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Geochemical Modeling of Acid Fluids in Los Humeros Geothermal Field, Mexico

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ABSTRACT

Los Humeros, located in the East of the Mexican central highland, is the third most important geothermal field in the country. In the past decade its electricity production has been affected by the occurrence of acid fluids. In this work, we present different geochemical models to shed some light upon the question of the origin of those fluids.

Geologically, Los Humeros is emplaced within a Quaternary caldera, 24 km in diameter, which is built of acidic to intermediary lavas, tuffs and volcanic ashes, upon a sedimentary-metamorphic basement with subordinated intrusive rocks. The geothermal system apparently consists of two reservoirs. The upper reservoir is located at depths between 1025 m and 1600 m a. s. l., it is fluid-dominated and it shows measured temperatures up to 300°C. The lower reservoir (between 850 m and 100 m a. s. l.) can reach temperatures up to 400°C and is steam-dominated.

Geochemical models were calculated using the software package SOLVEQ/CHILLER, due to its applicability for studying multiphase systems as well as boiling and mixing processes. Setting up a useful concept of acid development by means of the existing data was problematic. Our main difficulties were incomplete chemical analyses, the presence of fluids with enthalpy excess, as well as the lack of geological and geochemical data to distinct the lower from the upper aquifer. Principally, our models are based on the more complete data set existing for well H-1.

The first model explores the possibility of the acid fluids arriving to the reservoirs from a yet unknown deposit, probably a deeper magma chamber underneath the reservoirs. Our calculations show that a contribution of 0.009 moles of HCl and 0.005 moles of HF would be enough to reach pH values as low as 3.5. Alternatively, a second model was calculated in which the geothermal fluid from Los Humeros has reacted with the corresponding aquifer rocks of the lower reservoir, in order to explore whether mineral reactions are responsible for the presence of acid fluids. According to our computations this hypothesis could hardly be responsible for the low pH values observed in the field.

1. INTRODUCTION

The installed electric capacity of all geothermal fields in Mexico has reached 755MWe (620MWe at Cerro Prieto, 93MWe at Los Azufres and 42MWe at Los Humeros; Quijano-León and Gutiérrez-Negrín, 2000). Geothermal electricity generation represents about 3.2% of the total country electricity production. In the late 1960s the exploration work in Los Humeros began with geological, geophysical and geochemical investigations, followed by the first deep drilling in 1982. To date over 40 wells have been drilled. In 1990 the first of altogether six power-plants was installed, each producing 7MW.

Although most geothermal fluids in the field have near-neutral pH, acid fluids are responsible for accelerated corrosion of wells and other installation at Los Humeros. Former studies showed that the fluid conveyed by the well is generally not in thermo-chemical equilibrium with those minerals found during drilling process (e.g. Torres-Alvarado and Maldonado-Aranda, 2001). This is probably, at least partially, due to the fact that most wells extend through two different geothermal aquifers, generating a fluid mixture which is not able to come into balance with the wall rocks. Furthermore, there is the problem of excess enthalpy in most of the deeper wells, complicating an estimation of the produced water/steam mixture.

The objective of this paper is to verify whether the acid fluids in Los Humeros come from a deep magmatic source or are produced through fluid-mineral reactions. We use the fluid and gas data (Arellano et al., 2003 and Tello et al., 2000, Table 1) obtained from well H-1 for geochemical modelling following two main hypothesis. We presume first a deep magmatic source, contributing HCl and HF to the upper aquifer. The second model is based on the hypothesis that HCl may be produced from mineral (halite + silicate +/- calcite) and fluid reactions at high temperature.

2. GEOLOGICAL AND HYDROGEOCHEMICAL SETTING

Los Humeros geothermal field is situated in the eastern part of the Central-Mexican Volcanic Belt (CMVB), approximately 200 km East of México City (Figure 1).

The local geology and geochemistry has been extensively described, among others, by Ferriz and Mahood (1984) and Verma (2000). Four principal lithological units have been recognized using data from the exploration wells. The local basement is formed by a Mezozoic, folded sedimentary sequence intruded by Tertiary, granodioritic to syenitic intrusions, which caused different degrees of metamorphism (hornfels facies). Two Mio - Pliocenic, andesitic lava flows build up the main aquifer for the geothermal reservoir. Covering them is a Pleistocenic sequence of lithic and vitreous ignimbrites. Finally, andesitic lava flows, intercalated with some basaltic flows and pyroclastic rocks form the last volcanic materials in the area. The geothermal system is located inside a caldera with a complex structure of ring-shaped fractures and faults, avoiding any hydrological connection with the surrounding geology. The subsurface geology inside the caldera consists of a sequence of blocks arranged as grabens and horsts. Figure 2 shows a cross-section of the area close to well H-1 including petrology, stratigraphy and structure of the geothermal field. The Caldera system is less than 500,000 years old, while the last eruption occurred 20,000 years ago producing an olivine basalt lava flow.

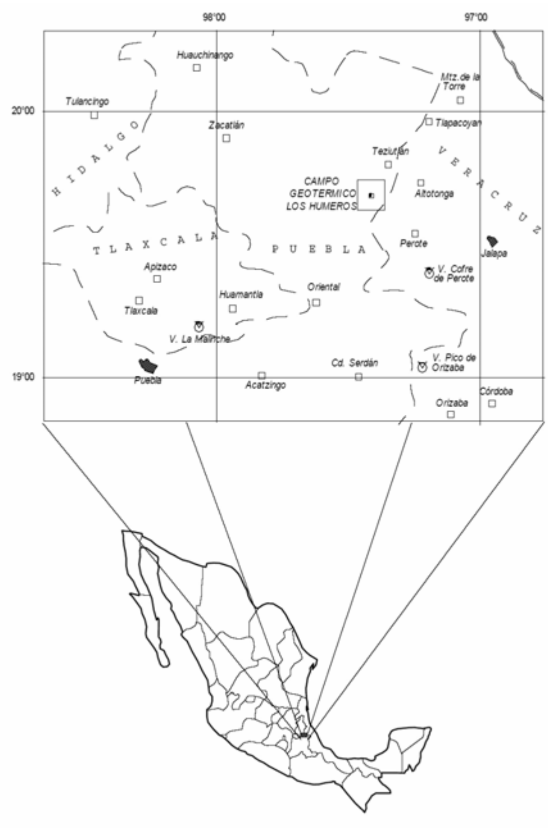

Figure 1: The location of Los Humeros Geothermal Field.

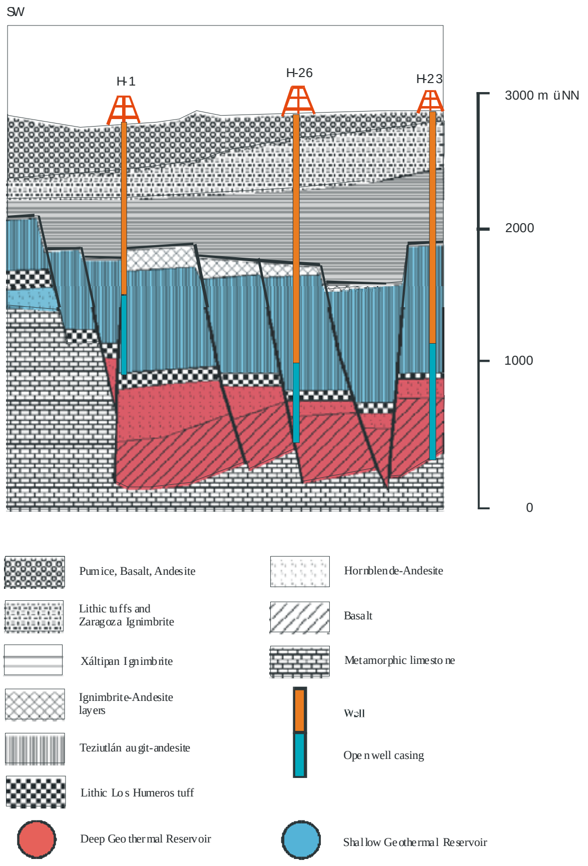

Figure 2: Geological cross-section. The two geothermal reservoirs are represented in color (Arellano et al., 2003)

According to Tello (1992) geothermal fluids are predominantly sodium-chloride waters, pH values 7-8, and high CO_2 concentrations. Shallow wells discharge a mixture of chloride and bicarbonate waters from a zone where deep geothermal fluid, steam heated waters and cold meteoric waters are mixed. Most geothermal fluids are very diluted (TDS around 800 to 1200 mg/l) and although Los Humeros is considered to be a two phase reservoir (Arellano et al., 2003), although the liquid saturation is in some wells remarkably low.

3. METHODOLOGY

The geochemical models were calculated using the programs SOLVEQ/CHILLER (Spycher and Reed, 1990). This software package was created to calculate multicomponent homogeneous and heterogeneous chemical equilibriums among solids, gases and an aqueous phase. They apply a Newton-Raphson numerical method to solve a system of mass-balance and mass-action equations. SOLVEQ computes the activities of all aqueous species and the saturation indices of solids and gases for a given temperature and composition of a homogeneous fluid. CHILLER, on the other hand, is able to compute the loss or gain of heat, pressure, gases, minerals or the mixing between two different kinds of water for temperatures up to 350°C. All these capabilities make both programs ideal for modeling the origin of acids in Los Humeros geothermal field.

Geochemical modeling was based upon geothermal fluid coming up from well H-1. Well H-1 is located in the upper aquifer, its fluids do not present an excess enthalpy and they show one of the smallest steam fractions (high liquid saturation) in the field. Therefore, the fluid produced in well H-1 is consequently usable for thermo-chemical calculations. Chemical analyses for the H-1 fluid have been published by Arellano et al., (2003) and Tello et al., (2000) (the analysis themselves were carried out in 1987 and 1994/ 1996 , respectively). It is important to note that the analyses of the second authors included a determination of HCl and HF (Table 1). We decided to use the data of Arellano et al., (2003) for modeling because this fluid falls closer to the full equilibrium line on the Giggenbach (1988) triangle-diagram than the fluid analyzed by Tello et al. (2000; Figure 3).

Total discharge compositions were calculated applying the methodology proposed by Henley et al. (1984) using the software section integrated into SOLVEQ for this purpose. Since no Fe^{++} or Al^{+++} had been analyzed, we assumed equilibrium with pyrite and an Al^{+++} concentration of 0.1mg/l. This later amount should be considered as a minimum value for Los Humeros geothermal fluids.

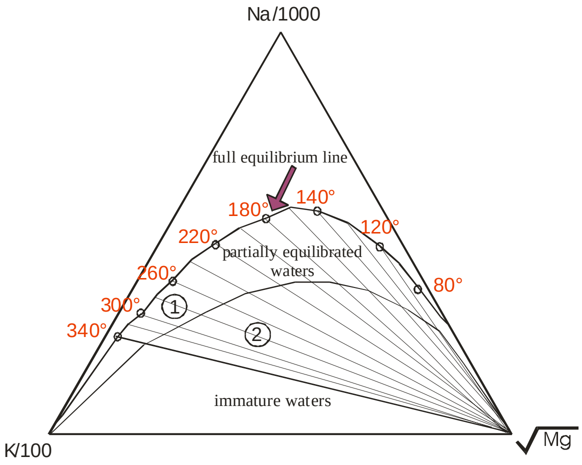

Figure 3: Na–K–Mg relative compositions of geothermal fluid samples from Los Humeros well H-1. Circle 1 shows the fluid composition data from Arellano et al., (2003), circle 2 the data from Tello et al., (2000).

4. MODEL RESULTS

4.1. Model 1

Model 1 assumes an unknown source (magma chamber?) for acids to the geothermal field. To perform this calculation, heating of the H-1 total discharge fluid was first simulated. Beginning at 50°C (analysis temperature) fluid temperature was rised up to 250°C, which is the reservoir temperature, estimated from the Na–K–Mg geothermometer (Giggenbach, 1988).

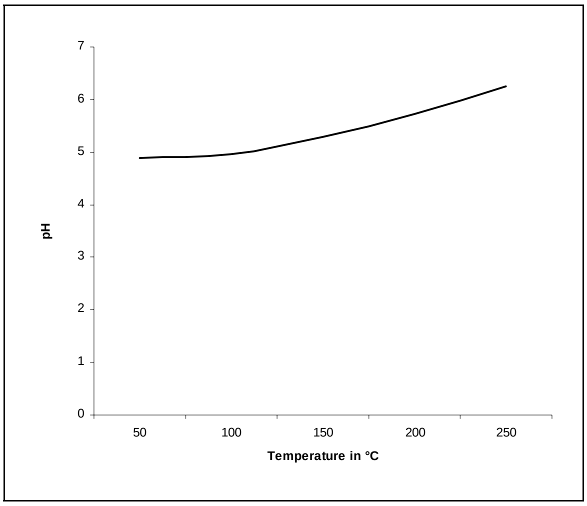

Figure 4: Modeled pH values of combined water and gas discharged (reservoir conditions) from well H-1 as a function of temperature.

Because of the stronger association of ion complexes at elevated temperatures (Henley et al., 1984) the pH rose from 4,8 at 50°C to 6,2 at 250°C (Figure 4). With increasing temperature most of the at first stable minerals started to dissolve (e.g. muscovite, illit, paragonite, kaolinite, feldspar, alunit, diaspor, several zeolithes, andalusite, staurolite) and had all disappeared above 250°C, apart from quartz which remained still stable.

To simulate the introduction of acid fluids from an unknown source, titration calculations were performed using the HCl and HF data from Tello et al., (2000) for *all* 24 well discharges in Los Humeros. The average values are 160 ppm HCl and 55 ppm HF. Considering a HCl:HF–ratio of about 3:1, it was then possible to titrate a conclusive amount of acids into the modeled fluid from the first step. A pH value of 3.5 was obtained after titrating 320 ppm HCl and 110 ppm HF (Figure 5), modeling a fluid with the capability to cause damages to the well casing. The total amount of Cl^- was still realistic after these calculations, considering the concentration analyzed by Tello et al. (2000) for well H-1. Excess Cl^- may separate into the vapor phase during boiling.

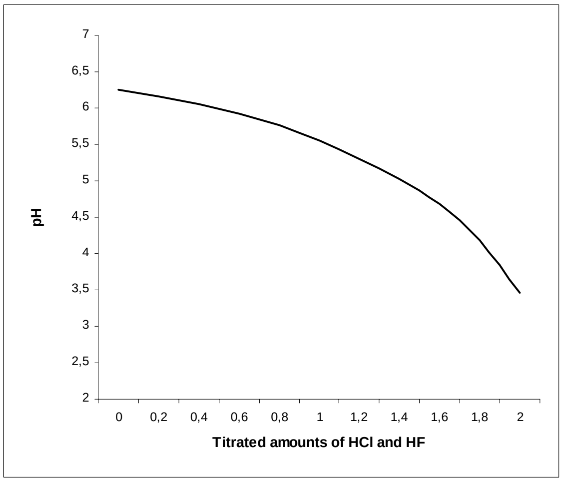

Figure 5: Modeled fluid pH as a function of rising amount of titrated acids at 250°C. Total concentrations of titrated acids were 320 ppm HCl and 110 ppm HF.

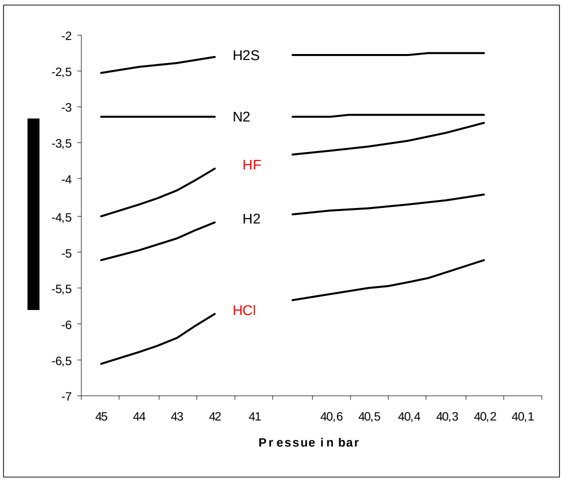

Figure 6: Gas production of the ascending geothermal fluid. The pressure was minimized so far that about 30% vapor was formed which is the corresponding vapor fraction of the total discharge of well H-1.

The last model step was to calculate the ascend of this acid fluid to the surface including boiling and separation of acids into the vapor phase to verify the analyzed acid amount of Tello et al. (2000). The produced amount of acids were 0,2 ppm HCl and 12 ppm HF. Since the drop in pressure happens in just one step at the well head, this last model step may not be too realistic. However, a conclusive amount of HF is produced. It is important to note that CHILLER tries to reach equilibrium at each calculation step. Reducing the pressure in too big steps, as we modeled, causes though convergence problems. The only way to solve this is to reduce the pressure in small steps, which however, do not produce the expected amount of HCl.

4.2. Model 2

Since the deeper reservoir is very hot (up to 400°C; Arellano et al., 2003), it is vapor dominated (low liquid fraction). On its way to the surface, mixing between this geothermal vapor and shallower water may occur, producing a chemically different geothermal fluid. Based on this idea, the objective of the second modeling approach was to calculate an "original" deep-reservoir fluid, which might be produced through chemical reactions between the reservoir rocks and geothermal fluids. This fluid should present remarkable concentrations of HCl, or as a second possibility, it should be capable to allow halite precipitation through evaporation, which in turn might react with silicates to produce HCl.

As a first step, we generated a fluid in equilibrium with the chemical compositions of the surrounding geology (andesite, rhyolite, basalt and limestone), under high-pressure (200 bar), and high-temperature conditions (350°C). After reacting 110 g of rock forming minerals (including 10 g of NaCl) into 1 kg of water, chemical equilibrium is reached in the system. The precipitation of minerals like feldspars, garnet, andradite, or antigorite is at this point observed. No halite formation was calculated.

The next step was to calculate the evaporation of the half of H_2O through pressure drop. After 50% of water in the system had been evaporated, gases and minerals showed in Table 2 were calculated. Table 2 shows that the computed amounts of acids are unrealistic low. This model can not explain the origin of the HCl or HF in Los Humeros. It is important to observe that no halite precipitated from the calculated solution, even after forced NaCl-supersaturation (addition of 20 g NaCl into the system and further evaporation).

5. CONCLUSIONS

According to Truesdell (1991) and D´Amore et al. (1990) there are two main theories about the origin of acids in the geothermal field of Los Humeros. The first one says that a yet unknown source (e.g. a magma chamber) underneath the geothermal system emits acids like HCl and HF into the aquifers. The second idea is that acids are produced through mineral reaction of halite + silicates + vapor under hot conditions.

Our models suggest that the first theory seems to be more likely, as an explanation for the origin of acids in Los Humeros. The presence of small amounts of HCl and HF, similar to those concentrations found in wire box compositions in the field, were enough to produce an acid geothermal fluid with pH values as low as 3.5.

A second model approach which considers the evaporation of fluid previously equilibrated with the host rocks, does not produce relevant amounts of HCl or HF. This modeled fluid may not allow halite precipitation, and therefore, a further reaction with silicates to produce HCl may not be probable.

Halite could only be present as part of the host rock but not being produced through chemical reactions in the geothermal system.

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Table 1: Water and gas analyses for geothermal fields from well H-1. Pc is the wellhead pressure, Ts the separation temperature, Cg is the gases total content in mmol per mol vapour.

Water anlysis	Date	Enthalpy kj/kg	pH	Na	K	Ca	Mg	Cl	SO4	HCO3	B	SiO2	Li	As
Tello et al., (2000)	04.01.1996	1179	8,3	267	45	264	0,119	90,2	233	162	218	1005	0,47	2,79
Arellano et al., (2003)	21.10.1987	1280,5	8	269	43,8	1,2	0,012	120	114	361	214	800	0,9	3,9
Gas analysis	Date	Pc Kg/cm2	Ts °C	Cg	CO2	H2S	NH3	H2	N2	CH4	HCl ppm	HF ppm	-	-
Tello et al., (2000)	14.04.1994	9,2	176	17,7	982,1	10,9	2	1,16	2,33	1,56	416,3	57,1	-	-
Arellano et al., (2003)	21.10.1987	14,5	125	8,72	963	29,5	3,7	1,25	2,32	0,6	-	-	-	-

Table 2: Partial chemical composition after the geothermal fluid equilibrated with the deeper reservoir host rocks was evaporated. Minerals saturated under these conditions are also shown. See text for details.

GAS OR MIN	MOLES	LOG MOLES	GRAMS	LOG GRAMS	WT PERCENT	VOL(CM3)
H2O gas	.3063E+02	1.486	.5517E+03	2.742	.9840E+02	.5327E+04
CO2 gas	.1973E+00	-.705	.8682E+01	.939	.1548E+01	.1384E+03
CH4 gas	.1300E-02	-2.886	.2085E-01	-1.681	.3718E-02	.6291E+00
H2S gas	.5347E-02	-2.272	.1822E+00	-.739	.3250E-01	.1575E+01
H2 gas	.4801E-01	-1.319	.9698E-01	-1.013	.1730E-01	.1632E+02
HCl gas	.9323E-07	-7.030	.3399E-05	-5.469	.6062E-06	.3019E-04
HF gas	.2435E-06	-6.614	.4869E-05	-5.313	.8684E-06	.7884E-04
SO2 gas	.2590E-10	-10.587	.1659E-08	-8.780	.2959E-09	.8387E-08
S2 gas	.2086E-12	-12.681	.1338E-10	-10.874	.2386E-11	.6755E-10
CO gas	.2703E-04	-4.568	.7571E-03	-3.121	.1350E-03	.8753E-02
albite-low	.3541E-01	-1.451	.9286E+01	.968	.1128E+02	.3543E+01
Andradite	.6265E-01	-1.203	.3184E+02	1.503	.3867E+02	.8271E+01
Grossular	.4025E-01	-1.395	.1813E+02	1.258	.2202E+02	.5044E+01
Antigorite	.4683E-02	-2.329	.2124E+02	1.327	.2580E+02	.8218E+01
Microcline	.3350E-02	-2.475	.9324E+00	-.030	.1132E+01	.3649E+00
pyrrhotite	.1029E-01	-1.988	.9047E+00	-.043	.1099E+01	.3619E+00