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Chemical and Isotopic ($\delta^{18}\text{O}, \delta\text{D}$) Behavior of Los Azufres (Mexico) Geothermal Fluids Related to Injection as Indicated by 2010 Data

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**ABSTRACT**

The Los Azufres (Mexico) geothermal field (188 MW installed power capacity), consists of two well-defined areas of production, Maritaro in the north and Tejamaniles in the south. The Comisión Federal de Electricidad (CFE) started field development in 1980 while commercial exploitation began in 1987. Injection started in 1983 and has been beneficial to the reservoir. All reinjection wells are located to the west of the field, at present time, there are two injection wells operating in the south zone and four in the north zone. Reinjection fluids are a mixture of separated water and condensed steam that is highly evaporated at ambient conditions before injection. In order to investigate the main processes occurring in the reservoir due to exploitation/reinjection processes, monitoring of chemical and isotopic compositions of fluids are routinely performed. In this work the distributions of geochemical indicators obtained in 2010 from chemical and isotopic data of fluids were related to reservoir exploitation and reinjection processes. Data for 50 wells provided by Comisión Federal de Electricidad were included. Geochemical indicators studied were: total discharge isotopes ($\delta^{18}\text{O}, \delta\text{D}$); Na/K temperatures for two-phase wells and gas FT-HSH2 temperatures of dry steam wells; $\text{CO}_2$; chlorides and $\text{N}_2$ concentrations, reservoir excess steam and reservoir liquid saturation.

The results indicate that chloride concentrations decrease but reservoir temperatures increase toward the northeast of the field where no injection takes place. Injection influence was noticed through minimum $\text{CO}_2$ concentrations in fluids. $\text{CO}_2$ concentrations increase from the west toward the east, with maximum $\text{CO}_2$ concentrations in the southeast but also in the northeast, where important natural upflow seems to occur. Because injection takes place by gravity at atmospheric conditions, air is unintentionally injected to the reservoir, together with separated water and condensed steam. Thus $\text{N}_2$ distribution provides actual trajectories of volatile species. Maximum $\text{N}_2$ concentrations are seen in the southwest of the field (where injection wells are located) with a decreasing trend toward the northeast. Isotopic results for 2010 showed enrichment at the west of the field, where injection wells are located. The 2010 $\delta\text{D}$ vs $\delta^{18}\text{O}$ relationship showed that some wells produce different proportions of injection returns and that injection effects are more important in the south zone. Most of the production of well AZ-2A (south zone) seems to consist of injection returns while well AZ-16 produced approximately 50% from injection. In contrast, in the north zone the wells are little affected by injection with the exception of well AZ-42 that shows a relatively enriched isotopic composition.

**Figure 1.** Location of Los Azufres geothermal field and schematic map of the field.
1. Introduction

The Los Azufres geothermal field with an installed power capacity of 188 MW, is located in the northern part of the Mexican Volcanic Belt (Figure 1). The Comisión Federal de Electricidad (CFE) started field development in 1980 while commercial exploitation began in 1987. The field consists of two well-defined areas of production, Maritario in the north and Tejamaniles in the south, separated by a distance of 2-3 kilometers with no surface manifestations in the intervening area. Injection in Los Azufres started in 1983 at an early stage of development of the field and has been beneficial for the reservoir (Torres-Rodríguez and Flores-Armenta, 2000). Since 2003, due to the 100 MW increase in power capacity installed at the north zone, concerns about reservoir performance due to fluids extraction have arisen. In order to estimate the occurrence of reservoir processes induced by exploitation (extraction and reinjection of fluids), the CFE routinely performs the monitoring of chemical, isotopic (Barragán et al. 2003; 2005a; 2009; 2010a) and production characteristics of wells (Arellano et al., 2005). The injection effects on the geochemical behavior of fluids produced during 2009 has been discussed by Barragán et al., 2010b). In this work, the geochemical behavior of fluids was investigated by the analysis of 2010 data. Geochemical data for 50 wells provided by CFE were included (Figure 1).

2. Methodology

In 2010 samples for isotope ($\delta^{18}$O, $\delta$D) monitoring from production and injection wells of Los Azufres geothermal field were collected under controlled conditions (Barragán et al., 2010a). The total discharge isotopic compositions of wells were obtained. The Na/K, (Nieva and Nieva 1987) was used to estimate reservoir temperatures of two-phase wells, while the FT-HSH2 method (Barragán et al. 2005b) was used to estimate temperatures of dry steam wells. From gas data, the reservoir excess steam along with the CO$_2$ for the total discharge and for the reservoir liquid were calculated by using the SCEXVAP program (Nieva et al. 1987). Average values for chemical compositions were used. Results were processed to produce iso-contours on the map of the field given in Figure 1. For reference, mass flow rates injected (2005-2010) are given in Figure 2; wells AZ-7A and AZ-8 are located in the southern zone while wells AZ-3, AZ-7A, AZ-8, AZ-15, AZ-52 and AZ-61 in the north. Injection fluids consist of a mixture of separated water, condensed steam and air, this mixture is highly evaporated at atmospheric conditions before injection.

3. Results

The total discharge enthalpy distribution of wells, according to January-July 2010 data is shown in Figure 3. As seen in the figure, high enthalpies (>2600 kJ/kg) occur in both the central part of the south zone and the east part of the north zone, where steam wells are located. In contrast, low-enthalpies are found to the west of the field where injection influence is significant, as in well AZ-2A, in the south zone. Previous studies have shown that this well produces high proportions of reinjection returns, i.e. in 2009 such proportion was estimated to be higher than 70% (Barragán et al. 2009). In the center of the field, in wells AZ-23 and 25, low enthalpies are also seen; however, according to previous geochemical data, the fluids from both wells are isotopically-depleted, thus, observed low-enthalpies could not be related to injection (Barragán et al. 2009).

As the injection fluids are evaporated at ambient conditions, they are highly saline and isotopically ($\delta^{18}$O, $\delta$D)-enriched as compared with typical reservoir fluids. For this reason, in wells producing returns from injection, among other characteristic changes, the salinity gradually increases. This is illustrated in Figure 4, where the distribution of total discharge chlorides for 2010 is shown. As seen in the figure, the higher values (~ 3000 mg/kg) are observed in wells AZ-2A and AZ-16 in the south zone, which largely produce returns from injection. In contrast, chlorides decrease towards the east, with the lower values in the north zone (well AZ-43). With respect to 2009 data, a slight dilution in chlorides is noticed in the north zone. In 2009 wells AZ-9 and AZ-28A were found along the 1500 mg/kg iso-contour while in 2010 both wells are close to the 1000 mg/kg contour. This could be due to a noticeable decrease in injection rates in wells AZ-15 during 2010 and well AZ-3 during part of 2010 (Figure 2).

Injection in Los Azufres takes place at about 40°C. Thus, although the injection mixture is heated by reservoir hot rocks, it is expected that in wells affected by injection, reservoir temperatures estimated by a “slow re-equilibration” geothermometer tend to decrease. Reservoir temperature distributions for 2010 (Figure 5) reflect the influence of injection. As seen in the figure, minimum temperatures (<240°C) are observed in the west of the field, in well AZ-2A of the south zone. Temperatures increase to values higher than 290°C to the east in the south zone, (well AZ-18) while in the north maximum temperatures (≥ 300°C) are found close to wells AZ-13 and AZ-32. Minimum temperatures in the north zone (>260°C) occur in well AZ-65D, close to injection wells.
Injection fluids are highly CO₂ depleted regarding reservoir fluids, then injection influence can also be noticed through minimum CO₂ in reservoir liquid contours. Figure 6 shows the CO₂ in the reservoir liquid distribution for 2010 data. As seen in the figure, CO₂ values increase from negligible values at the west toward the east. Such negligible values are clearly related to...
In contrast, maximum CO₂ in reservoir liquid related to natural up-flows values are observed at the southeast (around well AZ-34) but also at the northeast (around wells AZ-5 and 43).

Since injection takes place by gravity at atmospheric conditions, air is unintentionally injected to the reservoir. Thus, N₂ provides actual trajectories of volatile species in the reservoir and increases in N₂ in total discharges of wells are related to the production of injection returns. The total discharge N₂ distribution for 2010 data is given in Figure 7. In this figure, maximum N₂ values (7 mol %) are observed to the southwest of the field in wells AZ-16 and AZ-16AD which are strongly influenced by injection. Contours decrease towards the north and the east of the field, where typical values are lower than 0.5 mol %.

As was already mentioned, injection fluids are isotopically-enriched because of evaporation processes that take place before injection. Thus, the influence of injection is easily noticed through the isotopic behavior of fluids over time. The fluids δ¹⁸O total discharge distribution for October 2010 is given in Figure 8. In this figure, the more enriched values of -2.5 ‰ are located to the west of the south zone (well AZ-2A) because of important injection effects. δ¹⁸O values decrease to -4.5 ‰ in the steam wells AZ-17 and AZ-37 although south zone wells are characterized by δ¹⁸O values of -4 ‰. In the north zone enriched δ¹⁸O wells are found in the west (AZ-42, AZ-65D) but also in the east (wells AZ-13, AZ-9A, AZ-9AD and AZ-32). In the central part of the north zone depleted δ¹⁸O (< -4.5 ‰) values are seen from well AZ-51 to the center of the field (well AZ-23). δD distribution for 2010 data is given in Figure 9. As seen in the figure, the more enriched δD values (of -50 ‰) are found to the southwest of the field in wells AZ-2A and AZ-16 which are adjacent to injection wells AZ-7A.
and AZ-8. As in the case of δ\(^{18}\)O, δD decreases toward the central part of the field (AZ-23 and AZ-25) where the -64 ‰ contour is found. For the north zone, the more δD enriched fluids (-60 ‰) are found in the west, and are attributed to injection. A decreasing tendency towards the center is observed, where the -66 ‰ contour is located and then a δD increase is noticed toward east (wells AZ-13, 32 and 9 among others) where an important up-flow has been suggested. The minimum δD values aligned along wells AZ-51, AZ-48 and AZ-30 in the north and AZ-23 in the center of the field, match the minimum δ\(^{18}\)O values in Figure 8, indicating negligible effects from injection in such area. In Figure 10 δD vs δ\(^{18}\)O relationships for (a) the north zone and (b) the south zone are given. Isotopic results indicate mixing effects between reservoir fluids and injection returns in both zones of the field. The depleted end-members are the compositions of wells not affected (or little affected) by injection while the injection fluids constitute the enriched end-members. In Figures 10 (a) and (b) most of the steam wells are located above the δD vs δ\(^{18}\)O linear trends. This is due to the convection process in the reservoir at temperatures higher than 220°C. Above 220°C deuterium slightly partitions to the steam, leaving the reservoir condensate relatively δD depleted (Truesdell et al. 1977). Most of the wells located below the linear trends in Figures 10 (a) and (b) are two-phase. In these wells, the relative δD depletion regarding the δD vs δ\(^{18}\)O linear trend is caused by the production of some relatively δD depleted condensate which flows-down to the reservoir because of convection.

In Figure 10 (b) it is seen that about 70% of the fluids produced by the well AZ-2A consist of injection returns from well AZ-7A, according to Barragán et al. (2005) while well AZ-16 produces about 50% of injection returns. In contrast, in the north zone the wells are little affected by reinjection with the exception of well AZ-42. This well shows a relatively enriched isotopic composition related to injection into well AZ-52, as suggested by the high injection rates (Figure 2) maintained during part of 2010 into it that caused the shape of the -58 ‰ δD contour around well AZ-42 in Figure 9. In the past, according to Arellano et al. (2005) some of the fluid injected into AZ-52 has also reached wells AZ-5 and 43 while some of the fluid injected into AZ-15 reached wells AZ-13, 28 and 43. However, in contrast with the large effects related to injection in south zone wells, in the north the quantity of the injected fluid, does not seem high enough to produce large changes in the thermodynamic conditions of the fluids feeding wells.

4. Conclusions

The analysis of 2010 chemical and isotopic (δ\(^{18}\)O, δD) data of Los Azufres geothermal fluids was useful to investigate changes occurred due to injection. Geochemical and production indicators included: enthalpies, reservoir chlorides, temperatures, CO\(_2\), N\(_2\) concentrations and δ\(^{18}\)O, δD composition of fluids. The main results for 2010 showed that minimum enthalpies, minimum reservoir temperatures, maximum chlorides, minimum CO\(_2\) in reservoir liquid, maximum N\(_2\) in total discharges along with isotopic enrichment of produced fluids, occur at the west of the field, where injection wells are located. 2010 δD vs δ\(^{18}\)O relationships showed that some wells produce different proportions of injection returns and that injection effects are more important in the south zone.

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