CALCITE SCALING IN GEOTHERMAL PRODUCTION WELLS IN EL SALVADOR, CURRENT SITUATION AND CONTROL METHODOLOGY

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ABSTRACT

Formation of calcite scale in geothermal wells can be a serious problem and occurs in many geothermal fields in the world. Scaling can be controlled by adjusting the pH of the geothermal fluid, using mechanical or chemical cleaning, or by adding inhibitors. The injection of an appropriate dose of inhibitor makes it possible to produce geothermal energy with little or no deposition and at lower cost than periodic mechanical cleanout.

Parameters such as the selection of the right inhibitor, setting the depth to which the inhibition chamber should be placed, as well as controls during the process of injection, both chemical and operative, are crucial to the success or failure of the inhibition system installed.

1. INTRODUCTION

One of the principal problems in the exploitation of a geothermal resource is the precipitation of solid scales from the geothermal fluid. Three main categories of scale deposition can be distinguished. These are: deposition from a single phase fluid (injection pipelines), deposition from flashing fluid (wells, separators, two phase-pipelines), and deposition by steam carryover (separators, steam lines and turbines) (Corsi et al., 1985). Deposition or scaling occurs not only in the casing and surface equipment but, in some cases, it also occurs inside the reservoir. This can result in a marked decline in fluid yields, and consequently can limit the output of the geothermal installation.

Different types of scales are found in geothermal fields. The most common are calcite ($CaCO_3$), silica (SiO_2) and sulphides. These present different kinds of behaviour with respect to the precipitation conditions at which they form (temperature, pressure, and pH). The precipitation of calcite mainly occurs as a result of CO_2 evolution from the liquid phase. CO_2 degassing increases pH and strongly increases carbonate ion concentration (CO_3^{2-}). These factors drive the equilibrium reaction to the right, resulting in supersaturation and precipitation of calcium carbonate scale at the flashpoint, according to the following chemical reaction:

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_{3(s)} + H_2O + CO_2 \qquad (1)$$
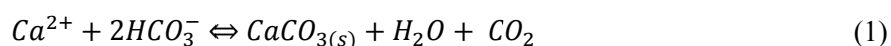
The deposition of calcite by this mechanism in the casing of production wells rapidly results in flow restrictions and loss of power production (Benoit, 1990).

Calcite scale control can be achieved by (Corsi et al., 1985):

a) Acting on the carbonate-bicarbonate equilibrium (pH and CO_2 partial pressure control) by injecting acid into the brine or CO_2 into the well with the use of downhole pumps;
b) Periodic cleaning (chemical or mechanical); and
c) Making use of scale inhibiting products.

The main objective of this report is to present an overview of calcite scaling in production wells in both fields under exploitation in El Salvador: C.G. Berlin and C.G. Ahuachapán, and to evaluate a proposal to implement a system of chemical inhibition and the controls necessary to monitor its effectiveness.

2. GEOTHERMAL FIELDS IN EL SALVADOR

The main use of geothermal energy in El Salvador is power generation. Geothermal energy production in El Salvador dates back to 1975, when the first 30 MWe unit was installed in Ahuachapán. Two geothermal fields are exploited in El Salvador, Ahuachapán and Berlín with an installed capacity of 95 MWe and 109.4 MWe, respectively. In 2010, the Ahuachapán and Berlín fields produced 26% of the total electricity generated in the country.

El Salvador, along with the rest of Central America, is a seismologically active region, situated atop three of the large tectonic plates that constitute the Earth's surface. The motion of these plates causes the earthquake and volcanic activity in the area. The geodynamics of the region are mainly controlled by the subduction process of the Cocos plate under the Caribbean plate, which has created the deep Middle American Trench lying off the coast of El Salvador (Figure 1). Parallel to this trench runs the Central American graben, a structural depression 20 km wide that crosses the whole country, with flanks defined by normal W-E trending faults. On the southern margin of the graben, a Quaternary volcanic chain with heights of 1,500 to 2,000 m constitutes the heat source that produces widespread geothermal activity (Jacobo, 2003).
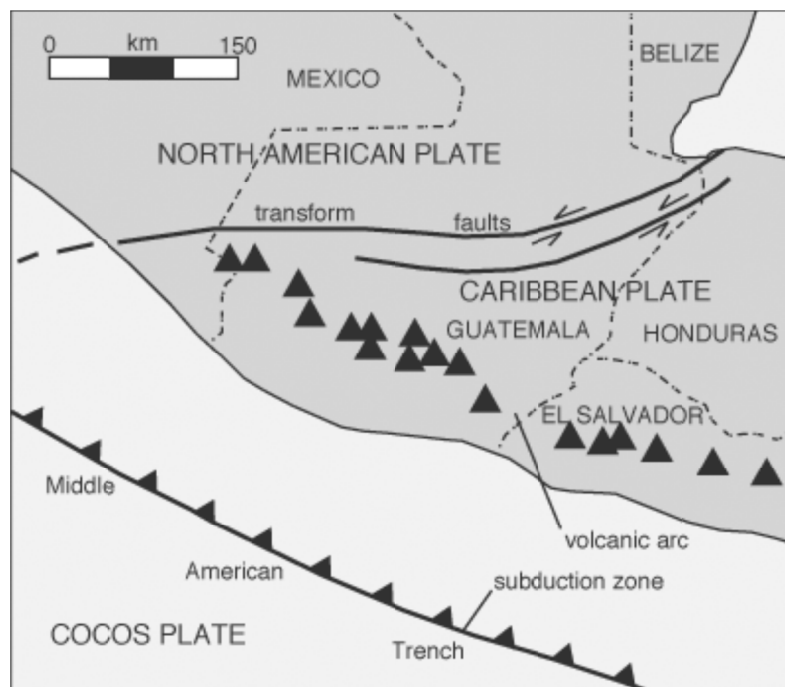

FIGURE 1: Simplified tectonic map of El Salvador and neighbouring region; subduction of the Cocos Plate beneath the Caribbean Plate produces the Central America arc; the arc is defined by the line of volcanoes (black triangles) (Jacobo, 2003)

2.1 Ahuachapán geothermal field

Ahuachapán geothermal field is located in western El Salvador about 100 km west of San Salvador. Lambert coordinates are between 411,000 and 417,000 m East, and 308,000 and 313,000 m North. The field covers an area of 4-6 km^2 at an average altitude of 800 m a.s.l. (Figure 2).

FIGURE 2: The Ahuachapán geothermal system and the Ahuachapán geothermal wells

The development of Ahuachapán started when the first well (AH-1) was drilled in 1968 with successful production results. Electricity generation in the field started with the installation of a 30 MWe unit in 1975, and a second one in 1976. The third 35 MWe unit was started in 1980, bringing the installed capacity up to 95 MWe (Montalvo, 1994). A total of 52 wells have been drilled (591-1645 m deep) in an area of approximately 5 km^2, of which 20 are production wells with an average steam fraction of 27% and an average measured enthalpy of 1240 kJ/kg. The temperature in the reservoir of the Ahuachapán field is in the range 210-250°C. All the brine produced is reinjected at an average temperature of 110-115°C into the Chipilapa geothermal field, located 6 km east of the Ahuachapán geothermal field.

2.1.1 Conceptual model (Montalvo, 2010)

Alteration mineralogy
Table 1 summarizes the different zones or facies in the production zone identified according to mineralogical alteration.

Heat source
The magmatic chamber is related to the volcanic group Laguna Verde – Laguna de las Ninfas in the Apaneca volcanic chain, which is very recent and probably somewhat shallow. MT and seismic studies have located the heat source at a depth of 9-12 km.

TABLE 1: Representative minerals in the production zone of Ahuachapán
geothermal field (Modified from Montalvo, 2010)

Facies	Mineral composition	Formation temperature
Phyllic 500-780 m	Chlorite – $(Mg,Fe)_5(Si,Al)_5O_{10}(OH)_8$ Quartz – SiO_2 Calcite – $CaCO_3$ Laumontite – $Ca(Si_4Al_2)O_{12}\cdot4H_2O$	150-200°C
Phyllic-prophylithic 780-1300 m	Chlorite – $(Mg,Fe)_5(Si,Al)_5O_{10}(OH)_8$ Quartz – SiO_2 Calcite – $CaCO_3$ Wairakite – $CaAl_2Si4O_{12}.2H_2O$ Anhydrite – $CaSO_4$ Epidote –$Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$ Ilithic – $K_{0.5}(Al,Fe,Mg)_3(Si.Al)_4O_{10}(OH)_2$	200-250°C
Prophylithic > 1300 m	Epidote –$Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$ Anhydrite – $CaSO_4$ Calcite – $CaCO_3$ Wairakite – $CaAl_2Si_4O_{12}.2H_2O$ Ilithic – $K_{0.5}(Al,Fe,Mg)_3(Si.Al)_4O_{10}(OH)_2$ Quartz – SiO_2	250-260°C

Fluid chemistry
The temperature measured in the liquid-dominated geothermal field of Ahuachapán is between 200
and 250°C. The discharged fluids are classified as sodium-chloride type with a chloride content of
3,600-9,000, and salinity between 7,500 and 20,000 ppm; the total carbonate content is between 11
and 96 ppm and the calcium content ranges from 83 to 428 ppm.

2.2 Berlin geothermal field

Berlin geothermal field is located approximately 110 km east of San Salvador, in the department of
Usulutan. Lambert coordinates are between 551,100 and 555,000 m East, and 265,200 and 269,000 m
North, between the cities of Mercedes, Umaña, and Berlin. The field covers an area of 4-10 km^2 at an
average altitude of 700 m a.s.l. (Figure 3) (Montalvo, 2010).

The stepwise development of Berlin started when the first exploration well (TR-1) was drilled in 1968;
production from the system started in 1992 with two 5 MWe backpressure units. In 1999, 18
additional wells were drilled and two 28 MWe condensing units went online. In December 2005, a
third condensation unit, 44 MWe, went online and 9 new wells were drilled in the southern region of
the geothermal field within the frame of a new exploration project, which aims to investigate the
boundary of the field (Renderos, 2009).

To date, 39 wells have been drilled in the Berlin field, of which 14 are production wells with an
average steam fraction of 22% and an average measured enthalpy of 1350 kJ/kg, with the exception of
well TR-18 A which is 100% steam with an enthalpy of 2,800 kJ/kg. The other drilled wells include
19 injection and 6 abandoned wells. A binary unit went online in 2008 which increased the power
generation capacity by 9.2 MWe with the conversion of thermal energy from low-pressure geothermal
brine into electrical energy. The current installed capacity is 109 MWe. The total produced brine is
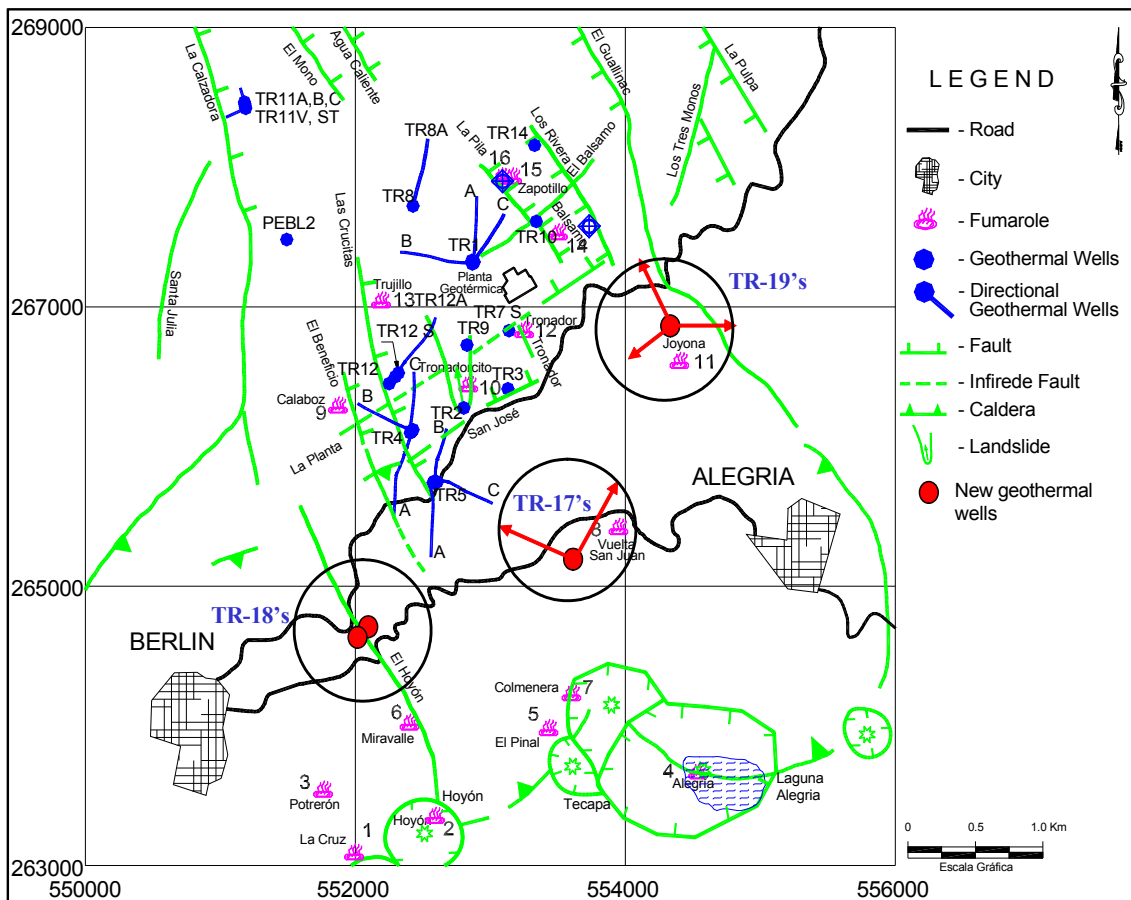injected at temperatures between 143 and 185°C in the northern part of the field (Renderos, 2009).

FIGURE 3: The Berlin geothermal system and the Berlin geothermal wells

2.2.1 Conceptual model

Alteration mineralogy (Jacobo, 2003)
The alteration mineralogy characterizing the Berlín geothermal field is due to the replacement of the original glass and minerals by secondary minerals. Table 2 summarizes the main hydrothermal mineral zones.

According to Renderos (2009), calcite is deposited naturally in the uppermost 1,000-1,250 m in wells, seen in wells TR-17 and TR-18 in Berlin field. This is consistent with the information in Table 2.

Heat source
The heat source of Berlin geothermal system is associated with the magmatic chamber of the Berlin – Tecapa volcanic complex, which is a layer of Quaternary age that emerged 1,000,000 years ago, after the formation of the Berlin caldera. The last magmatic activity was recorded 700 years ago, when there was a phreatic eruption in the El Hoyon crater. An indication of the activity of this magma chamber is the existence of hydrothermal alteration zones and hot springs in the southern part of the geothermal field, which are considered a result of continued release of heat. According to MT and seismic studies, it probably is located at an average depth of 9 km (Montalvo, 2010).

Fluid chemistry
The average temperature in the liquid-dominated geothermal field of Berlín is close to 300°C in the southern production zone in wells TR-2, TR-4, and TR-5. The discharged fluids are classified as sodium-chloride type with a chloride content of 3,000-7,000 ppm, pH values between 5 and 8, salinity between 7,000 and 20,000 ppm, a total carbonate content between 2 and 120 ppm and a calcium content of 82-160 ppm. The gas/steam ratio is usually between 0.001 and 0.003 (Renderos, 2002).

TABLE 2: Representative minerals in the production zone of
Berlin geothermal field

Facies	Mineral composition	%	Formation temperature
Phyllic 1000-1500 m	Chlorite – $(Mg,Fe)_5(Si,Al)_5O_{10}(OH)_8$ Calcite – $CaCO_3$ Quartz – SiO_2 Epidote –$Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$ Wairakite – $CaAl_2Si_4O_{12}.2H_2O$ Chlorite clay – $Mg_8Al_3Si_6O_{20}(OH)_{10}.4H_2O$	(3) 10-50 7-20 2-10 Tz-2 1 4	200-220°C
Phyllic-prophylithic 1500-1800 m	Calcite – $CaCO_3$ Chlorite – $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$ Sericitic/Ilithic – $K_{0.5}(Al,Fe,Mg)_3(Si.Al)_4O_{10}(OH)_2$ Epidote – $Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$ Quartz – SiO_2 Penine – $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$ Wairakite – $CaAl_2Si_4O_{12}.2H_2O$ Prehnite – $Ca_2Al(AlSi_3O_{10})(OH)_2$ Pyrite - FeS	20 5-10 5-25 1-10 3-15 1 30 1-7 1	220-250°C
Prophylithic 1800 - >2000 m	Chlorite – $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$ Prehnite – $Ca_2Al(AlSi_3O_{10})(OH)_2$ Epidote – $Ca_2(Al,Fe)Al_2O(SiO_4)(Si_2O_7)(OH)$ Actinolite – $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ Quartz – SiO_2	5-9 5-7 5-30 1-7 2-30	250-300°C

2.3 Calcite scaling in El Salvador

2.3.1 Ahuachapán production field

Tables 3, 4, 5 and 6 summarise the evidence of calcite formation encountered in four wells in the Ahuachapán production field.

2.3.2 Berlin production field

The evidence of calcite formation encountered in well TR-18 of the Berlin production field is summarized in Table 7.

2.3.3 Inhibitors used

Table 8 summarizes the principal problems encountered in handling the calcite inhibitors used in both power production fields in El Salvador.

TABLE 3: Calcite scaling in well AH-33B (Guerra, 2002)

Date	Inhibitor	Dosage	Event
August, 2001	------	------	Connected to generation (wellhead pressure: 7.65 bar-a, two-phase flow = 60.3 kg/s and steam fraction = 13%).
October, 2001	------	------	Decline in wellhead pressure, related to calcite scaling formation.
March, 2002	1340 HP (NALCO)	2 ppm	After mechanical and chemical cleaning (January, 2002), the well was connected to generation, operated with calcite inhibition system.

TABLE 4: Calcite scaling in well AH-35A (Guerra, 2002)

Date	Inhibitor	Dosage	Event
September, 2001	-----	-----	Connected to generation (wellhead pressure = 8.96 bar-a, two-phase flow = 58.0 kg/s and steam fraction =22%).
January, 2002	-----	-----	Decline in wellhead pressure, related to calcite scaling formation.
April, 2002	1340 HP (NALCO)	2 ppm	After mechanical and chemical cleaning (January, 2002), the well was connected to generation, operated with a calcite inhibition system.

TABLE 5: Calcite scaling in well AH-35B

Date	Inhibitor	Dosage	Event
May, 2003	-----	-----	Well was closed and cleaned chemically, due to a decline in production characteristics.
December, 2003	1240HP (NALCO)	2 ppm	After mechanical and chemical cleaning, the well was operated with a calcite inhibition system.
August 24, 2009	3505 (Alkemy)	2 ppm	The inhibitor 1340HP (NALCO) was replaced by 3505 (Alkemy).
October, 2009	-----	-----	Calcite inhibition was suspended due to problems with the inhibition system.
October, 2010	-----	-----	Well stopped production due to reduction of operating characteristics, mainly steam flow and wellhead pressure.

TABLE 6: Calcite scaling in well AH-35C (Jacobo, 2008)

Date	Inhibitor	Dosage	Event
July, 2007	1340 HP PLUS (NALCO)	2 ppm	Well was connected to operation. Since the beginning it had been operated with a calcite inhibition system.
February, 2010	1340 HP PLUS (NALCO)	2 ppm	The well had mechanical entrapment of the inhibition chamber; for that reason the inhibitor was substituted with 5200M (NALCO).
August, 2010	5200 M (NALCO)	2 ppm	Hydroxyapatite was found in the scattering chamber.
March, 2011	5200M + 3DT156 and formic acid	2 ppm	Started inhibition with the mix. Addition of formic acid was expected to prevent the formation of Hydroxyapatite. However, the capillary tubing was obstructed after 118 hours of operation.

2.3.4 Chemical monitoring

The chemical constituents in geothermal fluids have conveniently been classified into two groups, depending on their characteristics and the type of information they provide on the geothermal resource. The groups are conservative and reactive constituents. The conservative constituents have also been termed non-reactive, inert, incompatible or simply tracers. Once added to the fluid phase, they remain there. Examples of conservative components are: Cl, B and Br. The conservative constituents provide information on their own source as well as on the source of the fluid. Reactive constituents have also been termed geoindicators. They tend to reach equilibrium with other reactive constituents and/or the minerals of the rocks in the geothermal systems. Examples of reactive constituents are: Si, Ca, Na and K. They are useful in obtaining information on the physical state of the geothermal reservoirs such as temperature and steam to water ratios (Arnórsson, 2000).

TABLE 7: Calcite scaling in well TR-18 (Guerra, 2010)

Date	Inhibitor	Dosage	Event
September 8, 2008	-----	-----	First time that the flow of the well was stopped by calcite scaling problems.
October, 2008			Chemical and mechanical cleaning performed.
December 4, 2008	1340-HP (NALCO)	2 ppm	Well was connected back to generation, with a calcite scaling inhibition system.
October 5 - December 8, 2009	DP-3537 (BWA)	1.4 ppm of product with concentration of 12% V/V, diluted with condensed water.	Good inhibition results were observed, but when the scattering chamber was taken out, it came out with a small amount of solid (87% nickel sulphide and 13% Fe_2O_3).
March 23, 2010	DP-3537 (BWA)	2 ppm of product with concentration of 10% V/V, diluted with condensed water.	The well started generation again.
June 7, 2010	DP-3537 (BWA)		After 76 days of operation the inhibition system was stopped, because an obstruction was detected in the check valve: a solid deposit. XRD results showed that the solid was 100% nickel sulphide.
July 13, 2010	DP-3537 (BWA)		Obstruction at the end of capillary tubing, after 36 operation days. The inhibitor was changed to: NALCO pHfreedom 5200m.
August 17, 2010	pHfreedom 5200m (NALCO)	2 ppm	High strength green solid (nickel sulphide) obstructed the capillary tubing. According to XRD, the beige-white material formed inside the chamber was 100% hydroxyapatite, (calcium phosphate).
October 3, 2010	pHfreedom 5200m (NALCO)	2 ppm	The inhibition system was stopped, because it was difficult to pump the inhibitor. Within the check valve was found green-brown scale (100% nickel sulphide). The beige-white solid that formed inside the chamber was 100% calcium phosphate.
October 19, 2010	pHfreedom 5200m (NALCO)	3 ppm	The inhibition system was stopped, because it was difficult to pump the inhibitor. In the inhibitor mixture tank, a supernatant was seen. After 19 days of operation, the scattering chamber of the inhibitor was 50% filled with a white deposit.

Chemical monitoring of wells with high calcite scaling potential in El Salvador is based on monitoring the relationship between a reactive component (Ca) and a conservative component (Cl); this ensures that any changes in fluid composition can be detected.

It has been a practice to obtain daily samples of geothermal water to monitor the Ca/Cl ratio to determine if the fluids are likely to scale. Unfortunately, the analyses performed at the Ahuachapan laboratory have too much data scatter to be of use. This scatter seems to be a result of a poorly located sampling point and the analytical process. The sampling point needs to be moved further from a probable source of turbulence in the two phase flow line, and sodium analyses need to be performed to provide a semi-independent check on the quality of the chloride analyses and the sample point (Benoit, 2011).

The central laboratory of LaGeo has accreditation for 20 analytical techniques in the geothermal matrix under the international standard ISO/IEC 17025:2005 (Appendix I). That experience must be

TABLE 8: Problems with calcite inhibitors (Cartagena, H., 2011, personal communication)

Product	Storage	Mixing tank	Inhibition system
HP-1340-PLUS (NALCO)	Product stable	From 2009, the product had problems in dealing with mixtures, causing microbiological deposition.	During the operation in four wells, two losses associated with obstruction of the capillaries were also associated with the formation of deposits in the chambers of the inhibitor.
5200m (NALCO)	Product stable		During operation in the year 2010, hydroxyapatite was deposited in five wells. .
DP3537 (BWA)	The product shows formation of an insoluble compound on bottom of barrels, the compound has been classified as "normal" for BWA.	Product mix is stable	Associated with thermal degradation in check valves of the inhibition systems in wells TR18 and AH-35B
GT-30 (ALKEMY)	Product stable	Using dilutions of 5-7.5%	After 1.5 months of use, the product showed high growing of mold and yeast.
3DT-121 (NALCO)	Product stable	Little microbiological growth in the interface water-air	The product has not presented problems to date.

transmitted to the laboratories at Ahuachapán and Berlin, to improve the quality of the analyses of Cl and Ca, and to obtain better values for the Ca/Cl ratio in order to make faster and more precise decisions regarding the inhibition process.

3. CALCITE IN GEOTHERMAL WATERS

3.1 Calcite scaling

Calcite is abundant as a secondary mineral in many hydrothermal systems. Studies of geothermal fluid chemistry in different parts of the world indicate that the waters at depth in the reservoir are very close to being calcite saturated (Arnórsson, 1989). On the other hand, surface waters are often, yet not always, considerably undersaturated.

Experience has shown that calcite scaling in producing geothermal wells is generally only encountered as a problem if the first level of boiling is inside the well, as most often is the case. Yet, theoretical considerations indicate that calcite super-saturation always results when extensive boiling of geothermal water is induced in discharging wells, irrespective of whether this boiling starts in the well or in the aquifer. The principal cause of this apparent discrepancy is considered to be the big difference in the volume of the well bore compared to the anticipated volume of connected pores in the aquifer, even at a small distance from the well (Arnórsson, 1989). Calcite does typically not form significant deposits unless a certain degree of saturation is reached (Bai Liping, 1991).

Mineral deposition from the boiling fluid largely occurs in response to its cooling and degassing. Cooling causes geothermal waters to become over-saturated with minerals with prograde solubility. Degassing tends to produce over-saturated water with respect to minerals whose solubility decreases with increasing pH. The quantity of minerals precipitated from solution is not only determined by the degree of over-saturation but also by the fluid composition and the kinetics of the precipitation

reaction. The solubility of some minerals decreases with increasing temperature and increasing pH, an example being calcite (Remoroza, 2010).

In practice, the most troublesome calcite deposition usually occurs in the well casing at the level of first boiling, with a heavy band of calcite being deposited over a short length (a few meters). Calcite deposition may taper off to become minor or zero from this point upward. Wells should be run at a wellhead pressure sufficient to ensure that calcite deposition, if it is to occur, is within the pipe and not in the rock fissures outside the well (Ellis and Mahon, 1977).

3.2 Thermodynamic treatment of equilibrium (Arnórsson, 2000)

The free Gibbs energy (ΔG_r), of any chemical reaction is given by:

$$\Delta G_r = \Delta G_r^o + RTlnQ \tag{2}$$

where ΔG_r^o is the standard Gibbs energy of reaction, R is the gas constant, T the temperature in Kelvin and Q the reaction quotient. The standard Gibbs energy of reaction is related to the equilibrium constant (K) by:

$$\Delta G_r^o = -RTlnK \tag{3}$$

At equilibrium, $K = Q$ and thus $\Delta G_r = 0$. If $K \neq Q$, $\Delta G_r \neq 0$, there is no equilibrium. Considering that the dissolution of calcite is controlled primarily by reaction, then:

$$CaCO_{3(s)} + H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2HCO_3^- \tag{4}$$
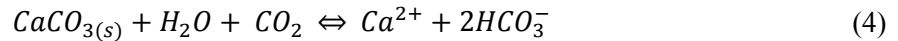
Aqueous CO_2 will be in equilibrium with CO_2 vapour if a gas phase is present. A movement of CO_2 from the liquid to the gas phase will decrease the concentration of aqueous CO_2 and thereby drive Reaction 4 to the left. CO_2 loss from solution, therefore, results in the precipitation of $CaCO_3$. The first dissociation of carbonic acid is given by:

$$CO_{2(aq)} + H_2O \Leftrightarrow H^+ + HCO_3^- \tag{5}$$

Loss of aqueous CO_2 to the gas phase will drive Reaction 5 to the left, and the pH of the solution will rise. The reaction quotient, Q, for Reaction 4 is given by:

$$Q = \frac{\alpha\,[Ca^{2+}](\alpha[HCO_3^-])^{\,2}}{\alpha[CaCO_3]\alpha[CO_2]\alpha[H_2O]} \tag{6}$$

The symbol "α" represents the activity of the species in brackets, and the activity is related to the concentration by the equation:

$$\alpha[Ca^{2+}] = m[Ca^{2+}]\gamma[Ca^{2+}] \tag{7}$$

The symbol "*m*" in Equation 7 is the molal concentration, and "*γ*" is the activity coefficient of the species. By convention, the activity of the crystalline solid and water is set equal to one, and the equilibrium constant then becomes a function of the activities of the aqueous species.

3.3 Saturation index of Calcite (SI)

The scaling potential of calcite is estimated using the saturation index (*SI*) of the mineral, which indicates the existence, or not, of excessive amounts of a mineral that should precipitate. The saturation index (*SI*) is expressed as:

$$SI = \log\left(\frac{Q}{K}\right) \tag{8}$$

where Q = Reaction quotient or activity product of a species in solution;
  K = Equilibrium constant, (theoretical);

For a mineral-solution $Q = K$ means that the system is at equilibrium, $Q > K$ means supersaturated solution and $Q < K$ means undersaturated solution. *SI* is therefore zero at equilibrium, positive for a supersaturated and negative for an undersaturated solution.

When studying whether a particular mineral-solution system is at equilibrium, thermodynamic data are needed on the respective equilibrium constant (K), and the value of the reaction quotient (Q) can be calculated from chemical analysis of the water.

3.4 Effect of boiling on calcite saturation (Arnórsson, 1995)

The solubility of calcite is most often expressed as:

$$CaCO_{3,calcite} \Leftrightarrow Ca^{+2} + CO_3^{-2} \tag{9}$$

It is, however, convenient to express calcite dissolution and deposition by the following reaction when envisaging the effects of boiling of geothermal water upon its state of calcite saturation:

$$CaCO_{3,calcite} + 2H^+ \Leftrightarrow Ca^{+2} + CO_{2,aq} + H_2O \tag{10}$$
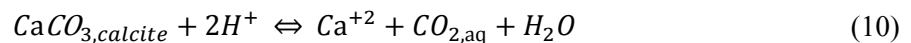
The equilibrium constant for Reaction 10 is given by:

$$\frac{\alpha_{Ca^{+2}}}{\alpha_{H^+}^2}\,\alpha_{CO_{2,aq}} = K'_{calcite} \tag{11}$$

But for Reaction 9, it is:

$$\alpha_{Ca^{+2}}\,\alpha_{CO_{3^{-2}}} = K_{calcite} \tag{12}$$

The symbol "α" represents the activity of the species. The relationship between the two equilibrium constants is:

$$K'_{calcite}K_{H_2CO_3}\,K_{HCO_3^-} = K_{calcite} \tag{13}$$

where $K_{H_2CO_3}$ and $K_{HCO_3^-}$ represent the first and second dissociation constants of carbonic acid, respectively. The equilibrium constant for the first dissociation constant of carbonic acid (aqueous carbon dioxide, i.e. $H_2CO_3 = CO_{2,aq}$) is given by:

$$\frac{\alpha_{H^+}\alpha_{HCO_3^-}}{\alpha_{H2CO3}} = K_{H_2CO_3} \tag{14}$$

If α_{H2CO3} decreases through degassing at constant temperature ($K_{H_2CO_3}$ = constant), it can be deduced from Equation 14 that the product $\alpha_{H^+}\alpha_{HCO_3^-}$ must decrease by the same amount. From the principle of conservation of charge, it follows that the decrease in bicarbonate must be equal to that of the hydrogen ion and since $HCO_3^- \gg H^+$ in geothermal waters, HCO_3^- can be regarded as approximately constant; so, a decrease in α_{H2CO3} by degassing will be accompanied by an approximately equal decrease in α_{H^+}. From this reasoning and the stoichiometry of Reaction 10, it can be deduced that CO_2 degassing will shift the chemical equilibrium reaction described by this equation from right to left, i.e. leading to calcite precipitation.

The solubility of calcite increases with decreasing temperature. When geothermal water cools by boiling and loses its CO_2 at the same time, it is the interplay of increased calcite solubility and decreased H^+ and aqueous CO_2 activities that determine the state of calcite saturation as a function of the temperature of boiling water. During the early stages of boiling, degassing always predominates causing initially calcite-saturated water to become supersaturated. However, as boiling proceeds and degassing approaches completion, the effect of increased calcite solubility takes over with the result that the water most often becomes progressively less supersaturated at lower temperatures and eventually even undersaturated with respect to calcite.

The effect of adiabatic boiling on the state of calcite saturation of selected geothermal well waters is depicted in Figure 4. As seen in the figure, the saturation index increase during the early stages of boiling is faster for lower temperature waters than for the highest temperature waters. This can be attributed to the effect of temperature on CO_2 solubility in water. In the range 150-350°C, CO_2 becomes more soluble with rising temperature. As a result, there is typically less CO_2 degassing in the early stages of boiling as the initial temperature of the water is higher.
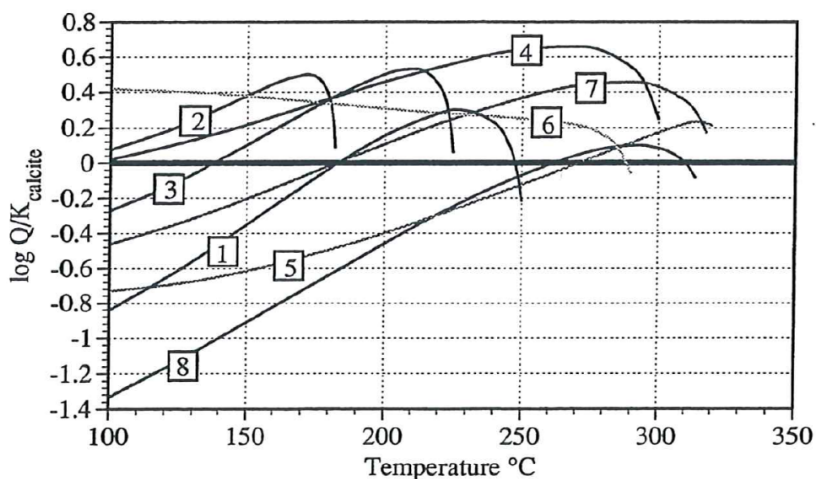

FIGURE 4: Calculated changes in the state of calcite saturation produced by one step adiabatic boiling of the geothermal waters from wells: (1) Amatitla 1, Guatemala, 250°C; (2) Hveragerdi 2, Iceland, 182°C; (3) Hveragerdi 7, Iceland, 225°C; (4) Krafla 6, Iceland, 300°C; (5) Námafjall 11, Iceland, 320°C; (6) Nisyros 2, Grecce, 290°C; (7) Palinpion 7, Philippines, 318°C; (8) Tongonan 407, Philippines, 314°C. (Arnórsson, 1995)

Variations between the calcite saturation curves in Figure 4 can be attributed to:

1) The effect of acids present in the water other than carbonic acid ($CO_{2,aq}$)   ;
2) The variation in the dissociation constant of all these acids with temperature; and
3) The temperature dependence of the stability of ion pairs that contain calcium ion or an anion of a pH-buffering acid.

The presence of acids other than carbonic acid causes H^+ to decrease less (or pH to increase less) than the aqueous CO_2 activity. The relationship between the decrease in $CO_{2,aq}$ and the increase in pH for the well fluids is depicted in Figure 5.

3.5 Methods to control calcite scaling

Many methods have been suggested to minimize and/or control the scaling problem in production wells; the methods can be divided as follows: a) Making the water calcite undersaturated; b) Periodic cleaning by mechanical and/or chemical methods; c) Controlling wellhead pressure; d) Chemical inhibitors.

3.5.1 Making the water calcite undersaturated

Chemical treatment of geothermal water, either by an acid or CO_2, to make it calcite

FIGURE 5: Relationship between relative decrease in aqueous CO_2 concentrations and increase in pH during adiabatic boiling of water; the number of each curve corresponds with the wells described in Figure 4 (Arnórsson, 1995)

undersaturated has been successful (Kuwada, 1982). It has, however, several disadvantages. Due to the relatively high pH-buffer capacity of geothermal waters, large amounts of acid may be required, making this treatment expensive and therefore, not attractive economically. Furthermore, acidification may render the water corrosive. The CO_2 partial pressure of many geothermal reservoir fluids is very high. Thus, large quantities of CO_2 may need to be added to make the reservoir water significantly calcite undersaturated, especially after it has flashed (Arnórsson, 1995).

3.5.2 Periodic cleaning by mechanical or chemical method

Mechanical cleaning has proven useful in many contries, including Iceland, Costa Rica and Tibet. The most successful mechanical cleaning method involves drilling out the scale with a small truck-mounted rig while the well is producing. By this method, the scale is brought to the surface, thus not accumulating at the well bottom, and the well can be connected immediately after the cleaning operation is completed, which takes one to two days. This method of coping with calcite scales appears to be feasible only if the deposition rate is not very fast and cleaning is required no more than about twice a year (Arnórsson, 1995).

3.5.3 Controlling wellhead pressure

This method is yields more total energy between each cleaning operation. The wellhead pressure is gradually decreased causing that flash point depth to increase gradually and, therefore, spread into the deposition zone. This doesn´t prevent scaling, but it is possible to retard the problem. This method is only feasible if the deposition rate is not very fast (Molina, 1995).

On the other hand, by controlling wellhead pressure, it is possible to choose the depth of the deposition zone by handling the downhole boiling point, shown in Figure 6. This saves cost when mechanical cleaning is required, because if the deposition is deeper, a more expensive drilling rig may be needed.

3.5.4 Chemical inhibitors

According to Hauksson et al. (1999), inhibitors are substances added to brines, usually at the parts-per-million level, to retard the growth of scale or the formation of a precipitate. The inhibitor must be
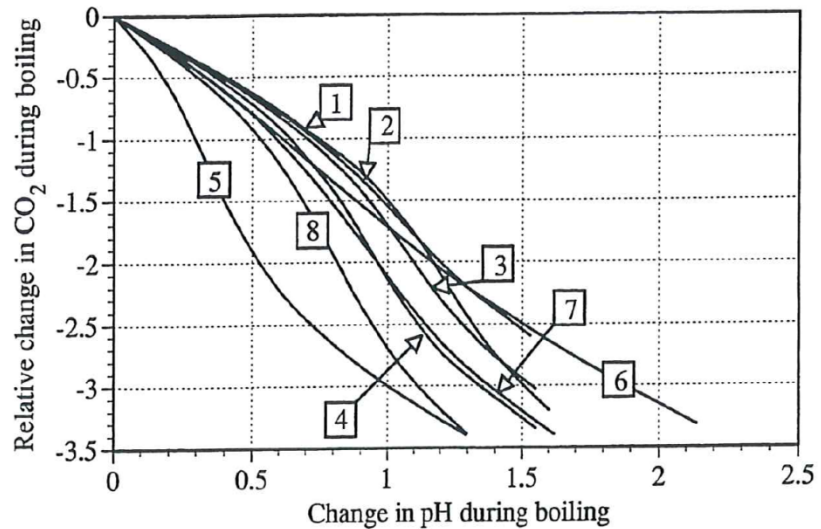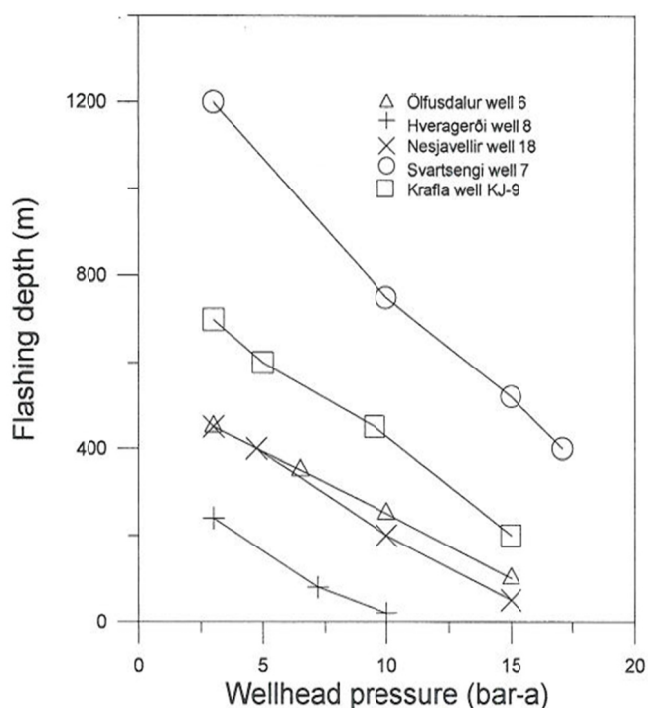
FIGURE 6: Calculated flashing depth with varying
pressures in five Icelandic geothermal wells
(Wangyal, 1992)

injected into the well at a depth that is below the level of first boiling. The inhibitors are tested and ranked in order of effectiveness and cost at high temperature. This testing and ranking procedure must be done at each site because the brine properties and flow conditions vary for each geothermal site.

The possible ways to prevent calcite scaling by chemical addition are divided into two groups. The first is to prevent crystal growth and the coagulation of the calcite particles that are forming, and the second is to reduce the activity of the ions that form the precipitate, calcium and carbonate, which thereby lowers their ion product and reduces the oversaturation. Only the first type is described below because it works better in high temperature wells.

Organic phosphate compounds (phosphonates, Phos) bind to the calcium ions on the crystal surface and are very effective calcite inhibitors. Examples are Dequest and Sequion. Phosphonates are either sold as acidic solutions, which are corrosive at high temperatures, or basic solutions which have been mixed with sodium hydroxide. At high temperatures it is known that phosphonates can decompose and become ineffective or form phosphates, which then leads to the precipitation of calcium phosphate.

Another group of inhibitors is composed of polymers with active acid groups, e.g. carboxyl groups, known as polyacids. Examples of such compounds are polyacrylates, polymethacrylates and polymaleicanhydrides (polymaleic acid). The polyacids bind to the calcite crystals causing a steric hindrance, thus disturbing regular crystal growth, in a similar manner as the phosphonates. They carry negative charges which cause repulsion between the crystal particles – if the length of the chains is right. If the chains are too long, they can connect the crystal particles and accelerate precipitation and if they are too short, they are ineffective as inhibitors. Examples of polyacids are Millsperse (polymaleic acid), Flocon (polycarboxylic acid) and Nalco 1340 (polyacrylate).

4. CALCITE INHIBITION SYSTEM – RECENT EXPERIENCES

4.1 Calcite inhibition system

Figure 7 shows the components of a calcite inhibition system. The tank system includes the pre-mix tank for the required amount of pure inhibitor, water tank, the mixing tank for the water-inhibitor mixture and the feed tank for the final injection solution. There are three pump requirements: a transfer pump that conveys the chemical from the original container to the pre-mix tank, a recirculating pump that ensures a homogeneous solution of the inhibitor and a metering or dosing pump that injects the desired concentration of chemical to the downhole injection system. A back-up dosing pump is required so that a switch-over can readily be done regularly (once-a-month) or during an emergency situation (Daco-ag and Belas-Dacilo, 2010).

The inhibitor is pumped into the production well through the capillary tubing to a depth of 50 to 100 m below the boiling point depth in the well. The capillary tubing is connected to the injection head and its weight bar. The weight bar helps to stabilize the components as well as lift and lower the inhibition head. The inhibitor is injected into the dynamic conditions of production wells; therefore, the inhibitor dosages in every well must be re-evaluated regularly. Also, the doses of the inhibitor must be checked if the weekly fluid monitoring shows

FIGURE 7: Simplified schematic diagram of the calcite inhibition system (CIS) (Daco-ag and Belas-Dacillo, 2010)

variations in the chloride and calcium concentrations, or if the bicarbonates monitored monthly show variations in their concentrations. It is very important to determine the injection depth of the inhibitor correctly. For doing this, it is necessary to use the data obtained from the dynamic temperature and pressure profiles, taking into consideration that the boiling point at maximum flow conditions will vary from some meters to up to hundreds of meters, depending on the well's permeability (Moya and Nietzen, 2010).

4.2 Mahanagdong, Philippines

The well discharges in Mahanagdong are generally of the neutral and mature NaCl-type of fluids (Daco-ag and Belas-Dacillo, 2010). The fluids towards the major natural outflow in the southeast are homogenous with lower T_{quartz} (260-280°C) and reservoir Cl levels (2000-3000 mg/kg). The fluids in the northern part of the reservoir are acid Cl-SO$_4$ waters (pH sampled at wellhead <4) with reservoir Cl concentrations of around 4000 mg/kg. The acidic fluids have elevated SO$_4$ (>100 mg/kg), Fe (>10 mg/kg) and Mg (>5 mg/kg) contents in the liquid phase and H$_2$S in the vapour (>25 mmoles/100 mole water) (Angcoy, 2010).

There are two existing Calcite Inhibition Systems (CIS) installed in the Mahanagdong sector of Leyte geothermal production field. The calcite saturation index (SI) of wells MG1 and MG19, which reached around 0.4-0.7, and the calcite mineral deposition were observed in these wells, requiring periodic mechanical cleaning during the initial commercial utilization in 1998.

4.2.1 Calcite inhibition system

MG1's calcite inhibition system was commissioned in April 2001 after the well was worked over in March 2001. In MG19, after the August 2001 work-over, a calcite inhibition system was installed and then commissioned in September 2001. Figure 7 shows the components of the calcite inhibition system. In MG1, the calcite inhibitor, at a 10% feed concentration and a dosing rate of 10-11 l/h (liters per hour), was injected at 1750 m depth starting April 2001; this sustained the well output for about three years until the next capillary tubing replacement and work-over. In MG9, the calcite inhibitor was injected at 1850 m depth with a similar dosing concentration and rate as MG1.

4.2.2 Monitoring

Pump parameters
Pump parameters, particularly the injection pressure, are closely monitored to check for the presence

of leaks or obstructions during run-in. After the capillary tubing is set at the injection depth, residence time is measured using a coloured tracer like sodium fluorescein. When stable pressure is attained, chemical inhibitor injection commences. The following parameters are then regularly monitored: injection pressure, pump stroke, injection rate, feed solution level and chemical stock. Of prime importance is the estimate of the required injection rate which must be updated when changes in the well's mass flow occurs; this is then calculated and compared with the target line concentration as specified by the chemical supplier.

Flow parameters

Flow parameters are important indicators in assessing inhibitor performance. Calcite scaling can be indirectly recognized by declines in mass flow and consequently steam flow. Also, some inhibitors cannot attain 100% inhibition efficiency such that declines in mass and steam flows still occur. Therefore, an observed decline in mass flow is an indication of blockage due to calcite deposition restricting the flow of the well.

Chemical monitoring

Geochemical monitoring in MG1 and MG19 generally observed that the reservoir calcium (Ca_{res}) concentration was quite stable. But the calcium level alone is insufficient when monitoring deposition or inhibition. During calcite deposition, calcium is expected to decline as it is consumed in the reaction process and deposited. Nonetheless, calcium (Ca_{res}) concentrations must be evaluated in tandem with other physical data such as flow parameters. The decline in mass flow will indicate if deposition is occurring.

4.2.3 Calcite inhibitor used at Mahanagdong

The use of chemical inhibitors to minimize calcite deposition problems has proven successful in wells MG1 and MG19 since the calcite inhibition system was commissioned in 2001. Two of these inhibitors are of the polyacrylate type (PAA#1(NALCO 9354), PAA#2(NALCO 1340HP PLUS)), and one inhibitor was of the polymaleic type (PMA (Millsperse 815)).

PAA #1 and PAA #2 are similar formulas except that PAA #1 has been neutralized with NaOH as shown by its higher pH levels, and PAA #2 is a high-purity version of PAA #1. Suppliers neutralize them to render these highly concentrated electrolytes less corrosive. PMAs, just like PAAs, are a polymer but with cyclic monomeric units. A PMA has almost the same action in inhibiting massive calcite crystal formation through crystal distortion and then dispersion. This type of inhibitor is known to be thermally stable up to ~300°C.

4.2.4 Problems encountered

When using PAA #1, the tubing was clogged only 5 days after CIS commissioning in MG19. When the tubing was pulled out, about a 5-mm deposit close to the nozzle tip was found. The deposit was very hard (metallic when pricked) with black adherent depositions. Scanning Electron Microscope (SEM) analysis of the deposit by the supplier yielded an elemental composition of Fe (65%), S (10%) with the minor element Ni (<10%) and other trace elements. Evaluation of the results showed that the deposits were corrosion products and degraded PAA #1.

Corrosion was believed to occur from the reaction of sulphur (which is a left-over in the manufacture of PAA #1) with the tubing material to produce metallic sulphide (e.g. iron sulphide), especially since the PAA #1 feed concentration was at 10% v/v. The inhibitor solution collected from the tubing (close to the nozzle tip) was likewise evaluated for inhibition efficiency using the National Association of Corrosion Engineers (NACE) standard test, method TM-0374-90. The sample was turbid with fine black deposits. The NACE test showed that the heated inhibitor had already exhibited poor inhibition properties. FT-IR spectra of the black deposit showed absorption bands in the 1000-3000 cm^{-1} region, characteristic of organic compounds, indicating that the inhibitor was chemically altered.

Note that PAA #1 was used in MG1 for more than one year of continuous dosing before the tube clogging problem was encountered. MG1 reservoir temperature during this period ranged from 242-264°C, which is lower than MG19 (>270°); this could be the reason why the clogging problem was not observed in MG1 during PAA #1 utilization. A new high-temperature calcite inhibitor of the polymaleic type was used after recommissioning MG19 CIS in October 2001. However, beginning in 2005, chemical suppliers offered PAAs, such as PAA#2, which were stable at higher temperatures. These PAAs are of high purity (unlike PAA#1) and were enhanced to withstand higher temperature, making them technically qualified for Mahanagdong CIS application at a temperature of ~280°C.

4.3 Miravalles, Costa Rica (Moya and Nietzen, 2010)

The temperature of the water-dominated geothermal reservoir is about 240°C and the main reservoir fluids have a sodium-chloride composition with TDS of 5300 ppm, pH of 5.7, silica content of 430 ppm and a tendency to deposit calcite in the wellbore.

4.3.1 Calcite inhibition system

The calcite inhibition system in Miravalles geothermal field has been used successfully in the production wells that supply steam and brine to the generating units since 1994. Experience has indicated that the injection of an appropriate dose of inhibitor makes it possible to produce the geothermal wells with little or no deposition. Currently, there are 21 calcium inhibition systems in operation. The field tests usually begin with an inhibitor overdose and then, when the calcium values under total inhibition conditions are found, the dosage is lowered until optimum values are determined. In other words, if when reducing the inhibition doses the calcium concentration is lowered, it means that the well is underdosed and will result in a partial scaling of the well.

4.3.2 Monitoring

Operating parameters
The operating parameters that are monitored are:

    a) Consumption time; this parameter is indicative of the rate of inhibitor flow;
    b) Pumping pressure; it is important for detecting possible problems in the capillary tubing such as partial or total obstruction or broken tubing; and
    c) Tank level; indicates the level of the inhibitor in the tank.

Chemical monitoring (Moya and Yock, 2001)
The chemical parameters are monitored periodically; if any parameter is out of range, a corrective action is taken to adjust the system to normal conditions. The monitored parameters are:

    a) Ca/Cl ratio: indicates the effectiveness of the inhibition process; and
    b) Bicarbonates: used to adjust the inhibition dosage.

In order to determine the baseline of the Ca/Cl ratio, at least 10 sets of samples must be taken before injecting the diluted inhibitor. While measuring the baseline, clean water must be injected through the capillary tubing. The time between sample sets is about 4-6 hours and each set comprises three water samples. The baseline ratio $(R)_{BL}$ is calculated in order to avoid extensive boiling or mixing:

$$(R)_{BL} = \left(\frac{ppm\ Ca^{+2}}{ppm\ Cl^-} \right)_s * (Cl^-)_r \qquad (15)$$

where $(R)_{BL}$ = Ratio baseline;
        s = Sample;
        r = Reservoir.

In order to monitor the performance of the inhibition system, at least one set of samples must be collected each week. Each set comprises three water samples. For each water sample, the chloride concentration and calcium content are determined, and the ratio is calculated in order to avoid extensive boiling or mixing:

$$(R)_{MC} = \left(\frac{ppm\ Ca^{+2}}{ppm\ Cl^-}\right)_s * (Cl^-)_r \qquad (16)$$

where $(R)_{MC}$ = Ratio monitored control.

The comparison of these ratios (R_{BL} & R_{MC}) determines the efficacy of the inhibitor. If the difference is greater than or equal to 3 units, the inhibitor is working properly, but if the difference is less than 3 units, a problem may exist with the inhibition system, and therefore, an inspection of the inhibition system must be performed.

Another chemical parameter useful for monitoring the inhibition system is the concentration of bicarbonates. In Costa Rica, bicarbonates are considered the limiting reagent in the formation of calcite (Sanchez et al., 2005); for that reason, bicarbonates are used to adjust the inhibition dose. If bicarbonate concentration increases, the inhibitor dosage may be lowered, but if the bicarbonate concentration decreases, the inhibitor dosage must be raised. After the initial evaluations have been performed, the concentrations of CO_2 in the steam and HCO_3^- in the liquid must be carefully monitored in order to watch the scaling tendency of each well.

4.3.3 Calcite inhibitor used

Different types of inhibitors have been tested in the Miravalles geothermal field since 2000. The inhibitors that passed the test were: NALCO 1340 HP Plus, Geosperse 8410CN+ and BWA DP 3537.

4.3.4 Problems encountered (Moya et al., 2005)

Table 9 shows a summary of the problems encountered during exploitation.

TABLE 9: Summary of problems encountered

Year	Product	Tubing	Comments
1990	Nalco 1340 (aqueous polyacrylate)	6.35 mm OD ASTM A-269 type 316L capillary tubing	The operation was stopped after three months due to scale deposits that blocked the capillary tubing. Chemical analysis of the material showed a high content of sulphur (38%), iron (40%) and Cr (14%). This deposit was probably formed by reaction of a sulphur impurity and the capillary tubing.
1992	Nalco 1340, sequion 40-30, and Exxon Chemical Surflo	a) ATSM A-269 type 316 b) Incoloy 825	Using Nalco 1340 inhibitor and ASTM A-269 type 316 capillary tubing provided the best technical and economic results.
1997	Henkel, Aquaquest 305 (aqueous Na-polyacrilate solution with a pH of 7.5-9.0)	SS 316-L capillary tubing	a) When the product was diluted with water, some bacteria grew with time, clogging the capillary tubing. b) The antibacterial used by Henkel to inhibit the bacterial growth had high phosphorous content that reacted with the SS 316-L capillary tubing, producing a solid that plugged the tubing.

5. METHODOLOGY

5.1 Sample collection

For geothermal wells, steam and water samples were collected at the wellhead using either a Webre separator or sampling ports installed at a cyclonic separator. Steam samples were collected in duplicate into evacuated gas sampling bulbs containing 50 ml of a 4N NaOH solution. Water samples from geothermal wells were collected at the same pressure as steam samples and filtered through 0.2 μm cellulose acetate membrane filters into high density polyethylene bottles using a filter holder of the same material. The sample was split into two portions, 250 ml each; one of them was preserved, adding 2.5 ml of suprapure concentrated HNO_3 for the analysis for major cations (Na, K, Ca, and Mg), boron and silica; the second portion was used for pH, chloride, total carbon dioxide and sulphate analysis.

5.2 Analysis of water and steam samples

Table 10 lists the analytical methods used for the analysis of the steam and water samples collected in the production wells.

TABLE 10: Analytical methods used for steam and water samples

Steam sample		Water sample	
Analyte	**Method**	**Analyte**	**Method**
CO_2	Titration with HCl	Na	AAS
H_2S	Titration with sodium thiocyanate	K	AAS
He	GC with thermal conductivity detector	Ca	AAS
H_2	GC with thermal conductivity detector	Mg	AAS
N_2	GC with mass detector	B	AAS
Ar	GC with mass detector	SiO_2	AAS
CH_4	GC with mass detector	Cl	Titration with $AgNO_3$
O_2	GC with mass detector	SO_4	UVS
		CO_2	Titration with HCl and NaOH
		pH	Potentiometric

GC = Gas Chromatography;   AAS = Atomic Absorption Spectrophotometer;
UVS = Ultra Violet Spectrophotometer

5.3 Data handling

Calcite scaling potential was calculated in 18 production wells in Ahuachapán production field and 13 production wells in Berlin production field, using the results of the chemical analysis of the water and steam samples collected. The study was carried out using samples collected in both production fields during the years 2009-2011. For the report, only liquid-dominant wells were considered. A special case was well AH-32st, which was not evaluated, because there were not enough samples in the evaluated period.

The calcite scaling potential is estimated by assessing the saturation index (SI) of the mineral; for this, it is necessary to establish the reference temperature to be used. The reference temperature was established using the average of the Quartz and Na/K geothermometers to minimize fluctuations in the reference temperature due to the chemical analyses of SiO_2, Na and K used in the calculations.

Chemical geothermometers depend on the existence of temperature-dependent mineral-fluid equilibrium at depth which must be preserved during the passage of fluid to the surface. This statement must be kept in mind, and it comprises the following assumptions (Arnórsson, 2000):

a) Fluid-mineral equilibrium at depth;
b) A temperature dependent reaction at depth;
c) An adequate supply of solid phase to permit the fluid to become saturated with respect to the constituents used for geothermometry;
d) Negligible re-equilibrium as the water flows to the surface; and
e) No dilution or mixing of hot and cold waters.

The solute geothermometers used in this report are shown in Table 11.

TABLE 11: Temperature equations for solute geothermometers

Geothermometer	Equation	Range (ºC)	Source
SiO_2[a]	$127.18 + 48.119Q + 82,135Q^2$	>180	Gudmundsson and Arnórsson, 2002
Na - K[b]	$733.6 - 770.551Y + 378.189Y^2 - 95.753Y^3 + 9.544Y^4$	0 - 350	Arnórsson et al., 1998

a) Q = log (mmol/kg), at 180 ºC (Calculated by Watch); b) Y = log (molal ratio Na/K)

Table 12 shows the reference temperature calculated for each well. The temperatures reported in Table 12, for each production well, correspond well with the temperatures reported by Jacobo in 2003, where estimation of the reference temperatures was done, using gas and water geothermometers, for both Ahuachapán and Berlín geothermal fields. Figure 8 shows each geothermometer temperature, plotted against the average temperature given by all the geothermometers used, for some wells in both Ahuachapán and Berlin production fields.

TABLE 12: Reference temperature (°C) for production wells in
Ahuachapán and Berlin production fields

Ahuachapán production field				Berlin production field			
Well	**RT**	**Well**	**RT**	**Well**	**RT**	**Well**	**RT**
AH-4Bis 1	224	AH-26	222	TR-2	274	TR-17A	251
AH-4Bis 2	226	AH-27	246	TR-4	280	TR-17B	261
AH-6	218	AH-28	234	TR-4B	279	TR-18	255
AH-16	244	AH-31	250	TR-4C	262		
AH-17	197	AH-33B	237	TR-5	285		
AH-19	221	AH-35A	220	TR-5A	271		
AH-20	223	AH-35B	224	TR-5B	277		
AH-21	231	AH-35C	224	TR-5C	272		
AH-22	222			TR-9	261		
AH-23	226			TR-17	270		

RT = Reference temperature (°C)

Figure 8 shows that the temperatures calculated using quartz and Na/K geothermometers follow a trend more or less linear with respect to the average geothermometer temperature; this indicates that there is a concordance between both geothermometers in the evaluated samples. Knowing the reference temperature for each well and using the chemical speciation program WATCH (Bjarnason, 2010), it was possible to calculate the saturation index (SI) of calcite.
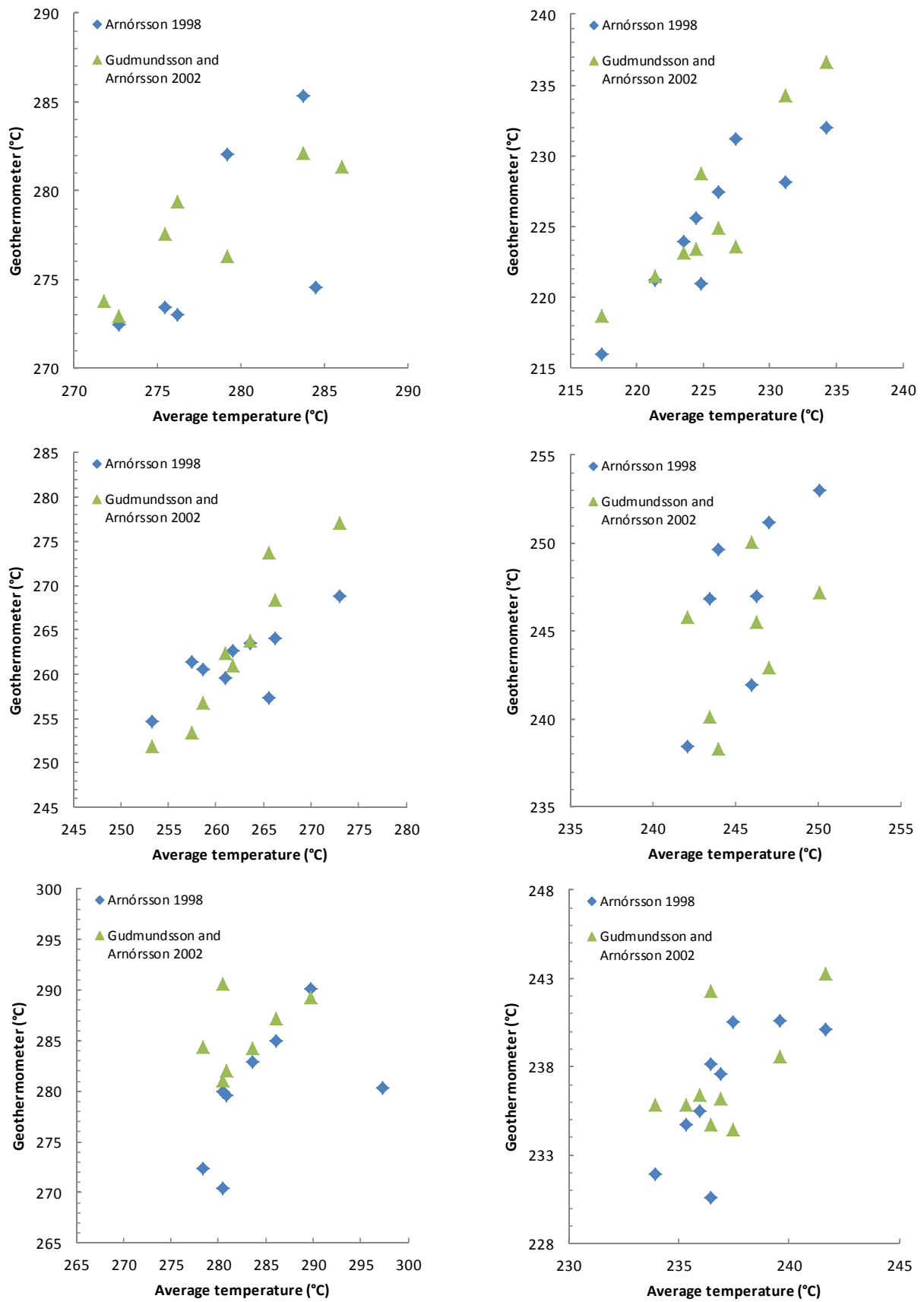
FIGURE 8: Temperatures based on solute geothermometer results (Arnórsson, 1998; Gudmundsson and Arnórsson, 2002); values are plotted against the average geothermometer temperature

The WATCH program can compute the resulting species concentrations, activity coefficients, and activity products and solubility products when the equilibrated fluid is allowed to adiabatically boil from the reference temperature to some lower temperature. This is particularly useful in the study of scaling. After the reference temperature has been chosen, the program will prompt for the temperature at which the water is assumed to have boiled and lost steam before sampling.

In this report, with the help of WATCH, an average of 10 samples for each well was studied. For each sample, adiabatic boiling from the reference temperature was simulated; the saturation index of calcite was calculated to 10 different temperatures, using the values of Q (Activity product of species in solution) and K (Equilibrium constant) from the aqueous speciation calculations and Formula 8, described before.

6. RESULTS

From the calculated calcite saturation index, obtained at the reference temperature, two graphs were drawn for each well. The first one describes the behaviour of the calcite saturation index with respect to time, during the period 2009 to 2011; the second one shows the computed results for calcite saturation curves for simulated adiabatic boiling. The saturation curves presented in the second graph are the samples with the highest and lowest SI, as well as the one closest to zero at the reference temperature, taken from the first graph.

Figures 9 and 10 show the calcite saturation curves for Ahuachapán and Berlin production fields, respectively. In the case of Ahuachapán, Figure 9 has been separated into two parts to facilitate the interpretation of the saturation curves. In both Figures 9 and 10, each curve represents the result of adiabatic boiling simulated at the reference temperature for each sample per well which is closest to equilibrium.

Negative values of calcite SI correspond to an undersaturated state, indicating no potential for calcite scaling formation in the well; according to the experience in El Salvador, calcite SI values between 0.0 and 0.2 correspond to an oversaturated state without risk of calcite scaling formation. However, calcite SI values higher than 0.3 correspond to an oversaturated state which indicates that the well has a high potential for calcite scaling (Guerra, 2008; Jacobo, 2011).

Following the approach described above and taking into account the results shown in Figures 9 and
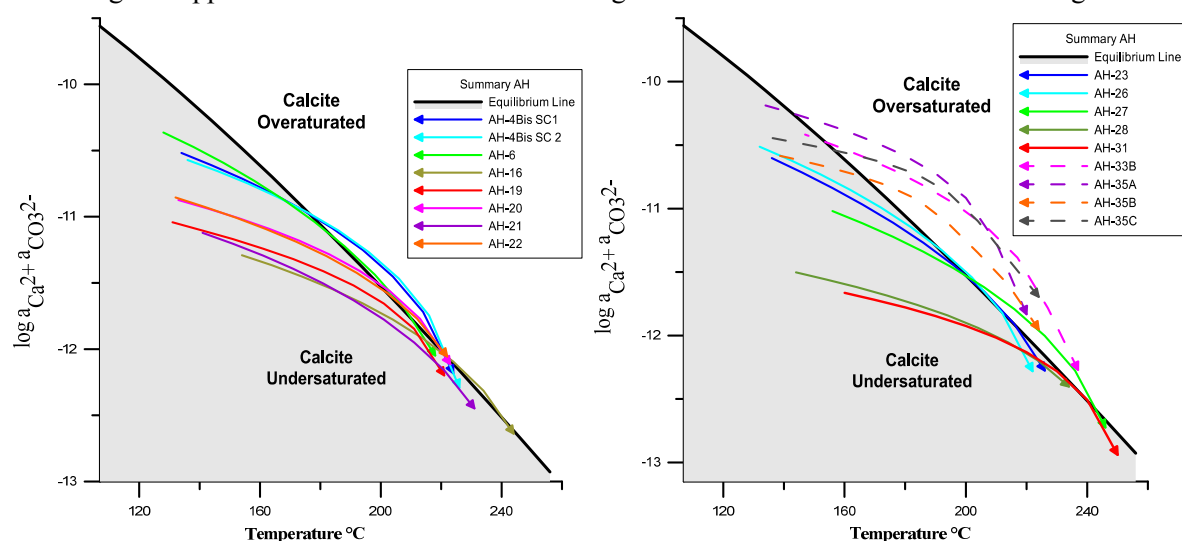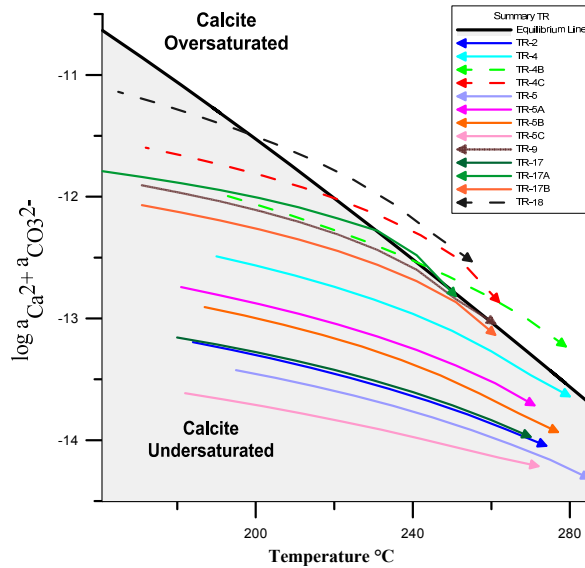

FIGURE 9: Calcite saturation curves for 18 production wells in Ahuachapán production field; dashed curves represent wells with high SI of calcite at reference temperature

10, it was established that of the 18 producing wells evaluated in Ahuachapán production field, 4 have a high potential for calcite scaling, while in Berlin production field, 3 out of the 13 evaluated wells have a high potential for calcite scaling.

6.1 Ahuachapán production field

Presented below are the results only for wells with a high potential for calcite scaling. According to the data used in this report, the production wells that have a high potential for calcite scaling in Ahuachapán production field are: AH-33B (Figure 11), AH-35A (Figure 12), AH-35B (Figure 13) and AH-35C (Figure 14). In the graphs for calcite SI vs. date, each symbol represents one independent sample; the red and blue symbols represent the maximum and minimum calcite SI, respectively, during the

FIGURE 10: Calcite saturation curves for 13 production wells in Berlin production field; dashed curves represent wells with high SI of calcite at reference temperature

evaluated period (2009-2011). On the other hand, in the graph for calcite SI vs. temperature, the red and blue symbols correspond to the red and blue symbols described for the first graph, and, thus, represent the maximum and minimum calcite SI calculated at reference temperature; the curves represent adiabatic boiling at the reference temperature.
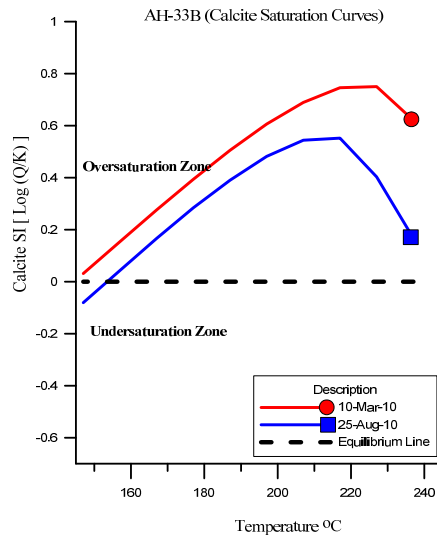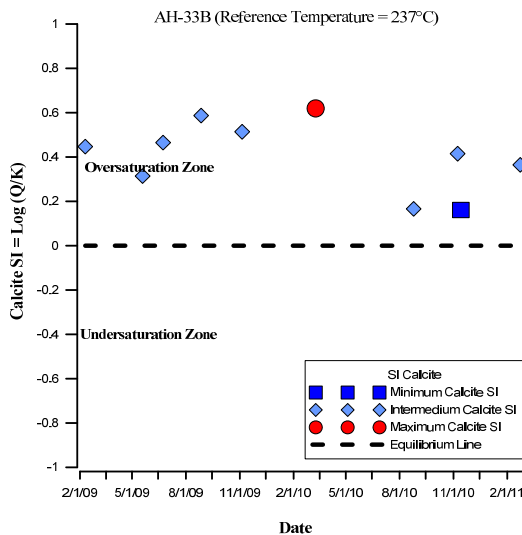
FIGURE 11: Well AH-33B, calcite SI (at reference temperature 237°C) vs. date (2009-2011); and calcite saturation curves

6.2 Berlin production field

Presented here are the results only for wells with a high potential for calcite scaling. According to the data used in this report, the production wells that have a high potential for calcite scaling in Berlin production field are: TR-4B (Figure 15), TR-4C (Figure 16) and TR-18 (Figure 17). In the graph of calcite SI vs. date, each symbol represents one independent sample; the red and blue symbols represent the maximum and minimum calcite SI, respectively, during the evaluated period (2009-
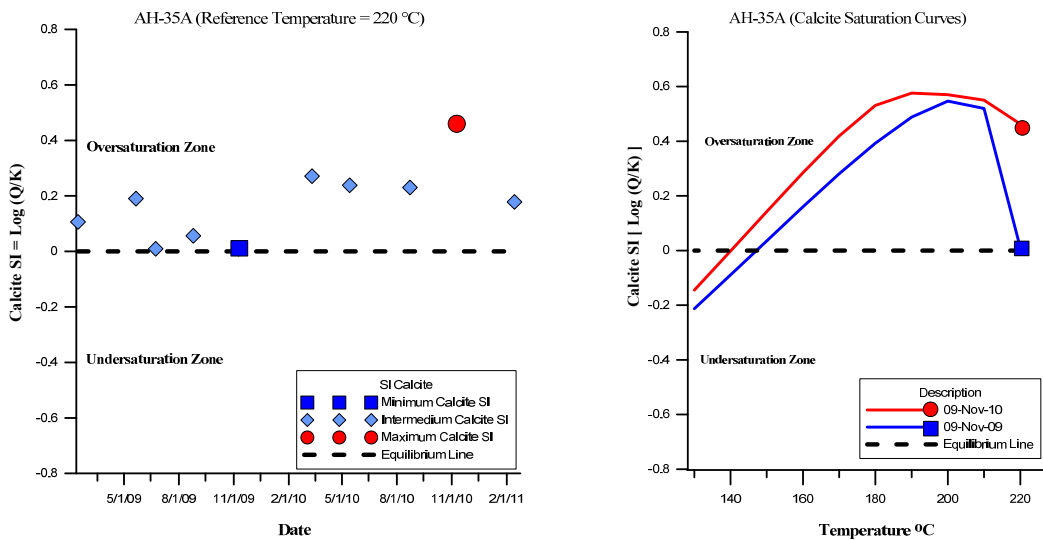
FIGURE 12: Well AH-35A, calcite SI (at reference temperature 220°C) vs. date (2009-2011);
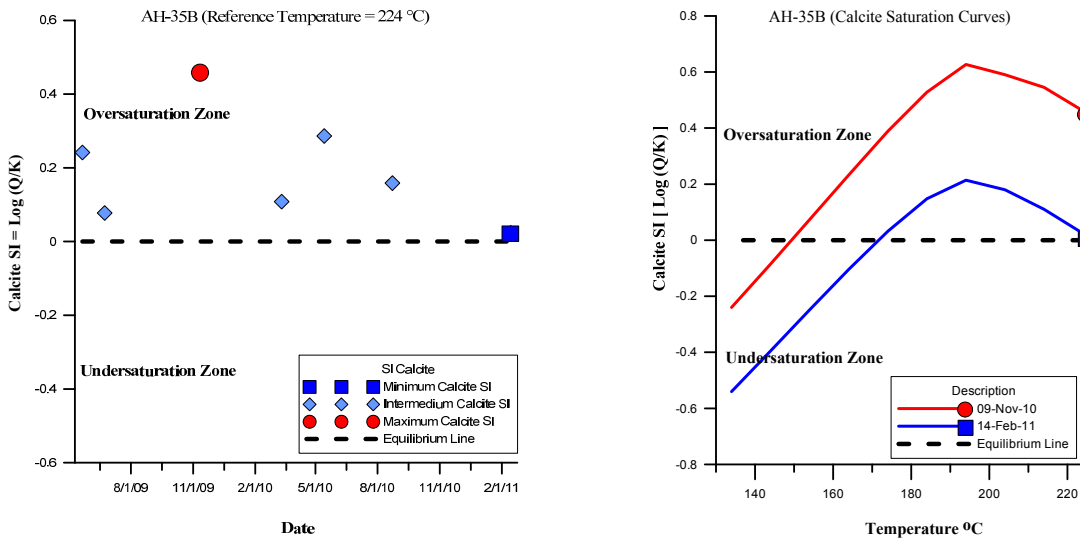and calcite saturation curves

FIGURE 13: Well AH-35B, calcite SI (at reference temperature 224°C) vs. date (2009-2011);
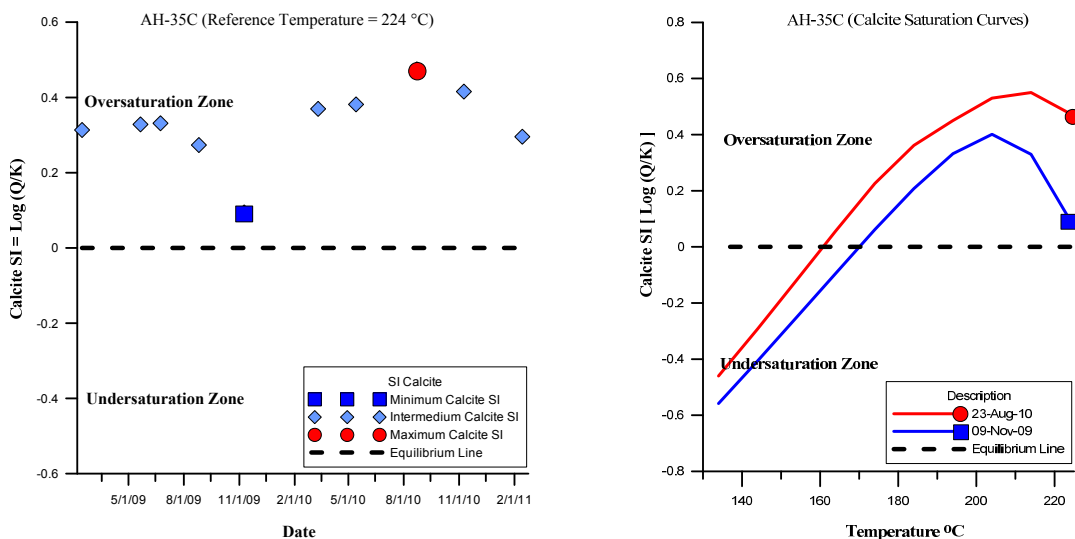and calcite saturation curves

FIGURE 14: Well AH-35C, calcite SI (at reference temperature 224°C) vs. date (2009-2011);
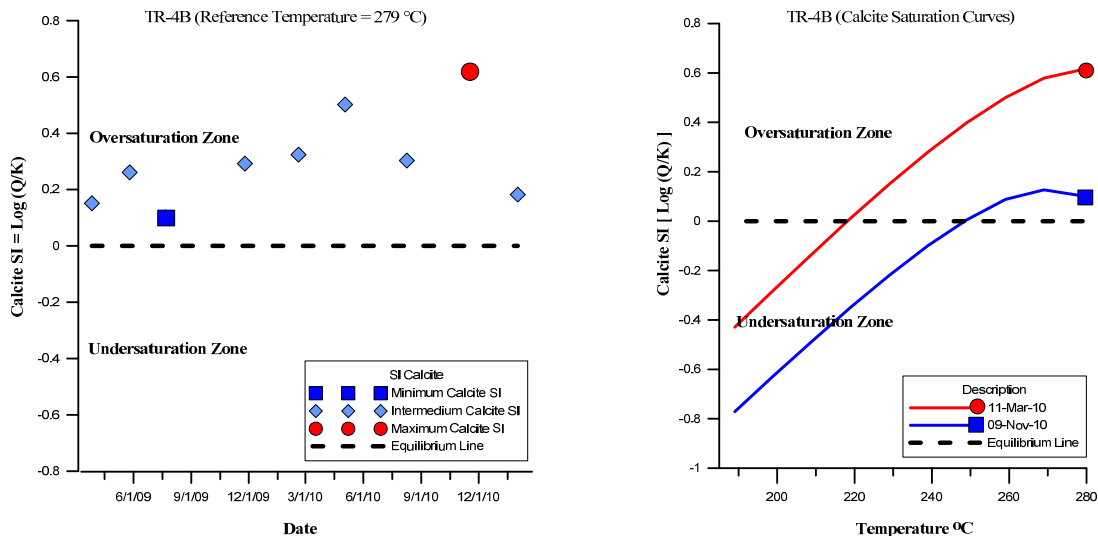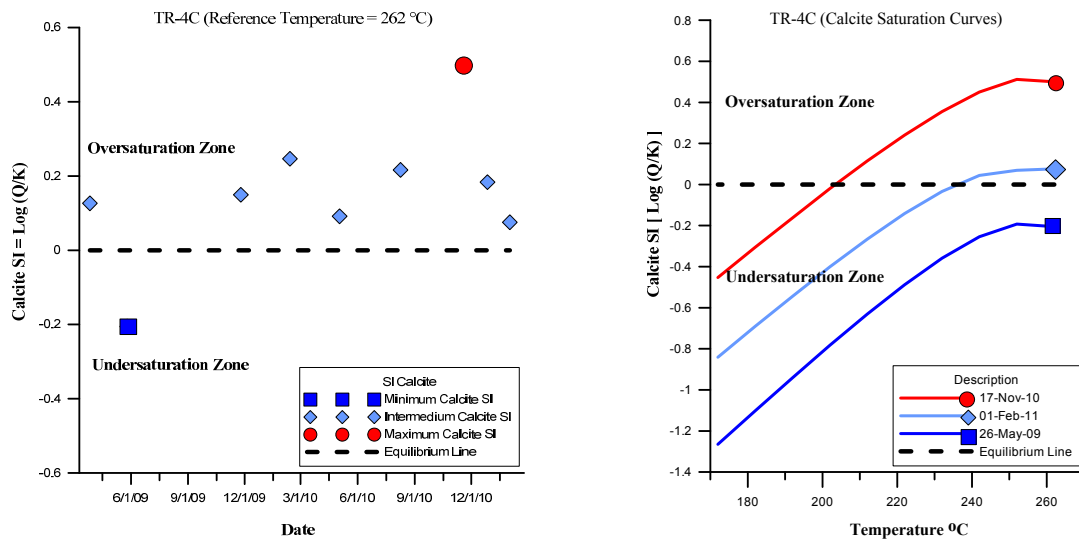and calcite saturation curves

FIGURE 15: Well TR-4B, calcite SI (at reference temperature 279°C) vs. date (2009-2011);
and calcite saturation curves

FIGURE 16: Well TR-4C, calcite SI (at reference temperature 262°C) vs. date (2009-2011);
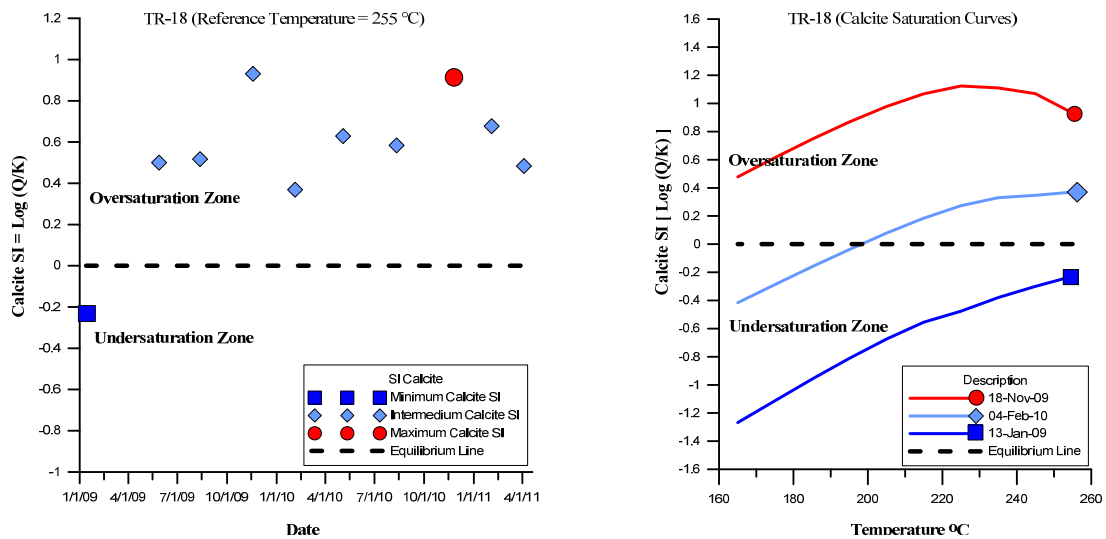and calcite saturation curves

FIGURE 17: Well TR-18, calcite SI (at reference temperature 255°C) vs. date (2009-2011);
and calcite saturation curves

2011). In the graph of calcite SI vs. temperature, both red and blue symbols correspond to the red and blue symbols described for the first graph, and, thus, represent the maximum and minimum calcite SI calculated at the reference temperature. The curves represent adiabatic boiling at this temperature.

7. DISCUSSION

Wells that have presented evidence of calcite scale formation in Ahuachapán (AH-33B, AH-35A, AH-35B and AH-35C) and Berlin (TR-18) geothermal fields in El Salvador correspond to the wells for which the results presented had a high potential of mineral scaling formation. The exceptions are wells TR-4C and TR-4B, for which the calculated saturation indices indicate a high calcite scaling potential; thus far, they have not presented evidence of mineral formation. This can be seen in the production characteristics of the wells shown in Appendix II. The production history shows that while well TR-18 was in production for almost 18 months in the same situation as wells TR-4C and TR-4B, production from well TR-18 since then has not been possible without a calcite inhibition system.

Therefore, it is important to establish whether the wells actually produce deposits of calcite and whether it is necessary to install an inhibition system to maintain the operating conditions, because installing a carbonate scale inhibition system in a well where it is not necessary adds additional and unnecessary risk to the overall field operation. For this purpose, it is advisable to use scaling coupons located at the flash point of the wells, to monitor physically and demonstrate the formation of calcite, as indicated by the chemical results. Capillary tubing could be used as a coupon (Benoit, 2011).

When determining whether a well must be inhibited or not, it is necessary to take into account the following:

   a) Chemical monitoring to know the mineral saturation index of the mineral;
   b) Locating a coupon in the wells to demonstrate the mineral deposition physically; and
   c) Estimating the flash point using dynamic registers of pressure, temperature and spinner.

Temperature, pressure, and spinner logs from each well are used to construct a basic model of the well. This will answer such basic questions as: where exactly the fluid-entry points in the wells are, how much the flash point depth changes with wellhead pressure, what percentage of the total flow enters in each zone, whether these entries are all single phase liquid, if there are any possible downflows in the wells, and most importantly how these flows change with time or changes in operating pressure. Only after these questions are confidently answered can LaGeo be certain that the current choice of inhibition depth is correct and that inhibition is truly necessary or advisable in certain wells (Benoit, 2011).

Experience in different countries like Costa Rica (Moya and Nietzen, 2010; Moya and Yock, 2001), Philippines (Daco-ag and Bellas-Dacilo, 2010) and Italy (Pieri et al., 1989) has indicated that injection of an appropriate dose of inhibitor makes it possible to produce geothermal energy from wells with calcite scaling problems, with little or no deposition of calcite, and that it is less expensive than performing mechanical cleanouts.

Drawing on the experience mentioned above to establish an efficient inhibition system of calcite in producing wells, it is necessary to take into account the following criteria:

   a) Selection of inhibitor;
   b) Location of the inhibition chamber;
   c) Dose of inhibitor; and
   d) Controls during the inhibition process.

Thermal stability and the inhibition efficiency on calcite deposition are fundamental characteristics

that must be evaluated before determining the inhibitor to be used. Perfecto Lim (2002) evaluated the thermal stability and efficiency of eight commercial inhibitors. Physical changes like charring and precipitate formation were noted during the thermal stability test at 250 and 300°C. The effectiveness of the inhibitors after the heat treatment was evaluated using the National Association of Corrosion Engineers (NACE) standard test method TM-0374-90. This test provides a way of quantifying the inhibition efficiency of a particular inhibitor based on its ability to retain the calcium ions in solution in a supersaturated solution of CO_2 and with high levels of calcium ions. On the other hand, Corsi et al. (1985) developed a laboratory test for evaluating calcite formation, using an autoclave filled with solutions of 0.5 M NaCl and 4.5×10^{-3} M Ca^{2+}, and using pressure and temperature to simulate downhole conditions. The test was carried out on fourteen commercial inhibitors.

When the inhibitor has been selected, using thermal stability tests and an inhibition efficiency test, it is important to determine the injection depth of the inhibitor correctly. The injection setting depth is indicated by the flash point depth where calcite initiates deposition. Experience in the Philippines (Trazona and Nogara, 2001) showed that the flash point depth is calculated using wellbore simulation, where the temperature and pressure were matched with the pressure-temperature-spinner log data. In Iceland (Wangyal, 1992), the flash point was calculated with the HOLA program, using measured pressure and temperature profiles. Based on the results and experience, it was found preferable to place the inhibition chamber about 50 to100 m below the flash point depth to ensure that there is full mixing and sufficient residence time for an effective inhibition.

The inhibitor dose to be injected is sometimes based on experience in the use of the inhibitor in other countries; however, the best way to select the starting dose should be based on the results of the inhibitor efficiency test. According to experiences in Costa Rica (Sanchez et al., 2005), inhibition usually begins with an inhibitor overdose. Subsequently, it should be adjusted, if required, by the interpretation of the chemical parameters monitored during the inhibition. An exception to this rule would be during the use of phosphates inhibitors, where it is advisable to start at a low concentration in order to prevent precipitation of calcium phosphate (Hauksson, 1999).

During injection, both operational and chemical parameters should be monitored.

In the case of operational parameters, it is important to adequately monitor and record the pumping pressure of the inhibitor in order to detect possible problems in the capillary tubing, such as partial or total obstruction or broken tubing. It is equally important to monitor and record the flow parameters; calcite scaling can be indirectly recognized by declines in mass flow and steam flow. Therefore, an observed decline in mass flow is an indication of blockage due to calcite deposition restricting the flow of the well.

In the case of chemical parameters, it is convenient to monitor and interpret the relationship between Ca^{2+} and Cl^- using the Ca/Cl ratio because it indicates the effectiveness of the inhibition process. It is important, as a first step, to establish the baseline ratio; therefore, it is necessary to take samples before the injection of the inhibitor. When the base line is established:

  1) If the ratio increases, it means that the inhibition is working properly; and
  2) If the ratio decreases, a problem may exist with the inhibition system.

Monitoring, recording and interpreting the parameters described above are crucial to the success or failure of the calcite inhibition system.

It is important to mention that the results for the saturation index of minerals are dependent directly on the reference temperature used; the results of the saturation index presented in this report may differ from those reported by LaGeo, because the calculations were run at reference temperatures calculated by geothermometry and not at temperatures measured in the wells. The best results of the evaluation of the saturation index are obtained from the measured temperatures in the wells.

8. CONCLUSIONS

Calcite inhibition systems implemented in El Salvador have made it possible for wells with high calcite scaling potential to be operated in stable conditions, as shown in Appendix II; however, there have been problems related to the inhibitors used such as microbial growth on mixtures, the formation of residues during storage, interactions with check valves, interaction with capillary tubing and especially trapping problems in the inhibition chambers.

Using as reference the tests developed in the Philippines to evaluate the thermal stability and efficiency of the inhibitor using the (NACE) standard test method TM-0374-90, it is important to implement this evaluation in inhibitors currently used in LaGeo in order to establish the concentrations and temperature with better results for each inhibitor, and to establish the optimum working range, under current conditions, for both geothermal fields in El Salvador. On the other hand, during such an evaluation, it is important to include capillaries available in the market to estimate the possible interaction between the inhibitor and the capillary under different temperature conditions.

According to experiences in Costa Rica, it is important to run tests on the baseline ratio of Ca/Cl in the production wells that have high calcite scaling potential in both production fields in El Salvador. This will establish the working range of the Ca/Cl relationship; this ratio can then be used as an indicator on the effectiveness of the inhibition process. The control is based on the concentrations of calcium and chloride; for that reason, it is necessary to have good precision and accuracy in analytical methods to ensure the quality of the chemical results. Better chemical analyses can generate better interpretations of the inhibition process, and better conclusions for making decisions related to the inhibitor dose.

In addition to chemical control, it is necessary to establish operating control parameters associated with the dosage of the inhibitor in the well, such as the injection pressure, pump stroke, and injection rate; these parameters, in conjunction with monitoring the well production conditions, form the basis of an efficient inhibitor monitoring system.

In the case of wells with high calcite scaling potential, but without evidence of scaling formation, it is advisable to use scaling coupons located at the flash point of the wells before starting with a calcite inhibition system, because it might not be necessary and adds additional and unnecessary risk to the overall field operation.

Finally, but not less important, I am very grateful to all the 2011 UNU Fellows, for the laughs and ideas we shared during the entire period; it was a real pleasure meeting and interacting with each and every one of you.

REFERENCES

Angcoy, E., 2010: *Geochemical modelling of the high-temperature Mahanagdong geothermal field, Leyte, Philippines.* University of Iceland, MSc thesis, UNU-GTP, Iceland, report 1, 79 pp.

Arnórsson, S., 1989: Deposition of calcium carbonate minerals from geothermal waters-theoretical considerations. *Geothermics, 18,* 33-39.

Arnórsson, S., 1995: *Calcium carbonate deposition from geothermal fluids: causes, operational problems and their solution.* World Geothermal Congress 1995, IGA pre-congress course, Pisa, Italy, May 1995, 79-94.

Arnórsson, S., 1998: Practical uses of chemical geothermometers (in Icelandic). Eyjar í eldhafi, Gott mál Ltd., Reykjavík, 241-267.

Arnórsson, S. (ed.), 2000: *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation.* International Atomic Energy Agency, Vienna, 351 pp.

Bai Liping, 1991. *Chemical modelling programs for predicting calcite scaling, applied to low temperature waters in Iceland.* UNU-GTP, Iceland, report 3, 45 pp.

Benoit, D., 2011: *Comments on scale inhibition in El Salvador.* LaGeo, internal report (unpublished), 4pp.

Benoit, W.R., 1990: Development of a carbonate scale inhibition program at Dixie Valley, Nevada. *Geothermal Resources Council Transactions, 14-II,* 1567-1573.

Bjarnason, J.Ö., 2010: *WATCH, version 2.4.* Iceland GeoSurvey.

Corsi, R., Culivicchi, G., and Sabatelli, F., 1985: Laboratory and field testing of calcium carbonate scale inhibitors. *Geothermal Resources Council Transactions, 9-II,* 239-244.

Daco-ag, L.M., and Belas-Dacillo, K.A., 2010: Experiences with different calcite inhibitor in the Mahanagdong geothermal field. *Proceedings of the World Geothermal Congress 2010, Bali, Indonesia*, 8 pp.

Ellis, A.J., and Mahon, W.A.J., 1977: *Chemistry and geothermal systems.* Academic Press, NY, 392 pp.

Gudmundsson, B.T., and Arnórsson, S., 2002: Geochemical monitoring of the Krafla and Námafjall geothermal areas, N-Iceland. *Geothermics, 31,* 195-243.

Guerra, E., 2002: *Monitoring of calcium carbonates inhibition in production wells AH-33B and AH-35A.* LaGeo, internal report (in Spanish).

Guerra, E., 2008: *Saturation index of minerals in Berlín production wells.* LaGeo, internal report (in Spanish).

Guerra, E., 2010: *Inspection of calcite inhibition system in well TR-18.* LaGeo, internal report (in Spanish).

Hauksson, T., and Benjamínsson, J., 1999: *Krafla and Bjarnarflag. Production of wells and chemical composition of fluids from wells and power plant.* National Power Company, report (in Icelandic), 60 pp.

Molina A., G.G., 1995: Rehabilitation of geothermal wells with scaling problems. Report 9 in: *Geothermal Training in Iceland 1995.* UNU-GTP, Iceland, 207-240.

Moya, P., and Nietzen, F., 2010: Performance of calcium carbonate inhibition and neutralization systems for production wells at Miravalles geothermal field. *Proceedings of the World Geothermal Congress 2010, Bali, Indonesia*, 10 pp.

Moya, P., Nietzen, F., and Yock, A., 2005: Benefits from the utilization of a calcium carbonate inhibition system for production wells at the Miravalles geothermal field. *Proceedings of the World Geothermal Congress 2005, Antalya, Turkey*, 6 pp.

Moya, P., and Yock, A., 2001: Calcium carbonate inhibition system for production wells at the Miravalles geothermal field. *Proceedings of the 26th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA*, 10 pp.

Jacobo, P., 2003: Gas chemistry of the Ahuachapán and Berlín geothermal fields, El Salvador. Report 12 in: *Geothermal Training in Iceland 2003.* UNU-GTP, Iceland, 275-304.

Jacobo, P., 2008: *Behaviour of calcite scaling potential in well AH-35C during 2007-2008.* LaGeo, internal report (in Spanish), 10 pp.

Jacobo, P., 2011: *Report on the scaling potential in fluids from production wells in Ahuachapán geothermal field.* LaGeo, internal report (in Spanish), 41 pp.

Kuwada, J.T., 1982: Field demonstration of the EFP system for carbonate scale control. *Geothermal Resources Council Bulletin, 11,* 3-9.

Montalvo, F., 1994: *Geochemical evolution of Ahuachapán geothermal field, El Salvador, C.A.* Report 9 in: *Geothermal Training in Iceland 1994.* UNU-GTP, Iceland, 211-236.

Montalvo, F., 2010: Geothermal field under exploitation in El Salvador. Actual status and development of geothermal resources in Central America (in Spanish). *DGCD/MAE, Pisa, Italy*, 50-79.

Perfecto, L., 2002: Thermal stability and efficiency of calcite scaling inhibitors. *Proceedings of the 23rd Annual PNOC-EDC Geothermal Conference, Makati City, Philippines,* 99-105.

Pieri, S., Sabatelli, F., and Tarquini, B., 1989: Field testing results of downhole scale inhibitors injection. *Geothermics, 18,* 249-257.

Remoroza, A., 2010: *Calcite mineral scaling potentials of high-temperature geothermal wells.* University of Iceland, School of Engineering and Natural Sciences, Reykjavik, MSc thesis, 99 pp.

Renderos, R., 2002: Chemical characterization of the thermal fluid discharge from well production tests in Berlín geothermal field, El Salvador. Report 12 in: *Geothermal Training in Iceland 2002.* UNU-GTP, Iceland, 205-231.

Renderos, R., 2009: *Carbon dioxide fixation by calcite and diffusive degassing in the southern region of the Berlín geothermal system, El Salvador.* University of Iceland, MSc thesis, UNU-GTP, Iceland, report 4, 41 pp.

Trazona, R., and Nogara, B., 2001: Operational dynamics in well SP-4D with a calcite inhibition, Mindanao geothermal production field, Philippines. *Proceedings of the 26th Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, CA,* 5 pp.

Sánchez, E., Vallejos, O., Rodriguez, A., and Guido, H., 2005: Chemical treatments of fluids on the Miravalles geothermal field: Investigation, application and its relationship with reservoir management. *Proceedings of the World Geothermal Congress 2005, Antalya, Turkey*, 7 pp.

Wangyal, P., 1992: *Calcite deposition related to temperature and boiling in some Icelandic geothermal wells.* UNU-GTP, Iceland, report 11, 33 pp.

APPENDIX I: Analytical methods accredited under the international standard ISO / IEC 17025:2005

Element	Method	Working range	Matrix	LOC (ppm)	Uncertainty (ppm)
Sodium	Atomic absorption (flame)	15-5,000 ppm	Geothermal water Surface water	12.0	± 31.4
Potassium	Atomic absorption (flame)	50-1,000 ppm	Geothermal water Surface water	11.0	± 5.45
Calcium	Atomic absorption (flame)	5.0-600 ppm	Geothermal water Surface water	0.77	± 1.73
Magnesium	Atomic absorption (flame)	0.0113-0.5 ppm	Geothermal water	0.0113	± 0.0022
Lithium	Atomic absorption (flame)	0.5-25 ppm	Geothermal water	0.20	± 0.152
Silica	Atomic absorption (flame)	50-600 ppm	Geothermal water Surface water	32.0	± 13.03
Boron	Atomic absorption (flame)	15-400 ppm	Geothermal water	15	± 2.35
Arsenic	Atomic absorption (flame)	1.12-20 ppm	Geothermal water	1.12	± 0.45
Chloride	Potentiometric	15-16,000	Geothermal water	15.0	± 90
Bicarbonates	Potentiometric	≤ 3.08	Geothermal water	3.08	± 0.765
Sulphates	Colorimetric	4.33 - 125.00	Geothermal water	4.33	± 2.35
Monomeric silica	Colorimetric	4.90 - 214.00	Geothermal water	4.90	±1.693
pH	Potentiometric	1.0-14.0	Geothermal water	-----	± 0.018
Elect. cond.	Potentiometric	2,000-125,000	Geothermal water	2000 µS/cm	± 1.42%
Elect. cond.	Potentiometric	0.05-100	Vapour	0.05 µS/cm	± 1.42%
Sodium	Atomic absorption (flame)	0.1000-0.5000	Vapour	0.1000	± 0.008
Iron	Atomic absorption (flame)	0.1000-0.5000	Vapour	0.1000	± 0.011
Silica	Colorimetric	0.011-4.28	Vapour	0.011	± 0.027
Chloride	Ion chromatography	0.073-50.0	Vapour	0.073	± 0.93%
Sulfates	Ion chromatography	0.076-50.0	Vapour	0.076	± 0.81%

APPENDIX II: Productive characteristics of wells with calcite inhibition system
in El Salvador during the period 2010-2011

WELL AH-33B

WELL AH-35A

WELL AH-35B

WELL AH-35C

WELL TR-4B

WELL TR-4C

WELL TR-18