mineralogical data was carried out in order to identify evidences of the interaction of acid fluids with the rocks of the Los Humeros.

The hydrothermal alteration of the subsurface rocks of the Los Humeros geothermal field can be recognized as neutral to basic pH alteration and according to Browne, (1991) can be defined as high rank and low intensity.

3.1.1 Calc-silicates and carbonates.

The low intensity of alteration in cores and cuttings is an indication of a low water-rock ratio in the hydrothermal system. The highest rank alteration is found in augite andesites. 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, amphibole, garnet, diopside and wollastonite have been recognized. In agreement with Reyes (1990), the pH conditions in which these minerals formed are considered to be as for neutral to alkaline conditions. The distribution of the epidote, amphibole, diopside, garnet and biotite in three cross sections of the field; indicate zones of high temperature. In wells drilled in the Colapso Central the distribution of these minerals indicates ascent of hotter fluids than in surrounded zones.

From the petrographic file, provided by the Comisión Federal de Electricidad, the percentage of some of the alteration minerals was taken; with calcite and epidote being the most indicative. Their distribution was represented in several geological sections (taken from Cedillo, 1997). Figures 3a and 3b show the distribution of calcite and epidote in wells located in the geological section L3 (H-21, H-31, H-15, H-30, H-16, H-33, H-29, H-4, H-10, H-26, and H-6). In Figure 3a it is observed that calcite is distributed from shallow depths to the augite andesite. At greater depth, calcite is scarce in wells that produce mixture of fluids and is absent in wells producing vapor. The absence of calcite at depth is the result of the low water-rock ratio that exists in the low liquid saturation zone (vapor rich). This same behavior is observed in Figure 3b where the distribution of epidote in the section L3 is presented. The biggest proportion of epidote is located in the upper andesite and extends to the lower andesite in wells producing a mixture of fluids. It is absent at depth in wells where vapor is the dominant phase.

3.1.2 Phyllosilicates

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 include: smectite, kaolinite, illite/smectite, chlorite/smectite, scarce kaolinite/smectite, illite, biotite and chlorite (Libreros R.E., 1991; Izquierdo M. G., 1993). No pyrophyillite was found. As is well known kaolinite may be formed either by alteration of a felsic rock at a temperature below 200°C or by interacion with an aqueous fluid of low pH. In Los Humeros kaolinite is found at shallow depths where the rock is felsic at temperatures lower than 200°C, discarding its formation as product of the interaction of the rock with an acid fluid.

3.1.3 Advanced Argillic Alteration

Acidity in geothermal fluids originating from 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, obtained from distinct zones of the field, shows the main crystalline specie of advanced argillic alteration: Alunite, kaolinite, gypsum, small amounts of jarosite, alunogen and scarcely potassium alum.

3.1.4 Fluid inclusion microthermometry

Microthermometric fluid inclusion data for some wells from Los Humeros have been evaluated. The microthermometric analysis was carried out in small transparent fragments of minerals such as quartz and calcite.

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). 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. Homogenization temperatures showed increase progressively from the shallowest levels to the deepest levels.

Deep small calcite fragments showed the presence of vapor rich fluid inclusions. From their behavior on heating, after cooling at –150°C, it is assumed the presence of CO_2, methane and hydrocarbons. No high salinity fluid inclusions were observed; instead the occurrence at depth of vapor rich inclusions may be an indication of mobility of deeper fluids favored by the permeability in the limestone.

3.1.5 Scale analysis

Not very much information could be obtained from scales since only a few have been recovered. Chemical and mineralogical composition showed the presence of minerals such as anhydrite, pyrite, microcrystalline quartz and opaque minerals (mostly sulfides). This mineral assemblage shows interaction with acid sulfate fluids.

3.1.6 Chemical composition of geothermal fluids

The Los Humeros geothermal system has been considered like a two phase system with low liquid saturation. The fluids have characteristics of condensed vapor. In general they have been classified as the sodium chloride type and in some cases as bicarbonate type (Tovar and López, 1998) and can be considered as a fluid of very low salinity.

As it was mentioned for some geothermal fields, excess of chloride in the liquid phase maybe related to the presence of HCl. From the CFE analytical files for Los Humeros, chemical composition of fluids from some wells shows an excess of chloride; which has changed with time. Since chemical composition has changed with time the apparent chloride excess is not a sign of acidity. It is worth mentioning that well H-16 has shown acidity but not excess chloride in its chemical composition.

4. CONCLUSIONS

Since there is no evidence of acidity in the evaluation of the chemical and mineralogical information for the Los Humeros geothermal field; we assume that the origin of acid fluids in the wells discharge is recent and that the formation of the HCl may be in a deep zone underlying the vapor dominated reservoir.

Results from the study of rocks and minerals recovered before the exploitation of the reservoir do not show the presence of hydrothermal minerals formed by interaction with low pH fluids like: kaolinite, dickite, pyrophyllite, diaspore, andalusite, zunyite, tourmaline, lazulite etc. Instead, typical assemblages of neutral or basic pH environments are observed: clay minerals, pyrite, calcite, epidote, quartz, zeolites, biotite etc.

The proportion and distribution of alteration minerals (in this case the most significative are calcite and epidote) in several geological cross sections of the reservoir show that there is a zone where the highest intensity of altered rocks occur and corresponds to the augite andesite. With increasing depth the intensity of the hydrothermal alteration of rocks decreases notably, indicating possibly low water : rock ratio.

In wells located in the Colapso Central, the absence of hydrothermal calcite in deep levels (except for calcite in limestones) is an indication of low water : rock ratio; the contrary occurs in upper levels where is observed the deposition of calcite. In some wells where two phase fluids occur, calcite is observed in low proportion at depth. It was thought that the absence of calcite in deep zones of the reservoir was due to fluid acidity. In a recent study (Arellano et al., 1998) two reservoirs have been recognized, being the deepest a low liquid saturation reservoir with temperatures above 300°C.

This same observation applies for epidote whose distribution is an indication of the water-rock interaction mainly in the upper andesite. At depth the intensity of alteration is lowered although very high temperatures have been registered

The presence of characteristic minerals of neutral alteration and the absence of typical minerals of acid alteration suggest that the acidity in the geothermal fluids was generated in a stage subsequent to the deposition of minerals formed in the rocks of the reservoir. It is probable that the alteration mineralogy does not reflect equilibrium with the present fluid and that the fluid from which the alteration minerals have formed had physical and chemical characteristics distinct to the present one.

Considering the occurrence of two reservoirs (Arellano et al., 1998), the chemical composition of fluids collected at atmospheric conditions is a mixture of condensed vapor and liquid, which obviously is not representative of the fluid of either of the reservoirs and consequently will not show equilibrium with the alteration minerals of the rocks of the reservoir.

The only evidences of the presence of acid fluids in the surface discharge are: corrosion of pipe lines, superficial advanced argillic alteration and in some wells excess of chloride in the chemical composition of their fluids.

Recently, alunite, alunogen, kaolinite, gypsum, jarosite and potassium alum formed by the interaction of sulfate waters with superficial rocks were identified in samples from different sites of the field. The contribution of sulfuric acid to the acidity of fluids should be considered apart from the presence of HCl.

The melting temperatures from fluid inclusions observations show a low salinity fluid trapped at the moment of crystallization of secondary minerals. Fluid inclusions showing the presence of hydrocarbons and gases, constitute evidence of the presence of organic of matter trapped in the limestone. The gases trapped in fluid inclusions may indicate activity in the deep calcareous basement.

At present, it is not possible to establish with certainty the origin of the acid fluids in the reservoir. However, from all the above conclusions and according to D'Amore (personal communication, December 1998) the origin of the vapor that constitutes the deep low liquid saturation reservoir should be a fluid (possibly of high salinity) which favored the formation of the HCl gas. When the exploitation of the reservoir started, the HCl gas moved to the zone of vapor (deep low liquid saturation reservoir) and was transported in the vapor toward the upper reservoir (liquid dominated reservoir) forming aqueous HCl, turning aggressive to the well casing pipes.

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6. REFERENCES

Arellano V.M., García A., Barragán R. M., Izquierdo G., Aragón A., Nieva D., Portugal E. and Torres I., (1998). Desarrollo de un modelo básico actualizado del yacimiento geotérmico de Los Humeros, Pue. Report IIE/11/11459/101/F. Instituto de Investigaciones Eléctricas for Comisión Federal de Electricidad, Cuernavaca, Mor., 450 p.

Browne P. R. L, (1991). *Notas del curso Hydrothermal alteration and geothermal systems*. pp. 14-16.

Cedillo R. F., (1997). *Geología del subsuelo del campo geotérmico de Los Humeros, Pue*. Internal report HU/RE/03/97. Comisión Federal de Electricidad. Gerencia de Proyectos Geotermoélectricos. Residencia de Los Humeros, Puebla.

D'Amore F., Truesdell A. H. and Haizlip J. R., (1990). Production of HCl by mineral reactions in high-temperature geothermal systems. *Proc. Fifteen Workshop on Geoth. Res. Eng. Stanford University, Stanford, Ca. January*. pp. 23-25.

Izquierdo M. G., (1993). Difracción de rayos-X en la caracterización de especies arcillosas: un caso de aplicación en el pozo H29 del campo de Los Humeros, Pue. *Geof. Int*. Vol., No 2, pp. 21-329.

Libreros R. E. P., (1991). *Caracterización de filosilicatos en el campo geotérmico de los Humeros, Pue., por medio de difracción de rayos-X.* BSc.

Thesis. Escuela de Ciencias Químicas. Universidad Autónoma de Puebla.

Quijano J. L. and Torres M., (1995). The Los Humeros geothermal reservoir, a case of very high temperature system. *Proceedings of the World Geothermal Congress 1995*, Florence, Italy. Vol. 3, pp. 1569-1573.

Reyes A., (1990). Petrology of Philippine geothermal systems and the application of alteration mineralogy to their assessment. *J. of Volc. and Geoth. Res.* Vol. 43, pp. 279-309.

Rye O. R., Bethke M. P. and Wasserman M. D., (1991). The stable isotope geochemistry of acid-sulfate alteration and vein forming alunite. *Reporte del US Geological Survey*. Open file report 91.

Tovar A. R. and López O., (1998). *Comportamiento geoquímico e isotópico del fluido de los pozos del campo geotérmico de Los Humeros, Puebla, México*. Comisión Federal de Electricidad. Subdirección de Generación. Residencia Los Humeros. 16-20 de noviembre de 1998.

Truesdell A. H., Haizlip J. R., Armannsson H. and D'Amore F., (1989). Origin and transport of chloride in superheated geothermal steam. *Geothermics*. Vol. 18, No ½, pp. 295-304.

Viggiano G. J. C. and Robles C. J., (1988a). Mineralogía hidrotermal en el campo geotérmico de Los Humeros , Pue. I: Sus usos como indicadora de temperatura y del régimen hidrológico. *Geotermia. Rev. Mex. de Geoenergía* Vol. 4, No 1. pp. 15- 28.

Table 1. Geology of the Los Humeros system, (Cedillo, 1997).

Lithologic Unit	**Description**	**Permeability**	**Hydrogeology**
1	Pumice, Basalts and Andesites	High	Cold and hot superficial aquifers
2	Lithic Tuffs	Medium	Possible aquifer
3	Vitreous and Lithic Ignimbrites	Low to None	Aquiclude
4	Intercalation of Andesites and Ignimbrites	Low	Aquiclude
5	Augite Andesites	Medium	Shallower geothermal reservoir
6	Humeros Vitreous Tuff	Low	Aquitard
7	Hornblende Andesite	Medium	Deeper geothermal reservoir
8	Basalts	Medium	Deeper geothermal reservoir
9	Limestone, Metamorphic Limestone and Intrusives	Low	Aquitard

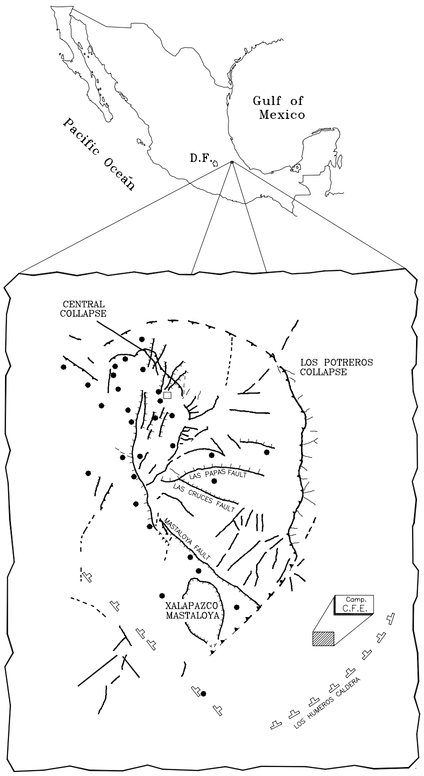

Figure 1.- Location of the Los Humeros geothermal field.

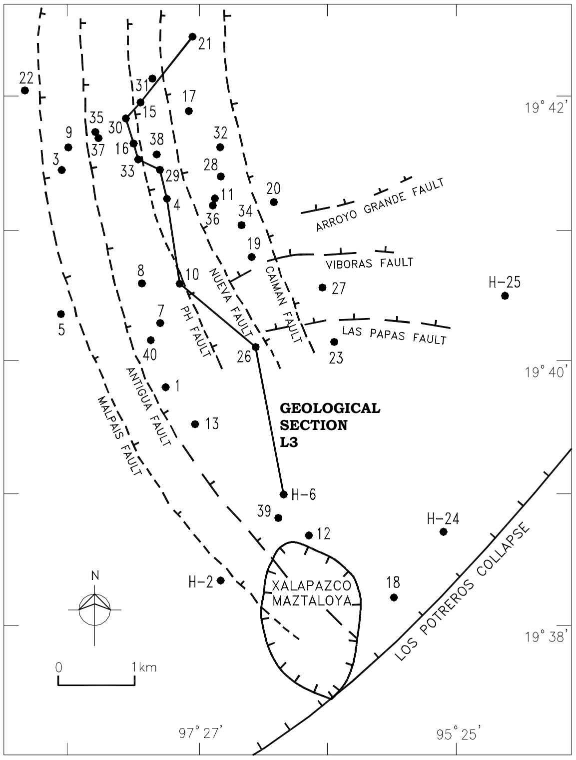

Figure 2.- Well location in the Los Humeros geothermal field.

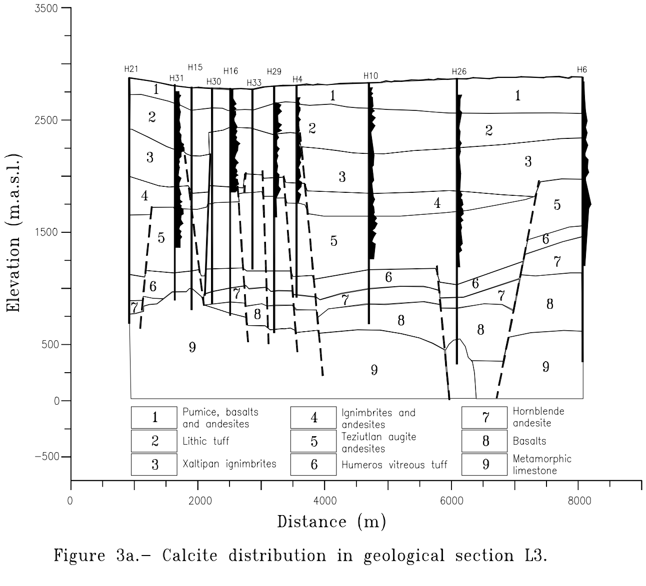

Figure 3a.- Calcite distribution in geological section L3.

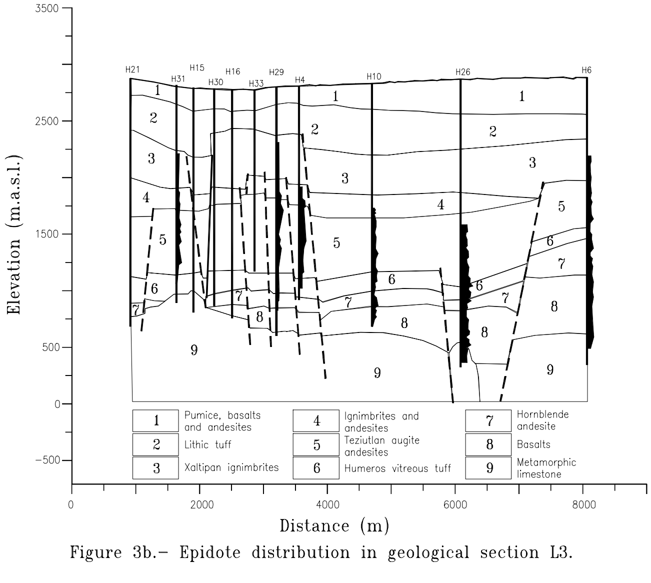

Figure 3b.- Epidote distribution in geological section L3.