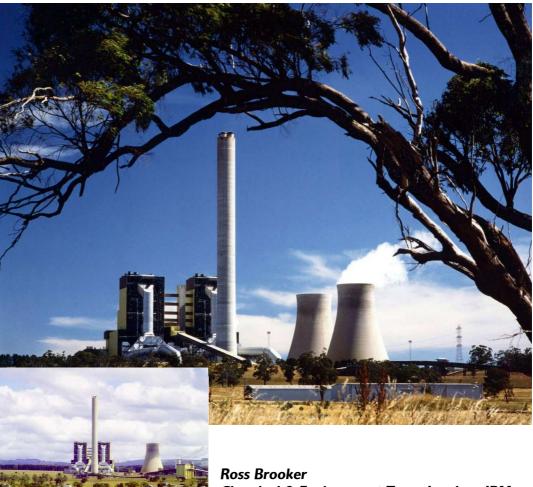
DEVELOPMENT OF A COOLING TREATMENT PROGRAM AT LOY YANG B POWER STATION



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API PowerChem May 2008

Introduction

The 2 x 500 MW Loy Yang B Power Station was commissioned during the period 1993 – 1996 as the newest of the base load, brown coal generators in Victoria.

Located adjacent to the 4 x 500 MW Loy Yang Power Station complex and open cut mine and given similar design and use of common support infrastructure the close proximity provided LYB chemistry personnel the invaluable opportunity of *"looking over the fence"* to gain an operational insight into the real issues to be faced in the early operating years of the Loy Yang B Plant.

The most significant of the *"foreseeable, chemistry management issues"* was the asset management problems to be faced with observed life of the copper alloy based unit condensers.

With the prospect of condenser plant failure at Loy Yang B 'mirroring' that experienced next door, the early asset management plans for the LYB condensers needed to be clearly focussed on Copper corrosion minimisation and delivery of asset life expectancy – in addition to addressing the significant environmental impact of Copper discharged to the local waterway.

Successful application of a Tolytriazole (TTA) based copper corrosion inhibitor program arrested the Copper loss from the LYB condensers and corrosion rate measurements indicated that the projected life expectancy for the condensers of > 35 years would be attained before the requirement for partial re-tube (with the cheaper Copper alloy option).

A complimentary project to the Copper corrosion inhibitor program has been the necessity to develop and implement a chemical biocide dosing program with the <u>dual aim</u> of the maintenance of heat exchanger performance and the implementation of OH&S risk management controls for the issues associated with Legionella.

This project has proven to be the most challenging – with the "development phase" now entering into its final design stage; some twelve years after initial investigations and plant trials. This development path has taken us through various plant trials starting from the original gaseous chlorine treatment programs through to sodium hypochlorite (NaOCl), *'stabilised'* bromine, ozone treatment of cooling tower make-up flows and finally to salt electrolysis – as the basis of a bromine program supported at this point by NaOCl.

The final process design of salt electrolysis, as the basis of a bromine program supported by NaOCl to achieve system 'disinfection', is now proving to deliver a cooling water treatment program that is achieving positive and balanced results in controlling Copper (and mild steel) corrosion (in conjunction with continuing TTA based programs) and controlling the risks associated with the ubiquitous Legionella, whilst at the same time providing effective control of biofouling.

One lesson to be learnt – don't lose focus on the primary objective of any cooling water treatment program – *maintenance of asset integrity and heat exchanger performance*. Both these aspects can have an immense impact on the bottom line of your business – get these

right and the 'secondary' issues of OH&S risks, such as Legionella, will be satisfactorily controlled.

As an example loss of *asset integrity and heat exchanger performance*, unit efficiency where significant bio-fouling events can have considerable revenue impacts on a generators bottom line. In one particular circumstance in June 2006 LYB generating units suffered significant generator off-loading due to Generator Hydrogen Cooler biofouling as "the loss of control in biofouling chemical programs". This single event resulted in the loss of some \$200,000 revenue and required "off-line condenser bakes" to displace bio-fouling from condenser heat exchanger surfaces to recover condenser performance. Had it not been at a time where system electricity prices were relatively low – the economic penalties may have been order of magnitudes greater.

LOY YANG B POWER STATION - PLANT PROFILE

Loy Yang B Power Station is located in Victoria's Latrobe Valley, 160 kilometres east of Melbourne.

The State's newest base load power station produces 1010 MW of electricity- 17 per cent of Victoria's power needs - using brown coal from the adjacent Loy Yang open cut mine.

Loy Yang B is jointly owned by a consortium of International Power plc (70 per cent) and Mitsui & Co. Ltd (30 per cent). The partnership trades as International Power Mitsui (IPM).

The power station was commissioned in 1993 when the first of its two 500 MW rated generating units began operation. The second unit commenced commercial operation in 1996.

The circulating water systems serving Units 1 & 2 is made up with water drawn from the Victorian Alps catchment via the Blue Rock Storage Dam, the Latrobe River and water supply infrastructure, that delivers cooling water to a local storage reservoir that serves the Loy Yang power station complex (some 3000MW of installed capacity across the Loy Yang Power and Loy Yang B Power Stations). The water supply is supplemented with artesian water which is drawn from the Loy Yang Open Cut brown coal mine for mine floor stabilisation and can constitute up to 30% of the make water supplied to Loy Yang B (LYB) Power Station.

The water supply quality to LYB is characterised (with seasonal variations) as shown in Table 1. 'Cycling up' the cooling towers in terms of salt loadings in circulating water due to the evaporative process involved in cooling, results in elevated water quality parameters as also shown in Table 1.

	Make Up	@ 5 Cycles	@ 13 Cycles
рН	6.0 - 6.5	8.0	8.6
Alkalinity (Total) as CaCO ₃ ppm	10- 15	90	190
Suspended Solids ppm	5 - 10	50	98
Total Dissolved Solids ppm	90 - 110	500	1300

The unit steam condensing plant at LYB consists of individual tube modules (of which there are three of per unit) each containing 7432 tubes, 7037 are Aluminium-Brass and 395 are 90/10 Copper-Nickel (being the air extraction zone).

Twin hyperbolic cooling towers serve the two 500MW units each having a circulation rate of $11.2 \text{ m}^3.\text{sec}^{-1}$ and total system volume of 25ML. Typical make-up water rate to each tower is 250 L.sec⁻¹ at MCR.

<u>WHERE WE STARTED - "LOOKING OVER THE FENCE" – INITIAL OPERATING</u> <u>CHALLENGES FOR LYB COOLING WATER SYSTEMS</u>

Located adjacent to the 4 x 500 MW Loy Yang Power Station complex and open cut mine and given similar design and use of common support infrastructure, the close proximity provided LYB chemistry personnel the invaluable opportunity of *"looking over the fence"* to gain an operational insight into the real issues to be faced in the early operating years of the Loy Yang B Plant The most significant of the *"foreseeable, chemistry management issues"* was the asset management problems to be faced with observed life of the copper alloy based unit condensers.

Early plant based measurements completed in 1995 indicated accelerated rates of metal loss for Aluminium Brass and Cupro-nickel condenser tubing and for mild steel components in the main and auxiliary systems of both units 1 & 2 at Loy Yang B.

Baseline corrosion rates determined by corrosion coupon surveys were as follows:-

•	Aluminium Brass	~50 µm/yr
•	Cupro-nickel	~ 18 µm/yr
٠	Mild Steel	~700 µm/yr

The corrosion of copper bearing alloys led to elevated levels of copper being discharged in to the Loy Yang Drainage Settlement Pond and ultimately the Traralgon Creek. Copper levels discharged to the Traralgon Creek from the Loy Yang complex to the Traralgon Creek were in excess of the Environment Protection Authorities limits for copper, peaking at just in excess of 1 ppm Copper.

At the baseline corrosion rates measured for Aluminium Brass (50μ m/yr) the expected condenser tube life was 12 years, based on a condenser tube failure criteria of 50% of tube wall diameter (1.22 mm) or 18 years for a 25% failure criteria. It is interesting to note that the LYA condenser failures fitted into this 12 year window - coincidence?

The question regarding the bio-toxicity of the copper being discharged from the Loy Yang Drainage Settlement Pond to Traralgon Creek was assessed at the time by a macroinvertebrate bio-monitoring program conducted on discharges water to the Traralgon Creek environment. This produced clear evidence that these water discharges were having an adverse environmental impact on the receiving water environment and thus become another clear driver to reduce copper discharge.

With the prospect of condenser plant failure at Loy Yang B 'mirroring' that experienced next door, the early asset management plans for the LYB condensers needed to be clearly focussed on Copper corrosion minimisation and delivery of asset life expectancy – in addition to addressing the significant environmental impact of Copper discharged to the local waterway.

It is also important to note that the LYB circulating cooling water systems were initially commissioned with chlorine gas treatment systems for control of biological fouling.

KEY PROGRAM OBJECTIVES & PRIORITISATION

The prioritisation of water treatment for the cooling towers has evolved in the twelve or so years of operation with a number of factors coming into play through the years. Corrosion monitoring programs and copper content in environmental discharges both clearly indicated that protection of copper bearing assets needed to be given highest priority in the early years – firstly to protect asset longevity and secondly to reduce copper losses to the water environment via cooling tower purge.

The cost associated with a condenser re-tube at this time was placed at some A\$7.5M per condenser for replacement with Titanium based metallurgy, whilst the projected ongoing costs of chemical treatment programs for circulating water systems became the key metric for justification of ongoing programs (Projected O&M costs for CW dosing program based on TTA, Sodium Hypochlorite, Iron Corrosion Inhibitor and Dispersant was A\$1.6M pa).

Whilst not immediately an identified issue, the health and safety aspects relating to Legionella in particular were a rapidly growing focus area – particularly after the Melbourne Aquarium Legionella outbreak in April 2000.

Subsequently the Australian Standard AS5059 Power Station Cooling Tower Water Systems—Management of Legionnaires' Disease Health Risk was published and become the guidance for managing risk within the energy sector for Legionella in circulating water systems.

At LYB the early chemical treatment program focussed on corrosion control with the 'secondary' elements of biological fouling of heat exchangers i.e. asset longevity took priority. This approach was to ultimately cost revenue as heat exchanger fouling, specifically in the main Unit condensers and generator hydrogen coolers caused a requirement for unit off-loading to rectify - therefore an intensive focus on biofouling was also required.

In more recent times with the continuing 2006 / 2007 drought conditions in southern Australia, water conservation initiatives have been a prime business driver with cycling of cooling towers recirculating water systems to higher levels of total dissolved solids in order to reduce water usage. Typically at LYB this has resulted in the number of cycles of being increased from five to thirteen resulting in a final TDS of some 1300 mg.L⁻¹ in circulating water and a reduction of 2GL in make-up water requirements. This has also necessitated the diversion of cooling tower purge to station coal ashing systems due to environmental restrictions on TDS discharges to local waterways.

COOLING WATER TREATMENT PROGRAM DEVELOPMENT PHASES

With LYB cooling water systems commissioned utilising chlorine gas as the primary disinfectant for fouling control, the strong oxidising chemistry approach compounded the issues of copper metal loss particularly in an environment complicated by low alkalinity and low Langelier Index (<1.0 LSI) resulting in corrosive water conditions.

In addition, high intensity maintenance resulting in poor availability of chlorine gas delivery systems (evaporators and injection systems) were drivers to explore alternative approaches

to biological and fouling management. The move to liquid chemical based disinfection programs based initially on sodium hypochlorite and bromine derivatives alleviated some of the chemical delivery system operation and maintenance issues - but increased overall chemical treatment costs i.e. chlorine gas versus 12.5 % sodium hypochlorite.

The introduction of the bromine chemistries to supplement the sodium hypochlorite based programs were generally founded on four key principles:

- Improved operating pH range
- Lower volatility of hypobromous acid compounds and decreased cross cooling tower stripping,
- Less severe interaction with copper bearing alloys; and
- Less severe interaction with Tolytriazole based filming corrosion inhibitors used for yellow metal protection.

Copper corrosion issues related to the low alkalinity cooling water have been successfully addressed through the implementation of a filming inhibitor dosing program based on TTA (and later the patented chemistries of Halogen Resistant Azoles). These programs have reduced Copper corrosion rates from > 50 μ m/yr to <2 μ m/yr, effectively increasing condenser asset life from 10 years to 35+ years – thereby meeting original design expectations.

Figure (1) provides a graphical timeline for the development phase of the LYB Cooling Water Treatment development program.

A major variant to the chlorine / bromine based chemistries as the basis for disinfections programs at LYB was trialled over a period in 2002 – 2004.

An ozone production plant was installed in 2003 to feed gaseous ozone into cooling tower make-up supplies primarily to remove chlorine demand and incoming biological fouling sources in an attempt to control major bio-fouling instances within the circulation water systems. The plant design was based on the production of ozone through the corona discharge effect with air as the carrier.

Many engineering design issues were encountered during the trial period, mostly relating to ozone feed control and degassing of product and carrier air in the make up water lines – which lead to motive water pump blanketing and the ozone plant tripping.

The trial did achieve effective ozonation of the make-up water supply to the cooling towers, which was reflected in improvements in make-up water quality, namely some reduced colour and biological content indicators of Heterotrophic Colony Count (HCC) and Total Legionella counts.

However, since the total volume of cooling tower make-up water being treated (~250 $Lsec^{-1}$ per cooling tower) constituted only ~3% of the total recirculating water rate within each tower system (11,200 $Lsec^{-1}$ per cooling tower) the impact of the "sterilisation" of the make-up water supply on the overall tower chemistry and biofouling fouling was negligible.

By the nature of operation of the hyperbolic design cooling towers, with the major function of evaporative cooling being achieved by ambient air being drawn into the base of the tower, therefore the tower acting essentially as an air scrubbing unit – the impact of the "sterilisation" by ozonation of the make-up water supply did not have the capacity to overcome the external contaminant load on the tower which was proven to be the greatest contributor of "nutrients and biological seeding" within the towers.

Figure (2) provides the cooling tower graphical timeline for the development phase of the LYB Cooling Water Treatment program overlayed with the system bio-logical profiles for HCC and Legionella.

For many bacteria found in cooling water, the optimum temperature for maximum growth is about 40° C, which is the level of temperature likely to be encountered in industrial water coolers, particularly in summer. At this temperature, small changes in temperature are likely to produce substantial changes in biofilm growth because microbial activity is very sensitive to temperature. For instance, it has been shown in one study that biofilm thickness increased by some 80% by raising the temperature from 30° to 35° C¹. The bacterium was E. coli. Figure (3) very clearly recognises this trend with a very clear seasonal variation in condenser cleanliness.

¹ "Bio-fouling in Water Systems" L.F. Melo & T.R Bott. April 17, 1996; revised September 15, 1996

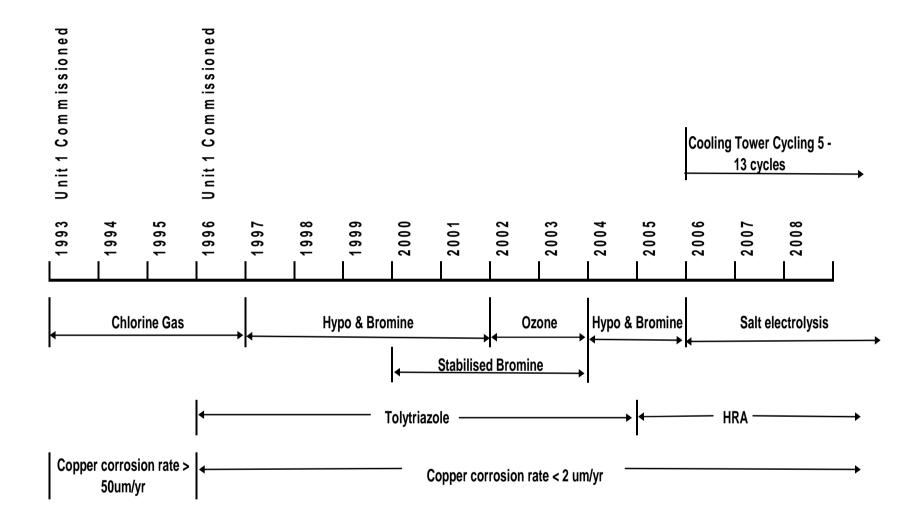
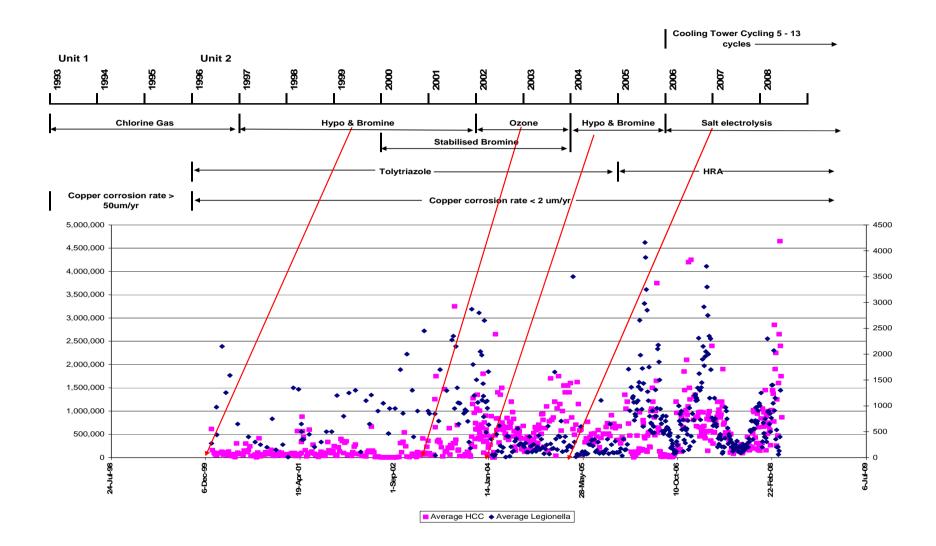


Figure No 1 – Loy Yang B Cooling Water Treatment Development Timeline





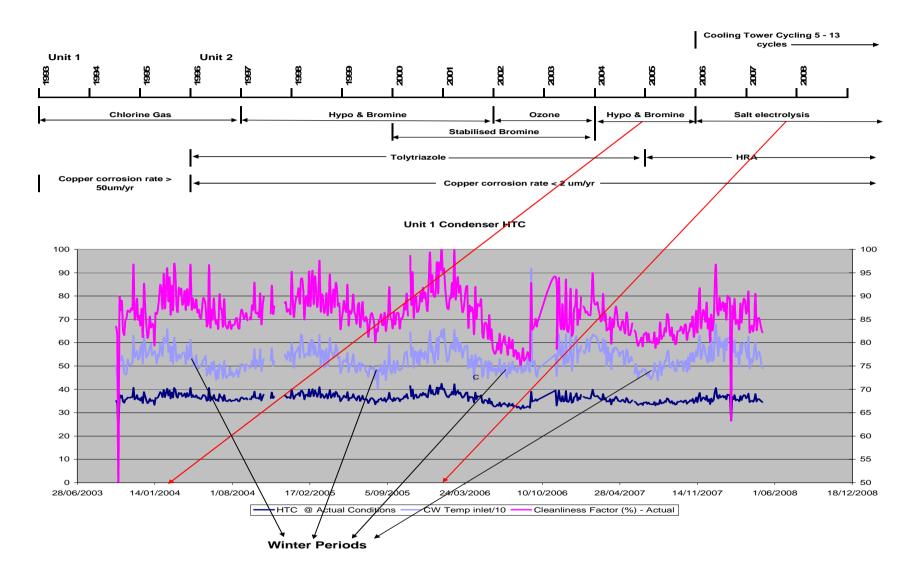


Figure No 3 – Loy Yang B Cooling Water Treatment Development Timeline overlayed with Condenser Performance Data.

<u> A BALANCING ACT – PLANT PERFORMANCE Vs OH&S</u>

The historical development of the Loy Yang B cooling water chemical treatment program was predicated on the delivery of the asset life longevity after "looking over the fence" at what might eventuate given the similar plant designs and water supply sources.

The first years of operation at Loy Yang B and the endeavours to deliver asset performance and longevity were largely successful based on the implementation of the yellow metal inhibitor programmes; that is Tolytriazole and later the halogen resistant azoles.

However, plant performance and efficiency measures and the health and safety drivers of Legionella soon become key players in the further development of the cooling water chemical treatment programme. In more recent times water conservation initiatives have driven chemistry programme redesign to consider higher cycling operations. The following issues are considered in greater detail within this paper:

- Water Conservation Initiatives (Cooling Tower Cycling);
- Biological Control Programs and
- Performance Monitoring Programmes.

WATER CONSERVATION DRIVERS

Large coal fired steam-electric power stations on inland sites in Australia rely predominately on indirect (recirculating) cooling systems with natural draft hyperbolic cooling towers. The cooling circuit of a typical 500MW unit contains up to 12ML volume recirculating water through the surface condensers and auxiliary cooling system.

Water loss is by drift and evaporation and accounts for some 20 ML.day⁻¹ per unit. Evaporation has the effect of increasing the concentration of salts and other contaminants including suspended solids in the system therefore a percentage of the concentrated water must be eliminated and replaced with lower concentration water to maintain these contaminants at a manageable level.

The water sources for many of these stations are rivers and lakes carrying varying levels of suspended and dissolved solids including potential run-off from agricultural activities and potentially discharge from wastewater plants. All of these inputs, have to some extent an impact on the usability of the water for station cooling purposes.

The extent of the latest drought and the consequent reduction in availability of water has focussed the industry on mechanisms for the reduction in the volume of water consumed by the industry in cooling applications. Indeed even with the reduction in the severity of water restrictions in some areas, some stations are under more strict limitations for access to water even if it is available.

Water trading markets in the State of Victoria have also reflected the supply shortfall under drought conditions with the price for water moving from 80/ML (2005) to 250/ML during the 2006/2007 period when bulk entitlements were exceeded and additional water was required to be purchased to insure continuity in generation. The price for water if required to be purchased in 2008 is placed at $1500.ML^{-1}$ minimum.

As a consequence of this an investigation was undertaken at LYB to determine the opportunities available to reduce water consumption and to improve treatment processes.

Initial review of the operational characteristics of the station pertaining to water quality and availability revealed some issues.

- Availability and quality of water would be compromised in the case where the drought worsened. This would have an impact on plant performance and potentially compromise generation.
- Due to the marginal design of the cooling system the plant faces potential cooling issues in hotter weather, particularly where increased cooling water temperatures impact condenser performance.
- A number of alternative biological control agents had been trialled over the years. The current sodium hypochlorite dosing program was only marginally effective and was a potential limit on more efficient water management.
- The make-up water while quite low in hardness is appreciably saline. The water is very corrosive to yellow metal and at low cycles requires the use of corrosion inhibitor. Make-up water has variable levels of iron and silica.
- There is a significant seasonal variation in water quality with high levels of silica and iron noted at periods through the year.
- The environmental licence sets discharge limits for blowdown water chemistry thereby placing constraints on cycling and discharges to Traralgon Creek.
- Other discharge points for blowdown were severely volume restricted i.e. station ashing systems.

Initially at LYB cooling tower cycling rates were dictated by environmental discharge limits, primarily on TDS, for blowdown discharged from the site to local receiving waterways.

Water conservation drivers were then key in the decision to increase cooling tower cycling of water, hence increasing TDS and necessitating diverting cooling tower blowdown to alternative discharge environments, namely the Loy Yang Ash Pond. This receiving environment ultimately is discharged to Bass Strait, a coastal marine environment – therefore more receptive to the high saline waters discharged from the station ashing systems and cooling tower blowdown.

Cycling Options

In order to meet the requirements for unit availability under reduced water reliability it was clear that more efficient water use need be made of existing and future water entitlement. Projections indicated that up to 2GL of water could be saved each year by increasing cycles of concentration in cooling towers from 4 to 13 cycles.

Figure 5 gives the modelled blowdown curve for the LYB cooling tower systems based on actual data.

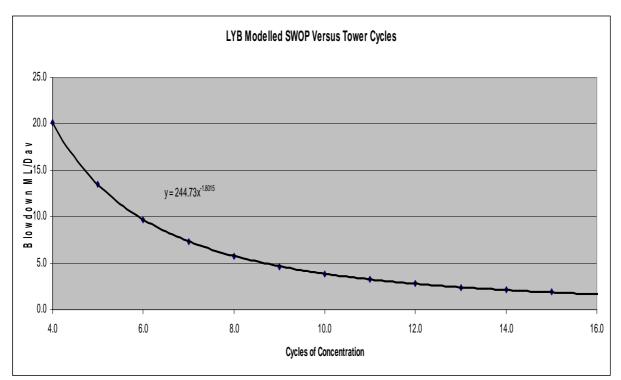


Figure No 4 – LYB Power Station Cooling Tower Blowdown Curve.

A comprehensive review of the water quality both current and historical revealed that there were a number of potential issues likely to be encountered if the cycling program was to be undertaken.

Challenges for the Water Cycling Program

The water quality at LYB as used in the make up for the Cooling Water system presents a number of challenges for use:

- Firstly the water is very soft but with relatively high salt content. Use at low cycles results in water that while low in scale potential up to 4 cycles is very corrosive and requiring yellow metal corrosion inhibition.
- Cycling the water above 4 5 cycles results in saturation of iron species and calcium/magnesium species in particular calcium carbonate, magnesium silicate and at higher pH levels potentially iron hydroxide.
- Cycling the water above 4 cycles without pH control would further increase pH thereby further reducing the efficacy of chlorine as a disinfectant.

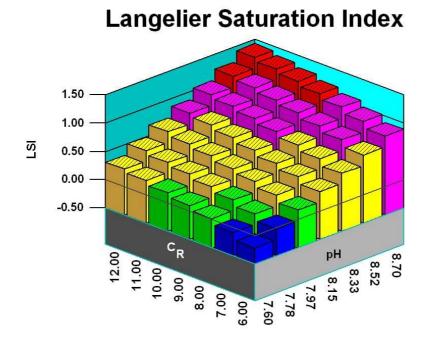
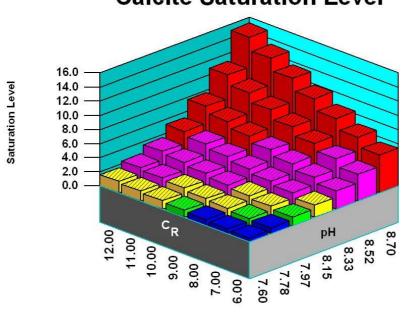


Figure No 5 -. LSI Saturation Model for LYB

As can be seen in Figure (5), 9 cycles at elevated pH calcium carbonate becomes a more significant issue with potential deposition in hotter areas of the cooling circuit.



Calcite Saturation Level

Figure No 6 –. Calcite Saturation Model for LYB

Figure (6) demonstrates the impact pH and cycling has on calcite deposition. As can be seen even at lower concentration ratios if pH increases above 8.3 then deposition will occur.

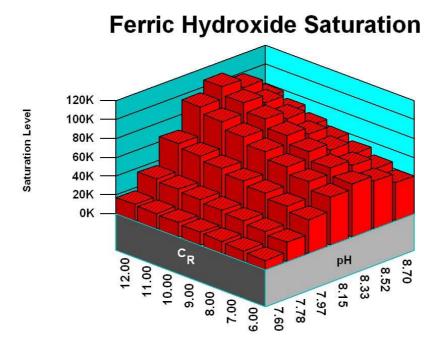


Figure No 7 –.Ferric Hydroxide Saturation Model for LYB.

The high level of iron in the incoming make-up was initially regarded as a significant concern as iron typically interferes with the performance of most scale inhibitors as well as being a potential foulant. However the absence of iron deposition at lower concentration ratios historically indicated that the iron might not be the issue the levels would suggest. (Figure (7).

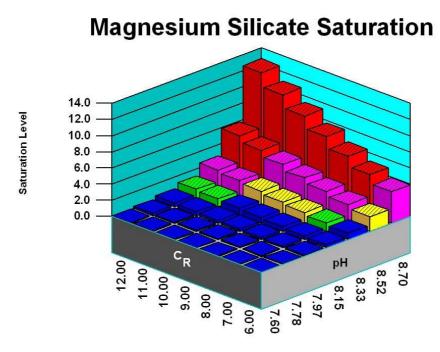


Figure No 8 – Magnesium Silicate Saturation Model for LYB

Magnesium silicate also is of some concern at elevated pH levels particularly when silica levels in the make-up are elevated. See Figure (8).

From this modelling we were able to develop a treatment regime to address the projected issues relating to:

- Calcium carbonate scale
- Iron fouling
- Magnesium Silicate scaling
- Biofilm and Biological Control

Laboratory evaluation of the water combined with modelling using Water Cycle allowed a chemical program to be developed to allow cost effective cycling to a maximum of 13 cycles with minimal fouling issues.

A water management program was developed comprising two major processes for IPM LYB in order to address a range of operational issues whilst not compromising performance or occupational health and safety of plant personnel.

The program comprised a biological control program incorporating ElectroBrom which was more suited to the operating regime likely to be encountered under increased cycles and an antiscalant/dispersant program able to control the fouling issues predicted as cycles were increased.

The program takes into consideration the high apparent iron levels in provision of an iron tolerant antiscalant (most antiscalants have very low tolerance to iron contamination) and very effective silt dispersant.

BIOLOGICAL CONTROL PROGRAMMES.

With LYB cooling water systems commissioned utilising chlorine gas as the primary disinfectant for bio-fouling control, considerable development time has been given to optimising biological fouling control programmes due to the <u>desire and need</u> to dispense with gaseous chlorine:

- the <u>desire</u> to dispense with gaseous chlorine largely based on the H&S and dangerous goods handlings issues with liquid / gaseous chlorine and the associated delivery systems; and
- the <u>need</u> to dispense with gaseous chlorine systems based on the fact that the chlorine plant and systems were highly prone to corrosion by the nature of the chemical involved and the reliability of the plant was less than satisfactory within 1 – 2 years of commissioning due to corrosion related malfunctions.
- A review of chlorine impact on yellow metal corrosion revealed a significant contribution by chlorine in destabilising the oxide film.

Prior to higher cooling tower cycle operations at LYB (pre 2006), the biological control program at LYB involved slug dosing of 12% sodium hypochlorite on a daily basis with an adjunct bio-dispersant on an indicative weekly basis. Sodium hypochlorite was added to give an ORP increase to 500mV and required some 600-700 litres per slug per unit.

Dosing was to a ring main around the circumference of the tower basin to an addition point at the furthest point from the pump forebay. This was to allow maximum dispersion thereby minimising the corrosive impact of the chlorine on the aluminium brass condenser tubes.

Problems were encountered with gassing of the hypo resulting in air-locking of pumps and inconsistent dosing as a consequence. This can be seen in the increasing trend for both HCC and Legionella in the period leading up to end 2005. (Refer to Figure 2). While, generally Legionella was effectively managed, there was evidence of biofilm on most visible wetted surfaces.

Problems Associated with Biofilms

A physical problem that biofilms cause in cooling systems is fouling. Algal biofilms foul cooling tower distribution decks and film and even splash fill where these surfaces are directly contacted by sunlight. Biofilm accumulations in these areas cause flow restrictions and result in decreased tower efficiency through channelling. Portions of the mass can also break loose and be transported to other parts of the system, causing blockages in sprays and other parts of the distribution system as well as providing nutrients for various strains of bacteria.

While biofilm can form on any wetted surface they cause issues most frequently on heat transfer surfaces as temperatures favour the rapid growth of many strains of bacteria. Biofilm fouling of heat exchangers is a major operational problem because of biofilms extreme resistance to thermal conductance. The data below shows the thermal conductivity values for several deposit-forming compounds compared to biofilm. A lower number indicates a greater resistance to heat transfer.

Substance	Thermal Conductivity (W M- ¹ K- ¹)
CaCO ₃	2.6
CaSO ₄	2.3
Biofilm	0.6

Thermal conductivity comparison of deposit-forming compounds and biofilm.

In addition to general fouling, biofilms can contribute to scale formation as well. Carboxylate functional groups in the biopolymer attract calcium ions from the recirculating water and fix them in place in the biofilm matrix. There they are available to react with carbonate ions which are also present at alkaline pH's. Once this nucleation of the calcium carbonate molecule has occurred, a crystal can grow. Biofilms can also trap calcium carbonate particles that have already precipitated. These particles can then serve as crystal growth sites further building the scale deposit.

In addition biofilm has been clearly linked with the proliferation of legionella and the potential amplification of the legionella bacteria in organisms within the biofilm.

Biofilm Control

There have been several trials of biocides at LYB in an effort to determine the most suitable cost effective biological control agent. A range of approaches from the initial gas chlorine to Ozone, Stabilized Bromine and liquid chlorine has been investigated with limited success. Each of the programs demonstrated limitations in their ability to deliver reliable and effective control over biofouling and pathogens while still not threatening plant longevity.

Further, in consideration of the chemical and physical constraints expected to be applied by the cycling program a further range of conditions needed to be satisfied by the biological program:

- Program needed to be able to be operated at relatively high pH conditions.
- Program needed to be effective against common pathogens including Legionella.
- Program was preferred to have minimal impact on OH&S.

Consideration of the above conditions narrowed the available options to bromine chemistry in general with electrolytic generation of hypobromous acid, ElectroBrom, ultimately being the preferred option.

ElectroBrom?

The generation of hypobromous acid as an active biocidal species is undertaken using an electrolytic process under the proprietary name '*ElectroBrom*'.

Bromine is generally accepted to be an effective oxidizing biocide, especially at cooling water pH levels above 7.0 where chlorine starts to lose much of its efficacy. When a halogen such as chlorine or bromine is added to water it hydrolyses to an acid form (hypohalous acid) and base (hypohalite) form. With regards to disinfection the hypohalous acid is by far the most effective. Chlorine and bromine ionize in this fashion and the balance between hypohalous and hypohalite form is very pH dependant.

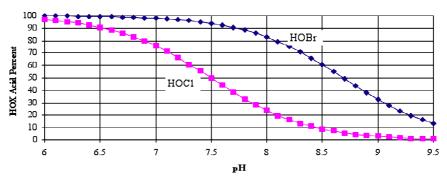


Figure No 9 – Chlorine / Bromine Speciation versus pH.

As can be seen at any given pH above 6 the active bromine biocide is at a greater concentration than for chlorine. Indeed at pH 8.5, the expected operational pH when LYB cooling towers were cycled, there would be in excess of 6X as much active bromine biocide.

Traditionally bromine has been used as an adjunct to chlorine in cooling water but with somewhat mixed results. Typically the hypobromous acid is generated by the addition of sodium bromide to sodium hypochlorite. Research carried out on bromide reaction chemistry in 1987 by K. Kumar and D.W. Margerum at Purdue University,² found that indeed, hypobromous acid was formed by reacting bromide with hypochlorous acid. The reaction was fast and complete if the hypochlorite solution was neutral, acidic, or slightly alkaline. However, if the hypochlorite solution was strongly alkaline (as would be the case for a concentrated commercial bleach solution), the reaction proceeded at a considerably slower rate. Kumar and Margerum reported that the reaction rate for hypochlorous acid was 1.5

² "Kinetics and Mechanism of General-Acid-Assisted Oxidation of Bromide by Hypochlorite and Hypochlorous Acid," Journal of Inorganic Chemistry, pp. 2,706–2,2711

million times faster than for hypochlorite ions. At a pH of 12, the bleach and bromide must be in contact for more than 45 minutes to convert just 50% of the bromide to hypobromite.

Other mechanisms to deliver bromine to the system have included a range of stabilised bromine products. To date they have at best delivered mixed results with less than satisfactory results obtained in larger power station cooling systems.

Another means of obtaining bromine is via on-site electrolysis of an aqueous sodium bromide solution, which is non-hazardous and relatively low cost. The major problem historically with electrolysis of sodium bromide solution to produce a hypobromite solution is a low bromide to bromine conversion efficiency, about 35%, which makes operation of such a process quite costly in terms of delivered bromine.

The new on-site electrolytic process obtains lower cost operation due to a bromide to bromine conversion efficiency exceeding 95%. This increase in conversion to the desired end product is obtained by use of an equimolar aqueous solution of sodium bromide and chloride. When such a solution is subjected to electrolysis at a direct current power input of one ampere per square inch of electrode area, an equal production of chlorine and bromine is obtained due to the equal probability that an electron will react with either a chloride or a bromide ion. This allows a production of up to 35% hypobromous acid and 35% hypochlorous acid that ultimately reacts with the excess bromide to form further hypobromous acid. The reaction is carried out under effectively neutral pH conditions so the reaction is very rapid.

At LYB the decision to adopt electro-bromination as the principle biocide program was screened against the criteria developed in the assessment process:

- Precursor salt or salt solution is non-hazardous, there is no risk associated with spills during transport, storage or employee handling
- Bromine has a lower vapour pressure than chlorine so less product escapes into the air from the cooling water circuit – cross towers stripping.
- The active disinfectant is generated as required and the precursors do not degrade in storage so there is no waste
- Bromine biocide reverts rapidly to harmless bromide ion in the environment so there is no toxic blowdown
- The Electrobrom Biocide System is suitable for providing continuous halogenation for control of Legionnaire's disease
- Cost is comparable to chlorine based disinfection, much less than non-oxidising biocides

Electro-Bromination Development Program

The electro-bromination programme was developed over the course of a two-year investigation, with three distinct programs of dosing have been used.

The first program installed was an ElectroBrom EBG40 unit with a graphite-electrode system capable of producing 18kg (as Cl_2) of oxidant per day, delivered as a 0.4% (4000 ppm) solution of hypobromous acid. The unit was fed from a mixed solution of sodium chloride and sodium bromide diluted with mains low quality water. The unit was designed based on performance data delivered from operation of a similar unit at IPL Plant at Petersburg,

Indiana, USA. This installation replaced a gas chlorine plant for a two unit station similar in output to LYB. In this instance a single EBG40 unit operating for 8-10 hours per day was able to provide equivalent disinfection capacity to the gas chlorination. Early indications were positive with HCC and Legionella numbers looking favourable after the previous poor bleach results. Clear improvements were visible in biological activity in visible wetted areas such as the CW return conduit. Removal of bio-film evident at the start of the trial was obvious with areas of clean painted surface becoming visible.

The change to on-site generation of a bromine disinfectant coincided with a move to higher tower cycles (as previously discussed). This increase in cycles contributed to an increased oxidant demand in the tower basins. As a consequence during the first few months the Electrobrom unit was operated continuously rather than intermittently as expected. This highlighted some design flaws in the unit where an accumulation of bromine apparently built up in the dead space at the bottom of the cell. Bromine is considerably more corrosive in its elemental form and this weakened the graphite undermining its integrity. After 6 months and a failure of 2 graphite cells the decision was made to install a reactor capable of delivering up to twice the oxidant of this original plant while overcoming the bromine build up issue.

At the relatively low oxidant solution strengths employed here, (<1%) an increase in total generation in addition to the design issue already discussed required a move away from graphite electrodes to the more expensive, but more efficient, coated-titanium electrodes. The new electrolysis unit installed was capable of producing up to 40kg (as Cl_2) of oxidant per day. In practice maximum conversion efficiency of halide to hyphalous acid – production of a 0.9% oxidant solution, was achieved at lower total flow rates giving a daily production of only 24kg. However satisfactory conversion of halide to hypoalous acid - a 0.5% oxidant solution - was achieved at total flow rates up to 6.0 L.min⁻¹, giving a daily production of over 40kg as Cl_2 . Installation of a second similar electrode unit, running in parallel, brought the total generation capacity to 80kg.day⁻¹.



Figure No 10 – ElectroBrom 40 kg.day⁻¹ Biocide Electrolysis Unit.

These larger units operate on a mix of three separate feeds – high-quality mains pressure water, a saturated brine solution and a 60% w/v sodium bromide solution. Individual control of each of these feeds allows adjustment of feed conductivity as well as chloride/bromide ratio.

	Daily Generation (kg as Cl₂)	Solution strength
EB-1-Gr	18	4000ppm
EB-2-Ti	40	5000ppm
Dual EB-2-Ti	80	5000ppm

The question of the discrepancy between the results obtained from the IPL operation and the LYB operation is accounted for in the absence of attention to Legionella control in the US and importantly the difference in biological challenge on a seasonal basis. The temperature range in Illinois is somewhat lower than that for Latrobe Valley with sub-zero temperatures encountered in winter where no disinfection is required at all to average summer temperatures of just 25° Celsius. In contrast temperatures consistently over 40° Celsius for extended periods are not uncommon in summer in the Latrobe Valley.

Consistently dosing the total output of both ElectroBrom units gave a good disinfection result even with increased cycles. However, the continual, low-level dosing did at no stage allow observation of a high, intermittent halogen residual or an elevated ORP. While there are advantages in terms of such aspects as corrosion control in continuous dosing at low levels for effective biological control there is still a requirement for an ORP shock to ensure effective control.

Disinfection of the towers (when run at lower cycles) had previously operated on an 'ORPcontrolled' dose of hypochlorite solution, so there was some experience in estimating system cleanliness from the ORP response following a hypo dose. It was decided to dose a standard hypochlorite solution to the towers on top of the ElectroBrom production and observe the ORP response. An immediate increase in ORP confirms that there is very little oxidant demand in the recirculating water and biological growth in the system is being controlled. In this way, the total amount of hypochlorite required to raise the ORP to a threshold level provides a *defacto* measurement of ElectroBrom performance.

Performance of the ElectroBrom system so far shows that a capacity of 80kg.day⁻¹ is sufficient for routine maintenance of a clean system. However, in practice a disinfection system must have 'spare' capacity to deal with periods of increased oxidant demand and be able to 'cleanup' a system that has suffered a period of increased fouling. In addition the ability to ORP shock the system to ensure effectiveness is considered advantageous. For this reason the final ElectroBrom system designed for installation at Loy Yang B will have a capacity of >180kg.day⁻¹ (as Cl_2).



Figure No 11 – Proposed ElectroBrom 180 kg.day⁻¹ Biocide Electrolysis Unit.

Plant Performance Impacts Post Implementation

As stated previously, much of the early focus of the cooling water treatment program was on delivering asset longevity.

The performance and efficiency of the various key heat exchangers was quite often overlooked – or at least "was out of sight" and hence out of mind!

Ongoing asset performance monitoring programs were tracking main condenser performance (cleanliness), however an event in mid 2006 proved to be a catalyst to 're-focus' our efforts on a more holistic control program, one not primarily concerned only with main condensing plant but also on key systems within the auxiliary cooling water circuits.

During a period in mid 2006, when ongoing equipment reliability issues had compromised the capacity of the biocide chemical dosing system to continually feed sufficient biocide to the cooling water system to maintain an effective halide residual, the 'cleanliness factor' measurements within the main condenser plant had degraded to less than the ideal design point, that is an 85% Cleanliness Factor.

Because of the seasonal timing of the event (early to mid winter) and cooler ambient temperatures, the overall condenser vacuum performance was not compromised. However, a more sensitive heat exchanger system within the auxiliary cooling system, the Unit Generator Hydrogen Coolers – did suffer loss of performance which necessitated the reduction of unit output and the removal and subsequent mechanical cleaning of the coolers. (See Figure 12).

The loss of revenue to the station as a result of this 'loss of control' was estimated to be ~ \$200k. Had it not been at a time where system electricity prices were relatively low – the economic penalties may have been order of magnitudes greater?

Corrective actions taken included:

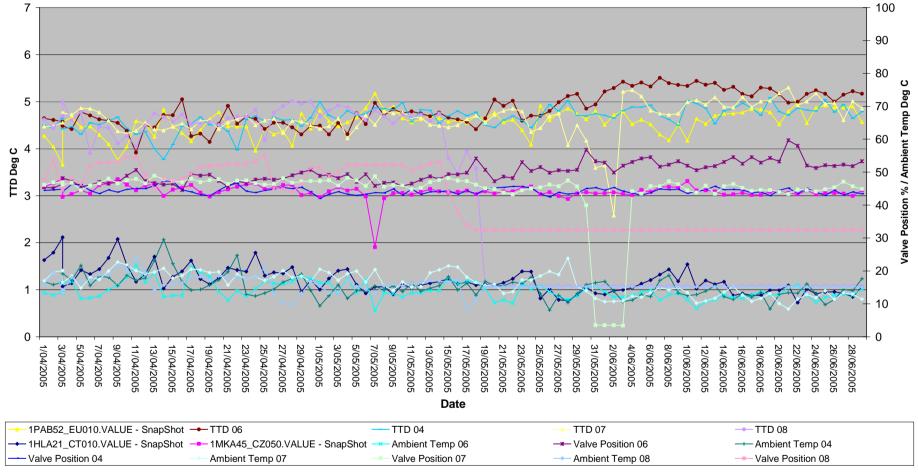
- Conducting main condenser plant "Bake Outs" a process where the cooling water is isolated in turn from each lung of the condenser and external water box doors are opened allowing steam side temperatures to dry condenser tube bio-fouling deposits to a friable state. Once the lung is placed back into service the heat exchange performance (i.e. Cleanliness factor) of the lung is restored.
- Mechanical cleaning of the generator hydrogen coolers; and
- Increased reliability in biocide delivery systems by upgrading the electrolysis units in the "ElectroBrom" process to a higher capacity.

Figure (13) shows the impacts of this event of condenser plant Cleanliness Factor.

As a result of the condenser bakes heat exchanger performance returned to optimum levels. (See Figure 14). The biocide delivery program has since proven effective in maintaining heat transfer performance. Through the remainder of 2006 and throughout 2007 effective biological control, as measured by condenser cleanliness, has been maintained.

Since 2006 the performance of the Unit Generator Hydrogen Coolers has also been monitored more closely. Subsequent analysis of plant performance in the time leading up to the fouling episode revealed that performance parameters of the hydrogen coolers were more sensitive to the gradual build-up of inorganic and organic deposit occurring in the cooling system. That is, fouling caused by silt deposition and biofilm growth could be detected earlier by monitoring the hydrogen cooler performance and ongoing monitoring of such performance gives confidence that the biocide delivery system is maintaining total system performance.

Figure (15) shows that active planktonic biological monitoring programs don't necessarily provide the predictive data trends needed to maintain effective plant conditions to avoid biofouling events. In this particular case there are no indicative (increasing) trends in either HCC or Legionella data that supported increasing bio-fouling potential. In fact to the contrary the HCC and Legionella counts where indicate a "relatively clean" and improving system dynamic – great from an OH&S perspective BUT! costly on plant efficiency and performance.



Unit 1 Heat Transfer (Hydrogen Cooler & Condenser TTD) April - June 2004/2005/2006/2007 Overlayed

Figure No 12 – Bio-fouling impacts on Hydrogen Coolers & Main Condenser

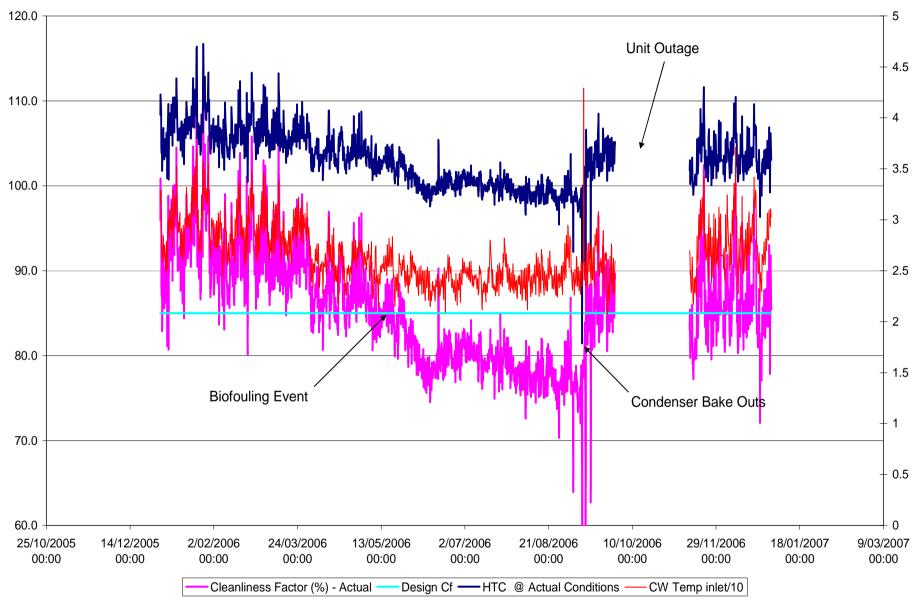


Figure No 13 – Bio-fouling impacts on main unit condenser plant 2006 Event

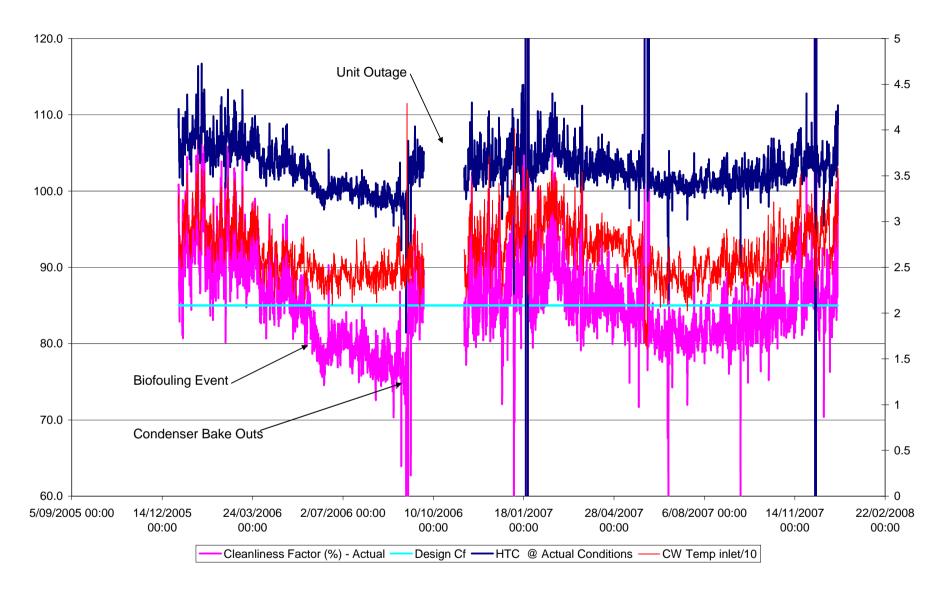


Figure No 14 – Bio-fouling impacts on main unit condenser plant – Recovery after 2006 Event

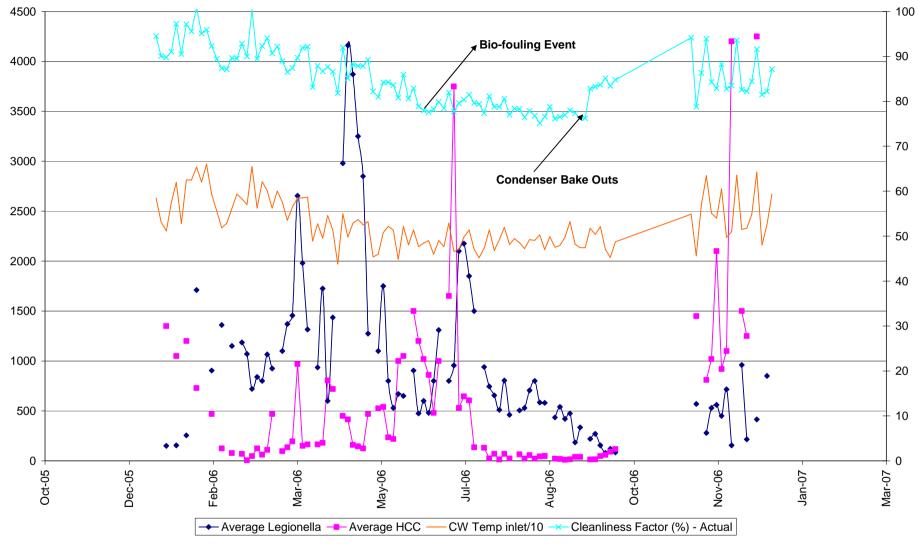


Figure No 15 – Bio-fouling impacts on main unit condenser plant and interrelationship with HCC & Legionella Data

<u>Performance Monitoring Programs – Corrosion, Condenser Heat Transfer, Biological</u> <u>Fouling & hygiene parameters</u>

The development of the cooling water treatment programs at LYB has also benefited in the evolution of plant performance and program performance monitoring systems. Data generated from this performance monitoring program has further improved the implementation of the chemical treatment and asset management returns.

The key elements of the monitoring program are:

• Corrosion Monitoring System

Corrosion was established as a KPI to be managed if plant lifespan was to be optimised. A test skid was assembled comprising a series of tube sections of various metallurgies, selected to mirror condenser and other key heat exchangers within the circulating water systems. The tubes are exposed to treated circulating cooling water at a matching flow velocity to that of the main condenser. The tubes are exposed for varying time periods from 30, 60 to 120 days and are then removed and analysed to determine corrosion rate and deposition rates. A fixed electronic corrator is also incorporated into the test rig and linked into the chemical dosing and data-logger control system.



• Water Quality Monitoring Panels

Circulating cooling water and make-up water quality is continuously monitored and data feed into the station's DCS and utilised for control functions within the CW Chemical; Dosing Program. Parameters such as pH, Conductivity, Turbidity, and ORP are routinely monitored.

• Condenser Heat Transfer Coefficient and Cleanliness Factor Monitoring

Main unit condensers are monitored for Heat Transfer Coefficient and Cleanliness Factor with data extracted from the DCS of each unit and calculated off-line in Excel spreadsheets. Examples of the data produced are seen in Figures (3), (12) & (13). Medium term trends (weekly - monthly) are examined as used as a decision making tool in modifying the hypochlorite dosing program in conjunction with ORP response data from the water quality monitoring panels to optimise dosing program.

• Legionella and HCC Routine Monitoring

Routine sampling and testing of circulating water systems is undertaken for Legionella (Fortnightly) and Heterotrophic Colony Count (HCC) (Weekly) to track biological fouling and OH&S indicators.

REFLECTIONS ON LESSONS LEARNT

Learning from one's mistakes is essential if progress is to be made. Learning from someone else's mistakes works every bit as well and is a lot less painful. The lesson learned from LYA allowed copper corrosion to be eliminated as a potential threat to station performance.

Don't lose focus on the primary objective of any cooling water treatment program – *maintenance of asset integrity and heat exchanger performance*. Both these aspects can have an immense impact on the bottom line of your business – get these right and the 'secondary' issues of OH&S risks, such as Legionella, will be satisfactorily controlled

HCC cannot be relied on in any way to indicate bio-fouling. In fact in some instances it could be 100% wrong.

Water management programs must be considered from a holistic perspective if they are to have most chance of success.

It is absolutely essential to set appropriate KPI's and ensure that they are correctly prioritised.

Water conservation will be the performance drivers over the next decade.

In Victoria the Eastern Water Treatment Plant Recycling Project will be the next hurdle for Latrobe Valley based electricity generators with 115 GL per annum of recycled water being considered for transfer to the region (115 Km) for direct use in the circulating water systems of the Power Stations. The projected multi-billion dollar infrastructure project will be based on the delivery of ultra-filtered recycled water with a TDS of ~ 700 mg.L⁻¹ (compare with existing supply quality of ~ 100 mg.L⁻¹) with elevated ammonia & nutrients.

Just what every power station with a copper condenser needs!!