Macrofouling Control in Power Plants

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Abstract Macrofouling organisms readily colonize artificial man-made structures, cooling water intake tunnels, culverts, pump chambers and heat exchangers. Cooling water systems if not properly treated invariably become susceptible to biofouling. The problem is particularly severe in the tropics and is site-, season-, and substratum-specific. Further, cooling systems serve as a source of macrofouling organisms and breeding grounds wherein invertebrate larvae are produced and colonize equipment downstream like pipelines, valves and heat exchangers. Once-through seawater or freshwater systems encounter severe macrofouling-associated problems like flow reduction, increased pressure drop across heat exchangers and equipment breakdown. Biocidal dose and regime for cooling water systems and heat-exchangers have to be tailor-made for a power plant and should be effective in controlling microbial biofouling as well as hard foulants (barnacles, mussels, tubeworms and oysters). With regard to macrofouling control in condenser-cooling systems of power plants, chlorination has been the method of choice for fouling control over the years due to its low cost, easy availability and handling, and known degradation pathways. Increasing awareness on the toxic effects of chlorination by-products and better understanding of the biocidal action, environmental issues and higher dosages required for sanitization of surfaces has resulted in replacement of chlorine by stronger oxidizing biocides like chlorine dioxide. Experimental studies using coastal seawater in plate heat exchangers, has revealed a chlorine residual of 1.0 ppm to prevent settlement of invertebrate larvae. However, an intermittent chlorination dose of 1.2 ppm residuals at a frequency of 0.5–2 h was sufficient in controlling slime formation. Side-stream monitoring of these heat exchangers in a nuclear power plant cooling circuit revealed barnacle fouling in spite of continuous chlorination of 0.2–0.3 ppm residuals and shock doses of 0.4–0.6 ppm twice a week for 8 h. In an operational plant, continuous monitoring of the fouling situation using side-stream monitoring devices is to be practised and the biocidal dose and regime

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Springer Series on Biofilms, doi: 10.1007/7142_2008_14

altered to overcome any spikes in settlement. This is essentially because biocidal doses required to kill established fouling communities are far higher than those for inhibiting settlement. Even if killing is achieved, accumulation of dead shell biomass (barnacles and tubeworms) often results in loading on equipment surfaces and increases surface roughness, facilitating settlement of other fouling organisms.

1 Introduction

Industrial fouling involves inorganic, organic, particulate and biological fouling (see Smeltzer 2008). Biofouling in industrial water systems is a recalcitrant problem not easily controlled and even then at a significant cost. Operationally, the problem due to biofouling manifests when "biofilm development exceeds a given threshold of interference" (Flemming and Griebe 2000). Microbial biofouling can alternatively be considered as a biofilm reactor in the wrong place, as cooling systems offer large surface areas for colonization and nutrients for growth (Flemming 2002). Biofouling in recirculating freshwater systems is less pronounced than in once-through seawater systems and generally manifests in the form of condenser slime (biofilms) in power-plant cooling circuits.

About 150 species of macrofoulants have been listed for seawater-cooled systems whereas Asiatic clams and Zebra mussels are the main macrofoulants in freshwater-cooled systems (Claudi and Mackie 1994). Macrofouling in the cooling water systems of power plants results in reduction of flow to the condenser tubes, blockage of intake pipes, condenser tube blockage, mechanical damage to pumps and condenser tubes, promotion of microfouling and enhanced corrosion of condenser tubes. Further settlement of hard-shelled fouling organisms causes damage to material integrity and often results in failure of equipments. Compared to shell and tube heat exchangers, plate heat exchangers (PHE) are finding increased applications recently in nuclear, thermal and desalination plants. Long-term data on the use of these heat exchangers in power plant cooling circuits revealed accumulation of corrosion products and particulate fouling on the plates. Initiation time for biological fouling in industrial systems ranges from a few hours to about 400 h (Bott 1993). For a successful antifouling strategy an integrated approach of monitoring the surfaces, including analysis of fouling situations, is important (Flemming 2002). In seawater-cooled systems macrofouling is a predominant problem and control measures should aim at a biocidal dose and regime to prevent settlement of organisms and development of biofilms, i.e. restricting biofilm development at the given threshold of interference. Environmental parameters such as fluid velocity, temperature, pH value, nutrient levels, cell concentration and surface roughness have all been demonstrated to have a measurable effect on the development of both biofilms and settlement of macrofouling organisms. A biocide dose should be effective from zero hours to keep the surface clean. The old approach of increasing biocide dosage to remediate a biofouling problem frequently fails in practice. Since biofouling is a surface-associated phenomenon it should be treated as such, by targeting treatments for controlling surface-associated or sessile organisms (Donlan 2000; Flemming 2002).

One of the major factors affecting power plant operation is the performance of the cooling water system (Brankevich et al. 1990; Bell 1977). This has led to the development of specific antifouling measures for power plants. The most common countermeasure as practised in a majority of power plants comprises filtration of debris and fouling organisms through intake and travelling water screens, biocide dosing (chlorine) and thermal shock treatment. Compared to chlorine dioxide, the use of a much stronger oxidizing agent such as ozone is not popular. Due to the high production cost and considering the volume of water to be treated in once-through systems, this does not seem to be a viable alternative. The success of these methods is dependent on the nature of the fouling organisms in a given geographical location (Strauss 1989; Sasikumar et al. 1992), quality of cooling water (Corpe 1977), thermal and biocidal tolerance ranges of different size classes of macrofouling organisms existing in a cooling circuit (Jenner 1980; Sasikumar et al. 1992; Rajagopal et al. 1995) and siltation (Jenner et al. 1998). The development of a macrofouling community in the cooling water system occurs as a result of passage of planktonic larvae of invertebrates followed by a settlement phase (see Murthy et al. 2008), during which the organisms metamorphose into adults by producing an outer shell. The high flow velocity ensures a continuous supply of oxygen, food for the growth of macrofoulants, avoids the accumulation of waste and results in increased colonization of macrofoulants (Jenner 1980). Over a period of time if the situation is left untreated a uniform fouling layer accumulates on the surfaces with a thickness reaching 30 cm from the wall (Kovalak et al. 1993). These cause problems in the condenser section as the fouling layer grows in thickness they are sloughed off due to high velocities, and such clusters are deposited in the heat exchangers blocking the flow (Kovalak et al. 1993).

The problem of macrofouling in heat exchangers leads to flow blockage in shell and tube heat exchangers (Fig. 1a) and deposition in plate heat exchangers (Fig. 1b). Fouling causes irreversible mechanical damage to the equipment surface due to the hard calcareous shells of fouling organisms. A 5 mm Hg reduction in condenser backpressure is equal to 0.5% improvement in turbine heat rate, which is approximately equal to an additional 3 MW(e) of generating capacity (Drake 1977). On the other hand, fouling of heat exchanger surfaces results in reduced heat transfer efficiency and increased fluid frictional resistance,resulting in additional maintenance and operating costs (Bott and Tianqing 2004). Apart from macrofouling, even a 250 micron-thick layer of slime may result in up to a 50% reduction in heat transfer in heat exchangers (Goodman 1987). In the case of heat exchangers, a decrease of the overall heat transfer coefficient due to fouling deposits leads to overdesign, and increased energy and cleaning costs, which are substantial (Bott 1995). As far as overdesign is concerned, fouling in plate exchangers leads to higher operational costs compared to shell and tube exchangers because of their higher efficiency (Muller-Steinhagen 1993; Hesselgreaves 2002; Kukulka and Devgun 2007). In seawater flow systems the fouling layer on a heat exchanger surface comprises chiefly of inorganic and biological fouling. If biofilm formation precedes that of inorganic film, the inorganic film develops in the channels existing in the biofilm

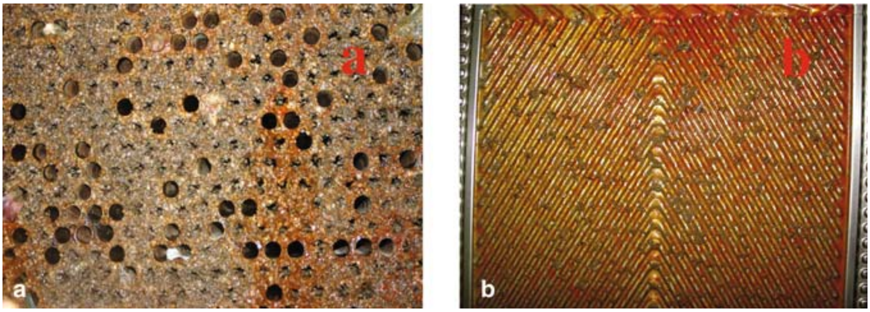

Fig. 1 **a** Flow blockage of tubular heat exchangers (PSWHX) of Madras Atomic Power station after one year of operation. **b** Fouling by particulate material and corrosion product on titanium plate heat exchanger surface after 69 days of operation at 0.5 m s^{-1} velocity in a side-stream study at the Madras Atomic Power Station, Kalpakkam

matrix. If inorganic fouling precedes organic fouling then it would attract adhesion of bacteria (Sheikholeslami 2000). However, these mechanisms are yet to be substantiated through experimental data. Some of the factors influencing fouling of heat exchangers are the material of construction of a heat exchanger, and its surface roughness will influence the development of biofilms (Mott and Bott 1991; Mott et al. 1994). Vieira et al. (1992) demonstrated that initial attachment of *Pseudomonas fluorescens* was more pronounced on aluminium plates than on brass or copper, which may be attributed to the release of toxic ions by these surfaces. Rabas et al. (1993) demonstrated that fouling was higher on spirally indented tubes than plain tubes. On the other hand, rough surfaces were more hospitable to microorganisms than smooth surfaces (Reid et al. 1992). On a rough surface, valleys provide shelter against removal by shear stress and hills act as nucleation sites; therefore the extent of fouling is high on rough surfaces. Surface properties like adsorption, surface charge and corrosiveness were also found to affect fouling (Epstein 1983).

2 Types and Features of Industrial Cooling Water Systems

Choice on the type of cooling water system is influenced by plant location and availability of water suitable for cooling purposes. Once-through cooling systems are used in plants sited beside large water bodies (sea, large flowing rivers and estuaries) that have the ability to dissipate waste heat from the steam cycle. For detailed system analysis and design of structures refer to Jenner et al. (1998), Neitzel and Dalling (1984). Design characteristics of once-through systems may allow or even increase the rate of fouling by promoting conditions that are conducive to sedimentation, macrofoulants and corrosion. Intake structures of once-through systems vary from plant to plant depending on environmental considerations and flow requirements. Most of the flow-through systems comprise of an offshore intake system (bored tunnel or a buried culvert), which conveys the water to a pump

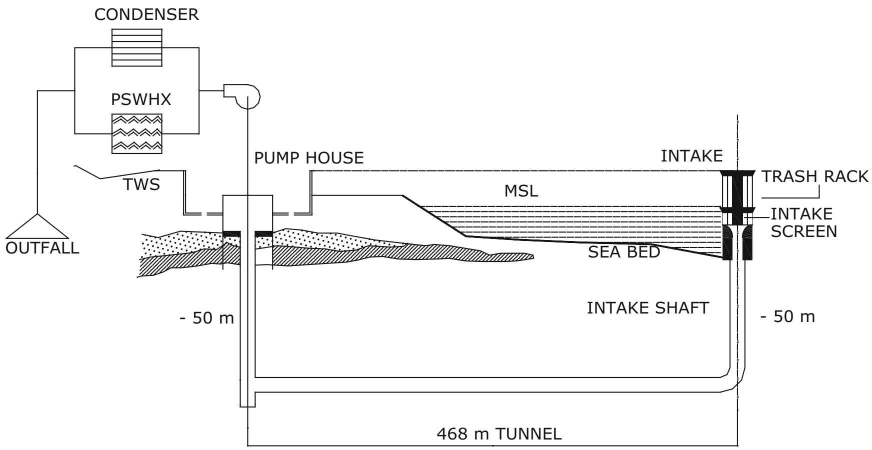

Fig. 2 Schematic view of a cooling water system of a power station (Madras Atomic Power Station, Kalpakkam, located on the east coast of India). *TWS* travelling water screens, *PSWHX* process seawater heat exchangers, *MSL* mean sea level

house located onshore from where the water is pumped through the condensers, and returns via a shore-based outfall (Fig. 2). Near shore intakes are not preferred as they may result in a severe siltation problem. Some of the design features incorporate physical water treatment methods like water velocities in the cooling water tunnel designed around 1.5–3.0 m s^{-1} to prevent sedimentation, and provision of trash screens at the offshore intake point and travelling water screens before the pumps. In addition, once-through systems typically have high flow velocities and mass flow rates for minimizing temperature effects on receiving waters. A typical 500 MW(e) unit would have a flow of 30 m^3 s^{-1} at an average velocity of 3 m s^{-1} in the cooling water circuits. Design factors influencing macrofouling of once-through systems are (1) flow velocity, (2) flow pattern, (3) frequency of use, (4) valve leaks, (5) unreliable and ineffective biocidal systems, (6) compartment size, (7) system configuration and (8) water temperature (Neitzel et al. 1984).

3 Economic Losses Due to Biofouling in Power Plants

An estimate of economic losses due to biofouling problems is large and emphasizes the importance of biofouling control measures in power plants. Most of the literature on losses due to biofouling dates to the late 1990s. Costs for one day of unplanned outage of a 235 MW(e) power plant can be around 0.3% of the earning. Hence control measures adopted to maintain cooling water cleanliness reflects on indirect earnings to the industry. Losses as a result of shutdown of a 235 MW(e) power station due to biofouling were estimated to be about Rs. 40 lakhs a day (about US$100,000) (Venugopalan and Nair 1990). The cost of removing macrofouling organisms from screening houses alone for two European power plants cost around US$ 25–30,000 every 2 years (Kovalak et al. 1993). In the USA, approximately 4% of failures in power plants >600 MW(e) is due to biofouling of condensers (Meesters et al. 2003). Fouling by Asiatic clams *Corbicula asiatica* in condenser tubes of power plants alone costs the USA over US$1 billion annually (Chow 1987; Strauss 1989). The problem is more pronounced in heat exchangers, where an increase in condenser backpressure due to fouling in a 250 MW(e) plant costs about US$250,000 annually (Chow 1987).

Cleaning of biofouling organisms from cooling water-circuits of power plants is a very expensive option for plant operations. Studies by Coughlan and Whitehouse (1977) showed that between 1957 and 1964, some 4,000 condenser tubes failed due to mussel fouling, leading to leakage of cooling water into the boiler. Apart from the loss of power generation, these leaks contaminated the feed-water system and accelerated the boiler waterside corrosion, resulting in boiler tube failures. This has necessitated the inlet culverts to be drained for manual cleaning once a year. The average quantity of mussels removed was estimated at 40 tons per year and the maximum was 130 tons per year. Similarly, 300 tons of mussels were removed from the Pools power station (Dorset). About 300 tons of mussels were removed following shock chlorination treatment from the atomic power station intake tunnel in a single occasion (Rajagopal et al. 1996). Similarly, 4,000 man-hours were used to clean the circuits and remove mussels (360 m^3) at the power station at Dunkerque (Whitehouse 1985). Another example of intense fouling is the Carmarthen Bay power station, where within a year of commissioning the problem became so severe that the plant was shut down periodically (James 1985). The underwater cooling conduits of the Tanagwa power station in Japan showed a fouling thickness of 70 cm (Kawabe and Treplin 1986).

3 Biofouling Control Methods in Once-Through Seawater-Cooled Systems

An important consideration in the operation of equipment subject to biofouling is its mitigation. Mitigation techniques broadly fall into (1) physical (Bott and Tianqing 2004; Melo and Bott 1997) and (2) chemical methods (Sohn et al. 2004; Meyer 2003; Ludensky 2003; Walsh et al. 2003; Rajagopal et al. 2003; Butterfield et al. 2002a, b; Prince et al. 2002; Ormerod and Lund 1995).

3.1 Physical Control Methods

3.1.1 Flow

Water flow is a major factor influencing settlement of marine invertebrate larvae (Table 1). Velocity is a design factor for cooling water systems (Strauss and Puckorius 1984; Tuthill 1985; Johnson et al. 1986). Flow velocities in cooling water conduits must be measured very close to the wall (1 mm) surface rather than

Table 1 Velocity as an antifouling measure

Velocity (m s^{-1})	Effects on organisms	References
Less than 0.9	Allows sedimentation and microfouling to occur	
>0 but <0.3	Allows Asiatic clam larvae to settle	Jenner et al. (1998)
>0.1 but <1.2	Allows blue mussel and oyster larval settlement	
>0.1 up to 1.5	Allows mussel settlement in intake tunnel *Branchidontes variablis*, *B. striatulus* and *Modiolus philippinarum*	Rajagopal et al. (2006)
>3.0	Does not detach mussels	Syrett and Coit (1983)
>0.01 up to 1.0	Allows Zebra mussel larvae to settle	Tuthill (1985)
0.15	Allows Zebra mussel larvae to settle. Data from ten European power plants	Kovalak et al. (1993)
Above 2.0	Inhibits Zebra mussel larval settlement	Leglize and Ollivier (1981)
<0.2; >0.6; >0.9	Settlement; growth inhibition; detachment of colonies of bryozoans	Aprosi (1988)
1.8–2.2	Allows settlement of mussels, barnacles, hydroids in circular conduits	Jenner and Khalanski (1998)
Up to 1.4	Allows mussel, barnacle, hydroid settlement in large rectangular conduits of (5–11 m^2)	Jenner et al. (1998)
>4	Required for preventing erosion corrosion of metal structures	Jenner et al. (1998)

the mean water velocity, as settling larvae are subjected to the velocity at the near surface boundary rather than in the bulk water. At high flow rates, the shear stress of the water often exceeds the shear strength of many organisms, hence they do not settle (Collins 1964). However this is not the situation in operational power plants, where barnacles were found to colonize even at velocities of 3.0 m s^{-1}, making the surface rough and creating sites for further settlement of mussels (Syrett and Coit 1983). Hence it is imperative to adopt a chemical control strategy to control the settlement and growth of macrofoulants. Conventionally a 1,000 MW(e) capacity power plant requires cooling water at the rate of 30 m^3 s^{-1} (Whitehouse 1985), which is drawn at a velocity of 2.0–3.0 m s^{-1} through inlet pipelines. In general, flow across the heat exchanger tubes is maintained around 1.4–2.0 m s^{-1}. Analysis of operational and experimental data from different power plants shows that velocities in the range of 3.5–4.0 m s^{-1} are required to prevent settlement of marine organisms. However, most power stations operate at velocities of 1.4–1.8 m s^{-1} across the heat exchangers and at around 2.0–3.0 m s^{-1} in pipe sections and cooling water circuits, which does not prevent the settlement of macrofoulants. The successional pattern of macrofouling organisms in cooling water circuits are also known to be driven by flow velocity. Larval forms capable of settling at high velocities are the primary colonizers and these established organisms were found to baffle water currents, which enabled attachment of larvae that preferred low velocities to settle (Corfield et al. 2004). An example of this effect was reported by Jenner (1980), whose study showed that barnacles were found to settle before mussels as they can attach at much higher velocities and their shells provide the roughness required for mussels to settle. In practice, there are low flow regions associated with the geometry of the cooling water circuit that may favour increased settlement, and it appears impossible to maintain a constant velocity throughout the cooling water circuit. Increasing the velocity requires additional pumping costs and does not seem to be a viable method. A possible antifouling method postulated by Jenner (1983) for controlling biofouling using velocity is to decrease the flow rate instead of increasing the flow rate, taking into consideration the sinking rate of different organisms at low flow velocities. However, this proposition is yet to be substantiated through experimental studies to be adopted in power stations. Alternatively the use of high velocities (1.5–2.5 m s^{-1}) with a smooth finish to the surface of the culverts could theoretically prevent settlement of mussel spat (Jenner 1982). With the advent of foul release coatings this seems to be a viable option, along with the flow and biocidal regimes in force. In general, the use of flow as an antifouling method is unlikely to be effective in power stations.

3.1.2 Travelling Screens

Another problem encountered in once-through offshore/near shore intake systems of power plants is impingement by large fish, driftwood, seaweed, jellyfish etc. The problem is overcome by the provision of single or double trash racks for the offshore intake systems, which serve as the first line of defense (Brankevich et al. 1990). Usually, travelling water screens are provided ahead of the heat exchangers to filter out the floating debris and adult macroorganisms. Screens of different mesh sizes (10 mm UK and Japan; 4 mm France and Italy; 4–10 mm Netherlands; 10–25 mm India) are in general use. Downstream of service water pumps, the water passes through basket strainers for removing particles and the water is taken to the condensers for cooling. Seawater-cooled plants are designed to minimize the number of components that interface directly with seawater because of the corrosive nature of seawater. Intermediate closed-cycle loops filled with demineralized water are used for cooling the auxiliary systems (process water heat exchangers). The use of travelling water screens is indispensable for plant operation.

3.1.3 Mechanical Cleaning Techniques

In spite of the presence of physical control methods like travelling screens and biocidal programmes, heat exchangers are often subjected to sedimentation and biofilm accumulation. Mechanical online and offline methods are available for cleaning of shell and tube heat exchangers. In the case of plate heat exchangers, online mechanical cleaning has been found to be economically non-viable and technically unfeasible warranting the use of chemical treatments. Ceramic, glass or sponge rubber balls have been used for online cleaning. Brush type online cleaning devices are also available. Two types of automatic cleaning systems are employed in power stations during normal plant operations: the Amertap system and the American M.A.N. brushes system. The Amertrap system can be operated on an intermittent or continuous basis depending on the severity of problem in the shell and tube heat exchangers. The Amertrap system comprises sponge rubber balls, slightly bigger in size than the tubes, that circulate along the length of the tubes (Bell 1977; Brankevich et al. 1990; Fritsch et al. 1977). The constant rubbing action keeps the surfaces clean and removes biofilms. The balls are collected in an outlet chamber and are again pumped into the heat exchanger. The American M.A.N system uses flow-driven brushes that are passed through the condenser tubes intermittently by reversing the flow. The brushes abrasively remove fouling and corrosion products. Automatic online mechanical cleaning methods are the most economical and are practised invariably in most of the power stations around the world. Even though these are a crude methods, no alternative technology is available at hand and the sponge rubber ball cleaning is again an indispensable method for microbial biofouling control in heat exchangers.

Offline cleaning is done by the hydrolazing method(specialized high pressure water jet cleaning) with a pressure of 10,000–20,000 psi for cleaning heat exchanger tubes. Tubes with scales showed that at a low pressure of 10,000 psi cleaning was relatively poor compared to 20,000 psi. Cleaning of dry tubes was more efficient with brass and spin grit brushes compared to wet tubes, which may be attributed to the lubricating effect of water between brush tips and tube surface. Hydrolazing was effective in cleaning wet tubes (Young et al. 2000). Other types of mechanical cleaning techniques involve moulded plastic cleaners (pigs) that are useful for cleaning light silt deposits. Spirally formed, indented or finned brushes are used for cleaning tubes. Hard calcite depositsare difficult to clean even by acids; rotary cutters similar to the ones used for cutting glass with a Teflon body are used for cleaning. Compressed airdriven devices are also available for cleaning of heat exchanger tubes. Offline cleaning methods are practised in power stations when the thermal resistance values in heat exchangers drop beyond an acceptable level. This results in shutdown of the equipment and affects production costs.

3.1.4 Thermal Treatment

Cooling water requirement of power plants are sized according to the upper thermal limits of discharge, i.e. 7–10°C above the ambient prevailing at a given location. Thermal treatment of cooling water circuits and inlet conduits is an effective environmentally friendly method for control of biofouling in power plants, wherein the cooling water temperature is raised above the thermal tolerance level (Table 2) of fouling organisms (Brankevich et al. 1990). The exact temperature and time required for mortality of fouling organisms is dependent on many factors; the main factor being the acclimation temperature, i.e. the difference between the ambient and treated temperature. A second factor is the rate of acclimation: if the temperature increase is slow, the mussels are found to acclimatize to the rate. Another factor

Table 2 Thermal tolerancelevels of common fouling organisms

Temperatures (°C)	Effect on organisms	References
35–37	Kills most macrofouling organisms	Jenner (1980); Gunasingh et al. (2002)
37 for 30 min; 38 for 15 min; 39 for 5 min	Causes 100% mortality in the mussel *Mytilus edulis*	Jenner (1980)
43 for 30 min	Causes 100% mortality in the green mussel *Perna viridis*	Rajagopal et al. (1995)
39 for 30 h; 43 for 30 min; >45	Tolerates; 100% mortality within 2.15 h; 100% mortality immediately for *Branchidontes striatulus*	Rajagopal et al. (1995)
35–47	Causes 100% mortality for barnacle *Megabalanus tintinabulum*	Sasikumar et al. (1992)

is genetic variations in local populations (Claudi and Mackie 1994). Before implementing a thermal treatment programme, the thermal tolerance of the major foulant species at a particular facility needs to be determined. This can be derived through simple experimentation and following the multiple regression formulae developed by McMahon et al. (1993) for 50% LT_{50} and 100% LT_{100} mortality of fouling organisms:

$$LT_{50}=34.57–0.035(\text{min}/1°\text{c}) + 0.149(°\text{C acclimation temperature})$$

$$LT_{100}=36.10–0.040(\text{min}/1°\text{c}) + 0.147(°\text{C acclimation temperature})$$

Thermal treatment procedures are very effective against macrofoulants compared to microfoulants as they are known to exist in condenser tubes (condenser slime) experiencing elevated temperatures (50–70°C). Thermal treatment methods have been successfully implemented at the Commonwealth Edison Heat plant, where 100% mortality of mussels was achieved by raising the water temperature from 31.6 to 37.2°C and maintaining this temperature for a 6 h period (Claudi and Mackie 1994). The method is also used in some power stations that have the option of dual intake pipelines and facilities for recirculation of water from the heat exchangers. One of the pipelines is used as an intake and the heated effluent from the heat exchanger is circulated through the other. After a certain period the direction of flow is reversed in these pipelines (Jenner 1982). The thermal method has been effective at Marsden B power station where the cooling circuits were treated with elevated temperatures (51.7°C). However, the periodicity of such operations depends on the intensity of fouling at a location. The effectiveness of thermal treatment is also dependent on the appropriate choice of water temperature, duration of exposure and frequency of exposure. For thermal treatment to be efficient, exposure periods no longer than 3 h should be adopted if it is to be economically and environmentally sustainable (Jenner 1982) for operational power plants. However, cooling water systems have a variety of macrofouling organisms, with different tolerance levels. Knowledge of the thermal tolerance of fouling species and information about the biological community that exists in a cooling water system is important for designing treatment strategies. Major disadvantages of thermal shock treatments are in regard to meeting the environmental regulations governing discharge of heated water and the availability of the option for thermal backwashing and losses involved in shutdown of the plant during the backwashing period.

4.2 Chemical Methods

3.1.5 Advantages and Disadvantages of Oxidizing Biocides

Oxidizing biocides are in use for treating cooling waters. In the oxidizing biocide category, chlorine has been the most extensively used and cost-effective biocide. The order of volatility is ozone > chlorine > chlorine dioxide > chloramines > hypochlorous acid > hypobromous acid.

Efficient chlorination treatments suitable both for biofilm and macrofouling control in condensers must be worked out for a given location. The addition of chlorine to water can be viewed as an instantaneous reaction resulting in an equilibrium mixture of hypochlorous acid (HOCl) and hypochlorite ions. Hypochlorous acid is the active biocide and its stability is dependent on the pH of the solution. At a low pH value of 6.0–7.0 relatively more concentration of hypochlorous acid is present than at a seawater pH value of 8.2. In addition, hypochlorous acid (HOCl) reacts with organic matter/nitrogenous compounds and is consumed readily (chlorine demand). This necessitates increased dosing to overcome the demand. In chlorination of natural waters, the chlorine demand has to be ascertained before administering the biocide. Chlorine demand is also found to vary seasonally and the demand of tropical coastal seawater usually varies between 0.7 and 1.0 mg L^{-1} (Murthy et al. 2005). To reduce biofouling, chlorination of seawater is usually practised, with typical applied doses of 0.5–1.0 mg L^{-1} (expressed as Cl_2) and a resultant residual oxidant level of 0.1 ± 0.3 mg L^{-1} in the cooling water. Chlorination can be an effective control technique for both bivalves and microbial slime. Different chlorine doses and regimes have been tested for fouling control (Jenner et al. 1998; Rajagopal et al. 1994, 2003; Rajagopal 1997; Gunasingh et al. 2002).

Some of the common chlorination practices adopted in power stations are:

- *Low level continuous chlorination*: Continuous application of chlorine at residuals of 0.1–0.2 mg L^{-1} is used to deter larval forms from settling. Mussel larvae close their shells in the presence of chlorine and the velocity in the system will flush them out without allowing the larvae to colonize the substratum (Claudi and Mackie 1994).
- *Intermittent treatment*: This method came into practice to reduce the cost of the treatment programme and also to meet the biocide discharge criteria. In addition, mussels are constrained to close their shell valves in response to continuous chlorination. However, studies by Rajagopal et al. (2003) have shown the method to

be ineffective as mussels were able to tide over periods of chlorine dosages by closing their shell valves. Alternatively, the more intelligent version of intermittent chlorination, namely pulse chlorination, developed at KEMA (Poleman and Jenner 2002) has been effective in achieving killing of mussels as well as reducing the biocide inventory and environmental burden.

– *End of the season chlorination*: This has been practised in some of the European power stations (Jenner and Janssen-Mommen 1993) where chlorine levels of 0.5 mg L^{-1} were maintained for 2 weeks at the end of the breeding season to cause 95% mortality of newly settled mussels.

Growing concerns over the harmful effects of chlorination by-products, i.e. trihalomethanes (THMs; volatile), haloacetonitriles (HANs; semi-volatile), halophenols (HPhs) and haloacetic acids (HAAs), resulted in chlorination being disallowed in several of the US, UK, Canadian and European power stations. Use of chlorine is subjected to increasing environmental regulations (such as the new Biocidal Product Directive, 98/8/CE, in European countries). The USEPA chronic and acute marine water quality guidelines for chlorine are 0.0075 and 0.013 g m^{-3}, respectively (USEPA 2002). CORMIX modelling done by the National Institute of Water and Atmospheric Research (NIWA) show that an eightfold dilution of the cooling water plume occurs in the mixing zone (Oldman et al. 2004). If residual concentrations in the cooing water outfall are in the range of 0.1 g m^{-3} after reasonable mixing, the maximum chlorine concentration would be 0.013 g m^{-3}, equivalent to the USEPA guideline (Corfield et al. 2004). The Safe Drinking Water Act (1979) enacted by the USA prescribes the maximum contaminated levels of total THM (TTHM) to 0.10 mg L^{-1} (100 ppb) and the disinfectants and disinfectant by-product rule has fixed the limits at 0.80 mg L^{-1} TTHM (USEPA 1994). Alternatives to conventional chlorination in power stations depends on the cost of the products proposed from the market, roughly these products are one to three orders of magnitude costlier than sodium hypochlorite.

An alternative biocide for controlling biofouling in power plant cooling systems is bromine. Bromine is a chemical halogen similar to chlorine and was introduced commercially in 1980. Since then, plant chemists have had the option of choosing either one or both biocides for their cooling systems. Bromination has been used for some time along with chlorine and can significantly reduce the total disinfectant and halogen application rates because bromine oxidants generated in water are more effective for controlling biofouling than their chlorine counterparts at high pH values, above the 8.0 found in seawater. Several forms of bromine are available, which include activated bromine, sodium bromide, bromine chloride and proprietary mixtures of bromine and chlorine. Commercial formulations like the Active Bromide (NALCO Chemicals), BromiCide (Great Lakes Chemical Corporation) and Starbex, a sodium hypobromite compound for microfouling control, have been adopted by some power stations along with chlorine dosing. Sodium bromide can be used to convert hypochlorous acid (HOCl) into hypobromous acid (HOBr). Literature on the toxicity of this biocide to marine organisms is limited. However, when used in combination with chlorination it is effective in reducing the total halogen load, and the bromine oxidants that are generated are more effective for controlling biofouling at pH values above 8.0 (Fisher et al. 1999).

Currently, chlorine dioxide is being adopted in several European power stations because of its effectiveness in killing macrofoulants as well as against microbial biofouling and because of the lesser formation of organo-halogenated by-products. Typical doses of ClO_2 for seawater cooling systems range from 0.05 to 0.1 mg L^{-1} (Petrucci and Rosellini 2005). Another oxidizing biocide being used for fouling control is ozone. The use of ozone as a biocide is still a very expensive method, estimated around 3.8 times that of the cost of sodium hypochlorite (Duvivier et al. 1996).

Oxidizing biocides have a similarity in their mode of action on biological organisms. The toxicity of chlorine has been reported to be due to the destruction of the respiratory membrane by oxidation (Bass and Heath 1977), oxidation of enzymes containing a sulfhydryl moiety (Ingols et al. 1953) and ion imbalances (Vreenegoor et al. 1977). An EPRI report (Electric Power Research Institute 1980) attributed the toxic effect of chlorine on mussels to a weakening of the strength of the byssal threads. The principle effect of chlorine was to depress the activity of the foot of mussels, leading to a reduction in the number of threads formed. Chlorinated mussels, with their weaker attachment systems, were swept from the walls of the cooling system (Claudi and Mackie 1994). In comparison, the biocidal action of ozone is on the bacterial membrane glycoproteins, glycolipids and certain amino acids such as tryptophan. Ozone also acts on the sulfhydryl groups of certain enzymes, resulting in disruption of normal cellular enzymatic activity. Bacterial death is rapid and is often attributed to changes in cellular permeability followed by cell lysis. Ozone also acts on the nuclear material, modifying the purine and pyramidine bases of nucleic acids (Roy et al. 1981).

The choice of the biocide for cooling water systems is primarily governed by the cost. The dose and regime depends on the nature and intensity of fouling organisms at a given geographical location, and on environmental conditions. There is no such concept as a best dose or a best biocide. Biocide doses and regimes must be tailor-made for each of the cooling water systems. Chlorine is effective but may require very high concentrations, which are not environmentally acceptable. Hence alternative biocides like chlorine dioxide or ozone may be considered, but here cost becomes a limiting factor. Hence, power plant operators have to strike a balance between cost and the cleanliness required. A comparative account of the properties and effectiveness of different oxidizing biocides are given in Table 3. The table has been synthesized based on experience and on data published by Jenner et al. 1998; Claudi and Mackie 1994; Corfield et al. 2004; Rajagopal et al. 1997; Cristiani 2005.

4.2.2 Biocidal Requirements for Prevention of Larval Settlement in Cooling Water Systems

Usually the problem of biofouling gains attention when it interferes with the performance of the station, even in the presence of a biocidal programme in place. This is due to the inadequacy of the biocidal programme in overcoming sudden increases in macrofouling settlement. Hence continuous surveillance, detection of fouling

Table 3 Comparison of properties of different oxidizing biocides

Parameters	Chlorine (Cl_2)	Bromine (Br)	Chlorine dioxide (ClO_2)	Ozone (O_3)	Peraacetic acid
Conc. used in CWS (doses)	0.2–1.0 mg L^{-1}	0.1–0.5 mg L^{-1}	0.1–0.5 mg L^{-1}	0.01–0.3 mg L^{-1}	1.5–3.0 g m^{-3}
Activity	Narrow spectrum at low concentrations	Moderately effective	Broad spectrum at low concentrations	Broad spectrum at low concentrations	Moderately effective
Contact time	Seconds to minutes	Seconds to minutes	Seconds to minutes	Seconds	Minutes
pH	Not very effective at pH higher than 7	Effective up to pH 9.0	Very effective up to pH 11	Not effective above pH 8.5	Effective up to pH 9.0
Temperature effects	Cannot be used at higher temperatures	Cannot be used at higher temperatures	Cannot be used at higher temperatures	Cannot be used at higher temperatures	Cannot be used at higher temperatures
Corrosiveness	Corrosive to handle	Not very corrosive	Not very corrosive	Moderately corrosive	Corrosive to iron substrates
By-products	Produces toxic tri-halomethanes; regulations on upper toxic levels	Used along with chlorine	Does not produce toxic by-products;chlorite ions are generated	Bromate and assimilable organic carbon	Readily biodegradable
Reaction with organics	Reacts with organics and is consumed. Reacts with NH_3	Does not react with organics	Does not react with organics and NH_3. Reacts with secondary amines	Reacts with NH_3. Removes organic matter, odour	Reacts with sulfites and sulfides
Storage	Conc. decreases slowly with time	Can be prepared fresh and dosed	Conc. decreases rapidly with time	Cannot be stored	Can be stored
Cost (arbitrary units)	Cheap	2.0 times cost of chlorine	2.5 times cost of chlorine	3.8 times cost of chlorine	10–20% more than chlorine

organisms, monitoring of the efficiency of the biocide, and fine tuning the dosages would help in reducing the biocidal requirement of power plants. Flow-through power stations use different biocidal doses and regimes for control of macrofouling organisms. In practice, a low level of continuous chlorination (0.1–0.2 mg L^{-1} residuals) coupled with shock dosing (0.5–1.0 mg L^{-1} residuals for 30 min once a week) is employed in power stations. Studies on the dosages required to prevent settlement of organisms are limited except for the available literature based on operational experiences at power stations. The gap in knowledge is due to the complexity of the cooling systems (geometry, flow, surface characteristics, diversity of organisms, cost involved in a biocidal programme and knowledge about larval settlement behaviour) encountered and to the interfacing of engineering aspects with biology and toxicology. Further complexity arises in the scaling of laboratory results to real-time cooling circuits. In general dosages required to inhibit or prevent settlement would be far less compared to those required for killing established fouling communities (Claudi and Mackie 1994).

Field observation on the effectiveness of continuous chlorination revealed a residual of 0.25 mg L^{-1}, sufficient for preventing attachment and growth of *Mytilus* species at water velocities as low as 0.4 m s^{-1} (Elecric Power Research Institute 1980). Laboratory studies showed that a total residual oxidant (TRO) level of 0.1 mg L^{-1} prevented attachment of mussels to concrete panels at water velocities as low as 0.76 m s^{-1} (Elecric Power Research Institute 1980). Alternatively, continuous chlorination at 0.2 mg L^{-1} had no effect on settlement of the blue mussel *Mytilus edulis*(L) at Maasvlakte power station, Rotterdam (Jenner 1983). Comparison of results from these two studies reveal the inadequacy of chlorine, i.e. through interaction with organics and being unavailable for killing, and the site-specific requirements of biocidal doses. Levels of 0.2–0.5 mg L^{-1} delayed settlement of 30% of mussel larvae (Khalanski and Bordet 1980). Compared to mussels, barnacles were more resistant to continuous low-level chlorination and required higher dosages. From the studies carried out at Astoria power station (NY, USA), a chlorine residual of 0.1 mg L^{-1} for 1 week during the spat settlement season reduced the density of settlement 15-fold. However, these concentrations were not effective in preventing the settlement of the barnacle *Balanus eburneus* (Sarunac et al. 1994). Continuous chlorination at concentrations above 0.8 mg L^{-1} were required to prevent settlement of coelenterate Hydroids and tubeworms on steel surfaces in flow chambers (Fig. 2a), whereas an intermittent chlorination of 1.2 mg L^{-1} with a 2 h-on/2 h-off regime was effective in bringing down the settlement of these foulants on plate heat exchanger surfaces (Murthy et al. 2005). In comparison, continuous application of chlorine dioxide at residuals of 0.1–0.2 mg L^{-1} resulted in clean surfaces (Ambrogi 1997) and elimination of the Mediterranean hydroid *Laomedea flexuosa*at residuals of 0.1–0.2 mg L^{-1} (Geraci et al. 1993). Chlorine dioxide treatments (0.22 mg L^{-1}) adopted at the Brindisi Nord power station on the Adriatic showed that test panels placed inside the condenser boxes were clean of both macrofouling and slime in comparison to periods before switching to chlorine dioxide, when 20 × 30 cm panels would accumulate a wet weight of 160 g over 3 months (Ambrogi 1997). Similarly, at the Taranto steel plant located in the south of Italy, fouling biomass on experimental panels were 60 kg m^{-2} $year^{-1}$. Continuous treatment with chlorine dioxide at a dose of 0.5 mg L^{-1} resulted in clean surfaces, as observed from fouling collectors (Belluati et al. 1997). The higher biocidal action against macrofouling organisms at low concentrations has resulted in many stations turning to chlorine dioxide. At present, the studies at the Brindisi Nord power station and the Taranto steel plant are the only literature available on dosages required to prevent settlement of larvae by chlorine dioxide. Application of ozone to cooling water systems was also found to be effective in preventing the settlement of mussel larvae by inhibition of production of byssal thread at concentrations in the range 20 –30 mg L^{-1}. Studies by Lewis et al. (1993) have indicated that a minimum contact time of 5 h was required for 100% mortality of veligers and post-veligers at concentrations of 0.5 mg L^{-1} at 15–20 C water temperatures. These biocides have to be evaluated under dynamic conditions at varying velocities to assess their efficacy and to arrive at some minimum dosages for cooling water systems.

3.1.6 Biocidal Requirements for Killing Established Fouling Communities in Cooling Water Systems

Often in an operating plant the problem of biofouling gains attention and importance when it leads to breakdown of equipment. The usual situation one encounters in an operational plant is an established fouling community as a result of lack of surveillance and monitoring and fine tuning of the biocidal dose and regime according to the requirements to keep biofouling at bay. As a result, the biofouling load exceeds the threshold limits and one is faced with the challenge of killing and removing the established fouling communities. It is all the more important to keep the cooling water systems clean from macrofouling as killing is not cleaning. An established fouling community offers surface roughness for larvae to colonize the substratum. In the case of macrofouling by hard-shelled organisms like barnacles, oysters and tubeworms irreversible damage to the surface occurs and can be cleaned only by mechanical methods like chiselling. Not all places in a cooling water systems are accessible to cleaning and may result in replacement of the equipment. In many power stations, bivalves are the most dominant of the fouling organisms. Dosages and regimes required for preventing bivalve settlement are different to those required for removal or killing of already settled mussels. Further, byssal threads of mussels dead or detached tend to remain in the system leading to under-deposit corrosion and can enhance attachment opportunities for incoming fouling larvae (Claudi and Mackie 1994). Discontinuous chlorination was not effective in killing mussels even at concentrations of 0.5–1.5 mg L^{-1} residuals. The biocidal action of chlorine in killing mussels of the species *Mytilus edulis* and *Mytilus galloprovincialis* was found to be dependent on temperature. Residuals of 0.2–1.0 mg L^{-1} required 15–135 days for mortality (Lewis 1983). Toxicity modelling showed a tenfold decrease in the required killing time for mussels, when comparing mortality rates at 10 C and 25 C. Low-level continuous chlorination was more effective against mussel spat than on adults (Travade and Khalanski 1986) Adult mussels were able to survive the continuous chlorination (residuals of 0.29 and 0.49 mg L^{-1}) practised at the Gravelines plant. Adult mussels survived up to 5 months whereas the recently settled mussels were far more sensitive to chlorine. Settlement of spat was inhibited and a large portion of existing spat were found to detach and die at continuous residuals of 0.49 mg L^{-1} within 20–30 days. At residuals of 0.29 mg L^{-1} growth inhibition and detachment of spat was observed (Travade and Khalanski 1986).

Intermittent chlorinationwas ineffective in removing mussel community lodged in the intake tunnel of the Madras atomic power station (MAPS), India. Alternatively, a continuous high-level chlorination at residuals of 1.4 mg L^{-1} followed by continuous low-level chlorination at 0.2 mg L^{-1} dislodged the mussel community and about 187 tons of fouling biomass was collected in the travelling water screens (Rajagopal et al. 1996). Low-level continuous chlorination of 0.2 mg L^{-1} led to reduction in the growth of the shell of the mussel *Mytilus edulis* as observed from the growth rates of mussels in the cooling culverts (Thompson et al. 2000). The findings were consistent with introduced mussels also exhibiting the same trend. High-level continuous chlorination has also proven to be effective in eliminating mussels due to two processes: a decrease in water filtration rate, which deprives the mussel of its food, or a progressive intoxication by oxidant compounds absorbed within small amounts of seawater in the mantle cavity (Khalanski and Bordet 1980). In comparison, low continuous chlorine residuals of 1.0 mg L^{-1} took 468 h (7 mm) and 570 h (25 mm) for 100% mortality in the brackish water mussel *Brachidontes striatulus,* whereas high chlorine residuals of 5.0 mg L^{-1} took 102 h (7 mm) and 156 h (25 mm) for 100% mortality (Rajagopal et al. 1997).

In a cooling water system different species of mussels co-exist, hence species-specific variability in tolerance of mussels to chlorination is an important aspect in framing a treatment regime. Small sized mussels are more susceptible to chlorination than larger ones (Rajagopal et al. 2003). Similarly, response of different species of tropical marine mussels, *Perna viridis*, *Perna perna*, *Brachidontes striatulus*, *Brachidontes variabilis*and *Modiolus philippinarum,* to chlorination showed that reduction in physiological activities is the lowest in *P. viridis* and the highest in *B. variabilis* (Rajagopal et al. 2003). Mussels were able to tide-over continuous low-level or intermittent chlorination by closing their shell valves to overcome the period. Consequently, the technique of pulse chlorination(Poleman and Jenner 2002; European IPPC Bureau 2000) developed by KEMA has been found to be effective in controlling bivalve fouling in European power stations as off-treatment intervals occur when the mussels have shut their valves tight in response to the biocide. Chlorine must be applied continuously at least during spawning seasons to control bivalve settlement. On the other hand, semi-continuous treatments coupled with high frequency treatments (i.e. 15 min-on/15 min-off and 15 min-on/30 min-off) has shown good results for controlling mussels at residuals of 0.5 mg L^{-1} (Wiancko and Claudi 1994). Compared to mussels, oysters (*Crassostrea madrasensis*) attach to surfaces by cementing one of the valves to the substratum, posing severe problems. A continuous residual of 1.0 mg L^{-1} took 21 days for 100% mortality in the size group 13 mm and 31 days for the size group 64 mm (Rajagopal et al. 2003). Compared to mussels, barnacles tolerated high chlorine residuals of 1.0 mg

L^{-1} for up to 15 days, where 75% of them survived up to 5 days only (Turner et al. 1948). Another species of barnacles, *Balanus improvisus,* required 2.5 mg L^{-1} for 100% mortality at short exposure times (5 min) (McLean 1973).

Further chlorine dioxide residuals of 0.2 mg L^{-1} were found to kill bivalve mussels more rapidly than chlorine at concentrations of 1.1 mg L^{-1} (Jenner et al. 1998). Comparison of the efficacy of chlorine and chlorine dioxide on killing mussels has shown chlorine dioxide to be more effective at a concentration of 1.1 mg L^{-1}. Long-term semi-continuous addition of chlorine dioxide at residuals of 0.2 mg L^{-1} with time intervals of 1 h-on and 2 h-off is as efficient as continuous treatment (Belluati et al. 1997). Chlorine dioxide has also been reported to be effective against serpulid worms at a concentration of 0.2 mg L^{-1}. Experimental runs with chlorine and chlorine dioxide conducted at the Vandellos II nuclear power station on the Mediterranean coast of Catalonia in Spain showed that macrofouling was eliminated at chlorine dioxide concentrations of 0.16–0.20 mg L^{-1} (residuals of 0.04 mg L^{-1}) and chlorine at 1.1–1.2 mg L^{-1} (residuals of 0.3–0.4 mg L^{-1}). However, the cost difference between chlorine dioxide and electro-chlorination was found to be 30% (Jenner et al. 1998). In contrast to chlorine dioxide, a far lower concentration of ozone (0.1 mg L^{-1}) was required to eliminate bryozoans (*Plumatella emarginata*) (Duvivier et al. 1996). Chlorine dioxide has shown to be effective against established fouling communities compared to chlorine and seems a promising candidate for cooling water systems in the future. The cost economics of application of chlorine dioxide needs to be worked out for the treatment to be widely adopted. In comparison, studies using ozone for treating cooling water systems in power plants are also limited. Concentrations of 0.25–0.5 mg L^{-1} were effective in eliminating the blue mussel (*Mytilus*) from European power stations (Claudi and Mackie 1994). In another study, concentrations of 0.5 mg L^{-1} ozone were required for a period of 7–12 days for 100% mortality of mussels (Lewis et al. 1993). The features of ozone that make it attractive for treating once-through cooling water systems are also its major drawbacks. One of the major disadvantages of ozone is that it dissipates more rapidly in water, which in a way minimizes the downstream environmental impact. However, the short life of ozone in water requires multiple injection points in the cooling water system to protect downstream equipment, which would be probably very expensive and is the main reasons why this biocide is not so popular for large once-through cooling systems.

3.1.7 Fouling Control in Once-Through Freshwater Cooling Systems

In freshwater systems, fouling by Asiatic clams, Zebra mussels and weeds poses a severe problem. In once through systems using freshwater clogging of heat exchangers by Asiatic clams has been related to changes in flow configuration in the service water systems. Continuous chlorination of 0.6–0.8 mg L^{-1} was required for controlling Asiatic clam settlement. Fouling by colonial hydroid *Cordylophora caspia*is a problem in several European and American power stations. Chlorine residuals of 0.2–5.0 mg L^{-1} with exposure time of 105 min and short intermittent exposure of 20 min did not kills the animals but reduced their growth (Folino-Rorem and Indelicato 2005).

Compared to marine mussels, the freshwater mussel *Dreissena polymorpha*was less tolerant to chlorine. Continuous chlorination employed at the Ontario Hydro experimental station on Lake Erie at Nanticoke showed that at residuals of 0.3 mg L^{-1}, attachment of the mussels was inhibited. Discontinuous treatments (half hour on, once in 12 h) were ineffective even at higher dosages of 0.5–1.5 mg L^{-1}. Similarly, another power station (Cleveland Electric illuminating company installation on Lake Erie) operating on a discontinuous mode failed to kill the mussels at 0.3 mg L^{-1} (Barton 1990). In contrast, semi-continuous chlorination has shown promising results at residuals of 0.5 mg L^{-1} with high frequency treatments like 15 minon/15 min-off and 15 min-on/30 min-off (Wiancko and Claudi 1994). In comparison, response of the Zebra mussels to shock chlorination showed that two successive shocks of 200 mg L^{-1} once every 24 h resulted in 100% mortality of mussels in 9 days (Khalanski 1993). The action of chlorine in killing Zebra mussels was found to be dependent on water temperature. For 95% mortality at 10°C, a time period of 42 days was required as against 7 days at a water temperature of 25°C (Van Benschoten et al. 1993). The study also demonstrated that compared to chlorine, chloramine concentrations above 1.5 mg L^{-1} were effective in controlling veligers of Zebra mussels in both static and flow-through tests. Exposure times of 1,080 h at 0.25 mg L^{-1} and 252 h at 3.0 mg L^{-1} are required for 100% mortality of these mussels (Rajagopal et al. 2003). Continuous chlorination at residuals of 0.5 mg L^{-1} was effective in killing the Asiatic clams*C. fluminea* with periods ranging from 2–3 weeks (Dohorty et al. 1986; Ramsey et al. 1988). In addition, monochloramine (NH_2Cl) was found to be effective against the Asiatic clams (Belanger et al. 1991). With respect to the freshwater Zebra mussel-*Dreissena polymorpha*brief exposure to chlorine dioxide at a concentration of 10 mg L^{-1} for 13 min or 50 mg L^{-1} for 3.2 min kills 50% of adult mussels, whereas at concentrations of 2 mg L^{-1} no mortality is observed (Montanat et al. 1980). Concentrations of 5 mg L^{-1} in closed recirculating systems of the Seraing power station on the river Meuse were found to be effective, giving 100% mortality of the bivalves (*Corbicula* sp. and *Dreissena* sp.) over a period of 18 days (Jenner et al. 1998). Synthesis of the above information reveals that biocidal requirements for fouling control in freshwater once-through systems are far less than for seawater-cooled once-through systems. In freshwater cooling systems (where Zebra mussels and Asiatic clams are the dominant foulers) chlorine has been found to be the most effective and commonly used method of mussel control in Europe, Asia and North America (Jenner et al. 1998; Claudi and Mackie 1994; Rajagopal 1997).

4 New Approaches for Fouling Control in Heat Exchangers

4.1 Electrolytically Generated Biocides

Currently, electrochemical methods are being tested for treating industrial waters with the goal of combating fouling without adversely affecting the environment. Metal ions particularly silver, copper (Cu anodes) hydrogen peroxideand potassium permanganate can be electrolytically generated (Martinez et al. 2004). In heat exchangers made of titanium, anodic polarization by a current of some tens of milliamps per square metre applied to titanium causes a low production of oxidant species (chlorine or bromine) at the metal–seawater interface. However, with heavy metal ions there is always the problem of occurrence of resistance in the organisms. The current is low but is enough to inhibit the growth of titanium on plates and tubes. Experiments to this effect at the Venetian Lagoon demonstrated the control of settlement of macroorganisms and algae with a polarization of about 100–200 mA m^{-2}. This technique is very interesting for heat exchangers considering the effect of the pH decrease in the water close to the anodic polarized surface of titanium (Cristiani 2005). Electrolytically generated biocides are particularly useful in cooling systems to combat biofouling of sensors for temperature, conductivity and pH. This technique is still in infancy and in-situ studies demonstrating this effect are lacking. Further application of this technique to large cooling systems seems to be an unviable proposition.

4.2 Surface Modification Approach to Control Biofouling

Surfactants or surface active agents alter the surface tension within the biofilm and at the biofilm–substratum interface, allowing enhanced penetration by biocide molecules and also more effective removal of the biofilm deposits from the surfaces. However, they only address one of the forces that provide cohesion and adhesion of fouling layers. Several studies on the positive effects of the use of surfactants have been reported from cooling water systems. Some of the most effective surfactants reported are ethylene oxide/propylene oxide block copolymer (Donlan et al 1997), dimethlyamide (DMATO) (Lutey et al. 1989), dinonylsulfosuccinate (Wright and Michalopoulos 1996), a combination of peracetic acid with ethylene oxide/propylene oxide (Meade et al. 1997), sodium dodecyl sulfate (SDS) in combination with urea (Whittaker et al. 1984), and Tween 20 (Fletcher et al. 1991). Recently, low-energy surfaces have been prepared by ion implantation (Yang et al. 1994). Low-energy surfaces can increase the induction period of fouling and facilitate detachment of foulants (Yang et al. 1994; Forster et al. 1999) during which stable nucleation takes place at localized sites and the lateral growth of individual nucleation sites results in a complete coverage of the surface. Another study to minimize particle adhesion on stainless steel plate heat exchangers used TiN sputter coatings, which decreased the surface energy and resulted in less deposition of particles (Rosmaninho et al. 2005). Ion-sputtered diamond-like carbon (Forster et al. 1999), self-assembled monolayers (SAMs) and electroless plated surfaces (Yang et al. 2000b) have been used to mitigate fouling due to the weak adhesion strength between the fouling layer and the heat transfer surface. SAMs of low surface energy can prolong the induction period of fouling. Also, thermally resistant (Yang et al. 2000a). SAM surfaces based on Si wafers exhibit no significant change after heat treatment up to 200°C (Shin et al. 1999) and SAM films of hexadecyl disulfide can withstand temperatures of up to 225°C (Nuzzo et al. 1987). SAMs can also protect metals against corrosion as they act as effective barriers against diffusion of oxygen and water. tThe cross-linking SAMs can result in more robust films with improved levels of protection (Itoh et al. 1995).Thus, SAM surfaces have great potential for use as heat transfer surfaces to reduce fouling. The technique has not been used widely in heat exchangers except for some small stations that require an improvement in the rate of heat transfer. The technique as such seems to be interesting for plate-type heat exchangers and needs to be evaluated under field conditions, provided the film lasts over an extended period of time. However, a breakthrough against fouling has not been achieved yet by the use of surfactants. Surfactants comprise only one of many more components of integrated antifouling strategies.

5 Concluding Remarks

The incidence of macrofouling in cooling water circuits of power plants varies considerably depending on the location and design of systems. The use of trash racks at the offshore intake point and travelling water screens before the pumps is a mandatory technique for removing debris and detached fouling biomass from clogging the heat exchangers. Thermal treatment is an effective option but many stations do not have the facility of recirculating effluent water in the cooling circuits. Chlorine or sodium hypochlorite is in common use internationally and requires high doses (0.5–1.0 mg L^{-1}) to overcome the demand in water and for killing macrofouling organisms. However, for effective plant operation the issue of killing established macrofoulants is secondary to preventing their settlement and colonization, right from the initial stages of commissioning the cooling water circuit. A fouled circuit provides a source of larvae, which colonize systems downstream, and dosages required for inhibiting settlement are far less than those for killing established communities. In general, power stations adopt low-level continuous chlorination (with residuals of 0.1–0.2 mg L^{-1}) at the outfall coupled with periodic shock or booster doses of the biocide depending on the intensity of fouling. The use of various techniques of chlorination, like shock chlorination and targeted chlorination of heat exchangers, has offered temporary relief to certain sections or equipment in the circuit. With the advent of the technique of pulse chlorination, up to 50% reduction in chlorine consumption can be achieved and bring down the environmental burden of toxic by-products (Poleman and Jenner 2002; European IPPC Bureau 2000). Commercial variants of bromine are in use in some of the European and Indian power stations. However, growing awareness of keeping biofouling levels within the threshold to minimize plant shutdown and the increasing regulations on effluent discharge has resulted in plant operators adopting the stronger oxidant, i.e. chlorine dioxide. The low concentrations required for killing and its environmentally safe nature have resulted in its use in power plants in spite of the higher cost of this biocide. Prior to the commissioning of a power station, effective biocidal dose and concentration need to be worked out on a site-specific basis. Dosages worked out elsewhere will not be effective for a given location.

Side-stream monitors(Biobox) (Jenner et al. 1998) or electrochemical probes need to be installed and monitored regularly. Spikes in settlement observed in side-stream monitors can be taken as a signal to alter the biocide dose or regime to achieve killing of new settlers. Continuous surveillance and monitoring of cooling water and fine tuning of the biocidal programme will ensure that biofouling levels are maintained well within the threshold limits. As biofouling is a surface-associated phenomenon, a combined approach of treating the cooling water and surface protection by the use of foul release coatings would offer long term solutions to macrofouling problems in cooling systems. Fouling release coatings have demonstrated their ability to resist macrofouling at high water velocities and are a potential option for cooling circuits (Leitch 1993; Kilgour and Mackie 1993; Claudi and Mackie 1994). With regard to heat exchanger fouling, mechanical methods like sponge rubber ball cleaning together with biocidal treatment is the only available method of control. In shell and tube heat exchangers flow blockage due to clogging of tubes by macrofoulants and biofilm is the primary problem. Contrary to the concept that high shear forces created by chevron angles in plate heat exchangers retard fouling, barnacle fouling on these heat exchangers has been observed. Sedimentation and accumulation of corrosion products on these heat exchangers is a problem to be overcome. Since online cleaning methods are not available for these heat exchangers a control strategy should take into account a biocide, cleaners and a corrosion inhibitor for optimum performance of these heat exchangers.

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