

# SULFUR DEPOSIT REMOVAL AND CONTROL IN A POWER PLANT COOLING TOWER: A CASE HISTORY FROM CERRO PRIETO, MEXICO'S LARGEST GEOTHERMAL FIELD

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## ABSTRACT

Effective deposit control is necessary to achieve optimum cooling efficiency in all cooling systems. Evaporative cooling systems in some geothermal power plants experience an unusual form of fouling – the accumulation of hard elemental sulfur deposits in hot water distribution lines and spray nozzles, on the tower fill, and in the condenser. This paper describes field trials of a sulfur deposit dispersant conducted in two 400,000 gallon cooling systems associated with 25 MW power generation units at the Cerro Prieto IV Geothermal Power Plant (Mexico). A successful 28-day field trial demonstrated the ability of daily cleaner/dispersant treatments to remove and disperse existing sulfur deposits and biofouling deposits from a fouled, underperforming cooling system. A successful 3-month trial demonstrated the ability of regular cleaner/dispersant treatments to prevent sulfur deposit formation and improve cooling efficiency in a cooling tower which was mechanically cleaned prior to the trial. Plant operating data and trial monitoring data are presented, along with a discussion of the characteristics of the operating environment in the geothermal cooling water system which make these plants susceptible to this unique and persistent form of fouling.

## 1. INTRODUCTION

The geochemistry and ecology of natural geothermal environments have been extensively studied (Hedlund, et al, 2012; Inskeep, et al, 2010; Shock, et al, 2005; Vetter, et al, 2010). These studies provide valuable insight into the abiotic and microbial processes which control the chemistry of these environments. The cooling water systems associated with geothermal power plants are impacted by the same abiotic and microbial processes. These processes, however, can cause unique fouling problems in industrial systems, which in turn require innovative solutions.

The cooling systems at the Cerro Prieto geothermal power plants are typical of those associated with many geothermal power plant operations. Soon after commissioning it became apparent that the performance of these plants was being impacted by the formation of both microbiological fouling and inorganic deposits. In this paper we describe the plants' efforts to identify the primary cause(s) of the cooling systems' deteriorating performance, and trials to evaluate a unique dispersant/penetrant for its ability to remove existing fouling

deposits, prevent the formation of new fouling deposits, and restore the cooling system to efficient operation.

## 1.1 Geothermal Power in Mexico

Mexico is the world's fourth largest producer of geothermal power, with net installed capacity of 1069 MW, and an additional 481 MW planned or under development (Geothermal Energy Association, 2016). Cerro Prieto, located in northern Mexico, is the largest of five major geothermal fields, with installed capacity of 720 MW in 13 operating units. The first two units of Cerro Prieto I were commissioned in 1973. Cerro Prieto IV (CP IV), commissioned in 2000, comprises four 25 MW single flash units (Flores-Armenta, 2012). In 2011, four of thirteen units at Cerro Prieto were decommissioned due to lack of steam, reducing capacity from 720 MWe to 570 MWe (Miranda-Herrera, 2015).

Other major geothermal power plant operations in Mexico include Los Azufres (194 MW installed, 75 MW near completion), Los Hornos (93 MW installed, 6 x 5MW noncondensing units decommissioned, 2 x 25MW units under development), Tres Virgenes (10 MW) and San Pedro Lagunillas (5MW installed, 2 x 25MW under development; (Flores-Armenta, 2012; Gutierrez-Netrin, et al, 2015). Cerro Prieto, Los Azufres, Los Hornos and Tres Virgenes plants are operated by the state-owned Compania Federal de Electricidad (CFE). The San Pedro Lagunillas plants are the first privately built and operated geothermal power plants in Mexico, and are operated by Grupo Dragon.

## 1.2 Geothermal Power Plant Cooling Systems

Many geothermal power plants utilize a cooling system to condense vapor exhausted from the steam turbine. Both air and evaporative cooling systems are used. In Dry Steam and Flash Steam plants using evaporative cooling systems, cooling water is used to condense the steam, either through a heat exchanger, or in a direct contact condenser. The condensed steam is often used as ultra-low TDS (Total Dissolved Solids) make-up water, replacing water lost from the cooling tower through evaporation and drift. As a result, impurities in the condensate (mainly dissolved gases associated with the steam) are mixed with the cooling water, and circulate through the entire cooling tower system. Condensate in excess of the amount required for cooling tower make-up is discharged from the cooling system, and is either reinjected along with the brine to recharge the geothermal reservoir, or discharged for surface disposal.

In binary cycle plants the hot geothermal brine is used to heat a secondary working fluid in a heat exchanger. The secondary fluid is then flashed to vapor to drive the turbine, and then cooled and condensed in a heat exchanger which interfaces with the cooling system. As a result, the geothermal brine and the secondary fluid never come in direct contact with the cooling water, and contaminants from the condensate or brine never enter the cooling system. For this reason, operational issues discussed in this paper apply to plants with evaporative cooling systems and direct contact condensers, but not to binary cycle plants.

### 1.3 Non-condensable Gasses in Steam Condensate

Geothermal brines and geothermal steam typically contain a number of non-condensable gasses (NCG's). NCG's are present in the dry steam, or appear in the gas phase when high temperature, high pressure brine is flashed to produce steam. NCG's typically make up less than 5% of the flashed vapor, but can make up to 27% of the total gas phase in some cases (Haklidi, et al, 2011). Carbon dioxide is the dominant NCG, followed by H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>. NCG's have a significant negative effect on the performance of both the steam turbine and the condenser (Khalifa and Michaelides, 1978). The presence of H<sub>2</sub>S in the NCG's also raises safety and environmental concerns, frequently requiring the application of sulfide abatement technologies.

In direct contact condensers NCG's will partition into the condensed steam, or condensed steam + cooling water mixture. Condensate/cooling water containing the NCG's flows from the condenser hotwell to the cooling tower. In this fully oxygenated environment H<sub>2</sub>S, NH<sub>3</sub> and CH<sub>4</sub> are susceptible to both chemical and microbiological oxidation. Microbial oxidation of H<sub>2</sub>S and NH<sub>3</sub> by specific microbial populations can produce sulfur and nitrogen-based inorganic acids, making pH control in the system necessary in order to minimize corrosion concerns (Clevinger, 1991; Islander, et al, 1991; Sarmago and Ho, 2001).

Oxidation of H<sub>2</sub>S to elemental sulfur is also frequently observed in geothermal power plant cooling systems (Chihiro, et al, 2003; Kudo and Yano, 2000; Richardson, et al, 2012). The elemental sulfur appears in the cooling system as particulate solids suspended in the recirculating cooling water, and as deposits in the cooling system piping, on cooling tower spray nozzles, on cooling tower fill surfaces, in the main and gas extraction system condensers, and at various locations in the auxiliary cooling systems. Sulfur deposits can (1) impede cooling water flow in pipelines, (2) accumulate in cooling tower fill, producing channeled flow and reduced cooling efficiency, (3) increase fill weights beyond design limits, (4) reduce heat transfer efficiency, and (5) accelerate corrosion. As a result, removal and prevention of sulfur deposits is a critical objective of all geothermal power plant cooling water treatment programs.

## 2. INVESTIGATION OF CP IV COOLING SYSTEM PERFORMANCE DETERIORATION

CP IV operating data provided clear evidence that deteriorating cooling system performance was having a direct impact on power generation. An investigation was undertaken to identify the cause(s) of poor cooling system performance, and develop a plan to remedy the problem(s).

### 2.1 CP IV Plant Operating Environment

CP IV consists of four single flash operating units (Units #10, #11, #12 and #13) of 25 MW each. Each Unit has an independent evaporative cooling water system with a volume of approximately 400,000 gallons (1514 m<sup>3</sup>). The cooling system includes a direct contact condenser where cooling water mixes with steam/condensate. The condensate serves as ultra-low TDS make-up to the cooling water system.

Cerro Prieto geothermal fluids contain the non-condensable gasses CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub> and CH<sub>4</sub>. CFE analysis of CP IV steam indicated 15,640 ppm CO<sub>2</sub>, 546 ppm H<sub>2</sub>S and 81 ppm NH<sub>3</sub>. Condensate pH was determined to be 5.34. Condensate TDS was 30 mg/L. Sulfate was not detected in the condensate.

The CP IV cooling system normally operates, with caustic additions, at a pH of approximately 6.7 to 7.0, although occasional acid pH excursions do occur. Among CP IV Units #10, #11, #12 and #13, cooling water TDS was reported to vary from 860 to 1470 mg/L (average, 1150 mg/L). Turbidity ranged from 7 to 27 NTU. Sulfate content of the cooling waters varied significantly, ranging from 240 to 1825 mg/L. Average sulfate concentrations in Units #10, #11, #12 and #13 at the time of this investigation were 904, 475, 707 and 676 mg/L, respectively. Nitrate and nitrite were previously detected in the ranges of 0.7 to 2.5 mg/L, and 0 to 2.0 mg/L, respectively. Prior to the trials the system was treated regularly with isothiazolone and methylene bis thiocyanate biocides to control microbial populations. Corrosion, scale and deposit inhibitors were applied as needed since commissioning.

### 2.2 Cooling Efficiency and Fouling in CP IV

CP IV cooling water systems performed as designed at commissioning, but over the first year of operation performance began to deteriorate, with cold-water temperatures gradually increasing. At the same time, power output from the plant declined despite increased steam use (Figure 1). Analysis of cooling system design performance curves showed that cooling efficiency was poor, and, after 3 years of operation, cold water temperatures were approximately 6 °C above design. All design considerations and operating parameters were evaluated in depth in an effort to identify the cause of the deterioration in cooling system performance.

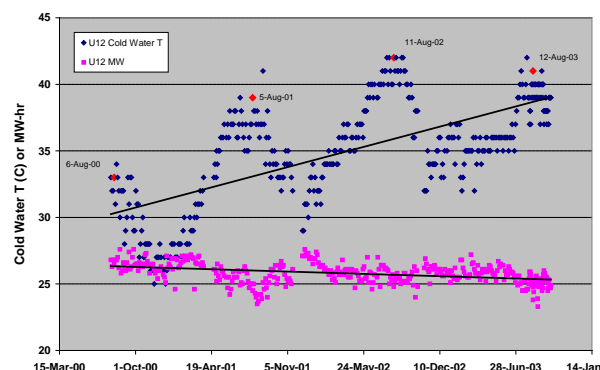


Figure 1. CP IV cooling system cold water temperatures gradually increased after commissioning in July 2000.

**Over the same period power output declined despite increased steam use.**

Design and operation of the cooling water system were determined not to be reasons for poor cooling system performance. Through the investigation, however, it became apparent that two types of fouling were occurring in the cooling tower, associated piping and equipment. Biological fouling (as microbiological and algal biofilms) was evident in the lower parts of the towers in areas with greater sunlight exposure, and was also observed to a lesser extent in the fill. Although present throughout the cooling tower, this fouling was not considered to be a major contributor to poor cooling system performance.

A second form of fouling was evident in the hot water distribution lines at the top of the tower, in the hot water spray nozzles on these distribution lines, and in the upper areas of the tower's high efficiency fill (Figure 2). This fouling appears as hard, white to yellow-white deposits, with thicknesses of up to 2 cm. Analysis of the deposits indicated their composition to be ~99% elemental sulfur. This is consistent with observations from geothermal power plant cooling water systems in Japan, New Zealand and the Philippines which experience similar sulfur fouling (Chihiro, et al, 2003; Kudo and Yano, 2000; Richardson, et al, 2013).



**Figure 2. Sulfur fouling of distribution lines (top), spray nozzles (middle) and tower fill (bottom).**

As noted previously, sulfur fouling in the hot water distribution lines at the top of the tower, if present at sufficient thickness, can restrict flow. Sulfur fouling in the spray nozzles results in an altered spray pattern which causes damage to the surface of the fill, and uneven accumulation of sulfur in the fill (Figure 3).



**Figure 3. Areas of heavy sulfur fouling beneath spray nozzles result in uneven water distribution through the cooling tower fill, and damage to the fill (red arrows).**

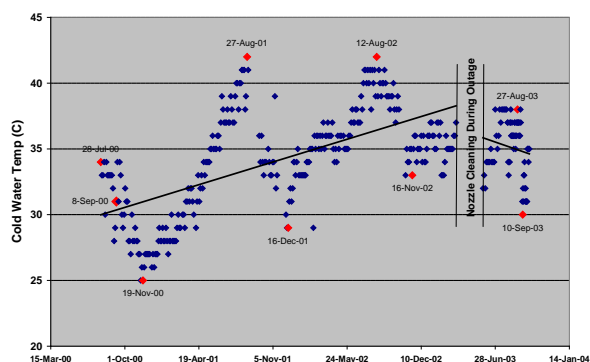
This pattern of nozzle/fill fouling results in uneven water distribution across the fill and channeled flow through the fill (Figure 4). The impact of this pattern of “channeled flow” is poor air-water mixing, and reduced cooling efficiency. A thermograph of a water curtain showing channeled flow in CP IV detected a 13 °C higher temperature in water from heavy flow areas (poor air-water mixing), compared to water in normal flow areas.



**Figure 4. Channeled flow due to uneven water distribution beneath sulfur-fouled spray nozzles.**

Extensive mechanical cleaning to remove sulfur deposits was shown to temporarily reverse the decline in cooling system performance (Figure 5), thereby confirming that this form of fouling had a significant impact on cooling system performance.





**Figure 5. Extensive mechanical cleaning of nozzles and distribution lines, and limited mechanical cleaning of the cooling tower fill resulted in improved cooling system performance in CP IV Unit #10.**

It soon became clear that restoring design cooling performance in this system would require two things: (1) removal of sulfur deposits from the distribution lines, spray nozzles and fill; and (2) prevention of the formation of new sulfur deposits once the system was cleaned. CP IV Maintenance Operations demonstrated that distribution lines and spray nozzles could be cleaned mechanically. Attempts to remove sulfur deposits from the cooling tower fill using mechanical cleaning methods, however, resulted in significant damage to the fill. Mechanical cleaning carries high manpower and equipment costs, and requires a complete system shutdown to conduct. Unscheduled maintenance outages result in lost power generation revenue. The inability to clean cooling tower fill by mechanical methods makes it necessary to budget for regular fill replacement. Between fill replacements fouling occurs and deposits accumulate, impacting cooling operations and reducing power generation efficiency. For these reasons, a chemical treatment which would be effective in removing existing sulfur deposits, and preventing the formation of new sulfur deposits was sought. An effective online chemical cleaning program would remove sulfur deposits from all wetted surfaces, including the cooling tower fill. Regular chemical treatments to prevent sulfur deposition would eliminate unscheduled maintenance outages, and would maintain full cooling system and power generation efficiencies. The costs and cost savings of mechanical methods vs. chemical treatments for the management of sulfur fouling will vary significant from country to country, and therefore must be carefully evaluated for each facility.

### 3.0 EVALUATIONS OF DISPERSANT TREATMENTS TO REMOVE SULFUR DEPOSITS, AND PREVENT BIOFOULING AND SULFUR DEPOSITION

Previous attempts to control sulfur deposits in other geothermal power plant cooling systems were based on surfactant, dispersant and deposit control chemical treatments (Chihiro, et al, 2003; Kudo and Yano, 2000; Sarmago and Ho, 2001). These treatment programs delivered varying degrees of success as preventative treatments. None, however, were reported to remove existing deposits in online treatment programs.

AMSA's BCP™ 5030 (DTEA II™) is used as an organic and inorganic deposit cleaner and penetrant aide. It has been used extensively in Biofouling Control Programs in industrial cooling

water applications. It has also been used for organic and inorganic deposit control in the oil and gas, mining and manufacturing industries. Based on this product usage profile and AMSA's understanding of the interrelated sulfur fouling and biofouling problems in the CP IV evaporative cooling systems, AMSA recommended to CP IV operations management a series of two evaluation programs. The objective of these evaluations was to demonstrate BCP™ 5030's ability to penetrate and disperse existing sulfur and biofouling deposits, maintain the system free of fouling deposits, and restore cooling system to as-designed performance.

#### 3.1 Unit #12 28-Day Trial

The plan for evaluation of BCP™ 5030 included a 28-day trial to assess the product's ability to remove existing sulfur and biomass deposits, followed by a 3-month trial to evaluate the ability of the product to prevent the formation of new deposits, and prevent deterioration of cooling system performance.

##### 3.1.1 Unit #12 28-Day Trial – Chemical Treatments

The initial trial of 28 days was conducted to determine if BCP™ 5030 was able to destabilize existing sulfur deposits in Unit #12. The tower's screens were cleaned before the trial, but no other cleaning was done in preparation for the trial. BCP™ 5030 was slug-dosed into the system daily; no other chemicals were applied during the trial. On the first day three doses of 138 ppm BCP™ 5030 (as 30% active product) were applied to the system. All other daily doses were 50 ppm BCP™ 5030 (15 ppm a.i.), except for approximately weekly higher doses of 75 or 100 ppm. A total of 825 gallons of BCP™ 5030 was added to the system in 31 doses over the 28 days of the trial. Routine operating data and water quality data were monitored throughout the trial.

##### 3.1.2 Unit #12 Trial -- Indications of Deposit Removal

Immediately upon commencement of BCP™ 5030 dosing, turbidity of the recirculating water began to increase. The water became increasingly milky/turbid (3 FAU before dosing, 15 FAU 3h after dosing, 40 FAU after 8 days, and 60 FAU after 23 days of daily dosing), suggesting dispersion of particulate sulfur from existing sulfur deposits. The tower's primary screen was lifted for inspection on the second day of the trial, revealing that biomass in the system was also effectively dispersed by the treatments. Populations of both general heterotrophic bacteria and sulfate-reducing bacteria were high ( $10^5$  to  $10^6$  CFU/mL and  $10^3$  to  $10^4$  CFU/mL, respectively), and highly variable, as biofouling deposits within the system were disrupted and dispersed. Initiation of detachment of algal fouling deposits also was observed. As the trial progressed, medium and large pieces of detached sulfur deposit (up to 7 cm on the long axis) were observed in the cooling system.

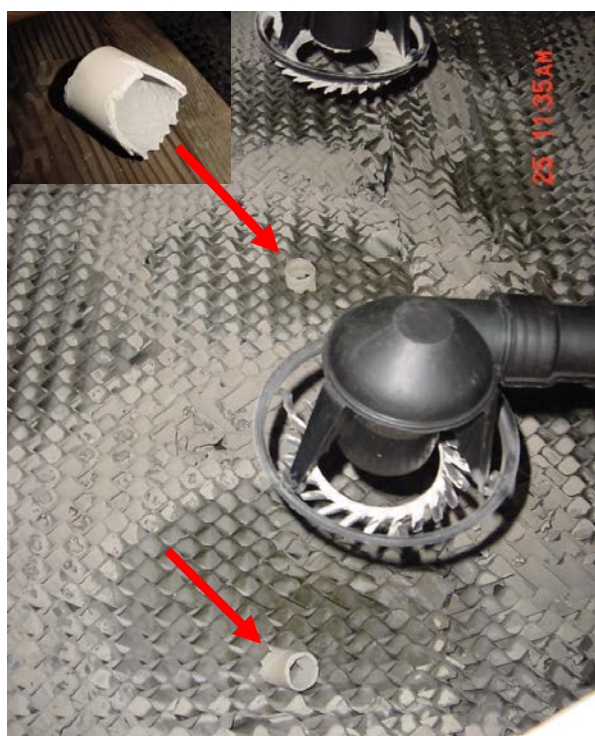
##### 3.1.3 Unit #12 28-Day Trial -- Inspection

An inspection conducted at the end of the trial revealed large pieces of detached sulfur scale on the top of the tower's fill, presumably released from the hot water distribution lines. Spray nozzles were significantly cleaner. At some locations intact sulfur cylinders matching the dimensions of the nozzle orifice were found on top of the fill immediately below the nozzles (Figure 6), suggesting adhesion of the deposit to the

nozzle surface had been reduced sufficiently for flow-induced shear to remove the deposit.

### 3.1.4 Unit #12 28-Day Trial -- Conclusions

The ability of BCP™ 5030 to destabilize and disperse hard elemental sulfur fouling deposits and biofouling deposits was confirmed in the 28-day trial. Sulfur was removed from surfaces as suspended particulate solids, small chips/flakes, and larger pieces (up to 7 cm.). The suspended particulate sulfur solids and smaller sulfur flakes leave the system with blowdown from the cooling tower. The larger sulfur pieces accumulate in the cooling tower basin and can be removed by basin vacuuming or during scheduled outages. Based on the results from the 28-day trial a 3-month trial to evaluate the ability of BCP™ 5030 to prevent sulfur fouling and maintain system performance was approved and planned.



**Figure 6. Spray nozzle orifice fouling deposits were expelled intact onto the tower fill.**

### 3.2 Unit #11 3-Month Trial

Based on observations of sulfur deposit removal in the 28-day trial in Unit #12, a 3-month performance metrics-driven trial was planned for Unit #11. Plant performance metrics monitored during the trial included: load, condenser vacuum, cold and hot water temperatures, wet and dry bulb temperatures, recirculation rate, and steam flow. Cooling water monitoring during the trial included: pH, TDS, turbidity, sulfate, nitrate/nitrite, general heterotrophic bacteria and sulfate-reducing bacteria.

Both Unit #11 and Unit #12 were cleaned mechanically immediately before the 3-month trial, and both began the trial operating with cold water temperatures 1.5 °C above design (08:00h data). Unit #10 had been cleaned approximately 7 months before the trial, and began the trial operating at 4.2 °C

above design cold water temperature. Unit #13 had not been cleaned within the year before the trial, and began the trial operating at 5.5 °C above design cold water temperature.

### 3.2.1 Unit #11 3-Month Trial – Chemical Treatments

Unit #11 was treated with BCP™ 5030 (30% active) throughout the 3-month trial. Unit's #10, #12 and #13 were not treated with BCP™ 5030. BCP™ 5030 was applied in Unit #11 6 days per week. The initial slug dose was at 137.5 ppm (as product). Slug doses on days 2 and 3 were at 68.75 ppm, and slug doses for the remainder of the first week, and for the subsequent 4 weeks were at 50 ppm. Slug doses over the remaining 8 weeks of the trial were at 37.5 ppm.

### 3.2.2 Unit #11 3-Month Trial -- Interim Inspection

One month into the 3-month trial Unit #11 was shut down for an interim inspection. This inspection documented that for the first month of the trial BCP™ 5030 treatments had prevented the formation of new sulfur fouling deposits on spray nozzles and tower fill.

### 3.2.3 Unit #11 3-Month Trial -- Cooling System Performance

Evaluation of cooling performance through the 3-month trial revealed that BCP™ 5030 treatments not only prevented deterioration of cooling performance in Unit #11, but actually improved performance as a result of additional cleaning of the cooling tower fill and other areas of the cooling system not accessible to mechanical cleaning. At the end of the trial Unit #11 was operating at 1 °C above design cold water temperature (08:00h data), an improvement of 0.5 °C (Figure 7).

In the absence of BCP™ 5030 treatments, the performance of Unit's #10, #12 and #13 deteriorated (Figure 7). Unit #12, cleaned before the trial and performing similar to Unit #11 at the beginning of the trial, but not treated with BCP™ 5030 during the trial, ended the trial operating at 3.9 °C above design cold water temperature, an increase of 2.4 °C. Units #10 and #13 ended the trial operating at 7.2 and 8.6 °C, respectively, above design cold water temperature, increases of 3.0 and 3.1 °C, respectively. These results demonstrate that BCP™ 5030 treatments will prevent sulfur fouling and the resulting deterioration in cooling performance in clean systems. In the absence of BCP™ 5030 treatments, both clean and fouled cooling systems experienced sulfur fouling and deterioration in cooling system performance while operating under the same conditions.

### 3.2.4 Unit #11 3-Month Trial -- Condenser pressure

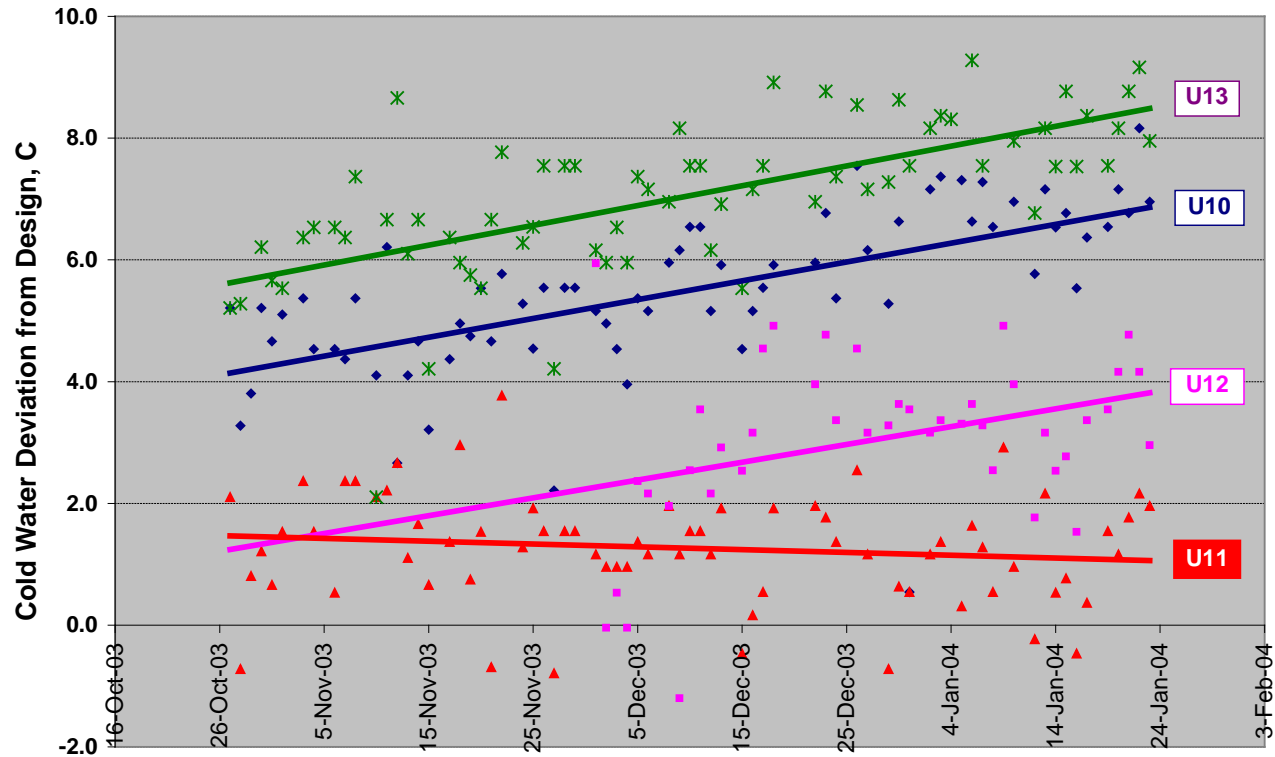
Improved cooling system efficiency results in colder cooling water, enabling more effective steam condensation, which in turn results in lower condenser pressures (i.e., greater vacuum). Lower condenser pressures translate into more efficient turbine operation, and result in greater power generation. Condenser performance over the trial period, measured as average condenser pressure (mm HgA) for Unit's #10, #11, #12 and #13 (08:00h and 14:00h readings) is shown in Figure 8. The results show Unit #11, treated with BCP™ 5030 and operating with the lowest cooling water temperatures, had the lowest condenser pressure. Conversely, Unit #13, with the highest cooling water temperatures had the highest condenser pressures. Over the long term it is

reasonable to expect that improved cooling system efficiency resulting from regular BCP™ 5030 treatments will result in improved power generation capability in geothermal power plants susceptible to sulfur fouling.

### 3.2.5 Unit #11 3-Month Trial – Cooling Water Sulfate

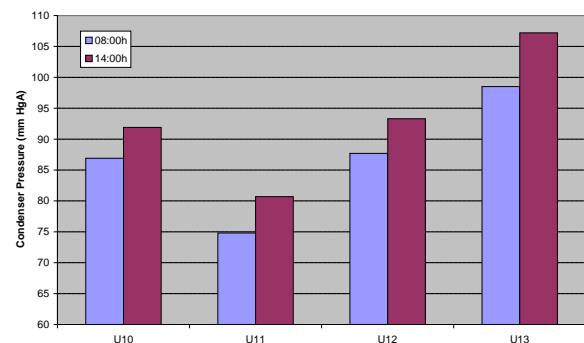
Cooling water sulfate concentration was monitored throughout the trial. Sulfate in geothermal cooling waters is primarily a product of SOB (Sulfur Oxidizing Bacteria) activity, although

some air oxidation of  $H_2S$  to elemental sulfur and more oxidized forms of sulfur undoubtedly occurs (Culivicchi, et al, 2005; Richardson, et al, 2013). An investigation comparing abiotic (chemical) and biotic (microbiological) sulfide oxidation rates concluded that chemolithotrophic (microbial) sulfide oxidation rates are in many cases three or more orders of magnitude greater than non-microbial rates, suggesting that in many environments, potentially including geothermal cooling system waters, microbial sulfide oxidation processes



**Figure 7. Cooling system performance of Units #10, #12 and #13 (not treated with BCP™ 5030) deteriorated over the 3-month trial. Cold water temperatures increased, and deviation from design increased. Over the same period and under the same operating conditions, cooling system performance of Unit #11 (treated with BCP™ 5030) improved.**

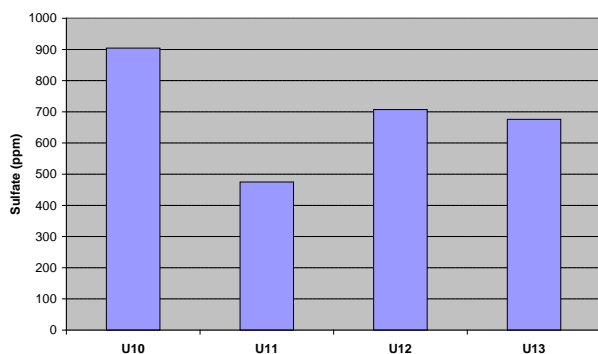
will be the primary mechanism of sulfur and sulfate generation from sulfide (Luther, et al, 2011).  $H_2S$  oxidation resulting in sulfur deposit formation is believed to be initiated in biofilms containing Sulfur Oxidizing Bacteria (Kudo and Yano, 2000). In systems where sulfur deposits have formed, the oxidation of elemental sulfur to sulfate will occur where the sulfur has accumulated, including at the surface of the sulfur deposits. Microbial oxidation of reduced sulfur compounds to sulfate (as  $H_2SO_4$ ) can produce highly acidic localized and bulk water pH's, resulting in accelerated corrosion of susceptible metals and concrete.



**Figure 8. Unit #11, treated with BCP™ 5030 throughout the trial, had the coldest water temperatures, and the lowest average condenser pressures.**

BCP™ 5030 treatments in Unit #11 prevented sulfur deposits from forming, and in general, prevented biofouling in the cooling tower and throughout the cooling system. Unit #11 also had the lowest average sulfate levels at the end of the trial

(Figure 9), suggesting the lowest overall conversion of H<sub>2</sub>S to sulfate in this system. This, in conjunction with prevention of sulfur deposition in the cooling system throughout the trial suggests BCP™ 5030 both prevented the accumulation of elemental sulfur deposits, and possibly through this mechanism, reduced the rate of oxidation of reduced forms of sulfur to sulfate. A reduced rate of sulfur-to-sulfate conversion in the cooling system would be expected to reduce the frequency of acid pH excursions in the cooling system.



**Figure 9. Average sulfate concentration over the final 6 weeks of the trial. BCP™ 5030 treatments in Unit #11 resulted in effective biofouling control, which in turn limits biofilm-based microbial processes, including sulfur deposition and sulfur oxidation to sulfate.**

### 3.2.6 Unit #11 3-Month Trial -- Nitrite, Nitrate

Further evidence of improved microbiological control during the 3-month trial can be seen in the cooling water nitrite and nitrate levels, which were lowest in Unit #11 at the end of the trial (2.3 and 2.4 mg/L, respectively, versus 3.6 and 3.6 mg/L, respectively, in Unit #10, 3.0 and 2.9 mg/L, respectively, in Unit #12, and 2.8 and 3.4 mg/L, respectively, in Unit #13). Nitrite and nitrate in geothermal cooling waters are typically products of the activity of nitrifying bacteria (ammonia oxidizing bacteria and archaea, and nitrite oxidizing bacteria); (Clevinger, 1991). Both Sulfide and Sulfur Oxidizing Bacteria, and Ammonia and Nitrite Oxidizing Bacteria and Archaea produce acidic metabolic byproducts (sulfurous and sulfuric acids, nitrous and nitric acids) which are frequently responsible for acid pH excursions in geothermal cooling waters (Clevinger, 1991; Sarmago and Ho, 2001). Aggressive sulfur deposit prevention treatments based on BCP™ 5030 have the added benefit of maintaining biofouling at a minimum in these systems, thereby providing some measure of sulfide/sulfur and ammonia/nitrite oxidizing bacteria control, and through this action, limiting the frequency of inorganic sulfur and inorganic nitrogen acid pH excursions.

### 3.2.7 Unit #11 3-Month Trial -- Aerobic Bacteria and SRB

The impact of aerobic heterotrophic bacteria on geothermal cooling water system operations has not been systematically studied, but is likely very similar to their impact on other industrial cooling water systems. These organisms grow primarily in biofilms, and, along with sulfide/sulfur-oxidizing and nitrifying microorganisms, contribute to the development of biofouling deposits in the system. Monitoring planktonic (water-borne) heterotrophic bacteria generally has limited value as an indicator of biofilm-based populations in a system.

However in systems not aggressively treated with biocides, these populations can be used as a general indicator of the overall level of microbial activity in a system. In the 3-month trial in Unit #11, clean surfaces were generally kept free of biofouling deposits by the BCP™ 5030 slug doses applied 6 days per week. Initial high concentration doses were followed by several Total Heterotrophic Bacteria population counts in the 10<sup>5</sup> to 10<sup>6</sup> CFU/mL range as biofouling deposits inaccessible to mechanical cleaning methods were disrupted and removed from the system. Total Heterotrophic Bacteria counts after the initial high concentration slug treatments were generally in the 10<sup>3</sup> to 10<sup>4</sup> CFU/mL range. SRB (sulfate-reducing bacteria) counts in recently-cleaned Unit #11 were low or below detection at the start of the trial, and remained at this level throughout the trial. Together, these observations suggest that regular BCP™ 5030 treatments to control sulfur deposits contribute generally to improved microbial population control, and specifically to biofouling control throughout the system.

### 3.2.8 Unit #11 3-Month Trial -- Conclusions.

Under operating conditions in which both clean (Unit #12) and already-fouled (Units #10 and #13) cooling systems experienced significant deterioration in cooling performance in the absence of BCP™ 5030 treatments, Unit #11 cooling system remained free of sulfur and biofouling deposits, and demonstrated improved cooling system performance (as indicated by lower chilled water temperatures) in the presence of BCP™ 5030 treatments. A summary of the key trial conditions and resulting changes in cooling system performance are summarized in Table 1.

Improved cooling system performance in Unit #11 also resulted in improved performance of the main condenser, as shown by Unit #11's lowest condenser pressure. Improvements in condenser vacuum allow for more efficient turbine performance and greater power generation.

In addition to de-aggregation and removal of hard sulfur deposits, daily BCP™ 5030 slug treatments also promoted dispersion of microbial and algal fouling deposits, and prevented the development of new biofouling deposits.

	Mechanically Cleaned Before Trial	Treated with BCP™ 5030 During Trial	Cold Water Deviation from Design <u>before</u> Trial (°C)	Cold Water Deviation from Design <u>after</u> Trial (°C)	Cold Water Deviation from Design <u>Change</u> (Δ °C)
Unit #10	No	No	4.2	7.2	+3.0
Unit #11	Yes	Yes	1.5	1.0	-0.5
Unit #12	Yes	No	1.5	3.9	+2.4
Unit #13	No	No	5.5	8.6	+3.1

**Table 1. Summary of 3-month trial conditions and changes in CP IV cooling system performance (as Cold Water Deviation from Design).**

Cooling water concentrations of sulfate and nitrite/nitrate, both products of microbial oxidation of NCG's H<sub>2</sub>S and NH<sub>3</sub>, were lowest in Unit #11, suggesting improved biofouling control also impacts these microbial populations which are known to contribute to sulfur deposition and acid pH control problems in geothermal power plant cooling systems.

## 4. CONCLUSIONS



Sulfur fouling, in the form of hard, tightly adherent deposits, was determined to be the primary cause of poor cooling system performance in CP IV. Removal of existing sulfur deposits from cooling system flow lines and spray nozzles by mechanical cleaning was shown to improve cooling system performance, but the fouling process resumed in the absence of preventative treatments.

In two evaluation trials BCP™ 5030 slug treatments were shown to remove existing sulfur deposits and prevent the formation of new sulfur deposits, delivering lower chilled water temperatures and improved condenser vacuum in CP IV's Unit #12 and Unit #11, respectively. BCP™ 5030 treatments also contributed to improved biofouling control. Lower sulfate and nitrite/nitrate levels in a cooling system treated with BCP™ 5030 suggests more effective biofouling control contributes to reduced activity of sulfide and ammonia oxidizing microbial populations. This may, in turn, contribute to reduced rates of microbially-mediated sulfur deposition and sulfur and nitrogen-based acid production.

Overall, the 28-day and 3-month chemical treatment trials in the cooling systems of CP IV demonstrate that BCP™ 5030 slug treatments can be used to control sulfur fouling and deliver conditions for optimal cooling system performance through online chemical treatments which reduce the need for regular shut-downs for mechanical cleaning.

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