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MIRAVALLES GEOTHERMAL FIELD, COSTA RICA -EVIDENCE OF THERMAL EVOLUTION AND A COMPARISON OF THE MINERALOGY OF AN ACID WELL AND A NEUTRAL WELL

Leyner Chavarría Rojas Instituto Costarricense de Electricidad Centro de Servicio de Recursos Geotérmicos Apartado 10032-1000, San José COSTA RICA *LChavarriaR@ice.go.cr*

ABSTRACT

The alteration mineralogy and the measured temperature data were used to find thermal fluctuations in the Miravalles geothermal field. Zones of relative heating were defined to the north and centre of the field; these correspond to zones where the measured temperature at the top of the epidote zone is at least 20°C higher than the temperature assigned to the epidote. A large north-south trending zone of apparent thermal equilibrium was defined along the main production wells in the field. In this zone, the measured temperature corresponds to the epidote temperature $(200\pm20^{\circ}C)$. Cooling zones indicate measured temperatures at least 20°C lower than the temperature corresponding to the epidote; these are located to the west and east sides of the main borehole field. The cooling zones may relate to the inflow of relatively cold water along NW-SE fracture systems, as indicated by the alignment of the zones. As part of the characterization of the acid fluid in geothermal wells, a literature survey was conducted and the main types, occurrences and characteristics are summarized. Similar literature review was done for the Miravalles geothermal field. The comparison between the alteration in a neutral and an acid well indicates that there are no major differences between those wells, which suggests that the acid fluids are likely to be restricted to very narrow zones that make identification difficult. This could also indicate that the acid fluids are not in equilibrium with the alteration mineralogy, probably due to the short time of residence.

1. INTRODUCTION

The Miravalles field is a high-temperature reservoir, located in the northwestern part of Costa Rica, in the Guanacaste Volcanic Range; about 150 km from the capital, San José (Figure 1). The field is located inside the Guayabo caldera in the southwestern flank of the Miravalles stratovolcano.

The first geothermal studies were carried out in 1963 and the first deep well was drilled in 1979. At present, the wells produce from a liquid-dominated reservoir characterized by sodium chloride waters and near neutral pH (Gherardi et al., 2002). However, in the northeastern sector of the field, 5 wells produce

sulphate-rich acid fluids. The occurrence and origin of acid fluids in Miravalles wells have been treated before by Truesdell, 1991; Gherardi et al., 2002; Sánchez et al., 2000; Mainieri, 2000; and Moya Sánchez, 2002. and Nevertheless, the characteristics of the acid aquifer are not yet fully understood. The permeability of the system mainly fracture is controlled. The reservoir is located below about 700 m depth with temperatures decreasing to the south and west (Vallejos, 1996).

With the data generated from drilling and evaluation of the wells, several volcanological, mineralogical, geo-



FIGURE 1: Main tectonic features in the Central America region (modified from Weyl, 1980)

chemical, stratigraphic and thermodynamic studies have been carried out. Some of them refer to several generations of alteration (Mainieri et al., 1980), and variations in the thermal conditions according to mineralogical data and present measured temperatures (Bargar and Fournier, 1988; Rochelle et al., 1989; Vega, 2000).

The field has been producing since 1994 and at present, the energy produced represents about 20 percent of the nation's total energy consumption. An additional second-stage flash unit of 19 MWe will be installed, which will increase the geothermal capacity in Miravalles to 162.5 MWe (Mainieri, 2000).

The first objective of this study is to use the alteration mineralogy and the measured temperature data to find zones of relative heating and cooling in the borehole field. The cooling zones could also be used to infer aspects related to the hydrogeology of the system. The second part of this report took into consideration the presence of acid fluids in geothermal wells. A literature survey was conducted and the main types, occurrences and characteristics were summarized. A similar literature review was done for the Miravalles geothermal field. Finally, a detailed description and mineralogical comparison between an acid and a neutral well was done.

1.1 Tectonic and geological setting

Costa Rica is located in the southern part of Central America, on the western margin of the Caribbean Plate, where the Cocos Plate subducts under the Caribbean Plate along the Middle American Trench. This subduction zone extends between Mexico and Costa Rica, and is bounded by the Polochic and Motagua faults in the north and by the Cocos Ridge and the Panamá Fracture Zone to the south (Figure 1).

As a result of the subduction, intense fracturing, seismic and volcanic activity developed. The last is represented by the Central and the Guanacaste volcanic ranges, which are parallel to the Mid-American

Trench and form a part of the Ring of Fire of the Pacific. The Miravalles geothermal field is placed inside the Guayabo caldera, in the southwestern flank of the Miravalles volcano, within the Guanacaste Volcanic Range.

The Guanacaste Volcanic Range comprises Tertiary and Quaternary volcanic rocks. The Tertiary complexes consist of a plateau of andesites, pyroclastites, and ignimbrites intercalated with detritical sediments. The Quaternary rocks are mainly lavas and pyroclastics, associated with the stratovolcanoes aligned along a NW-SE orientation. These volcanoes are characterized by basaltic-andesite to andesite compositions (Chiesa et al., 1992), and the existence of tuff deposits, ignimbrites and lahars at the base (ICE/ELC, 1986).

1.2 Surface geology

The Miravalles geothermal field is a hydrothermally active area located inside a caldera 15 km in diameter (Guayabo caldera), formed in various collapses between 1.5 and 0.6 m.y. ago (Chiesa et al., 1992). The last phase of volcanic activity was 7000 years ago (Mainieri et al., 1985). The indication of an active geothermal system is suggested by the presence of several fumaroles and hot springs in the area. The formation of the caldera was accompanied by great explosive activity with deposition of large amounts of pyroclastic flows of dacitic to rhyolitic compositions (Chiesa et al., 1992) (Figure 2).

The border of the Guayabo caldera is represented by the hills Mogote and La Montañosa to the west and north, and Espíritu Santo to the southeast. These are partially eroded relics of old stratovolcanoes (Chiesa et al., 1992). The Miravalles stratovolcano is located toward northeast of the last hills. Along the top, different eruptive vents are observed, mainly oriented NE-SW (Alvarado, 1989). The Santa Maria volcano, to the northwest of the Guayabo caldera, consists of andesitic to andesitic-basaltic products associated with the Santa María-Rincón de la Vieja volcanic complex. The western border of the caldera is represented by heterolithic breccias outcropping near Guayabo and in Cerro Mogote. To the southeast, the caldera edge consists of pre-caldera lavas and occasional breccias of andesitic to basaltic composition associated with the Cerro Cabro Muco and Espíritu Santo. Several laharic flows cover most of the caldera depression; and some of them continue also outside the caldera to the south, along the La Fortuna graben.

Several widespread pyroclastic flows have been identified to the south and southwest of the caldera border, evidencing phases of intense explosive activity during the formation of the Guayabo caldera. Towards the southern sector of the caldera, near the town of La Fortuna, some lacustrine deposits are present, which are evidence of periods of erosion and relative volcanic inactivity.

Gravimetrical interpretation given by Hallinan and Brown (1995), indicates a negative anomaly of -7.5 mGal over the centre of the Guayabo caldera (near PGM 15), and positive anomalies to the east at the Bajo Los Chiqueros area (+24 mGal) and well PGM 04 in the south. This gravimetric maximum over the Bajo Los Chiqueros was explained as being an intrusive body of intermediate composition, located at about 500 m depth.

Several tectonic features are present in the area. On a regional scale, an important old and deep fracture system is thought to trend in a NW-SE direction, parallel to the Guanacaste Volcanic Range. This trend is also observed in several eruptive centres at the Rincon de la Vieja volcanic complex (to the northwest of Miravalles). Another important structural system runs NE-SW, which is evident in some lineaments between some of the volcanoes of the Guanacaste Volcanic Range, as well as in several cones in the Miravalles volcano.

Inside the Guayabo caldera, four main fracture systems have been defined: N-S, NE-SW, NW-SE and E-W. An important arrangement of faults are oriented N-S, where the main fractures cross the Guayabo caldera and form graben structures to the south (La Fortuna graben). The NW-SE and the NE-SW systems



FIGURE 2: Geology of the Guayabo caldera and distribution of main structures and deep wells at the Miravalles geothermal field (modified from Hallinan and Brown, 1995; and Vega, 2000)

are also important for the permeability of the geothermal field. The E-W system is mainly developed in the northern sector of the field, of which the Las Hornillas fault is a good example. The E-W structures appear to be the youngest (Vega, 2000), and coincide with the highest thermal anomalies and surface manifestations in this sector of the field. Some of these fracture systems show morphological evidence, which could be related to reactivation processes due to tectonic or volcanic activity.

1.3 Well stratigraphy

At present, 52 deep wells have been drilled in Miravalles, including production, re-injection and observation wells (Figure 3). Based on cuttings and core samples, the stratigraphic sequence of the field has been defined in several previous works, including borehole geological reports and other technical reports. Vega (2000) presented an updated stratigraphic sequence for the geothermal field. This stratigraphy is also shown in the cross-sections in Section 2.



Lava basement (LB): The oldest unit identified inside the caldera structure. Consists of a sequence of lava flows deposited prior to the caldera formation. This unit has only been drilled in PGM 15 (deepest well in the field), below -1941 m a.s.l. It is formed by deposition of several lava flows which are moderately to highly altered. Most of the lavas were identified as andesites, in which the pyroxenes (and maybe amphiboles in some flows) are altered to chlorite. The plagioclase crystals are mainly transformed to clays, chlorite, calcite and epidote (Vega, 2000).

Ignimbrite unit (IGU): This unit is present in the central and southern sectors of the field, overlying the Lava basement unit. In well PGM 15, the total thickness of this unit is 1087 m. It consists of several tuff units; some of them are partially welded and are also formed with an abundant matrix, different lava fragments and occasionally compacted glass. The matrix is fine grained with crystals of plagioclase, pyroxene, opaque minerals and rare quartz. Most of the lava fragments are highly altered. These are formed by crystals of plagioclase, pyroxene and opaques altered to moderate and high temperature minerals (Vega, 2000).

Tuffaceo lava unit (LTU): This unit is widely distributed within the geothermal field; with a thickness ranging from 260 to 1900 m. It includes a sequence of andesitic lavas with occasional lithic and crystalline tuffs and rare epiclastic sediments. The lavas contain plagioclase, pyroxenes, sporadic amphibole and opaque minerals as the main constituents. The alteration intensity varies from moderate to high, usually with high-temperature minerals. The tuffs are mainly lithic and crystalline, related to several deposition events and some of them are separated by fine epiclastic sediments (Vega, 2000).

Volcano sedimentary unit (VSU): The unit is found in the geothermal field, except in the PGM 04. The thickness is between 255 and 1050 m. It is comprised of lithic and crystalline tuffs, epiclastic deposits and occasional lava flows. The amount of heterolithic fragments varies in the tuffs, which are immersed in a fine ash matrix. The crystalline tuffs are fine grained and contain altered plagioclase and pyroxene crystals in a fine matrix. Some epiclastic and lacustrine deposits have been recognized intercalated with the tuffs. These are very fine grained and are frequently banded. The thickness ranges from a few centimetres to several metres. There are some andesitic and basaltic-andesitic lava flows, usually with moderate to high alteration intensity (Vega, 2000).

Cabro Muco andesite unit (CMAU): This unit is widespread in the field (except not found in well PGM 15), probably due to the long distance to the source (thought to be near the Cabro Muco hill). It includes andesitic and andesitic-basaltic lavas and occasional tuffs. The lavas have crystals of plagioclase, two pyroxenes, opaques and sporadic olivine in a matrix of the same composition. The tuffs are generally lithic, containing fragments of andesitic lavas, crystals of plagioclase, pyroxene and magnetite (Vega, 2000). In the north-central part of the field, its emplacement was possibly favoured by the east-west fracture systems, where the thickness is higher and it was usually altered to microcrystalline quartz (up to 70% in some cases).

Pumitic unit (PumU): This unit was only found in well PGM 15 showing a total thickness of 310 m. The gravimetrical data indicate a possible distribution of these deposits in a 3 km wide fringe, trending N-S in the western sector of the field. It is represented by pumitic-pyroclastic products partially reworked. The pumice is formed by glass and crystals of plagioclase, pyroxene and microlithic fragments (Vega, 2000).

Post Cabro Muco volcanic unit (PCMVU): This unit includes lahar deposits, andesitic and andesiticbasaltic lavas, tuffs and lacustrine deposits. The lahars are formed by fragments of andesitic and andesiticbasaltic composition (from centimetres to metric sizes) with variable alteration intensities, immersed in a sandy matrix partially altered to clays. The lavas are relatively fresh, commonly altered to oxides of iron and low-temperature clays. Some thin lacustrine levels are present at different depths; these are mainly sands and clays and more frequently found in the southern sector of the field. Based on the inclination of the unit (to the southwest) a possible location of the source is thought to be towards the Miravalles volcano, probably at the Bajo Los Chiqueros (Vega, 2000).

2. THERMAL EVOLUTION ACCORDING TO EPIDOTE AND MEASURED TEMPERATURES

2.1 Introduction

In Miravalles, the primary mineralogy basically consists of intermediate composition, with plagioclase, pyroxenes (augite and hypersthene), magnetite and accessory quartz and apatite. The alteration mineralogy shows a progressive change, related to increasing temperature with depth (Rochelle et al., 1989).

The alteration mineralogy can be used to find thermal fluctuations such as cooling and heating zones. Epidote is used as an indicator of high temperature ($\geq 200^{\circ}$ C) and is compared with measured temperatures in the wells, in order to give a qualitative distribution of cooling and heating zones in the Miravalles geothermal field.

Epidote is a common secondary mineral in geothermal fields and occurs where the hydrothermal temperature generally exceed 230°C (Thompson and Thompson, 1996). In Miravalles, this mineral is observed at temperatures ranging from 78 to >240°C. However, in most of the wells it is present at temperatures higher than 175°C (Vega, 2000); although in other geothermal fields this mineral is found above 230°C (Table 1). The reference temperature assigned to the first appearance of epidote is 200°C, which is an average value according to its presence and measured temperatures in Miravalles and correlation with data from other geothermal fields. Although this temperature is affected by several geochemical and geological conditions, it is only used as a reference value to compare with the measured temperature at the top of the epidote, in order to estimate the relative distribution of cooling and heating zones. The error margin in this value is estimated about $\pm 20°C$.

TABLE 1: Distribution of some alteration minerals in the Miravalles geothermal field as a function
of the temperature (°C) and mineral temperature stability in other geothermal fields
(modified from Gebregziabher, (1998); the Miravalles data were taken from Vega, (2000; 2001))

Minerals	Miravalles (Costa Rica)	Cerro Prieto (Mexico)	New Zealand	Philippines	Tendaho (Ethiopia)	Iceland
Epidote	>175	>225	230	>230	>240	>240
Prehnite	?	>280	>220	>230	>220	(>250)
Wairakite	>200	>240	>230	210 - 310	>230	>200
Laumontite	-	-	<200	>110	>170	120 -
						200
Stilbite	-	-	<120	-	<175	70 - 120
Anhydrite	-	-	-	>180	>200	-
Quartz	-	150 - 330	>110	180 - 340	>190	>180
Smectite	25-120	-	-	20 - 180	<190	30 - 200
Chlorite	120 ->240	150 - 325	-	>120	>230	>230
Kaolinite	<100	<160	-	0 - 160	<225	-
Illite	≥ 220	150 - 325	>230	220 - 330	>130	230 -
						330
Mixed layer clays	140 - 220	200 - 225	-	-	160 - 230	200 -
						230
Vermiculite	-	>325	-	160 - 280	180 - 210	-
Illite+Chlorite	-	>145	>220	-	>230	-

In order to identify the zones of cooling and heating, some stratigraphic cross-sections and surface representations have been elaborated. The cross-sections (Figures 4 and 5) show the stratigraphic sequences, the distribution of the first appearance of epidote (theoretical value of 200° C), and the measured 200° C isotherm.



FIGURE 4: Cross-sections A-B (NW-SE) and C-D (E-W), showing the distribution of stratigraphic units, main faults, top of the epidote and the 200°C measured isotherm

Once the 200°C value was assigned to the top of the epidote (theoretical value for its deposition), the measured temperatures at those points in the wells were used to estimate the degree of cooling or heating. In this case, a subtraction between the theoretical value for its formation (200°C) and the measured temperature at the top of the epidote is proposed. Surface representations of the top of the epidote (in m a.s.l.), the 200°C isotherm, and finally the difference between epidote temperature (200°C) and the measured temperature at the top of the epidote, were elaborated. The measured temperature data were taken from GeothermEx, Inc. (1997) and additional data from ICE/ELC (1986) (Reservoir Engineering Group).

The presence of cooling zones in Miravalles, has been considered before by Bargar and Fournier (1988), Rochelle et al. (1989), Vega (2000) and others.

Bargar and Fournier (1988) carried out fluid inclusion



07 06

02

VSU

11

PCMVU



analyses in calcite and anhydrite crystals and their results indicate values from near the present measured temperatures to as much as 70°C higher than the maximum measured well temperature.

- Rochelle et al. (1989), based on alteration mineralogy assemblages, suggested temperatures in excess of 300°C in PGM 11, which is considerably higher than the present temperature (255°C).
- Vega (2000) considered that the presence of the epidote at relatively low temperatures in some of the wells (<175°C) may be related to the cooling of some aquifers, and its presence can be considered fossil alteration

According to Reyes (2000), cooling in a geothermal system could originate from

- Structurally controlled inflow of cold water into the system;
- Thermal decline of the heat source with time;
- Shifting of the focus of fluid flow in response to renewed intrusions.

The cooling and heating tendencies can also be used to define the hydrology of a system.

For the present study, it is necessary to mention some of the factors that can influence the results obtained by using the first appearance of epidote as a geothermometer:

The distribution of the permeability is an important factor in the circulation of fluids and mineral deposition;

Southeast

F

64

CMAU

Northwest

E

58

200

-200

14

60

- The effect of large fault displacements occurred after the onset of the deposition of the epidote;
- Large variation in rock composition in the stratigraphic column;
- Chemical composition of fluids and availability of CO₂.

In Miravalles, Viale et al. (1986) differentiated two aquifers: one shallower (200-300 m depth), subhorizontal with temperatures 200-210°C, sodium bicarbonate acidic water with a pH of 5, very low chloride and probably vapour-dominated. Bargar & Fournier (1988) also mentioned the presence of a shallow vapour-dominated zone at 150-450 m depth in the northern part of the field with temperatures close to 200°C. The deep reservoir is thought to be located at depths from 900 to 1600 m, with a temperature range of 236-255°C and neutral sodium chloride water. The deep aquifer seems to be in equilibrium with the minerals observed at that depth and in equilibrium with the measured temperatures (Viale et al., 1986). However, thermodynamic calculations made by Rochelle et al. (1989) suggest that the observed alteration mineralogy is not in equilibrium with the present fluid composition, unless estimates of the reservoir pH are incorrect.

2.2 Stratigraphic cross-sections with information on the tops of epidote and the 200°C measured isotherm

In order to show the distribution of the top of epidote and the 200°C measured isotherm, three stratigraphic cross-sections were elaborated through the borehole field. Stratigraphic units, faults and permeable zones are also shown. According to the temperature assigned to the epidote, the curve that represents the top of this mineral could be considered as representative of the 200°C isotherm. The location of the cross-sections is shown in Figure 3.

The section A-B, aligned NW-SE was drawn between the wells PGM 15 and PGM 50 (Figure 4). From this picture, the deepening of the epidote and the measured 200°C temperature near the edges of the borehole field are clearly evident. This trend is more pronounced in the measured temperature curve, where the difference of the two curves is larger to the northwest (PGM 15) and the southeast (PGM 50) sectors. This behaviour is probably related to the thermal distribution in the field and the tendency of cooling at the edges of the borehole field. Within the central part of the cross-section, between the wells PGM 28 and PGM 43, the curves are very close to each other, corresponding to zones where the temperatures seem to be stable with time, without heating or cooling of the system (equilibrium).

The section C-D has an east-west trend and lies between the wells PGM 25 and the PGM 55 (Figure 4). Similar to the A-B cross-section, towards the western edge of the borehole field (PGM 25), a deepening of the top of the epidote and the 200°C measured isotherm is evidenced. To the centre, close to the wells PGM 49 and PGM 47, both curves are very close indicating equilibrium. In well PGM 55 to the east, the epidote has similar elevation as in the centre of the field. However, the curve of the 200°C measured isotherm is located below the epidote curve, indicating cooling.

The cross-section E-F presents the distribution of the lithologic units, faults and permeable zones, distribution of the top of epidote, and the 200°C measured isotherm in the northern sector of the field (Figure 5). In this sector, there is a thermal anomaly, where the highest temperatures in the geothermal field have been measured. In this sector, the 200°C measured isotherm is above the top of epidote (except in PGM 07) which coincides with the thermal anomaly mentioned. The behaviour of the two curves seems to be related to a heating zone between the wells PGM 58 and PGM 06, as will be shown in the surface diagrams.

To the southeast, the top of epidote tends to be slightly deeper than in the PGM 02, and the 200°C measured isotherm is visibly deeper than in the other wells. Again a cooling zone is thought to become more pronounced towards the PGM 64.

2.3 Surface diagrams

In order to show the spatial distribution of the epidote, the 200°C measured isotherm, and the difference between the temperature measured at the top of the epidote and the theoretical value of formation of the mineral (200°C), three different surface diagrams were drawn (Figures 6, 7 and 8).

The distribution of the first appearance of epidote in Miravalles is shown in Figure 6 (in m a.s.l.). This diagram is also representative of the 200°C isotherm, according to the assumed temperature for the epidote. In the northern sector of the field, the epidote is present at shallower levels (wells PGM 63, 10, 01, 07 and 02) than in the rest of the field. Also to the centre and southern sectors, zones with similar behaviour (PGM 03, 04, 26 and 33) are observed. This tendency is also coincident with the distribution of the 200°C measured isotherm. According to Vallejos (1996), the main upflow zone is located in the northeastern sector of the field, in the vicinity of wells PGM 10 and 11; then to the south the temperature and pressure descend gradually and the fluids move in a lateral flow (Figure 6).

In Figure 7, the distribution of the 200°C measured isotherm is shown (m a.s.l.). The highest temperatures are located toward the northeast and central sectors of the field, as has been suggested before by Vallejos (1996), Vega (2000), and others. As mentioned above, this anomaly appears to correspond to the main upflow zone, and the temperatures decline gradually to the east, west and south.

In order to visualize the qualitative degree of heating and cooling in the borehole field, the distribution of the epidote and the measured temperature data were used. Figure 8 shows the difference in temperature between the measured temperature at the top of the epidote and the theoretical value for its formation $(200^{\circ}C)$. According to this figure, the main heating zone is again located towards the northern sector and continues to the centre of the field. Possible cooling zones are located toward the western and eastern sides of the geothermal field.



FIGURE 6: Depth to the first appearance of epidote (m a.s.l.) corresponding to the distribution of the 200°C isotherm (see text for further explanation)



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FIGURE 7: Distribution of the measured 200°C isotherm as measured in wells, in m a.s.l.



FIGURE 8: Difference in temperature between the theoretical temperature for the deposition of epidote (200°C), and the measured temperature at the first appearance of epidote

Based on Figure 8, three main zones have been distinguished in the borehole field: heating zones, zones in apparent equilibrium, and cooling zones. These are schematically shown in Figure 9. The heating zones correspond to the areas where the measured temperatures are at least 20°C higher than the temperature assigned to the epidote. These are located towards the northern sector (wells PGM 05, 11, 14, 60, 62, 63 and 65) and central sector of the field (PGM 45 and 66). The zone where the measured temperature corresponds to the epidote temperature $(\pm 20^{\circ}C)$ is aligned in the N-S direction, Most of the production boreholes are located in this zone. Zones of possible cooling were defined in the western sector (PGM 04, 15, 23, 22, 44 and 03), northeastern sector (PGM 10, 01, 02, 64 and 55) and southern sector (PGM 52 and 50) of the field. Here the measured temperatures are at least 20°C lower than the temperature assigned to epidote.

The pattern of the cooling zones was used to infer aspects related to the hydrology of the system. Some lineaments observed in Figure 9 suggest the possible control of two NW-SE geological structures, in the vicinity of wells PGM 03 and 44 (L1), and near the wells PGM 01 and 10 (L2).

These structures could be related to the inflow of relatively cold water towards the centre of the borehole field. More detailed mineralogical and stratigraphic studies are needed in order to establish the existence and importance of these structures with certainty.

3. COMPARISON OF THE ALTERATION MINERALOGY OF AN ACID AND A NEUTRAL WELL IN MIRAVALLES

3.1 Introduction

In Miravalles, most of the the 52 wells produce neutral sodium chloride fluids. However, 5 wells located in the eastern sector discharge acid fluids with pH 2.3-3.2. These wells require neutralization systems in order to avoid corrosion of casings, valves and pipes, and although neutralization has been done successfully in two of the wells, it imposes additional costs and some technical difficulties. For that reason, the understanding and characterization of the acid wells is of great importance. The origin of these fluids in Miravalles is not clear, and some geochemical studies have been done by Truesdell (1991) Giggenbach and Corrales (1992) and Gherardi et al. (2002).

This section presents an overview related to the origin, occurrence and alteration mineralogy associated with the acid fluids in geothermal wells. The objective is to provide a guide in finding clues for understanding and modelling these fluids in different geothermal wells.

Also, as part of the characterization of the acid wells in Miravalles, the occurrence and chemical characteristics of the wells were analyzed, and a comparison between the secondary mineralogy of an acid and neutral well was done. The purpose was to find differences and similarities in the alteration

mineralogy, which could help to understand and recognize the occurrence of acid wells. In this case, the acid well PGM 07 (northeastern sector) and the neutral well PGM 44, near the centre of the geothermal field were selected. The mineralogical identification was made by cutting (stereoscopic microscope) and petrographic analysis. Data from XRD analyses were used in the identification of some minerals.

3.2 Origin of acid fluids in geothermal wells

The presence of acid fluids geothermal well in discharges has been of great theoretical and practical interest (Truesdell, 1991). This acidity introduces engineering problems related to corrosion and scale formation to the point that some wells have been abandoned. It is important to know the source of acidity of these waters (Akaku et al., 2000), and try to find economically feasible In some solutions. geothermal wells, the acidic fluids have been successfully neutralized and although it means additional operation costs, the investment for neutralization can be

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recovered in a few days, depending on the production capacity of the wells (Sánchez et al., 2000).

The most important species in a geothermal system for causing acidity in a hydrothermal fluid are the volatile components coming from the magma, such as HCl, SO_2 , H_2S and CO_2 . The reaction of these components with geothermal fluids and the physical and chemical changes that take place in the reservoir can produce acid fluid, which are modified in the subsequent travel to the surface. An acidic aqueous

solution tends to be neutralized or become alkaline due to interaction over a long period with the rock minerals including feldspars, micas, reduced iron oxides and silicates (Giggenbach, 1988 in Truesdell, 1991; Truesdell et al., 1989; Izquierdo et al., 2000).

At deep levels in liquid-dominated systems, the gases are dissolved in the hot water, but when steam is formed by boiling, the gases pass into a steam phase. Boiling in the upper portion of geothermal systems is accompanied by the transfer of acid gases (CO_2 and H_2S) to the resultant steam, which may penetrate the surface as fumarolic activity or become condensed in the shallow groundwater, giving rise, with oxidation, to distinctive low pH sulphate bicarbonate waters (Henley and Ellis, 1983).

The CO_2 in geothermal systems may originate from decarbonation reactions of carbonate rich rocks, from dispersed organic matter, from solution in meteoric water or from magmatic sources (Henley and Ellis, 1983).

According to Izquierdo et al. (2000) and Matsuda et al. (2000), the two most common acid agents in geothermal environments are HCl and H_2SO_4 , and they can be classified into two groups:

- Hydrochloric acid type (HCL) or Cl-type; such as in Larderello (Italy), The Geysers (USA), Kakkonda and Onikobe (Japan), Los Humeros (Mexico), Tatun (Taiwan) and Krafla (Iceland).
- Sulphuric acid type (H₂SO₄ or SO₄-type); such as in Palimpinon and Mt. Apo (Philippines), Sumikawa (Japan), and Miravalles (Costa Rica).

Truesdell (1991) classified the acid fluids into two groups:

- Acid Cl-SO₄ waters with excess chloride;
- Acid SO₄-Cl reservoir waters.

In the first case, at least part of the acidity is introduced as HCl, most probably from a volcanic source, and the other is closely associated with active volcanism (as springs). In some fields, the excess chloride has not been neutralized by reaction with the host rock because the reservoir contains no minerals (feldspar or mica) capable of neutralizing acid. Acid SO_4 -Cl waters have been found at the margins of several geothermal systems associated with recent andesitic volcanoes (Truesdell, 1991).

3.2.1 Hydrochloric acid type (Cl-type or acid Cl-SO₄)

The occurrence of HCl is related to distinct geological origins, and its presence in steam depends on certain chemical and physical conditions (Truesdell et al., 1989). The main factors controlling the production of HCl are: pH, temperature and Cl concentration. Lower pH, higher temperature and higher chlorinity allow more HCl to be volatilized with steam (Truesdell et al., 1989). The HCl increases as a function of temperature (D'Amore et al., 1990; Izquierdo et al., 2000) and it is expected that this acid becomes a problem in all geothermal systems with temperatures above 300°C, when superheated steam is produced as a result of drying (D'Amore et al., 1990).

In order to reach the surface in a steam phase, the HCl cannot come into contact with liquid water (in which it is more soluble), essentially limiting the transport to superheated steam. In absence of liquid water, the HCl in vapour remains associated and is not strongly reactive (Truesdell et al., 1989). In contact with liquid water, the HCl is dissociated into H^+ and Cl^- , becoming corrosive to the casings, valves and pipes. It seems that the zones, most affected by corrosion, are the ones located in the zone of condensation of the HCl gas (zone of mixture between $HCl_{(gas)}$ and liquid water). (Sverrir Thórhallsson, pers. comm. 2003).

Two factors are considered by D'Amore et al. (1990) regarding the origin of HCl:

- Formation of HCl from a neutral or acid boiling brine at high temperature;
- Through reactions in vapour with NaCl (halite) and silicates producing HCl gas.

To explain the origin of HCl, several approaches are known (Izquierdo et al., 2000):

- From acid fluids of magmatic origin;
- Formation of NaCl (halite) from a deep boiling brine;
- Reactions between halite and silicates.

The prolonged boiling of the liquid beneath the vapour-dominated reservoir should result in the formation of brine. Even the loss of steam through surface venting results in solute accumulation and evaporative concentration can produce halite crystallization (D'Amore et al., 1990). Also the accelerated boiling due to exploitation would lower the level of the liquid surface and leave pockets and surface films of brine which could evaporate to precipitate halite. These conditions are not limited to deep parts of vapour-dominated systems and can also occur in liquid-dominated reservoirs as well. (D'Amore et al., 1990). In the Los Humeros geothermal field, once the exploitation started, the gas moved to the zone of vapour in the upper reservoir, formed aqueous HCl and an aggressive fluid (Izquierdo et al., 2000). The injection of liquid water can recharge the liquid in the reservoir and in most cases raise pressures and prevent the transport and ultimately the generation of HCl (D'Amore et al., 1990; Truesdell, 1991).

3.2.2 Sulfuric acid type (SO₄-type)

Various mechanisms for the formation of H_2SO_4 have been proposed, according to the environment in which it is produced (Izquierdo et al., 2000). Matsuda et al. (2000) emphasized the utilization of geochemical techniques (isotope data) to reveal the origin and characteristics of acid fluids enriched in SO_4 , in particular the sulphur species.

The formation of H_2SO_4 in magmatic hydrothermal systems can be related to reactions between SO_2 and H_2O at decreasing temperatures (Rye et al., 1991- in Izquierdo et al., 2000). The acid- SO_4 waters can either have a volcanic origin or be related to near surface oxidation of H_2S (Truesdell, 1991). The deep SO_4 -rich acid fluids become more aggressive as the fluids rise in the well to shallower levels (Sanada et al., 2000).

The steam separation processes produces fumaroles and steam adsorption by groundwater and oxidation of H_2S at the water table, giving rise to steam–heated acid sulphate-bicarbonate waters. Mixing may occur between deep neutral pH and steam-heated waters to give oxidising $Cl-SO_4$ waters (Henley and Ellis, 1983).

The sulphuric acid type fluids are generally formed by any of three different mechanisms (Matsuda et al., 2000):

- Oxidation of H₂S;
- Hydrolysis of SO₂;
- Hydrolysis of S (native sulphur).

Oxidation of H₂**S**: This is a typical mechanism to generate acid sulphate hot spring water, but is rarely the cause of acidity in deep geothermal fluids, due to the highly reduced conditions (Matsuda et al., 2000). When the oxidation of H₂S takes place at shallow depth, it would be partial and accompanied by isotopic re-equilibration (Matsuda et al., 2000). In some geothermal wells, the partial oxidation of H₂S is believed to be the main source of acidity (Hermoso et al., 1998). In the oxidation of the H₂S, Reaction 1 takes place:

$$H_2S_{(g)} + 2H_2O_{(liq)} + 2O_{2(g)} \rightarrow SO_4^{-2}_{(aq)} + 2H_3O$$
 (1)

Hydrolysis of SO₂: The hydrolysis of SO₂ (Equation 2) as well as the dissolution of HCl, is related to the source of acidity of many SO₄-Cl type hot spring waters. These types of acid fluids tend to exist at great depth, near the heat source (Matsuda et al., 2000).

$$4SO_2 + 4H_2O \rightarrow 3H_2SO_4 + H_2S \tag{2}$$

Hydrolysis of native S: The hydrolysis of native S is given by Equation 3. Here the production of sulphides is three times that of sulphates, as indicated by the equation. In the Hatchobaru field (Japan), this process is estimated to take place at temperatures lower than 224°C (Matsuda et al., 2000).

$$4S + 4H_2O \rightarrow H_2SO_4 + 3H_2S \tag{3}$$

The relationships between SO_4 and H_2S concentrations in the fluids may give some clues about the origin of the sulphur species in the acid fluids. In the case that the SO_4 enrichment in the acid fluids is due to the hydrolysis of SO_2 or the hydrolysis of native sulphur, in or around the reservoir without the fractionation of sulphur species, the SO_4/H_2S ratios would be close to 3 or 1/3 in accordance with the Equations 2 or 3, respectively (Matsuda et al., 2000).

In some cases, the air dissolved in the re-injected waters can oxidize the H_2S and produce a sulphuric acid fluid (Matsuda et al., 2000). Based on chemical and isotopic characteristics, they infer that the acid fluids are the result of mixing of neutral-pH fluid with low temperature SO4-rich fluids from shallower levels. The mixing of shallow high-SO₄ water with deep neutral high-Cl water is suggested to be the origin of acid SO₄-Cl waters in some geothermal fields (Truesdell, 1991; Matsuda et al., 2000).

In some SO_4 -rich acid wells, important discharges of H_2S have been recognized during the drilling process, such as in Miravalles (Costa Rica) and Hatchobaru in Japan (Matsuda et al., 2000). In Hatchobaru (Matsuda et al., 2000), Palinpinon (Hermoso et al., 1998) and Miravalles (Gherardi et al., 2002) it is thought that the H_2S ascends to near surface, then the SO_4 , formed by oxidation is dissolved in the groundwater and may infiltrate down to the deeper portions of the reservoir and produce deep acidity. In Hatchobaru, the oxidation of the H_2S is favoured by the air dissolved in the waste waters reinjected close to the acid wells' production area. Also the hydrolysis of sulphur along the Hatchobaru fault is an important process in the formation of acid fluids (Matsuda et al., 2000).

In the Hatchobaru field, the acid aquifer is located near the contact between geological formations; therefore the acid fluids are also likely to have some horizontal extension. In one of the wells, the acid fluid occurred only during a late stage in the discharge history, possibly in response to the inflow of shallower fluids as a result of pressure decrease in the reservoir (Matsuda et al., 2000).

The occurrence of SO_4 -rich acid fluids in geothermal wells is usually not restricted to shallow levels. In Tatun (Taiwan), acid water about 200°C was found at 500 m depth, probably related to zones of several percent of sulphur (Ellis and Giggenbach, 1971). In Miravalles, some permeable zones related to acid fluid are present at depths between 750 and 1700 m; and in the Philippines, acid fluids have been found as deep as 2500 m depth (Reyes, 2000).

3.2.3 Excess of H⁺ due to chemical reactions

Akaku et al. (2000), using numerical modelling based on chemical equilibrium for liquid-solid-gas phases, studied the formation processes of saline and dilute acid waters in the Fushime and Kakkonda geothermal systems (Japan). The model considers boiling in the reservoir, originated by production-induced pressure decrease near the wells and consequent reactions with wall rocks. Their results indicate that the H^+ supply from sphalerite precipitation during boiling is the most probable cause of the observed acidity in the saline

Fushime waters. The acidity observed in the dilute Kakkonda waters could be in response to the H⁺ supply from the reactions with pyrite and magnetite and from H₂ redox reactions. Their model demonstrates that production-induced boiling and consequent chemical reactions in the reservoirs are able to produce acidity, without any contribution of acidic volatiles such as HCl and SO₂. According to their models, the lowering in the pH is caused by the excess of H⁺ (product of Reactions 4, 5 and 6), over the H⁺ consumption by CO₂ degassing, shown in Reaction 7.

$$3\text{FeS}_2 + 6\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 0.5\text{SO}_4^{2-} + 5.5\text{H}_2\text{S} + \text{H}^+$$
(4)
(pyrite) (aq) (magnetite) (aq) (aq) (aq)

$$\begin{array}{cccc} H_2O &+& 0.25H_2S \rightarrow H_2 &+& 0.25SO_4^{2-} &+& \textbf{0.5H}^+ \\ (aq) & (aq) & (gas) & (aq) & (aq) \end{array} \tag{5}$$

$$ZnCl_{2} + H_{2}S \rightarrow ZnS + 2H^{+} + 2Cl^{-}$$
(aq) (aq) (sphalerite) (aq) (aq) (6)

$$\begin{array}{l} HCO_3^{-} + \mathbf{H} + \rightarrow CO_2 + H_2O \\ (aq) & (aq) & (gas) & (aq) \end{array} \tag{7}$$

3.3 Associated mineralogy and occurrences

When an acid fluid reaches the surface (or near surface), the volcanic host rocks become altered, producing secondary minerals such as alunite (or natroalunite), hematite, jarosite, kaolinite and pyrite (Izquierdo et al., 2000). The acid sulfate alteration is a special case of advanced argillic alteration in which it is common to find the association: alunite + kaolinite + quartz + pyrite (Izquierdo et al., 2000).

The deep acid geothermal fluids could be related to alteration mineralogy such as kaolinite-alunite-pyrophyllite, as in Matsukawa, Japan (Nakamura et al., 1970).

Reyes (2000) shows three types of acid alteration related to the water composition:

- Associated with low-temperature (<160°C) bicarbonate waters that produce the association: smectite and kaolinite with or without associated pyrite, goethite and/or calcite.
- Associated with acid sulphate waters with assemblages usually containing alunite, kandites, silica
 polymorphs and sulphides such as pyrite, bornite, enargite, covelline and chalcocine. When the acid
 waters start to neutralize by reaction with the host rocks, pyrophyllite, illite, diaspore and anhydrite
 appear. These shallow waters can percolate to a few hundred metres along open faults. The
 temperatures vary from ambient to 300-330°C.
- Associated with deep magmatic hydrothermal fluids. This type can overlap with the previous one. The mineralogy is similar to above, except that at temperatures over 330°C muscovite forms instead of illite, and minerals like andalusite and cordierite appear.

Two types of acid alteration are related to the virulence and corrosivity of the fluids, they are (Reyes, 2000):

- Virulent (Sulphur + alunite + abundant pyrite/marcasite).
- Deceptively benign (without sulphur and alunite; presence of kandites, pyrophyllite, diaspore, anhydrite and pyrite).

The acid alteration frequently changes from a virulent to a deceptively benign type and then into neutral pH alteration with depth, along a fault. It also changes laterally away from the main acid channel and across narrow zones (Reyes, 2000).

Several circumstances are given by Reyes (2000) about the occurrence acid alteration in the Philippines:

- They are structurally-controlled
- They are often narrow (few cm to as much as 750 m)
- They are formed contemporaneously with the neutral pH alteration
- They form sharp boundaries with neutral pH alteration
- Some shallow occurrences could be active solfataras
- They can occur as deep as 2500 m, mostly at 1600-1800 m
- Their range of ambient temperature is to >400°C
- They are frequently found where there was or still is high gas content
- They are commonly associated with abundant veins and intense to complete alteration
- They are fluid dominated alteration- immature hydrothermal systems.

3.4 Acid fluid wells at Miravalles

The Miravalles geothermal field has been in production since March 1994. At present, there are 52 geothermal wells including production, re-injection and observation. Their depths range from 850 to 3000 m. Most of the wells produce sodium-chloride type waters, coming from a ~240°C liquid-dominated reservoir with a pH average of 5.7 and they tend to have carbonate scaling within the wells (Sánchez et al., 2000, Moya and Sánchez, 2002). However, towards the eastern part of the field, there is a sector where pH conditions of the discharge fluids differ from the rest of the field. Five of the drilled wells produce high SO₄ acid fluids, with pH ranging from 2.3 to 3.2.

The location of the acid wells and possible distribution of the "acidic zone" are shown in Figure 3. In this sector, there are SO_4 - rich fluid manifestations at the surface (Las Hornillas), which discharge acid sulphate waters (1538-2020 ppm of SO_4). In these manifestations, the steam heating is the most important process in their formation, which is related to the low Cl content, high temperature (up to 94°C) and low pH values (1.8 - 2.2) measured. The pH conditions coincide with the widespread argillitic alteration at the surface (Gherardi et al., 2002).

The first evidence of acid fluids in a deep well in Miravalles was found in 1984, during deepening of well PGM 02. A neutral fluid typical of the producing reservoir was obtained in this well from zones at 850-1100 m depth, but the discharge fluid became acid after intersection with an acid aquifer located at 1600-1700 m depth. The acid fluid had pH 2.4 and was high in SO_4 concentration (around 690 ppm). The temperature and salinity were similar to those of the neutral fluids, but SO_4 was relatively high (Truesdell, 1991; Gherardi et al., 2002).

More acid fluids were found later with the drilling of the wells PGM 19, 07, 06 and 64. In well PGM 19, an acid aquifer with a pH 2.7 was intersected at 950-1000 m depth, but deeper new aquifers with neutral pH fluid were found in that well (Gherardi et al., 2002). During the evaluation of the well PGM 07 in 1998, it became evident that the well was producing from two zones of different chemical characteristics. One is chemically similar to the aquifer observed in the neutral wells; the other one is less saline and probably related to the low pH measured (3.2- 4.3). (Vega et al., 1998).

In Miravalles, the salinity composition of the acid and neutral fluids are similar; the most conspicuous differences are in the SO_4/Cl ratios, which are systematically higher in the acid fluids by about one order of magnitude. This ratio also showed significant variations in time, which suggests that SO_4 concentrations are not buffered by SO_4 -bearing minerals (i.e. anhydrite) inside the reservoir (Gherardi et al., 2002).

One possible source for SO_4 -rich fluids is the presence of S-rich magmatic gases (i.e. H_2S), which can be oxidized on contact with the reservoir or shallow fluids to produce SO_4 (Sakai and Matsubaya, 1977; Gherardi et al., 2002). However the H_2S concentrations measured at the wellhead remained constantly low and there seems to be no correlation between H_2S and SO_4 (Gherardi et al., 2002). However, during the drilling process of the wells PGM 07 and PGM 06, remarkable discharge of H_2S (and probably CO_2) was detected, and even caused problems during the cementation of the casings.

In a preliminary way, the results of Gherardi et al. (2002) suggest that two acidification processes could be operative in Miravalles:

- In well PGM 19, the occurrence of acid fluids above the neutral reservoir could be related to a mixing between SO_4 -bearing acid waters produced at shallow levels, similar to Las Hornillas. Alternatively the acidification could be related to an influx of large quantities of air during drilling. Because well PGM 19 produces very high quantities of gas (Mainieri, personal communication in Gherardi et al., 2002), the contact between the air and H₂S could have formed SO₄ (by oxidation), acidifying the water in the process.

- In wells PGM 02 and 07, the most probable mechanism for the formation of acid fluids is the contribution to the groundwater of "immature" volcanic-geothermal waters that are not fully equilibrated with the mineral paragenesis of the reservoir (Gherardi et al., 2002).

The data shown by Gherardi et al. (2002) indicates two possible sources for the SO_4 -acid fluids in Miravalles, either superficial H₂S oxidation or inflow of "immature" volcanic waters. However, Truesdell (1991) considers that the acid SO_4 -Cl waters at Miravalles (wells PGM 02 and 19) are likely to be immature volcanic-geothermal waters, which are not fully equilibrated with feldspar, mica and Fe minerals in the reservoir, originating from a deep origin not formed by mixing with surface-produced acid-SO₄ water. These SO_4 -Cl immature waters may be considered as the parent water of the neutral Cl waters (Giggenbach and Corrales, 1992).

The acid fluids at the Miravalles field have been successfully neutralized and the wells PGM 19 and 07 have been used for commercial production since the year 2000 and 2001 respectively (Sánchez et al., 2000; Moya and Sánchez, 2002).

3.5 Mineralogical comparison between an acid well (PGM 07) and a neutral well (PGM 44) at Miravalles

In order to characterize the alteration mineralogy in the neutral and acid fluids environment in Miravalles, a detailed mineralogical reconnaissance was done. The mineralogical identification was carried out in two deep boreholes: The PGM 07 is an acid well that produces SO_4 -rich fluids, located in the northeastern sector of the field, near a hydrothermally active zone which is related to the Las Hornillas fault. The other well analyzed was the PGM 44, a typical neutral Cl-rich fluid well situated at the centre of the geothermal field about 2.5 km from PGM 07 (Figure 3). The characterization of the alteration mineralogy was carried out by analysing cutting samples, thin sections and some x-ray diffraction analysis (XRD). The lithological control and the clay zones are based on the geological reports of the respective wells (Vega et al., 1998; Herrera et al., 1999).

3.5.1 Well PGM 07

Figure 10 lists all the alteration products identified in the well, along with the lithology, clay zones and main aquifers. The mineralogy sequence observed in this well is consistent with the results in most of the wells of the geothermal field.

In the first 500 m, the alteration is dominated by low to moderate high-temperature minerals, such as Feoxides, quartz, low-temperature clays (smectites and chlorite/smectite). Chlorite is also observed along with calcite, pyrite, anhydrite, titanite (sphene) and small amounts of heulandite (XRD), pennine, sericite, epidote and wairakite.



FIGURE 10: Lithology, location of aquifers, distribution of alteration minerals and clay zones in well PGM 07; the size of the squares represents the relative abundance of the respective minerals

Below 500 m, the Fe-oxides decrease as the temperature increases, and high-temperature minerals such as sericite, epidote, pennine, prehnite and adularia are more frequently found. High silicification is present in the interval 650-1000 m, where the microcrystalline quartz can locally reach more than 50% of the volume of the rock.

The secondary mineralogy is mostly alteration of the primary minerals with minor proportions of veins and vesicle fillings. In the lavas and tuffs their matrix is often altered to:

quartz / quartz-calcite-titanite-chlorite / quartz-titanite /

The phenocrysts of plagioclases can be partially to totally altered to:

calcite / chlorite / chlorite-calcite / quartz / epidote / sericite / sericite-epidote-pennine / prehnite / prehnite-epidote / pennine / adularia / apatite

The ferromagnesians are altered to:

chlorite / prehnite / chlorite-pennine / calcite / quartz / epidote / titanite

The dominant alteration is (quartz-epidote) - chlorite-pennine - sericite - titanite.

The presence of adularia was observed below 725 m depth, as a plagioclase alteration and as small crystals associated with quartz in the matrix and in sporadic veins. Adularia was also formed at 725 m where the first total circulation loss occurred. Small amounts of prehnite were found below the 420 m, mainly as alteration of feldspars and pyroxenes. According to Vega et al. (1998), the amount of pyrite in PGM 07 was anomalously high, compared to other wells of the field; even cubic crystals of 4 mm were recovered at the shakers during the drilling. The presence of high quantities of pyrite is probably related to the proximity of the well to the Las Hornillas fault. The amount of calcite in well PGM 07 is relatively low, compared to other wells of the field. Its first appearance was at 60 m depth and continues intermittently to the bottom of the well, with relatively high values between 300 and 500 m (3-8%). The epidote is present in small amounts and intermittently below 450 m depth, with local anomalies in the cores taken at 1702 and 1810 m (where it can reach up to 8%). The anhydrite has been identified in variable amounts in all the acid wells drilled, and although this mineral is also present in some neutral wells (i.e. PGM 44), it seems to be more common and in more quantity in the acid wells. In the PGM 07 it appears intermittently and in small quantities below 420 m depth, higher values are found locally at 1134, 1340 and 1285 m, as single crystals and veins; even crystals of 1 cm were recovered at the shakers during the drilling process (Vega et al., 1998). Titanite (sphene) is present below 60 m depth and continues to the bottom of the well. Usually, it appears as substitution and partial alteration of opaque minerals (magnetite?). For this reason, it is more common in the andesitic and basaltic-andesitic lavas.

In well PGM 07, no evidence was found of mineralogy characteristic of acid alteration, as described in Section 3.3.

3.5.2 Well PGM 44

All alteration products identified in the well PGM 44 are in Figure 11, along with lithology, clay zones and main aquifers. The alteration mineralogy in the uppermost 500 m, is characterized by low-temperature assemblages, such as Fe-oxides, chlorite, smectite, calcite and pyrite. High-temperature mineralogy such as pennine, sericite, epidote, wairakite and prehnite is present below 500 m.

The *Fe-oxides* are common in the uppermost 450 m, usually related to shallow, low-temperature aquifers. Below this depth they are intermittent and in small amounts, with anomalies at 1400 m and 1800 m,

possibly related to alteration at the margins of dykes, where values can be as high as 30%. The *clays* are present throughout the well, with anomalies between 250 and 400 m when they are, related to the cap rock of the reservoir. The main *quartz* anomaly is found between 750 m and 1050 m, as an alteration of crystalline tuffs and lavas. At high temperatures, quartz is present usually together with epidote and sericite. *Calcite* is present continuously below 165 m depth, with anomalies at 245 and 280 m (>15%)



FIGURE 11: Lithology, location of aquifers, distribution of alteration minerals and clay zones in well PGM 44; the size of the squares represent the relative abundances of the minerals

and also at 1370 and 1673 m (>10%). These values are much higher than observed in PGM 07, which could be related to the chemical characteristics of the fluids. As in PGM 07, the anhydrite was found in small amounts at variable intervals. It appears between 620 and 795 m and from 1255 to 1673 m depth. As in other neutral wells at Miravalles, the anhydrite is not restricted in the neutral wells, although apparently it is more common in acid wells than in neutral ones. The presence of anhydrite in PGM 44 could be related to old feed zones with immature acid fluids, which possibly react with the surrounding rocks to become neutral; it is also possible that those zones closed after tectonic activity or processes of self-sealing. In well PGM 44, the presence of sericite is notably higher than in PGM 07, which could be related to the pH of the fluids. The small quantities of sericite in the PGM 07 could be related to the formation of K-feldspars as alteration products (orthoclase, adularia?), instead of sericite. However, the amounts of these feldspars are not very high. The K-feldspars were not identified in PGM 44. In a preliminary state, it seems that the neutral PGM 44 exhibits similar silicate alteration as the acid well PGM 07. In this sense, the silicate minerals cannot be used to distinguish the acid from the neutral fluids in these wells, and probably not either the other wells of the field. The calcite (Ca_2CO_3) is present in both wells, although it appears to be less common in the acid well PGM 07 than in the neutral PGM 44. The anhydrite (CaSO₄) is also present in both wells, although it is slightly more abundant in the PGM 07. Frequently, the samples that contain anhydrite contain also some amounts of calcite, which could suggest different depositional episodes.

The mineralogical survey indicates that there are no major differences in the alteration mineralogy between the wells PGM 07 and PGM 44. It seems that the acid fluids are restricted to narrow zones, which makes identification of minerals characteristics of the acid fluids difficult. Also, it is possible that the residence time of the acid fluids is not enough to allow the formation of those minerals.

Based on the geochemical Miravalles volcano Acid well (Case B) Acid well (Case (Case Veutral wel well Cid

3.6 Preliminary geological-geochemical models for SO₄-rich fluid in Miravalles

FIGURE 12: Model for the formation of acid SO₄-waters in Miravalles by immature SO₄ deep waters; based on geochemical data from Giggenbach and Corrales (1992), and Gherardi et al. (2002) (see text for further explanation)

results obtained by Truesdell (1991),Giggenbach and Corrales (1992), and Gherardi et al. (2002), a geologicalgeochemical model was drawn for Miravalles (Figures 12 and 13). The model includes two possibilities for the formation of the SO₄-rich acid fluids, as described above.

Immature SO₄-rich waters: The acid fluids ascend from a deep source commercial depths to (<3km)along deep fractures (Figure 12), reaching the neutral reservoir and developing acid waters in narrow zones, restricted to the fracture systems. If an





FIGURE 13: Model for the formation of acid SO₄-waters in Miravalles by oxidation of H₂S; based on geochemical data from Giggenbach and Corrales (1992), and Gherardi et al. (2002) (see text for further explanation)

acid fluid-fracture crosses a neutral one, the latter According to

Oxidation of H₂S: In this case, the geothermal fluids, rich in H₂S, ascend to shallow levels and react with the groundwater to form SO_4 (by oxidation), which can be is dissolved

in the groundwater and percolates down to reservoir outputs along open fractures (Figure 13). The mixing of shallow high-SO₄ water with deep neutral high-Cl water is suggested as a possibility to the origin of acid SO₄-Cl waters in Miravalles.

4. **DISCUSSION**

Based on the measured temperatures and alteration mineralogy, the hottest zone of the geothermal system is located in the northern sector. Some geological elements that can influence the heat flow in this sector are the east-west fault systems (such as Las Hornillas fault) and a possible heat source towards the Miravalles Volcano (to the northeast). Even a heat source at the Bajo Los Chiqueros area is possible (around 3 km to the east), where an intermediate intrusion was interpreted to be located at shallow level based on gravimetrical data (Hallinan and Brown, 1995). However, the distribution of the mineralogy and measured temperatures indicate relatively colder zones towards the Los Chiqueros area, although this thermal behaviour could be in response to the inflow of relatively cold water from north to south, along open fractures such as the NE-SW fault systems (graben structures). It seems that in the northern and eastern sectors of the field, there is an interaction between relatively cold water and a heat source, in an open fracture environment. This combination could be very important in the generation of acid fluids in the northeastern sector of the Miravalles geothermal field either by inflow of acid SO₄ fluids from a deep source or oxidation of H_2S (by interaction with relatively cold water at shallow levels). It is even possible that a hydrolysis of native S has occurred along the Las Hornillas fault.

According to the distribution and proposed models for the formation of the acid fluids in Miravalles, it is believed that faults and fracture systems play an important role in providing permeable structures for

could become acid by migration of SO₄-rich waters. patterns in fractures and faults, a geothermal well can exhibit several types of feed zones, as indicated in Figure 12. An acid well could show a shallow acid feed zone and a deep neutral one (case A - well PGM 19); a shallow neutral zone and an acid deep zone (case B - well PGM 02); or even deep and shallow acid feed zones (case C); and several other combina-tions.

those fluids. It seems that the acid fluid zone is confined to the area between the Las Hornillas fault (F14) to the north, F38 to the south, F11 in the east and F8 to the west. Other fault systems that could be involved are the F10 and the F9 (Figure 3). It is thought that most of these faults are related to extensional settings (graben structures).

5. CONCLUSIONS

5.1 Thermal evolution

The comparison between the temperature assigned to the first occurrence of epidote (minimum 200°C) and the measured temperature at that location, allowed the division of the geothermal field into:

A heating zone, which corresponds to areas where the measured temperature is at least 20°C higher than the temperature assigned to the epidote. These are located towards the northern sectors (wells PGM 05, 11, 14, 60, 62, 63 and 65) and central sector of the field (PGM 45 and 66).

An equilibrium zone was defined where the measured temperature corresponds to the epidote temperature $(\pm 20^{\circ}C)$. This zone has a north-south alignment across the geothermal field and encompasses most of the production wells.

Cooling zones are classified as areas where the measured temperatures are at least 20°C lower than the epidote temperature. Zones of possible cooling were defined towards the west (PGM 04, 15, 23, 22, 44 and 03), to the northeast (PGM 10, 01, 02, 64 and 55) and in the southern sector of the geothermal field (PGM 52 and 50). The distribution of the first two cooling zones suggests the possible control of two NW-SE geological structures in the vicinity of the wells PGM 03 and 44 (L1) and near the wells PGM 01 and 10 (L2). These could be related to inflow of relatively cold water towards the centre of the well field.

5.2 Mineralogical comparison

There are no major differences in the alteration mineralogy of the wells PGM 07 (acid) and PGM 44 (neutral). The interpretation is that the acid fluids are restricted to very narrow zones which make identification difficult. This could also indicate that the acid fluids are not in equilibrium with the alteration mineralogy probably due to the short time of residence. More detailed sampling techniques could improve knowledge about the acid wells.

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