Plant Experience with Dosing Optimisation of an Environmentally Friendly Biocide

Hugh Fallon
Contact Energy
Hellabys Rd
Otara, Auckland
New Zealand
hugh.fallon@contact-energy.co.nz

George J. Licina
Structural Integrity Associates
3315 Almaden Expressway, Suite 24
San Jose, CA 95118

ABSTRACT

Initial experience with an environmentally friendly biocide at a brackish water-cooled power plant showed that the biocide was very effective in controlling microbiological fouling of piping and condenser tubes. Subsequent activities demonstrated that the biocide could be used more economically by closely tracking the biocide's effectiveness on biofilm activity using an electrochemical biofilm activity monitor.

Keywords: biocide, monitoring, biofilms, water treatment, cooling water

BACKGROUND

Water treatment, usually with biocides, is the most common approach for mitigation of microbiologically influenced corrosion (MIC) based upon its ease of use. However, the use of a biocide treatment alone is rarely effective for an already fouled system. The most commonly used biocides are oxidising agents that can also aggravate a corrosion condition that may have been established initially by microbiological activity, but which may proceed with no further microbiological involvement. In such cases, the use of a biocide, especially an oxidising biocide, may prevent further infestation but it can also provide alternative and stronger half-reactions that fuel the corrosion activity. Biocide treatments alone

are only likely to be effective when microbes actively participate in the corrosion process (e.g., by catalysis of the reduction of oxygen, or by cathodic depolarisation in anaerobic systems), or when microbes provide alternative reactions that exacerbate corrosion. In summary, biocide treatments are a very effective **preventive** measure against MIC; however, the condition of the corrosion process must be well understood before biocide treatment is used to remediate an apparent MIC condition.

Contact Energy LTD own and operate the Otahuhu B 380 MW gas-fired single-shaft combined cycle power station, located in South Auckland, New Zealand (Figure 1). Estuarine water is supplied to the main cooling water system where the recirculation rate to a 2-pass titanium-tube condenser is some 20,000 m^3/hr. The velocity through the condenser tubes is 2 m/s. A hybrid 8-cell cooling tower is used for heat rejection. The design ΔT across the condenser is 9.9°C. System losses (evaporation and purge water) are made up continuously to the main system. Over 22,000 m^3 of make-up water are taken from the estuary each day to maintain the design cycles of concentration of 1.25.

The conductivity of the brackish make-up water can vary significantly between the low and high tide cycles; by as much as 15 mS/cm. Seasonal variations are also notable due to high rainfall totals during winter and spring. In general, the make-up water conductivity varies between 5 and 35 mS/cm between June and November. During the warmer months the average conductivity is more stable, and changes tend to occur gradually in the range 35 to 50 mS/cm.

The make-up water is treated continuously with industrial grade bleach to provide a free halogen residual of between 0.5 to 0.8 mg/l. A proprietary stabilised bromine-based biocide is added to the recirculating water system to augment the primary (make-up) oxidant dosing. The bromine product is a unique, biomimetic, stabilised liquid bromine biocide, with excellent microbiological and biofilm control properties, while exhibiting lower toxicity and lower reactivity than traditional oxidising biocides. A total halogen residual in the range 0.1 to 0.40 mg/l is maintained in the main system. All residuals were reported in plant data as chlorine for convenience and for direct comparison with on-line chlorine analysers. However, the estuarine nature of the water and the injection of the stabilised bromine biocide ensure that the residuals consist of bromine in a mixture of free, stabilised and combined species. A proprietary scale inhibitor is also dosed to the recirculating water.

That treatment has effectively controlled MIC and biofouling throughout the cooling system.

Biocide Optimisation

Originally, the cooling water chemistry on the plant was quite reactive and the effects of fouling in the system were assessed off-line without the aid of any on-line techniques; clearly without any predictive indicators. Plant policy was to apply chemicals to provide fixed, target residuals. If a performance or fouling problem were noted, the amounts of chemicals would be increased. The chemical program was expensive while this policy was maintained.

A more sensible approach was considered to be the application of chemicals, especially the biocides, according to the system demand and the system performance. That biocide optimisation effort is a wide-ranging and thorough instrumentation project with the aim of using the smartest technology to fully monitor and optimise the system. As a part of that program, the plant installed two BI?GEORGE™ electrochemical biofilm activity probes (Figure 2), a DATS™ model heat exchanger, and other instruments in a test program intended to evaluate the suitability of the probe for use at the plant, then to use the probe output data as part of a water treatment control management system, which would add biocide on a schedule and at concentrations that would keep system surfaces free of biofilm

and any and all biofilm-related problems while using less of the biocide. The predictive and anticipatory characteristics afforded by the "lead factor" provided by the probe (i.e., fouling occurs on the probe before fouling occurs in the system) was considered to be a key component to the overall effort. With such a sensor in place, the system could then be monitored on a performance basis and the amounts of chemicals added varied according to that performance. The operational details associated with the biofilm probe have been reported previously, including other papers in this conference.[1-8] Biocide optimisation programs have been performed in other cooling waters using that probe as shown in Figure 3 and described in Reference 2.

The basic aims of the biocide optimisation effort here were to:

- Monitor the cooling water systems more closely to offset risks associated with biologically induced fouling.
- Reduce the costs of chemical treatment through the introduction of a performance-based approach to monitoring and dosing.
- As a consequence of the above, aim to minimise the toxicity of the discharge effluent to the receiving environment.

APPROACH

Because the system was quite clean to begin with, the plant was reluctant to degrade the process conditions in any way in order to foul the electrochemical biofilm probe. To this end the sidestream sample that runs past the probe (and only that sample), was manipulated such that only that area was subject to unclean conditions. In that way the probe was subjected to a worst-case scenario, and if fouling was to occur, it should occur there.

Following observations of fouling on the probe (from increases in applied and generated currents) the probe was then exposed to the actual process water. If the water has sufficient toxicity, then biofilm probe trends should again decrease. This approach also permitted evaluations of the process water's toxicity and capability to slough off and destroy biofilm, or determine what level of toxicity is required to do so. The goal of this exercise was to permit the plant to reduce the overall concentrations of residuals, or to apply intermittent dosing of the more costly stabilised bromine product (which is the real aim), and repeat the above – that is, artificially foul the probe (i.e., under conditions of reduced toxicity) and then let the process water clean it up. Eventually the plant will reach the stage where the process conditions will be efficient, just at the level where fouling may begin to occur, and the probe can continually contact the process water. Then, any microbial activity over and above the "normal" amounts that the system has been set up for will foul the probe in real time and the plant will have an on-line indication that the current dosing rates or times are insufficient and more chemical or other mitigation approach is required.

As such, from April to June 2002, the probe was installed in a 6-inch tapping point on the condenser's outlet header (Figures 4 and 5). The probe surfaces contacted water flowing to an automatic chlorine analyser. The flow rate past the probe was approximately 1.5 litres per minute. The process water velocity in the system is 2 m/s, slightly greater than what most of the probe surfaces experience. This slightly lower flow rate across the probe was selected to use a fairly representative flow condition while giving microbes a better chance to settle out, also taking advantage of the lead factor that the probe has over system surfaces. That is, the probe surfaces are encouraged to foul by the daily

polarisation cycle that is applied. As shown in other systems, the electrochemical biofilm probe will foul quite quickly (in a few days) and the trends for applied and generated currents will rise to significant values compared to the baseline if there is significant fouling potential in the system.

In the course of the optimisation activity, probes have been isolated from the biocide treated flow, have been exposed outside of the system in a bucket of make-up water, and have been exposed in both inlet and outlet streams.

RESULTS

Initial Exposures

Figures 6 and 7 illustrate the initial performance. When the probe was exposed to the biocide-treated water at a flow comparable to that experienced by the condenser tubes, little or no evidence of any biofilm activity was seen, which was consistent with visual examinations of system surfaces. This behaviour was not unexpected as noted above. There were indications of biofilm on April 29th and June 12th, however, in both cases, the system itself was able to clean up the probe.

Those initial results led to modifications of the flow conditions experienced by the probe, starting with a period of stagnation.

Effects of Flow Rate and Biocide Treatments

The objective of subsequent changes in the exposure of the biofilm probe in terms of flow rates and exposure to biocide were intended to permit the probe to foul, then to observe the response of the applied and generated currents to biocide dosing. In general, those conditions showed that once a system (including the probe surfaces) is fouled, it may not be easy to establish the previously clean conditions. It should also be pointed out that since the biofilm probe will be encouraging biofilm formation even while the water has oxidant in it, non-polarised surfaces may be recovered with more ease than the probe electrodes. Finally, the changes in flow and dosing conditions past the probe permitted the biofilm's response to stress to be observed.

As shown in Figure 8, on July 16th, the biofilm probe was exposed to dead leg conditions (i.e., flow through the condenser outlet tapping point was isolated). In addition, the applied potential was increased from 200 to 400 mV and the applied potential time was increased from 1 hour to 90 minutes. Baseline and alarm setpoints were not reset. The intent was to observe when and if the probe would foul, then to introduce process water to it and to note the response of that biofilm to flow.

As of July 18th the applied current trend started to increase dramatically. There was a coincident large negative deviation on the generated current trend at the same time.

On July 30th 2002 at 10:16, the process flow was introduced to the biofilm probe again at a low flow of less than 1-liter per minute. The applied current decreased somewhat from its earlier peak and was then steady, up to July 31st, when both the applied and generated trends started to increase significantly.

On August 7th 2002, flow past the biofilm probe was measured as 0.6 litres per minute. Biocide (stabilised liquid bromine) dosing was increased (from a 10% pump stroke setting to 20%) for approximately seven hours. The overall flow out of the rack was set to about 1.25 litres per minute for this time period. The generated current began to decrease from 12:15 on the same day.

On August 13th at 08:35 the flow from the rack was increased to about 6 l/min and the next day the bromine biocide dosing was doubled (10% to 20%) from 08:00 to 14:00. Between August 17th and 22nd, the rack flow decreased from 6 to 3 litres per minute, due to some mud accumulation further down the drain line, which decreased the flow rate over a number of days, and both the generated and applied current trends were starting to increase again.

On August 22nd at 15:30, the probe was swapped over to the inlet line tapping point (the line that furnished the DATS) with a flow of 28 l/min. The toxicity would only be slightly higher on the inlet side of the condenser; as such, this is more an indication of the effect of flow on the biofilm than the effect of toxicity.

At 15:00 on September 3rd 2002, the applied potential was again changed downward, from 400 mV applied for 90 minutes to 200 mV for 1 hour. Those adjustments reflect the pre-July 16th settings. Between August 22nd when the probe location tapping was changed, and September 3rd when the potential and time were changed, the applied current and generated currents changed from 3.4µA and 0.15µA, respectively (both being quite steady), to values after the setting changes of 1.75µA and (still) 0.15µA, respectively. On Friday September 6th, when the bromine biocide dosing was turned off from 10:45 to 15:15, the generated current values did not change significantly.

On September 10th 2002 the bromine biocide dosing schedule was changed from a continuous mode to a 1 hour off/1 hour on schedule from 19:00 to 08:00 on the 11th. The applied and generated current trends appeared to show a slight decrease during this on/off test. Note that the hypochlorite dosing was on as normal to the make-up water during that time.

The plant was shut down for the weekend on Friday September 13th. Just before shutdown the recirculating water temperature was a fairly steady 25°C. Over the weekend, the recirculating water temperature went as low as 6.5°C (on the 14th). Bromine biocide dosing was from 08:00 to 16:00 for the 14th and 15th. The plant restarted on the 15th at 17:00 and the recirculating water got to 31.5°C by 20:00.

On Monday Sep 16th, the bromine biocide dosing was set to a 1-hour off/ 1 hour on schedule. The applied current decreased from 1.43µA on the morning of the 13th to 1.11µA on the morning of the 17th while the generated current remained steady at -0.08µA. All or part of the applied current reduction may have been due to the temperature shock during the weekend.

On Tuesday September 17th, samples (swabs) were taken from the biofilm surfaces, the BioBox (a transparent Perspex box with a tortuous flow path, which encourages sedimentation and fouling), and the recirculating water corrosion coupon. Water samples were taken from the probe tapping point (upper level) and the BioBox. This completed this dead-leg/biofilm production trial.

In parallel with the tests of the on-line probe (as detailed above), an identical probe was exposed to another set of controlled test conditions. Initially, the unit was left suspended in a bucket of untreated seawater to which some sugar was added. The unit went quickly into alarm on a high applied current. The biofilm activity on that probe peaked on July 19th with significant scatter in the trend plots. The applied current levels had begun to decrease significantly after July 19th. The probe in the bucket test

appeared to indicate that the biofilm was dying since the environment was so rich, bugs grew rapidly and everywhere, polluting their own environment.

On August 22nd, when the on-line probe was changed from the condenser outlet to the inlet, the probe from the bucket test was put in the outlet tapping with a flow of about 4.5 l/min.

The summary conclusions from this exposure period were that the biofilm grew rapidly on the probe when flows and biocide dosages were low; that growth on the probe was most significant when nutrients and flow were at higher levels (with biocide levels still low), but that system water with "normal" levels of biocide effectively killed or deactivated the biofilm on the probe surfaces. The introduction of process water to the dead-leg where the probe was installed caused applied current and generated current trends to increase even further as the established biofilm, which was probably somewhat nutrient-poor, suddenly experienced a (relative) abundance of nutrients. The increased shear stress from introducing the process water flow at a low flow rate was not sufficient to slough off the biofilm on its own. However, the response of an already fouled probe to the changes in flow showed that flow is a factor.

The most significant event leading to higher applied currents (on September 15th) was the 31.5°C temperature of the water. During the plant shutdown from September 13th to 15th, the trends showed the biofilm's response to stress. Biofilm activity decreased during the shutdown with greater evidence of biofilm activity on the probe moved from the bucket test to the outlet line position.

In general:

- biofilm growth occurred during periods of stagnation
- the level of biofilm activity was greater than during exposure to biocide-treated water
- once (nutrient-rich) flow was resumed to the probe, activity flourished
- more rapid flow and higher biocide dosing rates almost immediately began to reverse biofilm activity
- Finally, once the biofilm was established it was hard to remove, to the extent that the system is not recovered fully. These tests also showed that biofilm can develop in low-flow areas, even if the water is toxic

Table 1 summarises the results of microbiological characterisation of the water and the probe and other surfaces. All samples exhibited a low diversity (note that more than 99% of viable microorganisms in a system are sessile). Total viable counts (TVC) for samples other than the probes matched the daily TVC values. TVC for the probes are noted to be higher than for all other samples, consistent with the probe's intent of encouraging biofilm development. Furthermore, flow velocity past probe is important.

Additional Biocide Optimisation Activities

Figures 9-11 illustrate the results of exposures of the biofilm probe in the cooling water location with no isolations of the probe or other activities designed to permit the probe to foul then to be cleaned up by the treated water flow. Those exposures are representative of the way that the probe is used in the plant now. Those results are representative of the partially completed biocide study. In general, this approach has permitted the plant to maintain the cleanliness of heat exchangers and other equipment while decreasing the amount of the clearly very effective bromine biocide. Figures 9-11 show that the current treatment regime continues to keep the biofilm probe's applied and generated current at low

levels that are consistent with, and in some cases, better than, the baseline conditions that were determined in the initial phases of the study.

Figure 12 shows the relative chemical treatment costs for the plant over the past 2½ years. The electrochemical biofilm activity probe has been incorporated into an overall water treatment management system that has allowed the site to optimise the use of the stabilised bromine-based biocide to the extent that a 25% saving in chemical costs has been realised to. Further, total savings of up to 40% compared to pre-optimisation costs are expected in the medium term as the dosing is changed to a fully performance-based approach, with the electrochemical biofilm probe system as an integral part of the overall biocide management program.

The biocide optimisation activities are continuing as the plant begins to approach its goal of continuously exposing the probe to actual process water that has been treated less aggressively with biocide such that the biocide content of the water is just sufficient to keep surfaces clean. These activities have continued to show that the stabilised bromine biocide is effective and that tools such as the electrochemical biofilm probe are effective in helping to optimise those treatments such that the plant has already reduced biocide usage.

CONCLUSIONS

The electrochemical biofilm activity probe was shown to be sensitive to biofilm formation in the plant system.

The electrochemical biofilm activity probe system definitely promoted preferential biofilm development on the sensor probe. That aspect of the system provides a useful “lead factor” for the plant, where fouling will develop on the probe before it becomes established on the general non-polarised surfaces of the main system.

Biofilm can become readily established if dosing control is lost; biofilm can also develop in stagnant areas.

Once established, biofilm is not easily removed, to the extent that it would be difficult to re-establish the previously clean conditions of the plant.

Maintaining clean conditions on the biofilm probe surfaces ensures the main plant conditions are also clean. Sessile analysis of the probe and cooling system surfaces supports this claim.

The stabilised liquid bromine biocide is clearly effective in maintaining surfaces free of biofilms, whether those surfaces are heat exchanger tubes or probe electrodes.

The biocide was also demonstrated to effectively return a probe surface with some microbiological fouling to a condition consistent with a clean surface.

The electrochemical biofilm activity probe has been incorporated into a total water treatment management system that is allowing the site to optimise the use of the stabilised bromine-based biocide to the extent that a 25% saving in chemical costs have been realised to date.

Further total savings of up to 40% compared to pre-optimisation costs are expected in the medium term as the dosing is changed to a fully performance-based approach, with the electrochemical biofilm probe system as an integral part of the overall biocide management program.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the cooperation and support of Mr John Rickerby, Mr. Harry Habib and Mr. Ralph Woulfe of Contact Energy Limited, Mr. Elie Tanos of Chemtrack, and Mr. Roy Menzies of Ondeo-Nalco.

REFERENCES

1. G. J. Licina, George Nekoksa, “The Influence of Water Chemistry and Biocide Additions on the response of an On-line Biofilm Monitor,” CORROSION/95, Paper No. 527, NACE International, 1995.

2. G.J. Licina, L.P. Venhuis, “Biocide Optimization Using an On-line Biofilm Detector”, International Water Conference, Paper 00-060, October 2000.

3. G.J. Licina, “Monitoring Biofilms on Metallic Surfaces in Real Time”, CORROSION/2001, Paper No. 442, NACE, Houston, TX, 2001.

4. M.H. Dorsey, et al., “Monitoring for Corrosion and Microbiological Activity in a Cooling Water System”, CORROSION/2002, Paper No. 441, NACE-International, 2002.

5. G.J. Licina, “Experience with On-Line Monitoring of Biofilms in Plant Applications”, Cooling Technology Institute, 2003.

6. P.G. Kutzora, L.B Peterson, G.J. Licina, “Monitoring Biofilms on Cooling Water System Surfaces”, Electric Utility Chemistry Workshop, University of Illinois, 2003.

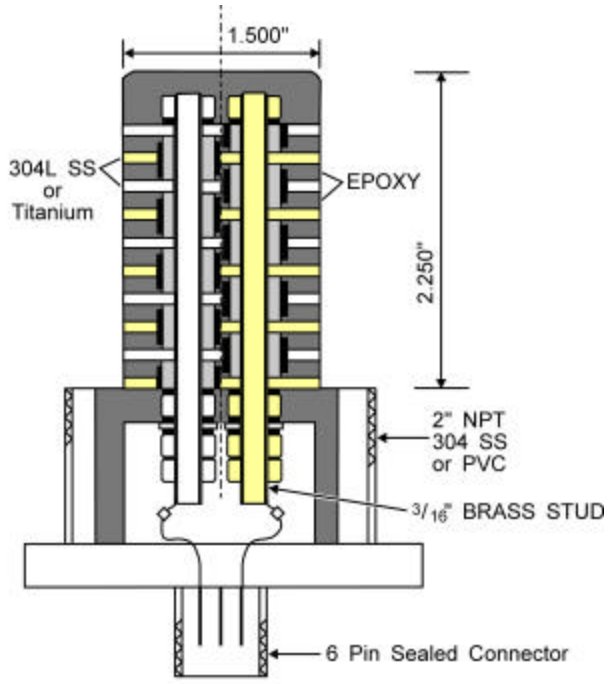
7. W.E. Garrett, G.J. Licina, "Monitoring Microfouling in a Once-Through Service Water System", Eighth EPRI Service Water System Reliability Improvement Seminar, 1995.

8. G.J. Licina, “Optimizing Biocide Additions via Real Time Monitoring of Biofilms”, CORROSION/2004, Paper No. 04582.

TABLE 1
RESULTS FROM SWABS FROM BIOFILM ELECTRODES AND EPOXY PROBE BODY

	Electrodes	Titanium	Epoxy	Titanium	Epoxy
Date	9/17/2002	10/25/2002	10/25/2002	10/31/2002	10/31/2002
Microscopic Examination (1000X Magnification)					
Sludge	+	-	-	-	-
Siliceous Material	-	+	-	+	-
Protozoa	-	-	-	-	-
Nematodes	-	-	-	-	-
Diatoms	+	-	-	-	-
Unicellular Algae	+	-	-	-	-
Filamentous Algae	-	-	-	-	-
Unicellular Bacteria	+++	-	-	-	-
Filamentous Bacteria	-	-	-	-	-
Amphipods (Larvae, nymphs etc)					
Yeast/Filamentous Fungi		-	-	-	-
Culturing(CFU/ml)					
Yeasts	ND	ND	ND	ND	ND
Moulds	100	10	10	10	10
TVC at 25 Deg C	14000	21000	800	21000	800
Anaerobic SRB	ND	10	ND	10	ND
Total Anaerobic Bacteria		600	50	600	50
Pseudomonas	ND	13000	700	13000	700
Clostridium	ND	50	ND	50	ND
Heterotrophic Iron ppt. Bacteria	100	200	20	200	20
Nitrifying Bacteria	ND	ND	ND	ND	ND
Denitrifying Bacteria	ND	ND	ND	ND	ND

FIGURE 1 - Aerial photograph of the site



97292r0

FIGURE 2 - Electrochemical Biofilm Activity Probe

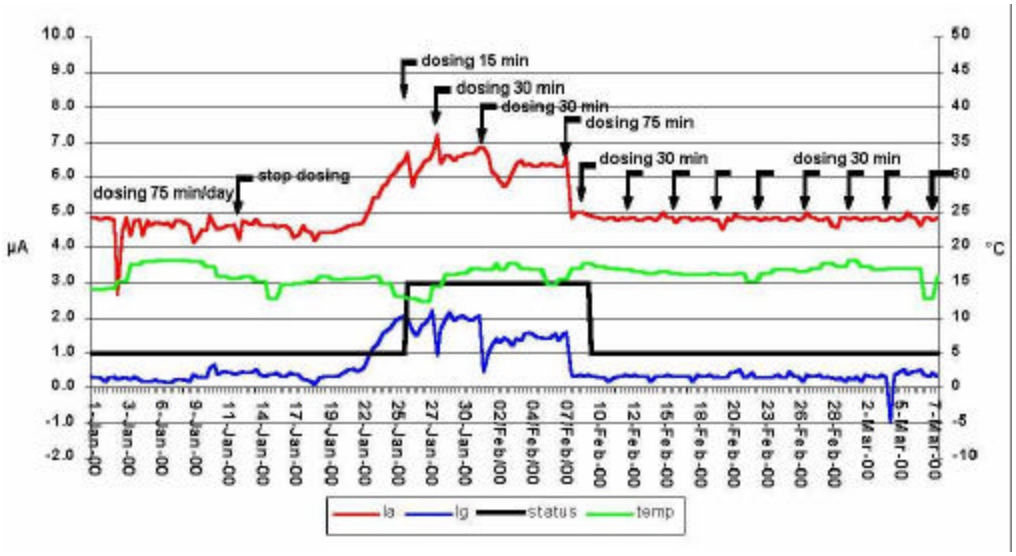


FIGURE 3 - Results from Biofilm Optimisation Study – Brackish Water-cooled Incineration Plant (from Reference 2)

FIGURE 4 - Probe Tapping on Cooling Water Return Line

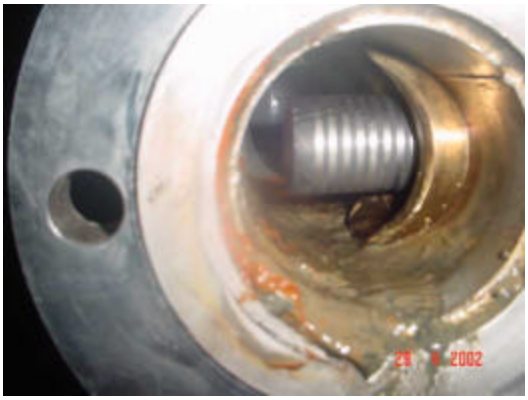


FIGURE 5 - View of Probe Installed in Tap

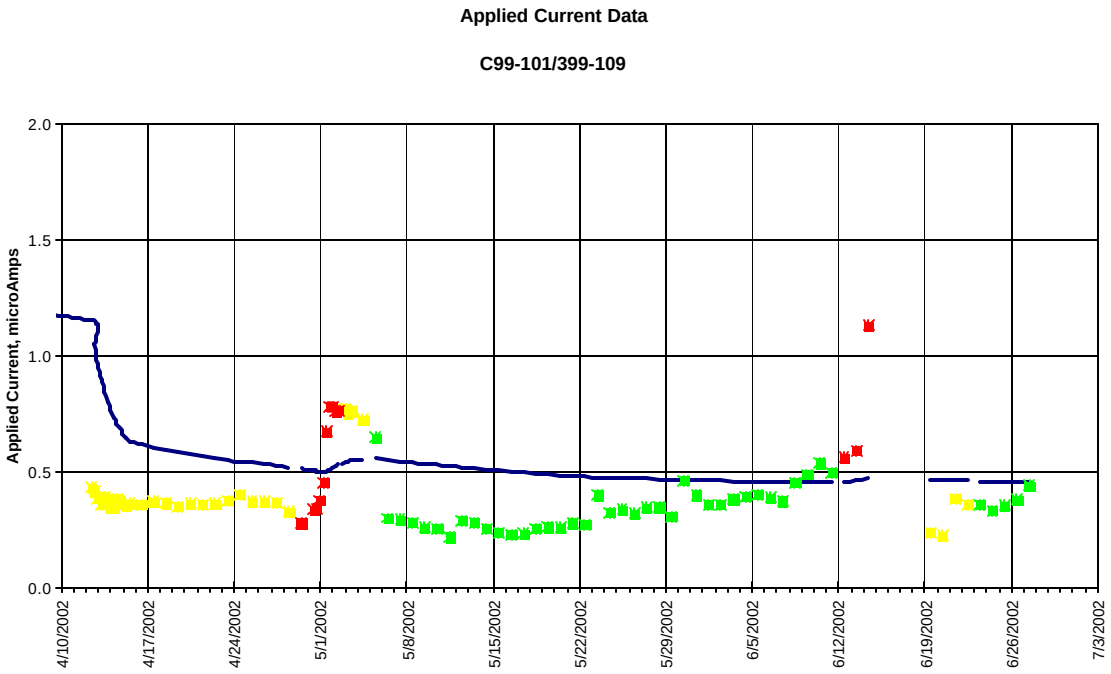


FIGURE 6 - Applied Current Trend – April 2002-June 2002 (Color code: Yellow = baseline being established; Green = probe is clean; Red = probe is fouled)

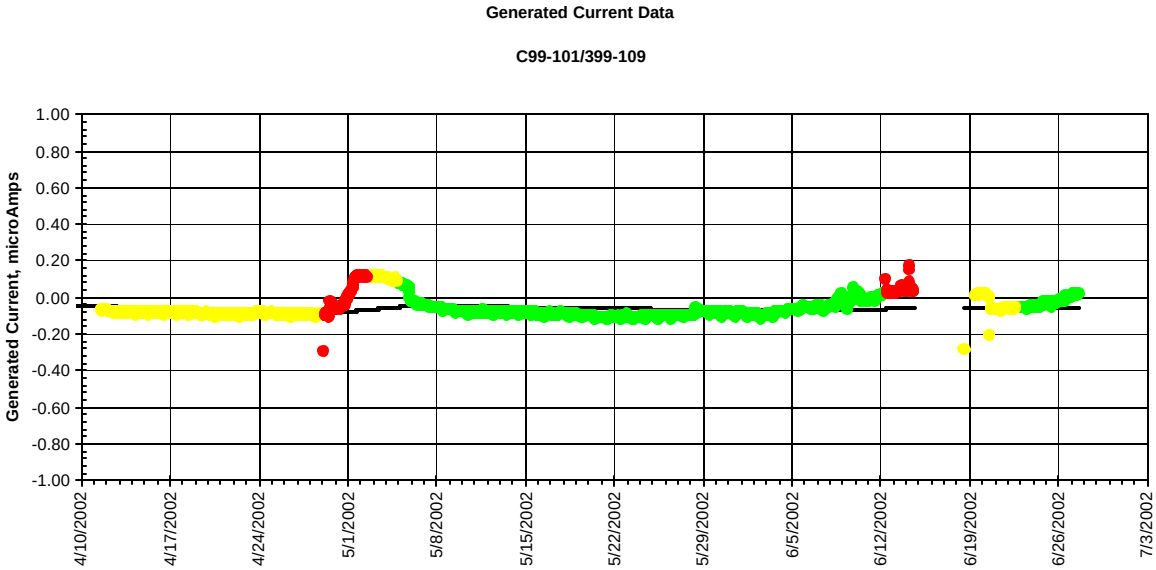


FIGURE 7 - Generated Current Trend – Aril 2002 – June 2002

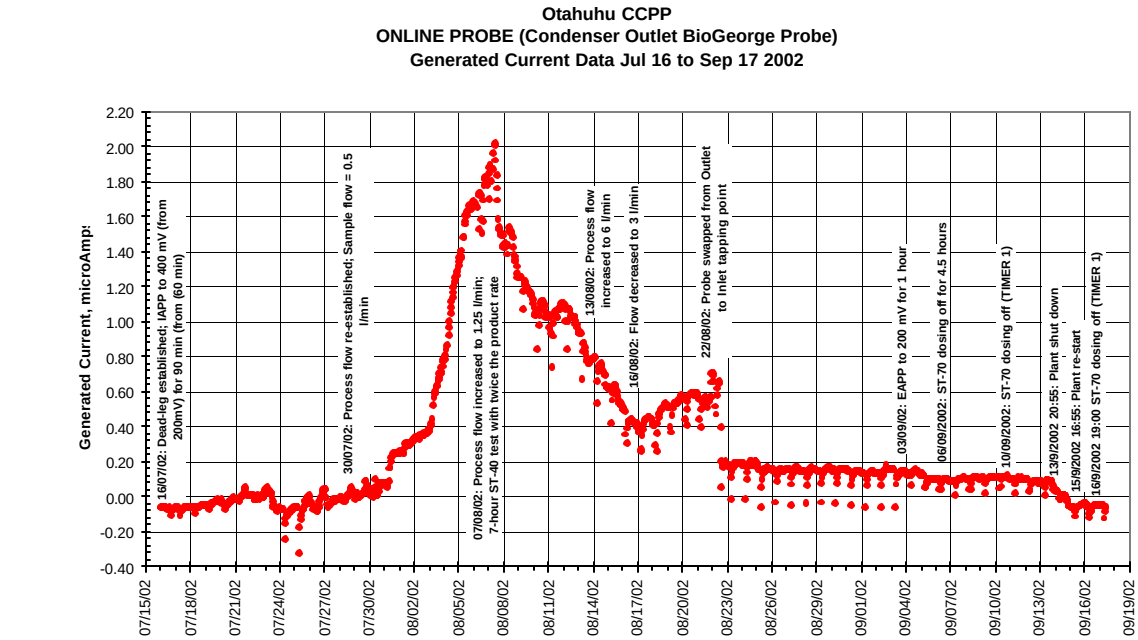


FIGURE 8 - Generated Current Trend – July 2002 through September 2002

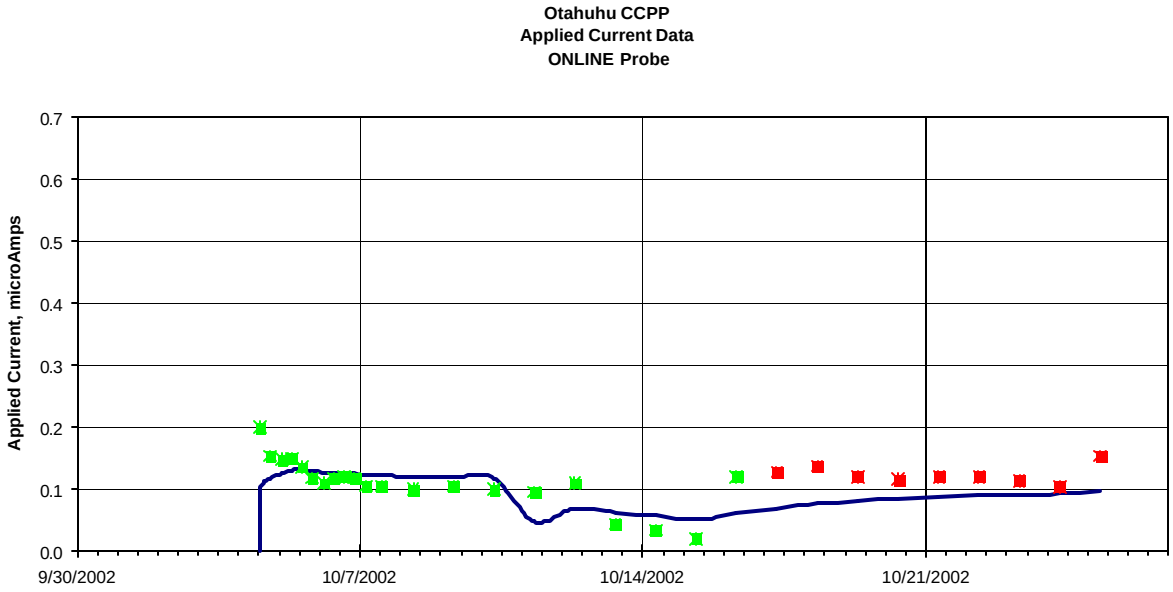


FIGURE 9 - Continuous exposure to treated cooling water

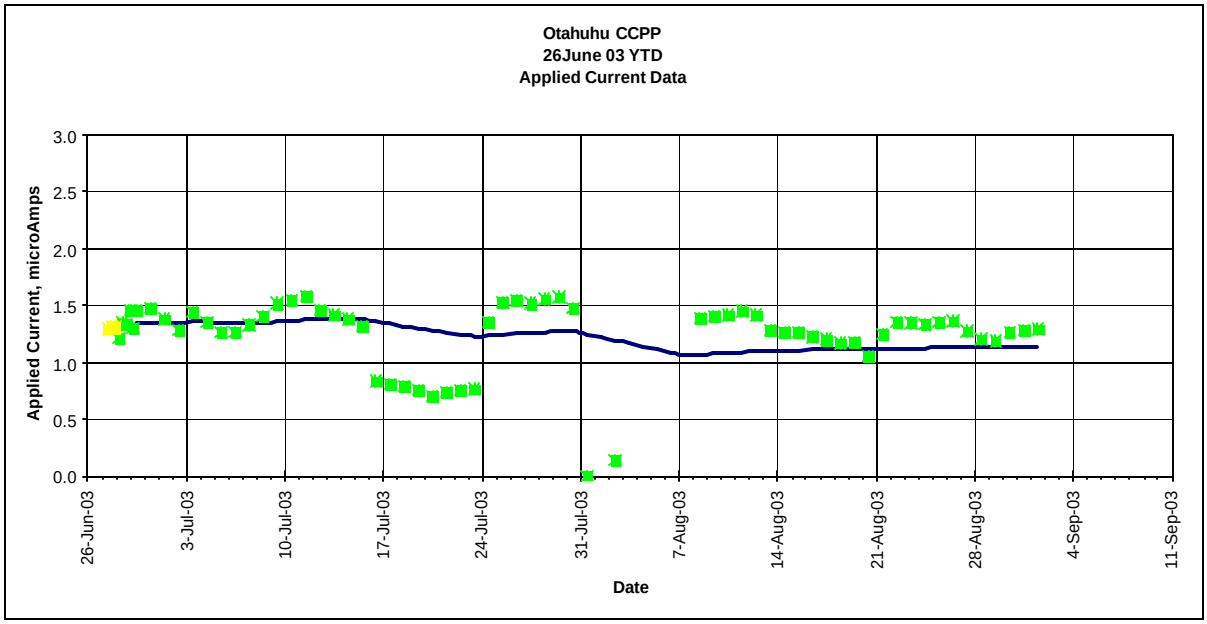


FIGURE 10 - Applied Current History –2003

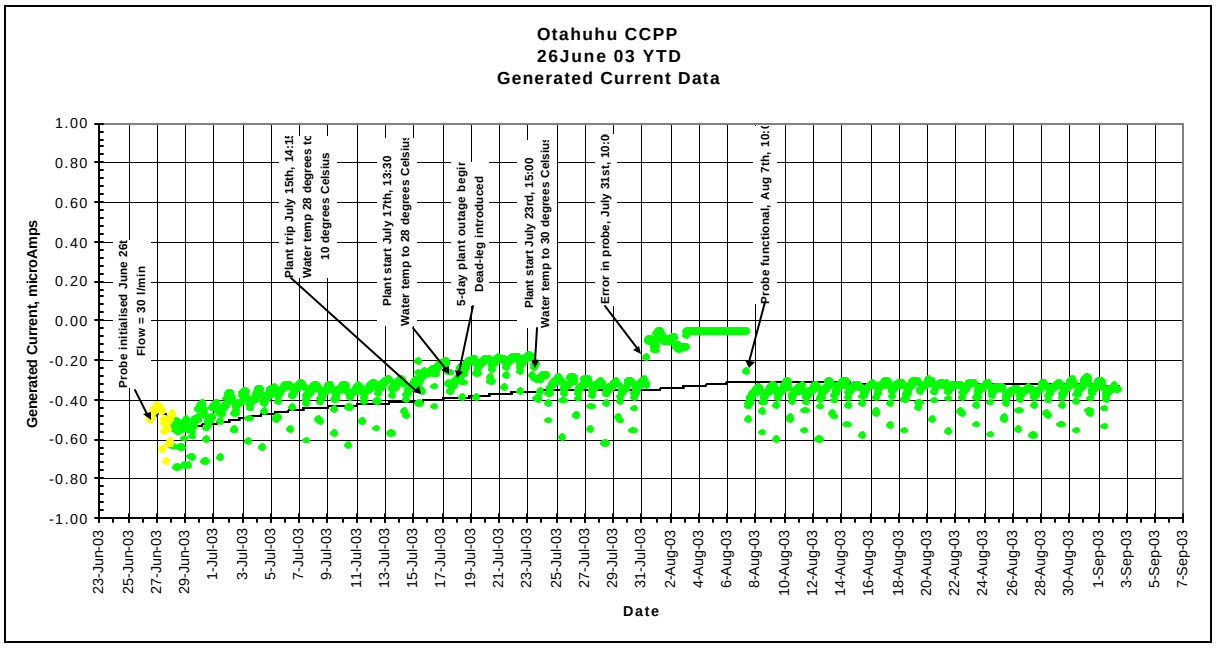


FIGURE 11 - Generated Current History –2003

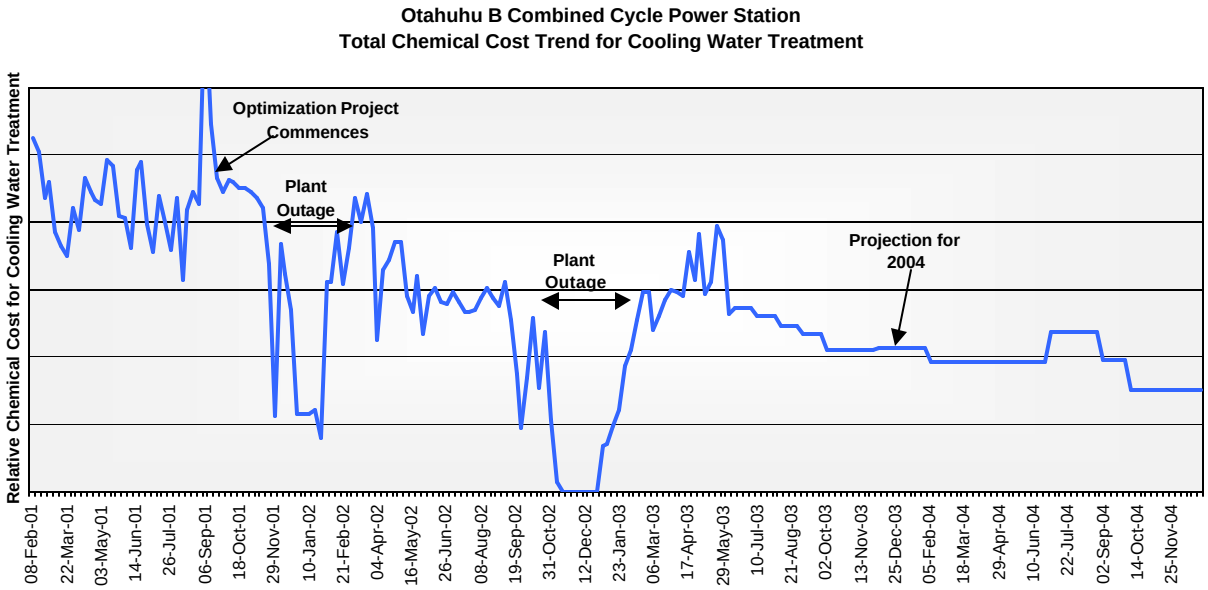


FIGURE 12. Relative Chemical Costs from Initial Biocide Optimisation Activities