NOTICE CONCERNING COPYRIGHT RESTRICTIONS

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

CORROSION AND SCALING IN THE WELL H-16 OF THE LOS HUMEROS GEOTHERMAL FIELD

Luis C.A. Gutiérrez Negrín and Julio C. Viggiano Guerra

Comisión Federal de Electricidad. Apdo. Postal 18-H, Morelia 58090, Michoacán, México.

ABSTRACT

The liner pipes of well H-16 from Los Humeros geothermal field were strongly corroded and incrusted by silica and iron sulphides. The corrosion process seems to be happened to an average rate of 0.752 mm/year and HCl from deep zones of the geothermal reservoir seems to be the cause. The scaling of the liner pipe was induced by mixing of the deep fluids and another fluids produced from a shallower zone (around 1400-1450 m depth). Future wells located at the same area of the (the Central Collapse), should to field avoid the mixing of fluids from both zones in order to prevent the scaling and to reduce the corrosion rates.

INTRODUCTION

Well H-16 was drilled in the Los Humeros, Puebla, Mexico, geothermal field in 1985. After its drilling was assessed resulting with 48 ton /hour of steam and 3.6 ton /hour of water, at 0.8 Mpa of separation pressure. Subsequently, the well was flowing by orifices of different well - head diameter and different pressures, and a progressive decrement of its production was observed. In August of 1988, the well production had descended to 31.2 ton /hour of steam and 6.5 ton /hour of water. In January and February of 1989 was observed that the well had been incrusted.

In May of 1989 a drilling rig was installed and 72.3 m of the 7" diameter liner pipe were recovered. Around a third part of that recovered liner presents advanced corrosion and scaling. This work reports the type of corrosion, scaling characteristics, and discuss some ideas about its origin and some suggestions to avoid them.

THE LOS HUMEROS GEOTHERMAL FIELD

This geothermal field is located between the eastern portion of the State

of Puebla and the western portion of the State of Veracruz (Fig. 1). The field lies into a volcanic Quaternary caldera, named Los Humeros Caldera, which is part of the eastern sector of the Mexican Volcanic Belt.



Igneous, metamorphic and sedimentary rocks outcrop in the geothermal field and its surrounding. Intrusive and metamorphic rocks represent a Permian basement over which Jurassic and Cretaceous sedimentary rocks, mainly limestones, were deposited (Alonso *et al.*, 1985). By middle of Miocene, about 14 million years (m.y.) ago, granitic stocks were intruded into limestones, and hornfels, skarns and marble were locally formed as a contact metamorphism products.

Volcanic rocks seem to have been formed during three volcanic periods (Gutiérrez N., 1982). First of them happened from Middle Miocene to Later Pliocene (11 to 2 m.y. ago), and formed thick mainly andesitic flows within which the geothermal fluids are presently enclosed. Second volcanic period started 0.51 m.y. ago, with the extrusion of rhyolitic domes followed by 180 km3 (Ferriz, 1985) of rhyolitic pyroclastic flows (Zaragoza Ignimbrite); a calderic collapse (the Los Humeros Caldera) in a surface of 21 × 15

km was formed as a consequence of such a sudden pyroclastic eruption. Two similar eruptions, but with minor amount of pyroclastic flows, formed two more calderic collapses (Los Potreros Caldera and the Central Collapse) inside the Los Humeros Caldera, between 0.1 and 0.06 m.y. ago. The Los Potreros Caldera has 10 km in diameter and the Central Collapse has around 3 km in diameter. Third and last volcanic period happened from 0.06 to 0.03 m.y. ago, and extruded basaltic, andesitic and dacitic lavas and some air-fall tuffs.

Thermal points in Los Humeros are only fumaroles and hot soils, lacking of hot springs; by the way, "humeros" means smoky, justly because of the large amount of fumaroles. Geothermal reservoir in Los Humeros seems to be confined to the subsurface of the Central Collapse, related to its circular structure, and to a narrow zone related to an important NW-SE trend fault, named Mastaloya Fault (Gutiérrez N., 1987).

Thirty three geothermal wells have been drilled in the field, whose depths range from 200 to 3280 m. Lithological analysis of cuttings and core samples, of these wells indicate that the geothermal fluids are included in the Miocenic to Pliocenic andesitic series with around 1600 m of thickness. Overlying to these andesites there are ignimbrites, which act as a sensu lato sealing cap, together with the upper portion of the andesitic unit (Viggiano and Robles, 1988). Metamorphic rocks, like hornfels, skarns and marbles, unmetamorphized limestones and some Miocenic granitic intrusives, are the basement underlying to the andesites. This presents low porosity basement and permeability, without exploitable geothermal fluids but with high temperature. Nevertheless, the basement seems to allow some deep geothermal fluids to Dass through it.

Rocks of the subsurface are hydrothermally altered by their interaction with the geothermal fluids. Three mineral zones have been classified; from the surface to bottom they are (Viggiano and Robles, 1988):

Zeolite zone.- Temperature from 50 to 150°C. Includes zeolites (except wairakite), hematite, calcite, pyrite, chlorites and quartz. This zone affects to andesites, basalts, air-fall tuffs and ignimbrites.

Epidote zone.- This zone has been divided into: <u>Epidote sub-zone</u>, with temperatures from 150 to 200°C and minerals like hematite, calcite, pyrite, rutile, sphene, clays, chlorites, quartz

and epidote (there are also some mineral relic of amphiboles and garnet); Epidotawairakite sub-zone, with temperatures from 200 to 300°C and hematite, calcite, anhydrite, pyrite, rutile, sphene, clays, chlorites, quartz, epidote, wairakite and prehnite. The epidote zone affects . essentially to the Tertiary andesites. The epidote sub-zone has been associated to low permeability, while the epidotewairakite has been considered as an indicative evidence from production zone of the reservoir.

Amphiboles zone.- This zone shows temperatures of 300°C or higher. Is characterized by pyrite, chlorites, quartz, epidote, prehnite, amphiboles, potassium-mica, biotite, garnet, diopside and wollastonite (these three last minerals have been identified also as primary minerals in metamorphic rocks from



Fig. 2.- Location of well H-16 at Los Humeros.

basement). Amphiboles zone affects to lower parts of the Tertiary andesites and some portions of the basemental rocks.

Most geothermal wells have an average production of 30 ton /hour of steam, with very low or zero water production. The greatest temperature is 340°C in the andesitic zone and almost 400°C in the The non-condensible gases basement. content (% in weight) in the steam is between 1 and more than 30; CO2 and H2S are the main gases in steam with significative H2 content (Table 1). HCl was detected (Alonso $et \; lpha$!., 1985) in well H-4, which had to be cemented and closed due to the high corrosion observed in the production casing.

	H-1	H-9	H-12	H-18	H- <u>3</u> 3
% wght. of gas	5.69	1.39	7.39	36.52	0.99
C02	98.27	84.97	94.36	95.66	80.28
H2S	0.92	10.52	3.76	1.73	14.27
NH3	0.638	1.740	0.497	0.220	3.530
He	1E-4	8E-4	0	0	0
H2	6.4E-4	0.17	6.2E-2	9.9E-2	0.12
N2	0.154	1.430	1.240	0.186	1.700
CH4	9.5E-3	1.17	0.80	2.10	9.98-2
Date of sampling: October 31, 1989.					

TABLE 1. CHEMICAL COMPOSITION OF GASES IN SOME WELLS IN LOS HUMEROS.

At this moment, four 5 MW backpressure units are under construction, and four more units of 20 MW are planned to be installed in the field. Two 5 MW units will be in operation this year.

WELL H-16

This well is located at the northern portion of Central Collapse (Fig. 2). Has a total depth of 2048 m, and its lithology is as follows (Viggiano, 1989):

> 0-150 m: Recent basalts 150-900 m: Quaternary ignimbrites 900-2000 m: Tertiary andesites 2000-2048 m: Tertiary hornfels

Well H-16 was constructed according to the diagram shown in Figure 3. During its drilling small circulation losses were observed in the last 500 meters, being 10 m3/hour the greatest. However, there were total circulation losses during the first 100 meters, as in Los Humeros often happens.

Microscopic evidences for stresses and faulting were observed in the recovered cuttings from the bottom of the well and from the intervals recorded in Figure 3. 319°C was the highest stabilized temperature at the bottom, but a temperature of 258°C was calculated since 1410 m depth.

Distribution and abundance of some hydrothermal minerals (calcite, pyrite, epidote, biotite and amphiboles) are also shown in Figure 3. It is remarkable the practical lack of calcite beyond 1100 m depth. According to the mineral zones above-mentioned, Zeolite zone would be from 0 to 900 m depth, Epidote zone from 900 to 1500 m, and Amphiboles zone from

The chemical composition of produced water of the well was initially of a sodium-bicarbonate type; after the water changed to a sodium-chloride type, but by ending of 1988 the water became to the sodium-bicarbonate type (Tello, 1989; see Table 2). It is important to remark the strong decrement of bicarbonates between June 1986 and July 1987: they descended from the first place of anions to the third one, after the chlorides and sulphates. But in just three months (from October 1988 to January 1989), the bicarbonates recovered the first place among the anions.

Date	C1	HC03	S04	Main anion			
86-02-14	208	393	150	HC03>C1>S04			
86-03-18	208	450	197	itid.			
86-06-12	309	900	-	ibid.			
87-07-14	263	144	191	C1>S04>HC03			
87-08-05	263	144	191	ibid.			
88-06-24	298	55	95	ibid.			
88-08-11	212	74	165	ibid.			
89-01-20	210	524	192	HC03>C1>S04			
89-02-14	210	523	197	ibid.			
89-10-13	99	464	142	HC03>S04>C1			
All sumpling of Of dispeter bolo							

All sampling at 2" diameter hole.

TABLE 2. GEOCHEMICAL WATER TYPE CHANGES IN THE WELL H-16



Fig. 3.- General characteristics of well H-16.

In May of 1989 it was attempted to recover the 7" diameter liner pipes with a drilling rig, after to confirm that it was blocked up and, likely, strongly damaged. It was believed that well could flow again without the incrusted liner. Only 72.3 m lenght of liner pipes were recovered. From them, 50.2 m are of unslotted liner (just four pieces) and 22.1 m are of slotty liner (two pieces, second uncomplete). Because of its advanced corrosion, the liner was broken around 1430 m depth, laying to the bottom of well (Figure 4; see also Figure 3 to compare).

Four pieces of unslotted liner are practically free of corrosion or scaling; only the lower piece presents scarce iron sulphid deposits. However, in two pieces of slotty liner three portions can be noticed (Fig. 4). Upper portion (1410 to 1415 m depth) presents essentially the same conditions of the lower part of unslotted liner: some annular deposits of iron sulphide with open slots. Middle portion (1415 to 1420 m depth) presents complete scaling, with sealed slots. Lower portion (1420 to 1432 m depth) presents high corrosion and thinning of liner pipe thickness; its slots are sealed with sulphides and, in some places, annular deposits of sulphides can also be observed (Lopez M., 1989).

ANALYSIS OF LINER AND SCALING

Recovered liner was analyzed bγ metallography in order to determine if its corrosion could be induced by a deficient manufacture. The liner pipe was analyzed in laboratories of the Instituto Tecnoldgico de Morelia and of the Instituto de Investigaciones Eléctricas. Results indicate that mechanical characteristics ٥f the steel of liner pipe are in concordance to the API (American Petroleum Institute) standards, but the analyzed samples present high density of nonmetallic inclusions and segregations (carbon and carbide, martensite, manganese sulphides). Even though these inclusions

increase the tensional strength of steel, act as favorable points for corrosion (IIE, 1989; Malagon, 1989).

The Rockwell C (Rc) hardness of the liner pipe was determinated in an average of 27.1, being the grain size between 8-9 (fine grain, after standards) and the chemical composition was qualitatively determined by X-ray fluorescence as follows (Malagon, 1989; Garcła, 1989):

- Heavy elements: Fe, Mo, Zn, Sb, Sr, Pb, Cu, Mn, Ba, Ni.
- Light elements: Al, S, Mg, Si, P.

The corrosion rate was determinated in a rank from 0.623 to 0.872 mm/year, with an average of 0.752 mm/year. Those rates are remarkable greater than current rates in geothermal fields, which varie from 0.03 to 0.3 mm/year (IIE, 1989).

The scaling products were analyzed by chemical, petrographical and X-ray diffraction methods. In Figure 4 have been marked two zones in the transversal section of the incrusted liner pipe. Zone 1 is peripherical, black coloured, hard, brittle and with high density (4.5 g/cm3 in average). Zone 2 is the central one, light coloured (white to yellow), glassy and with a lower density (2.21 g/cm3 average). The average chemical composition in average of both zones is (IIE, 1989):

Component (%)	Zone 1	Zone 2
Fe	94.28	1.83
Si02	2.90	90.97
S	8.76	0.56
A1	0.05	0.16
C1	0.31	0.01
Cu	0.02	t
Ca	0.02	0.14
Mg	0.02	0.02
Na	0.01	0.04
ĸ	n.d.	0.02
Pb	t	n d .
Insoluble	0.24	2.79

n.d.= No detection; t= traces

According to the microscopic analysis of scaling samples, the zone 1 is mainly formed by iron sulphides and oxides, with minor amount of amorphous silica, cryptocrystalline quartz and chalcedony in alternative layers (IIE, 1989). The zone 2 is essentially formed by amorphous opaline silica (Viggiano, 1989) and microcrystalline quartz (IIE, 1989); these silica minerals alternate with flakes of anhydrite and gypsum (Viggiano, 1989), and with some manganese and carbon minerals. Some iron sulphides and oxides (pyrite, magnetite, hematite) were also observed among the silica minerals; actually, some silica nodules seem to be formed around isolated pyrite minerals.



Fig. 4.- Status of well after the corrosion and scaling period.

In upper and lower portions of the scaling zone, there are some annular depositions of iron sulphides and oxides within the liner pipe, as was mentioned. Those deposits have a density of 4.07 g/cm3 in average, and average contents of: Fe: 89.17%, S:12.58%, and SiO2: 2.18% (IIE, 1989). The sealed slots of lower portions of the liner pipe present oxides (magnetite, marcasite) and sulphides (pyrite, pyrrotite, troilite) (Garcla, 1989).

DISCUSSION AND SOME CONCLUSIONS

It has been suggested that the well H-16 produced from two distinct production zones: one shallow (around 1400-1450 m depth) and one deeper (Löpez, 1989; Tello, 1989; IIE, 1989). Actually, this condition seems to be current in another wells drilled in the Central Collapse area (Lôpez, 1989). Deep zone would produce superheated steam (Tello, 1989) having a very low liquid phase (IIE, 1989), and shallow zone would produce steam and water (IIE, 1989) or condensated water from deep steam (Tello, 1989). Deep zone presents some amount of HC1 which corrodes the deeper portions of liner pipe, forming iron chlorides in deep fluids. These fluids, by mixing with shallower fluids -which has H2S and a lower pH--, allow the deposition of iron sulphides, starting then the scaling process of the pipes (IIE, 1989).

Temperature of the deeper zone in the reservoir has been estimated between 300 and 330°C, and a salinity of its fluids has been also estimated from 2000 to 7000 ppm of NaCl (IIE, 1989). pH of the same deep zone seems to be lower than 5.0, according to its hydrothermal mineralogy (Viggiano, 1989). Under such a conditions, deep fluids could have from 10 to 20 ppm of HCl; this acid would be drived in steam phase, because the liquid phase saturation should be low (IIE, 1989).

Existence of two production zones in the well H-16 was evidenced by the strong variances in the chemical composition of its fluids --sampling at different orifices and well-head pressures in the same month--, by the excess of enthalpy, and by the lack of water-rock equilibrium (Tello, 1989).

The evolution of chemical composition of the separated water can be seen in Figure 5. All the recorded analysis in that figure correspond to the same sampling condition, in this case hole of 2" in diameter. Last data (October 1989) were obtained after the liner was recovered.

Taking in account that boron is a typical component from deep origin, representative of the suggested deep production zone, and that the behavior of chlorides and sulphates are symmetrical (Fig. 5), as one can expect if the geothermal fluids are originated from two distinct zones, the evolution of well H-16 can be summarized as follows. At the beginning, perhaps the first half of 1986. the well produced from the two suggested zones, geothermal fluids presenting increasing characteristics from both: boron, chlorides amount of and bicarbonates. The remarkable variances in boron of the analysis performed in the months of 1986 at different first conditions and very near dates (Tello, 1989), also evidence the suggested just simultaneous production.

Probably since the second half of 1986, the fluids from deep zone became the prevailing, as the relatively high amounts of chlorides and boron and the relatively low amounts of bicarbonates suggest. This condition prevailed until middle of 1988, allowing the corrosion of the bottom liner pipes and the first deposition of iron sulphides on the shallow portions of the liner. By that date, sudden decrement of boron and chlorides and increment of sulphates and pH, suggest that scaling was happened and, then, the shallow production zone prevailed.

corrosion process The could he started practically since the first days of 1986, when the well started to flow, but certainly happened since the middle of that year, when deep fluids seem to become prevailing. In that date, deep geothermal fluids were flowing in vapor phase with 10 to 20 ppm of HCl. Near of the well or deep parts of it, a partial within condensation of steam was happening, allowing the appearance of a very acid condensate. During its rising along the liner pipe, this condensate reacted upon iron of the pipes, corroding them, and dissolving the iron.

When the condensate with dissolved iron, perhaps as iron chlorides (Lopez, 1989), reached the shallow supplying zone, reacted with its fluids depositing iron sulphides formed from H2S. Besides, the mixing of the rising condensate with the shallow fluids neutralized the acidity of condensate, as is shown in Figure 5.

Apparently, the deposition of silica did not occur inmediatly after of the sulphides one. Probably in June of 1988 its deposition had not started yet, because in that date the concentration of silica in the separated water was still high (Fig. 5). It is possible that the





Fig. 5.- Chemical variances of the separated water of well H-16

sulphates deposition (as anhydrite and gypsum) began before of the silica but after of the sulphides, because the sulphates content was relatively low in June of 1988 (Fig. 5).

However, two months after, the content of silica had a decrement. Therefore, it is evident that in August of 1988 the deposition of SiO2 (as quartz and amorphous silica) had started, and continued to February of 1989 at least (Fig. 5). The deposition of sulphates seems to be ceased or become lower from that date.

On the other hand, deposition of and presents silica sulphates some problems, because the water from well H-16 is not satured with relation to calcite, quartz and anhydrite (Tello, 1989). Nevertheless, if the deep steam is superheated could produce saturation in the liquid phase of shallow zone by mixing with it, allowing precipitation of quartz (IIE, 1989; Tello, 1989). Also has been suggested that silica can be deposited by reaction with some before deposited iron hidroxides (Tello, 1989).

The well H-16 was repaired in December of 1989. After the 8 1/2" diameter hole (see Fig. 3) was filled with high density mud from the bottom to around 1600 m depth, two plugs were placed: one obturanting plug and one cement plug, which top reached 1570 m depth. Thus, the deep zone was isolated, expecting that the well produce from the shallow one.

Evidently, more wells located at the Central Collapse of Los Humeros field will present similar corrosion and scaling problems. Actually, all the wells that have penetrated and produce from the two production zones will be affected by the same process. Therefrom, a repair as made in the well H-16 could be necessary in those wells.

On the other hand, in future wells would be appropriate to avoid the deep zone and to attempt that wells produce from the shallow one (IIE, 1989; Viggiano, 1989). Certainly, the amount of fluids could be lower, but the wells would be shallower. In some cases could be necessary to reach the deep zone, because the shallow one present too low permeability. Then, the shallow zone should be completely isolated with casing pipes and cement, to avoid the mixing with deeper fluids. Perhaps some corrosion would occur, but scaling could be saved. In such a cases, would be a good idea to leave the smallest diameter hole of well without liner pipes.

REFERENCES

Alonso E., H., González S., A., y Razo M., A., 1985 (Coords). Geologia de los yacimientos geotérmicos en México. CFE. Reporte DEX 3/85. Unpublished.

Ferriz, H., 1985. Zoneamiento composicional y mineralógico en los productos eruptivos del Centro Volcànico de Los Humeros, Puebla, México. *Geofísica Internacional*, Vol. 24, pp. 97-157.

García D., J., 1989. Reporte de estudios de difracción y fluorescencia de rayos X a tubería de CFE. ITM. Internal report. Unpublished.

Gutiérrez N., L.C.A., 1982. Litologła y zoneamiento hidrotermal en los pozos H-1 y H-2 del campo geotérmico de Los Humeros, Pue. CFE. Informe 45/82. Unpublished.

Gutiérrez N., L.C.A., 1987. Geotermia: Una fuente de energla al alcance de México. *Ciencia y Desarrollo* No. 73, pp. 35-47.

Instituto de Investigaciones Eléctricas, 1989. Caracterización del fenómeno corrosión-obturación de pozos de Los Humeros. Informe IIE/11/3753/I 15/P. Unpublished.

Lôpez M., J.M., 1989. Reporte geoquimico sobre la tuberia de producción recuperada en el pozo Humeros No. 16. CFE. Internal report. Unpublished.

Malagon R., H., 1989. Reporte metalogràfico de la tuberia de 7" de diàmetro del pozo H-16 del campo geotérmico de Los Humeros, Puebla. ITM. Report for CFE. Unpublished.

Tello H., E., 1989. Quimica de los fluidos de descarga del pozo Humeros 16. CFE. Informe 6/89. Unpublished.

Viggiano G., J.C., and Robles M., J., 1988. Mineralogia hidrotermal en el campo geotérmico de Los Humeros, Puebla. I: Sus usos como indicadora de temperatura y del régimen hidrològico. *Geotermia*, Vol. 4, No. 1, pp. 15-28.

Viggiano G., J.C., 1989. Incrustaciones en el pozo H-16, Los Humeros, Puebla. CFE. Informe 1389-010. Unpublished.