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Exclusion of Acid Sulfate Fluid in Wells at Tiwi Geothermal Field, Albay Province, Philippines

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ABSTRACT

Well Bar10 in the Bariis sector of the Tiwi field was drilled in 1996 and it produced highly corrosive acid sulfate fluids at a pH of ~3.7. The results of Bar10 and other previously drilled acid-sulfate producers in the same sector (Bar02, Bar03 and Bar09) were discouraging that further drilling in the area, despite its high reservoir temperatures and permeabilities, was shelved.

In 1996 a previously non-corrosive well, Bar08, started producing acid sulfate fluids. Fieldwide studies of the chemistry and occurrence of the acid sulfate fluids indicated that they form near the top of the reservoir, due to the interaction of H_2S-bearing reservoir steam with downflowing air-saturated meteoric water. Therefore, well Bar08 was redrilled in 2005 and cemented liner installed below the original casing shoe, with the objective of excluding the acid sulfate fluids from the wellbore. The well has been an excellent producer of benign fluids since then. A new well Bar11, was drilled in 2008 with a similar design and is also currently producing a similar high-temperature, benign fluid.

1. INTRODUCTION

The Tiwi Geothermal Field is located in the southern portion of the Luzon island in the Philippines, see Figure 1 below. It is the first field in the Philippines that utilized geothermal steam for power generation.

Chevron Geothermal Philippine Holdings, Inc. (CGPHI) through its 38-year history of developing and operating the Tiwi field has drilled approximately 28 wells that have shown the characteristics of acid-sulfate fluids, namely, elevated concentrations of sulfate ($SO_4^{=}$) and low pH. In most cases, the wells have been suspended or abandoned. Some were used as injectors while others were excluded from the steam gathering system. Still others, those that were drilled within the periphery of the field, are used as observation wells for monitoring reservoir pressures and temperatures as these respond to changes in the reservoir. There have also been cases when the wells initially produced neutral pH fluids then turned acidic and were eventually shut-in. The following table shows some of the wells in Tiwi that have produced acid sulfate fluids:

Currently shut-in - 530 kilo-pounds/hour (67 kg/s) of steam		Currently flowing to the system – 210 kph (27 kg/s) of steam	
Mat15	140 (18)	Mat17	80 (10)
Kap32	80 (10)	Bar05	130 (16)
Bar02 (flowtest)	50 (6)		
Bar03 (flowtest)	260 (33)		

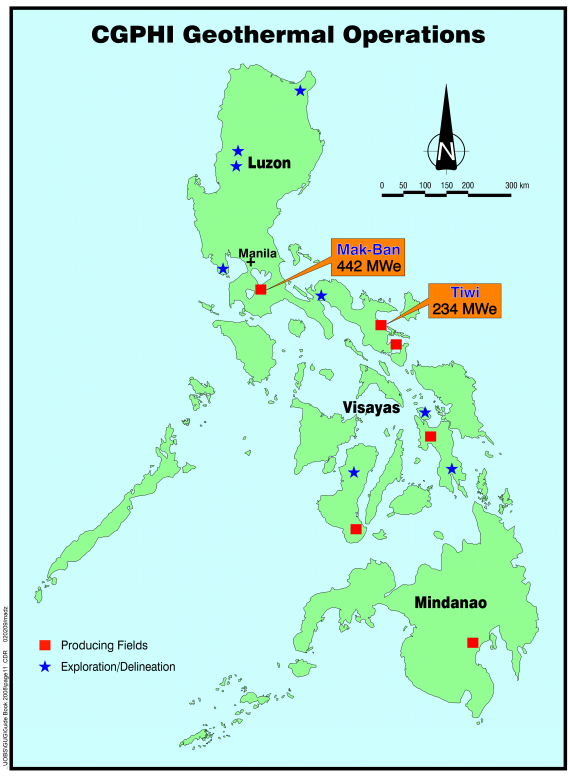

Figure 1. Location of the Tiwi Geothermal Field

Several acid sulfate wells were drilled early on in Tiwi's history within the Naglagbong sector. The more recent wells were drilled within the Bariis sector of the field. The Bariis area is one of four geographic sectors comprising the Tiwi Geothermal Field (see Figure 2 below). It is located near the southwest end of the bean-shaped field production area and overlies one of two postulated upflows (the other upflow being situated farther to the east in the Kapipihan sector). As an upflow area, Bariis would naturally attract attention for potential production well drilling given the high expected flowrates. Until about 1996, 10 wells were drilled in the Bariis area. Half of these wells produced highly corrosive fluids. The last well that was drilled in Bariis was Bar10 – it produced fluids with pH of around 3.7 and during corrosion tests showed corrosion rates of greater than 1000 mils per year! Another well, Bar08, initially produced benign fluids but produced acid fluids later. With these results, the large scale development of the sector was put on hold.

The corrosivity of acid fluids, specifically those with high sulfate concentrations, which is found in a lot of geothermal systems, has limited their development and utilization, see for example *Moya and Sanchez (2002)*, and *Villa, et al (2000)*. Various workers have described the occurrence of acid fluids containing high sulfate in geothermal systems

and these seem to be heavily dependent on the geology, see for example *Truesdell, (1991)* and *Giggenbach (1992)*. Some of the hypotheses suggest that acid sulfate fluids can be formed when the rising H_2S from the geothermal reservoir reacts with oxygen-containing groundwaters. Another suggested mechanism is that the acid sulfate waters are formed by the disproportionation of SO_2 from magmatic gases when it encounters shallow groundwaters. Leaching of previously formed acid alteration minerals may also give rise to localized acid sulfate fluids. It is, however, believed that acid sulfate waters derived from a direct magmatic source are limited in areal coverage to within a small region immediately surrounding the volcanic crater, see for example *Giggenbach (1987)* and *Chiodini, et al (2001)*. The characteristics of a predominantly magmatic origin for the acidic fluids have yet to be found in Tiwi, i.e., the acid fluids are of the acid sulfate-chloride type with no apparent excess chloride.

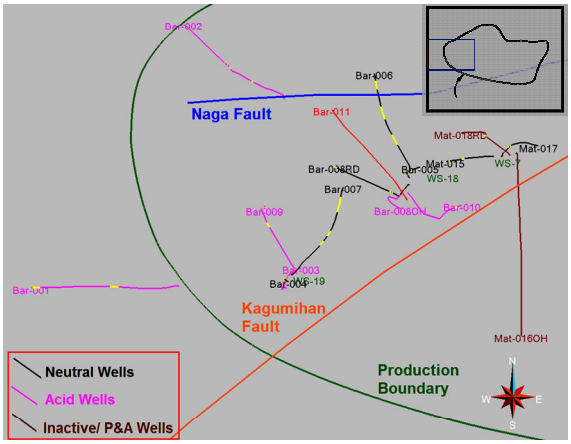

Figure 2. Bariis Sector in the Tiwi Field showing wells that produced acid sulfate fluids.

2. CORROSION MITIGATION AT WELL BAR08

One of the more notable cases of the occurrence of acid sulfate fluids in Tiwi is that of well Bar08. This well was drilled in May 1995 to target the high temperatures and pressures in the Bariis sector of the Tiwi field. The highest temperature measured was about 290°C at the well's bottom (1992 mMD). Initially, it was producing around 280 kph (35 kg/s) of steam, at a steam fraction of about 0.85. Its reservoir chloride concentration of around 6000 ppm was higher than one of the more stable wells in the Bariis sector, Bar07, at 4800 ppm, probably since the deepest production zone of Bar08 is around 1000' deeper than that of Bar07. Hence it may be thought that Bar08 was producing from a deeper neutral chloride reservoir. The fluid pH started out in the 4.6 to 5.2 range while the sulfate (SO_4) level was around 40 ppm.

Figure 3 shows a plot of some chemical species from Bar08 fluids. A typhoon that passed Tiwi from 30 October to 04 November in 1995 caused damages to the power plant units and led to a fieldwide shutdown of almost four months. No immediate changes in the chemistry of the well was noticeable though a few months after the shutdown, the fluid pH showed declining trends of pH while Mg and SO_4 contents gradually increased. The chloride concentration showed declines during these period. By late 1997, the well's fluids showed acid chemistry with pH values ranging from 3 to 4 and SO_4 concentrations in the 200 to 400 ppm range. The well was kept flowing for a while until the liquid pH became too acidic and it was shut-in during the 2nd half of 1997.

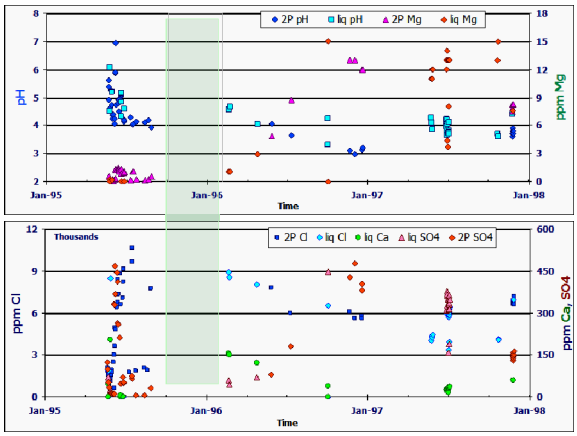

Figure 3. Plot of Selected Chemical Specie from Well Bar08

A downhole temperature and pressure survey done in January 1997 showed the possible presence of a blockage at around 1300 mMD. Subsequent scale probe surveys, as shown in Figure 4, indicate that by 1999 – 2000 a blockage had formed at a depth of about 1310 mMD and was spreading to the shallower portion of the well. The fact that the well was still producing despite the blockage suggests that the well was only partially obstructed. The formation of the blockage together with the change in the well's chemistry after the long shut down implies that the shut-in may have played a role in the formation of the blockage and subsequent change in chemistry.

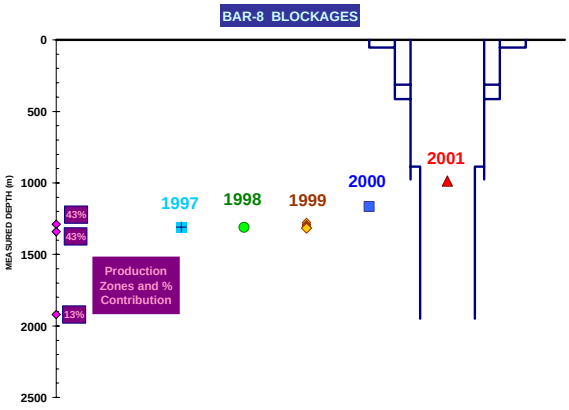

Figure 4. Scale probe surveys conducted at Bar08.

Based on the above, it is thought that the initial formation of the blockage started when the well was shut-in after 1996. Under this condition, fluids from the upper zone, which is assumed to contain H_2SO_4 from condensed steam within the steam zone, would enter the well. Due to its relatively lower temperature, and thus higher density, the acid sulfate fluid downflows and mixes with the Ca-containing and hotter neutral chloride waters from depth. The mixture of SO_4 and Ca sets up the following precipitation reaction:

$$SO_4^{=} + Ca^{++} \xrightarrow[T]{} CaSO_4 \downarrow \qquad (1)$$

$CaSO_4$ or anhydrite is a very insoluble salt which has a retrograde solubility, i.e., it is less soluble at high

temperatures. The formation of the anhydrite scale between the acid sulfate and neutral chloride inflows effectively suppresses the deeper feed zone (neutral Cl). With succeeding flowing of the well, the discharge fluid becomes more acid while the anhydrite scale presumably spreads and possibly covers a bigger portion of the liner diameter. The well's acidity will increase as the anhydrite progressively suppresses the deeper, neutral chloride zone. This model is presented as a cartoon in Figure 5.

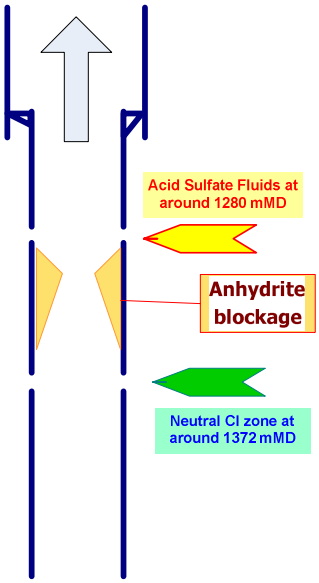

Figure 5. Mechanism of anhydrite blockage formation at Bar08.

Depending on the proximity or the presence of a steam feed zone, the formation of the anhydrite could also result in a decline in the well's discharge enthalpy (see Figure 6). This is normally accompanied by an increase in the brine rate. There may also be some decline in the flowing wellhead pressure as the contribution from the hotter, deeper zone diminishes.

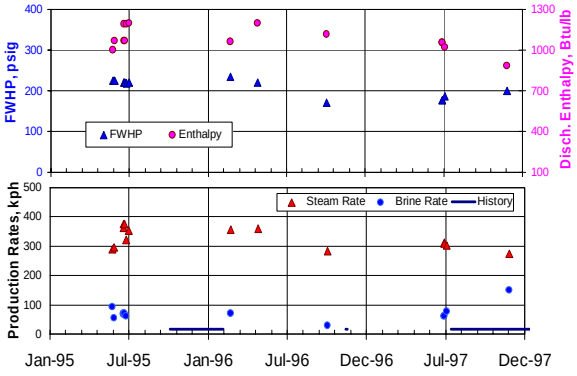

Figure 6. Enthalpy and Production Rate changes of Bar08

After a series of tests, a downhole corrosion mitigation system was constructed for Bar08. It essentially consisted of injection of a mild concentration of caustic soda as near as possible to the acid zone, (Villaseñor et al, 2001), through a corrosion-resistant capillary tube. The pH and corrosion rates were measured in real-time at the discharge line. Monitoring of the pH was used in formulating the concentration and injection rate of the caustic solution and a surface pH of around 4.5 to 5 was maintained. The corrosion rates were thus maintained at less than 15mpy. Scaling around the injection sub, however, prevented the pull-out of the sub for maintenance checks.

The plan for the subsequent workover consisted mainly of pulling out the injection sub and the capillary tube. This, however, proved to be difficult given the fact that the downhole equipment (injection sub and capillary tube) were all made of a corrosion-resistant alloy making it almost impossible to drill through it. The liner was eventually pulled-out including the injection sub encased in scale. The scale was analyzed to be a calcium silicate that forms at high pH. It apparently formed where the mild caustic solution initially mixed with the acid sulfate fluids.

Examination of the pulled-out liner also showed that the area just below the emplacement of the injection sub was severely corroded while the sections above it did not show signs of significant corrosion damage. This proved that the neutralization procedure was indeed successful in controlling the corrosive nature of the fluid. Another important finding was the presence of a highly corroded portion on the outside wall of the liner at ~1350mMD. This provided concrete evidence on the depth of the acidic zone.

2.1 Acid sulfate fluids in Bariis

Chemical modeling of the discharge fluids of some of the Bariis wells were done using the Chevron in-house software called Gcxl5. As a first approximation, the following simplifications were done in the calculations:

- No attempt was done to model the total composition of the fluid, i.e., only the composition of the separated liquid sample was used for all the wells considered;
- The calculations did not examine the effects of boiling nor mixing with another fluid;
- The effect of precipitation of solids, though included in the calculations, were not used to adjust the concentrations of the corresponding components, i.e., the total sulfate concentration was assumed to be constant and unaffected by deposition of anhydrite;
- In effect, the chemical speciation of the fluid was only calculated at high temperatures.

The results of the calculations were then plotted with the following equilibria in mind, with the species favored at high temperatures shown on the right side of the equation:

$$2H^+ + SO_4^{=} \underset{T}{\longleftrightarrow} H_2SO_4 \qquad (2)$$

$$H_2O \underset{T}{\longleftrightarrow} H^+ + OH^- \qquad (3)$$

Equation 2 is a simplified equation for the dissociation of sulfuric acid. It is seen that the undissociated acid is favored at high temperatures. The dissociation of water (Equation 3) was used to determine the pH of a pure liquid at high temperatures as will be shown below.

Figure 7 shows the plots of Bar10 with regards to its sulfate chemistry. The upper plot shows the speciation of Ca, $SO_4^{=}$, and $CaSO_4$ in the Bar10 separated liquid as these vary with temperature. The y-axes show the concentrations of the various species (in ppm) at elevated temperatures. It is

readily seen that the sulfate concentration declines with increasing temperature. The change in slope at around 250°C is possibly due to its association with Ca.

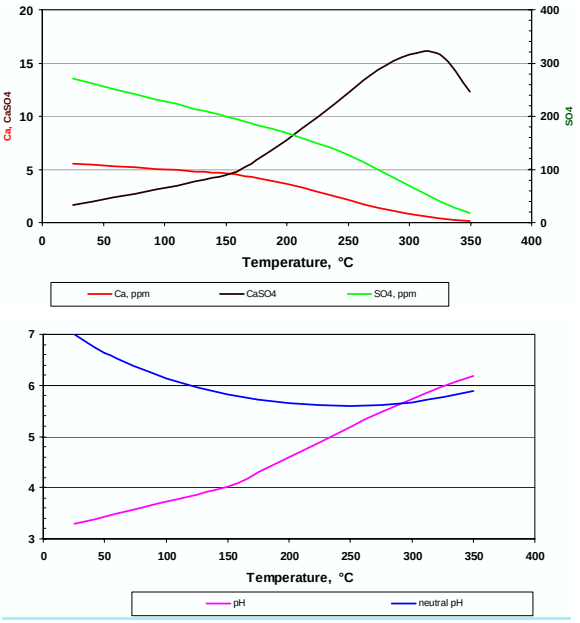

Figure 7. Sulfate chemistry and acidity of Well Bar10

The bottom figure shows the pH of the solution (pink line) while the blue line shows the pH of pure water which is taken to represent the neutral pH. Due probably to other buffers[1] in the system which tend to absorb the H^+, the pH of the Bar10 sample rapidly increases with temperature and is only one pH unit lower than neutrality at about 220°C. The same trend can be seen in Figure 8 which shows the same plots for the fluids of Bar08 prior to its redrill.

These plots show that anhydrite forms at high temperatures and hence supports the proposed model (Figure 4) with regards to the increase in Bar08's acidity and the possible continuation of scale development. Figure 9 shows the calculated ion products of Ca^{+2} and $SO_4^{=}$ based on the speciation at high temperatures. The ion products were plotted as the logarithm of the ratio with the anhydrite solubility constant at various temperatures. Log Q/K = 0 represents the equilibrium line. The curves for some of the acidic wells in Tiwi show that equilibrium is reached at around 225°C suggesting the formation of anhydrite for these sulfate-rich fluids.

With the sulfate concentration apparently being controlled by anhydrite solubility[2], it is believed that the fluid pH will tend to neutrality with low sulfate concentrations upon formation of anhydrite. This has been shown to be the case by the second plots in Figures 7 and 8.

[1] Some of the other buffers not shown in the plots but were included in the chemical modeling are those of the weak acids of borate, silicate, carbonate and sulfides.

[2] One other important factor in the formation of sulfate fluids at depth would be the availability of oxygen for the reaction with sulfides or H_2S. The oxygen fugacity in high temperature hydrothermal systems has been shown to be very low (see for example Giggenbach, 1987).

2.2 Tiwi Wells with Acid sulfate fluids.

Studies on the distribution of acid fluids in Tiwi wells, Powell, et al (1995), suggested a possible compartmentalization of these fluids along corridors possibly bounded by faults. It is realized that these structures could also provide pathways for the downflow of oxygen-containing meteoric water which could then react with H_2S in the rising steam to form acid sulfate fluids near or within a condensate zone. Leakage of geothermal fluids along these structures may also lead to localized lower temperatures either due to the inflow of cooler groundwater or because these serve as conduits for a drop in pressure leading to localized boiling in the hydrothermal system.

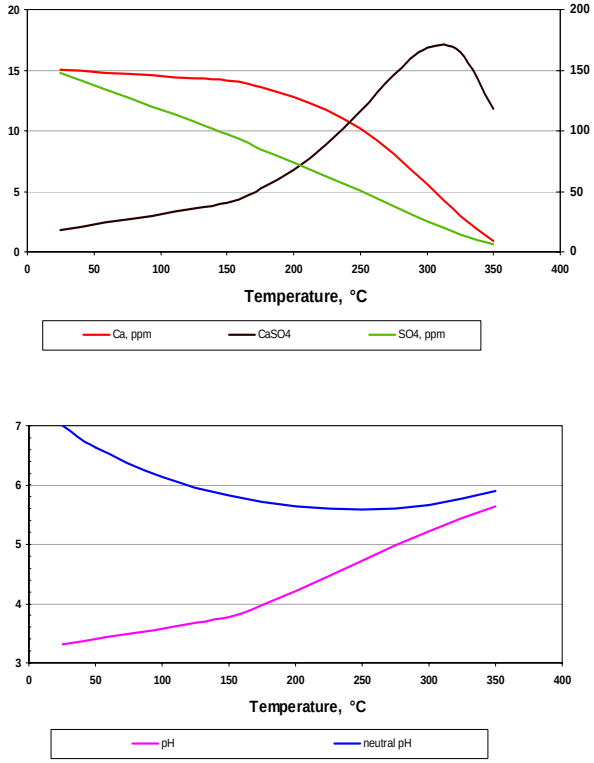

Figure 8. Sulfate chemistry and acidity of Well Bar08

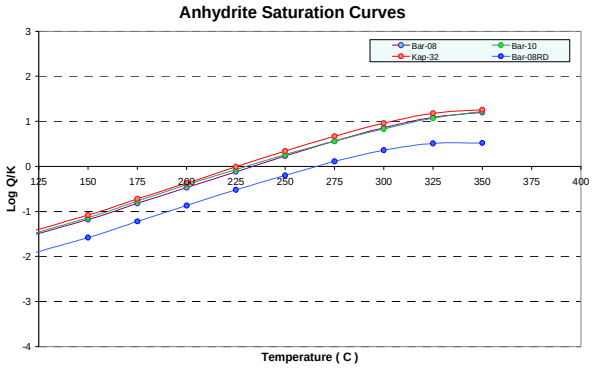

Figure 9. Anhydrite saturation indices of selected Tiwi wells

Some of the wells in the Bariis sector that produced acid sulfate fluids are shown as pink welltracks in the plan view in Figure 2. Some of these wells, Bar08 and Bar10, may have intersected the Kagumihan Fault while others were seen to have shallow production zones within the depth range of the top of the reservoir.

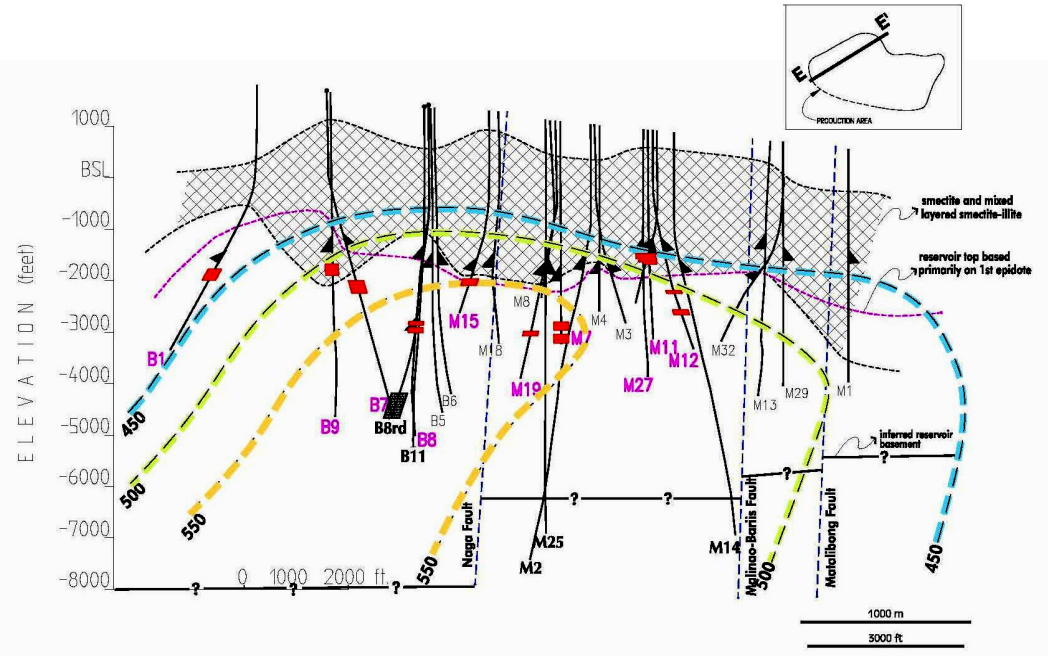

Figure 10. Cross section within the Bariis sector

The reservoir top as shown in Figure 10 has been interpreted from temperature and mineralogy data and it roughly coincides with a temperature of about 220°C. The other wells in Tiwi that showed the presence of acid sulfate waters are shown with pink font in Figure 10. Acid alteration mineralogy was also recognized in some of these wells, although these lenses of acidic alteration may or may not be reflective of the current conditions. The production zones that are thought to contribute acid sulfate fluids are highlighted in red in Figure 10. Noting that the inferred acid production zones occur near the top of the reservoir, a completion program for Bar08 was developed to exclude these zones.

3. BARIIS MAKE-UP WELL DRILLING

Bar08 was redrilled by directing the new leg away from Kagumihan fault. A deep cemented casing was also put in place to isolate zones that are interpreted to be the source of acid entry into the wellbore. Completion tests after the redrill showed that the well was mainly producing from a zone at 1740 mMD to almost 1900 mMD, Regulacion, 2005. The redrill operation in Bar08 was considered a success and the well produced fluids have since been neutral. Figure 11 shows the sulfate chemistry and the pH of the fluids produced by Bar08RD. It is currently producing around 30 kg/s of steam (~12MW).

The success of Bar08RD paved the way for the planning of new wells to be drilled in the same general area with the objective of producing solely from deep zones by isolating shallow and moderate depth entries. Recently, CGPHI drilled another well within the Bariis sector, Bar11. The concept behind the targeting of Bar11 was two-fold, similar to that employed n Bar08RD. First, faults that are believed to channel acid fluids were purposely taken out of the list of drilling targets. Second, a deep cemented liner was put in the design to case-off entry zones down to ~4500 ft-TVD (1372mVD). Such a design was a challenge to implement given the difficulty of cementing a section with multiple loss circulation zones and which is already within the reservoir section. Despite the difficulties, drilling of Bar11 was completed and completion testing verified the existence of a major zone at the bottom. Subsequent flow tests showed the well producing neutral pH fluids at commercial rates, adding 8 to 9 MW of generation at the power plant.

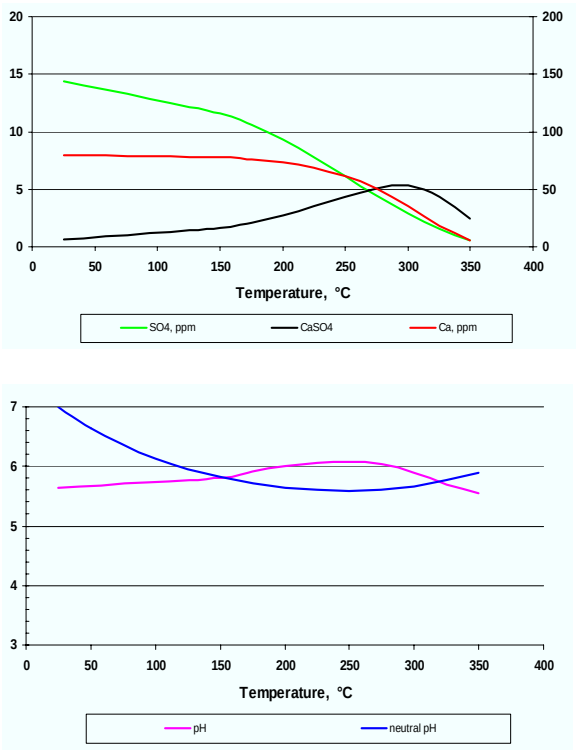

Figure 11. pH and Sulfate Chemistry of Bar08RD

Further drilling activities have been recommended in the same general area of the Bariis sector especially a section that has not been drilled yet. The successful redrill of Bar08

and drilling of Bar11 showed that corrosive acid sulfate fluids can be excluded from the wellbore, opening up new opportunities for developing the Bariis area.

4. CONCLUSIONS

The concept of the acid sulfate fluids being confined at shallow depths was also applied in maintaining wells that have shallow production zones. Some of these wells have already shown some tendency to produce acid fluids (Mat17 and Bar05). The operating philosophy for these wells has been to maintain these at flowing conditions so as not to induce the inflow of the shallow acid sulfate zones at shut-in conditions. To further minimize the entry of acid sulfate fluids, these wells are being flowed at slightly higher wellhead pressures to suppress production from the shallow zones. These have been incorporated in the operating procedures for these wells.

These concepts have also led CGPHI to the possibility of extending development of the Tiwi resource to zones below the acid sulfate zones and possibly into the high temperature areas south of Bariis and Kapipihan sectors.

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