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Emission of some rare gases at the Los Azufres, Mexico, geothermal reservoir

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RESUMEN

La química de los fluidos en el campo geotérmico de Los Azufres, México se originó a partir de procesos volcánicos y es controlada por temperaturas profundas, el pH, la solubilidad y el equilibrio minerales. En este reservorio la fase vapor es de composición heterogénea mostrando un rango amplio de concentraciones de gases no condensables (NCG), variando entre 1% y 9% del peso total del gas en la fase vapor. Los NCG medidos rutinariamente en este reservorio contienen típicamente CO_2 , H_2S, NH_3 , CH_4 , O_2 , H_2 , N_2, He y Ar; también hay Ne, Kr y Xe, pero estos no se registran. El bióxido de carbono es el mayor componente encontrado en el campo, representando entre el 70% y el 99% del peso total de los NCG. El más alto contenido de CO_2 se encuentra en pozos superficiales con alta calidad de vapor. El H_2S es el segundo gas más importante, variando entre el 0.2% y 13% del peso total. Simultáneamente a la extracción del fluido, cantidades significativas de salmuera fría y aire se inyectan dentro del reservorio, modificando su geoquímica natural. La concentración total de gas encontrada en algunos pozos se está incrementando a causa de la cantidad extra de N_2 y Ar atmosféricos inyectados. El cociente molar N_2 /Ar ha estado decayendo con el tiempo alcanzando, en algunos casos, el mismo valor que en la atmósfera. Ambos gases están empujando a los NCG cambiando su distribución espacial natural. El efecto termodinámico de la reinyección ha sido beneficiosa para la producción de energía y la longevidad de este reservorio. Los gases raros como el He y el Ar medidos en este campo muestran una tendencia, pequeña, pero general, a crecer cuando los pozos correspondientes están sujetos a producción continua, con algunas excepciones inusuales. Aparentemente, tal incremento es proporcional a la cantidad de fluido extraído y al tiempo de extracción. En otros casos la dependencia de ambos gases en la producción no está clara. En este trabajo se reportan la evolución observada y la distribución espacial de los NCG y de dos gases raros en el campo geotérmico de Los Azufres para el período 1981-1999.

PALABRAS CLAVE: Gases raros, helio, argón, evolución geoquímica, reservorio geotérmico, reinyección, Los Azufres, Mexico.

ABSTRACT

The chemistry of fluids in the Los Azufres, Mexico geothermal field originated from volcanic processes and is controlled by temperatures at depth, mineral solubility, pH values and mineral equilibrium. Vapor phase at this reservoir has an heterogeneous composition. It shows a wide range of non-condensible gases (NCG) concentration, which ranges between 1% and 9% of total gas weight in the steam phase. NCG are routinely measured in this reservoir and typically contain CO_2 , H_2S, NH_3 , CH_4 , O_2 , H_2 , He, N_2 and Ar; although there are also Ne, Kr and Xe, but these gases are not registered. Carbon dioxide is the major constituent found in the field, representing between 70% and 99% of total NCG weight. The highest CO_2 content is found in shallow wells with high steam quality. H_2S is the second most important gas, varying between 0.2% and 13% in the total weight. Simultaneously to fluid extraction, significant amounts of cold liquid and air are injected into the reservoir, modifying its natural geochemistry. Total gas concentration found in some wells are increased because of the extra amount of atmospheric N_2 and Ar injected. The molar quotient N_2 /Ar has been falling with time reaching in some cases the same value as in the atmosphere. Both gases are pushing the NCG changing their natural spatial distribution. The thermodynamic effect of reinjection has been beneficial for the energy production and longevity of this geothermal field. Rare gases such as He and Ar measured in this field show a low, but general trend to increase when the corresponding wells are subjected to continuous production, with few unusual exceptions. Apparently, such increment is proportional to the amount of fluid extracted and to the time of extraction. But, in other cases, the dependence of both gases on production is not clear. In this paper the observed evolution and spatial distribution of NCG and of those two rare gases at the Los Azufres geothermal field are reported for the period 1981-1999.

KEY WORDS: Rare gases, helium, argon, geochemical evolution, geothermal reservoir, reinjection effects, Los Azufres, Mexico.

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 existent 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, located at an average elevation of 2800 masl, in the central portion of the Mexican Volcanic Belt (Figure 1). Geochemical analysis were 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, or the chemical composition of fluids at depth, but in obtaining quantitative estimations of its global permeability and flow paths under exploitation conditions (Suárez *et al.*, 1997).

Rare, inert or noble gases have as a common characteristic to show an extraordinary stability in their atomic structure. They exist in very small quantities in the atmosphere, (He 5.4 ppm, Ne 18 ppm, Ar 0.93% in air at sea level). ^{36}Ar, Kr and Ne are not produced from rocks but act as atmospheric tracers. Natural rich sources of ^{3}He exist only in the mantle below the Earth's crust indicating magmatic sources. ^{40}Ar, He, ^{222}Rn and ^{136}Xe are continuously created from radioactive decay of U, Th and ^{40}K existent in the Earth's deep rocks (Ellis and Mahon, 1977). The presence of two of those gases, Helium and Argon, has been detected and routinely measured during the last 20 years in the Los Azufres geothermal reservoir; although there are also Ne, Kr and Xe (Prasolov *et al.*, 1999; Barragán *et al.*, 2000), these gases

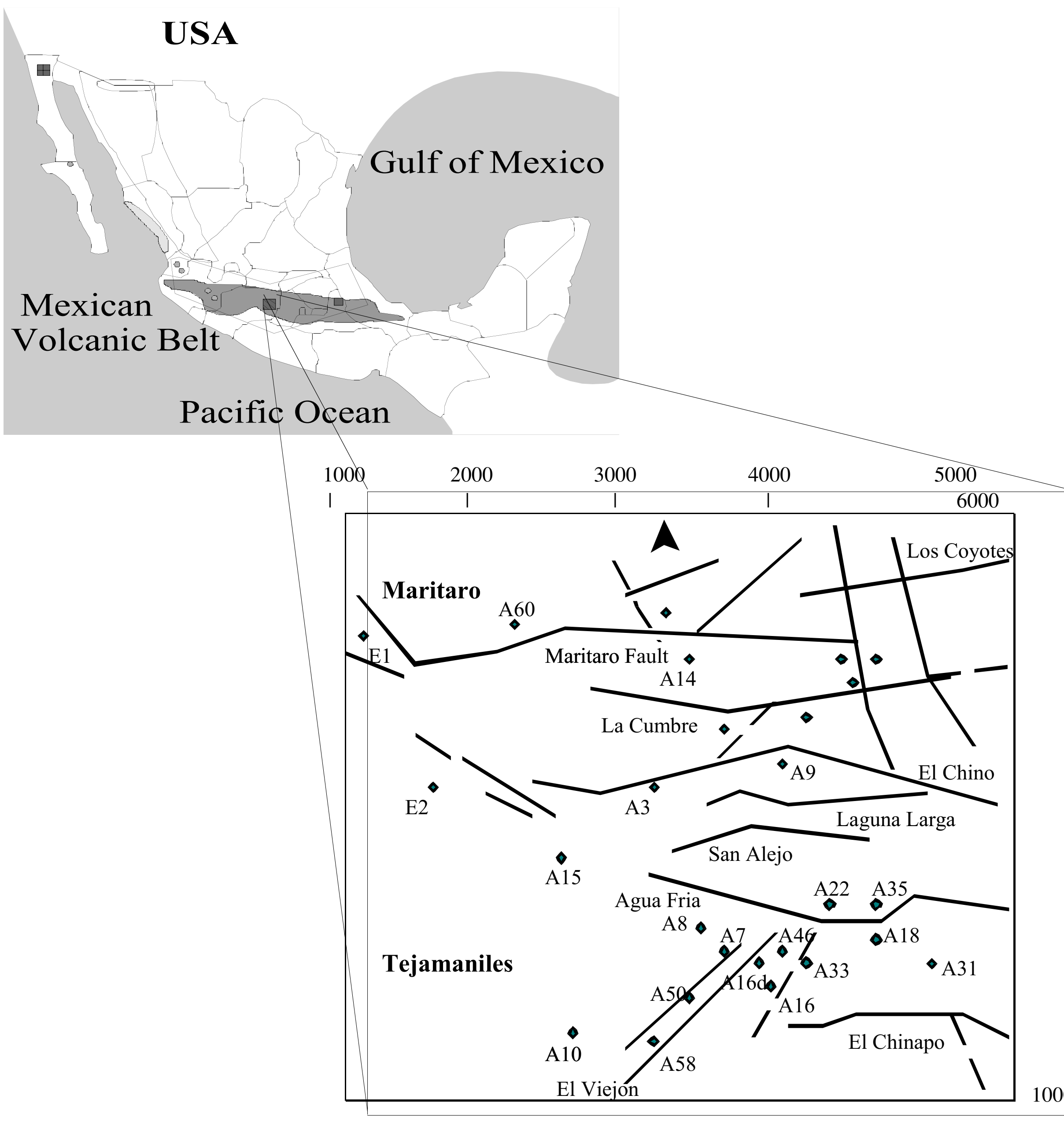

Fig. 1. A simplified map of Los Azufres geothermal field.

are not measured nor registered. Both gases He and Ar have also been observed in Larderello, Italy and in Wairakei, New Zealand. In other geothermal systems as Yellowstone, USA the presence of Ne, Kr and Xe is also detected (Ellis and Mahon, 1977). On the other hand carbon dioxide is the most important NCG constituent of the Los Azufres reservoir. The CO_2 emitted by the wells of this field, represents the fifth part of the same gas produced by a conventional thermal power plant having the same capacity. Since 1929 it is well known that NCG diminish the efficiency of the turbine, reducing notably both, the condensation and the global transfer heat coefficients (Kestin, 1980). This combined effect causes the efficiency of the geothermal power cycle to decrease. Due to the Los Azufres 50 MW_e plant technology, the turbine can only accept a maximum amount of NCG lower than 3% in weight. For this reason it is particularly important to observe the evolution of those gases. At the same time, their careful study allows the inference of important details on the fluid origin and its transport within the reservoir.

THERMODYNAMIC CONDITIONS AT LOS AZUFRES

The Los Azufres hydrothermal reservoir is composed by two volcanic subsystems with the same fluid and similar geochemical and mineralogical characteristics, but whose thermodynamics is 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 single liquid phase reservoir, located between 200 and 2200 masl. It is characterized by an hydrostatic (liquid) vertical profile at an average pressure of 90 bar and an average temperature of 300 °C (Suárez *et al.*, 1997). 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, originating larger steam segregation toward this area. Gases 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. Reservoir boiling processes are lower but also important in the northern zone, where some fluids have started to change their thermodynamic state towards vapor phase, because of pressure decrease.

TYPE OF GASES DETECTED IN THE LOS AZUFRES RESERVOIR

Since August 1982, at the beginning of massive fluid extraction, the vapor phase at Los Azufres reservoir had a natural heterogeneous composition, with a wide range of NCG concentration values between 2% and 8% in weight. Volcanic mechanisms produced the reservoir's fluid composition, which is characterized mainly by the presence of carbon dioxide and hydrogen sulfide. Carbon dioxide is the major constituent of NCG representing today between 70% and 99% in the wells. Noncondensable gases accompanying steam extraction at this field, is a mixture typically formed by 90.8% of CO_2 and 1.2% of H_2S as average values in the total weight of NCG. The remainder 8% of gases is formed by He, Ar, NH_3, H_2, CH_4, O_2 and N_2 (see Table 1 for their numerical values). Because of different boiling intensity of process occurring in both sectors, H_2S being more soluble than CO_2, the CO_2/H_2S quotient has values between 80 and 200 in the southern area and between 60 and 80 in the northern zone. The high concentrations of CO_2 and the existence of carbonate waters in few shallow portions of the reservoir indicate possible connections with thermo-metamorphic processes. The existence of carbonate waters in some upper layers of the reservoir can also be explained because of the ascent of condensed steam. The reservoir brine at Los Azufres is chloride type. Unsaturated hydrocarbons, mainly benzene, have also been detected in the steam extracted from some portions of the southern sector (Tello, 1997). The formation temperature of this hydrocarbon is 600°C. Initial studies of the composition of phases showed that concentration of fluid volatile components such as CO_2 and deuterium decreased with depth (deuterium starts to behave as volatile from 220°C), while concentration of non-volatile components such as oxigen-18 and ion-chloride, increased (Nieva *et al.*, 1983, 1987; Quijano *et al.*, 1989).

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 between 1981 and 1999, by direct sampling in wells at a separation pressure of 8 bar. Table 1 summarizes chemical composition of gases of some representative wells at two different dates. The first date is for the initial state, the second one represents the last measured value in 1998. The 2D contours shown in Figures 2 and 3 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.

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 maximums in the field, reflecting the existence of two natural rich regions of

Table 1

Geochemistry of gases at some wells of the Los Azufres Geothermal Field (concentration in % of total NCG weight)

WELL	DATE	TGAS	CO_2	H_2S	NH_3	**He**	H_2	**Ar**	N_2	CH_4
AZ-05	01/11/1985	2.6	97.40	2.300	0.030	0.0001	0.0180	0.0020	0.0033	0.017
AZ-05	07/24/1998	2.378	98.35	1.450	0.066	0.0014	0.0019	0.0019	0.1213	0.0082
AZ-06	06/20/1986	6.600	98.60	0.545	0.254	0.00030	0.0170	0.0050	0.003	0.027
AZ-06	03/22/1996	4.209	96.32	0.462	0.000	0.00065	0.0187	0.0432	3.1360	0.0164
AZ-09	06/02/1987	0.800	95.22	3.034	1.128	0.00013	0.0110	0.0030	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	0.092
AZ-13	01/11/1985	1.860	96.30	3.430	0.066	0.0005	0.0249	0.0022	0.0080	0.0127
AZ-13	07/24/1998	2.366	93.28	1.426	0.10	0.00119	0.0308	0.4428	4.8041	0.0141
AZ-17	01/11/1985	5.200	98.61	1.290	0.060	-	0.0110	0.0050	0.0003	0.0008
AZ-17	01/27/1997	3.332	82.67	1.217	0.258	-	0.0378	0.2022	15.6150	0.0064
AZ-18	02/20/1987	6.200	98.93	0.570	0.271	0.00010	0.0040	0.0010	0.211	0.1900
AZ-18	06/01/1998	9.974	99.33	0.296	0.054	0.00027	0.0037	0.0069	0.2735	0.0310
AZ-22	04/27/1988	1.100	96.02	2.987	0.158	-	0.0235	0.0531	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	0.0254
AZ-33	07/21/1986	6.600	98.58	0.497	0.435	0.00020	0.0180	0.0030	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	0.0232
AZ-41	03/25/1987	0.600	95.63	2.967	0.162	0.00017	0.0230	0.0240	1.1310	0.0570
AZ-41	05/30/1998	2.421	97.36	1.536	0.094	0.00017	0.0133	0.0129	0.9533	0.0322
AZ-046	07/21/1986	2.600	97.65	0.997	0.473	0.00020	0.0350	0.0140	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	0.0017
AZ-16D	06/20/1986	3.000	90.60	2.000	0.750	0.00003	0.0240	0.1230	6.500	0.0030
AZ-16D	11/21/1995	4.975	52.14	1.400	0.138	0.00286	0.0250	0.7043	45.7340	0.0005

NCG, having concentrations larger than 8% in weight. Both zones were located in the southern portion of the reservoir. The first one was to the west and corresponded to wells with the highest steam quality (*e.g.* Az17). The second one, at the eastern portion, was measured at well Az18 when it had little amount of steam. Toward the north, NCG concentration diminished and was notably minor than in the southern sector. A certain E-W alignment existed, corresponding to faults oriented in the same direction. A NCG gradient, originated by the higher concentration of gases in the southern sector, was also observable in S-N direction.

Distribution of NCG concentrations was altered by reservoir's exploitation between 1982 and 1999. This is shown in Figure 3. A clear trend of increasing NCG is observed. This trend follows a slightly WE direction in both central and northern areas. In the southern zone NCG increment has a remarkable growing drift toward the southeast, but restricted to the Y-coordinates between 1250 m and 2500 m. It is also observed that 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 the trend is minor, but conserves a similar profile between 5500 and 6500 m Y-coordinates. NCG concentration gradient follows the same orientation as Laguna Larga and Marítaro faults.

Rare gases such as He and Ar measured in this field, show a general trend to increase (Table 1, Figures 4 to 7) when the corresponding wells are subjected to continuous production, with few unusual exceptions. Apparently, such increment is proportional to the amount of fluid extracted and to the time of extraction. But in other cases the dependence of both gases on production, is not clear. Figures 4 and 5 show the time distribution or evolution of Ar and He concentration at well Az-16D. The observed behavior can be partially explained because of the continuous amount of reinjected liquid that is performed to the West of this well. Figure 6 shows the oscillations of He at well Az-05. The

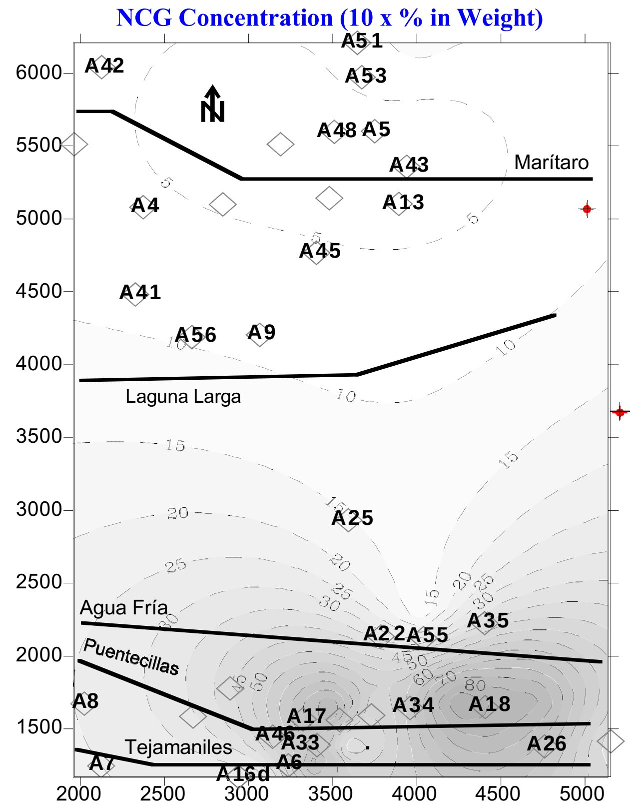

Fig. 2. Spatial distribution of total gases 1981-1984.

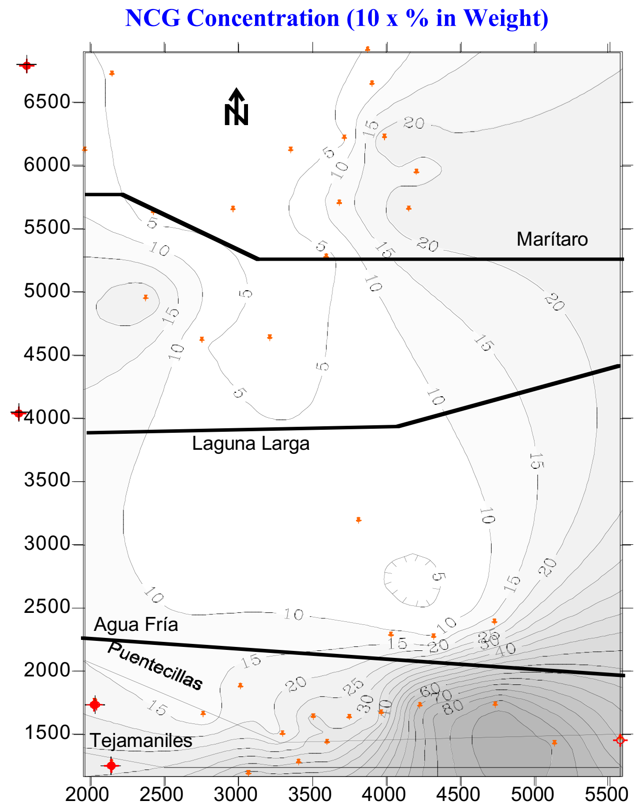

Fig. 3. Spatial distribution of total gases in 1999.

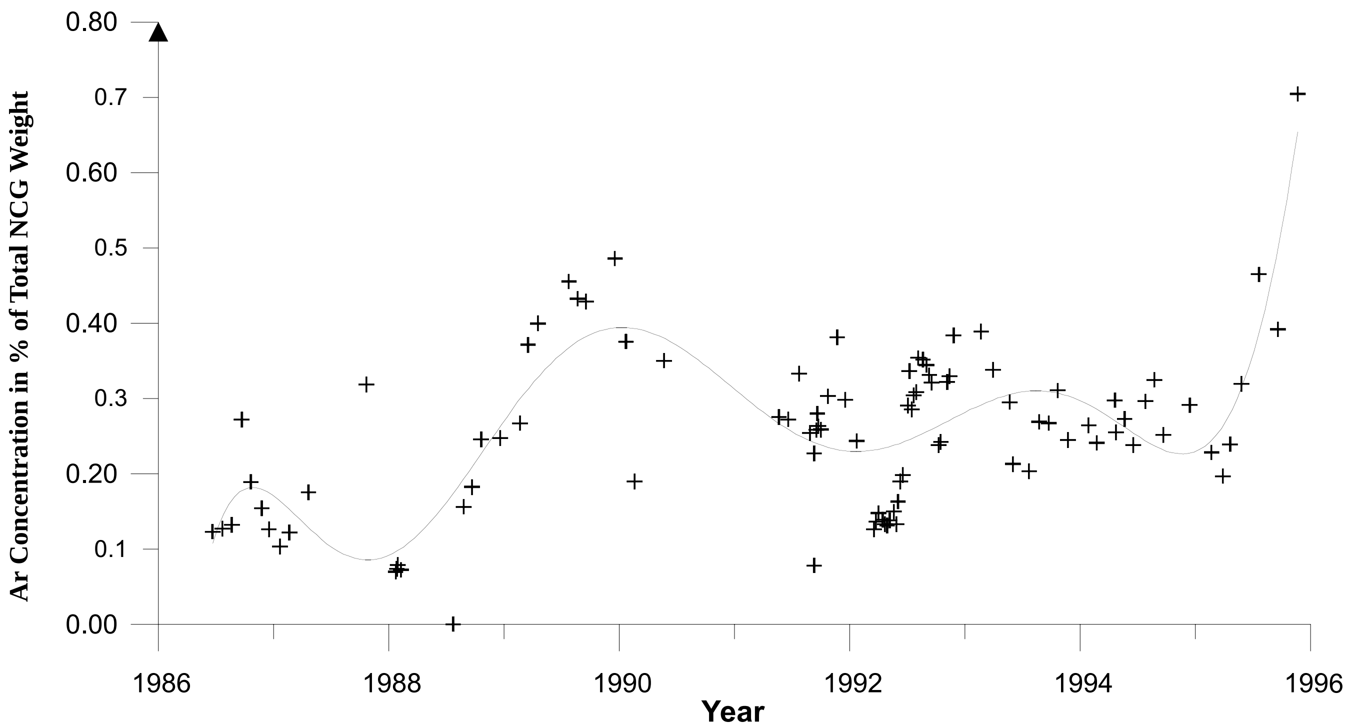

Fig. 4. Time distribution of argon in Well Az-16D.

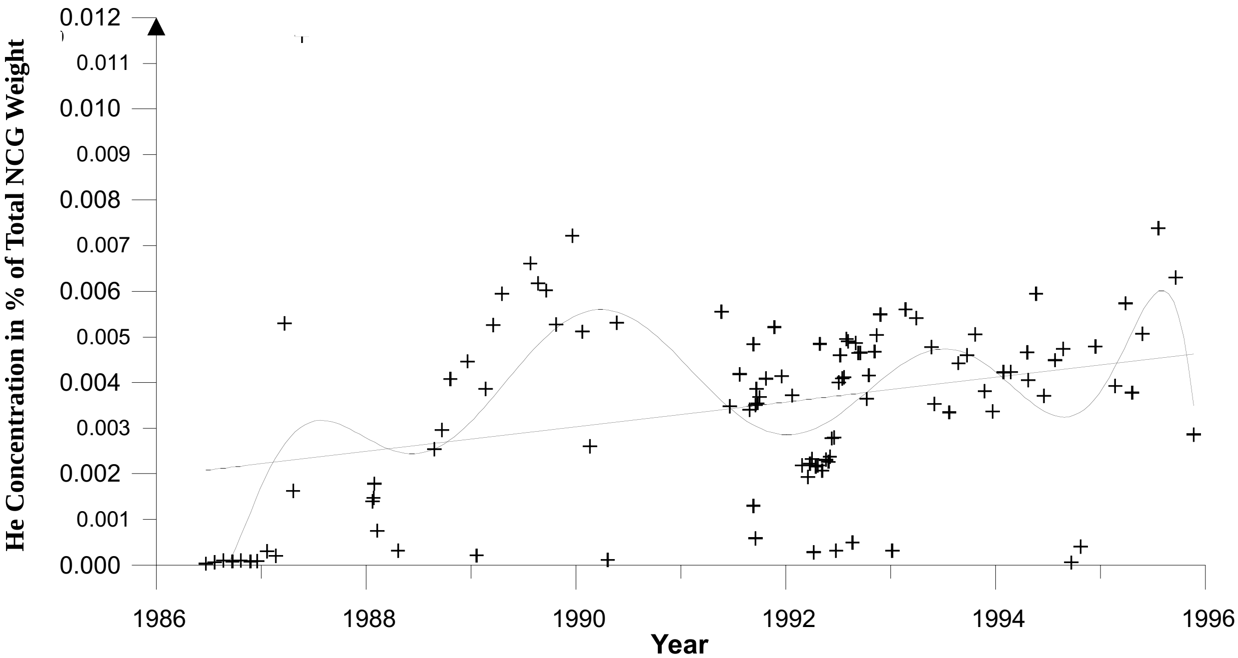

Fig. 5. Time distribution of helium in Well Az-16D.

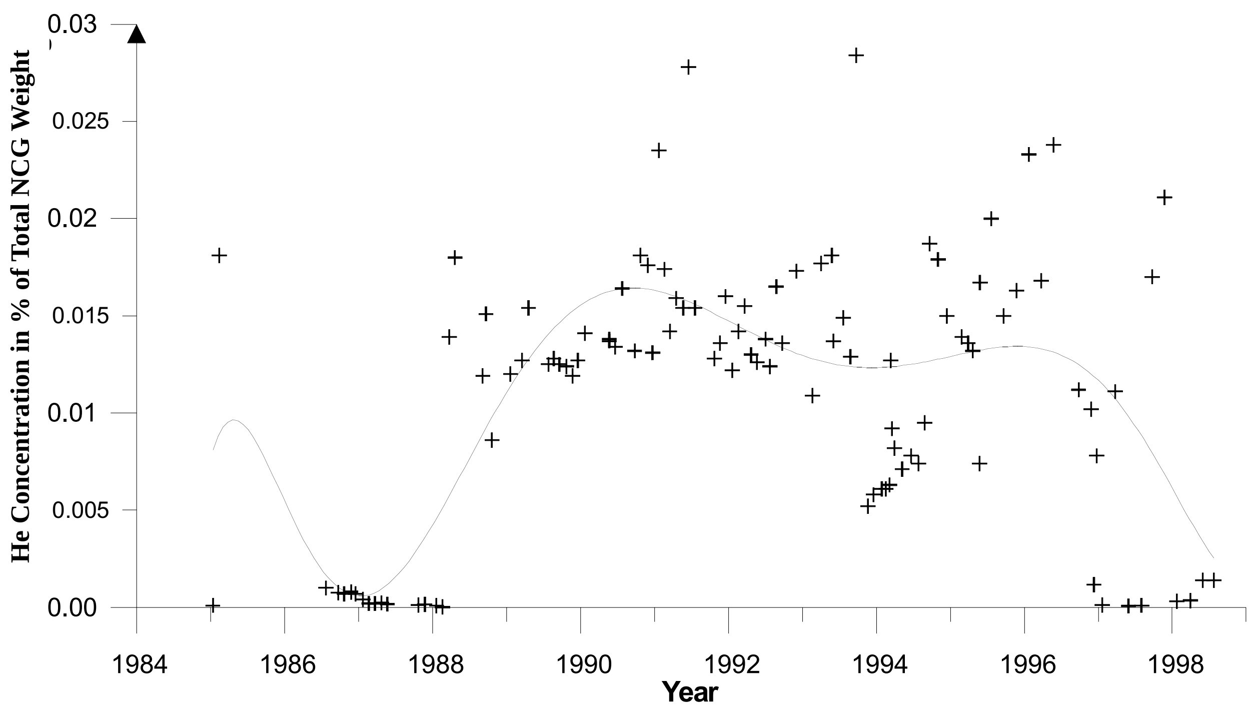

Fig. 6. Time distribution of helium in Well Az-05.

trend of Ar at well Az-17 is shown in Figure 7. Anomalous high concentrations of He have also been found as precursors of seismic events (Favara *et al*., 2001). As another example some important anomalies in He concentration at Los Azufres were reported by Santoyo (*et al*., 1991) as same precursors of seismic activity in Mexico in 1985.

DISCUSSION AND RESULTS

Original chemical composition of gases at Los Azufres field is analogous in some aspects to other volcanic geothermal reservoirs. The difference here is that NCG concentrations are higher and that reinjection of waste liquid and air is carried out parallel to the exploitation of the field since 1982. Simultaneously to fluid extraction, injected water drags air toward the reservoir through the injection wellheads (Horne *et al.*, 1989; Suárez *et al.*, 1997). Air arrives to deep reservoir zones and breaks down into its primary elements. Oxygen reacts immediately by combination with other components in the rock formation. Nitrogen and Argon are freely displaced from injection zones to production sectors. The concentration evolution of these two gases exhibits a remarkable increase in several producing wells. In some of them the increment is exponential, up to 6 times larger than initial concentrations (Figures 4 and 7). The molar quotient N_2/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 increase the total NCG in some wells due to the extra amount of atmospheric N_2 and Ar, pushing the reservoir gases in the same direction. Concentration changes of CO_2, Ar and N_2 are valuable indicators of communication between several zones of the reservoir. Their displacements show the traces of high permeability paths related to faults and fractures. A multicomponent numerical simulator has been used to study the reservoir using this geochemical information (Suárez *et al.*, 1997). Those results were useful to analyze non-isothermal pressure tests and to deduce global permeability values between 100 md (milidarcy) and up to 1000 md in both zones.

Carbon dioxide is the major constituent found in the field representing between 70% and 99% in total NCG weight. H_2S is the second most important gas in total weight, it varies between 0.2% and 13%. In some wells a relatively high He concentration has been detected (Table 1). This fact suggests slow circulation of magmatic fluids carrying the helium in the Earth's crust. At major depth the gas amount is minor; while in shallow zones NCG concentration increases. Wells affected by injection present a complex oscillatory behavior of its CO_2 concentration. The width and amplitude of oscillations are reflections of extraction, reinjection, permeability and production of CO_2 combined. NCG concentration has a close relationship with thermodynamic conditions of producing wells. Wells having rich or growing gas concentrations (NCG > 2% in weight) have high steam quality (75%). Wells with poor and constant gas concentrations (1%) have lower and constant steam qualities. There is a direct relationship between large amounts of NCG and high enthalpy wells with higher vapor fraction. It also exists an inverse relationship between bottom hole temperature-pressure and NCG: their concentration diminishes when pressure and temperature increase. This is because wells at these conditions have lower enthalpy and less or zero steam quality. Detailed descriptions of these relations were already reported (Suárez *et al.*, 1997).

CONCLUSIONS

- Los Azufres geothermal reservoir is a volcanic system in total chemical equilibrium. Its original magmatic fluids have been totally neutralized by geochemical water-rock

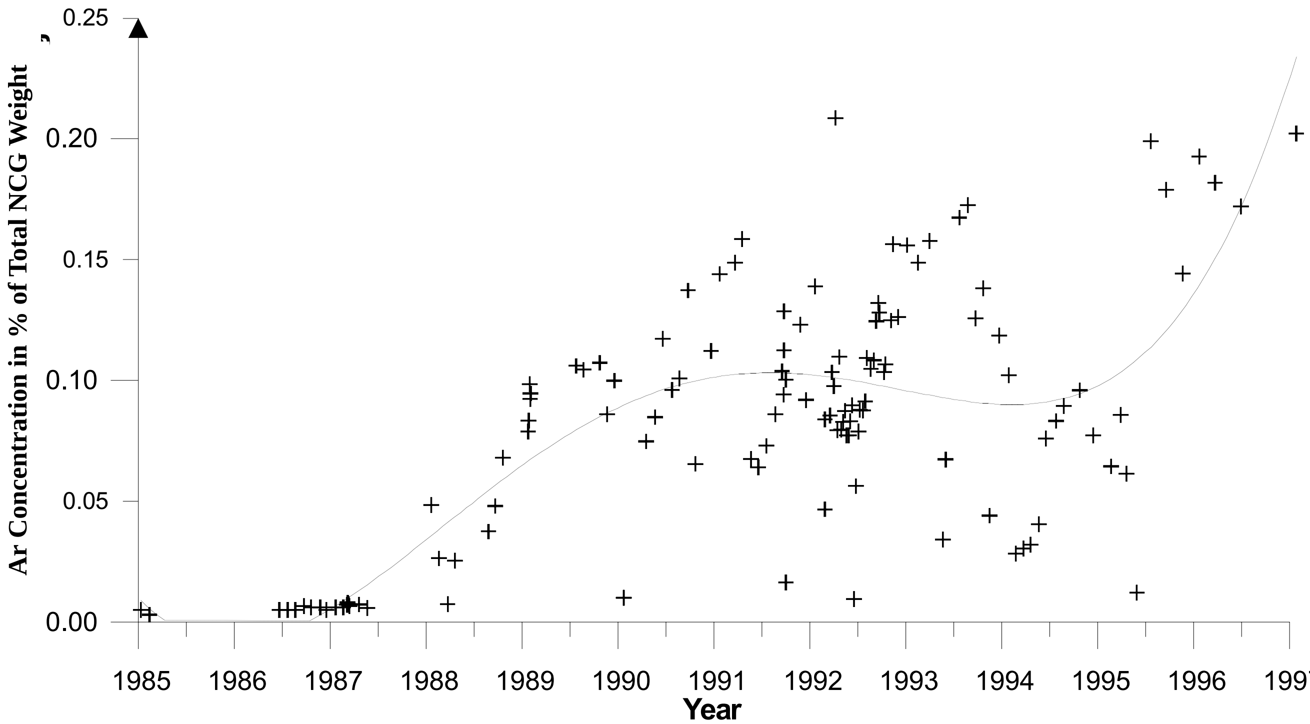

Fig. 7. Time distribution of argon in Well Az-17.

interactions. Its NCG concentrations are higher than in other volcanic fields.

- Steam phase at Los Azufres reservoir has an heterogeneous composition, showing a wide range of NCG concentration values between 1% and 9% in total weight. The general observed trend is that at depth the gas amount is minor; 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 reduction in the numerical value of the quotient CO_2/ H_2S in S-N direction.

- Rare gases such as He and Ar show a general trend to increase when the corresponding wells are subjected to continuous production. Apparently, such increment is proportional to the amount of fluid extracted and to the time of extraction. This is also an effect of air and brine reinjection into the reservoir.

- Wells having rich or growing gas concentrations greater than 2% in weight have both high steam quality and higher enthalpy. Wells with poor and constant gas concentrations have lower steam qualities.

- Injection of waste liquid and air contributes to increase total gas concentration in some wells because of the extra amount of N_2, Ar and other atmospheric gases.

- Reinjection modifies field's geochemistry because it pushes reservoir NCG toward the production zones, changing their current spatial distribution.

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