OPTIMISATION OF CHEMICAL DOSING FOR TE MIHI COOLING TOWERS

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ABSTRACT

Te Mihi Uenukukopako (eew-new-koo-kor-par-kor) (Te Mihi) Power Station was commissioned in May 2014 but started experiencing cooling water pH control issues after 12 months operation. The alternating dual biocide programme of dosing a quaternary ammonium biodispersant/biocide (quat) one week then glutaraldehyde biocide (glut) the following week was no longer able to maintain control.

Alternative biocides were trialed to initially regain pH control, but it was then determined that the most cost and performance effective solution was to implement continuous caustic dosing, to compensate for the low concentration of ammonia in the steam and hence poor buffering ability to changes in pH, and to move to a less frequent, performance-based biocide dosing regime triggered by on-line conductivity monitoring and caustic consumption rate.

Te Mihi Power Station is a 2 x 83 MW double flash plant fed by the Wairakei geothermal field. Each unit has a c.4,400 m^3 main cooling water system designed to withstand the corrosive environment associated with aerated geothermal fluid for a pH range of 4.5 to 8. Exposed materials are fiberglass, PVC, 316L stainless steel and epoxy-coated concrete.

1. INTRODUCTION

1.1 Open Cooling Water System

Cooling water is drawn from the cooling tower basin through a single mesh screen by vacuum then sprayed into the steam exiting the turbine in a direct contact condenser. Non-Condensable Gases (NCG) are extracted in the condenser through a combination of steam ejectors and a Liquid Ring Vacuum Pump (LRVP). There is also a backup 130% steam ejector for the LRVP. Two 50% (2,900 kg/s each) hotwell pumps per unit distribute the liquid phase over an eight-cell forced-draft cooling tower. The holding time index (half-life) of the open cooling water system is approximately 20 hours.

There are also two 100% (460 kg/s) auxiliary cooling water pumps that circulate water from the basin to plate heat exchangers and to the inter/after condensers after the steam ejectors and to the LRVP on the NCG system.

1.2 Microbiological Control of the Open Cooling Water System

Major types of bacteria commonly found in geothermal systems are: (Bacon, et al., 1995)

- Slime producers, such as Pseudomonas, form biofilm on surfaces creating a habitat for other bacteria.
- Sulphur Oxidising Bacteria (SOB).
- Nitrogen bacteria, such as blue-green algae which can convert nitrogen gas to ammonia, and nitrifying bacteria which oxidise ammonia to nitrate.

As Te Mihi was a new station, there was a fairly extensive monthly microbiological testing of grab samples from both cooling towers as listed in Table 1.

Table 1: Monthly Microbiological Tests for Te Mihi Cooling Towers.

Test	Target Value (cfu/mL)
Legionella	Not detected (<20)
Heterotrophic Plate Count @ 25ºC Heterotrophic Plate Count @ 37ºC	<10,000 <10,000
SOB *Thiobacillus thioparus* SOB *Thiobacillus neapolitanus*	<20,000 <20,000
Nitrifying bacteria	<1,000
Denitrifying bacteria	<10,000
Iron precipitating bacteria	<1,000
Pseudomonas	<1,000

Geothermal recirculating cooling water systems are renowned for their ability to become acidic as a result of the proliferation of Sulphur Oxidising Bacteria (SOB) (Bacon, et al., 1995). SOB require the same basic macronutrients as plants: a nitrogen source, phosphorus (PO_4^{3-}), carbon (from carbon dioxide, CO_2) and hydrogen sulphide (H_2S). While most of the hydrogen sulphide is removed with the NCG's in the condenser some remains dissolved in the condensate. Condensate from geothermal steam supplies all of these required nutrients except for phosphorous, which can be provided by nearby agricultural and forestry environments where dust, pollen and insects may provide sufficient quantities. Phosphorous can also be introduced from adding surface water to the cooling water system.

SOB obtain their energy from the oxidation of a number of reduced sulphur species:

$$2H_2S + 2O_2 \rightarrow H_2S_2O_3 + H_2O \qquad (1)$$

$$5S_2O_3^{2-} + 4O_2 + H_2O \rightarrow 5SO_4^{2-} + H_2SO_4 + 4S \qquad (2)$$

$4S + 6O_2 + 4H_2O \rightarrow 4H_2SO_4$ (3)

The production of sulphur (S) is mainly by chemical reaction from oxidation of hydrogen sulphide firstly to thiosulphate (1) then to sulphur (2) by atmospheric oxygen introduced by the open recirculating cooling tower, although only a limited amount of the hydrogen sulphide present undergoes these reactions. Elemental sulphur (S) is insoluble and deposits on surfaces potentially reducing the heat transfer effectiveness of the cooling tower by disrupting even water distribution from the spray nozzles and across the packing. The production of sulphuric acid (H_2SO_4) is predominately from bacterial oxidation of sulphur by SOB (3).

Almost all SOB and other microorganisms will be present as sessile populations within biofilm attached to surfaces of the cooling water system, only a relatively small number will be present as planktonic (free floating) bacteria in the water. Many biocides are not effective at penetrating the protective layer which forms on the outside of the biofilm in order to kill the SOB and other species within, and the use of a biodispersant is often necessary to facilitate the penetration of biocides into the biofilm or to help partially remove the biofilm from the surface.

Ammonia (NH_3) in the steam is highly soluble and practically all dissolves in the condensate as ammonium hydroxide (NH_4OH) which provides some pH buffering capacity to the condensate. Once the buffering capacity is exceeded from sulphuric acid produced by the SOB, the pH of the cooling water will rapidly begin to drop (observed as low as pH 3 at Te Mihi). The pH under biofilm can be lower than that of the bulk water.

1.2 Biocide Dosing Programme

In November 2012, tender responses from several reputable companies were reviewed for providing a biocide dosing programme that included chemicals and dosing services for the Te Mihi cooling towers. All companies proposed using two or three non-oxidising biocides dosed at regular dosing intervals. The successful provider began manually dosing and monitoring the cooling towers from October 2013. Originally the tender included design and installation of a permanent dosing and monitoring system, but this was instead later managed by Contact post commissioning. Unfortunately this resulted in considerable delay with on-line (and remote) monitoring of key chemistry performance parameters (pH and specific conductivity) and an automated biocide dosing system was not built and commissioned until 17 February 2016 (PI Historian not updated until 28 June 2016).

The automated dosing programme was for alternate weekly dosing of 94 kg over 72 hours of quaternary ammonium product (referred to as "quat") to achieve a 5 mg/L (ppm) product concentration in the basin one week (100 L), then dosing of 220 kg (200 L) over 1.5 hours of glutaraldehyde product ("glut") to achieve a 50 mg/L product concentration (product contains 30 to 60% glutaraldehyde) in the basin the following week. As the dosing system was common to both Units, only one particular chemical could be dosed to one cooling tower at a given time, but can dose different chemicals to separate towers simultaneously. The two biocides are dosed in the return line to the cooling tower, a dosing quill helps to mix the chemical evenly in the water to all eight riser pipes to each of the eight cells in the cooling tower.

For manual dosing, the chemical is either gravity drained or pumped from an Intermediate Bulk Container (IBC) into the cold well or cooling tower basin.

The original pH control philosophy was to dose sufficient biocide to keep the SOB population low enough to prevent the pH of the cooling water from becoming too acidic. Dosing of an alkali for pH control was only envisaged for occasional emergency use, in the event of a substantial SOB outbreak that lowered the pH below the effective application range of the glutaraldehyde biocide. Manual dosing of 30%$^{w}/_{w}$ sodium hydroxide (caustic soda, or more commonly referred to as "caustic") from an IBC was to be used for this purpose.

2. RESULTS AND DISCUSSION

2.1 Problems with pH Control

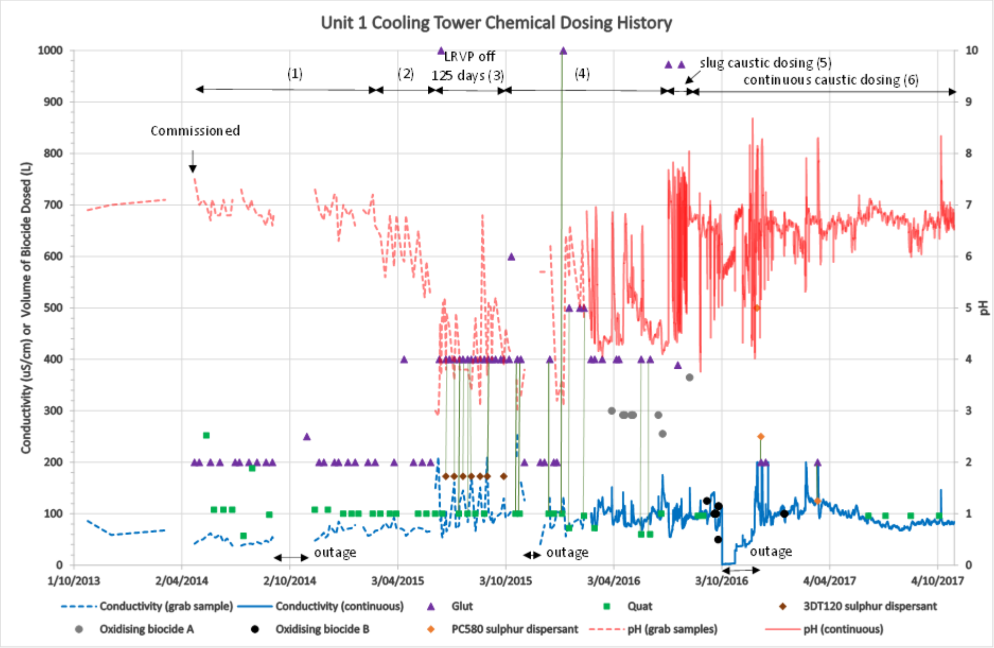
For the first 11 months from commissioning in May 2014, there was good control of the pH of the main cooling water circuits of both Units 1 and 2, from the alternative weekly dosing programme of quat and glut biocides. The cooling tower basin water ranged between pH 6.6 to 7.5 during this period with pH 6.8 to 7.0 being most typical.

From around March 2015 onwards, there was a gradual decline in the pH of the cooling tower basin water in both Units. For Unit 1, the pH would decrease to pH 5.6 to 5.9 until glut was dosed, then temporarily recover to pH 6.8 before decreasing again. Unit 2 was performing better, with the pH not dropping just below pH 6 until 12 June 2015.

More serious pH control issues on Unit 1 began as soon as the LRVP was out of service for 4 months (125 days) from 28 May 2015, with the cooling tower basin water as low as pH 3 on several occasions and mostly remained below pH 5 despite more frequent doses of double normal concentrations of glut and dosing trials with a sulphur dispersant (3DT120). After the LRVP returned to service on 30 September 2015, pH control issues and higher glut dosing continued over the following months with the pH often below pH 5. From July 2016, caustic was routinely then almost continuously dosed so the pH was mostly above pH 5. The pH control and dosing trends for Unit 1 are summarised in Figure 1.

Unit 2 experienced similar pH control issues when its LRVP was out of service for 6 weeks (41 days) from 16th July 2015, but recovered better once the LRVP returned to service, with cooling tower basin pH >5. However, once there was continuous on-line monitoring of basin water pH from February 2016, the pH was often dropping to pH 4 and higher concentrations of glut dosing resumed. Caustic buffering for pH control was introduced from July 2016. The pH control and dosing trends for Unit 2 are summarised in Figure 2.

Two oxidising biocides were also trialed on both Units between August and December 2016, oxidising biocide "B" refers to 50% hydrogen peroxide in Figures 2 and 3. While there was a rapid recovery of basin water pH after dosing peroxide, this only lasted between a few hours to a couple of days before the pH would drop below pH 6.



(1) pH controlled by weekly biocide dosing worked okay for 11 months from commissioning.
(2) Gradual decline in pH probably once biofilm became established.
(3) Further decline in pH when LRVP off due to increased steam flow through steam ejectors resulting in more H_2S in condensate. More frequent dosing of biocide.
(4) Some recovery in pH once LRVP back in service, but pH still too low between biocide doses.
(5) Up to daily slug dosing of caustic to control pH.
(6) Continuous caustic dosing to control pH (dose rate of 2 to 6 L/h of 30% caustic) and reduced biocide dosing frequency to 1 - 3 months.

Figure 1: Unit 1 Cooling Tower Chemical Dosing History

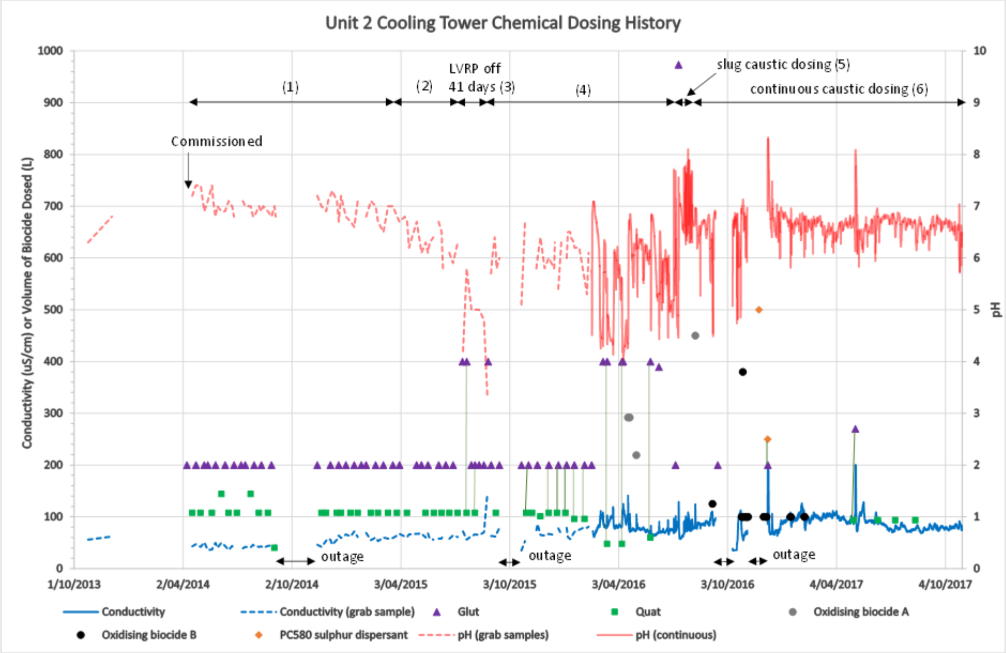


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Figure 2: Unit 2 Cooling Tower Chemical Dosing History

Te Mihi condensate has a very low buffering capacity (alkalinity) due to a very low concentration of ammonia in the steam resulting in a low concentration of ammonium hydroxide in the condensate and cooling tower water, Table 2 compares Te Mihi with Okaaki cooling tower basin water (Contact Energy internal data). This means that the pH of Te Mihi cooling tower water is very sensitive to small system changes which would not affect the pH at Ohaaki. The amount of SOB measured in the cooling water at Te Mihi was typically one to three orders of magnitude lower than measured in the cooling water at Ohaaki. It does not take many SOB at Te Mihi to produce enough sulphuric acid to lower the pH of the cooling water. Hence the difficulty in trying to control pH at Te Mihi by simply dosing biocide to control SOB numbers, especially once a stable biofilm was established within one year after commissioning.

The solution to pH control at Te Mihi was to add additional buffering capacity to the Te Mihi cooling water by continuously dosing small amounts of caustic. Caustic dose rates of between 2 to 6 L/h were cheaper than frequently dosing biocide alone to control the pH. This then allowed less frequent biocide dosing to control biofilm.

Table 2: Comparison between Te Mihi and Ohaaki Cooling Towers.

	Te Mihi	Ohaaki
Total Ammoniacal-N* (g/m^3)	6.6	60
Sulphate (g/m^3)	10 to 35 typical	46
SOB (cfu/mL)	10^2 to 10^5	10^5 to 10^6
Conductivity (μS/cm)	70 to 120	345 to 600

*can read as relative indication of levels of ammonium hydroxide

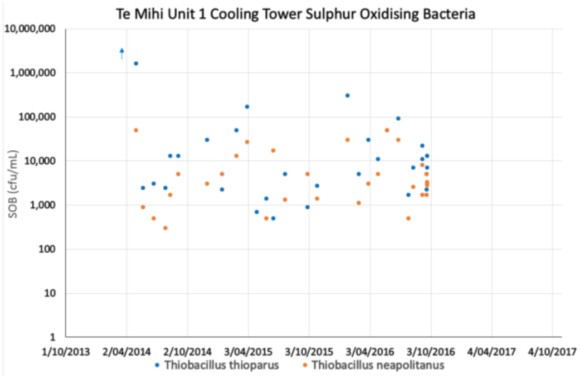

Figure 3: Te Mihi Unit 1 SOB Data

2.2 Microbiological Control Results for Te Mihi

Microbiological control targets in Table 1 are compared with actual test results from laboratory analysis of grab samples taken from the cooling tower basin water.

The SOB control target was <20,000 cfu/mL. This target was exceeded approximately a quarter of the time, and furthermore, did not given consistent expected results before and after shock dosing when an increased sampling period was taken during some biocide trials, Figure 3. Also, there was a large uncertainty associated with each plotted SOB value as listed in Table 3, which effectively made the results practically meaningless.

Table 3: SOB reported results with typical 95% uncertainty ranges.

Reported Value (cfu/mL)	Minimum (cfu/mL)	Maximum (cfu/mL)
5,000	2,000	20,000
11,000	4,000	30,000
22,000	10,000	58,000
30,000	10,000	130,000
50,000	20,000	200,000

The Pseudomonas results were >1,000 cfu/mL control target most of the time with values one or two magnitudes higher, although there were about a quarter of the results below the target value.

The Heterotrophic Plate Counts were mostly >10,000 cfu/mL control target. These are an indication of the amount of bacteria in general present in the water. More recent data for 2017 has shown values consistently below the control limit.

Nitrifying and denitrifying bacteria results were all below the detection limit of 1000 cfu/mL. There were no results for iron precipitating bacteria.

Legionella was always below 20 cfu/mL.

Overall, the comprehensive and expensive suite of microbiological results did not prove to be very useful in helping to control the pH of the cooling towers. Aside from the large uncertainly in the SOB results, it also took 9 days from when the sample was taken until a result was reported. This lead to looking for other more readily measureable parameters that could be used to indicate microbiological control. Routine microbiological testing was reduced to just monthly Legionella and Heterotrophic Plate Counts, plus the introduction of weekly dip slides as a simpler and cheaper general microbiological test that could be done on site.

2.3 Influence of LRVP out of service

The pH of both cooling towers became more acidic when the LRVP's were out of service. The possible reasons why are explained below.

The LRVP is the last vacuum device for NCG extraction after a series of steam ejectors and inter-condensers. All the steam ejectors are powered from IP steam taken after the IP steam scrubber vessel. All the inter-condensers return condensate back to the condenser above the condenser water level, and the seal water separator after the LRVP returns water back to the condenser by connecting into the water spray lines in the main cooling water circuit from the cooling tower.

When the LRVP is taken out of service a back-up 130% steam ejector is run instead. While the condenser vacuum does not significantly change simply from switching from the LRVP to the 130% back-up steam ejector, there is a significant increase in combined steam flow through all the ejectors. The 130% steam ejector increases the normal total IP steam flow to all ejectors from approximately 2.5 to 7 kg/s, and the condensate from the after-condenser for the 130% ejector drains directly to the cooling tower basin instead of to the condenser. Whether the condensate from the ejectors discharges to the condenser or to the basin is unlikely to be significant in terms of the amount of H_2S reaching the cooling tower, as this condensate does not pass through spray nozzles to enter the condenser (unlike the LRVP which would strip NCG more effectively) but simply drains into it after passing through a barometric loop seal, so hence would not provide sufficient liquid-to-gas surface area of the condensate to permit effective removal of dissolved H_2S despite the lower pressure in the condenser.

It is a combination of an additional 4.5 kg/s of IP steam going through the ejectors with the LRVP out of service and the condensate from the 130% ejector not spraying into the condenser, that results in more H_2S in the cooling water system than had this steam steam passed through the steam turbine instead with the LRVP in service.

There is insufficient data to quantify the increase in H_2S entering the cooling tower from running the 130% ejectors. However, the H_2S concentration in steam ejector condensate may be around seven times greater than that from condenser condensate from steam exiting the turbine (Mroczek, et al. 1995).

Hence additional H_2S enters the main cooling water circuit when switching to the 130% steam ejector when the LRVP is out of service, which provides more food source for SOB, which in turn produce more sulphuric acid to lower the pH in the cooling water.

2.4 Biocide Resistance

In August 2016, a review of the on-going pH control problems and ineffectiveness of the biocide dosing programme was undertaken. The conclusion was that the microbiology in the cooling water system had probably developed a resistant to glut from too frequent dosing of this chemical. Microbial resistance to both glutaraldehyde (glut) and quaternary amine (quat) biocides have been reported (SCENIHR, 2009). The later addition of caustic dosing was becoming too excessive (>6 L/h) and was not addressing the cause of the problem which had continuing for over 12 months of regaining microbiological control.

Glut is the primary biocide with the quat more for keeping surfaces clean by removing biofilm as a dispersant but also has mild biocide properties itself. There may have been some microbial resistance to the fortnightly dosing of quat, but it is difficult to say for certain as it was not dosed in combination with another biocide other than glut. The dispersant properties of quat work synergistically with glut by enabling the glut to better penetrate into the biofilm to kill microbes inside. Quat on its own would not be sufficient to regain microbial control.

Good practice is to have at least two (or better three) biocides that have different kill mechanisms. This helps to prevent microbial resistance. Glut is a protein inactivater, while quat is cell wall/membrane disrupter (Roscoe, 2009). The oxidising biocides that were trialed also have a different microbial kill mechanisms, but are not good at penetrating biofilm on their own and cannot be dosed in combination with quat as they are chemically incompatible.

2.5 Cooling Tower Inspection

In August 2016, the water in the cooling tower basins were very green in colour indicating poor microbiological control, Figure 4.

Deposits and biofilm on the basin wall was evident after draining during an outage, Figure 5.

The cooling tower spray nozzles and fill material showed little Sulphur deposits, Figures 6 and 7.

Figure 4: August 2016 Te Mihi Cooling Tower Basin

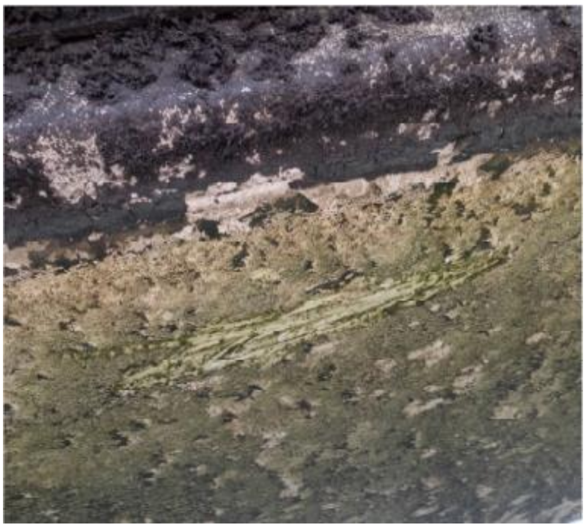

Figure 5: Deposits and biofilm on basin wall after draining, Unit 2 (Sep 2016)

Figure 6: Unit 2 cooling tower spray nozzle (Sep 2016)

Figure 7: Unit 2 bottom of top layer of fill (Sep 2016)

2.6 Effective Biocide Solution for Regaining Control

It was decided that the best option was to trial a different biodispersant/biocide to focus on getting the surfaces of the cooling system clean in order to regain microbial control. Initially is was thought that sulphur deposition may be more significant that was later observed.

An amide sulphur and biodispersant chemical PC580 (also known as DETA II and BCP 5030) was trialed on both cooling towers, firstly by itself and then in combination with glut. The latter worked well and was sufficient to regain microbial control. No chunks of sulphur solids were observed on the cold well screen or on the noise-attenuating splash screens under the fill confirming low sulphur deposits in the cooling water system as observed during earlier inspection of the cooling tower.

Note glut had not been dosed for five months in Unit 1 and almost three months in Unit 2 cooling towers with an oxidising biocide dosed multiple times during these intervals, before glut was dosed with PC580. Hence any microbial resistance to glut is likely to have diminished over these periods, plus the biofilm would have been already stressed from the earlier oxidising biocide shock-doses and earlier PC580 dose before finally experiencing a combined PC580 and glut dose. PC580 also has biocide properties and works synergistically with glut to penetrate into biofilm. The dosing was made more effective by raising and holding the pH of the cooling water to pH 8.0 to 8.5 overnight by dosing caustic at 60 L/h. PC580 removes sulphur deposits best at pH >7.5 and the optimum pH for glut in terms of rate of efficacy and half-life is in the range of pH 7 to 9 (Chemical supplier technical bulletin).

2.7 Performance-Based Dosing

After control was regained, for 2017 the glut and quat dosing has resumed but under a different dosing programme. Caustic is continuously dosed to control the cooling water pH and the on-line chemistry monitoring is used to help determine when shock-dosing with biocide is required. Quat dosing is presently dosed every one to three months and glut is only dosed occasionally when required based on the conductivity reading or to keep the chemical stocks within their 12 month shelf life. When glut is dosed it is immediately after quat dosing once the pH is increased to around pH 7.5 by increasing caustic dosing for a few hours (cheaper and still effective compared to raising to pH 8.0 to 8.5).

Cooling water quality is dominated by the concentration of sulphate (SO_4^{2-}) in the water, and measuring sulphate can be used as an indication of SOB activity (Richardson, et al. 2012). Measuring sulphate can be performed manually within minutes of taking a grab sample of cooling tower basin water. A better system is to have a continuous on-line monitor. As SOB produce sulphuric acid, this will increase the specific conductivity of the cooling water which is simple and easy to measure on-line with minimal maintenance.

In practice, the conductivity has proven to be a useful comparative indicator of sulphate for SOB activity along with the caustic dosing rate required to buffer the pH between pH 6.0 to 7.0. A high conductivty alarm limit of 120 µS/cm was set to indicate that SOB levels were too high and prompt biocide dosing is required.

On-line pH measurement is the primary control measurement as this determines whether cooling water is being maintained within the pH design limits of cooling water system of pH 4.5 to 8. The pH under biofilm may be lower than the bulk water where the pH is measured so the low level pH alarm has been set to pH <6.0.

CONCLUSIONS

1. Biocide dosing alone to reduce the already low levels of Sulphur Oxidising Bacteria (SOB) was not feasible to control pH of the cooling water after the first 11 months of operation once some biofilm inevitably forms on newly exposed surfaces.
2. Continuous low concentration caustic dosing is necessary to control the pH of the main cooling water at Te Mihi, due to the low levels of ammonia in the steam available to provide pH buffering to the condensate.
3. Too frequent dosing of glutaraldehyde biocide probably resulted in some microbial resistance. Alternative biocides had to be used to regain microbiological control.
4. Biocide dosing has successfully moved from regular scheduled weekly dosing towards performance-based dosing using on-line measurable parameters of specific conductivity, pH and caustic dosing rate. This reduces the chance of microbes developing a resistance to the particular biocides while still maintaining good microbial control. This has also resulted in significant chemical cost savings compared to the original chemical budget

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