# HYDROGEN PEROXIDE AS A GEOTHERMAL COOLING WATER BIOCIDE

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## ABSTRACT

Evaporative cooling water systems in geothermal power plants can pose a number of challenges for geothermal operators. The challenges of corrosion, deposition and biological control can be magnified in systems utilising direct contact condensers due to the presence of hydrogen sulphide in the cooling water. The presence of hydrogen sulphide results in the formation of elemental sulphur that can deposit throughout the cooling water system and restrict flow in pipe work, impact fill reliability and plant efficiency. Perhaps the most challenging aspect of the presence of hydrogen sulphide in the cooling water system is the limitations this places on biocide selection, and the resultant difficulties faced by some plants of maintaining effective cooling water control when faced with sulphur oxidising bacteria. This paper discusses the methods utilised by Mercury to monitor and control cooling water pH excursions as a result of sulphur oxidising bacteria in its geothermal cooling water systems, including the use of hydrogen peroxide to control sulphur oxidising bacterial activity.

## 1. INTRODUCTION

Mercury operates a range of geothermal power plants, including flash plants, binary plants and combined flash-binary plants. The two large flash plants, which utilise condensing steam turbines in the power generation process, are the 138MWe triple flash Nga Awa Purua (NAP) power plant and the 105MWe double flash Kawerau (KAG) power plant.

Both the NAP and KAG plants utilise direct contact condensers, and also have a similar non condensable gas content and composition in the geothermal steam. As a result, a significant amount of hydrogen sulphide is dissolved in the cooling water while it is in the condenser. While passing through the strongly aerated cooling tower, sulphide can oxidise to insoluble elemental sulphur. Hydrogen sulphide also provides a readily metabolised energy source for the growth of sulphur oxidising bacteria (SOB) which colonise the tower, forming a biofilm on the large surface area provided by the tower's fill material. The SOB bacteria oxidise hydrogen sulphide to either elemental sulphur or completely to sulphate, in the form of sulphuric acid. Elemental sulphur is believed to be an intermediate product, which can be further oxidised to sulphate or excreted from the bacterial cells, where it results in the formation of sulphur deposits within the cooling water system (Janssen et al. 1995; Jensen et al. 2009, 2011). In a mixed culture study of *Thiobacilli*, Janssen et al. (1995) showed that the formation of sulphur or sulphate as the end-product of sulphide oxidation is controlled by oxygen availability, with a restricted oxygen supply favouring elemental sulphur.

The sulphur deposits present a challenge to plant operators as they can restrict flow within the cooling water system, and foul the tower's fill-pack, resulting in efficiency degradation and, in severe cases, fill pack collapse. When the sulphur is further metabolised through to sulphuric acid, the quantity produced can overcome the natural pH buffering of the cooling water and cause the pH to drop as low as 2. Low pH cooling water presents a significant corrosion risk within the cooling water system itself (even where corrosion resistant materials are employed) as well as downstream in condensate/cooling water handling systems such as reinjection piping and wells.

New Zealand's geothermal cooling water systems have shown a propensity to reach a pH of 2 when sulphur oxidising bacterial activity remains unchecked, as previously described at this conference (Richardson et al. 2012). An example of such a period of pH instability for the Nga Awa Purua (NAP) cooling tower (in the early summer of 2015/16) is shown in Figure 1. The previous report of Richardson et al. (2012) described Mercury's experiences in controlling microbial growth in its cooling towers, including early experimentation with a range of non-oxidising biocides. This paper provides an update on this work and describes the evaluation and effectiveness of hydrogen peroxide as a novel oxidative treatment to control the SOB bacteria.

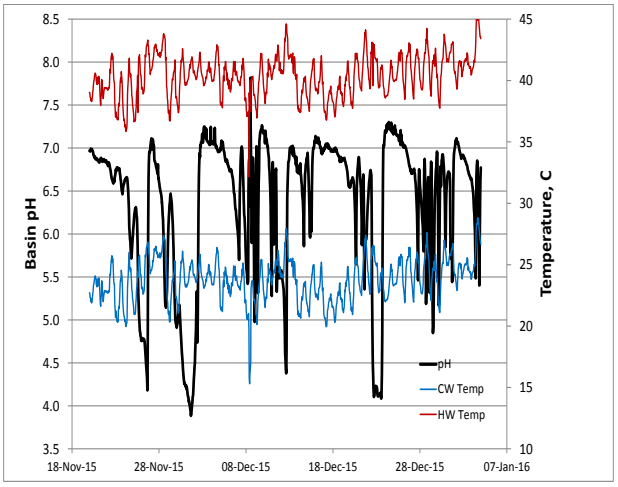


**Figure 1: Frequent cooling water pH excursions during the period late November, 2015 – early January, 2016**

## 2. GEOTHERMAL COOLING TOWERS

### 2.1 Cooling Water System Description

Figure 2 gives a schematic diagram of the cooling water system at Mercury's Nga Awa Purua (NAP) station, showing the design mass flows (for 100% station load).

With the recirculating flow to the tower at about 27,000 m³/h and an approximate system volume of 6,500 m³, the "recirculation time constant" of the tower basin is = 6,500/27,000 = 0.24 hours (~15 mins). In contrast, the dilution rate of the cooling water system is determined by the rate of "overflow" or "blow-down" from the Hot Well pumps to the reinjection well. Hence, the average retention time of water in the cooling tower is given by water volume/blow-down rate = 6,500 m³/278 m³/h ~24 hours. This is the retention time for the dissolved solids, since the water evaporated from the tower is essentially free of solids. With the hydraulic retention time being 100 times greater than the "recirculation time constant", the total system can be analysed as if it were a fully mixed system.

The NAP tower fill has a cross sectional area of 3000 $m^2$ and a depth of 2 m, giving 6000 $m^3$ of fill volume. The fill has a specific wetted surface area of about 133 $m^2/m^3$; meaning a total of 800,000 $m^2$ of internal surface area (0.8 square kilometers!)

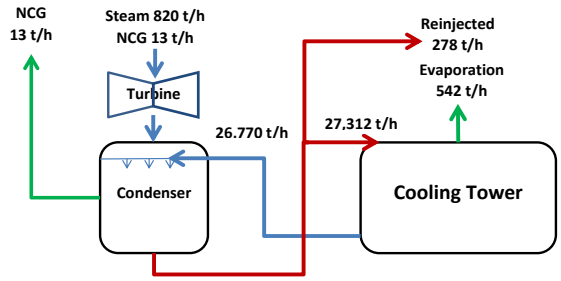


**Figure 2: Schematic drawing of the Condenser-Cooling Tower system, showing normal mass flow rates.**

### 2.2 Monitoring the Activity of the S-oxidising Bacteria

An effective way to monitor the activity of the Sulphur Oxidising Bacteria (SOB) is to measure the sulphate concentration in the cooling water. Since there is very little sulphate present in the steam to the turbine, any sulphate formed is essentially due to the activity of the SOB bacteria in oxidising sulphide to sulphuric acid. Abiotic oxidation of sulphide can also occur, but generally only accounts for a small proportion of observed sulphide oxidation, especially where active populations of SOB bacteria are present (Janssen et al. 1995; Jensen et al. 2009, 2011).

By reference to Figure 2, the hydraulic retention time of the NAP tower is (24/0.24) 100 times greater than the "recirculation time constant" of the tower. Hence, it is reasonable to analyse the cooling water system as if it were a completely mixed system ie. as if it were a stirred tank reactor of 6,500 m³ volume, with inflow as steam condensate and outflow as tower blow-down. Given this simplifying assumption and assuming the sulphate content of the steam to be negligible, we can calculate the rate of sulphuric acid (or sulphate) production from the following equation:

$SO_4$ Prodn Rate (kg/h) = $SO_4$ overflow rate (kg/h) + net accumulation of $SO_4$ (kg/h) ------- (1)

Figure 3 shows that cooling water conductivity is a very good predictor of sulphate concentration. This chart plots the monthly cooling water test results from 2010 – 2017 for the NAP cooling tower, for both the Hot Well and Cold Well sample points. In fact, the concentrations in respective Hot Well and Cold Well samples from each sampling event are essentially identical. Therefore, for practical purposes, the sulphate concentration in the cooling water can be estimated with reasonable accuracy from the on-line Conductivity measurement.

Cooling water pH is the other obvious indicator of the level of sulphuric acid production by the SOB bacteria. Figure 4 shows Cold Well pH versus sulphate concentration, plotting monthly Cold Well test results for the NAP cooling tower since 2010. The wide spread of results for both pH and sulphate concentration reflects the variations in microbiological condition of the cooling tower over the different seasons of the years. The shape of the curve clearly resembles an acid-base titration curve, reflecting the increasing amount of sulphuric acid produced by the SOB bacteria as pH declines. There is significant buffering capacity in the cooling water, mainly due to ammonia present in the geothermal steam condensate. This buffering explains the slow rate of change until about pH 7. But once this buffering is exhausted, the pH drops rapidly as acid concentration increases further. Based on the NAP cooling tower's normal blow-down rate, this pH drop occurs when the rate of sulphuric acid production exceeds about 45 kg/h.

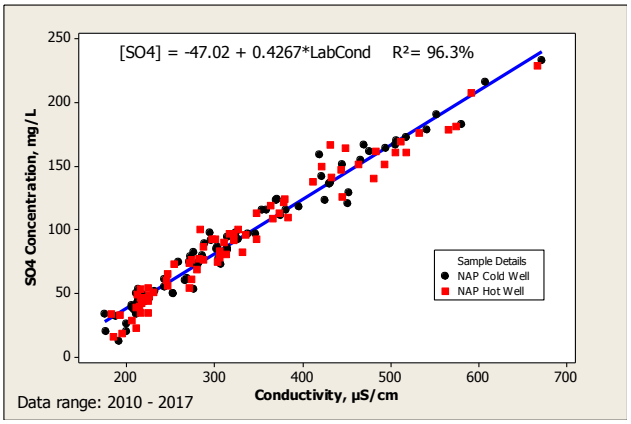


**Figure 3: Relationship between sulphate concentration and conductivity, sampled from the Hot and Cold Wells**

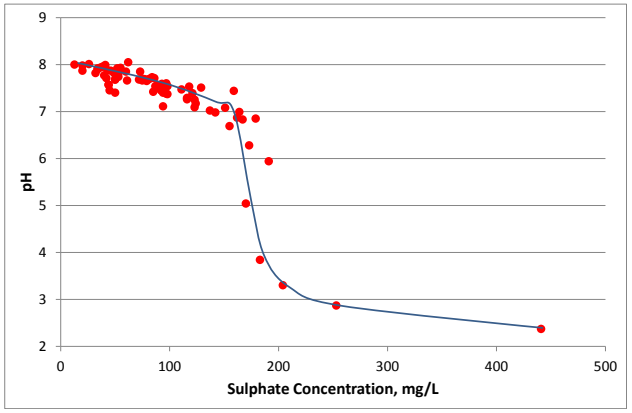


**Figure 4: Cold Well pH versus sulphate concentration, plotting monthly Cold Well test results for the NAP cooling tower, since 2010.**

### 2.3 The Partitioning Behavior of Hydrogen Sulphide in Geothermal Cooling Towers

Because of the central importance of sulphide oxidation in determining microbial growth potential in geothermal cooling towers, it is important to understand the behavior of hydrogen sulphide in the cooling water system.

This section makes use of a study by Baldacci et al (2002), who conducted a modeling and experimental validation study of the partitioning of $H_2S$ in both the direct contact condenser ($H_2S$ absorption) and cooling tower ($H_2S$ desorption) units of an Italian geothermal power station.

Their results for the desorption (stripping) experiments, using a pilot scale cooling tower apparatus, are reproduced in Figure 5. The desorption data are presented as ratios of total sulphide (as $H_2S$) in the outgoing liquid to that in the incoming liquid, over a range of pH values. The specific gas (air) and liquid loads ($m^3/h.m^2$ of packing cross-section) and the packing depth (2m) of this pilot system were comparable with these parameters for the NAP cooling tower. Hence, these results should be indicative of what happens in the Mercury cooling towers.

Somewhat surprisingly, these results (Fig. 5) show that the efficiency of sulphide stripping was only about 50% at neutral pH levels typical of normal cooling tower operation. They also show that stripping efficiency is relatively insensitive to the specific air load (or air velocity).

A conclusion from these findings is that a significant level of dissolved $H_2S$ and hydrosulphide ion should remain present and available to the SOB bacteria throughout the fill pack depth under normal operation. This is illustrated in Table 1, which presents a hypothetical profile of the concentrations of dissolved hydrogen sulphide ($H_2S$aq) and hydrosulphide ion through the fill-pack depth of the NAP cooling tower. An incoming total sulphide concentration (as $H_2S$) in the hot well water of 3.5 mg/L is assumed (similar to measurements from the NAP hot well water).

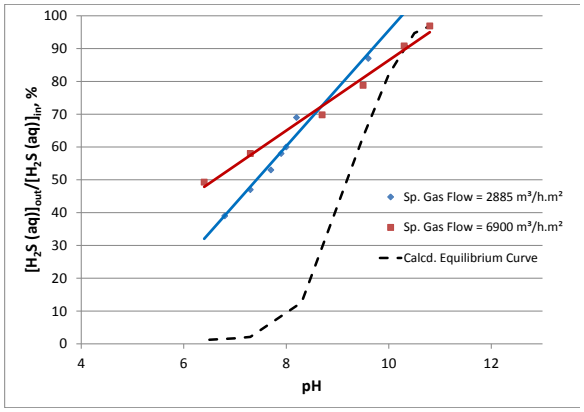


**Figure 5: Experimental results (reproduced from Baldacci et al, 2002) from $H_2S$ stripping trials conducted in a pilot scale cooling tower under two different specific air loads. Stripping efficiency is presented as the concentration ratio (as %) of total sulphides (as $H_2S$) in the outlet liquid to that in the inlet liquid. The dotted line shows the calculated "Equilibrium Curve", which assumes that the partitioning and dissociation of $H_2S$ between the liquid and gas phases reaches equilibrium at each pH level.**

The water's pH is assumed to change from 6.0 to 7.5 as it passes through the fill pack, which is also consistent with typical pH values measured for hot well and cold well samples. This analysis also assumes linear profiles for pH and the concentration of $H_2S_{(aq)}$ through the fill-pack depth and that the dissociation of $H_2S_{(aq)}$ reaches equilibrium with the concentration of $HS^-$ according to its first dissociation constant ($K_1 = 9.6 \times 10^{-8}$). Hence, it does appear possible to obtain nearly 90% removal of the dissolved $H_2S_{(aq)}$ species, while only achieving 50% removal of total sulphide, consistent with the experimental findings of Baldacci et al. (2002).

Table 1: A hypothetical profile for dissolved $H_2S$ and $HS^-$ ion through the depth of fill pack within a geothermal power station's cooling tower. A linear concentration profile has been assumed for $H_2S$(aq) and pH, with the dissociation of $H_2S_{(aq)}$ assumed to reach equilibrium with the concentration of $HS^-$ according to its first dissociation constant ($K_1 = 9.6 \times 10^{-8}$).

| Concentrations in mg/L (except pH) | pH | [$H_2S$(aq)] | [HS-] | Tot. Sulphide (as $H_2S$) |
|---|---|---|---|---|
| top of Fill Pack (2.0 m) | 6.0 | 3.22 | 0.30 | 3.5 |
| 75% Fill Pack height (1.5 m) | 6.4 | 2.52 | 0.56 | 3.1 |

| | | | | |
|---|---|---|---|---|
| 50% Fill Pack height (1.0 m) | 6.8 | 1.83 | 0.96 | 2.8 |
| 25% Fill Pack height (0.5 m) | 7.1 | 1.13 | 1.41 | 2.6 |
| bottom of Fill Pack (0 m) | 7.5 | 0.44 | 1.30 | 1.8 |
| **Average concentrations** | | **1.83** | **0.90** | **2.76** |
| **Removal Efficiencies** | | **86.3%** | | **50%** |

### 2.4 Cooling Tower Microbiology and Legionella

Autotrophic bacteria are those capable of synthesizing all their cellular material from just inorganic nutrients and using carbon dioxide as their sole C-source. Most sulphur oxidising bacteria (SOB) are "strict autotrophs" (they cannot grow on organic carbon sources) and obtain the energy required for growth by oxidising sulphur-compounds - sulphide, elemental sulphur and thiosulphate - mainly to sulphuric acid. In geothermal cooling water, the presence of aqueous ammonia provides a readily available N-source for the SOB bacteria. The cooling tower temperature and pH ranges are also ideal for the growth of these bacteria; incoming hot water at 38 – 43°C, pH ~ 6 and cold well water between 17 - 24°C and pH ~ 7.5.

Heterotrophic bacteria are those which require an organic carbon and energy source for growth. Heterotrophs are able to colonise and grow in the biofilms which develop on the cooling tower's fill pack by utilizing the organic extracellular products and cell detritus produced by the SOB bacterial population.

Legionella species such as ***Legionella pneumophila***, which can cause Legionnaire's Disease, are heterotrophs. Heterotrophic bacteria can only colonise a geothermal power station's cooling tower under conditions in which the autotrophic bacteria have been able to proliferate, unless there is some organic carbon source available. Hence, it is essential to control the SOB population, in order to minimise the growth of heterotrophic bacteria and, hence, the risk of a Legionella outbreak.

The enumeration of heterotrophic bacteria in cooling water is done using the Heterotrophic Plate Count (HPC) method. The HPC test provides an indication of the size of the heterotrophic population within the tower fill. Although not routinely measured, SOB bacterial species can also be enumerated. Figure 6 shows some past bacterial count results for NAP's cooling tower over a 3-year period, where counts of both HPC bacteria and of a typical SOB species, ***Thiobacillus thioparus***, were measured.. Like most ***Thiobacillus*** species, ***T. thioparus*** is a "strict autotroph" and is not capable of growth on organic carbon sources. Hence, the SOB bacteria will not be included in the HPC counts, since they will not grow under the laboratory conditions used for the HPC test.

We have previously described the variable effectiveness of biocide treatment programmes in maintaining control of the bacterial populations in the NAP cooling tower (Richardson et al. 2012). This is well illustrated by Figure 6. There were two distinct periods when the basin pH went below 5.0 for extended periods of time:

1. A two week period from 2 – 14 Feb, 2012; and
2. Four separate pH excursions of 1 – 3 days duration, over the period 17 Mar – 23 Apr, 2013

While the days when bacterial counts were measured don't always line up exactly with these pH excursions, some clear conclusions can still be drawn from the data:

- During the stable pH period (prior to Feb, 2012) ***T. thioparus*** counts were generally an order of magnitude lower that the HPC counts;
- During the first extended period of low pH (2 – 14 Feb, 2012) ***T. thioparus*** counts were up to an order of magnitude greater than the HPC counts. The response to this major pH excursion was to neutralise with NaOH and repeatedly dose with carbamate biocide, which proved ineffective in reducing bacterial counts. A subsequent treatment with glutaraldehyde biocide finally proved effective in reducing both the HPC and ***T. thioparus*** counts.
- During the second period of repeated low pH events ( 17/3 – 23/4/2013), ***T. thioparus*** counts were again greater than or equal to the HPC counts, with glutaraldehyde treatment used in each case to regain normal pH stability. Note how the ***T. thioparus*** count increased by more than 2 orders of magnitude between 20th March and 10th April, indicative of the rapid re-growth often observed following biocide treatments.

Bierre and Fullerton (2015) conducted a kinetic analysis of bacterial sulphide oxidation to sulphuric acid, studied at pilot scale during development of the Wairakei Bioreactor for reducing emissions of sulphide to the Waikato River. They showed that pipes coated with a biofilm layer of just 0.4 mm thickness can achieve a maximum oxidation rate of about 10 g $H_2S/m^2/d$; equivalent to production of about 29 g $H_2SO_4/m^2/d$. At this activity level and biofilm thickness, the SOB bacteria would only need to colonise about 5% of the wetted surface area of the fill in NAP's cooling tower to produce the 45 kg $H_2SO_4$/h required for pH depression (as described in section 2.2). The Bierre and Fullerton (2015) study also showed that the half saturation constant, $K_S$ for sulphide oxidation is just 0.24 mg/L; meaning that these bacteria are very efficient at utilising low sulphide concentrations in water ($K_S$ is the substrate concentration at which the SOB bacteria can grow at half their maximum rate).

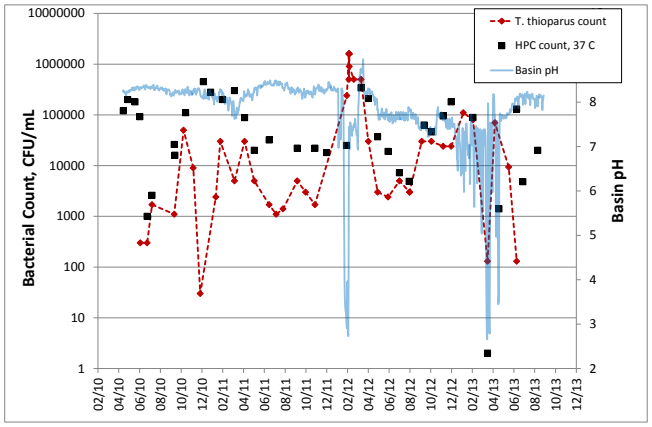


**Figure 6: Bacterial counts (monthly grab samples) of heterotrophic bacteria (HPC) and a typical sulphur oxidizing bacterial species (*Thiobacillus thioparus*) for the period May, 2010 – August, 2013, showing two periods of pH instability.**

### 2.5 Using Conductivity to Monitor the Activity of the Sulphur Oxidising Bacteria

Using bacterial counts to monitor the activity of the SOB bacteria does not provide fast enough feedback to allow timely application of biocide treatments. Because of the strong correlation between sulphate concentration and

conductivity (refer Fig. 3 above), basin conductivity (temperature corrected) has proven to be a reliable measure of the activity of the SOB bacteria. This is illustrated in Figure 7, where the effects of large diurnal temperature swings are mirrored in the changes in Cold Well conductivity. Note how the conductivity gradually decreased over the first 5 days, due to decreasing night-time temperatures, then significantly increased following two warmer days, and finally decreased again after two colder nights. This degree of sensitivity to ambient temperature is surprising, especially considering that the bacterial growth rate responds to the temperature of the cooling water, where the impact of ambient temperature changes is greatly attenuated.

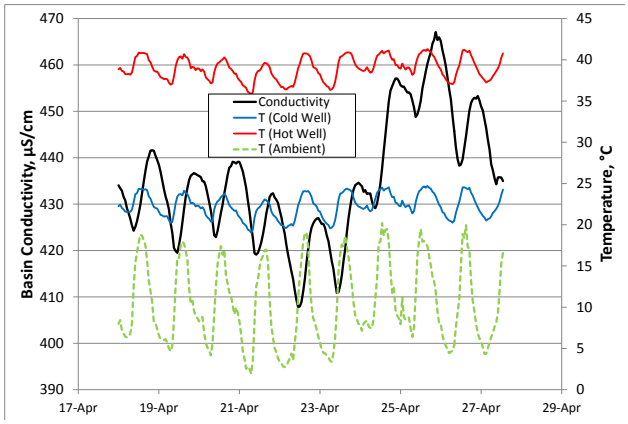


**Figure 7: Effect of diurnal temperature variation on basin conductivity changes.**

As described in Section 2.2, the Cooling Tower system can be modelled as a fully mixed bio-reactor, using conductivity as a predictor of sulphate concentration. In this way, the rate of sulphuric acid production within the tower can be indirectly estimated. Using this modeling procedure, the rates of sulphuric acid production (hourly averages) were estimated for different time periods (1 – 3 weeks duration in each case) selected from different times of the year and plotted against Cold Well temperature in Figure 8. The data from Figure 7 are represented by the green data points in Figure 8. The data fall into 3 distinct bands depending on the season and the slope of each band indicates the effects of temperature on SOB activity.

This plotting method normalizes for the temperature effect on bacterial activity. Therefore, the existence of different trend lines (or bands) indicates different levels of SOB activity (or biomass load) within the tower at different times of the year. Hence, it can be inferred that the load of SOB bacteria greatly increases as the seasons move from mid-winter to the hottest period of summer. As the data indicate, late summer 2016 was particularly hot, with a resultant high level of SOB activity (red data points). So it is no surprise that multiple pH excursions occurred during this hot summer period. Comparing the rates of sulphuric acid production (at the same Cold Well temperature) suggests that the mass or load of SOB bacteria in summer is about 4-5 times greater than in winter.

One other observation is that the slope of the curves becomes greater as the SOB biomass load increases, implying that the greater the amount of SOB bacteria in the biofilm, the more rapid is the increase in sulphuric acid production, as water temperatures increase. These large seasonal differences in SOB load will, of course, have been influenced by the tower's microbial control programme. Hence, it is likely that the chemical treatments proved more effective and gave more sustained "knock-down" in the cooler months.

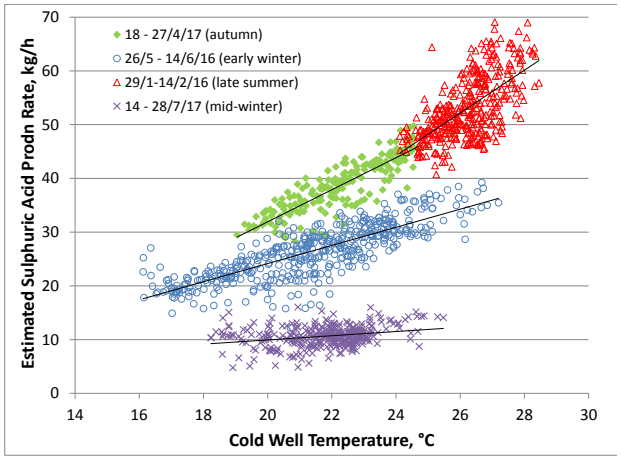


**Figure 8: Estimated sulphuric acid production rate versus Cold Well temperature for different seasonal time periods (data points are hourly averages, covering between 7 and 20 days duration)**

## 3. OXIDATIVE BIOCIDES FOR GEOTHERMAL COOLING TOWER APPLICATION

The selection of commercially available biocides that can be used successfully in Mercury's geothermal cooling water systems is limited by a number of factors, in particular, the chemistry of the cooling water. Hydrogen sulphide is readily oxidisable and reacts with the most commonly used oxidising biocides such as sodium hypochlorite. As a result, oxidising biocides are generally ineffective in cooling waters containing significant concentrations of hydrogen sulphide.

The Mercury stations have been using glutaraldehyde as the primary biocide, supplemented with quaternary amine and polyquat dispersants and the occasional use of MBT (methylene bisthiocyanate) and TTPC (tributyltetradecyl-phosphonium chloride) based biocides. However, maintaining control of the SOB bacteria and, hence, cooling water pH has continued to be problematic over recent summers. It became apparent that the bacterial populations were developing resistance to these non-oxidising biocides, even though the chemical applications were alternated to try and avoid this problem.

Because of these issues, a wider range of chemical treatments was sought, to help improve control of microbial growth in Mercury's cooling towers. While oxidative biocides had largely been discounted, they do have the advantage of being less susceptible to the development of microbial resistance. They are also much cheaper than typical non-oxidising biocides. Hence, we decided to look at oxidative agents again.

While control of the SOB bacteria is important to ensure the operational integrity of the cooling water system, the main reason for having a biocide programme is to minimise the

risk of the tower becoming colonised by ***Legionella*** species that can cause Legionnaires Disease. Hence, in the evaluation of any new biocide, it is important to confirm its efficacy against heterotrophic bacteria. This evidence is a necessary prerequisite for inclusion of a new chemical in a site's Legionella Management Plan.

Our initial work studied the in-situ generation of chlorine dioxide, through the acid catalysed reaction of hydrogen peroxide with sodium chlorate. Peroxide acts as a reducing agent in this reaction, which is used commercially in $ClO_2$ generators for the bleaching of wood pulps.

$$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + Na_2SO_4 + 2H_2O + O_2$$

We speculated that this chemistry could provide a "surgical approach", such that $ClO_2$ would only form within the biofilm in localised regions where sulphuric acid is being produced. However, the initial trials failed to show any significant formation of $ClO_2$, when the chlorate/peroxide mixture was dosed to the NAP cooling tower. This is probably because the acid concentration within the biofilm was too low for the above reaction to proceed. Despite this apparent lack of $ClO_2$ generation, a clear effect on tower pH and conductivity was observed. Further trials with hydrogen peroxide alone reproduced the same effect as seen with the chlorate/peroxide mixture. Hence, it appeared that hydrogen peroxide was causing the effect on pH and conductivity.

## 4. EXPERIMENTS WITH HYDROGEN PEROXIDE

### 4.1 Effects of Hydrogen Peroxide Treatment of Geothermal Cooling Towers

It was quickly found that quite low charges of hydrogen peroxide were effective in raising the cooling water pH and causing a gradual reduction in the water's conductivity. Figure 9 illustrates the effect of a 100 kg charge of 50% hydrogen peroxide, which is equivalent to a peak concentration of just 8 ppm in the 6500 m³ system volume. At this charge rate, when compared on a cost basis for control of SOB bacteria, peroxide can be as little as 5% of the cost of typical non-oxidising applications. Peroxide also has the advantage of generating environmentally benign break-down products ($O_2$ and $H_2O$), which reduces the limitations on condensate reuse, for industrial or agricultural purposes.

The treatment shows two characteristic effects:

1. A rapid increase in basin pH, starting almost immediately after peroxide addition. As a generalisation, the lower the starting pH, the greater the observed pH increase, which appears to be due to the reduced buffering present at lower pH levels.

2. Conductivity (sulphate concentration) declines almost linearly for about 24 hours after peroxide treatment. For reasons that remain unclear, the magnitude of the conductivity change can be variable, but lies mostly between 50 – 100 µS/cm (21 – 43 mg/L as sulphate). The gradual decline in conductivity is due to "wash-out" of sulphate, due to a sharp reduction in its production rate as soon as the peroxide charge was added (see later in Section 5 for more detail).

Experience gained following several trials with peroxide has shown the magnitude and longevity of the effect to be quite variable. In addition, it was unknown whether the peroxide treatment was having a biocidal effect on the heterotrophic bacteria. Hence, a dose-response trial was undertaken to better define the treatment's effect, looking particularly for evidence of biocidal activity with respect to the heterotrophic bacteria (see below).

### 4.2. Hydrogen Peroxide Chemistry in Geothermal Cooling Water

The rapid pH rise, following peroxide addition, appears to be mainly a result of its reaction with $HS^-$ ions. Under acidic and neutral conditions (pH < 8), hydrogen peroxide oxidises sulphide ions to elemental sulphur (in a colloidal form), with the consumption of one $H^+$ per hydrosulphide ion oxidised. The reaction with hydrogen sulphide is pH dependent, with the rate increasing under alkaline conditions with more complete oxidation to bisulphate and sulphate (Castrantas, 1980).

$$H^+ + HS^- + H_2O_2 \text{ ----------> } S^0 + 2H_2O$$

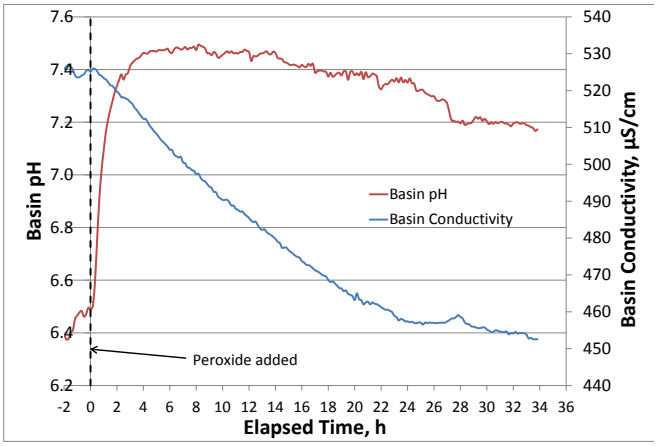


**Figure 9: Example of time course for basin pH and conductivity, following peroxide addition (100 kg of 50 % kg $H_2O_2$)**

Since $H_2S$ and $H_2O_2$ have the same molecular weight, 100 kg of pure $H_2O_2$ will oxidise 100 kg of $H_2S$, with the consumption of 100/34 = 2.94 kgmoles of $H^+$ ions. By reference to the titration curve of NAP tower's cooling water (Fig. 4) and the system volume, this amount of $H^+$ consumption appears to explain the observed "sharp pH rise".

Another possible reaction which will result in consumption of hydrogen peroxide, is the enzyme-mediated decomposition reaction. In the presence of the enzyme catalase, peroxide is rapidly decomposed to water and oxygen gas. This reaction neither produces nor consumes $H^+$ ions. Most aerobic organisms produce catalase and, hence, it is likely that this enzyme will be present in the cooling tower's biofilm.

$$2H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2$$

If significant, the catalase reaction will compete for peroxide with the hydrosulphide ion reaction. The test for catalase activity of bacterial isolates involves taking a small amount of bacteria from a single colony and dropping into a 3% hydrogen peroxide solution (30,000 ppm). Immediate and vigorous release of oxygen bubbles indicates a positive test (see Figure 10). We surmised that one reason for the observed variability in the effect of peroxide treatment may be the amount of catalase activity in the microbial biofilm and the possibility that repeated peroxide treatments would select for catalase-positive bacteria. Peroxide use in industries such as pulp and paper is known to be adversely affected when catalase activity builds up within the paper machine and bleach plant white water systems (Novozyme, 2005).

## 5. PEROXIDE DOSE-RESPONSE TRIAL

### 5.1 Trial Design

The purpose of this trial was to measure the biocidal effectiveness of hydrogen peroxide in the NAP cooling tower. The trial design was based on a series of three 1-day trials, at respective peroxide dose rates of 100, 200, and 300 kg (50%w/w solution). The three trials were conducted at approximately 14 day intervals in April 2017. Basin water samples were taken before and after each treatment and dispatched (chilled at < 4°C) for same-day HPC and catalase testing. A statistically representative number of bacterial colonies from the HPC agar plates (20 per water sample) were tested for catalase activity, in order to determine the percentage of heterotrophic bacteria that were catalase positive.

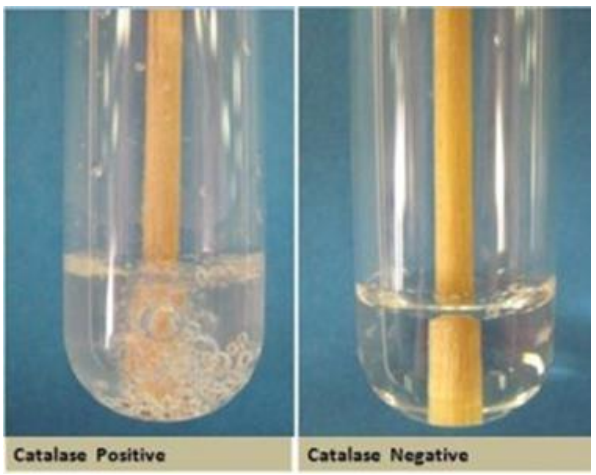


**Figure 10: Catalase positive and catalase negative tests**

Water samples were collected every 30 minutes, for 3 hours prior to application of the peroxide charge. Post-treatment sampling (also every 30 minutes for 3 hours) commenced 6 hours after peroxide was charged, allowing enough time for the residual peroxide to completely react. Hence, no peroxide residual should have been present in the samples.

### 5.2 Heterotrophic Plate Counts

Results for the 3 trial runs are summarised as box plots in Figure 11. The sampling methodology appears to have been satisfactory, since the HPC counts were quite consistent within each pre- and post-treatment sample set. The following observations can be made about the changes in HPC counts across the 3 trials:

- Only Treatment #2 (200 kg of 50% $H_2O_2$) showed a reduction in the cooling water's average HPC count, the post-treatment result being about 30% of the pre-treatment average.
- Treatment #1 (100 kg of 50% $H_2O_2$) showed a 2.5 fold increase, while Treatment #3 (300 kg of 50% $H_2O_2$) gave a 30 fold increase in average HPC count.

The concentration of viable bacteria in the cooling water is determined by its interaction with the biofilm layer. Therefore, one plausible explanation for increasing HPC counts is that the rate of bacterial release from the fill-pack's biofilm layer was increased by the peroxide treatments. To explore this explanation further a supplementary experiment was conducted during Treatment #3 (300 kg of 50% $H_2O_2$ charge). A 25 litre sample of the basin water was isolated from the main circulating flow (by filling a plastic bin, called the "basin water control"). This isolation was carried out immediately before peroxide was dosed to the cooling tower and a small volume of peroxide (1 mL of 50% $H_2O_2$) was added to the "basin water control" to achieve the same peroxide charge as was applied to the whole cooling tower. In parallel with the main trial, 3 samples were taken from the basin water control at 30 minute intervals, starting 6 hours after peroxide was dosed. HPC count results for this Basin Water Control experiment showed that the average count decreased to 30% of the pre-treatment count over the 6 hour period after peroxide addition. This reduction was due to either (or both):

i) the biocidal effect of hydrogen peroxide, and/or
ii) heterotrophic bacterial cell "turn-over", due to the water in the plastic bin having been isolated from the biofilm; the source of the nutrients required for heterotrophic growth.

As the concentration of residual $H_2S$ is normally very low in the tower basin, the peroxide added to the Basin Water Control would not have been consumed by reaction with $H_2S$. Additionally, the relatively low HPC count (7,000 CFU/mL) in the basin water is likely to have limited the rate of any peroxide decomposition due to catalase. Consequently, the peroxide (charged at 25 ppm) may have had enough "contact time" to explain the observed reduction in HPC count.

Despite the apparent biocidal effect observed in the Basin Water Control experiment, the main results from the three trial runs do not provide any clear evidence of significant biocidal activity due to hydrogen peroxide, at least in respect to the heterotrophic bacteria.

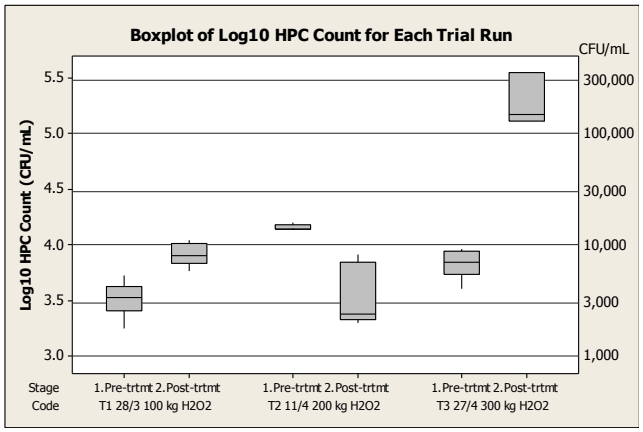


**Figure 11: Box Plots of $Log_{10}$(HPC bacterial counts) for basin water samples collected before and 6 hours after peroxide was dosed in each trial run (each data set consists of 6 samples taken at 30 min intervals)**

### 5.3 Catalase Activity of Heterotrophic Bacteria

A representative sample of bacterial colonies were randomly selected from the HPC agar plates and tested for catalase activity. Three of the six water samples, collected pre-treatment and post-treatment, were selected for catalase testing during Treatment #'s 1 and 2. With 20 bacterial colonies tested for catalase activity from each plate gave a total of 2 * 6 * 20 = 240 individual colonies.

All 240 colonies tested positive for catalase activity. These colonies were selected at random off the agar plates and the analyst attempted to avoid any biased selection (eg. by colony appearance). Therefore, it appears that almost all the heterotrophic species in the cooling tower are catalase positive, meaning they produce the enzyme which breaks down hydrogen peroxide to oxygen and water. Note that Legionella spp. are also aerobic heterotrophs and are known to be catalase positive.

Therefore it seems reasonable to suggest that hydrogen peroxide, at the charge levels evaluated in this study, is unlikely to be an effective biocide for controlling the Legionella risk, because of the presence of catalase, both within the bacterial cells, but also present in the biofilm (due to its release from lysed cells).

### 5.4 Effects of Peroxide Charge on pH and Sulphuric Acid Production

Figures 12 and 13 show, respectively, the pH and conductivity time courses for the 3 peroxide treatments. The initial pH's and conductivity levels varied between the 3 runs, mainly due to the ambient temperature history of the days and nights leading up to each trial (ie. average ambient temperatures were declining through April). Hence, a direct comparison of the pH and conductivity responses between each run is complicated by the sequential nature of the trials. Nevertheless, the following observations are clear:

- The sharp increase in pH started within about 10 minutes of the peroxide being dosed to the Cold Well
- The pH rose rapidly, stabilising after about 6 hours (refer back to Figure 9 for a close-up of the first 30 hours for the 100 kg 50% $H_2O_2$ treatment).
- The basin conductivity declined much more slowly, initially at a linear rate, then gradually slowing and reaching a minimum after about 24 – 30 hours.

For Treatment #1 (100 kg 50% H2O2) the pH started to rapidly decline after about 72 hours and a dose of glutaraldehyde was applied to halt the increasing rate of sulphuric acid production. Note how the pH response to the glutaraldehyde treatment is quite different from that after the peroxide treatments. The pH rise didn't start until about 2h after glutaraldehyde was dosed and the rate of pH increase was much slower than with peroxide.

Figure 13 also shows the calculated rates of sulphuric acid production during each trial, using the calculation procedure described in Section 2.2 (Eqn 1). Although there is some "noise" in the data, the effect of peroxide addition on the rate of sulphuric acid production can be clearly seen in all three trial runs.

- There was an immediate drop in the rate of sulphuric acid production of between 35% and 80% of the initial rate;
- The rate then stabilised and started to gradually recover after about 20 – 24 hours, regaining close to the original rate after about 72 hours.

Note that the effects of cooling water temperature changes on sulphuric acid production rate (due to ambient temperature changes) are confounded with the peroxide effect, but appear to explain most of the cyclical rate changes over the 80 hour time course shown in Figure 13 (temperature data not shown).

To quantify the reduction in sulphuric acid produced during each trial run, the area under each curve in Figure 13 was measured, giving the mass of sulphuric acid produced. These values were then subtracted from the amounts of sulphuric acid that would be expected from each trial, if the rate of production had stayed constant at the initial values. This dose-response effect is shown in Figure 14 as the kilograms of sulphuric acid that were not produced as a result of the peroxide treatment. A linear relationship appears to fit the data, confirming an increasing effect as the peroxide charge was increased. Inaccuracies in this quantification method are likely due to the effects of ambient temperature differences between each trial run.

The red dotted line in Figure 14 is a hypothetical reference line, showing the reduction in sulphuric acid production, based on the calculated amount of sulphide that could be removed by reaction with peroxide. Hence, this reference line assumes that any sulphide that is oxidised by peroxide is not then available to the SOB bacteria for conversion to sulphuric acid. In other words, it presents the maximum "chemical effect" that could be attributed to peroxide. The fact that the actual suppression of sulphuric acid production is much greater, confirms that peroxide has inhibited microbial activity.

In summary, it is clear that hydrogen peroxide is effective at temporarily reducing the rate of sulphuric acid production by the SOB bacteria. However, it remains unclear whether this effect is due to peroxide actually killing a proportion of the SOB's or simply inhibiting their activity.

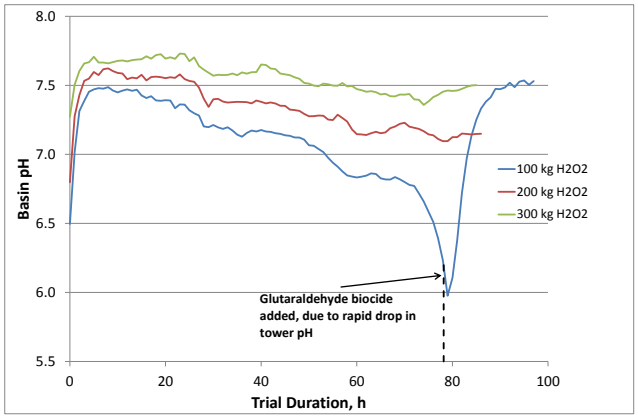


**Figure 12: Comparison of basin pH trends for each peroxide treatment. Peroxide addition was at time zero.**

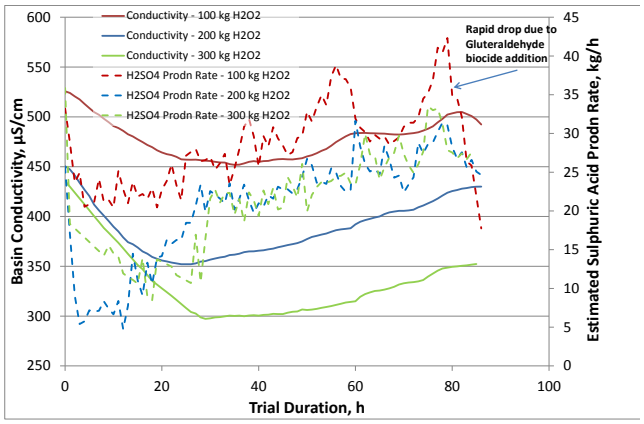


**Figure 13: Basin conductivity and estimated sulphuric acid production rates for the 3 peroxide dosage trials**

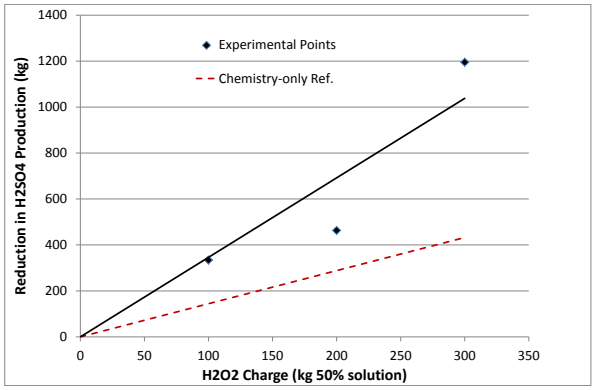


**Figure 14: Effect of peroxide charge on the reduction in sulphuric acid produced during each trial run. Reference line is the amount of sulphuric acid equivalent to the amount of sulphide-ion oxidized at each hydrogen peroxide charge level**

## 6. IS THE HYDROGEN PEROXIDE EFFECT BIOCIDAL OR INHIBITORY ?

Coughlin and Steimel (1997), in a laboratory-scale cooling tower study, showed that peroxide does demonstrate biocidal activity. However, experience from other industries shows that catalase activity in bacterial biofilms and white water systems is capable of rapidly destroying hydrogen peroxide (Novozyme, 2005; US Peroxide, 2017). While not constituting conclusive evidence of lack of efficacy, the presence of catalase activity in 100% of the bacterial colonies taken from the HPC plates in this study does provide a recognised mechanism to explain how the bacteria (especially in the biofilm) could be protected from hydrogen peroxide's "oxidative power". This result is unsurprising, since most aerobic bacteria are catalase positive, including most SOB bacteria (Veerender and Sridar, 2012; Sultan and Faisal, 2016).

So while the evidence is inconclusive, it seems prudent to take a conservative approach. Therefore, without proven efficacy, peroxide should not be relied on as part of the site's Legionella Management Plan.

Even in the absence of biocidal activity, there is clearly a "peroxide effect" on SOB bacterial activity. If this effect is attributable to inhibition, a plausible mechanism is required to explain it. The sudden removal of most of the hydrogen sulphide (after peroxide is dosed) temporarily removes the preferred energy source available to the SOB population. This will clearly reduce sulphuric acid production until the peroxide has been consumed. However, the recovery of sulphuric acid production does not start until about 20-24 hours after peroxide addition, much longer than the expected time that peroxide will remain present. However, it is conceivable that the SOB bacteria may shift their metabolism to using the abundant, but less energetically favoured, elemental sulphur as their energy source, as soon as the supply of $H_2S$ becomes restricted. Once $H_2S$ becomes fully available again (when the peroxide is consumed), an extended period of apparent inhibition could result from the bacteria then switching their metabolism back to sulphide. However, this hypothetical proposition doesn't explain why the sulphuric acid production rate didn't drop to zero, even at the highest peroxide charge level (see Fig. 13).

The following observations of pH and conductivity changes during a 23 hour plant trip at NAP do provide some interesting additional evidence. When the plant tripped on 4$^{th}$ of January this year, steam to the turbine was shut off, but the Cooling Tower kept running with cooling water circulation continued at half the normal rate, but with the fans turned off. The changes in pH and conductivity are shown in Figure 15. The increase in conductivity of about 50 µS/cm occurred over about 9 hours, despite the loss of $H_2S$ supply from the Condenser. This change in conductivity is equivalent to a 22 mg/L increase in sulphate concentration or 145 kg of sulphuric acid, calculated for the whole cooling water volume of 6,500 m$^3$.

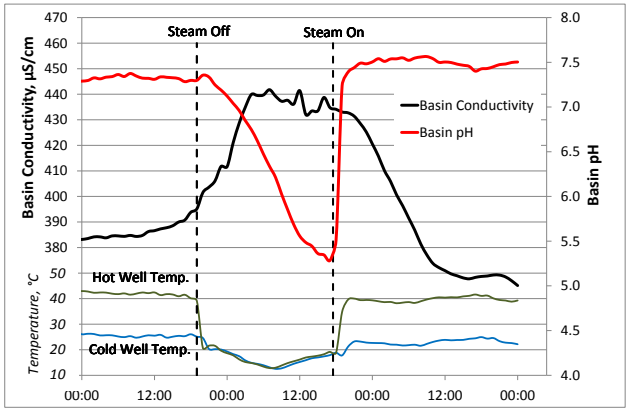


**Figure 15: Cooling water pH and Conductivity when the cooling system kept running during a 23 hour station trip (turbine off-line). The Hot and Cold Well temperatures are shown to indicate the plant trip's effect on cooling water temperatures.**

To explain the apparent continuation in sulphuric acid production, after loss of the $H_2S$ supply, suggests three possibilities:

1. That about 48 kg of dissolved $H_2S$ and hydrosulphide ion was "held up" within the tower biofilm and cooling water system and was oxidised by the SOB; or
2. The SOB bacteria immediately shifted to oxidising elemental sulphur to sulphuric acid, when the sulphide supply was exhausted.
3. That conductivity increased for some other reason (than on-going sulphuric acid production).

If explanation 2 is correct, it is unclear why sulphuric acid production abruptly stopped after about 9 hours, since the SOB bacteria can continue to grow at pH values as low as 2 and there is abundant elemental sulphur available in the fill-pack's biofilm layer. When the plant restarted, the shape of the conductivity decline curve fits with that expected when normal blowdown resumed and the sulphuric acid production rate returned to the pre-shut rate (the "wash-out" effect). Hence, this evidence suggests that the conductivity increase was due to sulphuric acid production.

Therefore, the first explanation appears the best fit to the available evidence, that a significant amount of sulphide was still available to the SOB bacteria, after the turbine and steam were off-line. This is perhaps an unexpected conclusion, given the expectation that sulphide is rapidly stripped from the cooling water on every pass through the tower. However, note the earlier hypothetical analysis of sulphide concentrations in the tower (see Table 1, Section 2.3) which indicates that significant steady-state levels of sulphide may be present through the fill-pack section of the tower.

## 7. CONCLUSIONS

Controlling microbial growth in these large geothermal cooling towers remains a challenge during the warm summer months. Conventional chemical programmes, based on non-oxidising biocides, are expensive and need to be regularly reviewed and adapted, to maintain their effectiveness. While further work is still required, this study has shown that hydrogen peroxide is a useful addition to the conventional chemical programmes.

Peroxide is able to raise the cooling water's pH and temporarily reduce the sulphide oxidising activity of the SOB bacteria. However, peroxide's effectiveness as a broad-spectrum microbial biocide seems doubtful at the low concentrations trialled. This is likely due to the presence of the enzyme catalase in most heterotrophic bacteria and, most likely, most sulphur oxidising bacteria as well. Hence, peroxide shouldn't be relied on for control of the Legionella risk, without evidence of efficacy. Nevertheless, peroxide offers promise when used as part of the overall chemical programme, in which control of the autotrophic, sulphur oxidising bacteria is of central importance.

Mercury will continue work with peroxide to better demonstrate the mechanism by which it inhibits SOB activity. This may lead to a targeted treatment strategy to maximise the effect and help maintain control of the SOB bacteria.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Baldacci, Aldo, Elisabetta Brunazzi, Chiara Galletti, and Alessandro Paglianti (2002) "Modelling and experimental validation of H2S emissions in geothermal power plants." ***Geothermics 31***: 501-517.

2. Bierre, E and Fullerton, R (2015) Hydrogen sulphide removal from geothermal power station cooling water using a biofilm reactor. In: Proc. World Geothermal Congress 2015. Melbourne, Australia, 19 -25 April, 2015.

3. Buisman, C.J.N, Jspeert, P.I., Hof, A., Janssen, A.J.H., ten Hagen, R., Lettinga, G. (1991) Kinetic parameters of a mixed culture oxidising sulphide and sulphur with oxygen. ***Biotechnology and Bioengineering***, Vol. 38.

4. Castrantas, H. M. (1980) Hydrogen sulphide abatement with hydrogen peroxide in geothermal operations. ***Geothermal Resources Council, Transactions*** Vol. 4, September, pp. 637 – 640.

5. Coughlin, M F and Steimel, L (1997) Performance of hydrogen peroxide as a cooling water biocide and its compatibility with other cooling water inhibitors. Paper No. 397 Corrosion 97 Conference.

6. Janssen, A J, Slyster, R, van der Kaa, C, Jochemsen, A. (1995) Biological sulphide oxidation in a fed-batch reactor. ***Biotechnology and Bioengineering***, Vol. 47.

7. Jensen, H.S., Lens, P.N., Nielsen, J.L., Bester, K., Nielsen, A.H., Hvitved-Jaconsen, T., Vollersten, J. (2011). Growth kinetics of hydrogen sulphide oxidising bacteria in corroded concrete from sewers. ***Journal of Hazardous Materials***, Vol. 189(3): 685-691.

8. Jensen, H.S., Nielsen, A.H., Hvitved-Jaconsen, T., Vollersten, J. (2009) Modelling of hydrogen sulphide oxidation in concrete corrosion products from sewer pipes. ***Water and Environmental Research***, Vol. 81(4): 365-373.

9. Novozymes North America (2005) Methods for controlling catalase. Patent WO 2005001056 A2 www.google.com/patents/WO2005001056A2?cl=en

10. Richardson, I, Addison, S., Addison, D. (2012). "Biological Control of Cooling Water in Geothermal Power Generation". In: Proceedings of New Zealand Geothermal Workshop. Auckland, Nov. 2012.

11. Sultan, S. and Gaisal, M. (2016) Isolation and characterisation of iron and sulphur oxidising bacteria from coal mines. ***Journal of Environmental and Earth Science***. Vol. 6(3):153-157.

12. US Peroxide Technologies. Activated sludge basin and dissolved oxygen. http://www.h2o2.com/pages.aspx?pid=168&

13. Veerender, K and Sridar, R. (2012) Isolation of autotrophic sulphur oxidising bacteria from marine environment. ***Advances in Applied Research***. Vol. 4(2):138-141.