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La Geo
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GEOCHEMICAL MONITORING PRACTICES IN EL SALVADOR

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ABSTRACT

Geochemical techniques for defining and monitoring chemical parameters have
been widely used in El Salvador with excellent results. During the geothermal
research stages: exploration, development and exploitation of the resource, they
have been proven to be of great value in obtaining the necessary scientific
information needed and in making decisions. In the exploration phase, several
geochemical processes such as defining the water origin (deep or meteoric),
estimating the temperature of the deep fluid, mixing of fluids circulating in the
system, boiling, evaporation and dilution are of vital importance in developing the
conceptual model of the system. During the development stage of a geothermal
resource, it is important to control the chemical evolution of new wells.
Parameters such as chloride and CO_2 allow the estimation of this evolution towards
the stability of fluids. Similarly, during the exploitation of a resource, it is relevant
to monitor the behaviour of the system as a consequence of the extraction of mass
from the reservoir. These techniques indicate when a system or geothermal well
presents boiling processes, dilution, possible mixing, etc.   The use of these
techniques has helped in understanding the geothermal systems and their behaviour
before and during the exploitation of the resource, and further provides for the
effective management of the system.

1. GEOCHEMISTRY IN SUPERFICIAL PROSPECTION

The objective is to classify the types of water in order to identify their origin (superficial or deep),
consider the original temperature (geothermometry) and processes occurring as a mixture of the fluids.

1.1 The chemical classification of waters

The chemical classification of waters is essential for a correct use of geochemical techniques, which
can be applied only to particular kinds of fluids with limited ranges of composition, reflecting the
environment of origin. For instance, most ionic solute geothermometers can be applied only to
samples representative of water-rock equilibrium at depth. This assumption is usually applied to
neutral sodium-chloride waters only. Therefore, these samples have to be properly identified and
selected. Furthermore, possible phenomena affecting the original characteristics of sodium-chloride
waters (i.e., addition of cold, shallow groundwaters, boiling, dissolution or precipitation of mineral
phases) have to be recognized and evaluated. The chemical classification of waters can be carried out
following different techniques, some of which are listed below.

The Cl-SO₄-HCO₃ triangular plot is used for an initial classification of geothermal water samples (Giggenbach, 1988; Giggenbach and Goguel, 1989). The position of a data point in this plot is obtained by first calculating the sum (Σan) of the concentrations C_i (in mg/kg) of all three species involved:

$$\Sigma an = C_{Cl} + C_{SO4} + C_{HCO3}$$

In this plot (Figures 1 and 2), the compositional ranges are indicated for the different kinds of water typically found in geothermal areas, such as:

1. Mature NaCl waters of neutral pH, which are rich in Cl and plot near the Cl vertex;
2. HCO₃ waters, indicated as peripheral waters; and
3. Volcanic and steam-heated waters, generated through absorption into groundwater of either high-temperature, HCl-bearing volcanic gases or lower-temperature H₂S-bearing geothermal vapours.
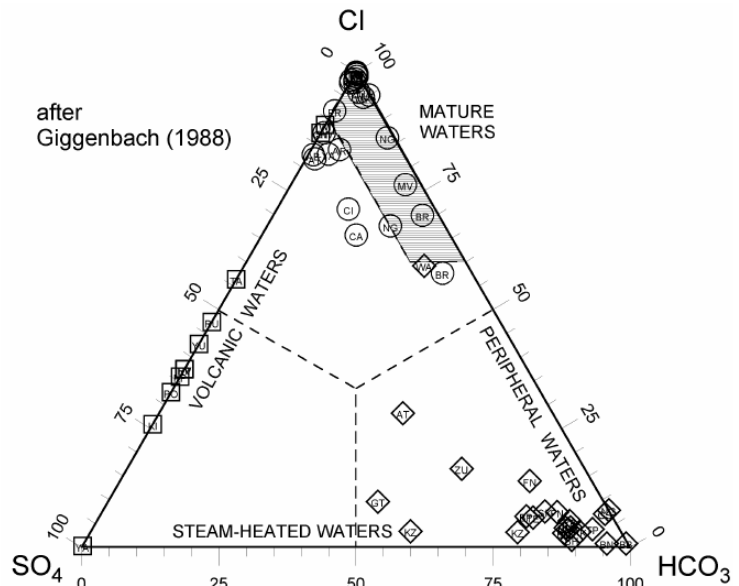

FIGURE 1: Relative Cl, SO₄ and HCO₃ contents (on weight basis) for different kinds of waters typically found in geothermal areas; squares = acid sulphate waters; diamonds = bicarbonate waters; circles= neutral chloride waters.
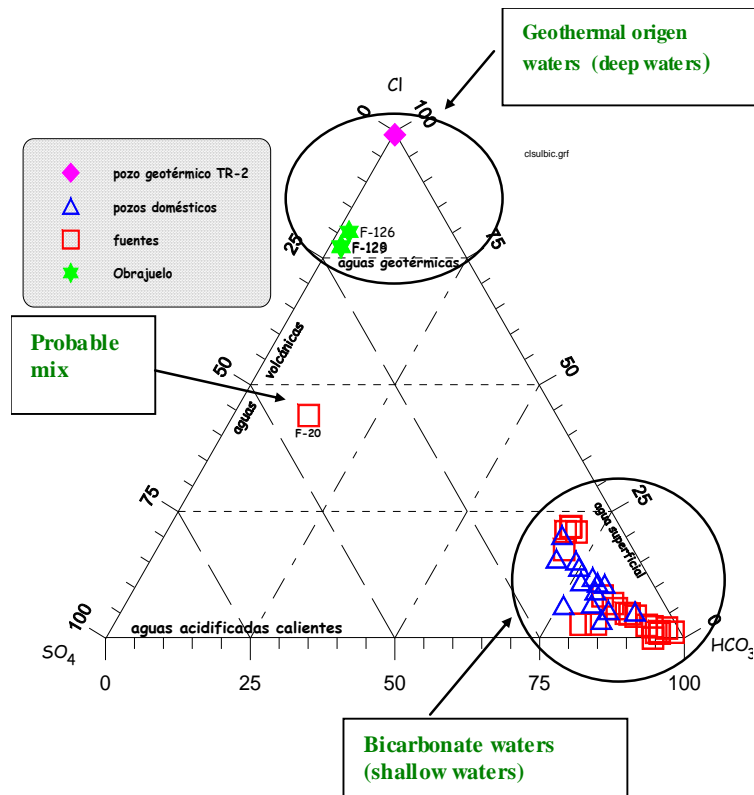

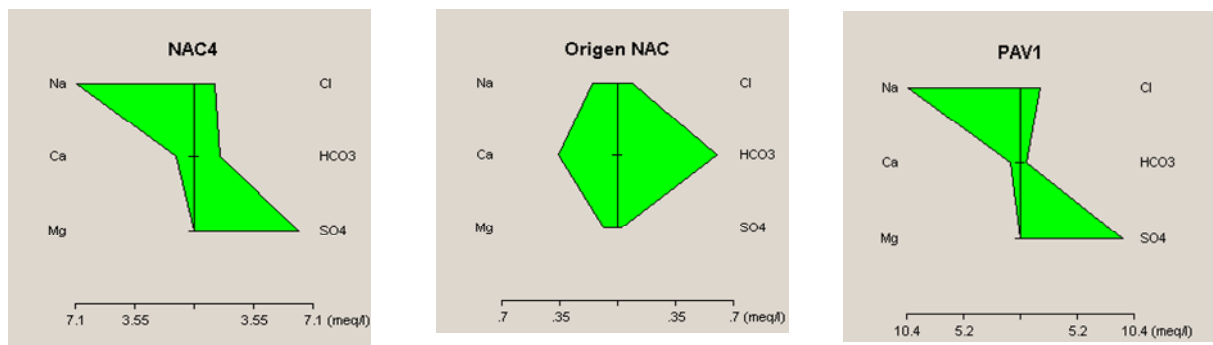FIGURE 2: Types of water in the Berlín geothermal area

FIGURE 3: Stiff plots for thermal waters

Another method to classify water is by using the Stiff diagrams (Figure 3), which is more accurate in identifying the chemical composition of the fluids.

1.2 Geothermometric methods for geothermal waters

Geothermometers and PCO$_2$-indicators (also called geobarometers) are relatively simple functions in which the chemical data of hydrothermal fluid samples, the equilibrium temperature, and PCO$_2$ are presumably present in the zones, where these hydrothermal fluid samples are thought to have attained chemical equilibrium. Partial pressure of water is usually assumed to be constrained by the coexistence of liquid and vapour phases (saturation). Total fluid pressure is then obtained by Cumming parameters P_{CO2} and P_{H2O}, and H_2O and CO_2, which are generally the two major constituents of hydrothermal fluids. The basic assumptions of geothermometry and geobarometry are:

(1) Chemical equilibrium is attained in the reservoir multiphase system, which is generally constituted by hydrothermal (secondary) minerals, the aqueous solution, and eventually a separated gas phase;

(2) The sample collected at the surface (from a hydrothermal manifestation such as a thermal spring or a fumarole) is fully representative of the hydrothermal fluid present in the reservoir.

Hypothesis (2) is not always satisfied. The parent hydrothermal liquid, during the ascent towards the surface, either mixes with shallow waters or separates a vapour phase, or precipitates some mineral phases or re-equilibrates at decreasing temperatures. The hydrothermal vapour, either present in the hydrothermal reservoir or produced through the boiling (steam separation) of the parent hydrothermal liquid, experiences secondary processes such as steam condensation and air entrainment at shallow levels. It is rather obvious that the modelling of the effects of these secondary processes for a correct application of geothermometric and geobarometric techniques is necessary.

The silica geothermometer.   The solubility of all silica minerals increases with increasing temperature. In the plot of the logarithm of dissolved silica versus the inverse of the absolute temperature, the data for several silica minerals (quartz, chalcedony, ά-cristobalite, opal-CT, and amorphous silica) lie along straight lines in the 20-250 °C range, even in the residual water after a single-step steam separation at 100 °C or maximum steam loss (Figure 4).

The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) is probably the most popular and uses an ionic solute geothermometer, although it is not a true geothermometer (Figure 5).
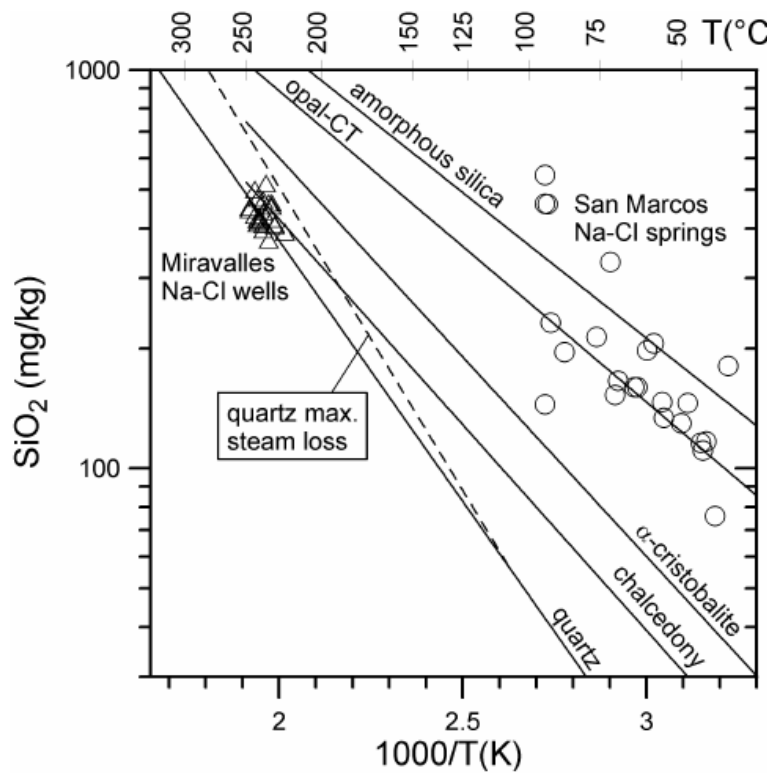
FIGURE 4: Solubility of several silica minerals in water at the vapour pressure of the solution (from Fournier, 1973; 1991). Also shown are the deep Na-Cl geothermal liquids of Miravalles, Costa Rica (Marini et al., 2003) and the Na-Cl thermal springs of San Marcos, Guatemala (Marini et al., 1998). The equations of these straight lines are as follows, where SiO2 indicates silica concentration in mg/kg (from Fournier, 1973; 1991)
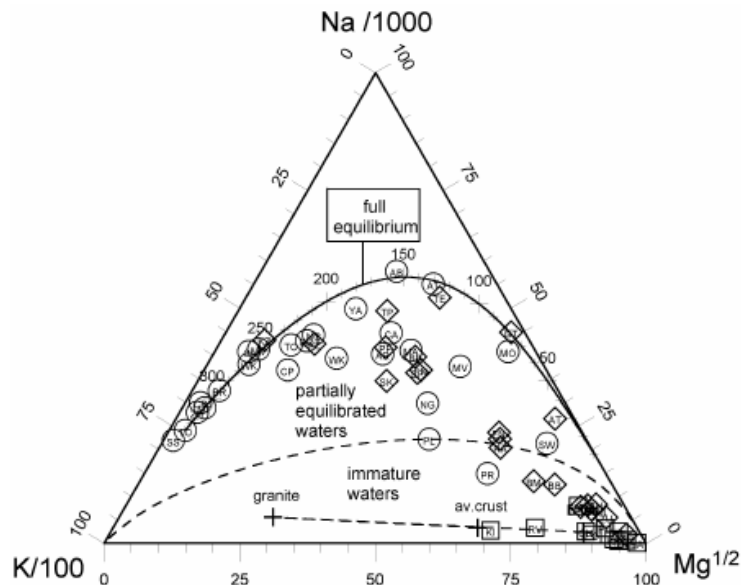

FIGURE 5: The Na-K-Mg1/2 triangular plot (from Giggenbach, 1988, modified); squares=acid sulfate waters; diamonds=Na-bicarbonate waters; circles= neutral chloride waters

2. GEOCHEMISTRY IN THE GEOTHERMAL DEVELOPMENT STAGE

Here the objective is to evaluate the thermal potential of the new drilled wells. In order to achieve the desirable information, time evolution plots are normally used. The chemical parameters to be monitored could be chloride, sodium compositions, or pH among others, as shown in Figure 6.

FIGURE 6: Chloride, electrical conductivity and pH time evolution, well CHI-3A

3. GEOCHEMISTRY DURING THE EXPLOITATION

The objective is to demonstrate some chemical techniques used to monitor the system behaviour under exploitation conditions.

Chemical changes with time. The data based on chemical concentrations deals mostly with water samples that are collected at the surface after the separation of the water and steam. It is of interest to convert them into the subsurface reservoir concentrations. This requires a set of simple formulas that are derived from the principle of mass and energy conservation. A major assumption for the derivation is that the dissolved solids are negligible in the separated steam phase as well as non-condensable gases in the separated water phase.

The computer program "WATCH" is a useful tool for the interpretation of the chemical composition of geothermal fluids and for non-thermal waters. Some chemical analyses of samples collected at the surface can be used to compute the composition of aquifer fluids. The program involves the calculation of several aqueous species using mass balance equations and chemical equilibrium. The

WATCH computer program can also be used to calculate the composition of the equilibrate sample after cooling or boiling (Bjarnason, 1994).

Several chemical species and ratios are plotted against time using the chemical data collected in the wells, from the start of exploitation until the present. In order to give a general overview of the evolution of water chemistry discharge, the chloride evolution with time is widely used in Ahuachapán and Berlín geothermal fields as shown in Figure 7.

The chloride history is shown in the discharge concentration and the reservoir concentration. With these plots, it is possible to assess the different processes occurring in the well or in the entire geothermal system.

The trend for reservoir chloride content in well TR-5C remains almost constant in time, decreasing from almost 8000 ppm in the early

FIGURE 7: Chloride evolution with time

years of production to 6500 ppm this year, representing a 19% dilution. The decline was gradual until 1987, but has been stable for the last few years.

Well AH-6 shows on the other hand, in spite of some scattering behaviour, a clear trend towards increased reservoir chloride content. Only in the last two years or so have lower values been observed than in previous years. Such changes could be related to a cyclic chemical behaviour and are possibly related to fluctuations in the water mass flow rate.

3.1 Chemical and thermodynamic indicators

The different responses of the NaKCa and quartz geothermometers combined with the enthalpy of each well affect the fluid state and fluid temperature around the wells.

In the Ahuachapán field, the wells' enthalpy evolution is summarized in the next table. Boiling lowers the fluid temperature within the expanding boiling zones, with progressively decreasing pressure (drawdown), and the fluid state corresponding to the two-phase liquid-vapour curve. The near well fluid is cooled by boiling, and the heat is transferred to the fluid from the reservoir rocks, probably resulting from flashing flow in the fractures (that is the case of Ahuachapán), which on a large scale may behave like a uniform matrix but may allow segregation of liquid and vapour (Aunzo et al., 1989).

According to the Table 1, six wells are affected by local boiling, but the rest (13 wells) produce diluted waters due to the mixing with relative "colder waters".
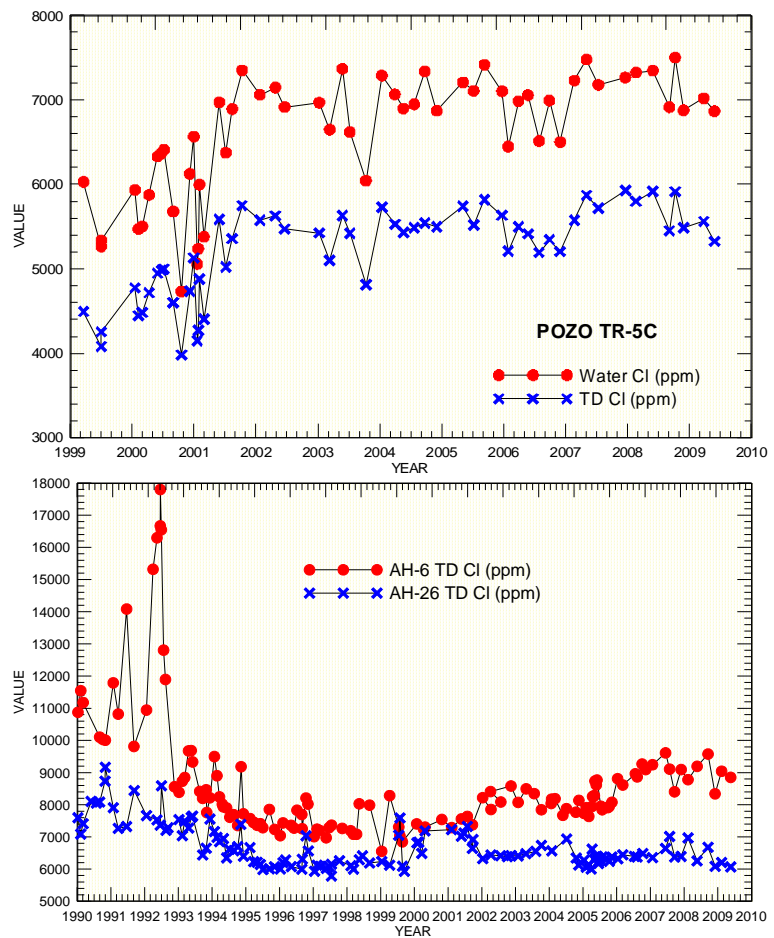
TABLE 1: Main thermodynamic processes occurring in Ahuachapán production wells
H_m: measured enthalpy, H_{NaKCa}: enthalpy at NaKCa geothermometer,
H_{SiO2}: enthalpy at quartz geothermometer

Wells	Prevalent order	Indicated process
AH-1, AH-7, AH-16A, AH-19, AH-20, AH-21, AH-24, AH-27, AH-28, AH-31, AH-33B, AH-35B, AH-35C	$H_{NaKCa} > H_{SiO2} > H_m$	Mixture of cooler more diluted water
AH-6, AH-4B, AH-17, AH-22, AH-23, AH-26	$H_m > H_{NaKCa} > H_{SiO2}$	Boiling during flow to the well

The enthalpy evolution of the Ahuachapán wells revealed by the comparison between the measured enthalpy and the liquid-phase enthalpy values calculated from geothermometer is summarized for all the wells in Table 1.

3.2 Processes in the reservoir: Enthalpy-chloride mixing model

The use of enthalpy vs. chloride plots is thoroughly discussed by Fournier (1979). This plot is a suitable tool to distinguish the effects of boiling and mixing, since both steam and cold waters, which generally have low chloride contents, are characterized by very different enthalpy values.
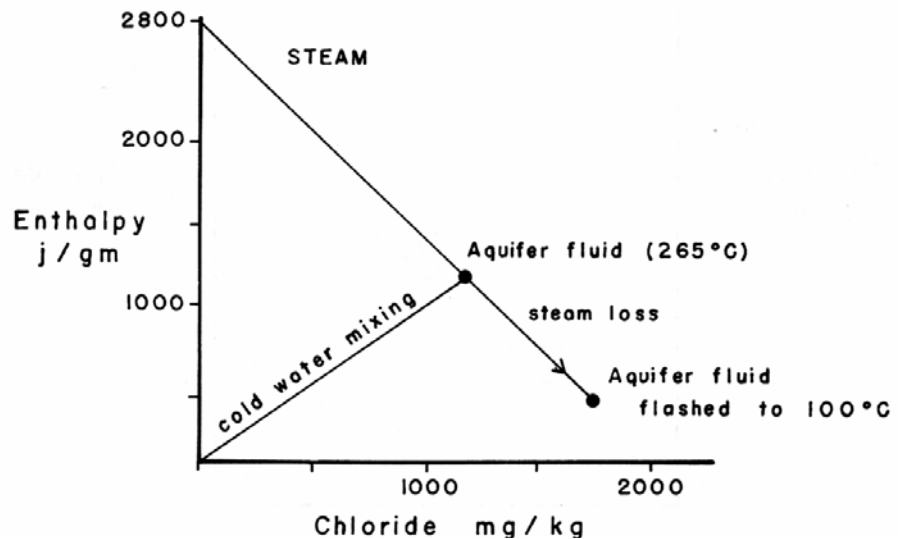
The enthalpy - chloride plot of Figure 8 shows that boiling (steam loss) moves the liquid

FIGURE 8: Enthalpy vs. chloride plot showing the effects of boiling and dilution on a geothermal aquifer liquid at 265°C (Henley et al., 1984)

from a point representative of the 265°C geothermal liquid towards higher chloride contents and lower enthalpies; whereas addition of cold, dilute waters result in the decrease in both enthalpy and chloride. If a deep hot water is cooled mainly through conductive heat loss, its enthalpy decreases but its chloride concentration remains unchanged. Figure 9 shows the local different processes in the Berlín geothermal field and theoretical considerations for the physical processes in the enthalpy vs. chloride plot.

3.3 Gases in the reservoir and the GRID method

The gas evolution in the reservoir presents an important factor to be considered in the evaluation of the deep recharge. Theoretically, in the first years of operation of a power plant, the geothermal reservoir becomes deficient from gases. The gas concentration rises to its maximum and then decreases until it becomes stable, like almost all the liquid dominant fields.

Figure 10 reflects the evolution of CO_2 in the reservoir and the percentage in weight of gases to total discharge for some of the Ahuachapán geothermal production wells.
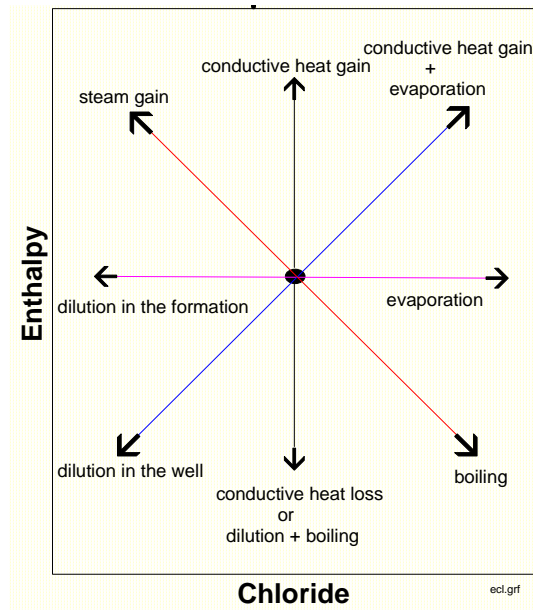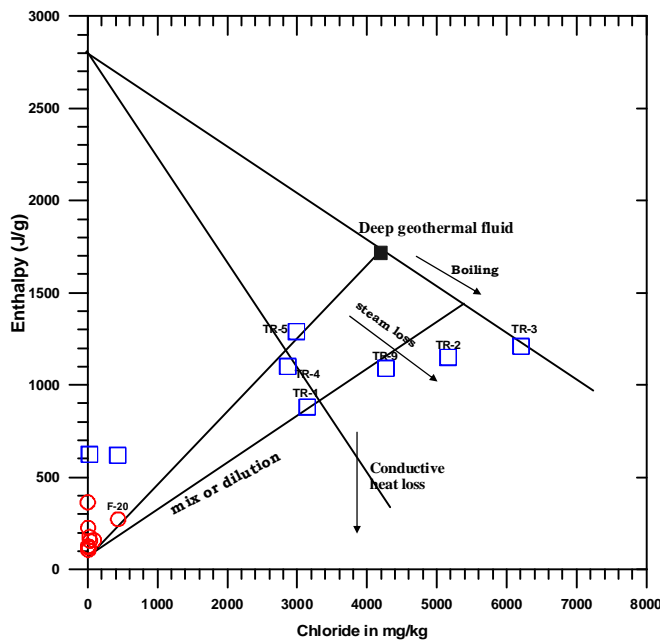
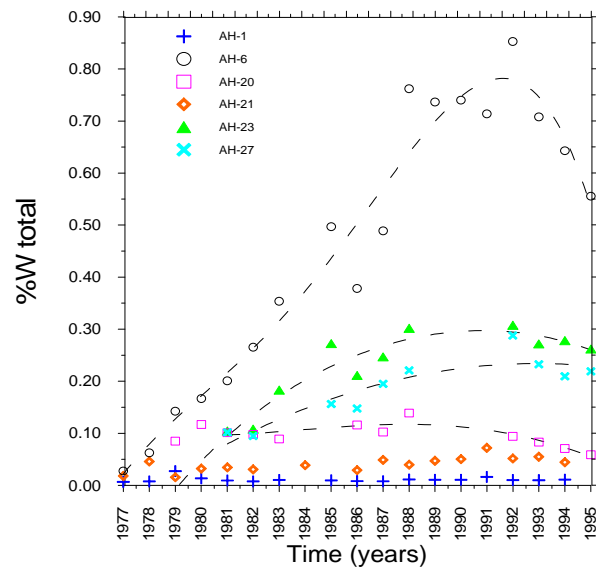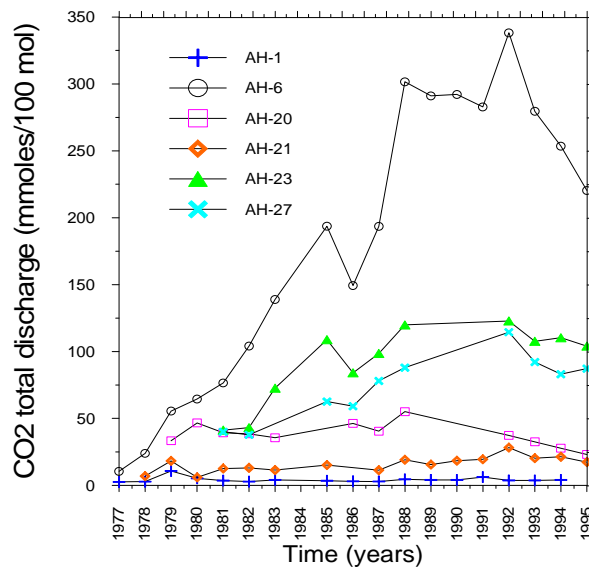FIGURE 9: Some physical processes for Berlín geothermal field

FIGURE 10: Evolution of CO_2 gas content in the reservoir and %-weight of gases

D'Amore and Truesdell (1985) demonstrated that using two equilibrium gas reactions expressing concentrations with respect to the water, it is possible to evaluate the temperature of a geothermal reservoir "T" and the steam fraction "y". The calculated nonlinear values can be solved graphically. As an example of this graphical method, using the equation Fisher-Tropsh and the pyrite-magnetite reaction it can be obtained that:

$$4 * \log (H_2/H_2O) - \log (CH_4/CO_2) = FT$$
$$3 * \log (H_2S/H_2O) - \log (H_2/H_2O) = HSH$$

The analytical chemical parameters FT and HSH are shown as coordinates in the diagram (Figure 11) whereas the physical parameters of temperature and steam fraction produce a grid within the diagram. In this model, sometimes, temperature values vary as opposed to those measured in a system under exploitation. These variations can be interpreted in two ways:

a. An increase in temperature and a decrease in steam fraction can indicate a contribution of fluid from a hotter and deeper source with a saturated affluent liquid;
b. An increase in both parameters can indicate an apparent increase of temperature. In this case, we assume a lateral steam source, with practically zero liquid (dry steam).
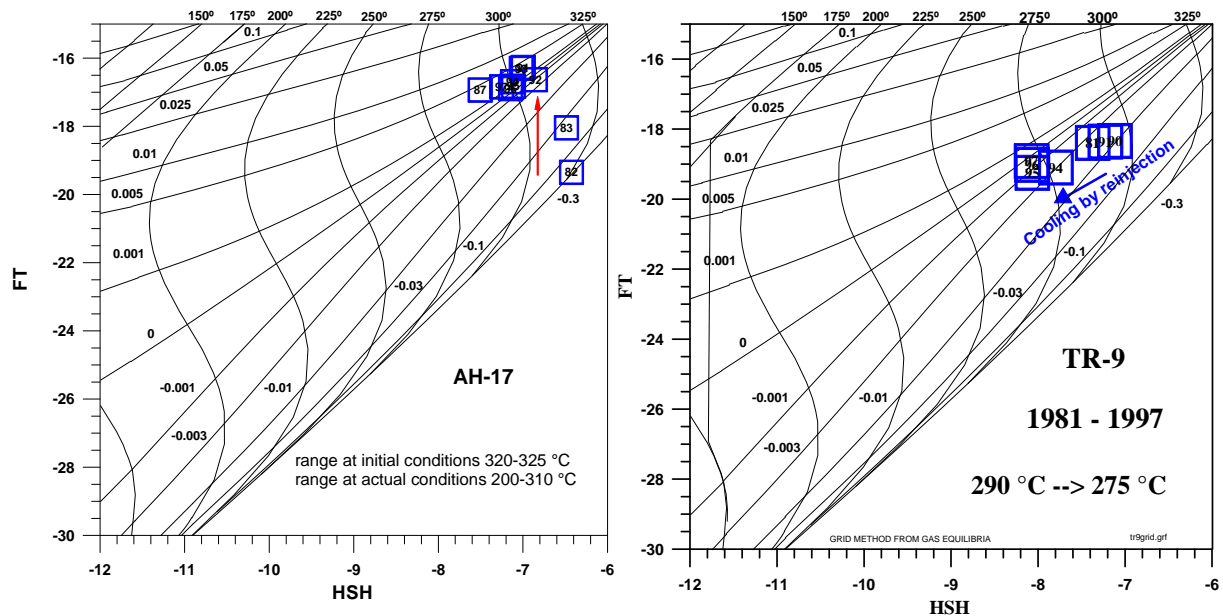

FIGURE 11: Grid diagrams showing the gas evolution for selected wells and physical processes in the Ahuachapán and Berlín fields

3.4 Isotopic composition of geothermal fluids

Isotope studies of the geothermal wells enable us to determine the recharge, discharge zone and also other physical processes like boiling, dilution or mixing with inflow of colder waters or reinjection fluids. For Ahuachapán, the baseline of the water's isotopic composition at initial conditions (see Figure 12) reflects that water-rock interaction process producing more positive values of $\delta^{18}O$ with respect to the isotopic composition of the groundwater.

Because of interaction with silicates of andesitic rock instead of carbonic sediments, this process is not locally predominant. For most of the wells with respect to hot springs, the observed slope of δ^2H vs. $\delta^{18}O$ is positive. This phenomenon cannot be due to boiling, at least for most of the wells, because the vapour-liquid exchange between 210 and 230°C in ^2H is practically 0. A different mechanism is carried out at initial conditions producing the positive
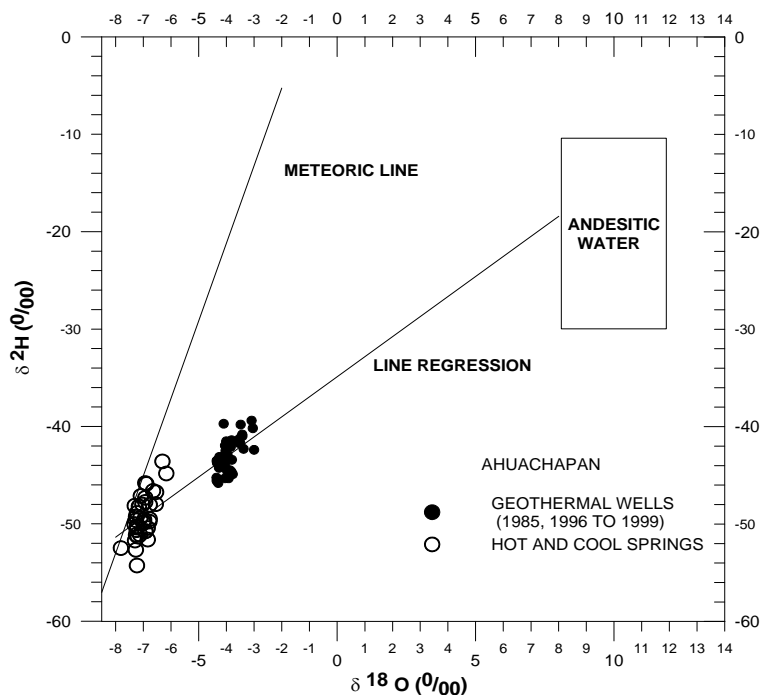

FIGURE 12: Isotopic composition from surface and deep fluids at the Ahuachapán geothermal field

slope. It could be inferred that an andesitic magmatic component is mixing with water rock $\delta^{18}O$ exchanged water.

3.5 Mineral saturation

Due to the development of different physical processes in the reservoir during the exploitation, the chemical composition of fluids can be modified, changing the equilibrium conditions of some particular minerals such calcite, silica (different phases), and anhydrite etc., and resulting in mineral super saturation that can negatively affect the production in some wells. Due to these chemical variations, it is necessary at the same time to observe the evolution of production data and also perform mechanical calibration inside the casing in the wells in order for there to be an agreement with the chemical results.

To predict the chemical mineral saturation, a computer programme like WATCH is used to compute the resulting species concentrations, activity coefficients, activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in order to evaluate the scaling potential of the fluids.

For the evaluation of the mineral state of the fluid, mainly for the quartz, calcite and anhydrite, several runs of WATCH programme were done for all the production wells. Evaluating the initial chemical discharge in the wells is needed to identify the calcite scaling potential, and define the use of calcite inhibitors at the beginning of the production. Figure 13 shows the computed results for calcite saturation curves for two wells. Well AH-4b produces under saturation curves, while well AH-33B presents oversaturation curves for calcite. Well AH-33B is operated with inhibitors.

FIGURE 13: Mineral saturation indexes for some production wells at Ahuachapán (with and without an inhibitor system)

3.6 Surface manifestations

Subsurface boiling creates fumaroles and alteration zones. Some hot springs of mixed composition indicate that cooler dilute fluids occurred above the geothermal system before production began (Aunzo et al., 1989; Laky and Dennis and others). The decrease in flow rate, salinity and temperature
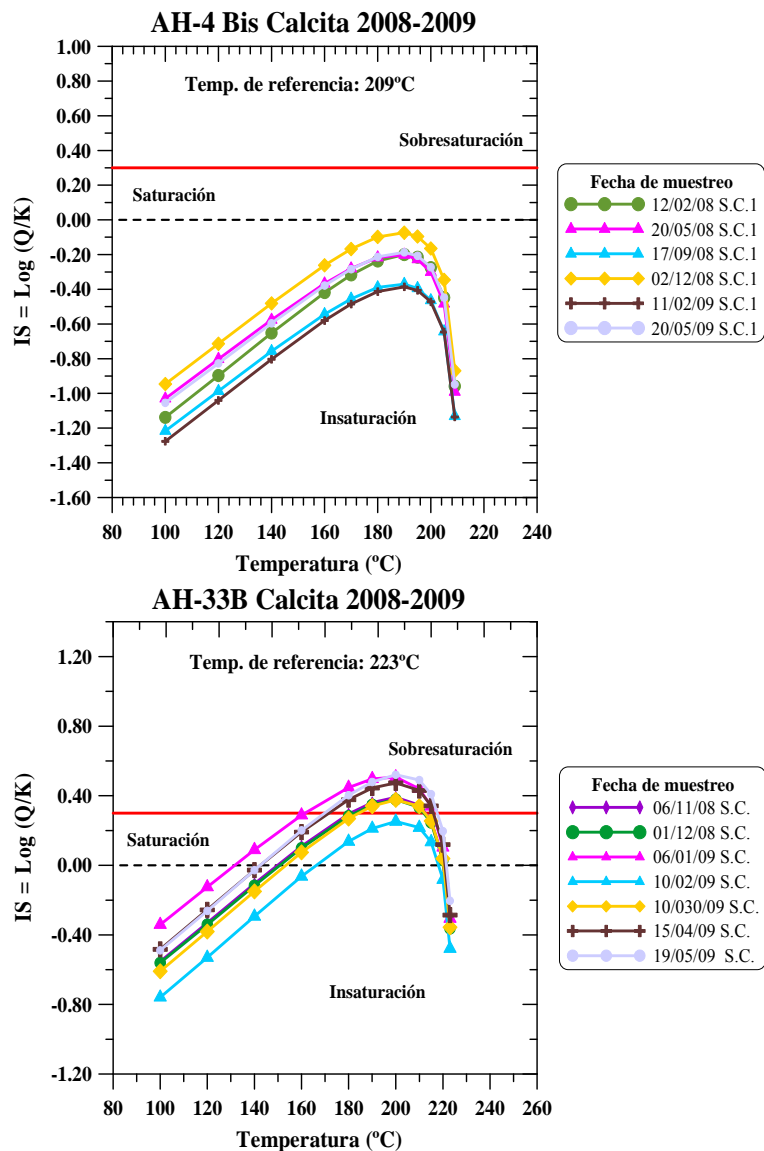
has been observed due to the pressure decline from overproduction in the area (Steingrimsson et al., 1991; Truesdell et al., 1989).

The main outflow for this system is the El Salitre springs area, located about 7 km north of the Ahuachapán field, where more than 1,000 l/s of 68-70°C were discharged prior to the exploitation in Ahuachapán, after that the flow rate and salinity have been decreased considerably. The fluid of El Salitre was a mixture of geothermal water (10-20%) and shallow aquifer fluid (Glover, 1970). Figure 14a shows the chloride, temperature and flow rate history of the El Salitre spring correlated with the reservoir pressure of the Ahuachapán geothermal field.

Numerous fumaroles are located on the northern flank of the volcanic range, but only the El Playón fumarole located in the main field (300 m to the south of the power plant building and surrounded by several producing wells) has a gas composition similar to the reservoir fluid, and its evolution clearly shows the effect of the exploitation of the field lowering the gas temperature (D'Amore and Panichi, 1980) from 280 to 240°C and the flow discharge from 50 kg/s to almost 0 by 1982 (Aunzo et al., 1989) as shown in Figure 14b.

It should be noted that the El Playón fumarole has a direct response to the drawdown in the reservoir pressure, while the Agua Shuca fumarole shows a different behaviour almost constantly against the time of the Ahuachapán exploitation history.
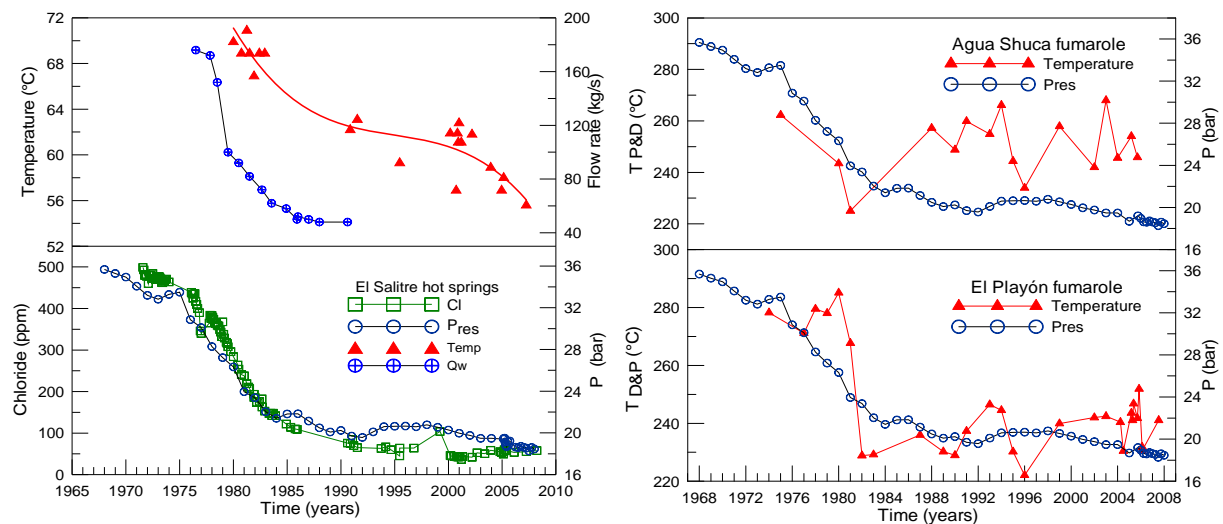
FIGURE 14: a) El Salitre spring and El Playón; b) Agua Shuca fumarolic zones evolution

7. CONCLUSIONS

The different geochemical monitoring techniques used as an important tool in the interpretation of wells and other manifestation features of the geothermal system prove to be very useful in the identification, definition and control of physical and chemical processes of interest. Similarly, they are applied in the control and monitoring of chemical changes as a result of the exploitation of geothermal fields especially when an intensive mass extraction has occurred.

Several chemical methodologies and physical parameters have been confirmed in order to select the most useful guides to show the chemical changes in time. Evolution of conservative compounds such as chloride, the chloride-enthalpy mixing model, the enthalpy temperature and the geothermometers (Truesdell, 1987) is important as indicators of different processes affecting the reservoir fluid like dilution, boiling and conductive heat transfer from the rocks. Such processes are common and occur

in liquid geothermal dominant fields like dilution, boiling, condensation, etc. producing mostly cooling in the reservoir fluids.

The chemical geothermometers in most of the cases agree with the measured temperatures in the wells, especially the quartz geothermometer. Other geothermometers reflect the highest temperatures of the deepest geothermal system.

Important information related to the mineral saturation indexes is also provided by the use of simulation code WATCH (Arnorsson et al., 1982).

The evaluation of steam reservoir evolution and estimation of the highest temperatures of the system is given by the Grid method (D'Amore and Truesdell, 1985) using the gas content of wells.

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