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# NEUTRALIZATION PROCESS OF ACID WELLS: DESIGN OF THE SAMPLING SYSTEM, MIRAVALLES GEOTHERMAL FIELD, COSTA RICA

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### ABSTRACT

In the year 2000, downhole pH neutralization was started in the Miravalles geothermal field with well PGM-19. Since then, three additional systems have been installed in the acid wells PGM-02, PGM-06 and PGM-07. Several changes have since been made in order to improve operative conditions. The online sampling process has not been implemented successfully but that is essential for the control and development of the neutralization and, subsequently, the exploitation of the acid sector of the field.

In this report, three scenarios for on-line pH monitoring were studied, two of them based on a flashing process; the third on a cooling process using a heat exchanger, where flashing is minimal. The computed saturation index for amorphous silica (log(Q/K)) indicates problems with silica scaling in most of the exchanger. The last scenario also needs fresh water and possibly other equipment to keep the readings continuous (another exchanger in parallel). However, this option would give the best results of pH readings as it minimizes the losses of volatile components that affect the value of the acidity, and approaches the real values inside the pipe. The disadvantages presented in the heat exchanger are not significant when compared with possible costs of an uncontrolled system: loss in production, the cost of mechanical intervention, the cost of the wells being out of production, associated costs in damages to casing, pipes and superficial stations and possible loss of a well. Hence, the cooling process (heat exchanger) should be selected.

# **1. INTRODUCTION**

Exploitation of geothermal energy began in Costa Rica in 1994 with the installation of a power plant of 55 MWe in the Miravalles zone (Figure 1). The current installed capacity is around 160 MWe (Table 1). Geothermal utilization in the country is primarily for electrical energy production (Mainieri, 2005), although there are some swimming pools that use natural geothermal water.

During drilling it was discovered that some of the wells belonged to an acid aquifer, or rather an *acid* sodium-chloride-sulphate aquifer (Na-Cl-SO4). The aquifer is located in the northeast sector of



Miravalles. The fluids from this aquifer have a high content of sodium-chloride sulphate, and pH values are between 2.4 and

3.2. These acid wells have high productivity (7 MW in average), however, it did not seem possible to exploit those wells for energy production due to corrosion problems in the pipelines, casing and other superficial stations. Therefore, it was necessary to develop a neutralization system. This system made it possible to take advantage of the resource, and also to recover the initial investment in drilling.

Several changes have been made since the initial application of the neutralization system, for example on the alloys in the capillary tube, the reduction of the NaOH concentration, and changes

in the operating system.

Unit	Power (MWe)	Туре	Start-up date	Final date	Owner
Unit 1 – Mir. 1	55	SF	March, 1994		ICE
WHU-1	5	BP	January, 1995	July, 2006	ICE
			December 2006		
WHU-2	5	BP	September, 1996	August, 1998	CFE
WHU-3	5	BP	February, 1997	January, 1999	CFE
Unit 2 – Mir. 2	55	SF	August, 1998		ICE
Unit 3 – Mir. 3	29	SF	February, 2000		GG
Unit 5 – Mir. 5	19	ORC	November, 2003		ICE
Total	163				

 TABLE 1: Installed capacity in Miravalles geothermal field

SF = Single flash;BP = Backpressure;ORC = Organic Rankine Cycle binary plant;WHU = Wellhead unit; one unit's location was changed in 2006;

ICE = Instituto Costarricense de Electricidad;

CFE = Comisión Federal de Electricidad (México);

GG = Geoenergía de Guanacaste Ltda., with a BOT (Build-operate-transfer);

In all processes, it is necessary to monitor and control the main variables. The sampling system plays a fundamental part in the recording and control of these variables. The commercial exploitation of the acid wells (its geothermal application) would not be possible without an adequate sampling system. Such a system shows if the neutralization process is being carried out correctly or not. The measurements must be made continuously. The main focus of this work is to suggest alternatives for

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sampling and measurements in order to find which one gives the best measurements (is most representative for the situation in the well). For that aim, it was necessary to:

- Analyse some plugs that formed in the capillary tube during sampling;
- Analyse and make plots of amorphous silica saturation curves, and estimate the temperature of silica scaling with the chemical characteristics of each well with the aid of geochemical reactions programs;
- Do pH measurements on site as well as measure the head pressure from equipment installed in the wells; discuss possible variations between readings and evaluate the feasibility of locations.

The general description of the neutralization process is treated in Section 2 of this work. Section 3 covers the design analysis (descriptions, results and discussions) and the conclusions are located in Section 4.

### 2. GENERAL DESCRIPTION OF THE NEUTRALIZATION PROCESS

# 2.1 Geochemical and thermohydraulic characterization of acid wells

The Miravalles geothermal field has 3 mains aquifers (Rodríguez, 2006). These aquifers are shown in Figure 2 and are described briefly here below:

*Neutral sodium-chloride aquifer (Na-Cl):* Its fluids have a sodium-chloride composition. It is located at the northern and central sectors. There is calcium carbonate scaling with chemical treatment required to control it.



FIGURE 2: Different zones of the Miravalles geothermal field. There are three mains aquifers: Na-Cl, Na-Cl-HCO<sub>3</sub> and Na-Cl-SO<sub>4</sub>; the acid wells are located in the Na-Cl-SO<sub>4</sub> aquifer, indicated in dark grey / red

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 $T_{\text{quartz}}$  (°C)

Enthalpy (kJ/kg)

239

1068

*Neutral sodium-chloride-bicarbonate aquifer (Na-Cl-HCO<sub>3</sub>):* Its fluids have a sodium-chloride bicarbonate composition. It is located in the southeast sector. There is severe calcium carbonate scaling with chemical treatment necessary to avoid it.

Acid sodium-chloride-sulphate aquifer (Na-Cl-SO<sub>4</sub>): Its fluids have a sodium-chloride sulphate composition. It is located in the northeast sector. It has a low pH (2.4-3.2). Chemical treatment is necessary to avoid corrosion in the well casings and surface equipment.

Four acid wells with their respective neutralization systems are located in the acid sodium-chloridesulphate aquifer (Na-Cl-SO<sub>4</sub>). These wells are PGM-02, PGM-06, PGM-07 and PGM-19. All of them have a low pH value and some similar characteristics. However, there are other production zones competing inside each one. Some zones contribute more than others, and this behaviour changes with time. These effects are responsible for the differences between the wells. Table 2 shows the chemical compositions of the acid wells (average values). In summary, these four wells are located in the same area that gives them the acid characteristics, but each well has its own chemical and thermohydraulic behaviour.

	PGM-02		PGM-06		PGM-07		PGM_19	
	(Oct06 to Agu07)		(2007)		(Oct06 to Sen07)		(Nov06 to Agn07)	
	(00000	Standard	(20	Standard	(00000	Standard	(1101000	Standard
	Average	deviation	Average	deviation	Average	deviation	Average	deviation
	menage	(±)	11, ci age	(±)	11 et age	(±)	11 et age	(±)
Sep_pressure (bar-a)	0 94	0.00	11	6	0 94	0.00	0 94	0.00
ηH*	5	1	5 17	0 74	57	0.5	5	1
Conductivity (uS/cm)	12494	716	12629	878	13590	185	13303	265
Na* (ppm)	2492	87	2417	221	2616	38	2522	69
X (ppm)	310	8	312	22	328	11	316	3
Ca (ppm)	40	1	34	5	47	3	47	4
Mg (ppm)	7.8	0.6	4	2	2.2	0.4	3.9	0.6
Fe total. (ppm)	4	6	1	2	1	1	1.5	0.4
Cl (ppm)	4008	85	3689	340	4244	67	4140	35
$SO_4$ (ppm)	305	32	536	68	168	23	166	44
HCO <sub>3</sub> (ppm)	0.8	0.1	4	4	1.4	0.4	3	3
F (ppm)	2.6	0.2	3.5	0.4	2.0	0.2	2.1	0.5
B (ppm)	67	2	94	5	71	2	67	2
$H_2S$ (ppm)	2.0	0.5	4	1	2	1	1	0
NH <sub>3</sub> (ppm)	15	2	29	7	10	3	14	4
As (ppm)	10.3	0.3	10	3	10.5	0.7	10	1
$SiO_2$ total (ppm)	618	20	624	28	674	18	538	34
$SiO_2$ mon.(ppm)	601	13	615	12	651	17	520	22
ГDS (ppm)	8118	175	8142	593	8282	354	8098	98
onic balance	0	1	0.1	0.6	0.8	0.8	0.1	0.7
$CO_2$ (mmoles/kg)	243	29	716	130	477	73	141	78
$H_2S$ (mmoles/kg)	3.0	0.5	14	2	7	2	1.4	0.6
$N_2$ (mmoles/kg)	1.4	0.4	2.2	0.5	1.6	0.2	1.1	0.5
$H_2$ (mmoles/kg)	0.21	0.07	0.3	0.3	0.51	0.05	0.11	0.03
Гotal	248	30	733	132	486	75	144	79
% of vapour	1.1	0.1	3.2	0.6	2.1	0.3	0.6	0.3
$\Gamma_{\text{Na/K}}(^{\circ}\text{C})$	237	2	240	3	237	3	237	2
$\Gamma_{\text{Na/K/Ca}}(^{\circ}\text{C})$	242	1	246	1	242	2	240.9	0.7

 TABLE 2: Chemical compositions of the fluids of the four acid wells during pH neutralization (average values)

\* affected by the neutralization process

1

0

245

1434

2

0

231

989

5

0

241

1700

2

0

### 2.2 Philosophy of the neutralization

The four acid wells in Miravalles are all producing energy for the power plants, and are located in the same zone. The fluids from these wells are highly corrosive unless previously treated. The materials in contact with the fluids (pipes, casing, capillary tube, separators, others) must be protected. The aim of a neutralization system is to protect all surface equipment from corrosion. A neutralizing fluid (like NaOH) is injected into the well at ~1000 m depth, close to the main production zone by means of a capillary tube and a pump. Neutralizing liquid is stored in tanks. Figure 3 shows the overall diagram of the neutralization system applied in PGM-19 and in most of the wells. Some elements of the system are detailed.



FIGURE 3: Fluid neutralization system in well PGM-19. The process begins in the tanks where the NaOH is stored (NaOH 1 and NaOH 2 in the diagram). The NaOH is transported through a low-pressure pipe to the pumps ("dosing pump"). Next, the NaOH is injected into a high-pressure pipe, which ends at the beginning of the capillary tube (located in the spool). The capillary tube transports the NaOH to the well and keeps its position thanks to the injection head. The dotted line represents electric signs (from equipment to the display) and the continuous line represents the route of the soda. Each part of the diagram is explained in Section 2

### 2.2.1 Neutralizator

The acid fluid from the wells is neutralized with 40 wt% NaOH solution. This concentration is reduced with water coming from another pump when the NaOH is injected into the well (dilution on line). In the beginning, NaOH 50 wt% (industrial grade) was used with dilution on line. However, this concentration was changed in order to reduce the work on the system pump.

# 2.2.2 Neutralizator storage tanks

There are two NaOH storage tanks located in a building close to each well (at a distance of around 35 m). Generally, the volume in each is  $10 \text{ m}^3$ , however, the PGM-19 well tanks have a different size (25 m<sup>3</sup>) (Figure 4). Storage time (between 15 and 30 days) depends on the NaOH consumption. The tank material can be carbon steel or polyethylene (high density).



FIGURE 4: Storage tanks for neutralizing agent; a) Metallic tank of 25 m<sup>3</sup>; b) Polyethylene tank of 10 m<sup>3</sup>

### 2.2.3 Pumping system

*Suction pipes.* The pipes are designed for low pressure flows. They connect the storage tanks with the system pumps. Generally the pipes are 50.8 mm (2") and the material is stainless steel (316). There are some valves on line for isolation of the system and for controlling the introduction of water for dilution of the NaOH (see Figure 5).

*System pumps*. Two pumps inject the NaOH into the well; one of them is for backup, although they work in an alternating way to maintain the internal components in operation. These pumps are specially designed for chemicals like NaOH and high pressure (more than 100 bar); the flow is between 10 and 50 l/h (depending on the well). There is another pump for water, which keeps the concentration of NaOH at around 30% (m/m), and the temperature of the fluid increases (solution

heat), reducing the viscosity, and thus, helping the pumps to work. All the pumps are positively displaced (diaphragm) (see Figure 5).

Discharge pipes. These pipes are designed for high pressure, between 12 and 60 bar, according to the flow. However, if the pressure gets higher than 100 bar, the system stops. The pipes are made of a special stainless steel (alloy 825), with a diameter of about 9.5 mm (3/8 "). There are some accessories on the pipe, like a damper (for softening the wave of the flows), a flowmeter (coriolis technology, which measures the flow of the NaOH / water mixture) and valves (for isolating the system) (see Figure 5). This line pipe connects the system pumps with the capillary tube (spool).



FIGURE 5: The low-pressure line, system pumps, high-pressure line and others accessories of the neutralization system



FIGURE 6: a) Capillary tube in the spool and the tower; b) Weight bar and neutralization head

# 2.2.4 Capillary tube

The tube is coiled in a drum (spool) (Figure 6a). During introductory and retirement operations, the spool is put above a truck and the depth (capillary in the well) is controlled. The capillary is made of a special stainless steel (alloy 825), with a diameter of about 9.5 mm (3/8 "). Its total length is approximately 1300 m, but its position in the well depends on the boiling zone and the configuration of the well (if there is a liner, general state of casing, etc.).

# 2.2.5 Stabilization system (neutralization head and weight bar)

The capillary tube needs to stay stable in the well. For this reason, the capillary is connected to a neutralization head by means of a subjection system. This head is connected with a weight bar, made of a special stainless steel tube (alloy 825), with a lead filling (Figure 6b). The diameter is approximately 50.8 mm (2"), with a weight up to 200 kg.

# 2.2.6 Sampling system (iron and pH)

There are two sampling systems: online (with special equipment), and manual (with operators) (Figure 7). The online system is continuous (Figure 7c). It is formed by a long tube from the production pipe to the equipment located in the neutralization hut (diameter 9.5 mm). It includes a pH-meter (maximum temperature 100°C) and a Fe-meter (maximum temperature 30°C, which has though been non-operative). In the middle of the long tube, there is a cooling system which reduces the temperature to approximately 30°C. The manual system is not continuous (Figures 7 a and b). Hourly, an operator takes a sample from the open channel of the well, waits for cooling and measures the pH and the concentration of Fe with tests and a digital pH-meter. The same operator controls several variables of the neutralization system (percent of pumping, flow, pumping pressure, system energy, work of the pumps, water supplied, etc.). If the well is out of control (e.g. if pH is too low or too high), the operator reacts immediately to avoid corrosion or scaling in the well.



FIGURE 7: Sampling systems; a) Manual – digital pH-meter; b) Manual – test for Fe (in ppm); c) Online – pH-meter

# 2.2.7 External systems for keeping the neutralization process working

The NaOH is bought from a chemical industry in great quantities, the deliveries are, however, not continuous. The refilling is shown in Figure 8a. A tank containing 20,000 kg arrives at the well every 15 or 30 days, depending on consumption. The safety measures for personnel and environment are the responsibility of the supplier during transport. At the well, the responsible party is ICE.

Figure 8b shows the spool truck, which has the function to lift or introduce the capillary into the well (an essential part of the neutralization system). This is a big truck with a rising hydraulic system. The system which turns the spool is also hydraulic and has a high torque. Care should be taken, when the system is ascending, of not applying so big a force as to rupture the point of the capillary. Changing the torque during operations is recommended.



FIGURE 8: External systems; a) Recharge of NaOH; b) Spool truck

# 2.3 Optimizations applied in the operative process

# *Capillary (internal scaling – ruptures):*

Several alloys for the capillary were tested in the acid wells. Some examples are 316L, Sanicro 128, Incoloy 825. One of them led to internal scaling due to dilution of nickel (and others components) in NaOH; the well had to be closed and production was lost for many hours. Sometimes, the capillary has broken inside the well due to chemical reasons (acid action or by NaOH). This leads to the closing

of the well while an attempt is made to fish out the neutralization head and weight. If that is not successful, mechanical intervention is inevitable with a high cost in materials and production.

One of the better alloys was Incoloy 825. This alloy has resistance to a variety of oxidizing substances such as nitric acid, nitrates, and oxidizing salts. The titanium addition serves, with an appropriate heat treatment, to stabilize the alloy against sensitization to intergranular corrosion (Painc Com, 2007). Also, the risk of nickel dilution during the NaOH injection was decreased, by reducing the concentration of NaOH (from 45 to 30 % m/m). Now there is a policy of capillary change every six months, independently of its state, to avoid ruptures at a later date.

#### *Fishing activities*

The part of the neutralization system which is inside the well is based on a thin capillary tube, with a weight on the end to give it stability. Sometimes, when the system is stopped, the capillary tube may break. In such cases, the weight and part of the capillary remain inside the well, preventing its replacement with new system for chemical treatment. Hence, it is necessary to begin "fishing" activity to retrieve the broken system. The first step is to "kill" the well with fresh water to a high pressure and close the main valves. A series of tubes (approximately 3 m each) are threaded and incorporated into the well to the location of the obstruction, with a help of a hydraulic crane. A harpoon is located at the end of the tube series. The harpoon is used to try to catch hold of the broken capillary by means of a turning motion. When the capillary is hooked, it is taken instantly from the well, using the crane. If the operation is successful, the well can be restarted; else the operation needs to be repeated.

#### Scaling in casing

New studies have been conducted in order to optimize the pH value to better control corrosion and reduce scale formation. An agreement between NEDO (New Energy Development Organization, Japan) and ICE has allowed studies to be carried out to determine the rate of corrosion and scale formation, using different values of pH in well PGM-07. Figure 9 shows the various pH values that have made it possible to operate well PGM-07 without a mechanical cleanout for more than a year. These results are already very positive, because they indicate that the frequency of mechanical well cleanouts can be reduced in the future, making the operation and maintenance of the acid wells less expensive (in the past, around 2 cleanouts per year were required for each well) (Moya et al., 2005).



FIGURE 9: Channel scaling rates at different pH values in PGM-07

### 3. DESIGN ANALYSIS

### 3.1 Amorphous silica in the sampling system (log(Q/K))

In the sampling systems, amorphous silica formation is a critical problem. One way to quantify the beginning of amorphous silica formation at a given temperature is to estimate the saturation index, SI, for the following chemical reaction in equilibrium:

$$SiO_{2 (am)} \rightleftharpoons SiO_{2 (aq)}$$

The saturation index is:

$$SI = log\left(\frac{Q}{K}\right) = log(Q) - log(K)$$

= Calculated ion activity product [dimensionless] as in the following: where Q

$$Q = \frac{a_{SiO_2 (aq)}}{a_{SiO_2 (am)}} \cong \frac{a_{SiO_2 (aq)}}{1} \cong a_{SiO_2 (aq)} \cong [SiO_2]$$

where  $a_i$ 

= Activity of species *i* in solution, where  $i = \text{SiO}_{2 \text{ (am)}}$  or  $\text{SiO}_{2 \text{ (aq)}}$  [dimensionless];  $[SiO_2]$  = Concentration of silica oxide in an aqueous solution [mol/l];  $SiO_{2 \text{ (am)}}$  = Solid silica oxide (as amorphous silica);  $SiO_{2 (aq)}$  = Silica oxide in an aqueous solution; = Equilibrium constant [dimensionless]. Κ

The SI value for the amorphous silica gives an estimation of the equilibrium state. Values of SI higher than 0 represent supersaturation (formation of solids), equal to 0 represent equilibrium, and less than 0 represent undersaturation (Zheng Xilai, 1993). It is possible to plot a log (Q/K) vs. temperature and to find the point of operation where the amorphous silica begins to form. The WATCH program is used for finding the different operational points of the plot. It is necessary to know the temperature where the amorphous silica begins to form. The online equipment needs a sampling temperature of about 100°C (maximum temperature). The sample should cool down (by flashing process or heat exchange). For this reason, silica is formed in the system.

Well PGM-02 shows a typical behaviour in a plot showing SI vs. temperature (Figure 10). For different SiO<sub>2</sub> concentrations in the samples, there are different temperatures of amorphous silica formation, however, these differences are not very significant. In the same graph it is possible to see a pH plot of PGM-02, as well as a pH plot of Well SV-11 in Svartsengi geothermal field, Iceland (both refer to the right axis of the graph). The data from SV-11 were taken on June 7<sup>th</sup> 2006. The different pH plots show different temperature dependent behaviours between the wells. These differences are due to the distinct acids that control the pH in each fluid. For PGM-02, the important acid is H<sub>2</sub>SO<sub>4</sub> which is not volatile (acid is not lost on boiling). In SV-11, the acid is H<sub>2</sub>CO<sub>3</sub> (and H<sub>2</sub>S); both are lost upon boiling. The chemistries are different in each case and the pH effects of the fluids are opposite.

### 3.2 Studied scenarios

In general, the engineering design is an interactive process. The design is modified continually until it is complete with an acceptable criterion of quality defined by the factors of security, cost, convenience and aesthetics. In the case of the sampling system, this process was applied for three different systems: two of them installed in well PGM-02: the other was modelled (Figure 11). Each well has different characteristics (chemical and thermohydraulic). All of Miravalles' four wells have a low pH



FIGURE 10: SI (log(Q/K)) and pH vs. temperature for well PGM-02. For different concentrations of SiO<sub>2</sub> in solution (631.5, 601.0 and 658.0 ppm in different days), it is possible to see three different plots and three different temperatures where the plot crosses zero and scaling begins (at 141, 136 and 145°C, respectively). Also there is a difference in the behaviour of the pH plot for different wells; the acidity of the well in Svartsengi is dominated by volatile acid that is lost during boiling, while the acidity of the well in Miravalles is dominated by a non-volatile acid that becomes concentrated during boiling

in their fluids as a result of their common acid aquifer. Well PGM-02 was chosen for this study as it is the most recent of the acid wells (with an active neutralization system) to be put into production and its fluids go to Unit 3 (Miravalles 3, private unit based on a BOT contract).



FIGURE 11: Location of equipment for sampling in the well. The continuous line toward the digital pH meter corresponds to installed equipment (flashing); the discontinuous line is the possible location of the exchanger (no flashing). Two-phase flow is shown in red, hot water in blue and steam in green. Some pictures of the actual equipment are shown in Figure 12

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When the neutralization process began, the fluid sample was carried to the neutralization hut through a capillary tube (a distance of 25-30 m). The equipment sensors were in the hut. During this process, several problems were encountered in the capillary tube (obstructions being the most frequent). The studied scenarios altered the sampling method. The main change was to conduct the measurement at the well and to send the signal to the hut, not the fluid. Then the length of the capillary tube was reduced while sampling (to approximately 2-3 m). With that, the obstruction problems were reduced considerably. It was also necessary to change the location of the equipment sensors (from the hut to the sampling system). The scenarios are detailed in Table 3 and are shown in Figure 12.

The first two systems in Table 3 (E1 and E2) use a flashing method in order to reduce the temperature; with the flashing, the sample temperature is reduced to a temperature corresponding to atmospheric pressure (around 0.94 bar, with a temperature of  $97.9^{\circ}$ C). The second system (E2) is put in the open channel of the well (the separated water from the two-phase fluid flows through this channel, in a small separator). The sensor takes pH readings directly from the water; the retention time is minimal in the separator. The third system reduces the sampling temperature with a heat exchange of fresh water (from 165 to  $95^{\circ}$ C); in this method, flashing is not used. The dimensions of the heat exchanger were based on the effectiveness and number of transfer units (Perry, 1999). Calculations were carried out using the EES program (see Appendix I).

In August and September, scenarios E1 and E2 were used to collect data. Scenario E3 was designed to avoid flashing during the sampling process; however, it has not been tried to date.



FIGURE 12: Studied scenarios; a) E1 – measurement of pH installed near the wellhead on the production pipe, using flashing; b) E2 – Installation in the open channel of well PGM-02, using flashing; c) E3 – Heat exchanger for reducing the sample temperature from 165 to 95°C, no flashing; the connection to the well is the same as that of E1

Equipment	Variable	Symbol	Units	Values
Π1	Outside diameter tank	OD <sub>E1</sub>	m	0.1683
E1 – Equipment installed	Wall thickness	$\mathbf{th}_{\mathrm{E1}}$	m	0.0071
Equipment instance	Water level	$LW_{E1}$	m	0.07
flashing)	Volume	$V_{E1}$	m <sup>3</sup>	0.001557
nashing)	Residence time	$t_{E1}$	S	45.5
E2 -	Length of the sampling tube	$L_{E2}$	m	6
Equipment installed near the open channel (with flashing)	Internal tube sampling diameter	$di_{\rm E2}$	m	0.0093
	Internal tube sampling diameter	di <sub>E3</sub>	m	0.0093
	Final sampling temperature	$T_{ho}$	°C	95
Е2	Temperature of the cold water	T <sub>ci</sub>	°C	15
EJ - Heat exchanger	Final cold water temperature	$T_{co}$	°C	85
nronosed to minimize	Cold water flow	F <sub>coldwater</sub>	kg/s	0.05
the flashing effect	Typical overall heat transfer	U	$W/(m^2 \cdot K)$	1277.61
the masning effect	Heat capacity of sampling	$Cp_{\text{sanpling}}$	J/(kg·K)	4353
	Heat capacity of cold water	Cp <sub>water</sub>	J/(kg·K)	4184
	Length of the heat exchanger	$L_{E3}$	m	3.226

TABLE 3: Equipment used in different scenarios

### 3.3 Results

### Scenarios with a flashing process (E1 and E2)

Data from scenarios E1 and E2 (flashing process) are shown in Figures 13 and 14 for the period from August  $23^{rd}$  to  $28^{th}$ . It is interesting to see that the pH for E1 is always lower than that of the fluid in E2 (Figure 13); the difference is not due to the calibration of equipment (both were calibrated in the test with patron solutions of pH 4 and 7, the temperature was also calibrated with gauged thermometers, its values were corroborated and the equipment worked correctly).

The reason for the differences may be due to the chemical composition of the fluid. There are two

main components in the fluid: non-volatiles and volatiles. The acid characteristics of a well depend on some chemical compounds dissolved in each component; the main non-volatile is sulphuric acid and the volatile main component is CO<sub>2</sub> (see Table 2). The nonvolatile component is always dissolved in the liquid phase, however, the volatile component goes from liquid to a gas phase according to conditions of fluid pressure. If а



FIGURE 13: pH data, the data from the open channel are always higher than those from the samples taken near the head; with only minor variations in the difference (green line), being close to the value 0.70





geothermal fluid loses the volatile part, its acidity decreases and the pH increases. An analogy can be made to what happens with lemon juice and coke. If lemon juice is kept in contact with the atmosphere, its acidity does not change in time as the lemon has a non-volatile part responsible for the acidity. However, if a coke is exposed to the atmosphere, the volatile part  $(CO_2)$ goes to the atmosphere, and the pH of the fluid changes with time.

FIGURE 14: pH vs. temperature with a degassing coefficient during a boiling process (235 to 98°C), in well PGM-02, August 10<sup>th</sup> 2007

The plots of Figure 13 show the effect of the non-volatile and volatile components. Scenario E1 is a small tank with a cover; it is likely that during the flashing process some components stay in liquid phase (not all of the volatile components go to the atmosphere, the recipient is semi-closed and some transfer phenomena could not have been carried out in a complete way). On the other hand, in scenario E2, there are two flashing processes, one of them to 7 bar-abs (separation of the steam for use in generation), and the other to atmospheric conditions towards the well's silencer in a completely open system; it is guaranteed that most of the volatile component passed to the atmosphere.

The data from Figure 14 show the effects of a non-equilibrium process (degassing coefficient = 0.01) in comparison with an equilibrium process (degassing coefficient = 1.0). According to the WATCH program, the boiling process with a degassing coefficient of 0.01 results in a lower pH than the boiling process with a degassing coefficient of 1. It is possible that scenario E1 does not reach equilibrium due to its semi-closed state that is evidenced in the pH values. On the other hand, scenario E2 seemed to have complete equilibrium (degassing coefficient = 1.0). In summary, the pH readings are different for the two scenarios; the equipment with a complete flashing process (in theory - E2) showed less acidity (higher pH) due to the loss of the volatile part.

The temperatures of the sampling systems are almost the same for both E1 and E2 (Figure 15). The trendline near zero corroborates this statement (black line shows the differences between equipment). There are more variations of the tendency in the equipment close to the wellhead (E1); this behaviour is possibly due to a combination of the configuration effects (valves cross, valve production, change of fluid direction, etc.), and the high residence time of the equipment (non-continuous). Of note is that sampling temperature decreased in time for both scenarios; the outdoor temperature (changes under climatic conditions during the test) affected the values of the sampling temperature.

There is a scaling effect in both E1 and E2 with the temperature drop; however, it is not critical due to their configurations. The solid particles were deposited in the bottom of the tank in scenario E1, and easy to clean during maintenance; in scenario E2, the scaling process occurred in the separator and in the open channel.



The third scenario (E3) does not have a flashing process. The heat exchanger takes the sampling fluid in the liquid phase to a temperature of around 165°C and cools it to 95°C with fresh Only a very water. small part of the volatile components goes to the gas phase and is kept in the equipment and the pH meter all the time. However, when the temperature decreases in the heat exchanger, scaling by amorphous silica occurs.

Figure 16 shows the saturation index  $(\log(Q/K))$ for the four acid wells as a function of temperature. as calculated by the WATCH program. For every well, the temperature, where the plot crosses the zero line, is slightly different. as the chemical characteristics are slightly different. The range is though For small. well PGM-02, the temperature is 137°C where the scaling starts in the exchanger.



FIGURE 15: Temperature data; the values from both scenarios are similar; the difference between the methods (green line) has both negative and positive values, but the average tendency is close to zero (black line) (August 23 - 28, 2007)



FIGURE 16: Saturation index (log(Q/K)) as a function of temperature for the four acid wells. The data were taken on dates in 2007 when the concentration of SiO<sub>2</sub> was high for each well. The plots cross the zero line at 137, 140, 143 and 128°C for wells PGM-02, 06, 07 and 19, respectively

The temperature profile for the sampling fluid in the heat exchanger is shown in Figure 17, as well as a diagram of the equipment. The EES program used for the calculations is shown in Appendix I. The length of the equipment is about 3.2 m. However, the problem with scaling begins at 137°C; according to the profile, this temperature corresponds to 0.9 m. In other words, there is a problem for a major part of the equipment as approximately 2.3 m will have experience scaling.

Periodic maintenance should be carried out for the E3 exchanger during operation for cleaning away scaling from the internal tube. Air or water with high pressure would probably help to remove the



FIGURE 17: Profile of the sampling temperature in the heat exchanger (E3). The silica scaling begins at 137°C, corresponding to 0.9 m of the exchanger; the vertical line in the profile shows the location in the equipment

silica, as it is not recommended to use chemicals due to damage risk to the equipment (Sverrir Thórhallsson, pers. comm.). Maintenance is necessary after the efficiency of the equipment has decreased with time (at temperatures higher than 98-99°C). Only experience can define the time period between cleaning operations in each acid well. The use of two exchangers is necessary to maintain continuous control of the neutralization system, where one should be working while the other is being cleaned.

Acid fluids are formed by a mix of different zones in the well. One of them dominates (the main component is the sulphuric acid which is not volatile). However, some zones could increase their participation at any moment and change some characteristic, such as the head pressure, pH, gases content, etc. The effects would be reflected in the sampling system that minimizes loss by flashing non-volatile components in the heat exchanger.

### 3.4 Comparison of alternatives and selection

The main features and results of the different scenarios are listed in Table 4, including also some comparison between them (advantages and disadvantages for each feature in each one).

From Table 4, it can be deduced that the heat exchanger (E3) has the highest costs (start-up, operation and maintenance) and needs external fluids (fresh water). The problem of silica scaling is also more critical in this equipment than in the others. However, when minimizing the loss of the volatile component in the geothermal fluid (that affects the acidity and the pH values), E3 would give readings closer to the actual acidity in the system pipes.

The main focus of the sampling systems is to secure the data readings and control the neutralization systems. For this reason, the heat exchanger (E3) should be selected, although it has some disadvantages. The disadvantages are minimal when compared with possible costs generated in a system out of control: silica scaling in the casing and pipes due to high pH (loss in production, cost of mechanical intervention and cost due to the well not being in production) or corrosion in systems in contact with the fluid with low pH (damage in casing, pipes and superficial stations, with associated costs, and possible loss of the well).

			Scenarios				
Priority	Feature	E1 installed near the wellhead (with flashing)	E2 installed near the open channel (with flashing)	E3 heat exchanger, proposed to minimize the flashing effect			
1	Dependability in the treatment of the sample	Low – flashing system. Most of the volatile phase will be lost from the fluid, affecting the pH values	Low - flashing system. Most of the volatile phase will be lost from the fluid, affecting the pH values	High - the system is not affected by flashing. Most of the volatile phase will stay in the liquid phase			
2	Dependence of climatic conditions	Low - semi-closed system	High - open system (silencer and open channel). The pH value may be influenced by ambient conditions like rains, wind, etc.	No - closed system			
3	Dependence on the separation process of the geothermal fluid	No - the sampling is on the production line of the two-phase fluid	Yes - the sampling is in the open channel of the well, where the separated water is.	No -the sampling would be on the production line of the two-phase fluid			
4	Flexibility for changes in the well (e.g. production, chemical changes, thermohydraulic)	Poor - flashing system. Most of the volatile phase will be lost from the fluid, affecting the pH values	Poor - flashing system. Most of the volatile phase will be lost from the fluid, affecting the pH values	High - the system is not affected by flashing. Most of the volatile phase is preserved in the liquid phase			
5	Problems of formation of silica scaling in the equipment	Low - there is silica scaling. However, it is easy to remove. The deposits are formed in the tanks's interior part.	Low - there is silica scaling. However, it is formed in the separator, silencer and open channel of the well. The effect on the sampling tube is minimal.	High - silica scaling is located in the internal part of the sampling capillary tube, reduces the efficiency with time, and increases the maintenance			
6	Necessity of other fluids (fresh water)	No	No	Always - water is indispensable for the cooling system.			
7	Maintenance costs	Low - see the last row.	Low - see the last row.	High - see the last row.			
8	Period of maintenance and frequency	Low - simple equipment, few parts, scaling is located in the interior part of the tank and easy to remove.	Low - simple system, which does not have several parts, scaling is located in the separator, silencer and open channel of the well.	High - equipment more complex, with more parts. Scaling located in the internal part of the capillary tube which hinders its cleaning, increasing maintenance time and frequency.			
9	Initial cost	Medium - cost of tanks, tube connections, supports, electrical and mech. installations, etc.	Low – cost of tube connections, supports, electrical and mechanical installations, etc.	High – cost of heat exchangers, tube connections, supports, electrical and mech. installations, etc			

TABLE 4. Main characteristics of the studied scenarios. E1, E2 and E.	TABLE 4:	Main characteristics	of the studied	scenarios:	E1, E2 and E3
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It may be possible to find some relationships in pH readings between E1 and E3, and use these relationships to reduce the cost and problems generated in scenario E3; however, it is first necessary to put scenario E3 into practice.

# 4. CONCLUSIONS

There are three main aquifers in Miravalles geothermal field, Costa Rica. One of them has acidic characteristics, being an acidic sodium-chloride-sulphate aquifer (Na-Cl-SO4). Four acid production wells are located in the vicinity of this aquifer. Their fluids have low pH and need chemical treatment for neutralization. The acidity is due to the presence of two main components in the fluids: non-volatiles (originating from the sulphate part of the aquifer) and volatiles (due to the  $CO_2$  in solution). For this reason, when the volatile part enters a gaseous phase during the flashing process (to 1 or 7 bar-a), the pH of the liquid phase increases slightly.

Originally, the neutralization system of the acid wells kept the pH value at around 7. However, at this pH value there were scaling problems in the casing. The production of the wells decreased over time and mechanical intervention was inevitable (with associated costs of the intervention, the reduction of production and time without production). Hence, it was necessary to change the pH value to minimize silica scaling. This value is now between 5.5 and 6.0. For values lower than 5.5, corrosion problems will be significant (damage in casing, pipes and superficial stations, with associated costs, adding a possible loss of the well). In contrast, for values higher than 6.0, the scaling problems will occur (loss in production, cost of mechanical intervention and cost due to the well being out of production).

The sampling system is an important factor in controlling the pH value. It is indispensable for getting reliable readings. Three scenarios were analysed, two of them based on a flashing process, the third one based on a cooling process. The cooling process was preferred, mainly due to the fact that it minimizes the loss of volatile components (those influencing the readings of pH) so that the readings will be closer to the real pH values in the pipe. However, the sampling system presents some disadvantages, the main one being silica scaling. The scaling starts at around 137°C (for well PGM-02), corresponding to 72% of total length of the equipment (with scaling problems in 2.3 m out of a total of 3.2 m, according to the equipment temperature profile). Periodic maintenance of this equipment would be necessary while it is in operation, to clean away scaling from the internal tube. Probably air or water for increasing the pressure would help remove the silica. Use of chemicals is not recommended due to damage risk to the equipment.

In summary, the scenario based on a cooling process (heat exchanger) should be selected to minimize the loss of the volatile component in the geothermal fluid (which affects the acidity and the pH values). The disadvantages of this system are minimal when compared with possible costs generated in a system out of control.

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# **APPENDIX I:** The EES program for design of the heat exchanger

"Boundary condiitons" "for process" F\_t=120 [kg/s] X=85 [%] D\_ipipe=0.508 [m] d\_itube=0.0093 [m] P flow =700 [kPa]

"For exchanger"

T\_final=95"[C]" T\_coldwater=15"[C]" F\_coldwater=0.05 [kg/s] U\_overhall=1277.609175 "[W/m^2-K]" "from TABLE 11-3 Typical Overall Heat-Transfer Coefficients in Tubular Heat Exchangers, (Perry, 1999)

"Suppose" F sample=F tube2

T\_flow=TEMPERATURE(Water,x=0,P=P\_flow) "[C]" rho\_flow=DENSITY(Water,x=0,P=P\_flow) "[kg/m^3]"

area\_ipipe=(pi\*D\_ipipe^2)/4[m^2] area\_itube= (pi\*d\_itube^2)/4[m^2] Nietzen S.

F\_water=F\_t\*X/100 [kg/s] v\_flow=F\_water/rho\_flow/area\_ipipe "[m/s]"

### "Flow in the tube"

F_tube=v_flow*area_itube	"[m^3/s]"
F_tube2=F_tube*rho_flow	"[kg/s]"
F_tube3=F_tube*1000*60	"[l/min]"

"Find length of a concentric tube HX. knowns:" T h i=T flow "[C]" T h o=T final "[C]" T c i=T coldwater "[C]" m\_dot\_h=F\_sample "[kg/s]" m dot c=F coldwater "[kg/s]" U=U overhall "[W/m^2-K]" D=d itube+0.0002 [m] "[m]" rho oil=DENSITY(Water,T=T coldwater,P=101.3) "[kg/m^3]" rho water=rho flow "[kg/m^3]" C p oil=CP(Water,T=T coldwater,P=101.3)\*1000 "[J/kg-K]" C\_p\_water=CP(Water,x=0,P=P\_flow)\*1000 "[J/kg-K]" "nu oil=1e-5" "[m^2/s]"

"a) What is the heat transfer and the water outlet temperature?" C\_h=m\_dot\_h\*c\_p\_oil "[W/K]" C\_c=m\_dot\_h\*c\_p\_water "[W/K]" q=C\_h\*(T\_h\_i-T\_h\_o) "[W]" q=C c\*(T c o-T c i) "[W]"

"b) What is the HX length?" C\_min=min(C\_h, C\_c) "[W/K]" TypeHX\$='counterflow' q\_max=C\_min\*(T\_h\_i-T\_c\_i) "[W]" epsilon=q/q\_max

Ntu=HX(TypeHX\$, epsilon, C\_h, C\_C, 'Ntu') Ntu=(U\*A)/C\_min

A=pi\*D\*L