# GEOCHEMICAL EVOLUTION OF THE LOS AZUFRES, MEXICO, GEOTHERMAL RESERVOIR. Part II: NON-CONDENSIBLE GASES

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### **ABSTRACT**

The Los Azufres, Mexico geothermal field has been under continuous exploitation since 1982. The vapor phase at this reservoir has an heterogeneous composition, showing a wide range of non-condensible gas concentrations between 1% and 9% of total gas weight. NCG's measured in this reservoir typically contain CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>, He, N<sub>2</sub> and Ar. Carbon dioxide is the major constituent found in all the field, representing between 70% and 99% in total NCG weight. The highest CO2 content is found in shallow wells with high steam quality, located near important conductive faults. H2S is the second most important gas in total weight, varying between 0.2% and 13%. The chemistry of fluids in this reservoir originated from volcanic processes and is controlled by temperatures at depth, mineral solubility, pH values and mineral equilibria. Simultaneously to fluid extraction, significant amounts of cold liquid and air are injected into this reservoir, modifying its geochemistry and changing, in a complex way, the NCG spatial distribution. Total gases in some wells have increased because of the extra amount of atmospheric N<sub>2</sub> and Ar injected. The molar ratio N<sub>2</sub> / Ar has been falling with time reaching in some cases the same value as in the atmosphere. Both gases follow flow paths related to high permeability, pushing the reservoir gases in the same directions and changing their natural spatial distribution. This geochemical information can be used together with a multi-component numerical simulator to deduce global permeability values between both zones and to analyse non-isothermal pressure tests with real geothermal fluid. The thermodynamic effect of reinjection has been beneficial for the energy production and longevity of this geothermal field. In this paper the observed evolution and spatial distribution of NCG's at Los Azufres geothermal field are reported for the period 1981-1999.

### 1.- INTRODUCTION

The Los Azufres, Mexico geothermal field was officially discovered and studied in the 50's, when Mexican engineers carried out geochemical analysis of the fumaroles. Twenty years later those studies were reactivated and in 1976 the first producing well was drilled. This success confirmed the existence of an energy potential of considerable magnitude inside a naturally fractured reservoir formed by andesites, at an average elevation of 2800 masl, in the central portion of the Mexican Volcanic Belt (Fig. 1).

Geochemistry was important in the initial characterization and during the development of this geothermal project. In particular, analysis of reservoir geothermal gases has been useful in understanding not only its subsurface state, and the chemical composition of fluids at depth, but also in obtaining quantitative estimations of the global permeability and flow paths under exploitation conditions. From the electricity production point of view it is particularly important to observe the concentration and evolution of non-condensible gases (NCG). The practical effect of NCG in any geothermal project is to cause the efficiency of the geothermal power cycle to decrease, by diminishing the turbine's efficiency. At the same time, their careful study allows the inference of important details of fluid transport as well as the environment of the geothermal reservoir. An updated general description of the field is reported in the first part of this paper. In this second part of this work, we restrict our analysis to the presentation of the observed evolution of the main gases in the fluid of the Los Azufres geothermal field, because of the extreme complexity of reservoir's geochemistry.

## 2.- THERMODYNAMIC CONDITIONS AT LOS AZUFRES

The Los Azufres hydrothermal reservoir is composed of two volcanic subsystems with the same fluid and similar geochemical and mineralogical characteristics, but whose thermodynamics are very different. Consequently the coupled processes of mass and energy flow are also different in each sector. The northern sector, known as Marítaro, is a liquid single phase reservoir, located between 200 and 2200 masl. It is characterized by a hydrostatic vertical profile at an average pressure of 90 bar and an average temperature of 300 °C (Suarez et al., 1995). The southern sector known as Tejamaniles, presents three different profiles: a shallow two-phase steam-dominated stratum, located between 1800 and 2600 masl, at initial average conditions of 55 bar and 270 °C; an intermediate two-phase liquid-dominated stratum, located between 400 and 1800 masl, at 100 bar and 300 °C; and a deep compressed liquid stratum, located between -50 and 400 masl, at 180 bar and 350 °C. Boiling processes are more intense to the south of the field, causing larger steam segregation toward this area. Gas concentrations in the southern sector have always been larger than in the northern zone. Thus a direct relationship is established between these gases and the high enthalpies of the producing wells in the southern reservoir.

#### 3.- TYPE OF GASES DETECTED IN LOS AZUFRES

Since August 1982, at the beginning of massive fluid extraction, it was detected that the vapor phase at Los Azufres reservoir had an heterogeneous composition, with a wide range of NCG concentration values between 2% and 8% in weight. Initial studies of the composition of phases in the reservoir showed that the concentration of fluid volatile components such as CO<sub>2</sub> and deuterium decreased with depth, while concentrations of nonvolatile components such as oxygen-18 and chloride ion, increased (Nieva et al., 1983, 1987; Quijano et al., 1989).

The composition of fluids in this reservoir resulted from volcanic mechanisms and are characterized mainly by the presence of carbon dioxide and hydrogen sulfide. Noncondensible gases (NCG) accompanying steam extraction at this field, are a mixture with typically 90.8% of CO<sub>2</sub> and 1.2% of H<sub>2</sub>S in the total gas weight. The remainder 8% of gases is made up of NH<sub>3</sub>, H<sub>2</sub>, CH<sub>4</sub>, He, O<sub>2</sub>, N<sub>2</sub> and Ar (see Table 1 for their actual values). Because of the intensity of boiling occurring in the south, H<sub>2</sub>S being more soluble than CO<sub>2</sub>, the CO<sub>2</sub> /H<sub>2</sub>S ratio has values between 80 and 200 in the southern area and between 60 and 80 in the northern zone. Carbon dioxide is the major constituent of NCG representing today between 70% and 99% in weight in different wells. The high concentrations of CO<sub>2</sub> and the existence of carbonate waters in some portions of the reservoir indicate possible connections with thermometamorphic processes. Unsaturated hydrocarbons, mainly benzene, have been also detected in the steam extracted from some portions of the southern sector (CFE, 1995). The temperature of formation of this hydrocarbon is 600°C. This fact suggests that part of field is closer to the reservoir heat source.

# 4.- INITIAL AND FINAL DISTRIBUTION OF NCG IN THE RESERVOIR

Few NCG data were obtained at Los Azufres between 1981 and 1983. Systematic measurements of NCG began in 1984, when the use of gas chromatography was introduced in this field. The data were measured by direct sampling in wells at 8 bar separation pressure, between 1981 and 1999. The 2D contours shown in figures 2, 3 and 4 were obtained through a Kriging interpolation method. Coordinates of figures are referred to those of well Az-10, whose absolute Mercator coordinates are: X= 322,000.3, Y=2,186,615.7. Table 1 sumarizes chemical composition of gases of some representative wells at two different dates. The first analysis is for the initial state, the second one represents the last measured value.

Figure 2 shows the state of NCG concentration between 1981 and 1984 when the first measurements were carried out and the reservoir was almost in its initial natural state. In that time there were two relative maxima in the field, reflecting the existence of two regions naturally high in NCG, having concentrations larger than 8% in weight. Both zones were located in the southern portion of the reservoir. The first one, to the west, corresponds to wells with the highest steam quality (Az17, Az36). The second one, to the east, was measured at well Az18 when it had a small amount of steam. Toward the north, NCG concentration diminished and was notably less than in the southern sector. A certain E-W alignment existed, corresponding to faults oriented in the same direction. A S-N gradient with a higher

concentration of NCG in the south, is also observable.

The distribution of NCG concentrations, as affected by exploitation of the reservoir between 1982 and 1996, is shown in Figure 3. A clear trend of NCG increasing toward the East is observed. The trend follows a slightly SE direction in both field areas. In the southern zone the gases increment has a remarkable increase in the S-N direction, but restricted to the v-coordinates of 1250 m and 2000 m. It is observed that the NCG concentration gradient is aligned in two sections following the orientation of two main fault systems, Puentecillas (Az17, Az34, Az18) and Agua Fría (Az22, Az55, Az35). In the northern zone there is a minor increment, but with the same trend and a similar profile between the v-coordinates of 5500 and 6000 m (Fig. 5). The NCG concentration gradient follows the same orientation as the Laguna Larga and Marítaro faults (Az42, Az19, Az43). The present distribution of NCG concentrations, measured in 1998, is shown in figure 4. It confirms the N-S trend in the southern sector, where an absolute maximum of 9% appears. In the northern zone, two lower relative maxima appear in both extremes of the sector.

#### 5.- DISCUSSION AND RESULTS

The original chemical composition of gases at Los Azufres field is analogous to other volcanic geothermal reservoirs. The difference here is that reinjection of waste liquid and air has been carried out parallel to the exploitation of the field since 1982. Simultaneously, injected water drags air toward the reservoir through the injection wellheads (Horne et al., 1989; Suárez, et al., 1997). Air arrives at the deep reservoir zones and breaks down into its primary elements. Oxygen reacts immediately, combining with other components in the neighboring formations. Nitrogen and argon are freely displaced from injection zones to production sectors. The concentration of these two gases exhibits a remarkable increase in several producing wells. In some of them the increase was exponential. up to 6 times larger than initial concentrations (Fig. 5). The molar ratio N<sub>2</sub>/Ar has been falling with time, reaching in some cases the same value as in the atmosphere (83.6). Reinjection accompanied by air is contributing to an increase in some wells of total NCG due to the extra amount of atmospheric N<sub>2</sub>, pushing the reservoir gases in the same direction. Evolution and displacement of CO2 and N2 are valuable indicators of the communication between various zones of the reservoir, showing the existence of high permeability paths related to faults and fractures. Using a multi-component numerical simulator, this geochemical information can be useful to deduce global permeability values between both zones and it could help to analyse non-isothermal pressure tests with real geothermal fluid.

Carbon dioxide is the major constituent found in all the field, representing between 70% and 99% in total NCG weight.  $\rm H_2S$  is the second most important gas in total weight, varying between 0.2% and 13%. In some wells, a relatively high amount of He has been detected (Table 1). This fact suggests very slow circulation in the Earth's crust of magmatic fluids carrying the helium. At great depth the gas amount is minor; while in shallow zones NCG concentration increases. Wells affected by injection present a complex oscillatory behavior of  $\rm CO_2$  concentration. The width and amplitude of oscillations are reflections of extraction, reinjection, permeability and

production of  $CO_2$  combined. NCG concentration have a close relationship with thermodynamic conditions of producing wells. Wells having large or growing gas concentrations (NCG > 2% in weight) have high steam quality ( $\geq$  75%). Wells with low and constant gas concentrations ( $1\% \leq NCG \leq 2\%$ ) have lower and constant steam quality ( $\leq$  50%). Wells with only small amounts of gas (NCG < 1%) could have any thermodynamic condition. There is also an inverse relationship between bottomhole temperature-pressure and NCG: their concentration diminishes when pressure and temperature increase. A detailed description of these relations was reported by Suarez et al.(1997). Figures 4, 5 and 6 show the change of carbon dioxide and hydrogen sulfide concentrations in the period 1984-1999.

#### 6.- CONCLUSIONS

- Los Azufres geothermal reservoir is a volcanic system in total chemical equilibrium. Its magmatic original fluids have been totally neutralized by geochemical water-rock interactions.
- The steam phase at Los Azufres reservoir, has an heterogeneous composition, showing a wide range of NCG concentrations between 1% and 9% in weight. The general observed trend is that at depth the gas amount is small; while in shallow zones the gas concentration increases, but there are some exceptions.
- $CO_2$  and  $H_2S$  are the main gaseous components of the geothermal fluid in Los Azufres reservoir. There is a general decrease in the  $CO_2/H_2S$  ratio in a S-N direction.
- Wells having large or growing gas concentrations have high steam quality. Wells with low and constant gas concentrations have steam qualities lower than 50%. Wells with very small amounts of gas could have any thermodynamic condition. Reinjection modifies the field geochemistry.
- Injection of waste liquid and air contributes to an increase in total gas concentration in some wells because of the extra amount of atmospheric N<sub>2</sub>. Reinjection pushes reservoir NCG toward the production zones, changing their current spatial distribution.

- The changes in carbon dioxide points out that realistic modeling should include production of CO<sub>2</sub> from depth.
- Chemical behavior of wells is different at each zone and the reinjection effect contributes to modify their behavior in complex ways, according to their production depth.

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Table 1.- Geochemical Evolution of Gases at some Wells of Los Azufres Geothermal Field

WELL	DATE	TGAS	CO <sub>2</sub>	$H_2S$	NH <sub>3</sub>	Не	$H_2$	Ar	$N_2$	$O_2$	CH <sub>4</sub>
AZ-05	01/11/1985	2.6	97.40	2.300	0.030	0.001	0.0180	0.0020	0.0033	0.1780	0.017
AZ-05	07/24/1998	2.378	98.35	1.450	0.066	0	0.0019	0.0019	0.1213	0.0117	0.008
AZ-06	06/20/1986	6.600	98.60	0.545	0.254	0.00030	0.0170	0.0050	0.003	0.5310	0.027
AZ-06	03/22/1996	4.209	96.32	0.462	0.000	0.00065	0.0187	0.0432	3.1360	0.9251	0.0164
AZ-09	06/02/1987	0.800	95.22	3.034	1.128	0	0.0110	0.0030	0.2000	0.3880	0.0110
AZ-09	07/24/1998	0.416	93.57	5.010	0.527	0.0042	0.0140	0.0371	0.7464	0.441	0.092
AZ-13	01/11/1985	1.860	96.30	3.430	0.066	0.001	0.0249	0.0022	0.0080	0.1171	0.0127
AZ-13	07/24/1998	2.366	93.28	1.426	0.1	0.00119	0.0308	0.4428	4.8041	0.0155	0.0141
AZ-17	01/11/1985	5.200	98.61	1.290	0.060	0	0.0110	0.0050	0.0029	0.0003	0.0008
AZ-17	01/27/1997	3.332	82.67	1.217	0.258	0	0.0378	0.2022	15.6150	0.02	0.006
AZ-18	02/20/1987	6.200	98.93	0.570	0.271	0.00010	0.0040	0.0010	0.211	0.2110	0.1900
AZ-18	06/01/1998	9.974	99.33	0.296	0.054	0.00027	0.0037	0.0069	0.2735	0.2204	0.0310
AZ-22	04/27/1988	1.100	96.02	2.987	0.158	0	0.0235	0.0531	0.6752	0.6752	0.0843
AZ-22	07/27/1998	1.117	96.83	2.279	0.189	0.00017	0.0102	0.0097	0.0654	0.1004	0.0254
AZ-33	07/21/1986	6.600	98.58	0.497	0.435	0.00020	0.0180	0.0030	0.0000	0.4300	0.0360
AZ-33	07/27/1998	3.163	97.53	0.697	0.078	0.00059	0.0096	0.0226	1.6393	0.0000	0.0232
AZ-41	03/25/1987	0.600	95.63	2.967	0.162	0.00017	0.0230	0.0240	1.1310	0.0000	570
AZ-41	05/30/1998	2.421	97.36	1.536	0.094	0.00017	0.0133	0.0129	0.9533	0.0000	0.0322
AZ-046	07/21/1986	2.600	97.65	0.997	0.473	0.00020	0.0350	0.0140	0.0000	0.8270	0.0008
AZ-46	08/28/1998	2.460	95.22	1.369	0.099	0.00074	0.0203	0.0611	3.2340	0.0000	0.002
AZ-16D	06/20/1986	3.000	90.60	2.000	0.750	0.00003	0.0240	0.1230	0.0000	6.5000	0.0030
AZ-16D	11/21/1995	4.975	52.14	1.400	0.138	0	0.0250	0.7043	45.7340	0.0000	0.0000

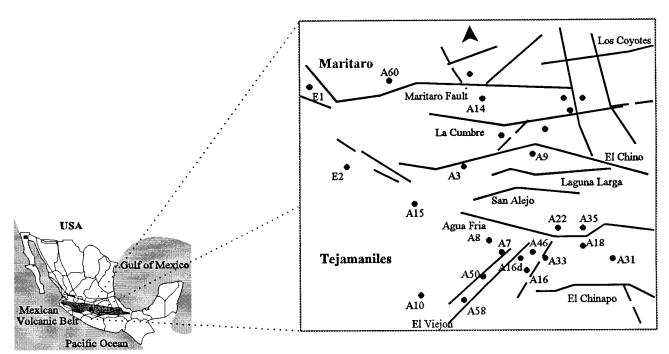


Fig. 1.- A Simplified Map of the Los Azufres, Mexico Geothermal Field.

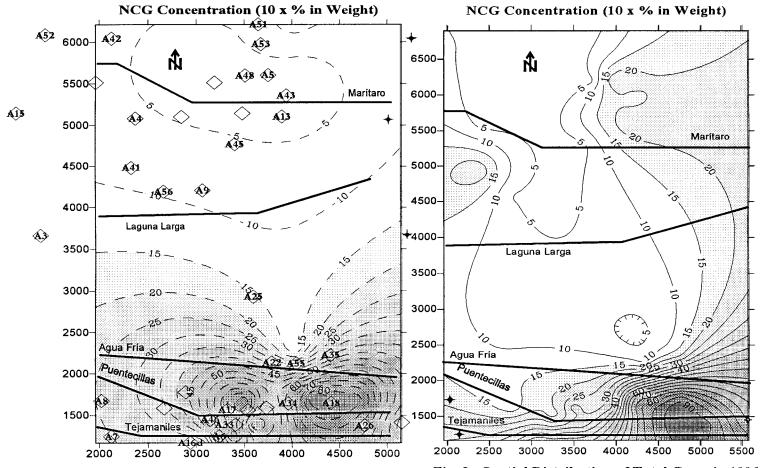


Fig. 2.- Spatial Distribution of Total Gases 1981-1984 Fig. 3.- Spatial Distribution of Total Gases in 1996

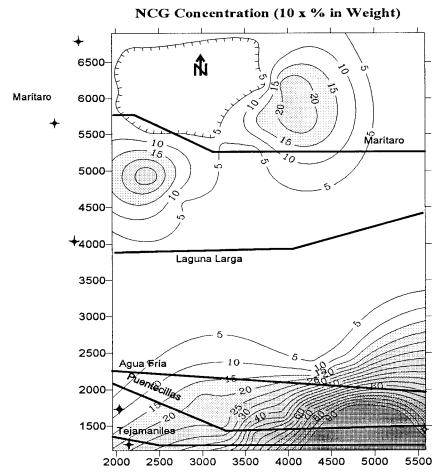


Fig. 4.- Spatial Distribution of Total Gases in 1998

Fig. 5.- EVOLUTION OF CARBON DIOXIDE AT THE NORTHERN SECTOR

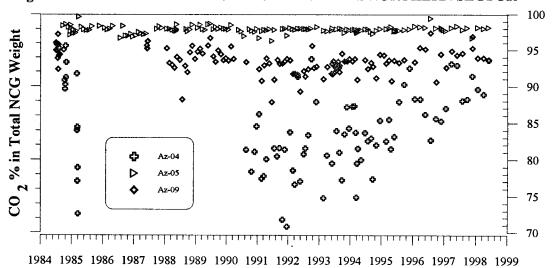


Fig. 6.- EVOLUTION OF CARBON DIOXIDE AT THE SOUTHERN SECTOR

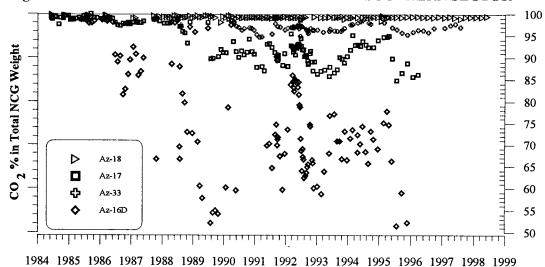


Fig. 7.- EVOLUTION OF HYDROGEN SULFIDE AT BOTH SECTORS

