

## Acid Fluids in Geothermal Systems: Case Study of Cerro Prieto IV Sector, México

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### ABSTRACT

Fluids of low pH are common in active geothermal fields under exploitation. More often they occur in geothermal systems associated with recent volcanism and may also occur in superheated steam containing HCl. In Mexico two of the main geothermal fields have produced corrosive fluids. In the Los Humeros geothermal field during the early exploitation stage some wells produced highly aggressive fluids. In the Cerro Prieto geothermal field, particularly in the Cerro Prieto IV sector, some wells started to produce low pH fluids; the main evidence is observed as accelerated corrosion of conduction pipe lines and changes in the chemistry of fluids.

In both fields the formation of acid fluids may be related to a deep zone where the liquid fraction is low and the highest temperatures have been recorded. In a recent study (Arellano et al., 2009) found that in the early exploitation stages the Cerro Prieto IV sector seems to be divided in two blocks by the Fault H. One with high enthalpy ( $> 2000$  kJ/kg) and low salinity compared to the block with enthalpy between 1400 and 1800 kJ/kg and high salinity. Evidence of acid fluids in Cerro Prieto IV are present in wells from the high enthalpy block.

### 1. INTRODUCTION

The occurrence of acid fluids in the discharge from geothermal wells has been of practical interest, especially by their corrosive effect on conduction pipes. Several approaches on the nature of these fluids have been proposed. Knowing the origin of acid fluids production, can assist in management decision during exploitation of geothermal resources. A common practice has been to treat fluids chemically, isolation of acid reservoir fluids and some times abandonment of wells or fields (Truesdell, 1990).

Acid waters may come to the surface through springs or drill holes originated from acid reservoir fluids. Also that boiling of high temperature neutral or acidic brines or reactions in vapor halite-silicate assemblages could generate HCl gas that is carried in superheated steam and becomes corrosive when the steam condenses, usually at the wellhead. Ascending superheated steam containing HCl may also mix with neutral waters to produce acid solutions that corrode and scale casing; possibly without acid fluids appearing at the surface (Truesdell, 1990).

Acidity in Mexican geothermal fields has occurred in Los Humeros and in Cerro Prieto. The former is considered the third geothermal resource and the later the first geothermal resource in the country. In the Los Humeros geothermal field (LHGF) the occurrence of acid fluids has been associated to a post exploitation process (Izquierdo et al.,

2003, 2005, 2007). At the early stages of production neutral brines were collected at the surface. Except well H-4; this from the beginning had to be closed and abandoned due to very high H<sub>2</sub>S concentration, high pressure and accelerated corrosion of casings. Later after few years of production, some wells in a particular sector of the field started to produce low pH fluids. To avoid low pH fluids, cement plugs where placed (H-16), isolating pipes from what was believed to be an acid reservoir. In reality cement plugs acted as a fence to avoid mobility of deep magmatic fluids (Izquierdo et al., 2005). After some time fluid pH started to decrease again.

Recently in the northeastern part of the Cerro Prieto geothermal field, particularly in the Cerro Prieto IV sector (CPIV) evidences of corrosive fluids were noted. Production data of some wells from CPIV have shown unusual features and a different response to exploitation compared to other sectors of the field. Also changes in the fluid chemistry have been registered. It is probable that acidic brines in both fields have formed under the same mechanism. In the two fields, acid fluids appeared in zones where the highest enthalpy and the lowest liquid fraction have been registered. These zones are related to the nearness to the heat source.

The purpose of this paper is to present and discuss some evidence of the occurrence of aggressive fluids in the Cerro Prieto IV sector

### 2. THE CERRO PRIETO GEOTHERMAL FIELD

The Cerro Prieto Geothermal Field (CPGF) is a liquid-dominated field, located in the northwest part of Mexico close to the United States border (Figure 1). It is the largest producing field within Mexico and has 720 MWe of installed capacity. It is the second largest producer in the world. At present more than 300 wells have been drilled not all of them are in use.

For administrative purposes the entire field has been divided into four areas known as CP-I, CP-II, CP-III and CP IV; being CP IV the shortest in productive life.

Two reservoirs have been inferred (Lippmann et al., 1991). The Alpha reservoir in the west part of the field is the shallowest and was the first to be exploited. It is found at depths between 1000 and 1500 m (Cerro Prieto I). The deeper Beta reservoir extends underneath the entire area of the Cerro Prieto at depths between 1500 and 2800 m with temperatures higher than those in the Alpha reservoir.

The Beta reservoir is located in high porosity, permeable sandstones underlying a low porosity, relatively impermeable shale unit.

In the year 2000, the condensing type 100 MWe CP IV power plant entered on line to increase to 720 MWe the

total installed capacity in the field (Gutiérrez-Negrín and Quijano-León, 2005).

The northeastern Cerro Prieto reservoir has shown unusual features and a different response to exploitation compared to other sectors of the field. A particular feature is that compared to the whole field, the CP IV area has the highest average production enthalpy (Rodríguez M, 2003). Also wells in the same area show evidence of cool water recharge; which is the predominant process in the western part of the field.

The Cerro Prieto geothermal field is located in the southern portion of the Salton Trough, an actively developing rift basin (Lippmann et al., 1997). The Salton Trough-Gulf of California is the result of tectonic activity that has created a series of spreading centers and transforms faults, which link the East Pacific Rise, an oceanic ridge, with the San Andres fault system, serving as a transform boundary. According to the model of Lachenbruch et al. (1985), in Lippmann et al. (1997), upwelling of magma from the asthenosphere creates new oceanic-type crust. Based on this model the extended crust is being intruded by gabbroic magma from the mantle. The rifting of a gabbroic intrusion is the result of high heat flows and metamorphism of the sedimentary rocks at relatively shallow depths. A seismicity area connects the Cerro Prieto and Imperial faults, possibly corresponding to a zone where magma is intruding to form a complex of dikes and sills. Some of these dikes, mainly of mafic composition, have been found in wells drilled in the eastern part of Cerro Prieto.

In 1984 Elders et al., proposed that the heat source of Cerro Prieto is large and not deep; and that Cerro Prieto could be considered as an active magmatic-hydrothermal system. In the same paper, Elders gave evidence of the occurrence of a

subsurface dike or sill rocks at the eastern part of the field; where at that time wells H-2, NL-1 and M-189 were drilled. At present low pH fluids in wells in the eastern part of the field known as Cerro Prieto IV may be the evidence of Elders et al., assumptions.

## 2.1 Geological Setting

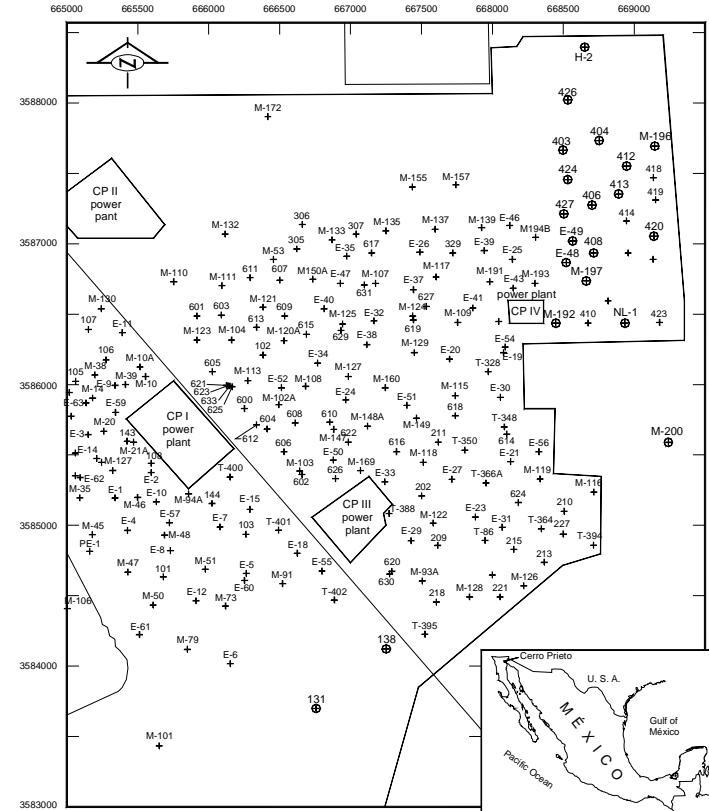
The sediments at Cerro Prieto were deposited mainly in alluvial, deltaic, estuarine and shallow-marine environments during Pliocene to middle Pleistocene (Halfman et al., 1984).

The hydrological model developed by Halfman et al. (1984, 1986) for the entire field indicates that the geothermal fluids circulate horizontally through permeable stratum from east to west and vertically through faults.

From the distribution of hydrothermal minerals Elders et al. (1984) also proposed the same direction of fluid circulation pattern and suggested that the heat source was located to the east of the field. Recharge of the beta reservoir has been considered to occur laterally along the edges of the geothermal reservoir (Truesdell and Lippmann, 1990), there is also an evidence of inflow of descending cooler groundwater.

Recently, Lira (2005) has identified five lithological units: The first (oldest) unit is the basement, represented by metamorphic and granites rocks.

The gray shale is the second unit, formed by intercalated shales and sandstones; average thickness: 3000 m. The thickness of sandstone in the gray shale varies from a few meters to 300 m; it has been called the silica epidote mineralized zone (SEMZ) and it is considered as the production zone.



**Figure 1: Location of wells and power plants in the Cerro Prieto geothermal field; CP IV roughly corresponds to the northeastern part of the field. Distances are given in meters.**

The third unit is known as the brown shale. The top is found at 600 m to the west and at 2500 m to the east (well M-205).

The fourth is the siltstone unit. It has a random distribution mainly in CP IV. It is found mainly to the east of the field. Layers of sandstone are also found in it.

Non-consolidated clastic sediments form the fifth unit that is composed of sand, gravel, silt and clay. It is of variable thickness, thin at the west and thicker to the east.

Izquierdo et al. (2000, 2001) carried out detailed mineralogical studies of cutting samples from the producing strata from wells all over Cerro Prieto. Hydrothermal mineralogy is common in other geothermal systems. It reflects interaction with neutral to alkaline pH fluids. In most drilled holes in Cerro Prieto it was observed that the intensity of the hydrothermal alteration is low and most of the secondary minerals are in the order of traces.

### 3. CERRO PRIETO IV

The Cerro Prieto IV area is located at the north east of the Cerro Prieto geothermal field. At present 31 wells have been drilled in this area; some of them for different reason are not on line. Figure 2 shows CP IV wells as well as main faults in the area.

Drilling in the area of CP IV started in 1985 with few wells (E-48, E-49, M-192, M-197, M-198 and NL-1) considered as an extension of the field. Most of the wells in CP IV were drilled from 1998 to 2005. So the operation of CP IV and information related to production is limited to a few years.

Four 25-MWe single flash units had been installed in CP IV; raising to 720 MWe the total installed capacity in the field (Gutiérrez-Negrín and Quijano León, 2005).

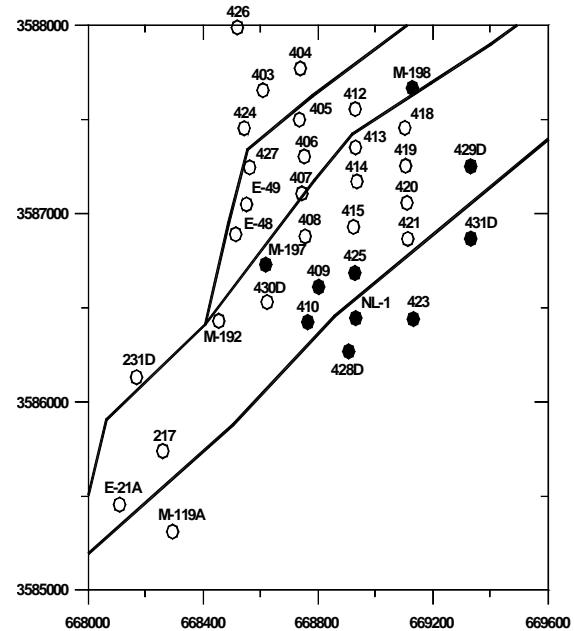
In CP IV the lithological units are deeper than in the west part of the field. At the west of the field, the top of the gray shale (SEMZ) is at a depth of 398 m; in CP IV it is found on average at 2000 m deep. The brown shale; which has been considered as impermeable strata, is a narrow layer overlaying the gray shale. The non-consolidated clastic sediments also have variable thickness being thicker at the east in CP IV. The siltstone unit is found at the east, it has a variable thickness and a random distribution.

Using epidote as a marker, the top of the SEMZ in CP IV is found at deeper than other areas of Cerro Prieto. The SEMZ has an average of 1750 m at the west part of the field and 2100 m to the east. So, all of the wells in CP IV have been drilled to depth greater than 2100 m; between 2500 m and 3000 m.

Being a liquid dominated reservoir, most of the CP-IV wells produce a mixture of steam and liquid at the wellhead. The liquid fraction has a chemical composition characteristic of geothermal brine and pH near to neutral. According to the Piper classification, the CP-IV brine can be defined as of sodium-chloride type. The content of potassium and calcium are high, while that of lithium, boron and sulfate is very low (Arellano et al., 2009).

Stable isotopic composition ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) for wellhead fluids are in the range of  $-89.8\text{\textperthousand}$  to  $-96.7\text{\textperthousand}$  for deuterium and  $-7.3\text{\textperthousand}$  to  $-9.4\text{\textperthousand}$  for oxygen-18. The stable isotopes indicate that the natural recharge to the reservoir consists of groundwater from the alluvial aquifer located in the western

part of CP-IV area. The main gases for CP-IV are  $\text{CO}_2$  (91 wt.%),  $\text{H}_2\text{S}$  (4 wt%) and  $\text{CH}_4$  (3 wt%); i.e. represent over 98 wt% (dry basis) of the non condensable gases (Portugal et al., 2005).



**Figure 2: Location of wells and main inferred faults (solid lines) in CP IV. Distances given in meters**

#### 3.1 Hydrothermal Mineralogy in CPIV

Hydrothermal mineralogy, petrographic and X-ray analysis of samples from the production zone (SEMZ) of CP IV wells (Izquierdo et al., 2000, 2001) revealed calcite, quartz and epidote as the main phases. Minor amounts of illite, chlorite, and smectite were reported and minerals like wairakite, pyrite, amphiboles and biotite were in trace amount and randomly distributed. Na-smectite, Ca-smectite, illite, chlorite and scarce interstratified minerals were identified in the clay fraction. All of these minerals occur in active hydrothermal systems where neutral to alkaline pH sodium-chloride fluids are present. Minerals that could indicate interaction with low pH fluids like kaolinite was reported in hand samples only in well 429 at 1593 m. More abundant from 2500 m to 2700 m where wall rocks are formed by almost 1:1 gray shale and sandstone. From 2826 m to 2868 m kaolinite is reported as 50% of the rock.

Optically, rock alteration was estimated to be close to 40 % in the cutting samples; it was defined as high rank and moderate to low intensity. In most of the samples, the rocks were terrigenous having shale more abundant than sandstone. According to minerals assemblages, the temperature in the SEMZ was in the range of 150 to 300 °C and higher when amphiboles were present.

#### 3.2 Fluid Production in CP IV

According to the data provided by the Comisión Federal de Electricidad (Federal utility responsible for the administration of the geothermal resources in Mexico), the wells in CP IV have produced about 150 million tons of fluids (77 million tons of steam and 73 million tons of liquid) between the dates each well started to produce and present. In that part of the field, the best of the liquid producers under wellhead conditions were wells 406, 407,

M-192 and 414, while wells 423, 403, 424 and 425 are the best of the steam producers.

The chemistry of liquid samples was characteristic of a neutral and of the sodium chloride geothermal brine type. Recently, liquid samples from few wells from CP IV showed pH below neutral, changes in their chemistry; as well as corrosion in pipe lines. These changes in composition may be indicative of processes that were occurring in the system.

According to production and chemical data from CP IV sector at least two groups of wells may be differentiated and probably are associated to geologic features in the field.

Table 1 shows some chemical components in the brine, sampled at the wellhead, produced by the best CP IV liquid and steam producers. Some of the liquid producers have different chemical characteristics. For example, wells M-192 and 414 present higher values for all ions than wells 406 and 407, indicating the effects in the borehole, such as entrance of fluids from different strata.

Liquid producers wells show a chemical composition characteristic of geothermal brines and pH near to neutral. Wells indicative of aggressive fluids show variations in their chemistry, most are steam producers.

#### 4. DISCUSSION

The chemical composition of the brine sampled from the main steam producers also show differences (Table 1). Apparently steam production in well 403 occurs under a mechanism different than in wells 423, 424 and 425. This may be related to the location of 403 in the field. The particular chemistry of well 425 in 2005 may reflect the effects of condensation; the brine collected has very low salinity and the highest B value determined in CP IV brines.

Recently well 425 was repaired, a cement plug was placed in order to avoid deep fluids migration. Table 1 shows new data for well 425. It is well known that B tends to be transported in the vapor phase of high-temperature fluids. Its relatively high B concentration may indicate deep volatiles migration; the study of the origin of B is an ongoing project. The relatively high values of Mn and Fe in the brine are related to the corrosion of the well casing. Data from 2007 show a very different composition of the fluid sampled in well 425. B is considered as an indicator of two groups of wells. The value below 30 ppm is related to high liquid fraction wells and a value greater than 30 ppm may be related to low liquid fraction wells.

Truesdell et al. (1992) associated the difference in several well parameters, like inlet vapor fraction, temperature,

isotopes and Cl concentration, observed at CP II and CP III to the location of the wells with respect to the downthrown and upthrown blocks of the beta reservoir. At CP IV these two fault blocks are not so evident; however where the top of the SEMZ is slightly displaced may indicate the location of the Fault H that limits these blocks. Using data provided by the Comisión Federal de Electricidad, several geological sections across CP IV were prepared, which showed slight offsets of the lithological units. The offset between NW wells (e.g. 403) and SE wells (e.g. 423) is between 150 m and 250 m.

Black circles in Figure 2 correspond to wells which have shown brines of low salinity. Most are located from south-west to south-east in direction to north-east close to branches of Fault H which was considered as a source of hot fluids (Halfman et al., 1984). So, it is possible that deep hot fluids are ascending through Fault H and reach the productive zone. Considering the two fault blocks mentioned by Truesdell et al. (1992) the difference in well fluid chemistry seems to reflect structural effects. For example, well 423 – the best steam producer and one of the deepest (2991m) in the southern part of CP IV – is located SE of Fault H (Figure 2), possibly in the downthrown block.

Casing corrosion has been observed in well 423. The recharging deep hot fluids might be corrosive or become corrosive on their way to the surface. Physical and chemical characteristics of the CP IV steam wells suggest that condensation of very high-temperature steam may occur in the reservoir (Truesdell et al., 1992) or as it flows up the borehole toward the surface.

Recently, some of the CP IV wells have shown corrosion effects in their casings; also some black solids have been recovered from fluids sampled at the wellhead. X-ray diffraction analysis of these solids shows that they are mainly magnetite with minor amounts of halite and calcite. Also siderite, chalcopyrite, marcasite and pyrrhotite have been identified by XRD in scales from vapor producer wells. In contrast scales identified in liquid producer wells consist mainly in calcite.

The pH measured in samples collected from the wellhead does not show low values (Portugal et al., 2006). However the effects of corrosive fluids and most of the differences found in fluid chemistry of CP IV wells may be associated to the processes occurring in the reservoir in response to exploitation of the field or be related to different sources of fluid recharge; which may be controlled by geologic structures in the geothermal system, like Fault H. Well 445, the latest drilled in the SE part of CP IV, has shown pH close to 5.

**Table 1: Chemical composition of the brine sampled at the weirbox of some CP IV wells. Concentration is given in mg/kg. Metals analyzed by ICP (b. d. = below detection limit).**

Well	CP IV Liquid producers						
	Na	K	Ca	Cl	B	Mn	Fe
406	5850	1344	115	10805	15.3	0.39	0.06
407	7032	1529	133	11952	16.5	0.62	n.c.
M-192	7829	2854	294	18866	21.8	1.80	0.35
414	11020	2006	169	13863	22.3	2.41	3.69
CP IV Steam producers							
423	3188	853	137	5629	43.3	4.75	12.2
403	7997	1933	255	14245	34.5	0.99	0.85
424	4652	1059	103	8408	45.9	1.29	6.86
425(2005)	7.57	b.d.	b.d.	285	99.2	2.02	1.48
425(2007)	4737	1022	142	8550	4211	n.a	2.07

Evidence of deep fluid migration is shown by the amount of B and CO<sub>2</sub> which may be used to differentiate wells that produce acid fluids from those which do no. B concentration in fluids from wells producing high liquid fraction, low enthalpy and low CO<sub>2</sub> is below 30 ppm in wellhead samples. In contrast wells with low liquid fraction, high enthalpy and high CO<sub>2</sub> B have values greater than 40 ppm.

Similarities among the Los Humeros geothermal field and Cerro Prieto IV sector may indicate that the origin of low pH fluids is similar.

In both fields the presence of characteristic minerals of neutral alteration and the absence of typical minerals of acid alteration suggest that the acidity in the geothermal fluids was generated in a stage subsequent to the deposition of minerals formed in the rocks of the reservoir. Kaolinite in well 429 is the only mineral that could indicate interaction with low pH fluids. Well 429 is located in the eastern part of CP IV and may be close to the magmatic source. As kaolinite was observed only in hand samples there is not certainty of its hydrothermal origin in this well.

In the Los Humeros geothermal reservoir rocks close to the heat source show low hydrothermal alteration intensity, this fact has been considered as an indication of the low liquid fraction (Gutierrez-Negrín and Izquierdo, 2009). In CP IV the same interpretation may be given for wells included in the high enthalpy block (low liquid fraction and low salinity). In the two geothermal systems the acidity may be associated with drying of the reservoir and exploitation of hotter areas.

It is probable that the alteration mineralogy does not reflect equilibrium with the present fluid and that the fluid from which the alteration minerals have formed had physical and chemical characteristics distinct to the present one.

Boron may be considered as a magmatic volatile, as the wall rocks in Cerro Prieto are not the source of B, it tends to be transported in the vapor phase.

In both fields acid fluids form in wells with low liquid fraction showing high enthalpies. The only evidence of the presence of acid fluids is accelerated corrosion of pipe lines. No excess of chloride in the chemical composition of fluids has been observed.

## 5. CONCLUSIONS

From production data and chemical composition of fluids, in CP IV there are at least two groups of wells (Arellano et al., 2009). Data from wells at the center of CP IV suggest entrance of shallower low temperature fluids. While wells at the east and south east show the highest temperatures of CP IV sector and tendency to decrease the liquid fraction.

The two groups of wells in CP IV should be related to the subsurface geology in this zone.

Acid fluids formation is a post exploitation process in wells located not only close to faults but near the heat source conduits; where magmatic volatiles are transported by vapor.

This is reflected in two zones with similar characteristics, one near well 424 and the other in the eastern part of CP IV (wells M198, 429D, NL-1, 428D, 423). The two zones show the higher enthalpies, low chloride, low salinity brines and higher CO<sub>2</sub> and B content. The fluid chemistry of wells 428 and 429 was modified after they were repaired.

Wells which showed evidences of corrosion coincide with the wells located in the eastern part of CP IV (425, 428D, 429D etc).

In CP IV, Boron in fluid discharge may be considered as a good indicator of deep volatile species migration; which on their way to the surface may turn almost neutral fluids in low pH fluids.

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