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### EVOLUTION OF HELIUM AND ARGON AT A VOLCANIC GEOTHERMAL RESERVOIR

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### ABSTRACT

Vapor phase at volcanic reservoirs has a heterogeneous composition, showing very often a wide range of non-condensible gases (NCG) concentration. For example, 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. The NCG concentration at this field ranges between 1% and 9% of total gas weight in the steam phase, and it typically contains  $CO_2$ ,  $H_2S$ ,  $NH_3$ ,  $CH_4$ ,  $O_2$ ,  $H_2$ ,  $N_2$ , He and Ar. It may also contain Ne, Kr and Xe, but these gases are not recorded. Carbon dioxide is the major constituent found in the field, representing between 70% and 99% of total NCG weight. H<sub>2</sub>S 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. Total gas concentration found in some wells are increased because of the extra amount of atmospheric N<sub>2</sub> and Ar injected. 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. In other cases, the dependence of both gases on production is not clear. Nevertheless, important anomalies in He concentration at Los Azufres were observed before the occurrence of some earthquakes in Mexico.

### **INTRODUCTION**

The Los Azufres, Mexico geothermal field is a reservoir of considerable magnitude inside a naturally fractured medium formed by andesites, located at an average elevation of 2800 masl, in the central portion of the Mexican Volcanic Belt (Fig. 1). 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 <sup>3</sup>He exist only in the mantle below the Earth's crust indicating magmatic sources. <sup>40</sup>Ar, He, <sup>222</sup>Rn and <sup>136</sup>Xe are continuously created from radioactive decay of U, Th and <sup>40</sup>K existent in the Earth's deep rocks (Ellis & 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 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 & Mahon, 1977). On the other hand carbon dioxide is the most important NCG constituent of the Los Azufres reservoir. The CO<sub>2</sub> 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<sub>e</sub> 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.

### THERMODYNAMICS OF LOS AZUFRES

This 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 (Suarez 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

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<sub>2</sub> and 1.2% of H<sub>2</sub>S as average values in the total weight of NCG. The remainder 8% of gases is formed by He, Ar, NH<sub>3</sub>, H<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> (see Table 1 for their numerical values). Because of different boiling intensity of process occurring in both sectors, H<sub>2</sub>S being more soluble than CO<sub>2</sub>, the CO<sub>2</sub>/H<sub>2</sub>S 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<sub>2</sub> 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). Few NCG data were obtained at Los Azufres between 1981 and 1983. Systematic measurements of NCG began in 1984, with the use of gas chromatography. Table 1 summarizes chemical composition of some 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.

Rare gases such as He and Ar measured in this field, show a general trend to increase (Table 1, Figs. 2 - 5) 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 2 and 3 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 4 shows the oscillations of He at well Az-05. This behavior could be partially explained by the influence of micro-seismological events on rock poroelasticity 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. The trend of Ar at well Az-17 is shown in figure 5.

# 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 (Figs. 2 and 5). 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<sub>2</sub>, Ar and N<sub>2</sub> 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 (Suarez 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<sub>2</sub>S is the second most important gas in total weight, it varies between 0.2% and 13%. In some wells a relatively high He concentration have 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.

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

- 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.

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WELI	DATE	TGAS	CO	H <sub>2</sub> S	Ho	Ar	Na
AZ 05	DATE 01/11/1005	26	07.40	2 200	0.0001	AI	0.0022
AZ-05	01/11/1985	2.0	97.40	2.300	0.0001	0.0020	0.0055
AZ-05	07/24/1998	2.378	98 35	1 450	0.0014	0.0019	0.1213
112 05	0772471990	2.370	20.55	1.450	0.0014	0.0017	0.1215
AZ-06	06/20/1986	6.600	98.60	0.545	0.00030	0.0050	0.003
1	00,20,1900	0.000	20100	010 10	0100020	010020	01002
AZ-06	03/22/1996	4.209	96.32	0.462	0.00065	0.0432	3.1360
AZ-09	06/02/1987	0.800	95.22	3.034	0.00013	0.0030	0.3880
AZ-09	07/24/1998	0.416	93.57	5.010	0.0042	0.0371	0.7464
	0112111990	01110	20107	01010	0.00.12	010071	017 101
AZ-13	01/11/1985	1.860	96.30	3.430	0.0005	0.0022	0.0080
1	01,11,1900	11000	20120	01.00	010000	010022	010000
AZ-13	07/24/1998	2.366	93.28	1.426	0.00119	0.4428	4.8041
AZ-17	01/11/1985	5.200	98.61	1.290	-	0.0050	0.0003
	01/11/1900	0.200	20101	11200		0.00000	010002
AZ-17	01/27/1997	3,332	82.67	1.217	_	0.2022	15.6150
	01/2//1///	01002	02107	11217		0.2022	1010100
AZ-18	02/20/1987	6 200	98.93	0 570	0.00010	0.0010	0.211
112 10	02/20/1907	0.200	20.25	0.570	0.00010	0.0010	0.211
AZ-18	06/01/1008	0.07/	00.33	0.296	0.00027	0.0069	0.2735
112-10	00/01/1990	5.574	<i>))</i> .55	0.270	0.00027	0.000)	0.2755
17 22	04/27/1088	1 100	06.02	2 087		0.0521	0.6752
AL-22	04/27/1988	1.100	90.02	2.907	-	0.0551	0.0752
17.00	07/07/1009	1 117	06.92	2 270	0.00017	0.0007	0.0654
AL-22	07/27/1998	1.11/	90.85	2.279	0.00017	0.0097	0.0654
17.00	07/01/1007	6.600	00.50	0.407	0.00020	0.0020	0.4200
AZ-33	07/21/1986	6.600	98.58	0.497	0.00020	0.0030	0.4300
AZ-33	07/27/1998	3.163	97.53	0.697	0.00059	0.0226	1.6393
AZ-41	03/25/1987	0.600	95.63	2.967	0.00017	0.0240	1.1310
AZ-41	05/30/1998	2.421	97.36	1.536	0.00017	0.0129	0.9533
AZ-046	07/21/1986	2.600	97.65	0.997	0.00020	0.0140	0.8270
AZ-46	08/28/1998	2.460	95.22	1.369	0.00074	0.0611	3.2340
AZ-16D	06/20/1986	3.000	90.60	2.000	0.00003	0.1230	6.500
112 102	50,20,1900	2.000	20.00	2.000	0.00005	0.1200	0.000
A7-16D	11/21/1995	4 975	52.14	1 400	0.00286	0 7043	45 7340
	11/21/1995		52.14	1.100	0.00200	0.7045	10.70-10
				I		1	

 Table 1.- Some Gases at Wells of the Los Azufres Geothermal Field (concentration in % of total NCG weight).







Fig. 2.- Time Distribution of Argon in Well Az-16D

Fig. 3.- Time Distribution of Helium in Well Az-16D







Fig. 4.- Time Distribution of Helium in Well Az-05