

GAS GEOCHEMISTRY OF THE LOS HUMEROS GEOTHERMAL FIELD, MÉXICO

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ABSTRACT

Gas data of the Los Humeros geothermal field were analyzed. A new method which is based on equilibrium of the Fischer-Tropsch reaction and on the combined pyrite-hematite and pyrite-magnetite reactions was used. Reservoir temperature and reservoir excess steam were estimated for the initial state of the field by using early data taken from producing wells at controlled conditions. The same parameters were also obtained for the present stage by using 1997 gas data. Reservoir temperatures ranged from 275 to 337°C and positive values for reservoir excess steam fractions were obtained for the starting stage. For well H-1 no excess steam was found since this well was fed by the shallower liquid-dominated reservoir. Results for 1997 showed lower scattering compared to earlier data and the possible occurrence of a heating process in the shallower stratum which could be due to exploitation.

1. INTRODUCTION

Gas geochemistry has proved to be a successful tool in geothermal exploration and exploitation, mainly in vapour-dominated fields. Several gas geothermometers have been proposed (D'Amore and Panichi, 1980; Arnórsson et al, 1983; Arnórsson and Gunnlaugsson, 1985), which are based on the variation of gas ratios with temperature in producing aquifers. Also methods to estimate the reservoir excess steam have been proposed (Giggenbach, 1980; D'Amore and Celati, 1983), which are useful when the reservoir temperature is available. Methods to estimate both, the reservoir temperature and the reservoir excess steam were developed by considering fluid equilibria with alteration minerals in the reservoir (D'Amore and Truesdell, 1985; 1995). Although those methods were successfully applied to other geothermal fields, they provided unrealistic low values for excess steam for the Los Humeros data. Recently D'Amore (1998) developed a new method based on equilibria for the Fischer-Tropsch reaction and the combined expressions for pyrite-magnetite and pyrite-hematite. In this method more local oxidant conditions are assumed, implying the occurrence of high concentration of H₂S and relatively low concentration of H₂ and NH₃ in the fluid. Siega et al. (1999) described this method and other additional based on the pyrite-pyrrhotite reaction, they concluded that the one that best fits mature and magmatic systems data is that based on pyrite-hematite. Previous works dealing with gas geochemistry for the Los Humeros geothermal field showed that gas geothermometers provided better estimations than those obtained by cationic geothermometers (Barragán et al, 1988; 1997), this could be result of the lack of full water-rock equilibrium in the reservoir (Tello, 1992; Prol-Ledesma, 1998).

2. THE LOS HUMEROS GEOTHERMAL FIELD

The Los Humeros geothermal field is located in a calderic structure in the eastern part of the Mexican Volcanic Belt (Figure 1). At present 40 wells have been drilled and 40 MW electrical energy are produced (Tovar 1998). The field is located at an average altitude of 2800 masl. The reservoir producing zones are located between -12 and 1610 masl. Figure 2 shows the location of the wells.

Most of the wells produce high steam fraction at separating conditions and exhibit excess steam phenomenon (Barragán et al, 1989; Tello, 1992). The existence of two reservoirs was proposed by Barragán et al, (1988) when studying the behaviour of chemical data; a shallower liquid-dominated one at a temperature of about 250°C and a deeper vapour-dominated one at a temperature higher than 300°C. Then when wells were fed by both strata a mixing process occurred. In 1989 well H-16 and others located in the Colapso Central zone were deviated or cemented due to corrosion-scaling in deep pipes. HCl was found in the vapour phase which originated such problems (Barragán et al, 1989; Gutiérrez-Negrín and Viggiano-Guerra, 1990). HCl caused corrosion while mixing of fluids caused scaling. Well H-1 located in the Corredor de Maztaloya was also deviated because of deep scaling, this well produces from the upper aquifer.

Few wells produce a significant fraction of liquid (H-1, H-6, H-7, H-8 and H-12). According to Giggenbach (1988), the water shows partial equilibrium with the rock at reservoir conditions (Figure 3). Variations in water composition with time also occur, these are due to the input of lower temperature waters to the reservoir as seen in Figure 4. Most of the waters are classified as bicarbonate type according to Giggenbach (1988). This is due to the presence of a high fraction of condensed steam which is concentrated in bicarbonate and sulfate ions in the reservoir fluid. Thus, only few points are located in the zone corresponding to chloride "mature waters" type (Figure 5).

3. GAS GEOCHEMISTRY

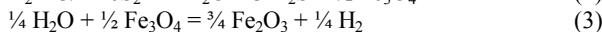
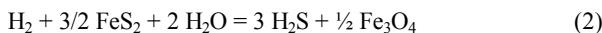
Although water geochemistry provided some clues in defining important characteristics of the Los Humeros reservoir, it was restricted to wells that produce two-phase fluids. For vapour wells gas composition has been used to estimate reservoir temperatures and excess steam values (Barragán et al, 1988). Calculations were performed by a method developed by Giggenbach (1980) and improved by Nieva et al. (1987) in order to make it applicable to samples with a high content of non-condensable gases, as those for Los Azufres or Los Humeros geothermal fields. However in order to obtain more realistic values for the reservoir excess steam, a good estimation of the reservoir temperature is needed and whenever possible the measured or stabilized temperature should be taken. This fact was a complex matter in Los

Humorous, because of the occurrence of strong thermal perturbations in the reservoir (Quijano-León and Torres-Rodríguez, 1995). Stabilized temperatures were obtained by Arellano et al, (1998), by using a spherical approach which proved to be more reliable than radial methods used before. D'Amore and Truesdell (1985) developed a method which was able to estimate both the reservoir temperature and the excess steam based on equilibria for the Fischer-Tropsch reaction and the pyrite-magnetite mineral buffer. The solution of equations produced a grid from which in a graphical way the reservoir temperature and the excess steam were obtained. Since it produced unrealistic high temperatures and low excess steam values for some wells in geothermal fields of México and The Philippines, D'Amore (1998) developed a new method using the Fischer-Tropsch reaction and a new chemical reaction for the H₂S-H₂. The pyrite-hematite equilibrium was combined with the original pyrite-magnetite equilibrium to obtain a new equilibrium expression named HSH2. This method is described as follows.

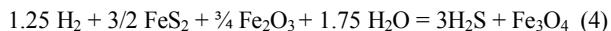
The Fischer-Tropsch (FT) reaction is given in equation (1):



Equilibrium for pyrite-hematite and pyrite-magnetite reactions (HSH2) are given by equations (2) and (3):



By subtracting reaction (3) from reaction (2) equation (4) is obtained:



The thermodynamic equilibrium constant for every reaction is given in equations (5) and (6), in terms of P, the partial pressure;

$$\log K_{\text{FT}} = 4 \log P_{\text{H}_2} + \log P_{\text{CO}_2} - \log P_{\text{CH}_4} - 2 \log P_{\text{H}_2\text{O}} \quad (5)$$

$$\log K_{\text{HSH2}} = 3 \log P_{\text{H}_2\text{S}} - 5/4 \log P_{\text{H}_2} - 7/4 \log P_{\text{H}_2\text{O}} \quad (6)$$

and writing the constants in terms of the water partial pressure, according to (D'Amore, 1992):

$$\log P_i = \log (n_i/n_{\text{H}_2\text{O}}) - \log A_i + \log P_{\text{H}_2\text{O}} \quad (7)$$

where $(n_i/n_{\text{H}_2\text{O}})$ is the molar ratio of "i" component regarding the total water. The coefficient A for every species "i" is defined as a function of temperature and the steam fraction "y":

$$\text{If } y \geq 0: A_i = y + (1-y)/B_i \quad (8)$$

$$\text{If } y < 0: A_i = 1/(B_i(1+y-yB_i)) \quad (9)$$

B_i is the distribution coefficient for every gas and it is a function of temperature (Giggenbach, 1980; D'Amore, 1992). For temperatures between 100 and 340°C, (t in °C):

$$\log B_{\text{CO}_2} = 4.7593 - 0.01092 t \quad (10)$$

$$\log B_{\text{H}_2\text{S}} = 4.0547 - 0.00981 t \quad (11)$$

$$\log B_{\text{CH}_4} = 6.0783 - 0.01383 t \quad (12)$$

$$\log B_{\text{H}_2} = 6.2283 - 0.01403 t \quad (13)$$

By substituting in equations (5) and (6) every P expression, as given in equation (7):

$$\log K_{\text{FT}} + 4 \log A_{\text{H}_2} + \log A_{\text{CO}_2} - \log A_{\text{CH}_4} - 2 \log P_{\text{H}_2\text{O}} = 4 \log (n_{\text{H}_2}/n_{\text{H}_2\text{O}}) + \log (n_{\text{CO}_2}/n_{\text{H}_2\text{O}}) - \log (n_{\text{CH}_4}/n_{\text{H}_2\text{O}}) \quad (14)$$

$$\log K_{\text{HSH2}} + 3 \log A_{\text{H}_2\text{S}} - 5/4 \log A_{\text{H}_2} = 3 \log (n_{\text{H}_2\text{S}}/n_{\text{H}_2\text{O}}) - 5/4 \log (n_{\text{H}_2}/n_{\text{H}_2\text{O}}) \quad (15)$$

The left side of equations (14) and (15) are defined as the FT and HSH2 parameters:

$$\text{FT} = \log K_{\text{FT}} + 4 \log A_{\text{H}_2} + \log A_{\text{CO}_2} - \log A_{\text{CH}_4} - 2 \log P_{\text{H}_2\text{O}} \quad (16)$$

$$\text{HSH2} = \log K_{\text{HSH2}} + 3 \log A_{\text{H}_2\text{S}} - 5/4 \log A_{\text{H}_2} \quad (17)$$

According to D'Amore (1992), the expressions for the equilibrium constants ($\log K_{\text{FT}}$ and $\log K_{\text{HSH2}}$) are given by:

$$\log K_{\text{FT}} = -4.33 - (8048/T) + 4.635 \log (T) \quad (18)$$

$$\log K_{\text{HSH2}} = 7.609 - (6087/T) - 0.412 \log (T) \quad (19)$$

$$\log P_{\text{H}_2\text{O}} = 5.51 - (2048/T) \quad (20)$$

where T is given in K.

The graphic solution of equations (16) and (17) provides a grid in the coordinates (HSH2, FT). The parameters FT and HSH2 are obtained from the gas composition according to equations (21) and (22):

$$\text{FT} = 4 \log (H_2/H_2\text{O}) + \log (CO_2/H_2\text{O}) - \log (CH_4/H_2\text{O}) \quad (21)$$

$$\text{HSH2} = 3 \log (H_2\text{S}/H_2\text{O}) - 5/4 \log (H_2/H_2\text{O}) \quad (22)$$

where concentrations of gas species are taken in the total fluid.

Alternatively the analytical solution of equations (23) and (24) provides the temperature and excess steam fraction:

$$\text{FT} = 4 \log (H_2/H_2\text{O}) + \log (CO_2/H_2\text{O}) - \log (CH_4/H_2\text{O}) = 15.35 - 3952.8/T + 4.635 \log T + f_1(y, B_i) \quad (23)$$

$$\text{HSH2} = 3 \log (H_2\text{S}/H_2\text{O}) - 1.25 \log (H_2/H_2\text{O}) = 7.609 - 6087/T - 0.412 \log T + f_3(y, B_i) \quad (24)$$

where T is given in K, and:

$$f_1(y, B_i) = 4 \log A_{\text{H}_2} + \log A_{\text{CO}_2} - \log A_{\text{CH}_4}$$

$$f_3(y, B_i) = 3 \log A_{\text{H}_2\text{S}} - 1.25 \log A_{\text{H}_2}$$

The following considerations should be taken when this method is used (D'Amore, 1998):

- Thermodynamic equilibrium must be attained in the considered reactions.
- All the considered chemical species (including water) must be in both chemical and phase equilibrium.
- No water gain or loss is allowed after the original equilibrate system.
- The fluid at wellhead generally consists of fluids coming from various sources of the reservoir with different chemical and physical characteristics. Then what it is obtained through the application of this method are integrated values of the steam fraction and temperature for all these different sources. This is important when the different sources have different gas/water ratios. When a deep hot zone of the reservoir located below the exploited reservoir, rich in reactive gas species and CO₂, becomes an important fraction of the total produced gas, an overestimation of the local reservoir temperature and y values are obtained.
- It is assumed that there is no re-equilibration of the chemical species from the source or sources to wellhead.

4. RESULTS AND DISCUSSION

Figures 6, 7 and 8 show the grids obtained for the reservoir starting conditions. Reservoir temperature estimations are in the range 275°C-337°C but for well H-23 this estimation was more than 350°C. Positive values for excess steam were obtained except in well H-1. Wells H-12, H-9 and H-19 show an excess steam of 100%. Wells H-11, H-13, H-20, H-3, H-32, and H-33 show excess steam values lower than 10%. For the original well H-16 a reservoir temperature of 337°C and an excess steam of 20% were estimated. Wells H-17 and H-18 show excess steam values of around 75%. For one sample of well H-23 an excess steam of 100% and a reservoir temperature of 315°C were estimated. Reservoir temperatures estimations through this method are slightly lower than stabilized temperatures (Arellano et al, 1998), which could be due to mixing of fluids. In contrast, for well H-35 this temperature was slightly higher than that stabilized. For well H-1 the temperature estimation was slightly higher than that obtained through logs.

Reservoir temperature estimations indicate that the gas phase comes from an equilibrated high temperature (about 350°C) liquid, otherwise estimations could have been very high corresponding to the system's formation (D'Amore, 1998). Thus, results support the hypothesis that in Los Humeros a hypersaline liquid is likely to occur at depth.

Figures 9, 10 and 11 show the grids obtained for 1997 data. In well H-1 an overestimation of the reservoir temperature is seen which is due to a high gas content, since there is not enthalpy increase in total discharge. Reservoir temperatures for all the wells are higher than 300°C. In well H-31 the highest reservoir temperature is obtained (335°C). Results for 1997 show less scattering compared to those corresponding to the initial state. An explanation could be the occurrence of a heating process in the exploited reservoir probably due to exploitation since fractures allow hotter deeper fluids to rise. This statement was also pointed out by D'Amore et al (1999), who also presume that the shallower aquifer would become thinner as exploitation increases.

Figure 12 shows the excess steam against the location of producing zones according to 1997 data. The highest values for excess steam were found for well H-15R located in the upper stratum and for well H-12 in de deeper stratum. A slightly positive slope is indicated in the shallower stratum which seems to be caused by a convective process since as depth decreases, excess steam increases. However, some wells (as well H-15R) do not obey this tendency.

5. CONCLUSIONS

In the Los Humeros geothermal system fluid geochemistry is strongly masked by the existence of at least two reservoirs. Thus liquid phase does not show full equilibrium conditions because of the presence of high bicarbonate and sulfate concentration condensed steam fraction in the reservoir fluid. Cationic geothermometers tend to underestimate reservoir temperatures. The separated water shows mixing effects and fluid classification varies with time. Water from well H-1 is classified as bicarbonate type, well H-33 is the only classified as chloride type, well H-6 became bicarbonate type and well H-7 became sulfate type, (they were classified before as chloride type). It is established that because of the vapour phase is dominant in the reservoir, gas geochemistry becomes very useful. Then it was

justified to use a new method (FT-HSH2) that considers equilibrium for the Fischer-Tropsch reaction and the pyrite-magnetite, pyrite-hematite combined equilibrium in order to obtain both, reservoir temperatures and reservoir excess steam fractions.

For the initial state, reservoir temperatures in the range 275°C-337°C were obtained. Excess steam fractions values from 0 (well H-1) and 1 (wells H-9, H-19 and H-12) were estimated. Data for 1997 showed less scattering in the grids compared to initial conditions data. Higher reservoir temperature values compared to initial values were obtained for wells H-3, H-6, H-7, H-9R, H-11R, H-12, H-17R, H-19, H-30 and H-31. Excess steam values corresponding to 1997 were found to be from nearly 0 (well H-1) and 0.25. For well H-15R the highest value was found, it was about 0.8.

From the results for the present reservoir conditions, it is inferred that a heating process in the shallower stratum (which is under exploitation) has occurred. This is due to the ascent of hotter deeper two-phase fluids through fractures. Estimated reservoir temperatures were slightly lower than stabilized temperatures. Results indicate that the reservoir vapor phase is probably originated from a deep liquid source in equilibrium probably at 350°C.

6. ACKNOWLEDGMENTS

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7. 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 de Los Humeros, Puebla*. Report IIE/11/11459/01/F for the CFE, 450 p.

Arnórsson S. and Gunnlaugsson E. (1985). New gas geothermometers for geothermal exploration-Calibration and application. *Geochim. Cosmochim. Acta*, Vol. 49, (6), pp. 1307-1325.

Barragán R. R. M., Santoyo G. E., Nieva G. D., Portugal M. E. and Verma M. P. (1988). *Caracterización de yacimientos geotérmicos por medio de la determinación de parámetros fisico-químicos, Cap. 7, Parte 2, Observaciones geoquímicas preliminares de los fluidos del campo geotérmico de Los Humeros*. Internal Report IIE/11/2386/I 01/F, pp. 195-239.

Barragán R. R. M., Cervantes M., Díaz R., Garduño V. H., González E., Holguín S., Meza F., Nieva D., Oliver R., Rosas N. and Sampedro J. A. (1989). *Caracterización del fenómeno de corrosión-obturación de pozos de Los Humeros*. Report IIE/11/3753/I, for the CFE, 83 p.

Barragán R. R. M., Nieva G. D., Santoyo G. E., González P. E., Verma M. P. and López J. M. (1991). Geoquímica de fluidos del campo geotérmico de Los Humeros (Méjico). *Geotermia, Rev. Mex. de Geoen.*, Vol. 7, (1), pp. 23-48.

Barragán R. R. M., Portugal M. E., Arellano G. V. M., Tello L. M. and Tello H. E. (1997). Comportamiento isotópico de fluidos de pozos del campo geotérmico de Los Humeros, Puebla, México. *Geotermia, Rev. Mex. Geoen.*, Vol. 13, (2/3), pp. 87-101.

D'Amore F. and Panichi C. (1980). Evaluation of deep temperatures of hydrothermal systems by a new gas geothermometer. *Geochim. Cosmochim. Acta*, Vol. 44, pp. 549-556.

D'Amore F. and Truesdell A. H. (1985). Calculation of reservoir temperatures and steam fraction from gas compositions. *Geoth. Res. Coun. Trans.*, Vol. 9, pt. 1, pp. 305-310.

D'Amore F. (1992). Gas geochemistry as a link between geothermal exploration and exploitation. In: *Applications of geochemistry in geothermal reservoir development*, F. D'Amore (Coordinador) UNITAR/UNDP pp. 93-117.

D'Amore F. and Truesdell A. H. (1995). Correlation between liquid saturation and physical phenomena in vapor-dominated geothermal reservoirs. *Proc. 1995 World Geothermal Congress*, pp. 1927-1931.

D'Amore F. (1998). *Time evolution of chemical and physical parameters of the reservoir fluid in Ahuachapan geothermal field (El Salvador)*. Report for IAEA, 125 pp.

D'Amore F., Truesdell A. H. and Haizlip J. R. (1999). Acidic geothermal fluids containing hydrochloric acid: A review. *Proc. 20th Annual PNOC-EDC Geothermal Conference*, Manila Filipinas, pp. 61-72.

Giggenbach W. F. (1980). Geothermal gas equilibria. *Geochim. Cosmochim. Acta*, Vol. 44, pp. 2021-2032.

Giggenbach W. F. (1988). Geothermal solute equilibria. Derivation of Na-K-Mg-Ca-geoindicators. *Geochim. Cosmochim. Acta*, Vol. 52, pp. 2749-2765.

Giggenbach W. F. (1992). Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. *Earth and Planetary Science Letters*, Vol. 113, pp. 495-510.

Giggenbach W. F. (1992). Chemical techniques in geothermal exploration. In: *Applications of geochemistry in geothermal reservoir development*, F. D'Amore (Coordinador) UNITAR/UNDP, pp. 119-144.

Gutiérrez-Negrín L. C. A. and Viggiano-Guerra J. C. (1990). Corrosion and scaling in well H-16 of the Los Humeros geothermal field. *Geoth. Res. Coun. Trans.* Vol. 14, pp. 1591-1598.

Nieva D., Verma M., Santoyo E., Barragán R. M., Portugal E., Quijano J. L. and Ortiz J. (1987). Chemical and isotopic

evidence of steam upflow and partial condensation in Los Azufres reservoir. *Proc. Twelfth Workshop on Geothermal Reservoir Engineering*, Stanford University, pp. 253-259.

Prol-Ledesma R. M. (1998). Pre- and post-exploitation variations in hydrothermal activity in Los Humeros geothermal field, Mexico. *J. Volcanol. Geotherm. Res.*, Vol. 83, pp. 313-333.

Quijano-León L. and Torres-Rodríguez M. A. (1995). The Los Humeros geothermal reservoir, a case of a very high temperature system. *Proc. World Geothermal Congress 1995*, Florencia Italia, V. 3, pp. 1569-1573.

Siega F. L., Salonga N. D. and D'Amore F. (1999). Gas equilibria controlling H₂S in different Philippine geothermal fields. *Proc. 20th Annual PNOC-EDC Geothermal Conference*, Manila Filipinas, pp. 29-35.

Tello H. E. (1992). Características geoquímicas e isotópicas de los fluidos producidos por los pozos de Los Humeros, Puebla. *Geotermia Rev. Mex. Geoen.* Vol. 8, pp. 3-48.

Tovar A. R. and López O. (1998). Comportamiento geoquímico e isotópico del fluido de los pozos del campo geotérmico de Los Humeros, Puebla, México. *Proc. Symp. IAEA-CFE*, Los Azufres, Mich., 22 p.

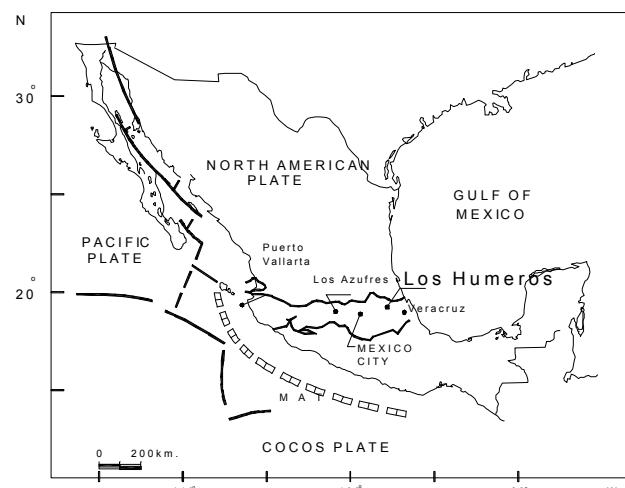


Figure 1 Location of the Los Humeros geothermal field.

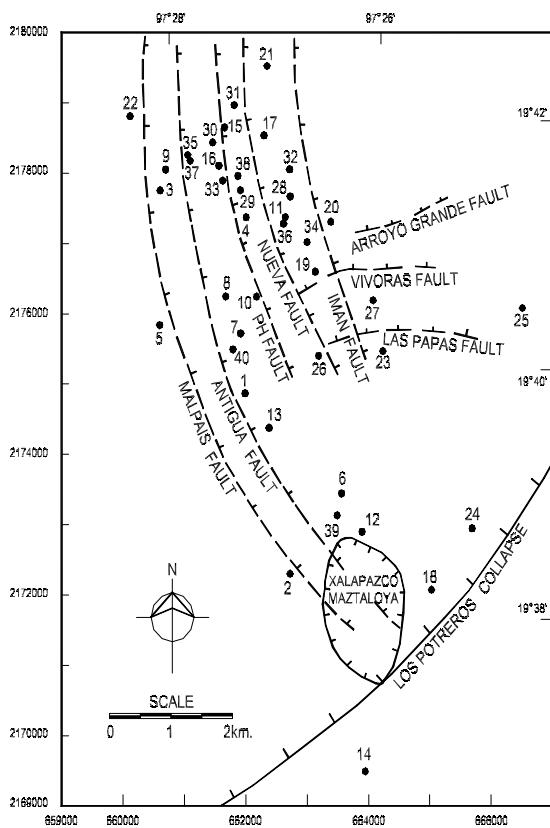


Figure 2 Location of wells in the Los Humeros geothermal field.

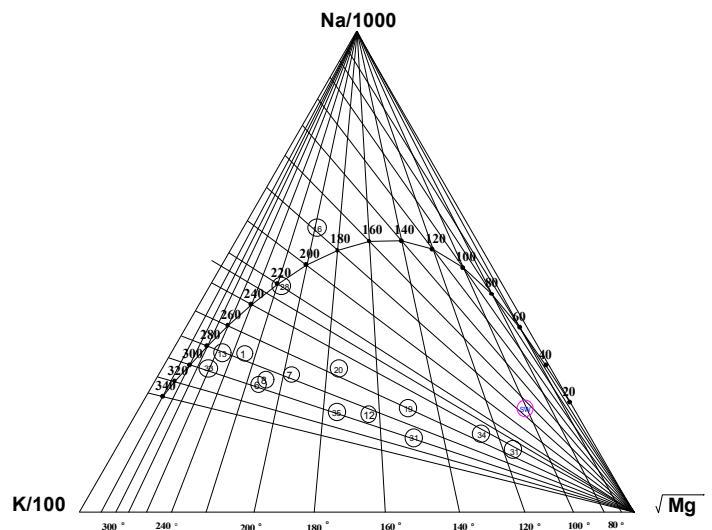


Figure 3 Na-K-Mg diagram for the fluids in the initial stage.

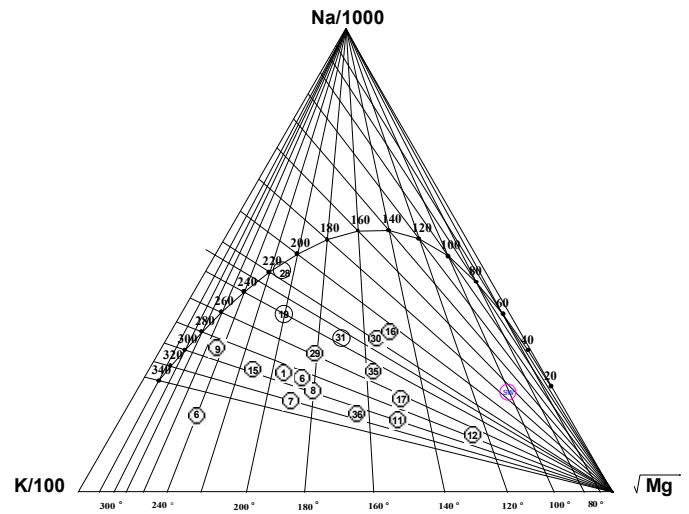


Figure 4. Na-K-Mg diagram for June 1996 data.

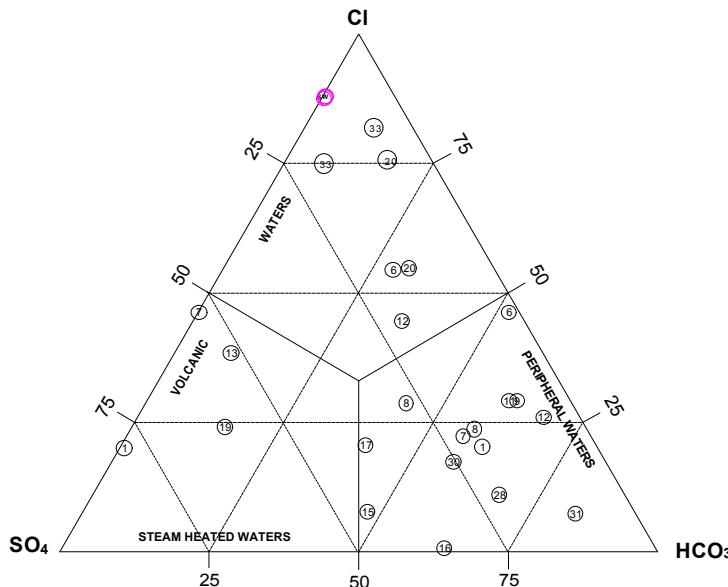


Figure 5. Chloride-sulfate-bicarbonate diagram for Los Humeros fluids.

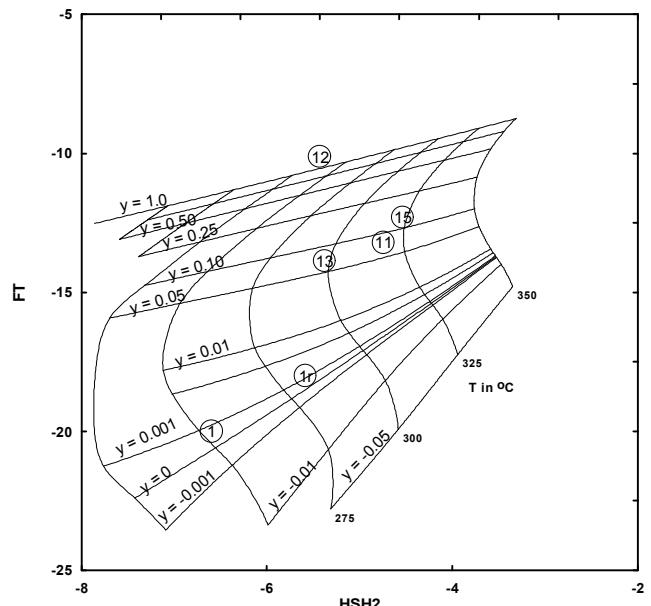


Figure 6. FT vs HSH2 grid diagram for initial state data.

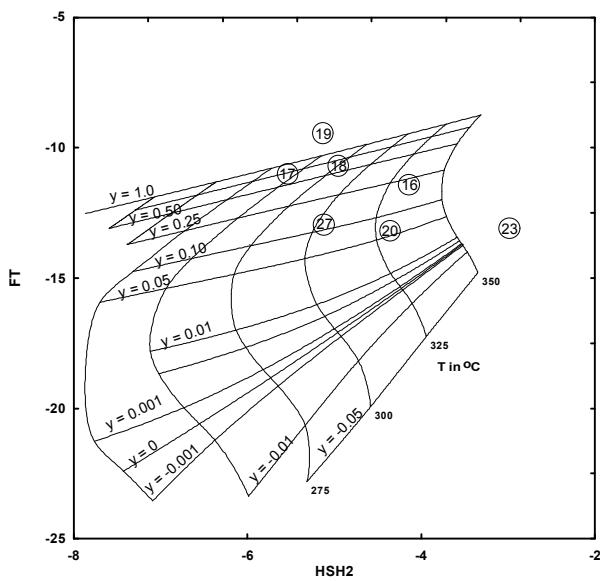


Figure 7. FT vs HSH2 grid diagram for initial state data.

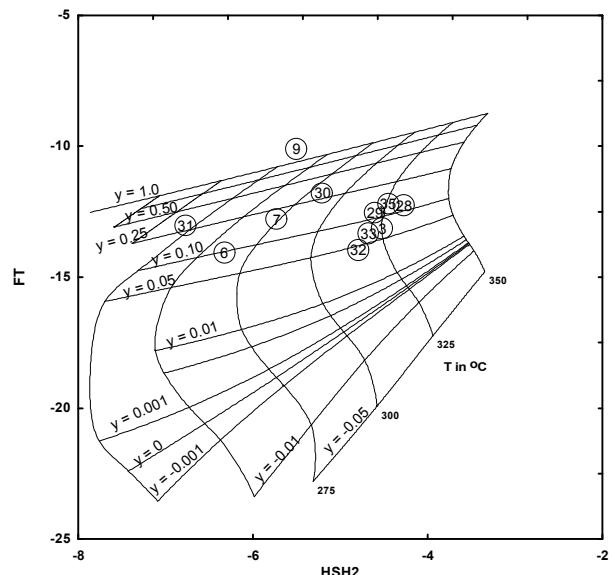


Figure 8. FT vs HSH2 grid diagram for initial state data.

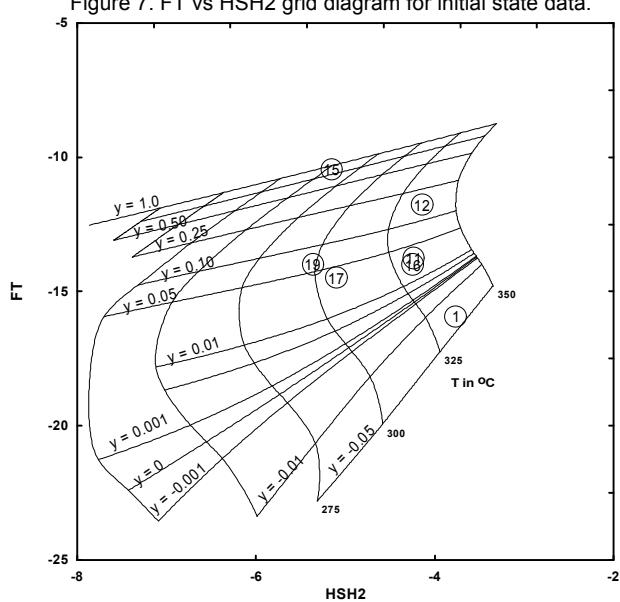


Figure 9. FT vs HSH2 grid diagram for 1997 data.

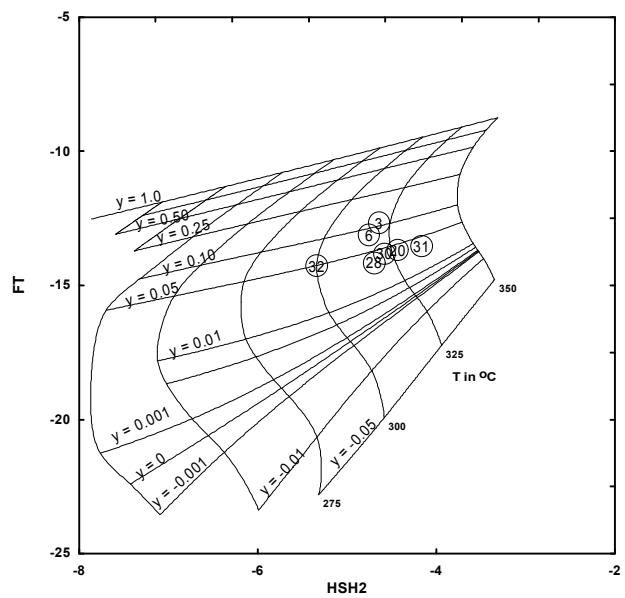


Figure 10. FT vs HSH2 grid diagram for 1997 data.

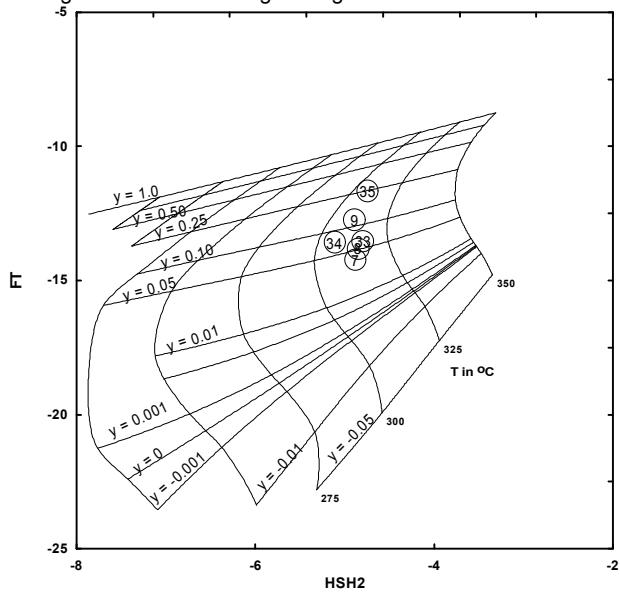


Figure 11. FT vs HSH2 grid diagram for 1997 data.

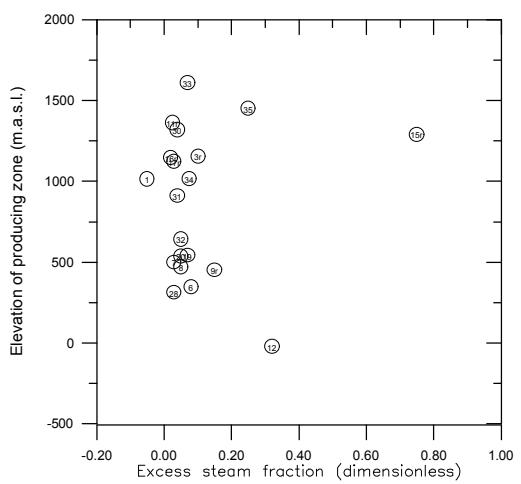


Figure 12. Elevation of producing zones vs the excess steam fraction for 1997 data.