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## Bouillante geothermal fluid: mixing and water/rock interaction processes at 250°C

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ABSTRACT: In the geothermal Bouillante area, electricity is presently produced from well BO-2 only. Following a successful stimulation operation in 1998, a second well BO-4 will be soon connected to the power plant. This paper presents relevant geochemical data obtained for both wells during 1998 and 2000. For some dissolved species, results show discrepancies between surface and down hole samples. In this case, additional information from thermal springs can be very useful to reconstruct the chemical composition of the deep fluid. Despite an high water-rock ratio, the deep NaCl brine (20 g/l) composed of about 58 % seawater and 42 % freshwater reacts with volcanic rocks at about 250°C reaching chemical equilibrium with a mineralogical assemblage as shown by its composition and by saturation calculations.

#### 1 INTRODUCTION

The geothermal Bouillante area is located on the western coast of Basse-Terre (Guadeloupe, French West Indies), which belongs to the active volcanic island arc of the Lesser Antilles (Fig. 1a). This area is developed near the seaside and around the town of Bouillante, where numerous hydrothermal events such as hot springs, mud pools, steaming ground and fumaroles occur (Fig. 1b). Presently, out of 4 exploratory wells drilled in the 70's, only the well BO-2 (around 120 t/h of brine and 33 t/h at 5.5 bar-g separation pressure; 240-250°C at 320 m depth) is connected to a power plant. After a positive stimulation operation carried out on well BO-4 in 1998 and several production tests, it has been decided to connect this second well to the power plant. Its production is presently similar to that of BO-2 (Sanjuan et al. 1999, 2000). The most significant water levels are between 550 and 1100 m where a maximum temperature of 248°C was recorded (Sanjuan et al. 2000).

The aim of this paper is to discuss data obtained for the wells BO-2 and BO-4 during 1998 and 2000 and to try to reconstruct the chemical and isotopic composition of the deep geothermal fluids using well and spring waters. The predictable nature of the fluid composition is useful in understanding potential scaling and environment problems during the production stage and for future exploration drilling related to the development of the geothermal field.

#### 2 SAMPLING AND ANALYTICAL DATA

Two Multiple Tracer Tests (MTT) using several organic tracers were carried out between BO-4 and BO-2 before (March-June 1998), during and after the stimulation operation by thermal cracking (August-October 1998) in order to evaluate the hydraulic connections between both wells. Around 8000 m<sup>3</sup> of cold seawater were injected into BO-4 during the stimulation experiment. Details of the MTT procedure are presented in Sanjuan et al. (1999).

The geochemical monitoring was performed at well BO-2 and 3 neighbouring thermal springs S1, S2 and S3 (Fig. 1b). The geothermal brine was collected at about 35°C after cooling in the high pressure separator. High-pressure steam condensates and non condensable gases were sometimes sampled. Except for temperature measurements, all other on site analyses (pH, specific conductivity, Eh, alkalinity and dissolved Ca, Cl, SiO<sub>2</sub>, NH<sub>4</sub>, HS, fluorescein, Na-naphtionate concentrations) were carried out in the laboratory of the geothermal power plant using classical analytical techniques. The Na-benzoate tracer was analysed in the BRGM laboratories.

During the geochemical monitoring, 17 fluid samples (6 from BO-2 and 11 from the springs) were selected and conditioned according to the required specifications for chemical analyses (major and trace species, artificial tracers) and isotopic measurements ( $\delta D$ ,  $\delta^{18}O$ ) actually used in the BRGM laboratories.

On the first production test (from July 15 to 17, 1998), reliable and accurate physical and chemical

data on separated brine, steam and non condensable gas were collected from BO-4. The main aim of the 3 subsequent tests (from October 3 to 10, 1998; from July 1 to 14, 1999; from February to May 2000) was to monitor any potential change in the fluid characteristics due to the stimulation and production.



Figure 1a. Location of Bouillante area in the Guadeloupe Archipelago (FWI).



Figure 1b. Location of the geothermal wells and thermal springs used for the geochemical monitoring.

At the end of the tests, more than 65,000 m<sup>3</sup> of total fluid were discharged from BO-4. Sampling of separated fluids at separator and weir-box, on site and Gas/Steam Ratios (GSR) measurements carried out for the geochemical monitoring are described in Sanjuan et al. (1999; 2000).

During the 1<sup>st</sup> and 3<sup>rd</sup> test (short term tests), only 1 sampling of fluids from weir-box and separator was performed for complete chemical and isotopic analyses. During the 2 other tests, 5 fluid samples were collected at separator and 12 brine samples at weir box for detailed analyses. 9 GSR measurements and 7 chemical gas analyses were performed for BO-4 against 2 measurements and 1 analysis for BO-2. Three down hole fluid samples were collected from BO-4 between 330 and 640 m (August 1, 1998; July 1 and 2, 1999) and one from BO2, at 320 m (July 7, 1999), using a KUSTER sampler. Most of on site measurements and sample preparations were performed immediately after sampling.

Several submarine thermal springs (outflow temperatures up to 95°C) were sampled in October 1998 from the Bouillante Bay. Chemical and isotopic analyses similar to those performed for BO-2 and BO-4 fluid samples were carried out.

All the analyses were performed using standard water analytical techniques such as titration, ion electrode, potentiometry, colorimetry, atomic absorption spectrophotometry, ion and HPLC chromatography, inductively coupled plasma-mass spectrometry (ICP-MS), mass spectrometry. The precision of major and trace species is better than  $\pm 5$  % and 15 % respectively. The precision of  $\delta D$  and  $\delta^{18}O$  determination is  $\pm 0.8$  ‰ and  $\pm 0.1$  ‰. Ion balance values lower than 5 % suggest a good quality and coherence of the major species analyses.

#### **3 DISCUSSION**

#### 3.1 Chemical composition of gases

All measurements carried out between 1998 and 2000 indicate that GSR ranges from 0.5 to 1.0 % in mass for BO-4 and is close to 0.4 % for BO-2. These values are consistent with that determined for BO-2 in previous studies (0.4 %; Demians D'Archimbaud and Munier-Jolain 1975). The chemical gas composition is similar for both wells and that considered as the most representative (less contaminated by atmospheric gases) is reported in Table 1.

Table 1. Corrected chemical gas composition (mol %) for wells BO-2 and BO-4.

Gas	%	Gas	%
$\overline{CO_2}$	95.1	He	0.0035
$\overline{\mathbf{O}_2}$	0.09	$H_2S$	2.78
$N_2$	3.60	$\tilde{CH_4}$	0.40
Ār	0.04	$C_2H_6$	0.005
$H_2$	0.48	$C_3H_8$	0.0005

The N<sub>2</sub>/Ar volume ratio (90) is close to the atmospheric value (84). Given the low  $O_2$  content, this ratio is probably the result of the presence of atmospheric N<sub>2</sub> and Ar in the reservoir. These gases come with seawater and superficial freshwaters which mix in the reservoir, as shown in the next chapter.

The <sup>13</sup>C value of the BO-2 fluid is -2.6 ‰, a value far above that of typical data of basaltic magmas (about -7 ‰). This probably reflects a mixed origin of CO<sub>2</sub> (magmatic and sedimentary origin).

According to Allard (pers. comm.), a significant part of He has a mantellic origin.  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio in BO-4 is 3 to 4 times higher than the atmospheric ra-

tio. These gaseous leaks would be controlled by regional tectonics rather than by a relatively small magmatic extrusion. The value obtained in BO-4, about 2 times lower than the value measured at the top of the Soufrière volcano, also suggests a mixing with crustal helium.

Gas geothermometers such as  $CO_2/H_2S/H_2/CH_4$ (D'Amore and Panichi 1980) and  $H_2/Ar$  (Giggenbach and Goguel 1989), applied on the chemical composition of gases selected in Table 1, give temperatures of 226 and 251°C respectively. These are close to the measured temperature which suggests that these gases are near equilibrium state at reservoir conditions. Partial CO<sub>2</sub> and H<sub>2</sub>S pressures (P<sub>CO2</sub> and P<sub>H2S</sub>) were estimated at 240-250°C using the D'Amore and Truesdell equation (1985). With a GSR value of 0.4 % in mass and a water pressure of 42 bar (Sanjuan et al., 1999), P<sub>CO2</sub> and P<sub>H2S</sub> are close to 1.8 and 0.015 bar, respectively. Brombach et al. (2000), using the K-Ca geobarometer (Giggenbach 1988), have calculated a value of P<sub>CO2</sub> of 0.32 bar.

## 3.2 *Chemical and isotopic composition of the deep brine*

Chemical and  $\delta D$ ,  $\delta^{18}O$  analyses of the BO-2 and BO-4 fluids collected at surface were corrected using the steam-liquid proportions at separation temperature and pressure (Sanjuan et al. 1999). Steam condensate is essentially composed of H<sub>2</sub>S and NH<sub>4</sub>.

Accurate pH values are necessary for the mineral saturation index determinations. The steam condensate has a pH of about 4.5, whereas neutral conditions are found for the surface brines. The values of pH measured in the down hole samples at 25°C range from 5.5 to 6.0. A value of 5.3 was estimated for the pH of the deep fluid using the EQ3NR geochemical code (Wolery 1995), a P<sub>CO2</sub> of 1.8 bar and assuming that the deep brine is in equilibrium with calcite at 250°C. The corresponding HCO<sub>3</sub> concentration was found to be 38 mg/l. This value is higher than that measured in the surface brine samples (24 mg/l) but is lower than that obtained from the down hole samples (80 mg/l). A contamination during down hole sampling, due to the presence of carbonate deposits in the KUSTER sampler which are dissolved at lower temperature, could explain this last discrepancy. The use of an higher value of  $P_{CO2}$ would allow to increase the HCO<sub>3</sub> concentration but would yield a much lower pH. A  $P_{CO2}$  of 0.32 bar leads to a pH value of 5.7 and a HCO<sub>3</sub> concentration of 16 mg/l. These values seem less reliable.

A decrease in Ca, Mg, Al, Si, Fe, Sr, Li and trace metal concentrations of the surface fluids is observed relative to the down hole samples (Sanjuan et al. 1999, 2000). A slight precipitation of carbonate, alumino-silicate and poly-metallic sulphide minerals is suspected during the deep fluid rise from the wells. Deposits of silica in major part, calcite, chalcopyrite, sphalerite, galena, silver, anglesite were found in very small amounts after two caliper tests into BO-2 in 1993 and 2000. Reconstructed chemical and isotopic composition is reported in Table 2. Eh value and  $H_2S$ , Fe, Ag and Cd concentrations are not presented because they remain poorly constrained.

Table 2. Reconstructed chemical and isotopic composition of the deep geothermal fluid.

Species	value	Speci	es value
pН	$5.3 \pm 0.3$	В	12.5 ± 1.3 mg/l
TDS	$20.0 \pm 1.0$ g/l	Li	$5.0 \pm 1.0$ mg/l
Cl	$12.0 \pm 0.6$ g/l	Sr	$17.5 \pm 2.0$ mg/l
Na	$5.1 \pm 0.3$ g/l	Ba	$6.5 \pm 1.0 \text{ mg/l}$
Ca	$1.8 \pm 0.1$ g/l	Mn	$15.0 \pm 3.0$ mg/l
K	$750 \pm 40$ mg/l	Rb	$2.0 \pm 0.3$ mg/l
HCO <sub>3</sub>	$50 \pm 20$ mg/l	Cs	$260 \pm 30 \mu g/l$
Mg	$12.0 \pm 2.0$ mg/l	Cu	$15.0 \pm 1.0$ mg/l
$SO_4$	$13.0 \pm 2.0$ mg/l	Ni	$2.0 \pm 0.5$ mg/l
SiO <sub>2</sub>	$500 \pm 30$ mg/l	Zn 65	$0 \pm 100 \mu g/l$
$NH_4$	$1.7 \pm 0.2$ mg/l	As 45	$0 \pm 50 \mu g/l$
Al	$110 \pm 20 \mu g/l$	Pb	$4.0 \pm 1.0 \ \mu g/l$
Br	$42.0 \pm 5.0$ mg/l	Co	$13.0 \pm 1.0 \mu g/l$
F	$0.9 \pm 0.1$ mg/l	Cr	$15.0 \pm 2.0 \mu g/l$
δD	$-1.2 \pm 0.8$ ‰	$\delta^{18}O$	$-1.1 \pm 0.2$ ‰

As shown in Figure 2, knowing the Cl concentration of the geothermal brine, the thermal submarine springs may be useful to validate or determine the concentrations of most major species and some trace elements (B, Sr, Li, Rb, Cs) in the geothermal brine. Indeed, the fluids from these springs reflect simple



Figure 2.  $Cl-SO_4$  and Cl-Li diagrams for seawater, submarine thermal springs of the Bouillante Bay and deep geothermal brine.

mixing between geothermal fluid and seawater.

The geothermal fluid is a Na-Cl brine with a TDS  $\sim 20$  g/l. All the results suggest a probable common origin of the deep geothermal fluid discharged from BO-2 and BO-4. However, the MTT indicate no direct hydraulic connections between the two wells and the 3 neighbouring springs. As recognised by

Sanjuan et al. (1999, 2000), Cl and Br concentrations and  $\delta D$  and  $\delta^{18}O$  values indicate that the geothermal fluid represents a mixture of about 58 % seawater and 42 % freshwater (surface waters fed by rainfalls in the western side of the Bouillante Pitons). This type of mixture can be explained by the N100-120° trending fractures (Fig. 1b).

The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios of the BO-2 and BO-4 fluids (0.705000  $\pm$  0.00004) characterise an interaction process with basalt or andesite close to an equilibrium state (Pilot 1974). Relative to a diluted seawater, the geothermal fluid is depleted in Mg, SO<sub>4</sub>, Na and enriched in K, Ca, Si, B, Li, Sr, Ba, Mn, Cs, Rb, As and trace metal ions. These trends are generally observed for basalt-seawater interaction studies. There was no significant change in the composition of the BO-4 fluids produced before and after stimulation and during the long term production.

After stimulation, the very low amount of injected seawater always observed in the discharged brines from BO-4 is indicative of a relatively large interconnected reservoir volume and of a high water-rock ratio. This is in agreement with the isotopic signature of <sup>18</sup>O in water and <sup>34</sup>S in dissolved SO<sub>4</sub> (19.4 ‰). A similar conclusion can be drawn for the BO-2 reservoir in which the fluid has the same isotopic signature as in BO-4, and from which a cumulated volume of about 1.4 million tons of water was extracted without any apparent drop of the field pressure (Demians D'Archimbaud and Munier-Jolain 1975).

#### 3.3 Saturation calculations and scale deposit risks

As indicated by saturation calculations using the EQ3NR geochemical code and by classical geothermometers (Nicholson 1993), the deep geothermal fluid reacts with volcanic rocks at about 250°C reaching chemical equilibrium with a mineralogical assemblage constituted of albite, K-feldspar, quartz, calcite, disordered dolomite, anhydrite, illite, smectites and zeolites. The use of the inhibitor IDOS 130 during the stimulation operation has prevented anhydrite scale deposits predicted by modelling and observed during the first production test. These deposits doubtless occurred during the interference test performed in March 1998 whereas less than 100 m<sup>3</sup> of seawater had been injected.

#### 4 CONCLUSIONS

The results of all geochemical studies carried out between 1998 and 2000 indicate that:

1. No direct hydraulic connections could be detected between BO-4 and BO-2 (presence of subvertical and parallel faults or opposite flow direction).

- 2. Most physical and chemical production characteristics of BO-4 are similar to those of BO-2, suggesting a common origin for the deep geothermal fluid. Except for Eh value and H<sub>2</sub>S, Fe, Ag and Cd concentrations, an accurate chemical and isotopic composition was obtained for the geothermal fluid. In spite of a relatively high water-rock ratio, this brine resulting of a mixture of seawater and freshwater reacts sufficient time with volcanic rocks at 250°C to reach chemical equilibrium with a specific mineralogical assemblage.
- 3. Additional information from submarine thermal springs which expelled a mixture between seawater and geothermal brine can be very useful to reconstruct or validate the chemical composition of the deep geothermal fluid.
- 4. No significant scaling occur in the wells during their exploitation if  $CO_2$  degassing is low and temperature and pressure remain high at well-head. In future drillings, it is highly recommended to inject a scale inhibitor to prevent anhydrite formation if seawater is used as a drilling fluid.

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