FOULING PREVENTION IN DESALINATION PLANTS[1]

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ABSTRACT

Combined low concentrations of copper (5 μg/l and chlorine (50,μg/l have been effective in preventing both micro and macro-fouling in over 120 seawater installations since 1987. This paper will outline the development of the technology, and demonstrate how it can be applied to the desalination industry. Recent trials with a copper/chlorine dosing unit on a reverse osmosis RO) test rig in the Gulf will be discussed.

KEY WORDS

Copper, chlorine, biofouling, desalination.

INTRODUCTION

The BFCC copper/chlorine system prevents the attachment and growth of micro and macrofouling organisms by the simultaneous use of low levels of copper (5μg/l and chlorine (50 μg/l The effect of the two together is synergistic, such that the combined antifouling effect is greater than would be predicted by summing the effects of the individual components.

Laboratory research at the University of Sheffield indicates that in the case of macrofouling the mode of action of the BFCC system is sub-lethal. Copper and chlorine were used to discourage the post larval settlement stage of the mussel Mytilus edulis (L.) from attaching to an otherwise suitable substrate. Once in clean water, the mussels rapidly recovered (1). In field trials with the now privatised Central Electricity Generating Board (CEGB - UK), untreated natural seawater was pumped on a continuous basis once through a number of mild steel pipes. The pipes were treated as follows; 2 with electrolytically generated copper ions at 35μμg/l (ppb), 1 with

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electrolytically generated copper and aluminium (35 μg/l copper & 5 μg/l aluminium, manufacturer's standard), 1 with conventional chlorination at 200 μg/l 1 with combined copper/chlorine treatment (5 μg/l copper & 20 μg/l chlorine) 1 control. The results are summarized in Figure 1.0. In pipes treated with 200 μg/l total residual chlorine (TRC) there was a significant reduction of biofouling compared to the control. In lines protected by the copper/chlorine system, the greatest degree of protection was observed. Copper/aluminium and copper alone had no significant effect in reducing fouling biomass.

The effectiveness of the copper/chlorine system against bacteria and microalgae can be inferred from microfouling studies conducted by the University of Miami, Department of Engineering, using a purposely built US Electricity Power Research Institute (EPRI) designed condenser tube test heat transfer resistance (Fig. 2). Conventional chlorination and the BFCC copper/chlorine treatment were tested against a control. In the chlorination line, chlorine was dosed at the maximum level permitted in the USA (200 μg/l Total Residual Chlorine (TRC) for 2 h/d). In the copper/chlorine treated lines 5 μg/l of copper was used in conjunction with 20 μg/l of TRC for 2 h/d. The copper/chlorine treatment prevented microfouling, and was more effective than the conventional chlorination regime (Fig. 3). The use of copper alone was not tested since copper is known to increase bacterial sliming and hence heat transfer resistance (2). The development of the copper/chlorine system is described in full elsewhere (3).

It is postulated that chlorine alters the permeability of the cell membrane, thereby facilitating of passage of copper into the cell where it attaches to enzymes, causing cellular disfunction. This is borne out by permeability experiments on artificial membranes (Nelson, personal communication with BFCC).

Problems caused by macrofouling include reduced water flow, pump head losses, blockage of screens caused by the sloughing of large sections of the fouling mat and blockage of coarse filters. The growth of micro-organisms, especially bacterial, reduces the efficiency of heat exchange processes, increases corrosion of susceptible materials and predisposes surfaces to colonization by macrofouling organisms. In RO plant, bacteria can adversely affect the process by growing on the RO membrane. Symptoms of fouling are a rapid build up of differential pressure followed by a reduction in flux and decrease in salt rejection (4). An additional problem, specific to RO desalination, is that the usual method of bacterial control is via chlorine. Whilst chlorine is effective in the control of bacteria, it will physically damage polyamide (PA) membrane material at the concentrations of chlorine required to control growth (5). For this reason, certain membrane manufacturers specify a zero mg/l chlorine content for water entering certain designs of PA permeator (6). The use of high concentrations of chlorine has also been implicated in bacterial aftergrowth on RO membranes through the formation of assimilable organic carbon (AOC) from organic material, which then acts as a food source for bacteria (7).

The BFCC copper/chlorine solution offers the prospects of being able to:

(1) Prevent macrofouling in the seawater intake system of thermal and RO desalination plants with minimal chloriane and copper usage.
(2) Prevent microfouling at all stages of the RO process without causing membrane damage, and without stimulating bacterial growth.
(3) Prevent biofouling without adversely affecting coarse and fine filter performance.

THE EXPERIMENT

In view of the success of the BFCC technology in preventing biofouling in a range of marine installations around the world, a joint project was set up between the Saline Water Conversion Corporation SWCC) and BFCC to explore possible applications of the copper/chlorine technology in the desalination industry.

In June 1993, an electrolytic copper/chlorine dosing system was installed at the SWCC Research Development and Training Center at Al-Jubail, Kingdom of Saudi Arabia, to demonstrate the effects of a copper/chlorine system on the seawater inlet pipe-work and pre-treatment stage of an RO process train.

The layout of the trial plant is shown in Fig. 4. Between 36 m^3/h and 66 m^3/h of raw, unchlorinated seawater was drawn from the inlet bay of the Al-Jubail plant by one of 2 pumps on a floating platform. Between 25% and 100 % of the main flow was directed through a purposely built dosing chamber where it was treated with copper and chlorine. The dosed water was then reintroduced into the main seawater flow, travelling through 900 m of 110 mm ID pipe to the pretreatment skid. The effective BFCC copper/chlorine dose is 5 µg/l and 50 µg/l respectively. However, in view of the transit time (6 to 13 minutes) of the water between the dosing point and the pretreatment plant (sand filters), 200 µµg/l of chlorine was added along with 5 µg/l of copper.

The copper/chlorine dosing unit comprised a single 200 mm diameter, 300 mm high mild steel dosing chamber with one vertically mounted copper anode and one vertically mounted Mixed Metal Oxide MMO) chlorine producing anode. The inside surface of the dosing chamber acted as the cathode in the electrolysis reaction. Constant direct current was impressed on the electrodes from a transformer rectifier control panel. The magnitude of the impressed current determines the mass of chlorine formed, according to Faraday's Law. The current, and hence mass of chlorine produced, remained constant throughout the experiment. The water flow rate varied, however, so the recorded copper and chlorine concentration were not constant. The direct current to the copper and MMO electrodes was pulsed 1 minute ON and 1 minute OFF. This is standard BFCC practise in industrial installations, its purpose being to reduce cathode scaling and extend anode life.

The facility for biofilm monitoring at different stages of the RO process was included in the design by providing removable pipe sections at various points in the process train.

Water quality was measured as Silt Density Index (SDI). Copper and chlorine concentrations were determined using colourimetric methods. Copper was assayed with sodium diethyl-di-thiocarbamate, colour absorbance being measured at 440 nm with a spectrophotometer. Chlorine was measured using the standard DPD (N,N Diethyl-P-phynylenc diamine) technique, absorbance being measured at 565 mm. At very low concentrations (less than 500 μg/l chlorine was determined using the Orion 9770 residual chlorine electrode which measures the amount of iodine liberated from potassium iodide added to water samples. The iodide is oxidized by chlorine produced oxidants (CPO) in the water.

Samples for chemical and bacterial analyses were taken at different stages of the RO process, i.e., raw seawater (RSW), before the feed entered the pre-treatment (BPT), after coagulation and sand filtration (ASF) and after the cartridge filter (ACF). as shown in Figure 4.

RESULTS

The measured chlorine concentrations in the outflow of the dosing chamber varied between 190 μg/l and 22,500 μg/l This variation was mainly due to variation in flow rate plus changes in chlorine demand and the effect of pulse dose timing. Pulsing the current to the electrodes ON and Off results in slugs of copper/chlorine treated water passing through the process plant. If a water sample is taken when the current to the electrodes is OFF, relatively low chlorine levels will be measured, and vice versa. The further away the sampling point is from the dosing chamber, the harder it is to predict whether a treated or untreated slug is being sampled. In any event, Faraday's Law of electrolysis make it possible to state that the mass of chlorine generated remained constant throughout the trials, based on the fact that a constant direct current output was impressed on the MMO electrode.

Copper concentrations (copper normally present in the water plus BFCC generated copper) ranged from 3 μg/l to 9.1 μg/l at the inlet of the pretreatment plant. Coagulation and sand filtration resulted in a reduction in concentration to between 0.9 μg/l and 1.5 μg/l This was due to the complexation of the copper ions (Cu^{2+}) with organic material in the water, and the subsequent coagulation and rcmoval of the chelated copper in the filter.

Both copper and chlorine concentrations were reduced in the time that it took the treated water to get from the BFCC treatment unit to the entry of the pretreatment plant. The chlorine would have been consumed in demand reactions, whilst the copper would have been complexed with organic material in the water.

DISCUSSION

In terms of plant performance, the slug dosing effect is not significant. Biofouling can be defined as the growth of organisms on surfaces (periphytic growth). Once a fouling organism leaves a water flow and becomes fixed relative to the flow of water, it experiences the slug doses and either detaches or is killed. Planktonic organisms entrained in the water flow that pass straight through the system do not constitute a biofouling problem.

It is possible that the BFCC system is acting as a bactericide and/or a bacteriostate. If there is a bacteriostatic action then water sampling will remove the inhibitory effects of a copper/chlorine mixture. Once a seawater sample has been taken, chlorine will rapidly disappear from the sample through demand reactions. When the sample is subsequently poured onto a cultivating medium and left to incubate in an oven, the medium, the temperature and the time will destroy any residual chlorine. This effect would not be seen in an industrial application, since the BFCC treatment would be applied on a continuous basis.

The 5 μg/l of added copper is well within the 23 μg/l water quality criteria level set by the Unites States Environmental Protection Agency (EPA), and one third of that emitted by a thermal desalination plant (8). The 200 μg/l (0.2 ppm) added chlorine compares favorably with the typically 1 ppm concentrations added by conventional chlorination systems. A reduced chlorine requirement has capital expenditure, maintenance and environmental advantages. It also reduces the risk of PA membrane damage, and reduces the requirement for feed water dechlorination. The use of sodium bisulphate (SBS) as an oxygen scavenger and/or chlorine scavenger can provide a food source for sulphate reducing bacteria (SRB) which reduce bisulphite to sulphide ions (9).

It may not be necessary to achieve 100% bacterial kill at the pretreatment stage. Dead bacteria are more likely to release organic material into the water through autolysis, thereby providing a potential food source for bacteria downstream. Frequent backwashing of filters would help in this respect, minimising the opportunity for bacterial degradation in the sand filters. Keeping in mind that backwashing frequency must remain within appropriate limits as dictated by other process restrictions. The data for bacterial numbers before and after the sand filters highlight the effectiveness of filtration in controlling bacterial numbers.

It was not expected that the BFCC system would have any direct effect on filtration, however, increased frequency of filter backwashing was required when using the BFCC system. In view of the importance of pre-treatment in removing bacteria, the coagulative effect of the BFCC system is a useful feature which is likely to lead to a reduction in the usage of coagulants such as $FeCl_3$.

The results reinforce the potential benefits of target dosing copper and chlorine. Target dosing involves introducing small doses of copper and chlorine treated seawater at different stages in the RO process (Fig. 3). Results of second injectiaon of low dose of copper and chlorine after pretreatment will be reported in a later work. This is preferable to adding high (parts per million) concentrations of copper/chlorine at the seawater intake. for a number of reasons.

(1) The addition of high chlorine concentrations in the raw seawater feed will result in increased available organic carbon (AOC) concentrations, which will then predispose the Reverse Osmosis (RO) membrane to bacterial fouling (7). Dosing with small copper/chlorine concentrations at key points in the process is the preferred water treatment strategy (Fig. 5).

(2) Copper introduced into the raw seawater is likely to be scavenged in the coagulation/filtration phase. Any residual chlorine produced oxidant, (CPO), will most likely be eliminated during filtration, especially if an activated carbon filter is in use. Therefore, it is wasteful to try and control biological fouling with one large copper/chlorine dose at the intake and/or ahead of the pretreatment.

(3) The use of a number of low copper/chlorine doses at strategic points in the process train minimises the possibility of chlorine induced polyamide (PA) membrane damage. It may also be possible to prevent fouling without having to add a reducing agent (e.g. sodium metabisulphite) to destroy excess chlorine prior to filtration in the membrane stack.

(4) One of the main difficulties in maintaining an effective antibiofouling dose is the short half-life of chlorine. However, filtration removes organic matter, which represents a major part of the chlorine demand of the seawater. The more the chlorine demand is reduced, the longer the chorine will last, and the easier it will be to maintain stable concentrations of copper and chlorine in subsequent stage of the RO process. Chlorine concentrations of 20 μg/l can be used in conjunction with 5 μg/l of copper just before the permeator, in comparison with concentrations of 200 μg/l of chlorine used at the inlet of the system (10).

(5) The introduction of chlorine into natural waters can give rise to the formation of trihalomethanes (THMs) and other halogenated organics (11). These are persistent molelcules, some of which are carcinogenic. There is concern about their accumulation in the food chain. Efforts are under way in a number of countries to limit the discharge of chlorine into fresh water and marine environments. The use of low initial concentrations of chlorine in conjunction with copper will help to minimise the concentrations of THMs produced. This would have a tangible effect if organic matters are removed by

coagulation/filtration process ahead of copper/chlorine injection. In view of the fact that small halocarbons are poorly rejected by some membrane (12), any measure which will reduce overall chlorine usage in the RO process must be attractive.

CONCLUSIONS

Biological fouling in Gulf desalination plants may be controlled with low concentrations of copper and chlorine, the technology offers a number of benefits over other antifouling technologies. Due to the relatively small masses of copper and chlorine required, the size of generating plant employed is small compared to other systems. Environmental impact is minimised through reduced copper and chlorine emissions. The formation of trihalomethanes is minimized, which is important both in terms of carry over into potable water, and the impact of rejected brine on marine ecosystems. The use of low chlorine concentrations minimises corrosion. The need for dechlorination prior to the RO membrane would thus be eliminated. Reduced chlorine concentrations may also improve filter performance, thereby improving the efficiency of the pre-treatment stage, and possibly resulting in a reduced requirement for their coagulations. Of interest to RO operators is the concept that reduced chlorine usage will remove the possibility of chlorine induced bacterial aftergrowth on RO membranes due to the formation of assimilable organic carbon (AOC).

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Fig.1 Results of a macrofouling experiment using mild steel rig after 4 months. Copper dosage was at 35 ppb in the copper/aluminium treatment; total residual chlorine was at 200 $\mu g.l^{-1}$; 5$\mu g.\ l^{-1}$ copper and chlorine at 20$\mu g.\ l^{-1}$ were used for the copper/chlorine (BFCC) treatment

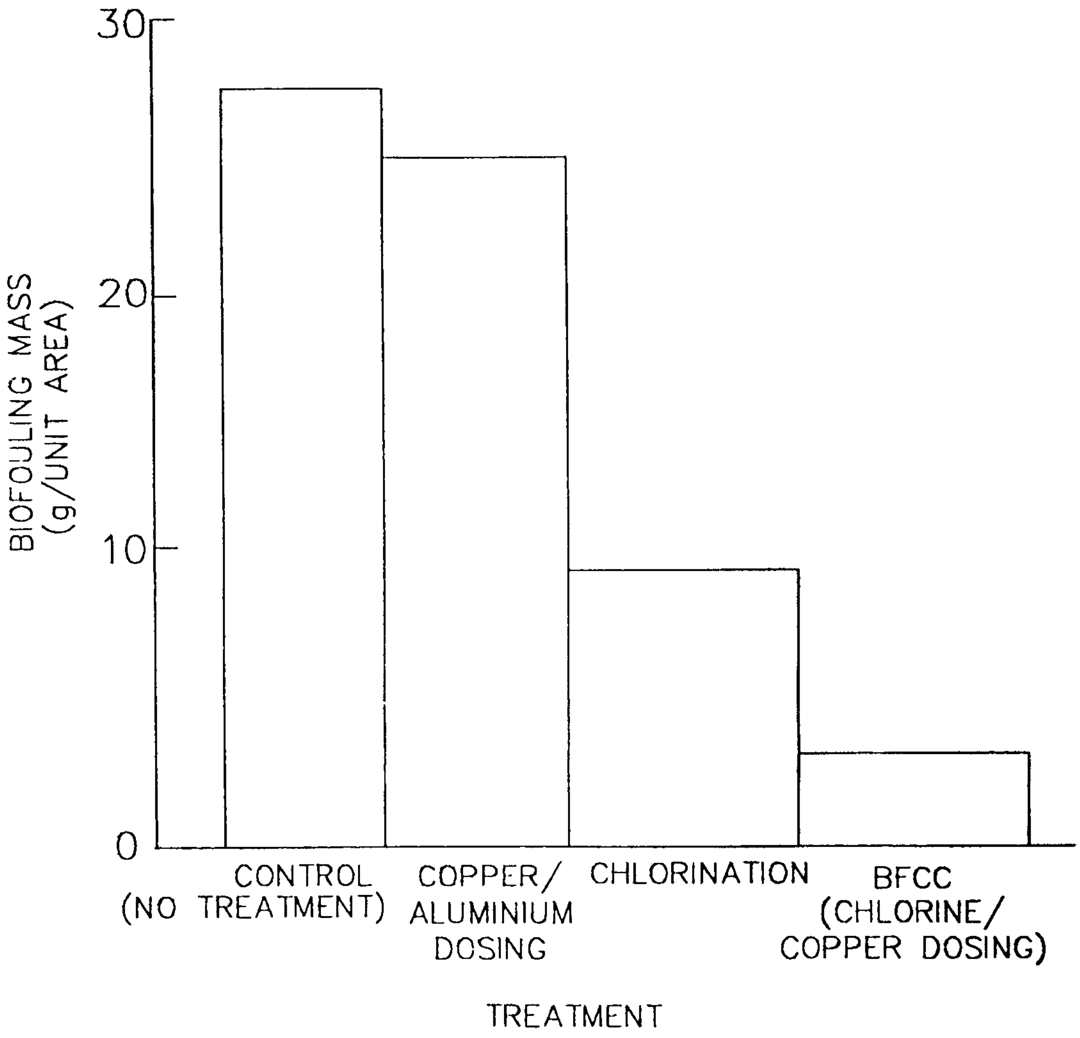


Fig.2 Schematic of US electricity Power Research Institute (EPRI) heat exchanger test facility. Shells A and B contained 7HE tubes. A,B,C and D contained the copper and chlorine electrodes

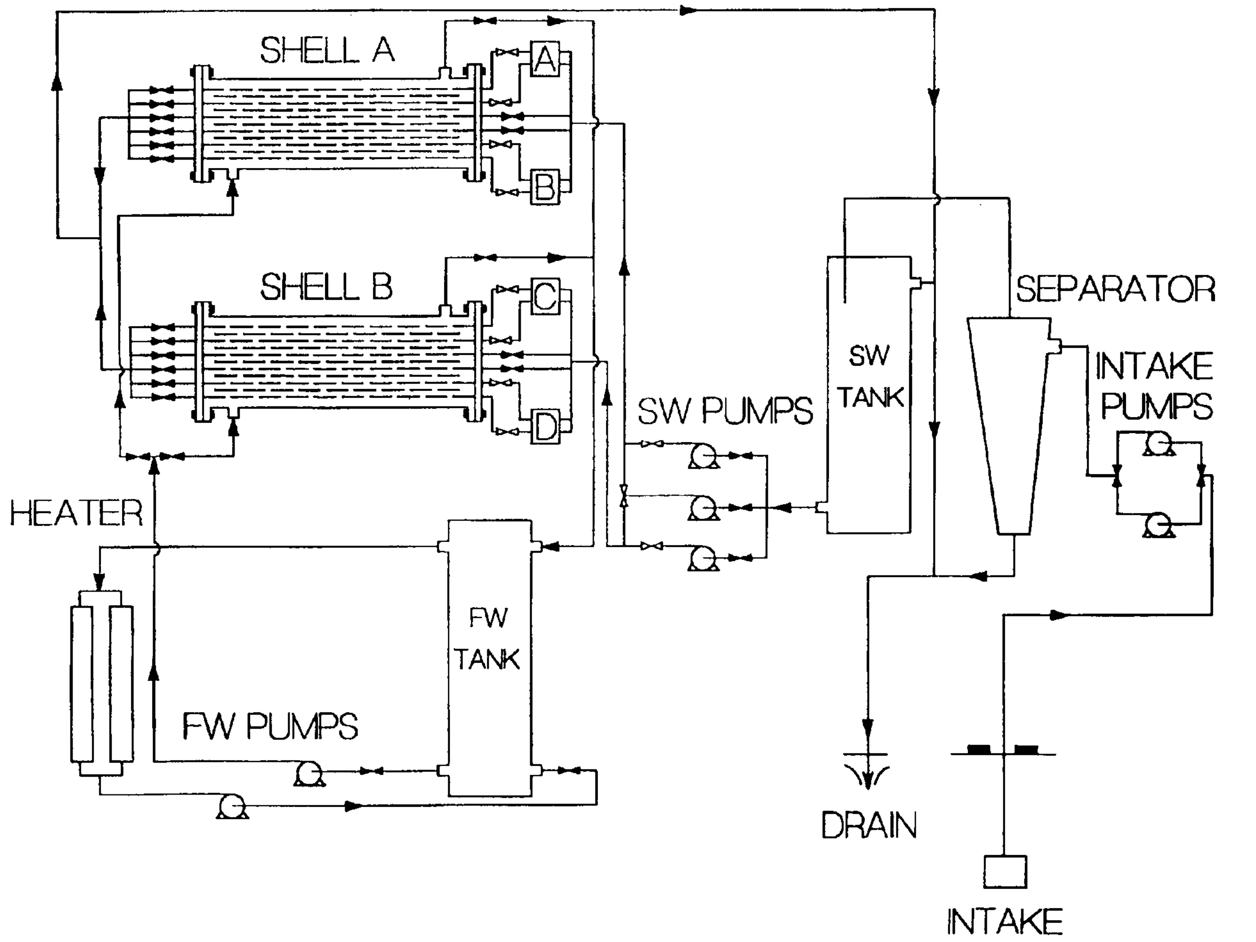
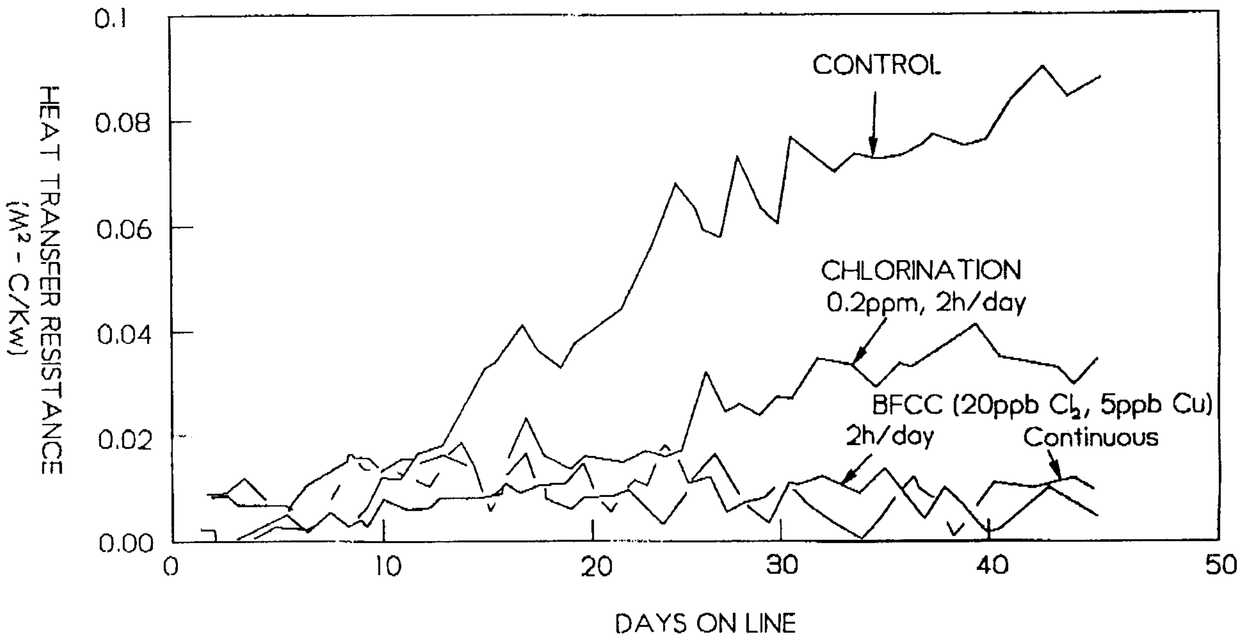


Fig.3 Microfouling experiment test results, using the EPRI test rig to compare conventional chlorination (200 mg $.l^{-1}$ for 2h . d^{-1}) and BFCC copper/chlorine (5ppb copper/20 ppb chlorine) treatments.



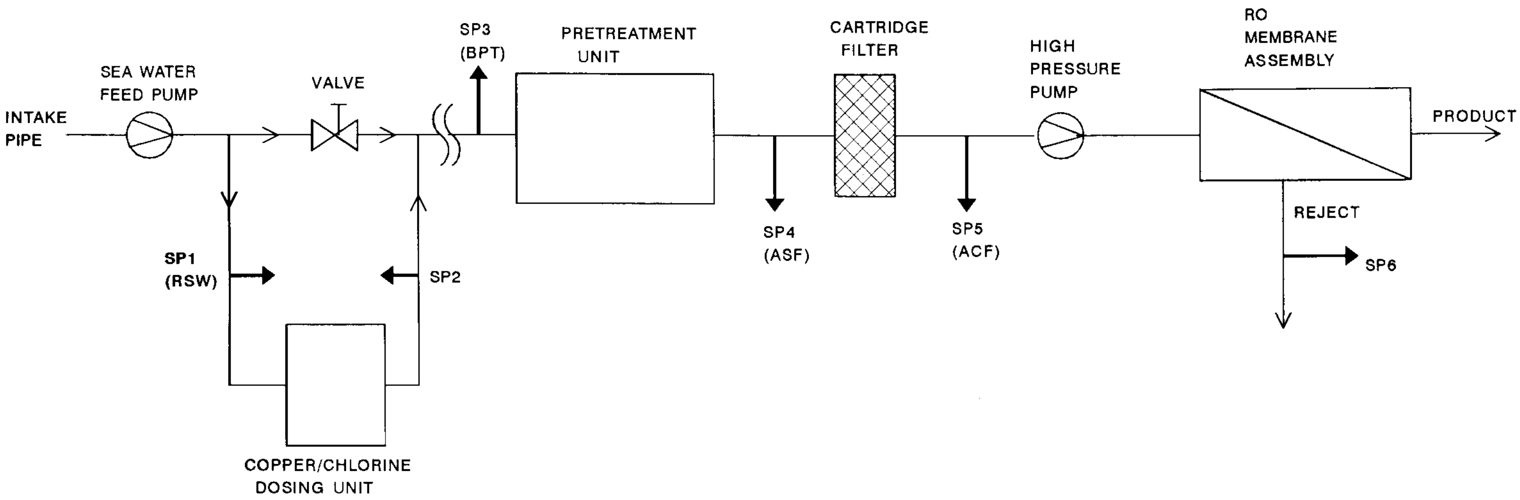


Fig.4 Layout of SWCC experimental Reverse Osmosis (SWRO) pilot plant, showing Sampling Points (SP). See text for legend

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Fig.5 Targeted copper/chlorine system