

## Production Chemistry of Wells in the Southern Part of Los Azufres, Michoacan, Mexico

Mirna Tello-López , Stuart Simmons and Mario-César Suárez-Arriaga

Alejandro Volta No. 655, Col. Electricistas, Morelia, Mihc., México, CP 58290

[mirna.tello@fce.gob.mx](mailto:mirna.tello@fce.gob.mx), [sf.simmons@auckland.ac.nz](mailto:sf.simmons@auckland.ac.nz), [msuarez@zeus.umich.mx](mailto:msuarez@zeus.umich.mx)

**Keywords:** Well geochemistry, Mexico, Los Azufres, equilibration, boiling processes.

### ABSTRACT

The Los Azufres geothermal field is located in the state of Michoacan in the central portion of the Mexican Volcanic Belt and is divided into two zones: the northern and the southern ones. In this paper, an updated analysis of the wells geochemistry is presented together with a discussion about the main processes that have been occurring in the southern part of this reservoir. The southern zone of the geothermal field is a two-phases system. In the deeper zone the reservoir is of a liquid dominated type. Some wells initially discharged a mixture of steam and water and some of them only produce steam. Most wells produce high enthalpy at their discharge and the dominated aqueous components are sodium, chloride, and potassium. The fluids also contain high concentrations of silica and boron. The main processes observed during the commercial exploitation of the wells are steam loss, cooling and boiling, depending on location of the feed zone. The liquid discharged by the wells is sodium-chloride water with near neutral pH and hot equilibration temperature of about 300°C. On the other hand, the gas composition is derived from magmatic sources, where carbon dioxide (CO<sub>2</sub>) is the major component of non-condensable gases (NCG).

### 1. INTRODUCTION

The Los Azufres geothermal field is located in the state of Michoacan in the central portion of the Mexican Volcanic Belt (Figure 1). The geothermal field is an intensely fractured, volcanic-hosted, high temperature hydrothermal system at an elevation of about 2800 masl. It has surface thermal activity that covers an area of about 60 km<sup>2</sup>.



Fig. 1. Location of the Los Azufres field.

Geothermal development began in 1976 with geochemistry, geological and geophysical studies. A total of 67 wells have been drilled by CFE (Comision Federal de Electricidad) to depths between 600 and 3500 m. In the southern zone 17 of the total number of wells are in production and 2 are for injection.

Los Azufres is the second geothermal field in Mexico, and it has been in continuous production since 1982. The total installed capacity is about 88 MW for which 61.5 MW is generated by the production wells located in the southern sector.

The geochemistry studies are important during the exploitation of geothermal fields, because knowing the chemical composition of water and gases and their evolution are useful to know the main processes that occur in the geothermal system.

### 2. CHARACTERISTICS OF THE GEOTHERMAL FIELD

The Los Azufres geothermal field is formed by a fractured andesitic massif of Tertiary age. Basaltic and andesitic lavas dominate the extensive Neogene volcanic rocks. The south-west area consists of sandstone and conglomerates from Eocene to Oligocene age (Dobson & Mahood, 1985).

Los Azufres is a silicic volcanic center that has three major eruptive groups: 1) Agua Fria rhyolites, 2) San Andres dacites and 3) Yerbabuena rhyolites (Figures 2 and 2a). (Dobson and Mahood, 1985).

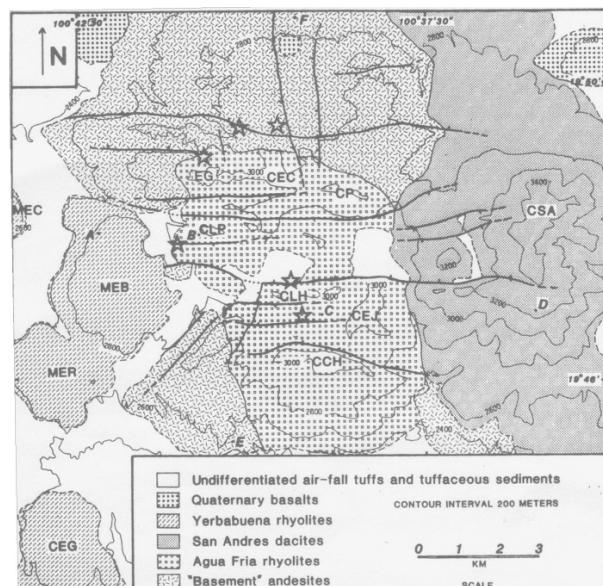
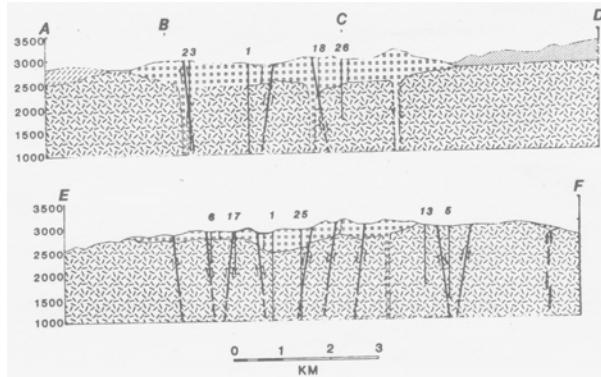


Fig. 2. Geologic map of the Los Azufres volcanic center. Hachured heavy lines indicate high-angle normal faults. Cerro El Gallo (EG), Cerro El Chino (CEC), Cerro Pizcuaro (CP), Cerro La Providencia (CLP), Cerro Las Humaredas (CLH), Cerro El Jilguero (CEJ), Cerro Chinapo (CCH) are Agua Fria rhyolite domes. Mesa El Carpintero (MEC), Mesa El Bosque (MEB), Mesa El Rosario (MER), and Cerro El Guagoche (CEG) are Hierbabuena rhyolite domes. Cerro de San Andres (CSA) is a vent complex for the San Andres dacites. Stars mark hot springs and fumaroles. A-B-C-D and E-F mark cross section locations.

The Agua Fria rhyolites has an estimated volume of 8 km<sup>3</sup> and consist of lava domes which contain phenocrysts > quartz > biotite > Fe-Ti oxides ± hornblende ± orthopyroxene. The Yerbabuena rhyolite forms the youngest major eruption group of the Los Azufres center. The normal faults cut the Agua Fria rhyolite and the San Andres dacite units (Dobson and Mahood, 1985).



**Fig. 2a. Geologic cross-sections of the Los Azufres center. No vertical exaggeration. Vertical scale in meters above sea level. Symbols as in Figure 2. Numbers mark well location. Figure by Dobson (1985).**

The Tejamaniles sector is in the southern part of Los Azufres; it has shallow permeable zones, due to the presence of fractures in the upper strata. The surface hydrothermal activity (steaming ground, mud pools, fumaroles) as well as the fluid production of geothermal wells at depth, is mainly controlled by E-W faults. Highly-fractured rock forms the main reservoir (Tello and Suarez, 2000).

The southern zone of the geothermal field is a two-phase system. Wells were drilled into most of the high-temperature part of the system. These wells initially discharge a mixture of steam and water and some of them only produce steam.

On the other hand, after a period of exploitation with steam and water discharge, the well characteristics may gradually change. The water fraction decreases and the chloride concentration increases due to steam loss, and this occurred in some wells in south zone at relatively shallow depths.

In deeper zones the reservoir is liquid dominated. The wells produce high enthalpy discharge between 1100 to 2700 kJ/kg. Chloride concentration in waters ranges from 2500 to 8500 ppm (mg/kg). The Na/K ratios indicate hot equilibration temperatures of around 300°C (Giggenbach, 1988).

### 3. METHODOLOGY

The southern part of the Los Azufres geothermal field was selected for this study. The water and gas chemical compositions from the production wells Az-2, Az-16, Az-18, Az-22, Az-25, Az-26, Az-33, Az-36, Az-46, Az-16AD, (mixture of steam-water) Az-6, Az-17, Az-34, Az-35, Az-37, Az-38, (only steam) and Az-62, were studied for the period 1990 to 1998.

Some calculations are necessary to interpret the chemical results, which includes the enthalpy of the fluid discharged from the wells, separation pressures and the chemical analysis of water and steam samples. The solute concentrations in waters and gas concentrations in steam vary with the conditions of sampling, therefore the results

need to be recalculated to a standard condition. The methodology of analysis was as follows:

- Calculate of ion balances. To determine the quality of the analysis.
- Total Discharge Conditions. These are calculated to help understand steam-water separation processes in the reservoir.
- Aqueous and gaseous Geothermometers: Quartz-no steam loss, Na/K and K/Mg (Giggenbach, 1988). Are calculated to determine deep equilibration temperatures in the reservoir.

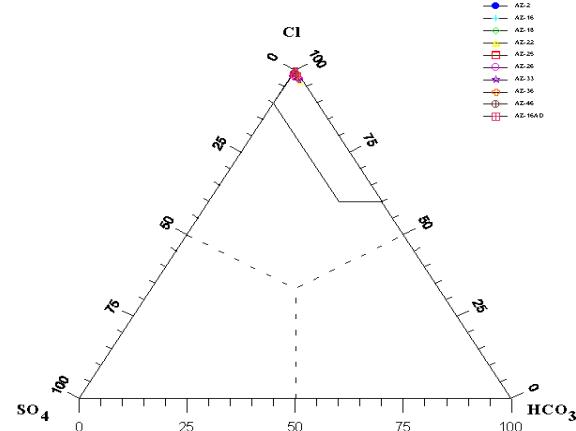
### 4. GEOCHEMISTRY COMPOSITION OF LIQUID PHASE

#### 4.1. Source of geothermal water

The most dominant aqueous components in the fluid from the Tejamaniles sector are chloride, sodium and potassium and also contain high concentrations of silica and boron. The water also has significant concentrations of bicarbonate, sulfate, lithium, rubidium, cesium, calcium and arsenic.

All values of the ion balance calculation are less than 5%, and were obtained from representative chemical analyses of water from the production wells used for this study.

The Cl-HCO<sub>3</sub>-SO<sub>4</sub> ternary diagram (Figure 3) shows the composition of waters from the wells, which fall in the chloride water region. All of the well waters are sodium-chloride waters with near neutral pH. The ratio of the most soluble constituents, such as Cl/B represents water compositions from deep wells. The samples located close to the B corner may suggest absorption of high B/Cl steam.



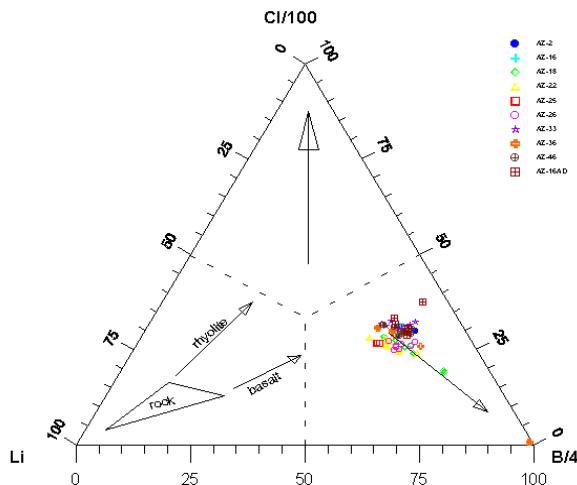
**Fig. 3. Cl-HCO<sub>3</sub>-SO<sub>4</sub> ternary diagram showing the well composition.**

The Cl-B-Li ternary diagram (Figure 4) shows the source of the geothermal brine from the production wells. The samples fall in the boron region where the Cl/B ratio is nearly the same, suggesting they originated from the same depth. Hence they have the same source, possibly related to reaction with rhyolite and basaltic composition igneous rock.

#### 4.2 Equilibrium State

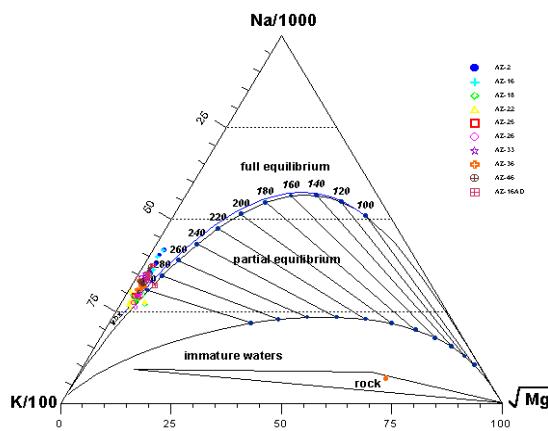
The Na/K ratio, the concentration of silica and magnesium in the water discharged from a well is helpful to calculate the temperatures. Silica concentrations are thus directly

associated with reservoir temperature in a particular zone, while the Na/K may represent conditions at some greater depth. Because water rock interaction affects fluid composition, the Na/K temperatures reflects equilibrium with Na and K-feldspars.



**Fig. 4. Cl-B-Li ternary diagram showing the well composition.**

The Na-K-Mg ternary diagram (Figure 5) shows the most representative reservoir temperatures of the Tejamaniles sector. The majority samples are scattered close of the full equilibrium line and the temperature of Na/K geothermometer (Giggenbach, 1988) relating 270 to 330 °C. The samples from the well Az-22 fall in the full equilibrium line showing the highest Na/K temperatures, on the order of 300 °C to 330 °C. The K/Mg geothermometer shows high temperatures that oscillate between 220 °C to 410 °C, this geothermometer is very sensitive to any slight addition of Mg from rock dissolution. This geothermometer gives high temperature, indicating that probably water-rock interaction occurred at high temperature.



**Fig. 5. Na-K-Mg ternary diagram showing the reservoir temperatures.**

On the other hand, the silica geothermometer (quartz-no steam loss) gives the reservoir temperatures between 180 °C – 330 °C, giving a maximum temperature based on quartz solubility.

#### 4.3 Reservoir and Total Discharge Composition

The chemical composition of the water extracted from wells in the southern zone of the field, was corrected to the total discharge conditions. The water produced by the wells, contain high chloride and silica concentrations which indicate important processes that occur in the reservoir. The solute concentrations in waters discharged from wells change with time due to physical processes occurring in the system during exploitation, such as loss or gain of steam, dilution, heat transfer between rock and water. Figure 6 shows the evolution of enthalpy, chloride and silica concentration with respect time in the total discharge.

The highest chloride concentrations are found in wells Az-16 and Az-2 showing increase from 2500 to 5000 ppm and 4000 to 6000 ppm, with time. Chloride prefers the liquid water phase, hence this behavior suggests that the wells produced from a liquid dominant zone that is influenced by steam loss (Figure 6).

All the other wells have decreasing chloride concentrations of 2600 to 500 ppm, suggesting the wells are producing two phase fluid. The enthalpy discharge increases due to depletion of the liquid phase (Figure 6).

The trend in enthalpy shows an increase while the solute concentration decrease, due to processes that occur in the reservoir. However, the trend from wells Az-2 and Az-16 is almost constant, between 1200 and 1300 kJ/kg and well Az-26 also is almost constant between 1300–1400 kJ/kg, with a small increase in the last two years (Figure 6).

The silica concentrations are sensitive to changes in subsurface temperatures in the deeper parts of the system, and show a quick response to cooling.

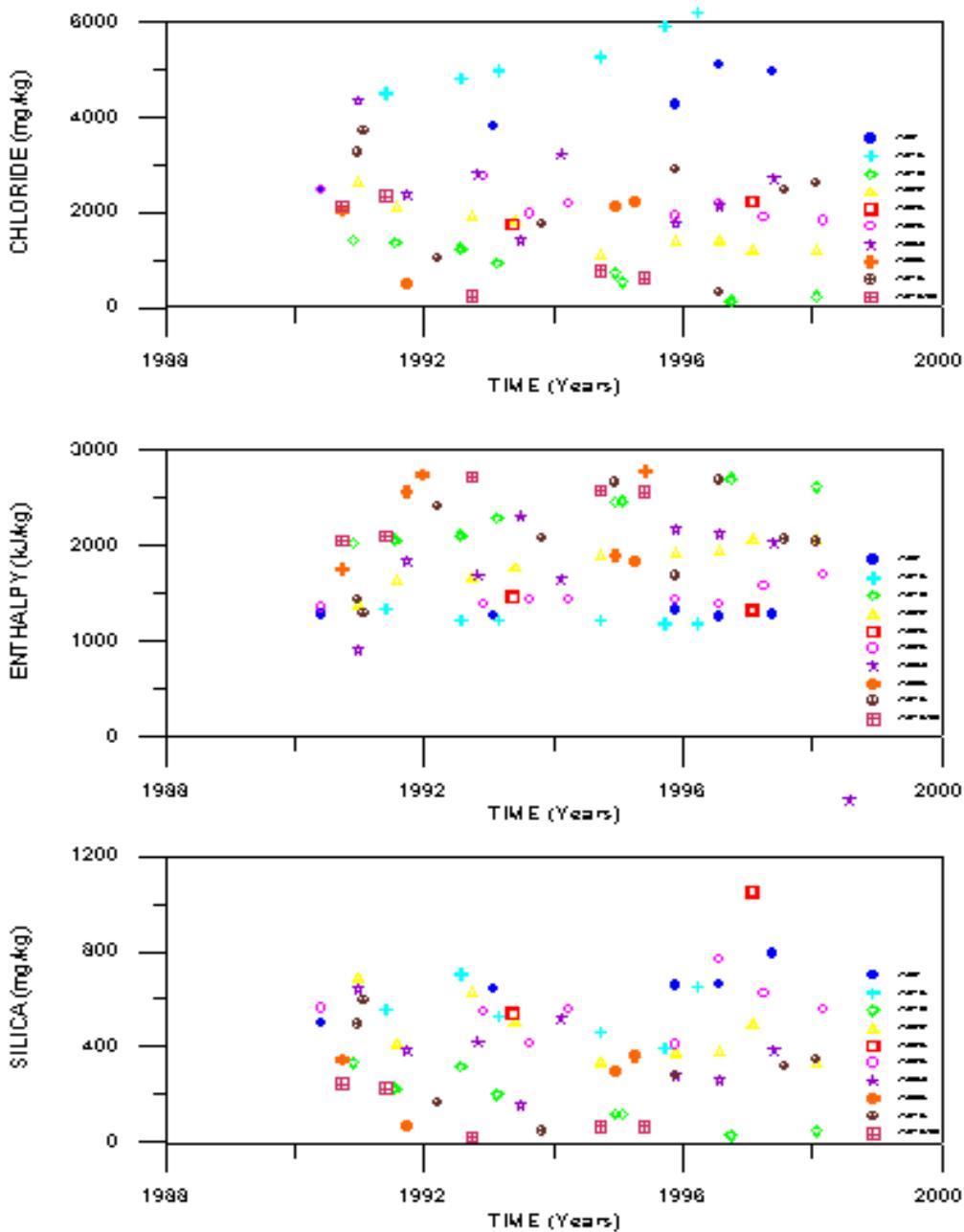
The evolution of the silica concentration with time represents change in the reservoir conditions. In the first years the silica concentrations of the wells decreases with time, but in the last four years the concentrations increase (Figure 6). The main effect that occurs is decreasing solubility due to cooling and increasing the silica concentration due to steam loss.

### 5. GEOCHEMISTRY COMPOSITION OF GASES

#### 5.1. Gas composition

The concentration of gases in the steam occurs because of the effect of exploitation into the reservoir. The steam phase includes gases initially dissolved in the water, such as CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, He and Ar. The total gas content is between 0.4 and 13.5 wt %, where carbon dioxide (CO<sub>2</sub>) is the major component of non-condensable gases (NCG), representing between 70 and 99 % and H<sub>2</sub>S comprises 0.5 to 4.0 % of weight in the total gas.

The N-He-Ar ternary diagram (Figures 7) shows the main sources of the gases (Giggenbach, 1991). The samples from wells Az-2, Az-16, Az-17, Az-25 fall in the meteoric component represented by air saturated groundwater. The majority of the samples are scattered near the magmatic region associated to volcanic gases. The samples from Az-18, and some samples from Az-26 fall in between the magmatic and meteoric region, which suggest that gas is a mixture of gases from both sources. One sample from wells Az-18, Az-22, Az-25, Az-26 and Az-36, plots close to He corner, which represents the basaltic field and some samples from Az-34 and one of Az-36 plot close to the andesitic field (Figure 7).



**Fig. 6. Evolution of Chlorides, enthalpy and silica with time in Los Azufres wells, at total discharge.**

### 5.2. Geothermometry of gases

The chemical composition of the gas is useful to estimate deep temperatures using gas geothermometers. Temperatures calculated for the (D'Amore and Panichi, 1980) gas geothermometer range from 250 °C (Az-34) to 370 °C (Az-26). They are the most realistic temperatures representative of reservoir conditions. These temperatures in some cases are coherent with temperatures assessed by means of the K/Mg and Na/K geothermometer (Giggenbach, 1988).

### 5.3 Reservoir state

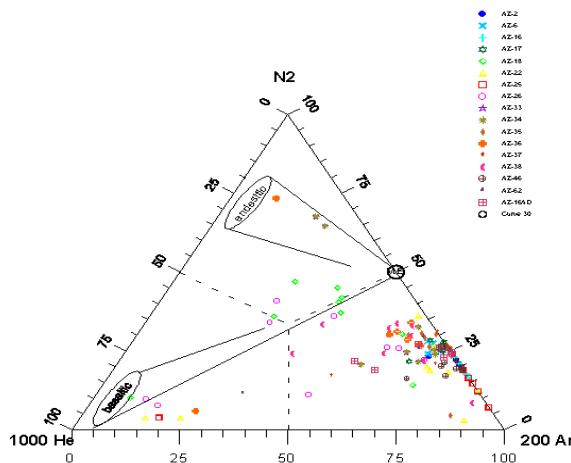
The gas composition was corrected to the total discharge composition for NCG data. The change in CO<sub>2</sub>/H<sub>2</sub>S ratio and CO<sub>2</sub> were calculated for multi-step steam separation from 300 °C (parent fluid) to assess the effects of steam loss in gas composition. The most soluble gases such as NH<sub>3</sub>, H<sub>2</sub>S and CO<sub>2</sub> are partially retained in the residual

liquid hence we can assess the gas concentration in liquid and vapor phases.

Wells Az-6, Az-17, Az-34, Az-35, Az-37 and Az-38 produce dry steam.

The plot of CO<sub>2</sub> (mmol/100 mol) vs CO<sub>2</sub>/H<sub>2</sub>S ratio for total discharge composition (Figure 8) shows the state of the reservoir. The majority of samples are scattered between the liquid and the vapor curves. The difference between high CO<sub>2</sub>/H<sub>2</sub>S ratio from the wells of dry steam and lower CO<sub>2</sub>/H<sub>2</sub>S ratio from the wells of two phases (steam-water) can be due to steam and gas loss from the boiling liquid.

When CO<sub>2</sub> is lost, the temperature decreases and the amount of vapor increases as boiling intensifies. The main process that occurs in the reservoir is simple boiling.



**Fig. 7. N<sub>2</sub>-He-Ar ternary diagram showing the well composition.**

## 6. RESULTS AND DISCUSSION

The reservoir rocks are rhyolitic domes and basaltic lavas. The wells of the southern zone produce from deeper regions, between 400 and 1200 masl where the reservoir conditions are liquid dominated (Tello and Suarez, 2000).

The thermodynamic properties of water and gas at higher temperatures and pressures are essential to know the origins of geothermal fluids. In some volcanic geothermal systems the liquid become concentrated in dissolved salts.

The sodium cation and chloride anion are present in large concentrations in the reservoir water. The water in the southern part of the Los Azufres Geothermal field is a sodium-chloride water with near neutral pH. The ion balance of the chemical analysis is less than 5% that suggests good analyses.

High chloride and silica concentrations reveal important processes. Boiling increases the chloride concentration and the discharge enthalpy of the reservoir fluids.

The Na/K geothermometer (Fournier) gives reservoir temperatures in the range of 250°C to 350°C and Na/K (Giggenbach) temperatures between 270°C and 330°C. The gas geothermometer (D'Amore and Panichi) is between 250°C and 370°C, similar to temperature calculated with aqueous geothermometer.

Trends in Na-K (Giggenbach) and silica temperatures in the majority of the wells show a decrease with time; this could reflect mixing of two hot waters before equilibration at different temperatures. From the Cl-HCO<sub>3</sub>-SO<sub>4</sub> ternary diagram, the fluid shows no evidence of mixing with cold waters.

The presence of high gas concentrations such as carbon dioxide and hydrogen sulfide (NCG) in the fluid of the reservoir is typical of a geothermal system. Their concentrations are affected by temperature and pressure. At constant wellhead pressure (WHP), the steam discharge increases and the CO/H<sub>2</sub> ratio increases.

The wells Az-6, Az-18, Az-26, Az-33, Az-34 and Az-38 have the highest value of CO/HS and shows high enthalpy discharge, suggesting that the wells produce from a two phase (steam and water) zone.

The liquid phase has lost CO due to the intensity of boiling in the reservoir, hence the proportion of steam increased.

Boiling processes are more intense in the southern zone, causing large steam segregation toward this zone of the field.

## 7. CONCLUSIONS

- The fluid produced by the wells is sodium-chloride water typical of the geothermal system. Chloride water type has not changed its composition due to mixing with other water types.
- The chloride concentration increases due to boiling.
- The range of the reservoir temperatures is 270°C to 330°C based on the Na/K geothermometer (Giggenbach). These temperatures approximate the reservoir temperatures, because mixing and dilution do not affect Na/K geothermometer.
- Water-rock interaction is occurring at high temperature of about 300°C.
- The gas composition is derived from the magmatic source associated with a volcanic system.

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