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Amorphous Iron Silicate Scales in Surface Pipelines: Characterization and Geochemical Constraints on Formation Conditions in the Miravalles Geothermal Field, Costa Rica

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ABSTRACT

Scales formed in surface pipelines as a result of mixing between neutral and acid fluids at the Miravalles Geothermal Field have been characterized by chemical analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). They consist of a chemically homogeneous amorphous iron silicate with a stoichiometry similar to the mineral minnesotaite ($(Fe^{++},Mg)_3Si_4O_{10}(OH)_2$). With the aid of computer programs for geochemical aqueous speciation (WATCH and EQ3NR) and for reaction path modelling of aqueous geochemical systems (EQ6), the geochemical constraints of the formation of the scales were modelled. The mixing experiments simulated with EQ6 between neutral and acid fluids, determined a range of log K for the dissolution reaction of the scale phase between 11 and 13 units. Above this range, the probabilities of over saturation of this compound are very high. On the basis of a series of mixing scenarios, an acidification of the neutral fluids to a pH value of 6.0 is suggested in order to prevent the formation of these scales.

1. INTRODUCTION

The Miravalles Geothermal Field (Figure 1) is located in the north-western part of Costa Rica. Deep drilling started in 1979, when a high-temperature reservoir was discovered. Subsequent drilling stages completed the steam necessary to feed three flash plants commissioned in 1994, 1998 and 2000, and one binary plant in 2004, totaling an installed capacity of 163 MW. Three wellhead units of 5 MWe each have produced for different periods, and one of them is still producing and belongs to ICE (Instituto Costarricense de Electricidad).

During the year 2008, the geothermal energy installed capacity was 7.0% of the total installed capacity of Costa Rica, and the energy produced at Miravalles during the same year represented 12.1% of the total energy generated in the country (Mainieri, 2009).

At Miravalles, 53 wells have been drilled, 31 of them are or could be used for producing steam and 13 for brine reinjection. Among the production wells, 5 produce acid fluids and 4 of them are now producing by means of deep neutralization of such fluids. The total production of the wells in Miravalles is about 300 kg/s of steam, and about 1350 kg/s of brine (about 800 kg/s are used for a binary plant) are injected back to the reservoir.

1.1 Chemical Characteristics of the Different Types of Fluids

At Miravalles there are four different geothermal aquifers. A shallow steam-dominated aquifer is located in the north-eastern part of the field (Vallejos, 1996). The chemical characteristics of the other aquifers will be described below (Figure 2) (Table 1).

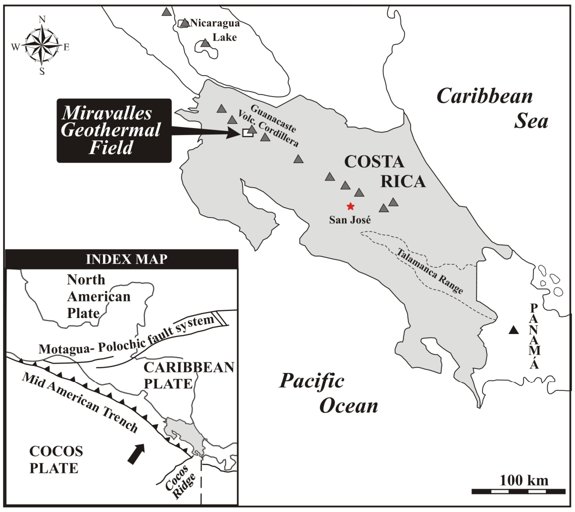

Figure 1: Location map (modified from Vega et al. (2005)

1.1.1 Neutral Sodium-Chloride Aquifer (Na-Cl)

The neutral sodium-chloride aquifer is located at the northern and central sectors of the field. It is the most important in terms of production. The fluids from this aquifer have a sodium-chloride composition. After flashing at 98°C and cooling to ambient temperature, pH values are from 7.6 to 8.0, chloride content from 4,100 to 5,000 ppm, silica from 580 to 620 ppm, calcium from 70 to 130 ppm, bicarbonate from 15 to 70 ppm, and TDS (total dissolved solids) between 8,000 and 10,000 ppm. Calcium carbonate (CaCO3) scaling has been observed in production wells of this sector of the field. These scales could result in complete obstruction of the wells in the periods from weeks to several months if an inhibition system were not employed.

1.1.2 Neutral Sodium-Chloride-Bicarbonate Aquifer (Na-Cl-HCO_3)

The neutral sodium-chloride-bicarbonate aquifer is located at the southeast sector of the field. The fluids have a sodium-chloride-bicarbonate composition. After flashing at 98°C and cooling to ambient temperature, pH values are between 7.4 and 8.2, chloride content from 4,000 to 4,300 ppm, bicarbonate from 160 to 215 ppm, silica from 550 to 560 ppm, calcium from 60 to 70 ppm, and TDS between 8,000 and 8,400 ppm. The $CaCO_3$ scaling tendency of these wells is severe. Production from these wells without inhibition systems will clog the casing in matter of few days.

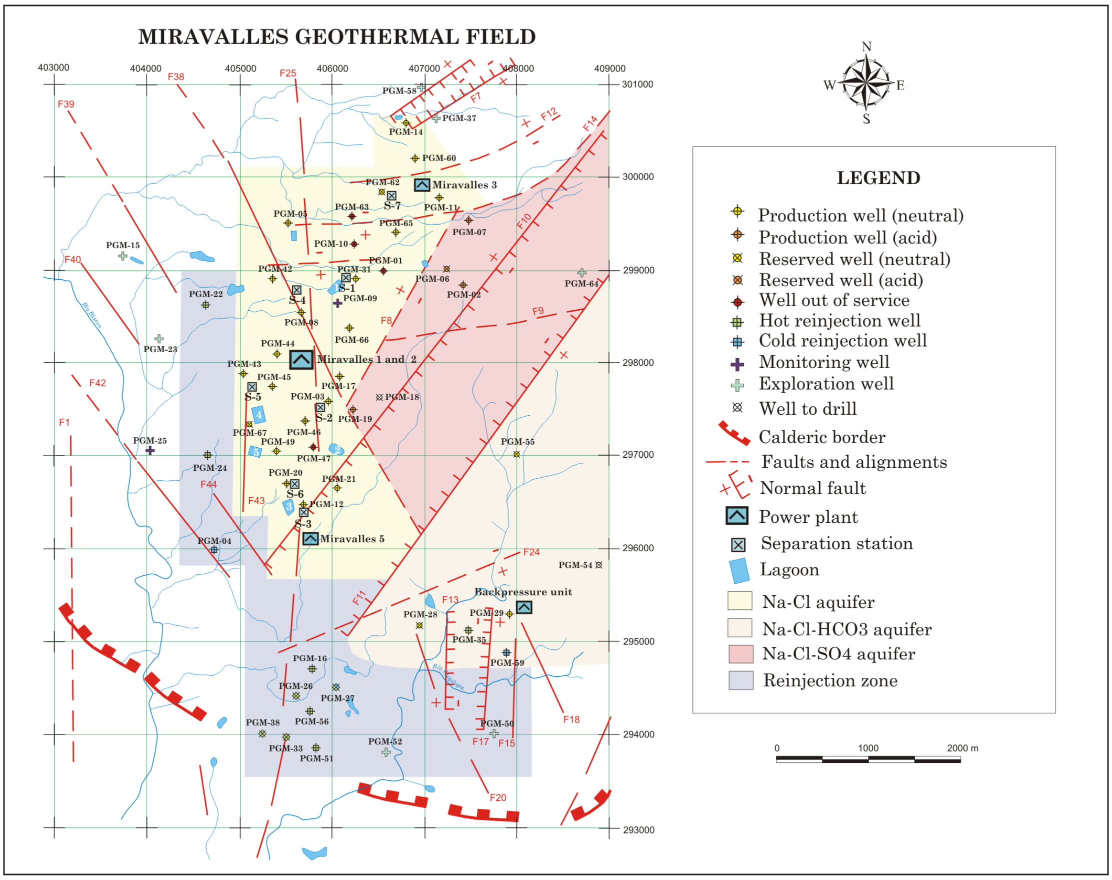

Figure 2: Miravalles Geothermal Field

1.1.3 Acid Sodium-Chloride-Sulfate Aquifer (Na-Cl-SO_4)

The acid sodium-chloride-sulfate aquifer is located at the north-eastern sector at Miravalles. The fluids from this aquifer have a sodium-chloride-sulfate composition. After flashing at 98°C and cooling to ambient temperature, pH values are between 2.4 and 3.2, chloride content from 3,900 to 4,300 ppm, sulfate from 170 to 300 ppm, silica from 550 to 650 ppm, calcium from 35 to 50 ppm, bicarbonate from 0 to 2 ppm, and TDS between 7,240 and 7,395 ppm. Without an appropriate neutralization system, the corrosive character of these fluids would rapidly cause catastrophic and irreparable damages to the well casings and surface equipment.

In summary, it can be said that the commercial exploitation of fluids at Miravalles would be impossible without the application of deep chemical treatments in the wells. However, although calcite scaling and corrosion problems can be prevented in individual wells, scaling is still a problem were neutralized acid fluids come into contact with fluids from the neutral wells. This investigation is intended to study the composition of these scales, explain their formation mechanisms, and to propose a solution to the problem.

1.3 Objectives of This Study and Applications

The formation of scales on equipment surfaces exposed to geothermal fluids can have serious economic consequences, arising from energy losses, increased cost of cleaning and maintenance, loss of production, or even abandoning a production well. In recent years, considerable effort has been made worldwide to characterize geothermal scale deposits.

The objectives of this work are:

- To chemically characterize scales formed as a result of the mixing of neutral and acid fluids, mainly between the wells PGM-66 and PGM-17, on one hand and PGM-19 on the other.
- To understand the geochemical constraints and the formation mechanisms of the scales and to model those with the aid of geochemical speciation and reaction path programs.
- To suggest measures for mitigating the problem.

The results of this work are an improved understanding of acid geothermal fluids in order to mitigate the problems that arise as a result of their use. This is of considerable importance since at Miravalles 4 acid wells (PGM-02, PGM-06, PGM-07 and PGM-19) produce the equivalent of 30 MWe which is a significant proportion of the total production at Miravalles. Also, in the near future, the exploitation of the acid aquifer could be extended in order to satisfy steam requirements, mainly at the northern zone for the Miravalles 3 power station.

Table 1. Chemical Characteristics of the Deep Aquifers at Miravalles.

Aquifer	*pH*	*Cl (ppm)*	*HCO3 (ppm)*	*SO4 (ppm)*	*Ca (ppm)*	*SiO2 (ppm)*	*TDS (ppm)*
Na-Cl	7.6 – 8.0	4,100 – 5,000	15 - 70	50 - 60	70 - 130	580 - 620	8,000 – 10,000
Na-Cl-HCO3	7.4 – 8.2	4,000 – 4,300	160 - 215	66 - 80	60 - 70	550 - 560	8,000 – 8,400
Na-Cl-SO4	2.4 – 3.2	3,900 – 4,300	0 - 2	170 - 300	35 - 50	550 - 650	7,240 – 7,395

2. UTILIZATION OF ACID FLUIDS AND THEIR SECONDARY EFFECTS AT MIRAVALLES

The first experiments on neutralizing acids fluids from wells at Miravalles were carried out in 1996. The neutralization process consists of injection of a solution of sodium hydroxide (NaOH) to a depth below the casing shoe with the aid of a pump and capillary tubing. This neutralizes the acids, thus raises the pH. Since February 2000 and October 2001, PGM-19 and PGM-07 wells have been, respectively, neutralized successfully. These wells produce a steam equivalent to approximately 17 MWe to the power plants. Logistical and scientific aspects of the commercial integration of acid wells have been discussed by Sánchez (1997), Castro and Sánchez (1998), Sánchez *et al*. (2000), Moya and Sánchez (2002) and Sánchez *et al*. (2005). Also, during June 2006, two more acid wells, PGM-02 and PGM-06, were integrated to the systems. Those wells produce 3.5 and 10 MWe respectively. Thus, the power that can be obtained at Miravalles from acids wells accounts to around 30 MWe.

The first attempts to neutralize acid fluids resulted in scaling problems. Soon after the implementation of neutralization systems in wells PGM-19 and PGM-07, it was observed that amorphous siliceous scales were formed in matter of months, as a result of the neutralization process. Also, similar scales formed inside separator, water tanks and pipelines located at the site of each well. The scaling problems were so severe that mechanical cleanings had to be performed every 6 months at PGM-07. Mechanical cleanings were very expensive, risky and time consuming operations that result in long periods in which the well could not produce. Furthermore, after each cleaning operation, PGM-07 could not be returned to stable production conditions, partly because of cold water injection as a part of the cleaning process.

Corrosion and scaling studies performed at PGM-07 from October 2003 to March 2004 in cooperation with NEDO (New Energy and Industrial Technology Development Organization) of Japan concluded that in order to minimize corrosion and scaling, a pH value of 5.0 inside the wells must be maintained (Rodríguez and Sánchez, 2004; NEDO, 2004). This pH value is lower than the one of 6.0 that was used before. pH measurements in samples collected at different separation pressures, demonstrated that a pH of 5.0 would correspond to a pH between 5.8 and 6.0 if the sample was boiled at 98°C and cooled to ambient temperature for the case of PGM-07 fluids, and to a pH between 5.5 and 5.7 for the case of PGM-19 fluids. With these small adjustments in neutralization conditions, both corrosion and scaling were minimized at depth and inside surface equipment located at the site of acid wells.

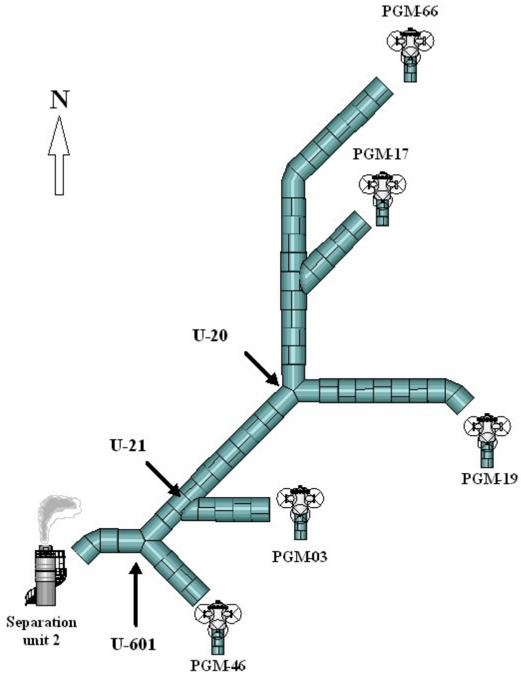

Figure 3: Location where scaling occurred

Before the optimization of neutralization processes, two-phase fluids from wells PGM-07 and PGM-19 were conducted to a separator located at each site. From there, the steam was sent to the power station and the brine to the cold reinjection system. Later, when the scaling and corrosion problems seemed solved, both wells were integrated directly to the separation units 7 and 2, respectively, during the end of July 2004. During an inspection for maintenance performed on October 2004, it was observed that at separation unit 7 the surface equipment like separators, water tanks and pipelines were completely clean. On the other hand, at separation unit 2 (“Satélite 2”), the presence of thick, black and vitreous scales were observed inside the equipments. Furthermore, it was observed that the first occurrence of the scales was at point U-20, where fluids from wells PGM-66, PGM-17 (both neutral), and PGM-19 were mixed (Figure 3).

Although at separation unit 7 there were no scaling problems, soon it was realized that a geochemical incompatibility between the neutral and acid fluids existed. The immediate solution to this problem was to avoid the mixing between those fluids and to resume separation of PGM-19 fluids at the site and send the brine trough the cold reinjection system. The consequences of that change were that when the brine separated at PGM-19 is discharged at atmospheric pressure, there is an over saturation of amorphous silica that creates thick deposits at the canal and surface pipelines.

3. AMORPHOUS IRON SILICATES, FORMATION AND OCCURRENCE

Many different types of precipitates from geothermal fluids have been documented and characterized. Iron-rich silicate scales are deposited from hyper saline brines produced at the Salton Sea Geothermal Field, California. The scales appear as brown-black, vitreous solid resembling obsidian (Gallup, 1989) and have been observed to deposit in brine-handling equipment and wells at rates ranging from ~0.5 cm/yr in production wells (>200°C) to over 50 cm/yr in injection pipes and wells (150 – 175°C) (Gallup, 1993). The occurrence of similar scales has been also documented at Cerro Prieto, Mexico (Mercado *et al*., 1989), Milos, Greece (Karabelas *et al*., 1989), Tiwi, Philippines (Gallup, 1993) and Reykjanes, Iceland (Kristmannsdóttir, 1984; Hardardóttir, 2004; Hardardóttir, 2005 and Hardardóttir *et al*., 2005).

In previous studies, iron-rich scales deposited from Salton Sea geothermal brine at high temperature were shown to consist of what is believed to be a compound exhibiting an empirical formula near $Fe(OH)_3{\cdot}SiO_2{\cdot}xH_2O$ or $Fe_2O_3{\cdot}2SiO_2{\cdot}xH_2O$ (Gallup, 1989). Spectroscopy (Mössbauer and IR) and X-ray diffraction studies undertaken at Salton Sea by Gallup and Reiff (1991) to improve the understanding of the nature of these deposits, detected mainly ferric (Fe^{3+}) but also ferrous (Fe^{2+}) iron, believed to be present as hydrous silicates resembling the mineral hisingerite and exhibiting a variable composition. According to those authors, other iron minerals were also detected and the bulk of the mineral phases present were microcrystalline, poorly-crystalline or glassy. Iron deposited in scales appears to derive primarily from brine, but is also found to be present as poorly-crystalline steel corrosion products (Gallup and Reiff, 1991). These authors concluded that ferric iron in the scale was deposited as a result of oxidation of ferrous iron in the brine by water.

Also Manceau *et al.* (1995), using X-ray diffraction and spectroscopic techniques, confirmed that high-temperature (250°C) scale precipitated from non-oxidized geothermal brines at Salton Sea contains polymerized ferric iron and silica and identified the mineralogical nature of this precipitate as hisingerite. Hisingerite is a poorly-crystallized, non-stoichiometric nontronite. Furthermore, they identified a low-temperature (100°C) scale precipitated form the same brines as a mixture of A-opal and micro- or nano-crystalline hydrous ferrous silicate structurally related to minnesotaite and/or greenalite. However, these components are difficult to identify by XRD alone.

High scaling rates of ferric silicate at Salton Sea severely plagued the operation of steam-gathering facilities. More traditional methods to control that deposition have been unsuccessful, such as the injection of a wide variety of commercially available scale inhibitors, some of which them have actually aggravated the scaling problem (Gallup, 1993). The process that has been used to prevent the scale deposition is brine acidification. In this process, a small amount of hydrochloric acid (HCl) is injected into the brine near a wellhead separator. The lowering of pH by 0.5 to 0.3 units has successfully inhibited ferric silicate formation (Hoyer et al., 1991). According to these authors, acidification of the brine is believed to: 1) increase the solubility of ferric ions and thereby decrease the driving force for precipitation either as ferric oxyhydroxide and/or 2) retard the kinetics of iron silicate polymerization reactions. The fact that the scales become enriched in a hydrous ferrous (Fe2+) silicate component as the brine temperature is decreased, suggested that ferrous silicate is somewhat more soluble than the corresponding ferric (Fe3+) silicate phase (Gallup and Reiff, 1991). Based on that solubility behaviour, Gallup (1993) saw the possibility of using chemical reducing agents capable of reducing trivalent iron to divalent iron as scale inhibitors. The results of a series of pilot unit test conducted at Salton Sea, provided conclusive evidence that addition of an amount of sodium formate (NaHCOO) approximately 2.8 times that required to reduced the ferric ion contained in untreated brine is effective for converting up to 99% to the more benign ferrous state (Gallup, 1993). Moreover, the reduction of ferric ions in geothermal brine by reducing agents is expected to have a mitigating effect on corrosion of mild steel equipment since ferric ions are well-know corrosive agents toward many metallic materials of construction (Gallup, 1993).

A major benefit of including the reducing agent in the brine pH modification process was corrosion mitigation. The addition of sodium formate with hydrochloric acid significantly reduced corrosion compared with acid injection alone. For those tests, sufficient acid was added to reduce the pH by 0.5 units and twice the stoichiometric amount of sodium formate necessary to reduce the ferric ions in the brine to the ferrous state were injected separately into the brine (Gallup, 1993).

The formation of iron silicates in conjunction with other minerals also seems to occur when fluids with different chemistry are mixed. Since those fluids in many cases are geochemically incompatible, some minerals reach over saturation conditions and tend to precipitate. For example, iron silicates in conjunction with iron oxides have been found on bacterial surfaces collected near hydrothermal vents in the north-eastern Pacific Ocean, where bacterial surfaces provide nucleation sites for poorly ordered oxides and silicates (Fortin et al., 1998). In that case, as high-temperature, reducing, and acidic solutions mix with sea water, various minerals precipitate around the vents. According to Todaka et al. (2003), at Onikobe Geothermal Field, in Japan, two types of fluids are encountered in the reservoir, one is neutral and the other acidic (pH = 3). The same authors have modeled mixing scenarios between those fluids and concluded that manganese-rich smectite precipitated due to mixing of the two fluids, forming an impermeable barrier that would explain why those fluids are separated in the geothermal reservoir.

4. SCALE CHARACTERIZATION

4.1 Macroscopic Description of the Scale

The samples collected for inspections are from sites U-20, U-21 and U-601 in the pipeline to separation unit 2 (Figure 3). U-20 corresponds to the point where neutral fluids from wells PGM-66 and PGM-17 encounter the acid fluids from PGM-19. At U-21 the fluids from PGM-03 are added to the system. Finally, at U-601, PGM-46 fluids are mixed with the ones that come from all the wells mentioned. The scales appear as a black, relatively hard solid with vitreous luster intercalated with softer light brown layers. Frequently, a transitional change exists between these layers. The thickness of a single layer is from 1 to 5 mm, and the intercalations as a whole can reach thicknesses up to 1 cm. They develop both parallel laminations and asymmetrical ripples (Figure 4). The different layers are generally difficult to separate mechanically from each other. Generally, it was observed that at U-20, the black material was more common than at U-33.

4.2 Chemical Analysis

Scale samples collected were taken during the cleaning operations of pipelines performed on October 2004. Chemical analyses performed at the ICE laboratories at Miravalles of both black and light brown layers of the scales are shown in Table 2. Those analyses were carried out on a wet basis. It can be seen that silicon and iron are the main components of the scales.

4.3 X-Ray Diffraction (XRD) Analysis

Scale samples from both sites U-20 and U-601 were analysed with X-ray diffraction (XRD) technique at ÍSOR (Iceland GeoSurvey) laboratories. Dark and light brown coloured layers were separated with the aid of a scalp. The solids were milled combined with acetone to a fine powder in an agate mortar. Then the mixture was dried at ambient temperature and the powder was put into an acrylic plate and the sample was scanned in a Bruker AXS D8 Focus model diffractometer equipped with a Bragg-Brendano goniometer, and a Cu anode lamp with a NaI crystal type scintillation counter. All samples were run in a step scan mode at 0.04°/1.0 s from 4 to 64° 2θ. The diffractograms of the scales exhibit poorly defined patterns that suggest the presence of a poorly crystallized material (Figure 5). There are a few broad humps in the patterns and this material is clearly different from amorphous silica. A typical pattern of amorphous silica is presented for comparison, but the presence of this phase in the scales analyzed is unlikely. In general terms, the black layers of the scales show a more even pattern compared with the light brown layers. Weak reflections that occur at ~7°, ~20°, ~35° and at ~60° 2θ are common in the light brown layers and do not appear in the black ones.

4.4 SEM Analysis of Scale Morphology and Composition

Scanning Electron Microscopy (SEM) analyses were carried out on scale samples collected at sites U-20 and U-601. In order to study their morphology and chemical composition, small pieces of the scales were carefully embedded in epoxy resin, polished and then coated with gold before they were placed in the SEM. The analyses were performed at the Technology Institute of Iceland (IceTec). The apparatus used was a Leo Supra 25 scanning electron microscope, equipped with a Gemini field emission column and an energy dispersive X-ray spectrometer (EDS) for performing geochemical analyses. The SEM was operated at 15.00 kV accelerating voltage, 8.5 mm working distance and with a 60 μm aperture size. Prior and subsequent to analysis, cobalt (Co) standard was run in order to adjust the dead time during analysis to approximately 25% and to correct for instrument drift.

The SEM micrographs were taken with the backscatter electron detector which detects contrasts between areas of different chemical compositions in the sample. The uniform gray color suggests that the chemical composition of the scales is homogeneous (Figure 6). Micrograph A, shows that parallel laminations of scales result from a change in texture, between porous and compact layers of the material. The morphology of the asymmetrical ripples can be observed in micrograph B. Areas with a linear array consisting of more dense material cross those ripples by their crest. Micrograph C corresponds to a closer view of the porous layers. They seem to be formed by aggregates of particles that develop a network of chains with branches. Micrograph D shows that in some parts, those particles become more and more compact until their identity is lost. The network structure can be appreciated in micrograph E. The size of the particles in the scales is around 1 μm. In micrograph F can be seen that each particle tend to bond with another one by means of fibrous structures.

The formation mechanism of the scales appears to occur in two stages. First, silicate particle growing occurs and seems to continue until each particle reaches a diameter of about 1 μm, which corresponds to the size of the particles of a sol. Second, from this point, particles bond each other to develop chains structures which grow forming branches. Later, those structures compact in a way that they develop a uniform pattern and none of this particles or chains can be observed. From here, the process seems to be interrupted and the growing starts again.

The results of spot analyses performed by an X-ray energy dispersive spectrometer (EDS) are presented in Table 3. The sampling points were selected as representative as possible of the different types of textures described previously. The composition of each element is reported as its respective oxide. This is done conventionally, even when it is know that probably the oxides are not the most common form in which the element is present. The reason for this is that the stoichiometry calculations were performed on oxide basis.

It is observed that scales consist mainly of silicon, oxygen, iron and manganese. Other elements like aluminum and magnesium are present but are not very important. Calcium, sodium and potassium appear only in small quantities. There were not significant differences in chemical composition between the porous and compact layers.

In conclusion, the laminations present on the scales seem to be due to changes in the texture rather than changes in the chemical composition. Differences in texture are probably due to variations in the growth rate of silicate which could be attributed to pH changes over time. It is well known that pH plays an important role in the kinetics of silicates deposition.

4.5 Stoichiometry of the Compound Present In Scales

Based on weight percentages of the constituent oxides given by EDS spot analyses, the calculation of a chemical empirical formula was performed. The details of this procedure and its theoretical background can be consulted in Deer *et al.* (1992). The calculations were done with the following considerations:

- Because of the reducing conditions were scales were formed, most of the iron, if not all, must be in the form of ferrous ion (Fe^{+2}).

- Based on chemical and EDS spot analyses, the main compounds of scales are silicon, oxygen and iron.

- Because amorphous minerals do not have a crystalline structure, they easily can accept other anions and cations that not necessary take part in the majority of the mass. That, in fact, could explain the presence of other elements in minor quantities.

- The macroscopic description of scales formed at Miravalles agrees with the ones belonging to amorphous iron silicates reported in other places around the world.

Table 2. Chemical Characteristics of the Deep Aquifers at Miravalles.

Site	% SiO_2 (±0.6)	% Fe_2O_3	% CaO (±0.02)	% MgO (±0.1)	% Na_2O (±0.04)	% K_2O (±0.01)
U-601 (l-b)	52.1	13.7 ± 0.3	0.81	3.9	2.66	0.28
U-601 (b)	49.6	24.6 ± 0.5	0.85	4.1	2.10	0.35
U-21 (l-b)	49.0	16.6 ± 0.3	0.85	4.7	2.68	0.26
U-21 (b)	46.1	25.3 ± 0.5	0.45 ± 0.01	2.8	1.94	0.25
U-20 (l-b)	47.3	27.7 ± 0.5	0.70	2.4	2.13	0.28

b: black layer, l-b: light brown layer

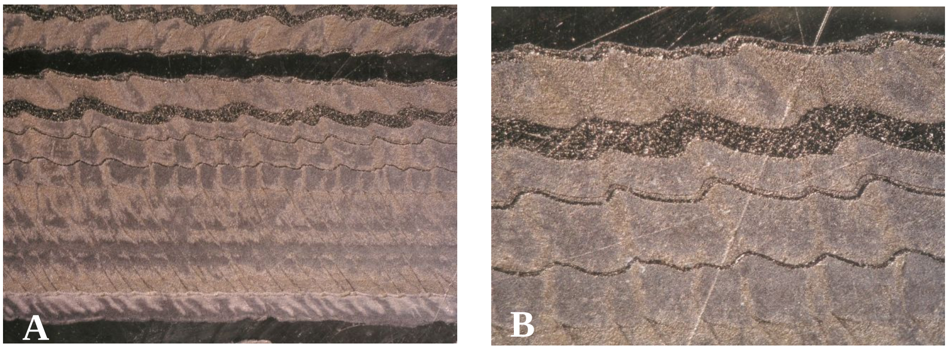

Figure 4: Photographs showing the structures of the scales (12.5 to 25x)

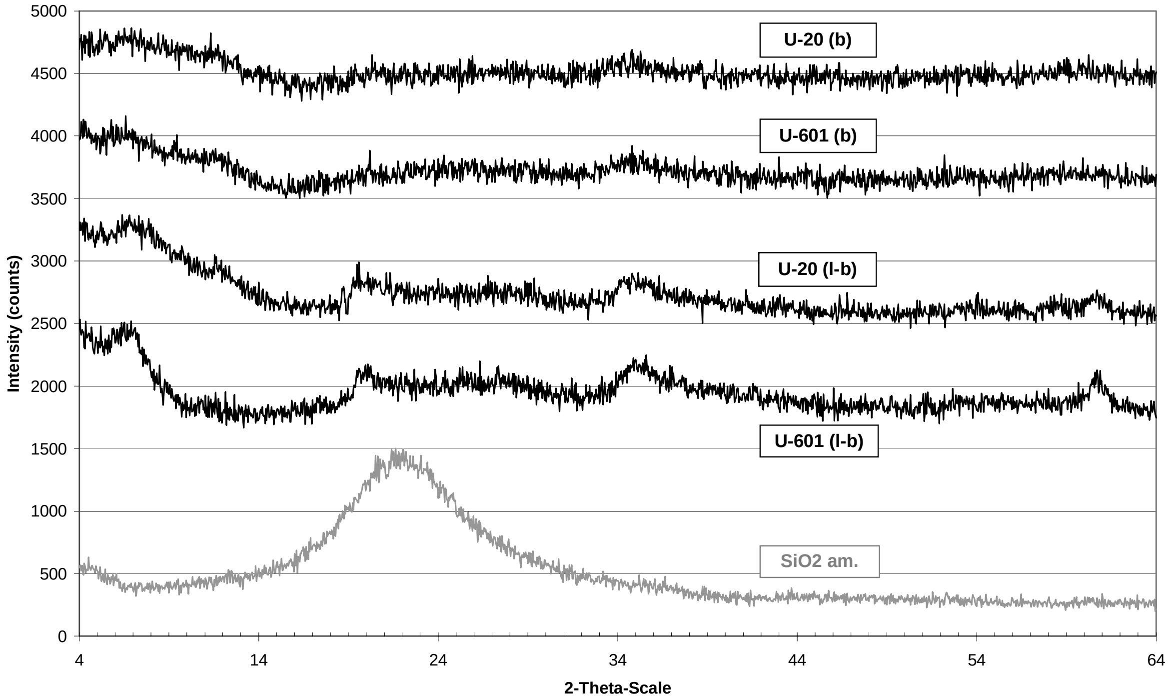

Figure 5: XRD patterns of scales collected at sites U-20 and U-601 (l-b: light brown, b: black; patterns offset by 1000 units)

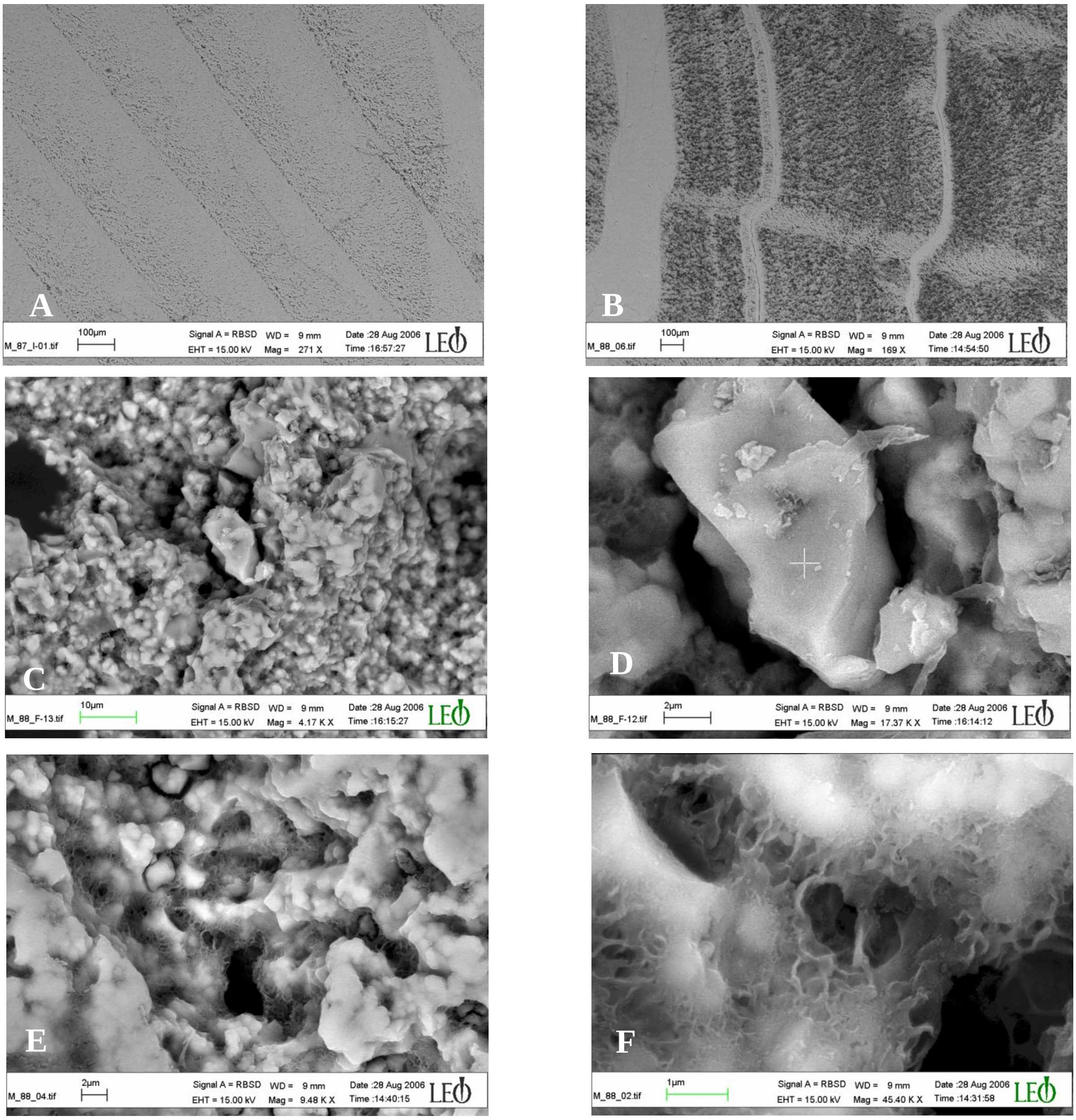

Figure 6: SEM micrographs

- Those facts point out that the phase under these considerations could be an amorphous ferrous silicate.

- The calculations were based on 11 oxygen atoms or equivalents per formula unit.

Atomic ratios between the main cations in scales (iron, manganese and magnesium) and silicon are presented in Figure 7. The results of some authors which have reported the occurrence of iron silicate scales around the world are also presented for comparison. It can be observed that the stoichiometry of scales at Miravalles is intermediate between nontronite ($Na_{0.3}Fe^{3+}{}_2(SiAl)_4O_{10}(OH)_2 \cdot n(H_2O)$) and minnesotaite ($(Fe^{2+},Mg)_3Si_4O_{10}(OH)_2$). Some iron oxides were plotted on the y-axis in order to represent different oxidation states of iron. Since the scales plot in the area defined by the lines that connect amorphous silica with FeO and magnetite, it is very likely that the iron present in the scales is in the form of ferrous (Fe^{2+}) ion, as it was supposed. All this led to the conclusion that the compound present in the scales at Miravalles is an amorphous ferrous silicate which has a stoichiometry similar to minnesotaite. Magnesium can substitute part of the iron in its formula. Actually, minnesotaite is very similar to the iron end member of talc ($Mg_3Si_4O_{10}(OH)_2$) which is sometimes referred to ferrous talc (Deer et al., 1992).

4.6 Thermodynamic Considerations

Having defined the stoichiometry of the scale phase, an expression for its dissolution can be expressed as:

$$\begin{aligned} &6H^{+}+Fe_3Si_4O_{10}(OH)_2 \Leftrightarrow \\ &3Fe^{2+}+4SiO_2+4H_2O \end{aligned} \qquad (1)$$

The equilibrium constant of reaction (1) can be written as:

$$K = \frac{(a_{Fe^{2+}})^3 \cdot (a_{SiO_2})^4 \cdot (a_{H_2O})^4}{(a_{H^+})^6 \cdot (a_{Fe_3Si_4O_{10}(OH)_2})} \qquad (2)$$

Assuming that the activities of pure phases are equal to 1, then (2) becomes:

$$K = \frac{(a_{Fe^{2+}})^3 \cdot (a_{SiO_2})^4}{(a_{H^+})^6} \qquad (3)$$

It can be deduced from equation (3) that the precipitation of scales is a reaction that strongly depends on the activity of H^+ or, in other words, the pH. Equation (3) will be used to evaluate the conditions under which the scales form.

5. GEOCHEMICAL MODELLING

5.1 Wells Involved in the Present Study

The wells involved in this study are those which contribute to the formation of the scales in the surface pipelines where two-phase fluids are transported to the separation station 2 (Figure 3). The scales formed during an approximately 3 month period, between July and October 2004. During this period, a mixture of fluids from PGM-66 and PGM-17 was combined with PGM-19 acid fluids at U-20. At that point, the scales started to deposit. The presence of the scales was also observed at U-21, where the fluids from PGM-03 combined with the mixture downstream from the addition of PGM-19 fluids. At the separation station 2, scales deposition occurred inside separators and water tanks. During that time, well PGM-46 was integrated to the separation station 2. At U-601, where PGM-46 fluids mixed with the ones coming from the addition of PGM-03 fluids, scales were also deposited.

For the calculation of deep fluid compositions and mineral saturation states, liquid phase samples collected between 2003 and 2005 at atmospheric pressure and gas samples collected at a different pressure from wells PGM-03, PGM-17, PGM-66 and PGM-19 were selected in order to be as representative as possible of the normal operating condition. Fluids from wells PGM-03, PGM-17 and PGM-66 are very similar with respect to their chemical composition. Although iron was not analyzed in samples from wells PGM-03, PGM-17 and PGM-66, it is usually in low concentrations (≤ 0.05 ppm) in neutral fluids. The neutralization system at PGM-19 was not operating on September 18th, 2005, while samples were collected. On the other hand, samples from October 13th, 2005, were collected during normal operating conditions. It can be seen that there are big differences with respect to iron concentrations and pH on both samples.

Samples from PGM-46 were not taken into account because this well is normally integrated to the separation station 6, only in a few cases to the separation station 2. Because only PGM-19 is acid, the point of interest is the intersection where the two types of fluids mix. Fluid temperatures in the pipeline are estimated to be between 190 and 200°C (pers. com. Sánchez, 2006). For calculation purposes, an average temperature of 195°C was used.

5.2 Assessment of the Deep Fluid Composition

In order to calculate the deep fluid composition, liquid phase samples collected at atmospheric pressure (98°C) and gas samples recalculated to those conditions were input to WATCH chemical speciation program version 2.3 (2004). The program reads chemical analyses of water, gas, and steam condensate samples, collected at the surface and computes the chemical composition of downhole, or aquifer fluids at a chosen reference temperature. This includes the pH, aqueous speciation, partial pressures of gases, redox potentials, and activity products for mineral dissolution reactions. The background of the program and the general methods of calculation used were described by Arnórsson *et al.* (1982).

PGM-03 and PGM-19 present excess enthalpy, which means the measured discharge enthalpy is higher than the value that could be expected derived from the measured temperature in the well below the level of first boiling (aquifer temperature). From measurements and observations performed in wells at Miravalles, an excess enthalpy is considered when a difference between those values is higher than 50 kJ/kg.

The excess enthalpy refers to the situation when the steam to water ratio in a well discharge is higher than can be produced by pressure drop of the initial aquifer fluid. According to Arnórsson (2000) this can be due to 1) flow of heat from the rock to the boiling water that flows through the zone of depressurization to the well and 2) phase segregation, in which the steam flows into the well but the water is partly or totally retained in the aquifer. In Miravalles, the cause of the excess enthalpy is deep boiling in the formation, resulting in phase segregation.

For calculation purposes, the downhole temperature measured in dynamic temperature logs was utilized as the reference temperature value in the case of wells PGM-17 and PGM-66. For PGM-03, the reference value was the temperature of the quartz geothermometer of Fournier (1977) and in the case of PGM-19, an estimated temperature based on dynamic temperature logs ran before the excess enthalpy was detected in the well.

The scheme followed with the input data from each well in the WATCH program was:

a. Calculation of the aquifer composition at the reference temperature.

b. Performing of boiling steps from the reference temperature to the following sequence of temperatures: 195, 170, 165, 159 and 98°C. The boiling process was assumed to be adiabatic and degassing in equilibrium (degassing coefficient = 1).

c. After the last boiling step was performed (98°C), the calculate composition of the fluid was compared with the analysis of the sampled fluids at the same temperature, in order to evaluate how appropriate the reference temperature value was.

d. Saturation indexes of amorphous silica and pH values were calculated because initially it was inferred that those parameters were playing an important role in the scaling problem studied in this work.

e. Special attention was paid regarding to the composition of the fluids calculated at 195°C, because that is the estimated temperature in the mixing point between neutral and acid fluids. Also, the composition at that temperature will be used in the mixing calculations that will be explained later in this study.

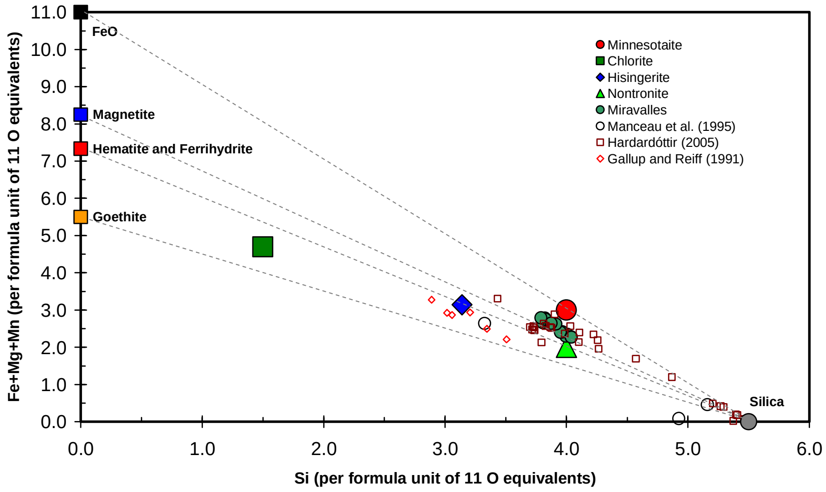

Figure 7: Atomic ratios between major cations and silicon in scales at Miravalles

5.3 Saturation Indexes Considerations

The chemical composition of the samples obtained after simulating boiling to 98°C using WATCH were very close to the analyses of the samples collected at the same temperature. Saturation indexes calculated by WATCH showed that amorphous silica did not reach super saturation above 98°C in any of the wells considered in this study (Figure 8). Similarly, there were no significant differences in the degree of saturation of calcite, amorphous silica and also pH within the time interval considered (2003 – 2005). If two or more solutions at the same temperature are under saturated with respect to amorphous silica, then the resulting mixture will be also under saturated. As a result, the scales formed at Miravalles cannot be related to amorphous silica.

5.4 Mixing Calculations

Before describing the work carried out for modeling fluid mixing, some considerations must be explained. It is clear at this point that scales formed because the mixing of fluids with different chemical compositions lead to a pH increase. That added to the fact that acid fluids are richer in iron than neutral fluids, sets the scenario for the amorphous iron silicate to precipitate. However, it has to be taken into account that the main problem there is the pH increase. That can be deduced by taking a look at the equilibrium constant in equation (3) and observe that it is very sensitive to pH, even to a small change of it.

Since the scaling begins at the point where neutral fluids from wells PGM-66 and PGM-17 are mixing with acid fluids that come from PGM-19, only this case was analyzed. Furthermore, to simplify things, only the fluids from PGM-17 were taken into account for modeling. This is justified because the fluids of wells PGM-17 and PGM-66 are chemically very similar and also because no scales have been formed in the pipelines where the mixture of fluids from wells PGM-66 and PGM-17 occurs.

Chemical composition data of fluids boiled to 195°C from PGM-17 and PGM-19 taken from WATCH were run in EQ3NR (v. 7.0), aqueous speciation software. EQ3NR, like WATCH, computes the distribution of chemical species in the solution, including simple ions, ion pairs, and complexes, using standard state thermodynamic data and various equations which describe the thermodynamic activity coefficients of these species. More details of this software can be reviewed in Wolery (1992). The reason for using EQ3NR was that its results serve as an input file to EQ6 (v. 7.0), a reaction path modeling code for aqueous geochemical systems. Complete information of this software is given by Wolery and Daveler (1992).

A reaction path modeling represents the process by which a set of irreversible reactions proceed to a state of thermodynamic equilibrium (Wolery and Daveler, 1992). Irreversible reactions might begin in a metastable equilibrium state and end in a stable equilibrium state, but in between these states the system must necessarily pass through states of disequilibrium. The general aim is to be able to trace what happens during irreversible reactions or processes, such as dissolution or precipitation of minerals, mixing solutions, cooling or heating systems (Zhu and Anderson, 2002).

There are many reaction path models. Mixing or titration modeling simulates the process of addition of reactant into a system. The reactant can be a mineral, a chemical reagent, a glass, a gas, another aqueous solution, a rock, or anything for which the chemical stoichiometry can be defined (Zhu and Anderson, 2002). This kind of model is the most suitable for understanding the processes that occur during the mixing between fluids from wells PGM-17 and PGM-19.

In order to have a more representative view of the situation, mixing experiments between PGM-17 and PGM-19 were carried out with samples belonging to the same time period. It means, for example, that is very unlikely to mix fluids sampled at PGM-17 during 2003 with fluids sampled at PGM-19 during 2006. During each run in EQ6, fluids from PGM-17 and PGM-19 were mixed at 195°C. Fluids from PGM-17 were titrated with fluids from PGM-19 until a mixture of equal parts of each was achieved. On the other hand, in order to have the whole spectrum of the mixing experiment, fluids from PGM-19 were titrated with fluids from PGM-17. Thus, two runs per mixing experiment were done.

An important consideration concerning the paths followed by the code of EQ6 software in order to reach a state of equilibrium is related to the precipitations of secondary phases. The default condition is that EQ6 will precipitate of any phase to avoid supersaturating the aqueous solutions, no matters if one phase, geochemically speaking, makes more sense that another. However, to make things less complicated, any phase to be precipitated was suppressed.

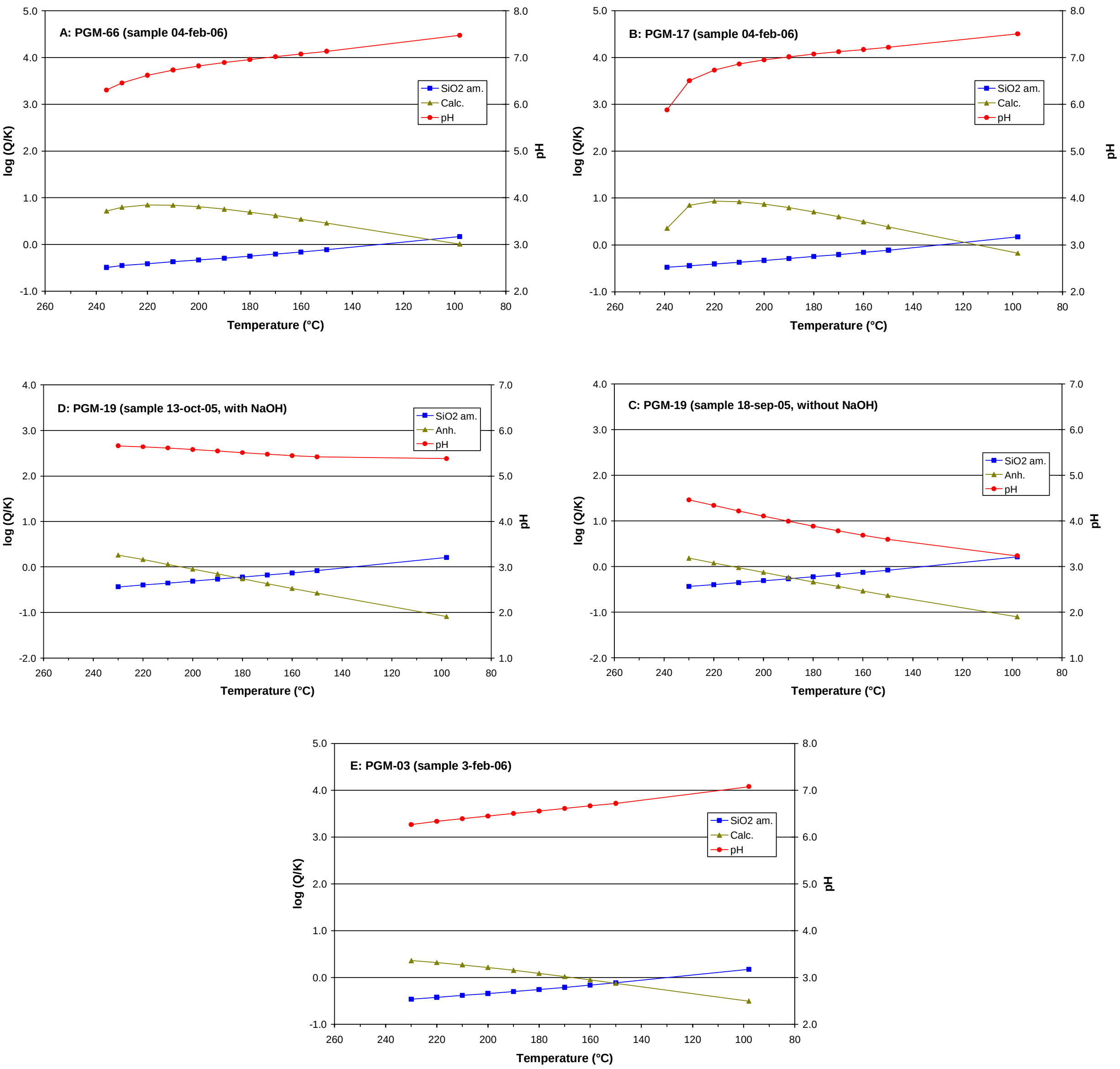

Figure 8: Saturation indexes of calcite, anhydrite, amorphous silica and pH of the fluids from wells PGM-66, PGM-17, PGM-19 and PGM-03. Notice than in PGM-19, different producing conditions are compared (with and without NaOH)

The activities of Fe^{2+}, SiO_2 and H^+ resulting from each run were used to calculate the reaction coefficient (Q) of the dissolution reaction of the scale phase at every step of the reaction path, as showed in equation (4).

$$Q = \frac{(a_{Fe^{2+}})^3 \cdot (a_{SiO_2})^4}{(a_{H^+})^6} \qquad (4)$$

If a given reaction is in equilibrium, then Q = K. A convenient way to evaluate the state of saturation of an aqueous solution with respect to a mineral or phase would be to calculate the saturation index (Q/K). The search of K for minnesotaite in literature was unsuccessful. However, it does not imply that important deductions about saturation states of minnesotaite cannot be derived in combination with observations carried out in pipelines and mixing proportions.

5.4.1 Actual Mixing Scenarios

The results of mixing experiments carried out by EQ6 are presented in Figure 9. The log Q of the scale phase is plotted against the mixing ratio between PGM-17 and PGM-19. All of PGM-19 samples, except during September 2005, correspond to periods when those fluids were neutralized by means of NaOH. At the extremes of x-axis, the end members of the mixture between PGM-17 and PGM-19 are plotted. Iron content in PGM-17 fluids is in non-detectable concentrations, thus log Q of the scale phase at PGM-17 extreme is not defined. In the starting solutions, the scale phase is assumed to be under saturated. Otherwise, scales would have been observed in two-phase pipelines in the way to the mixing point between those wells. On the other hand, PGM-19 solutions are richer in iron. Concentrations between 0.23 and 0.81 ppm are present in neutralized samples and between 3.66 and 19.49 ppm in non-neutralized samples.

In the case of neutralized PGM-19 samples, log Q rapidly increases in the firsts mixing stages of PGM-19 with PGM-

17 until a mix ratio of 80% and 20% respectively exists. Beyond that point both log Q and pH slowly increase. In Figure 9, the mixing ratios that represent the conditions prevailing when the scales formed at the mixing point between PGM-19, PGM-17 and PGM-66 fluids are illustrated. According to Sánchez (pers. com., 2006) at that site there were 100 kg/s delivered by PGM-66, 100 kg/s by PGM-17 and the contribution of PGM-19 was about 110 kg/s. That makes 64.6% of neutral fluids and 35.4% of acid fluids. Because scaling occurred, it is deduced that over saturation of the minnesotaite-like phase existed at these mixing conditions.

Considering that in this experiment the starting solutions are under saturated with respect to the scale phase and that at a certain point of their mixing path the mixture becomes over saturated, it is inferred that log K would be located somewhere between 11 and 13 on the y-axis, thus $11 \leq \log K \leq 13$. Therefore, if log Q values exceed this range, scaling is very likely to occur.

Results from the mixing experiments show that the scale phase over saturation was reached with the slightest addition of PGM-19 fluids to PGM-17 fluids until the mixing ratio contained more than 70% of PGM-19 fluids. Of course, those ratios are variable and depend on the degree of neutralization of PGM-19. An interesting situation appears in the mixing experiment that corresponds to the samples taken on September 2005. For a short period, PGM-19 was not being neutralized, so the pH of the mixing fluids is lower compared to the other mixing experiments. Furthermore, the scale phase under saturation remained until PGM-19 fluids constituted more than 32% of the mixture. That behaviorc suggests that a pH decrease will result in a decrease of the saturation of the scale phase.

Iron, silica and pH play an important role in the formation of the scales. pH is in fact, the most sensitive parameter and the only one that can be directly controlled by means of neutralization. At this point, question arises about how the degree of saturation of the scale phase could change if an acid solution of PGM-19 is neutralized.

The result of a titration experiment carried out by EQ6 is present in Figure 10. The NaOH solution utilized was at a concentration of 30% w/w; similar to the one employed for deep neutralizations treatments at Miravalles. The PGM-19 titrated solution corresponds to a non-neutralized sample taken on September 2005, with an initial iron content of 19.49 ppm. The titration was run in a temperature of 195°C. According to scaling and corrosion rate studies performed on acid fluids at different pH values of neutralization (Rodríguez and Sánchez, 2004; NEDO, 2004), it is very likely that beyond a pH of 5.0 scaling will occur at the same temperature conditions of the titration experiment made here. Taking into account all those observations, the log Q of the scale phase seems to be in a range from 14 to 15.

These results are somewhat higher than what was found in the mixing experiments. However, it has to be considered that this case is different with respect to the mixing experiment because the iron contents here are much higher. Therefore, it is expected that the log Q values rise to a higher values sooner than in the mixing experiments. The most important conclusion of this experiment is that this process resembles the case when neutralization is carried out inside an acid well with the purpose of avoid corrosion.

5.4.2 Simulated Mixing Scenarios

With the goal in mind of giving a solution that could solve the scaling problems due to the mixing between neutral an acid fluids, some scenarios were modeled. One possible solution involves acidifying fluids from neutral wells. That would involve doing this operation in wells PGM-17, PGM-66 and PGM-03. In order to simply things, the mixing models were done as if only PGM-17 fluids were acidified.

Three scenarios considered mixing acidified PGM-17 fluids to the next pH values: 6.5, 6.0 and 5.5, with neutralized fluids from PGM-19. The results are presented in Figure 11. The pH 5.5 and 6.0 scenarios show curves that run well below the over saturation threshold of the scale phase. On the other hand, under the pH 6.5 scenario, the curve touches that threshold; therefore scaling may occur under those conditions. An important consideration about all this mixing models is that they are giving a starting point for future field tests. All the results of these experiments are theoretical and must be confirmed by scaling and corrosion rates tests using coupons in specific locations inside the pipelines.

6. DISCUSSIONS AND CONCLUSIONS

Chemical and EDS analyses determined that scales formed at Miravalles as a result of combining neutral with acid fluids are mainly composed of silicon, oxygen and iron. That composition corresponds to a ferrous silicate with a stoichiometry very similar to minnesotaite $((Fe^{++},Mg)_3Si_4O_{10}(OH)_2)$.

XRD patterns suggested that the scales are mainly amorphous or poorly crystallized. Because of the amorphous nature of scales they can easily accept many other ions into its bulk mass and that could explain the presence of other elements in minor quantities.

SEM micrographs showed the layered structures observed in hand specimens of scales are due to textural differences, rather than chemical differences. The dark layers presents a compact texture meanwhile the light brown ones develop a porous texture consisting of particle aggregates.

The correlation between the chemical compositions of the scales and minnesotaite, permitted to define a reaction for the dissolution of the scale phase. Iron, silica and pH control the precipitation of the scales, but the latest is the most sensitive parameter and the one that could be directly controlled. A high iron content provided by PGM-19 acid fluids with a pH increase that occurs during the mixing between those fluids with the neutral ones, are the key factors that control the saturation state of the scale phase.

As it was demonstrated with a titration experiment in which a PGM-19 fluid was neutralized with NaOH, this is the same case when a pH is raised too much inside an acid well in order to avoid corrosion.

The mixing experiments between neutral and acid fluids determined a threshold of log K of the scale phase between 11 and 13. Above this range, the probabilities of over saturation of this compound are very high. Decreasing pH values of neutral fluids seems to be a feasible solution to avoid scaling. According to the mixing models performed, with a pH 6.0, it seems that no scaling occurs. A minimum value could be around 5.0, according to the corrosion test performed at PGM-07 in 2002.

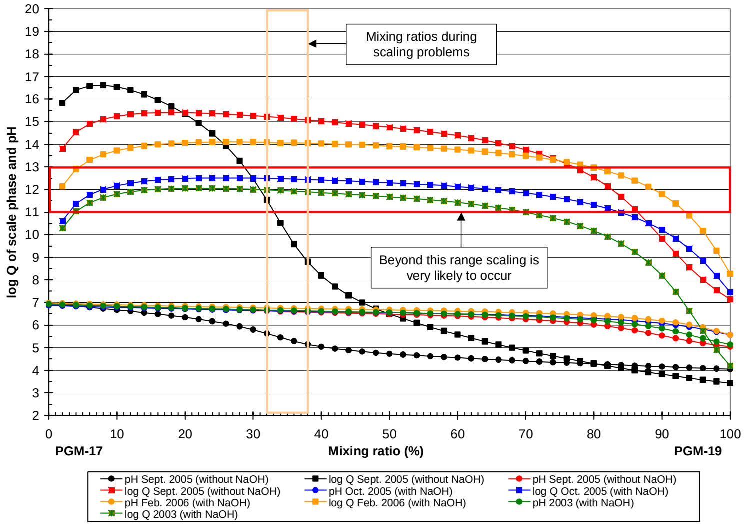

Figure 9: Mixing models between PGM-17 and PGM-19 fluids

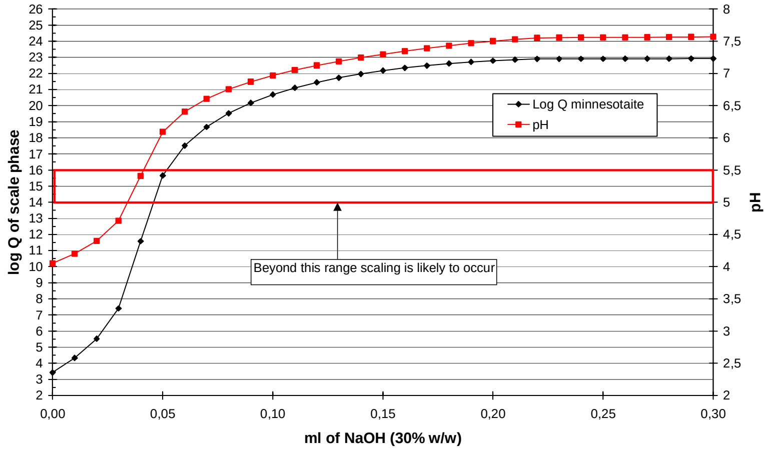

Figure 10: Titration of a non-neutralized fluid with NaOH (30% w/w) at 195°C

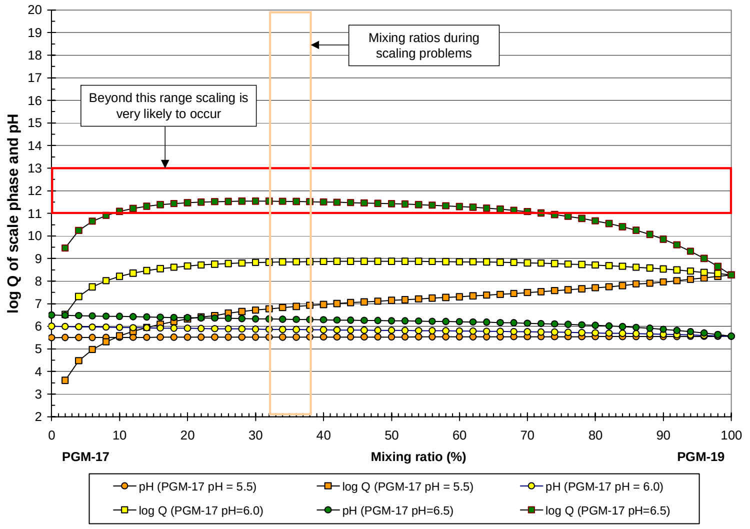

Figure 11: Mixing models with pH value scenarios of 5.5, 6.0 and 6.5

RECOMMENDATIONS

- Decreasing the pH of neutral fluids with an acid (HCl, for example) to a maximum value of 6.0 would be recommended.

- However, corrosion and scaling rates studies are highly recommended in order to optimize this value and reach a good balance between corrosion and scaling.

- Additional studies of the scale such as IR and Mössbauer spectroscopy would be of great value to further investigate the nature of the scales.

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