

Biofouling control in recycled cooling water with bromo chloro dimethylhydantoin

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Introduction

Recirculating cooling tower systems (RCT) that contain high concentrations of organic matter present significant challenges to control of biofouling. Organic concentrations in cooling water are increasing because environmental regulations and higher water costs are stimulating recycle schemes involving cooling water systems.

Three of the more common water reuse schemes are:

1. Use of low dissolved solids process effluents as cooling water makeup
2. Decrease of blowdown water rate to conserve water
3. Treatment and reuse of blowdown.

Use of any of these water reuse schemes can result in relatively high organic concentrations in cooling water. An RCT in a plant that reuses much of its process water as makeup and also treats and reuses its blowdown will have high organic concentrations that will stimulate biofouling.

USS Chemicals, Houston, Texas, began operating a recycle/reuse RCT system in 1979. Effluent streams, including stormwater, process wastewater, and boiler blowdown, were added as makeup to the RCT system. The only effluent streams not reused were the demineralizer regeneration and rinse waters. Blowdown was treated in a lime softener for calcium, magnesium, and silica removal and recycled to the RCT system. See Figure 1 for a schematic of the system.

The theoretical chemistry of the sidestream softening system has been described elsewhere^{1,2} and approximates the actual working system in terms of precipitation/crystallization processes (scaling). Within six months of startup, process operation was satisfactory and no chemical scale problems were observed.

However, biofouling was such a problem that by January 1981, production was limited by the resulting

loss of heat transfer. Organic levels, in terms of total organic carbon (TOC), had increased to approximately 500 mg/L. In contrast, most RCT systems rarely rise above 50 mg TOC/L.

Conventional biofouling control methods were not effective so a different approach was attempted. This article describes the new approach as illustrated by the experience at USS Chemicals.

Methods

A fouling monitor system* was installed on a slipstream from the cooling water return line to monitor biofouling and to determine effectiveness of various biocide treatments. Its purpose was to simulate conditions in the main system and provide a real time readout of the extent of biofouling as measured by reduction in heat transfer.

In the plant control room, surface condenser vacuum was monitored. Although influenced by a variety of factors, vacuum reading was sensitive to biofouling. Rapid decreases in vacuum, in absence of other causes, was directly attributable to biofouling.

The total halogen residual in the cooling water was measured six times per day by the DPD colorimetric method.³ The TOC was analyzed daily. Microorganism counts in the cooling water were also conducted on a daily basis.

The Fouling Monitor System

The fouling monitor system consists of two major components:

1. A 0.0127 m (0.5 in) I.D. carbon steel tube which contains ports for pressure drop measurement and a

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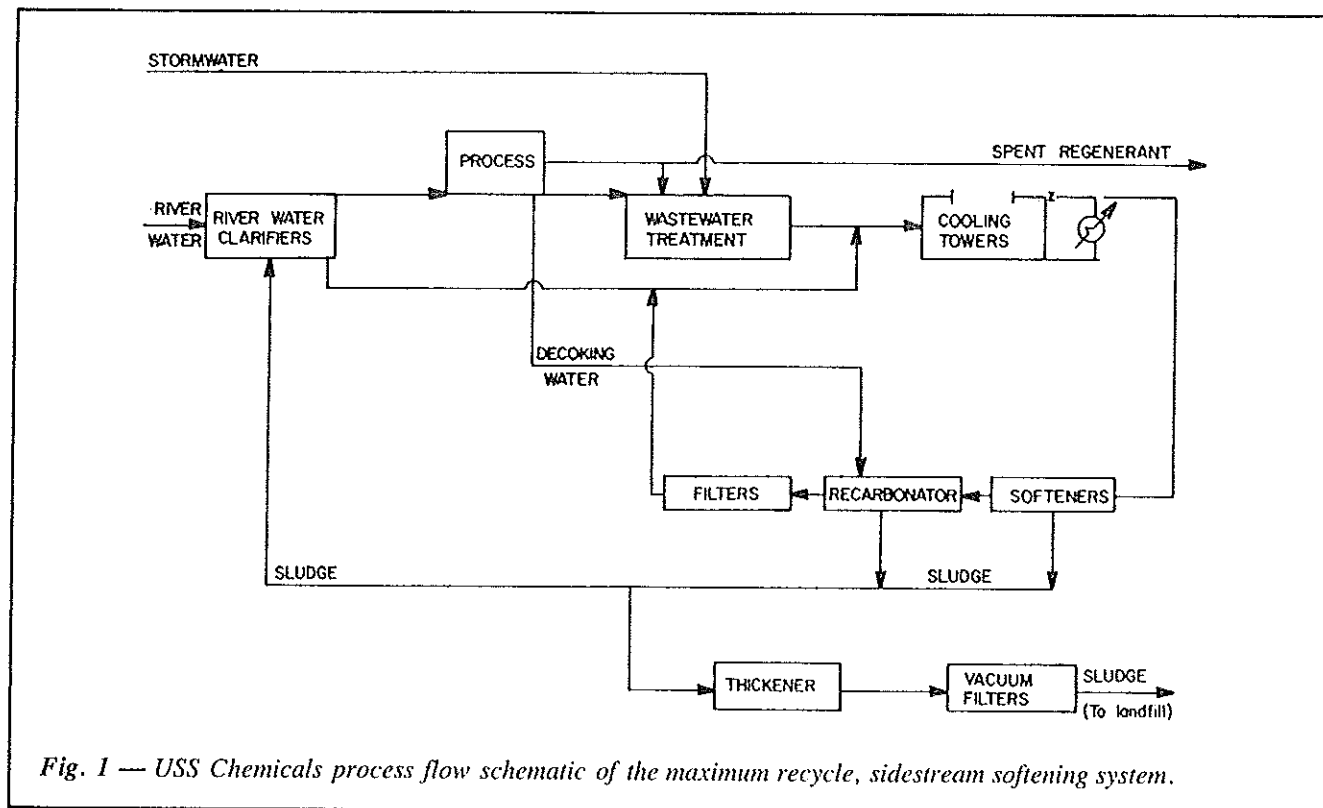


Fig. 1 — USS Chemicals process flow schematic of the maximum recycle, sidestream softening system.

heat transfer section consisting of an electrically heated block which is clamped around the tube. Temperature probes are inserted in the block to determine the radial temperature profile. The system also includes a flow meter and bulk water temperature probes. The pressure drop and entrance length section is heated to match surface temperature conditions in the heat transfer section.

2. A microcomputer calculates frictional resistance and overall heat transfer coefficient. Output from the microcomputer is displayed on a television monitor and includes all pertinent measurements and calculations. A cassette recorder stores the data.

The fouling monitor was operated at the following conditions to simulate a composite heat exchanger in the plant:

1. Flow rate at 3fps (0.90 ms^{-1}) was maintained by using a constant head feed tank and a manually controlled valve
2. Feed water temperature was maintained at 40°C by a manually controlled heat exchanger
3. Electric power to the block was 100 watts

Data was averaged for each hour of operation and recorded on an hourly basis.

Output consisted of the following:

1. Bulk water temperature at the tube inlet, T_{B1}
2. Bulk water temperature at the tube outlet, T_{B2}
3. Block temperature at two radii, T_1, T_2
4. Flow rate, F
5. Pressure drop, Δp

The computer calculated the following:

1. Overall heat transfer coefficient, U , using a heat flux calculated from the thermal conductivity of the block and the difference between T_1 and T_2
2. Friction factor, f , from pressure drop and flow rate data

Data and calculations were recorded on cassette tape and transcribed at a later date.

Manual determinations of temperatures and pressure drop were conducted approximately every three days as a check of computer results and to anticipate a computer failure. Bulk water and block temperature were measured manually using a Yellow Springs Instrument Tele-Thermometer and pressure drop was measured with an inclined mercury manometer.

Overall Heat Transfer Coefficient

Overall heat transfer coefficient is defined by

$$U = \frac{q}{2Lr_{ii}(T_2 - T_1)}$$

Overall heat transfer resistance, U^{-1} , is the inverse of U . The heat flux, q , was maintained constant and was calculated from T_2 and T_1 and the thermal conductivity of the heated block.

$$q = \frac{2 L k (T_2 - T_1)}{\ln (r_{ii}/r_i)}$$

Frictional Resistance

Frictional resistance is characterized by the dimensionless friction factor.

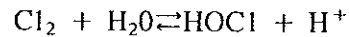
$$f = \frac{2 d \Delta p \rho_{Hg} g}{L_p 8f v_m^2}$$

where ρ_{Hg} is the specific gravity of mercury, ρ_f is the fluid specific gravity, L_p is the pressure drop length, and v_m is linear mean velocity.

Control Strategy

The chemicals originally used for biofouling control were chlorine, a surfactant, and a non-oxidizing biocide. Chlorine was added continuously to the RCT by bubbling the gas through the water in the cooling tower basin. Free chlorine residual levels were maintained in the 0.05 - 0.2 mg/L range. The surfactant (chlorine helper) was also added continuously. The non-oxidizing biocide (a quaternary amine) was batch fed to the system three times per week. In response to excursions in which heat transfer was reduced, additive rates were increased to maximum levels.

The alternative control strategy was to utilize Bromocide[®], bromo chloro dimethylhydantoin, manufactured by Great Lakes Chemicals, as a complement to gaseous chlorine. The rationale was as follows. The pH of the cooling water at USS Chemicals was controlled in a range of 7.6 to 7.8. In this pH range, chlorine is less effective as a biocide than at lower pH. The gaseous chlorine when added to water reacts as follows:



The product, hypochlorous acid, establishes an equilibrium with the hypochlorite ions:



At low ionic strength and temperatures of 20°C, the pK

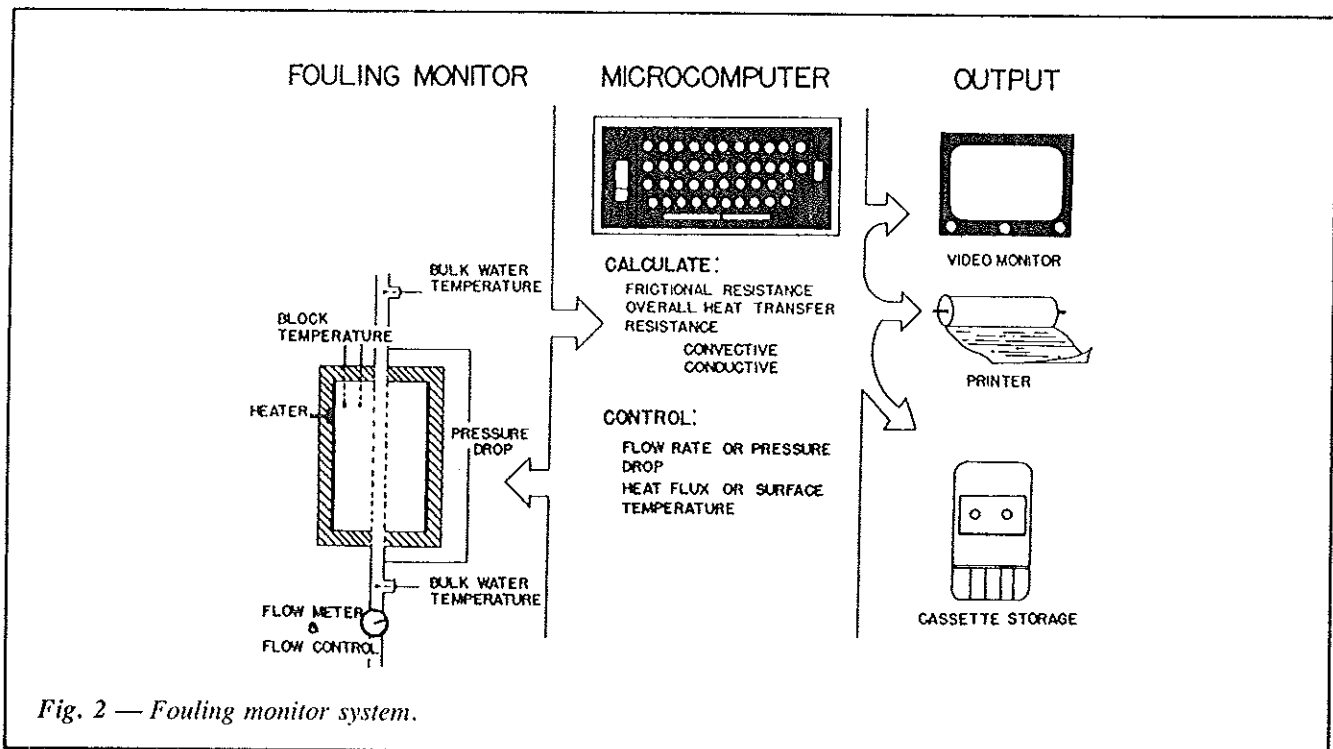


Fig. 2 — Fouling monitor system.

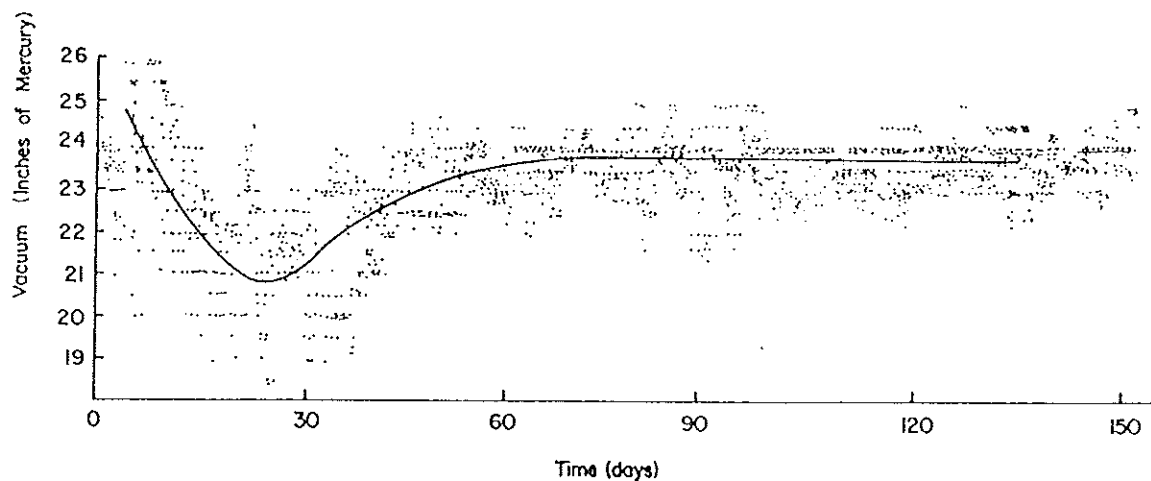


Fig. 3 — Surface condenser vacuum as a function of time.

equals 7.5. At higher ionic strengths and temperature, the pH decreases. In the cooling water at USS Chemicals, the pK approaches 7.0 at a temperature of 30°C and ionic strength of 0.5. Thus, the predominant species is the hypochlorite ion.

There are two major disadvantages to the predominance of hypochlorite ion over hypochlorous acid. First, the hypochlorite ion is a much stronger oxidizing agent and reacts quickly with organic material and dissipates. Second, hypochlorite ion is a less effective biocide because the micro-organisms can more easily repel the charged ions. Conversely, the uncharged hypochlorous acid can diffuse readily into a microbial cell.⁴

Bromine chemistry is analogous to chlorine chemistry in that the bromine will form hypobromous acid and hypobromite ion. Moreover, the pK is approximately one pH unit higher than chlorine. Therefore, the predominant species of bromine in the USS Chemicals cooling water is hypobromous acid.

Results and Discussion

Debugging of the biofouling monitor system was completed in late 1980. In Jan. 1981, the comprehensive monitoring system including analysis of halogen residual, viable cell counts, and measurement of condenser vacuum was in operation.

During the first 30 days, the condition of the cooling water deteriorated. The impact of intensified biofouling is shown in Figure 3, which indicates that the surface condenser vacuum decreased from a high of 25 inches of mercury to a rough average of 21. In an attempt to counteract the biofouling, increased

amounts of chlorine were added to the cooling water system. As shown in Figure 4, the free residual rose to an average of 0.5, but the biofouling condition persisted.

On day 30, the chlorinators were shut down and the BCDMH at a rate of 100-150 lbs/day was added to the system. The results shortly before the DCDMH addition and after are shown in Figure 5, which indicate the progression of fouling by the change in heat transfer resistance and frictional resistance, respectively, in the fouling monitor.

Figure 5 indicates the progression of heat transfer resistance (inverse of heat transfer coefficient). Heat transfer resistance increases steadily due to fouling, up to approximately day 10 (actually day 30 of the test). After that, heat transfer resistance decreases to approximately clean conditions. The decrease in heat transfer resistance begins immediately after the change to BCDMH treatment.

Figure 5 also indicates the progression of friction factor. The results are almost identical to heat transfer resistance. Friction factor increased steadily until BCDMH was added, then the friction factor decreased to clean conditions.

For the next 30-day period, BCDMH was added with the surfactant and non-oxidizing biocide. As Figure 3 shows, the condenser vacuum gradually increased into the 23 to 24 range. There was also visual evidence of biofilm reduction. Stringers on the cooling tower slats gradually disappeared.

The TOC and viable cell count measurements were not indicative of biofouling conditions in the cooling water system. The TOC actually increased during the month of February as shown in Figure 7. However, the

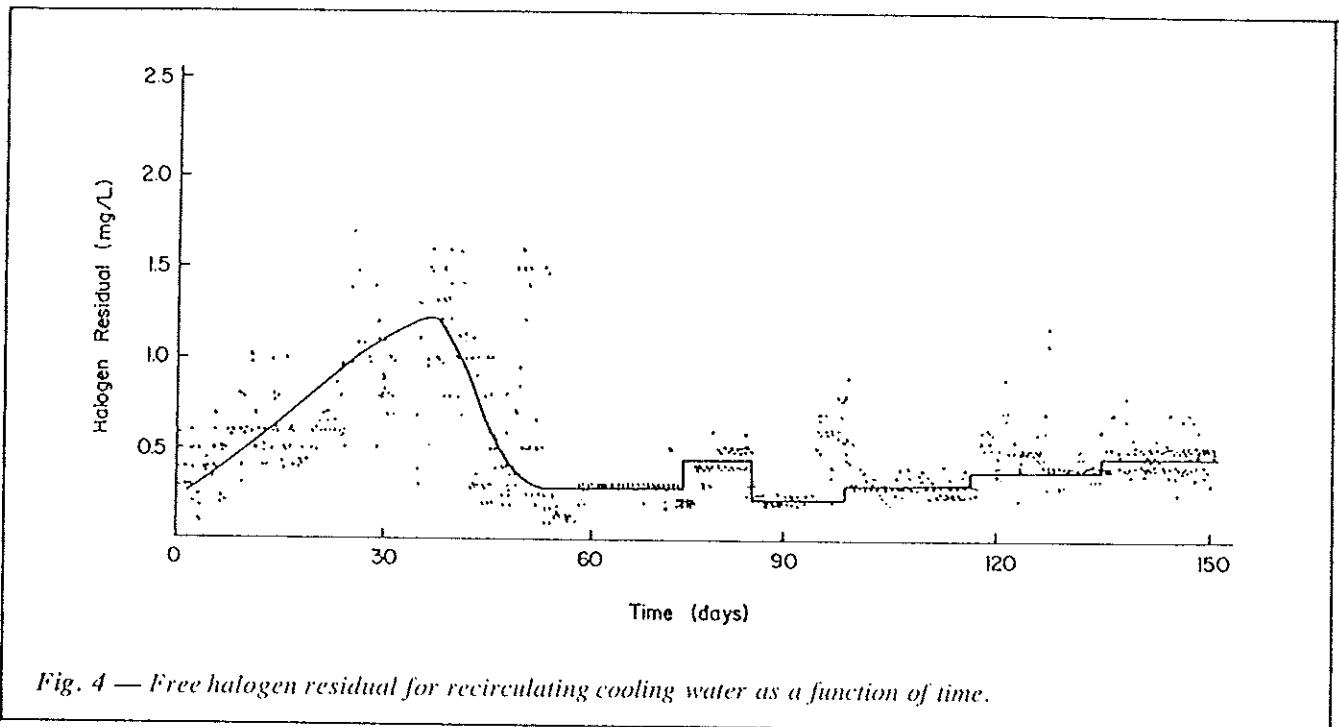
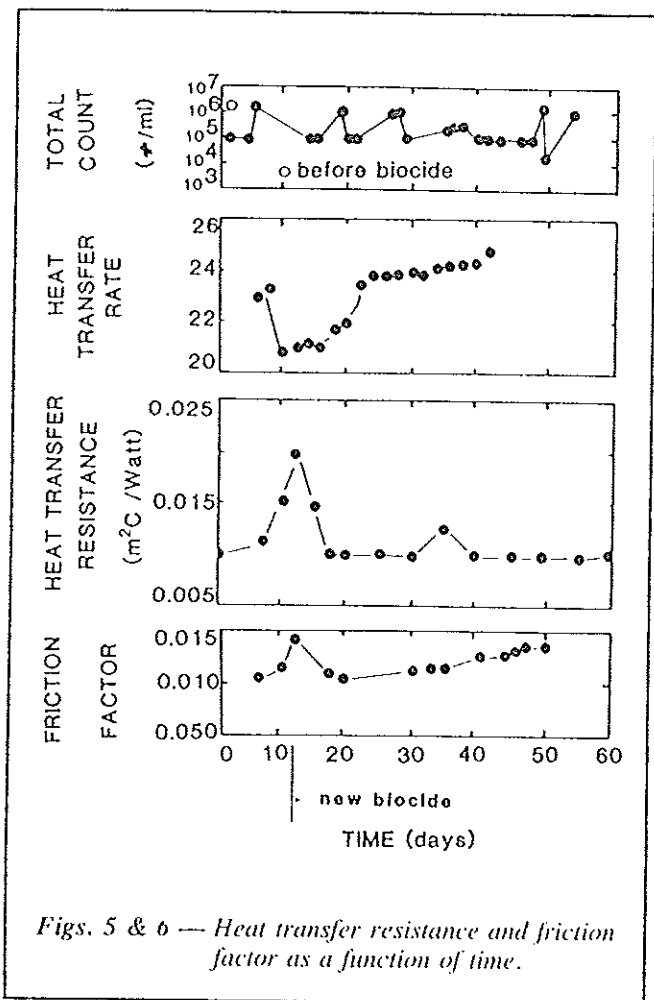


Fig. 4 — Free halogen residual for recirculating cooling water as a function of time.



Figs. 5 & 6 — Heat transfer resistance and friction factor as a function of time.

increase may have been an artifact of the cleanup operation rather than evidence of higher organic loadings to the system. The viable cell counts showed no sensitivity to biofouling or the resultant cleanup operation, as shown in Figure 8.

Starting at day 90, BCDMH was blended with chlorine on a 1:10 weight ratio basis which was roughly 30 lbs: 300 lbs/day to decrease the cost of biofouling control. The cooling water system was considered to be in good condition.

Over the next 90-day period, an operational strategy involved. The free halogen level was gradually increased in step changes from 0.25 to 0.45 at 0.05 mg/L intervals. The goal was to establish minimum residual level at which biofouling incidences were negligible. At 0.45 mg/L, this level was achieved. The condenser vacuum gradually increased and stabilized at an acceptable level.

Today, stable operations are continuing. The usage of surfactants and non-oxidizing biocides have been phased out. The TOC in the cooling water has decreased to below 300 mg/L, due to improved plant operations. Halogen dosage based on the 1:10 BCDMH to chlorine weight ratio is set to maintain a halogen residual of 0.45 mg/L.

Conclusions

1. The bromine compound BCDMH was effective in the control of biofouling in a high pH, high organic content cooling water.

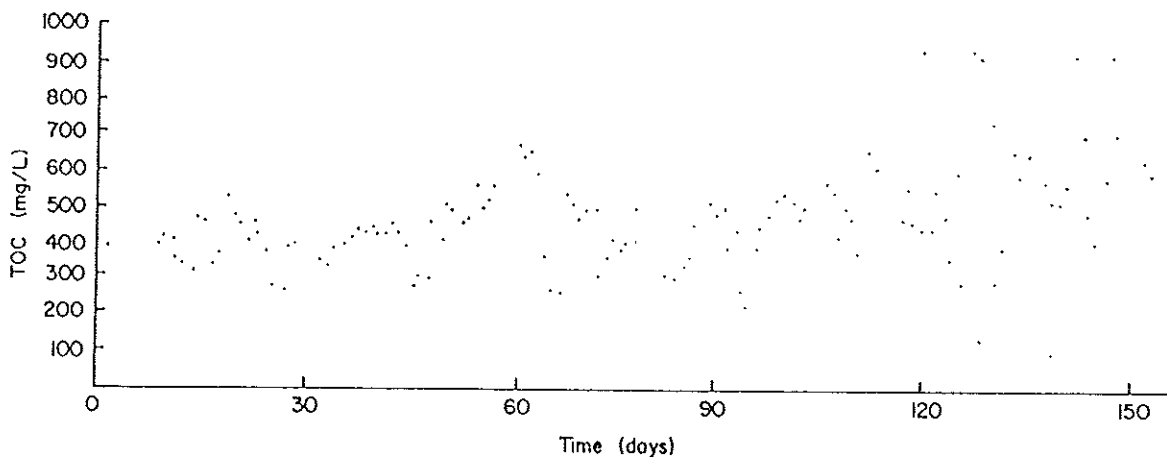


Fig. 7 — Cooling water total organic carbon as a function of time.

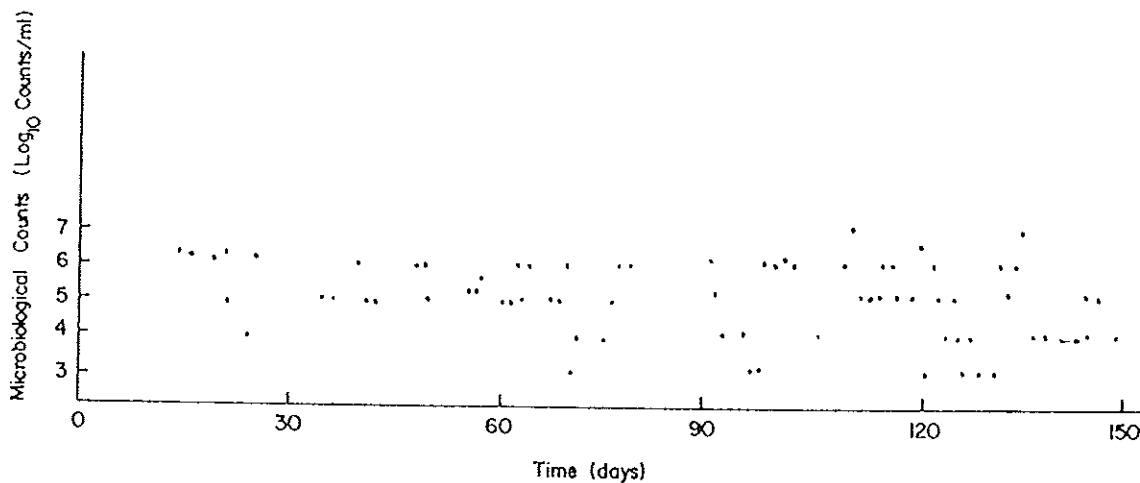


Fig. 8 — Cooling water viable microbial cell counts as a function of time.

2. Free halogen residual control was an effective strategy in biofouling control.
3. The biofouling monitor was a sensitive, real time indicator of biofouling.
4. Condenser vacuum was a key parameter for the detection of biofouling.
5. Viable cell counts and total organic carbon did not correlate with biofouling conditions.

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does this constitute an endorsement by EPA of any products or views contained herein.

References

1. Matson, J.V., "Zero Discharge of Cooling Water by Sidestream Softening," *Journal of the Water Pollution Control Federation*, Vol. 51, No. 11, 1979.
2. McGaughey, L.M. and Matson, J.V., "Prediction of the Calcium Carbonate Saturation pH in Cooling Water," *Water Research*, Vol. 14, November 1980.
3. APHA, *Standard Methods for the Examination of Water and Wastewater*, 15th Ed., American Public Health Association, Washington, D.C., 1981.
4. Rice, J.K., "Drew Principles of Industrial Water Treatment," Drew Chemical Corporation, Boonton, NJ, 1977, p. 100.