# GEOCHEMICAL EVOLUTION OF THE LOS AZUFRES, MEXICO, GEOTHERMAL RESERVOIR. Part I: WATER AND SALTS

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## **ABSTRACT**

The Los Azufres, Mexico volcanic reservoir is characterized by fluids of neutral sodium chloride type at depth. High temperatures, and different concentrations of soluble components in the rocks affect the amount of chemical elements such as Cl, B, Br, Li, Cs and As observed in its water. There are in the liquid other less soluble components such as SiO<sub>2</sub>, Ca, Mg, Rb, K, Na, SO<sub>4</sub>, NH<sub>4</sub> and HCO<sub>3</sub>. This geothermal field has been under continuous exploitation since 1982; reinjection of waste liquid and air is carried out parallel to exploitation. These actions contribute to modify the reservoir's geochemistry. Chemical composition of fluid feeding the wells is not the same everywhere, indicating that there are several production sections from different formations. Measured enthalpies show that boiling occurs within the reservoir. Initial chemical data showed that the concentration of volatile components in the fluid such as CO2 and deuterium, decreased with depth, while concentration of non-volatile components such as oxygen-18 and chloride, increased. In a few lateral portions of the field there is isotopic evidence of mixture of meteoric water and shallow groundwater with geothermal fluids. An efficient caprock exists only in the southern sector where the main recharge must be lateral and deep. Data from many two-phase production wells, show that concentrations of chloride, boron. sodium, calcium, lithium and cesium, dissolved in the liquid, have been increasing since 1984, while rubidium and arsenic decreased in the same wells, during the same period. This effect is closely connected to the constant injection of cold liquid into the reservoir. Reinjection produces successive concentration of those salts in the water within the production zones. Wells not affected by injection are increasing their steam quality and show the opposite behavior. Potassium, sulfates and silica are constant or vary slightly in all the wells, independently of whether or not they are affected by reinjection. Some wells do not show any significant trend in their overall chemical behavior, suggesting the existence of large, well-connected high porosity zones around such wells.

#### 1.- INTRODUCTION

The Los Azufres geothermal field is an intensely fractured, two-phase, volcanic hydrothermal system located at an elevation of about 2800 masl in the central portion of the Mexican Volcanic. Belt, in the state of Michoacan. The coordinates of the center of the field are 100°37′, 100°43′ longitude W, and 19°48′, 19°51′ latitude N. This field was known and used by its original inhabitants in Pre-Columbian times, officially discovered in the

50's and studied in the 70's. CFE drilled the first successful well in 1976. At the present time 63 wells, with depths varying between 452 m and 3544 m and wellhead elevations between 2700 and 3200 masl, have been completed in this reservoir. Los Azufres generates 600 GWh/year with 88 MWe installed. We estimate its maximum potential as around 500 MWe for 30 years.

Fifty years ago, geological and geochemical studies were the first type of research carried out in this field. Today, the field's explored area covers about 140 km², but the actual exploited field's surface is only 30 km². Exploration techniques include reservoir engineering, geology, geochemistry, geophysics and mineralogy. Regional and detailed aeromagnetic surveys and LandSat-5 images were previously done. These studies are described in many CFE internal reports; some of them were published in different international forums (Gutiérrez & Aumento, 1982; Nieva et al., 1983; Dobson, 1984; Cathelineau et al., 1985; Wright et al., 1989; Geotermia-CFE, 1991; Suarez et al., 1995; Tello, 1997). In this paper the observed evolution of geochemistry at Los Azufres geothermal field is reported for the period 1979-1999.

## 1.1.- Methodology of Analysis

Information on the chemical composition and evolution of the fluid extracted from wells in this field is abundant. We processed data from wells where considerable variations of concentrations are observed and present herein the main trends. The methodology of analysis was as follows: a) analysis of chemical composition of solutes at atmospheric pressure; b) estimation of chemical composition of solutes corrected to total discharge and to reservoir conditions; c) geothermometry of the aqueous phase and d) analysis of chemical composition of gases. This last point is described in the second part of this paper. Because of the extreme complexity of the reservoir's geochemistry, we restrict here our analysis to the presentation of observed chemical evolution of salts in this geothermal field.

### 2.- GENERAL FIELD CHARACTERISTICS

## 2.1.- Geology and Reservoir Thermodynamics

The highly-fractured rock forming the main reservoir hosts two geothermal subsystems: Marítaro in the north and Tejamaniles in the south. They differ in their thermodynamic characteristics, but geochemically their fluids are the same. The evolution of this field is better understood by regarding both zones as separate entities. The reservoir is formed by andesites with rhyolites at the upper layer in the southern sector. Several regional faults cut the field (Fig. 1) and are intersected by wells

at different depths. Apparently the mass and heat transport processes are slightly different in each subsystem and therefore their petrophysics and mineralogy are also somewhat different. In the southern sector there is a narrow circulation zone, with fumaroles, boiling mud pools and steaming ground. These superficial manifestations are distributed between faults. Both fields produce high enthalpy fluids, between 1500 and 2800 kJ/kg. There are two relative maxima of steam saturation toward the center of each zone. In deeper regions the reservoir is liquid dominated in both sectors.

The most important production zone is a two-phase portion located in the Tejamaniles sector, between 1600 and 2300 masl, at 55 bar and 270°C in its initial state. A deeper liquid-dominated zone has been found between 400 and 1200 masl, at higher temperature but with lower permeability. The maximum measured temperature was 358 °C (at 185 bar), in well Az-47 at 2800 m depth. The northern sector, known as Marítaro, is a single liquid phase reservoir, located between 200 and 2200 masl. Its natural state was characterized by an hydrostatic vertical profile at an average pressure of 90 bar and an average temperature of 300°C.

#### 2.2.- Reinjection

Eight deep wells are used to inject about 650 T/h of separated water and condensed steam from the cooling towers. Reinjection is performed in wells that are close to the assumed field boundaries in both sectors. The maximum amount of fluid accepted by some wells is about 350 T/h, indicating an extremely high permeability of several darcys. The temperature of injection varies between 40 and 50 °C at 0.73 bar, the local atmospheric pressure. The horizontal distances between reinjection wells and the nearest production wells ranges between 1000 and 2000 m; injectors are completed 500 to 1000 m deeper than productors. In spite of the fact that production and injection zones are connected by faults and fractures, the reservoir's thermodynamic evolution shows that the liquid is reinjected at adequate depth and distance from production zones (Suarez et al., 1995). Reinjection has been beneficial for the energy production and longevity of this geothermal field.

## 3.- GEOCHEMISTRY OF LIQUID AT LOS AZUFRES

## 3.1.- Composition of Spring Waters

Springs are the most frequent thermal manifestations found in the field, with temperatures close to the boiling point (90°C), pH lower than 4.0, high content of sulfates (1500 ppm) and low concentration of chlorides (20 ppm). These conditions are produced by geothermal vapor discharged into the shallow ground waters. The deep fluid of the reservoir is altered during its passage to the surface by addition of calcium, bicarbonate and acid sulphate components. CFE engineers have measured the water composition of 62 hot springs of the Los Azufres area (Tello, 1997).

The majority of springs are located in zones whose measured temperatures are between 100 and 160°C. Some springs around the El Chino, Laguna Verde and Agua Fria faults (Fig. 1), are located over the region of partial equilibrium (Fig. 2) at

temperatures of  $330^{\circ}\text{C}$ . These waters, heated by steam, are acid sulphate waters because of the oxidation of  $\text{H}_2\text{S}$  from geothermal origin. This type of acid sulphate water is most common in fumarolic areas where steam rising from boiling hot water zones condenses as it approaches the surface. Some peripheral springs are characterized by waters of neutral sodium chloride type, their fluid is of meteoric origin representing superficial lateral discharges from the reservoir. Springs with sodium-bicarbonate type water, have lower K/Mg temperatures around  $100^{\circ}\text{C}$ , indicating that probably water-rock interaction occurred at low temperature.

## 3.2.- Composition of Reservoir Water

Chloride, sodium and silica are the most abundant elements present in the fluid extracted from the Los Azufres geothermal field. Its composition reflects important processes occurring in the aqueous phase of the reservoir. The composition of water in this reservoir is related to volcanic processes. The fluids extracted are characterized by sodium chloride waters in all the wells and a total equilibrium exists in every drilled zone. The only exception is well Az-14 with sodium-bicarbonate fluid, having influence from a shallow aquifer. Distribution of chloride concentrations show that boiling processes are more intense in the southern zone than in the northern sector. Sulphate/chloride waters characterizing oxidizing zones, have never been observed in this field. Table 1 sumarizes chemical composition of separate water of some representative wells at two different dates.

### 3.3.- Water-Rock Equilibrium State

Figure 2 shows the relative Na-K-Mg content in waters of the Los Azufres reservoir. The current state of equilibrium in wells and springs and the temperatures of water-rock equilibrium are presented in a Giggenbach-type diagram (Tello, 1997). Except for wells Az-14 fed by shallow waters and Az-30 which has high concentrations of calcium and magnesium, every well falls on the line of total equilibrium at temperatures between 300 °C and 360°C (300- 340°C, after Tello, 1997).

#### 4.- RESULTS AND DISCUSSION

The sodium chloride water of the Los Azufres reservoir has a pH close to neutral at depth. When the fluid approaches the surface, it loses steam and carbon dioxide, becoming slightly alkaline. Chloride is the most common anion present and the ratio of chloride to sulphate is high. The principal cation present is sodium. These characteristics are common in large reservoirs. Figures 3, 4 and 5 synthesize the evolution of salts in representative wells of both sectors. A gradual decrease of chloride concentration, from 3300 ppm to 1000 ppm, is observed in a SW-NE direction. At wells Az-13 and Az-32 a remarkable chloride decrease is observed. Well Az-13 is fed by two phase steam-dominanted fluid. This causes boiling in the area and an increase of its discharging enthalpy. Consequently, condensation at the surroundings is produced, causing dilution of the neighbouring water.

Data from many two-phase production wells, show that the concentrations of chloride, boron, sodium, calcium, lithium and

cesium, dissolved in the liquid, have been increasing since 1984, while rubidium and arsenic decrease in the same wells, during the same period. This effect is produced by the constant injection of flashed liquid into the reservoir. The operation induces successive concentration of salts in the water going to the production zones. On the other hand, wells that are not affected by injection are increasing their steam quality and enthalpy and the same salts are decreasing, with increase of Rb and As. This means that their chemical behavior is reversed. Potassium, sulfates and silica are constant or have small variations in all the wells, whether they are or not affected by reinjection. Some wells do not show any significant trend in their overall chemical behavior, suggesting the existence of well connected, high porosity, high permeability, large source zones feeding such wells.

Figures 3 and 4 plot the evolution of chloride and sodium of wells representing the reservoir. They reflect the effect of reinjection affecting wells Az-16D and Az-18 during the period 1979-1999. We deduce that the production volumes of these wells have direct communication with the western reinjection sectors (Fig.1), through faults and fractures. In same figures it is observed that the production zone of well Az-05 is not affected by injection. Figure 5 shows concentration evolution of several salts for well Az-16D. Using a multi-component numerical simulator (Battistelli and Pruess, 1997), this geochemical information is useful to deduce global permeability values between both zones, effective volumes of feeding fluid and could help to analyze non-isothermal pressure tests with real geothermal fluid.

Undesirable aspects of reinjection such as serious interference of lower enthalpy water with the energy outflow of the producing wells, or formation permeability decrease by chemical deposition, or contamination of groundwater have never been noticed at this field.

### 5.- CONCLUSIONS

- Los Azufres geothermal reservoir is a volcanic system in total geochemical equilibrium. Fluids extracted from its wells are sodium-chloride waters, characteristic of deep circulation geothermal brine
- The reservoir is of convective type with high enthalpy fluids and the water-rock interaction occurred at high temperatures. Equilibrium was attained at temperatures between 300°C and 360°C.
- Concentration of salts in this reservoir are extremely sensitive to exploitation and to reinjection. Chemical changes in twophase reservoirs are very important to detect the response of the field to fluid extraction and reinjection, at any stage of development of the project.

- Intensive boiling processes are occurring, partially because of field's exploitation. This process together with reinjection effects, are producing increases of chloride and other salts in several zones under exploitation. Reinjection affects mostly wells closer to injection zones.
- Liquid is reinjected at adequate depth and distance from production zones. Reinjection has been beneficial for the energy production and longevity of this geothermal field.

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TABLE 1.- GEOCHEMISTRY OF LIQUID WATER IN SOME WELLS OF THE LOS AZUFRES GEOTHERMAL FIELD

WELL	DATES	CL	В	HCO <sub>3</sub>	SiO <sub>2</sub>	SO <sub>4</sub>	NH <sub>4</sub>	Na	K	Li	Rb	Cs	CA	Mg	As
Az-02	04/03/1978	2449.5	131.0	162.2	689.0	28.00	5.600	1376.0	316.00	32	3.5	2.4	9.60	0.4	18.2
Az-02	07/28/1997	6284.6	521.5	2.51	986.3	23.62	0.3	3722.4	510.10	30.10	6.370	16.28	302.90	0.045	12.90
Az-05	08/14/1979	2964.8	221.3	46.4	1089.9	43.90	5.900	1664.0	427.40	24.50	4.9	3.1	12.80	0.200	23.8
Az-05	05/29/1998	2995.1	267.3	1.39	1521.8	26.78	1.6	1631.6	353.80	17.88	4.420	3.89	7.15	0.003	18.00
Az-09	02/19/1982	5427.1	371.5	63.8	118.2	320.00	1.21	2740.0	900.00	44.20	6.600	3.60	152.00	10.600	9.70
Az-09	05/30/1998	3607.7	307.5	1.59	1434.3	17.80	2.8	1954.4	456.30	20.72	5.420	4.26	14.48	0.026	20.80
Az-13	05/07/1980	2481.4	302.1	80.5	1245.6	65.30	2.900	1456.3	350.00	26.00	4	2.3	26.4	26.100	21.60
Az-13	03/31/1998	10.2	33.7	9.89	48.6	15.30	0.2	27.4	2.60	0.10	0.340	0.05	0.03	0.007	1.60
Az-16	12/01/1981	2339.9	155.1	61.9	1096.0	59.00	6.05	1340.0	214.00	16.00	1.800	1.40	17.20	0.550	16.50
Az-16	01/22/1996	8305.1	611.1	11.90	897.3	48.40	1.9	3859.0	757.00	30.01	7.300	14.10	287.00	0.060	5.90
Az-18	01/20/1981	2305.8	207.7	71.4	782.0	23.50	11.000	1440.0	385.00	28.2	4.8	2	22.3	0.04	22.1
Az-18	01/27/1998	3121.2	467.6	6.78	642.5	55.82	2.7	1697.1	379.80	16.78	9.550	18.36	64.61	0.054	20.60
Az-22	02/12/1981	2580.6	237.2	74.3	1007.7	52.00	5.800	1500.0	418.80	26.00	5.000	2.00	18.60	0.03	20.00
Az-22	07/27/1998	3641.6	318.3	18.01	1546.9	9.25	0.1	1897.2	492.20	19.22	4.440	5.20	22.50	0.004	22.60
Az-32	04/01/1985	2304.4	669.2	153.46	766.7	195.00	3.060	65.5	276.00	1.11	1.590	1.49	16.09	1.130	41.3
Az-32	03/31/1998	54.4	27.8	18.64	120.4	32.70	-	59.3	5.90	0.53	0.570	0.07	0.06	0.002	0.40
Az-33	07/21/1983	3742.7	284.3	126.2	993.4	58.60	7.3	2157.1	421.90	23.00	2.400	3.10	30.10	0.200	24.50
Az-33	07/28/1997	7424.2	544.8	4.96	814.3	27.84	0.06	4254.9	747.50	32.17	9.530	22.66	376.80	0.046	11.10
Az-46	10/31/1983	3180.1	225.1	113.2	737.1	35.50	0.193	1824.0	358.60	20.00	0.100	2.30	23.70	0.020	19.20
Az-46	01/28/1998	7011.1	553.2	7.64	941.0	27.46	0.06	3734.4	614.40	31.17	17.700	36.63	287.16	0.040	9.50
Az-16D	11/15/1982	3904.0	629.8	83.3	394.0	86.50	7.600	2270.3	445.80	20.90	2.800	2.20	60.90	0.800	23.70
Az-16D	09/22/1992	8595.8	545.5	65.03	800.0	25	-	4538.0	816.00	36.00	9.600	11.50	275.20	0.120	8.20
Az-16D	05/25/1995	5596.9	448.6	11.90	614.2	32.00	4	3106.0	557.00	26.10	7.3	13.7	97.10	0.040	5.00

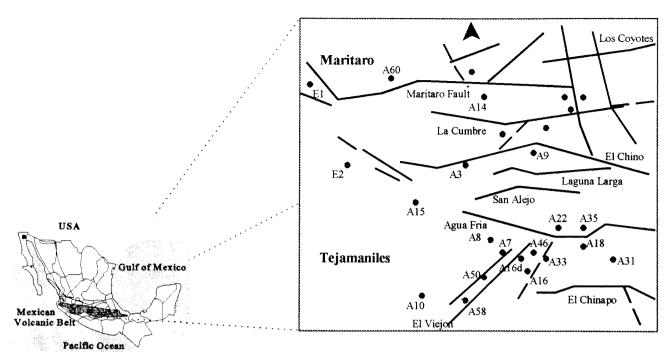
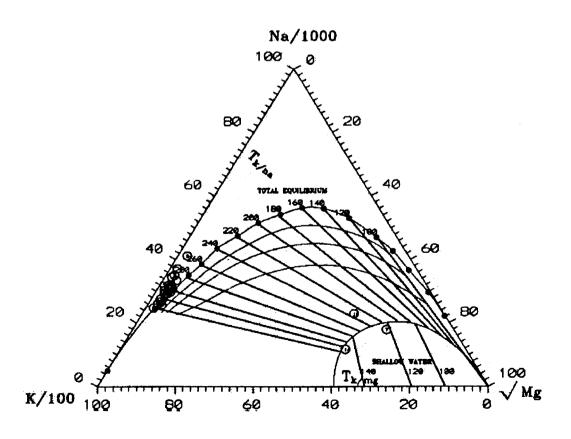
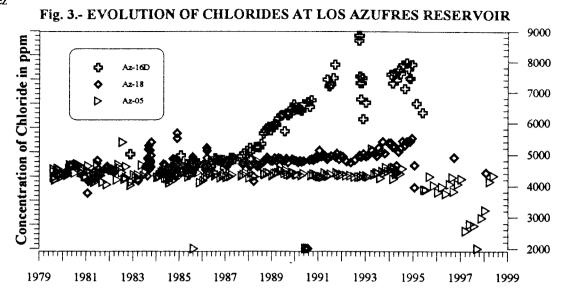
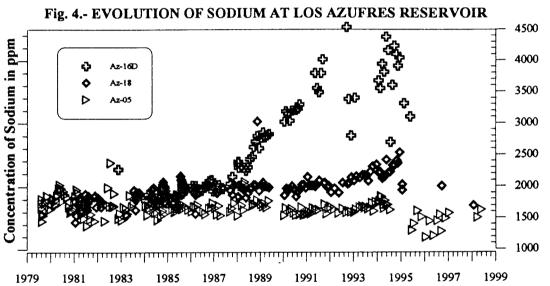


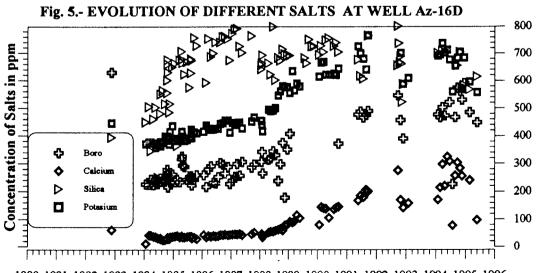
Fig. 1.- A Simplified Map of the Los Azufres, Mexico Geothermal Field.

# FIGURE 2.- RELATIVE CONTENT OF Na-K-Mg IN WELL OF THE LOS AZUFRES RESERVOIR









1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 YEAR