ASSESSMENT OF PHENOL DERIVATIVES IN COOLING TOWER SYSTEM AS BIOCIDES

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ABSTRACT:
One of the major problems facing the industrial utilities especially cooling towers is biofouling. Many techniques and measures have been taken and still continuing researches are under way. Biocides and water qualities were the main area of research for evaluation. Friendly biocides are preferable for controlling viable count and fungi, but many harmful still in use.

The main objective of this research work is to predict a relationship covering the concentration of Cl and Br – containing compounds as biocide and the performance.

It was concluded that the chlorophenol is the major effective biocide used (reduce it for about 80%, while bromophenol to about 65%) and that material although they are highly approved, but suffer pitting corrosion.

الخلاصه:
يعتبر الفشل البايلوجي أحد أهم المشاكل الرئيسيه التي تواجهها ابراج التبريد في المرافق الصناعية. فبالرغم من استخدام و توظيف عدة تقنيات و اساليب سيطرة و تحكم إلا أن المشاكل مازالت تستثير أهتمام الابحاث و استمراريتها في هذا المجال.
في الوقت ذاته تلعب المياه و نوعيتها و مصادرها دوراً رئيسياً في تحديد استخدام المضادات الحيوية(بايوسايد) خاصة تلك التي تعتبر من اعداء البيئة و منها مشتقات الفينول التي لازالت تستخدم الى وقتنا الحاضر ، لكن التفتيش عن عن مضادات حيوية صديقة للبيئة لازالت قيد الاهتمام و التفتيش.
البحث يهدف الى ايجاد علاقه بين استخدام مشتقات الفينول الحاوية على الكلورين و البرومين و تحديد كفائتها كقاتل احيائي ،النتائج المستحصلة من البحث تظهر تفوق الكلوروفينول كقاتل احيائي على البروموفينول(حيث اظهر الاول انخفاضاً بنسبه 80% في العدد الحي بينما الثاني بنسبة 65%) ،مع الاخذ بنظر الاعتبار كمية المواد العضوية المترسبة و التي تسببت بأحداث بعض التنقر لبعض السبائك الفائقة.

KEY WORD: Biocide, chlorohenol, cooling tower, pitting corrosion.

INTRODUCTION:
From a water cycle shown in Fig. (1) For a factory, it can be concluded that a cooling tower system is the main part in single train process.
Such waters scheme although subjected to a pretreatment before using, but still dangerous to materials being used in the process such as heat exchangers and main piping systems. Some containing floating materials being mainly organic carbon widely differed in their content

depending on operating parameters and the quality of the make-up water but will always support microbial growth [Cloete TE, Brozel VS, and Van Holy A, 1992].

As heat exchanger experienced a large surface area already, they provide favorable conditions for bacterial attachment [Characklis WG (1990)]. Leading to form a tangled mass of fiber termed a biofilm [Characklis WG and Cooksey KE (1983)]. Formatting of a biofilm begins with attachment of free floating microorganisms to a surface, these are first colonists. Although biofilm are beneficial for removing undesirable substance from rivers and waste – water treatment systems they are responsible for biofouling. The industrial problems associated with biofouling are essentially those that accrue to all fouling mechanisms – namely, increased back pressure, for a given flow rate and, in heat exchangers reduced heat transfer for a given temperature difference [Fletcher M. (1992)].the major economic impact caused by biofilm in cooling water system is because of energy losses due to an increase in the fluid fractional resistance and increase in heat transfer resistance [Michael L., 2003].

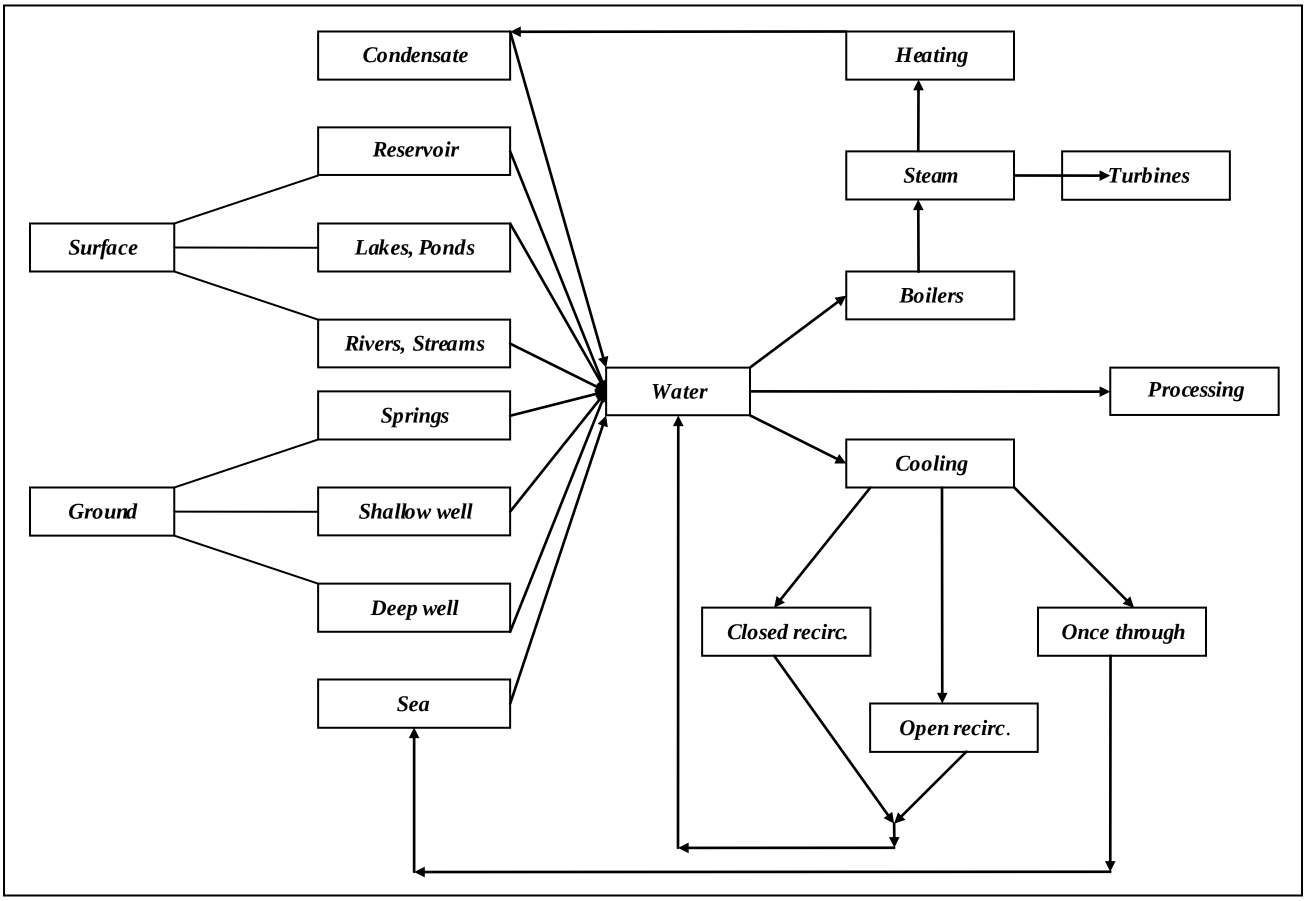


Fig. 1: The water cycle in a factory.

Also the presence of microorganisms that adhere to different surface can damage the metal surface by bio-corrosion [Michael L.2004].

One of the most effective tools to minimize their biofilm in industrial water system is by chemical treatment using biocides, to reduce the vial content or synthetic dispersant or enzymes for removal of such biofilm formed. It is of great desire that the biocide should meet the following criteria [Favstritsky et al (1992)]:

1- Wide kill spectrum – the agent should be effective against a wide variety of microorganisms, such as, for example, algae, bacteria, fungi, mold, and other aquatic organisms.
2- Fast rate of kill.
3- Low cost.
4- Useful in wide range of PH.
5- Non- corrosive to metal.
6- Compatible with commonly used cooling tower treatment chemicals such as scale inhibitor and corrosion inhibitor**.**
7- Unaffected by organic contaminants or nitrogen compound in the water recirculation system.
8- Ease of handling and application.

Biocide can be grouped into two general categories, oxidizing and non –oxidizing depending on the mechanism used to kill target organisms [John A.Viel, et al, (1997)].

In general the non-oxidizing biocides function primarily by altering the permeability of the cell walls of the microorganisms and interfering with their biological process. Numerous non-oxidizing chemicals have been used as their primary biocide or as supplement to oxidizing biocide application. One product that is widely used in electrical power industry is quaternary ammonium salts (quits). Some other non-oxidizing biocide used includes organo-sulfer compound, chlorinated phenolics, and glutaraldehyde, isothiozoline, triazine, di-bromonitriloproionamide (DBNPA), and heavy metals compounds [Tanji Y., et al, (2002)].

Oxidizing biocide cause irreversible oxidation /hydrolysis of protein group in the microorganisms and of the surface to the cooling tower equipment. The result of this process is loss of normal enzymes activity and cell death. Most oxidizing biocide are chlorine or bromine compounds. Chlorine is generally an excellent algaecide and bactericide although some strains of bacteria can develop chemicals resistance to chlorine. Liquid bromine has also been used in the treatment of biofouled cooling towers. Chlorine and bromine when they added to water, they form hypochlorous acid (HOCl) and hypobromous acid (HOBr), which acts as the active ingredient. Historically chlorine gas was widely used because of it is low cost. However in recent years many users have switched to other form of chlorine because of the health and safety risk associated with handling chlorine gas. Bleach (sodium hypochlorite) is now widely used as source of HOCl. Sources of HOBr are becoming increasingly popular in place or in addition to sources of HOCl. Sodium bromide is often added along with bleach. The sodium bromide reacts with the HOCl to form HOBr, which is an effective micro biocide over a wider PH range than is HOCl. Another biocide, 1-bromo, 3-chloro, 5, 5-dimethylhydanation (BCDMH) serve as chlorine and bromine donor and can generate HOBr.

Several phenols are used for disinfectant or preservation purposes [McDonnel,G. and Russell, D.1999].Phenol induces progressive loss of intracellular constituents from treated bacteria and produces generalized membrane damage with intracellular coagulation occurring at higher concentration [Hugo,W.B.1999,Russell,A.D.2003]. The plasma membrane of fungi is also damaged [Russell, A.D. and Furr, J.R. 1996]. Although A.niger and C.albcans are less susceptible than bacteria [Goddard, P.A. and McCue, K.A. 2001]. Low concentrations are claimed to lyes growing culture of E.Coli, staphylococci and streptococci, but this effect has not been examined in detail. Fentichlore, a chlorinated phenol, acts as an uncoupling agent against susceptible bacteria.

Bacterial spores are very resistant even to high concentration of phenol, but germination is inhibited by low phenol concentrations [Russell A.D. 1990]. Mycobacteria may be inactivated by phenolics, the damage being presumably membrane-orientated.

This paper describe the result of laboratory studies comparing the efficiency of two non-oxidizing biocide , chlorophenol and bromophenol and a mixture of them , for control of biofilm development in laboratory cooling tower and the effect of these biocide on the 904L and 316 SS was noticed.

EXPERIMENTAL SETUP*:*

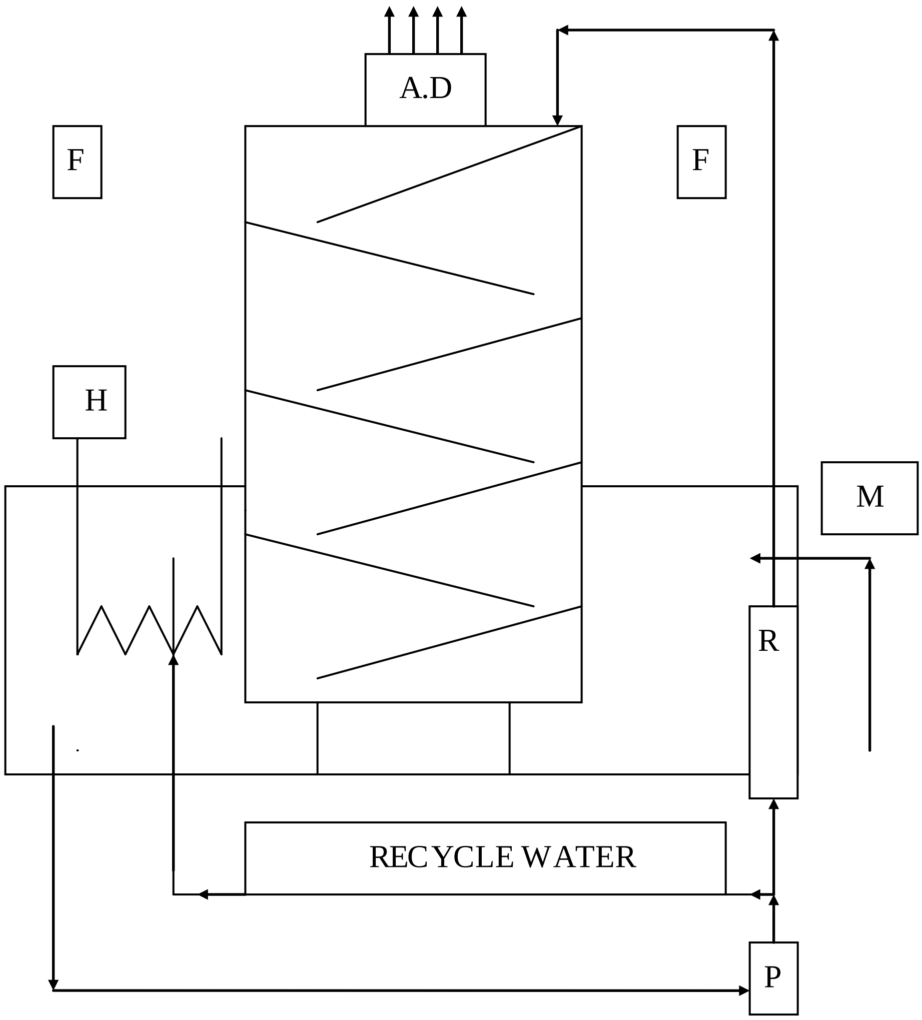
An assimilation of cooling tower has been designed and fabricated by the research group advised and approved by the scientific group of the department. The main constituent of such is shown in figure (2).

The system consists of pyrexpex tower (30*30*60 cm) contained within (50*50*40 cm) basin. The basin contains an over flow port positioned to provide a constant 40L working volume in the system , the tower contained water flow distribution box at the top and a series of slates (covered by sponge) which were positioned to provide a uniform cascade of recirculation water. The system has a recirculation water flow regulator and a make-up water supply. A portion of the recirculation water flow was diverted at the bottom of the basin to supply mixing within the system, the remainder where returned to the distribution box. An air draft fan has been positioned in the top of the tower to pull air out side the tower from the top with a temperature of about 43˚C (the air in to the tower from holes in the bottom with a temperature of 35˚C). The tower received a daily supplement of sodium nitrate (23mg/l) and sodium phosphate (20 mg/l) and once per week (50 mg/l) of kaolin to support microbial growth these condition has showed the maximum growth of microbial [Melo L.F., Bott T.R. 1997]. The cooling tower received a daily inoculation of (10 ml) of mixed population of algae and bacteria which was obtained from surface scraping from industrial cooling tower. The pH of the recirculated water was maintained at 8.5 using NaOH and H_2So_4 . The slats which served as the sampling sits were pre-fouled prior to each experiment to provide an initial biofilm. At the start of each experiment, the slats where brushed to remove the majority of the adherent biofilm and placed in the tower directly beneath the distribution box.

In the first run the tower served as the no treatment control, the other runs received two per week sludge doses of biocide to the water in the basin which where as follow; (25 ppm chlorophenol, 12.5/12.5 ppm mixture of chlorophenol and bromophenol, 25 ppm bromophenol) after two weeks of operation to each of the biocide the biofilm developed where assayed.

The total solid content was determined by drying (5 ml) of samples at 103˚C over night, the samples then weighed and then ignited at 550˚C for one hour in furnace to calculate the volatile solid content. Total viable hyperopic bacteria were determined by preparing special media for bacteria and fungi, the media for bacteria was a nutrient agar antisepticises by the auto clave, and the media for fungi was saboured agar or potato dextrose agar (PDA). A serial of dilution were prepared and 1 ml of the medias were raised in dishes, the bacteria were incubate at 37˚C for 1 to 2 days and the fungi at 20-30˚C for 5 to 7 days. Then we count the cells according to the following low: CFU (cell/ml) =colony number * dilution inverse (Department of Biology, college of Science, Baghdad University).

For the investigation of the corrosion of 904 and 316 SS, coupons of 10*30*1 of them were prepared, they were wet polished with polishing paper and then cleaned with acetone and dried and weighed.



M make up water **P Pump**
R rotameter **H Heater**
F Fluorescents **A.D air draft fan**

Fig. 2: Experimental set-up cooling water system.

RESULTS AND DISSCUTION:

For more than a century, phenol, and phenol derivatives are known to be the most available antiseptic agents, and also as antibacterial of microbial organisms. One of their major drawbacks that these are hazardous and not as friendly as naturally occurring chemicals to the environment. Their action as a biocide is located within the intucellur penetration of the cytoplasm of the living cells. Such a penetration will act to precipitate the proteins. Further more phenol derivatives are membrane dissolving action agents. They penetrate into the liquid phase of the cytoplasm membrane causing a leakage of its constituents. It is advisable to recall some important problems encountered in cooling water systems before discussing the results obtained. Such problems are interrelated as corrosion proceeds , an electrochemical reaction will take place which involve the dissolution of metal ions into circulated water , as water is slightly alkaline, the recirculation water in this study was of pH = 8.5 , scaling of sparingly soluble carbonate films will develop on surfaces of the pipes and heat exchangers components.

In meantime fouling due to attachment of inert debris of organic and inorganic, organic usually very loosely bounds to the metal surfaces affecting heat transfer and fluid flow. At the end microbiological growth were cells of bacteria , fungi and algae multiply to such proportions that they forms deposit easily visible to the eye which cause fouling. The principle area of this study was the performance of two non-oxidizing biocides (chlorophenol and bromophenol) against the growth and development of microorganisms in biofilm. Such results shown in the histogram chart(fig. 3) reveal clearly that under these circumstances of using one biocide i.e. chlorophenol at 25 ppm concentration, for 2 weeks time, greatly reduced the vial count(about 80%) but the fungi did not show the same decrease(65%) , while total solids (fig.4) mainly related to algae growth , still much higher than expected, the volatile solids parameters is a reflection to the total biomass present and is an important consideration in maintaining optimum performance of heat exchangers. The use of bromophenol with chlorophenol as a ratio of 1:1 and bromophenol alone at 25 ppm also show a decrease in vial count but it was not like the use of chlorophenol alone(about 65% for the vial count and 50% for the fungi). The same behavior for total solid, while the volatile solid show more decreases than the total solid.

The reasons for the variations in non-susceptibility arising between types of microorganisms can then be ascribed to: (I) the considerable difference in adsorption by and the uptake into cells resulting from the dissimilarities in composition and architecture of the outer cell layers;(ii) possible slight marked difference in actual target sites so that the affinity of sites for biocide is modified ;(iii) possible differences in the amount of available target sites; (iv) the presence within some type of cells of protective chemicals such as the spore-specific that protect against DNA damage ;(v) stress responses , i.e. the manner in which cells respond to harmful agent; and (vi) the presence of biofilm .

One can conclude that unless a multi-systems inhibiting formulation is used, still some other constituent will grow faster on the expenses of other parameters. So biocides, together with anti-scaling , anti-fouling with continues dosing is the only way of treating heat exchanger cooling systems to be trouble –free in service.

Biocide of chlorophenol as stated earlier are intercellular penetrate , causing a destruction of living cells of microorganisms and note algae controlling systems , as already seem from the green deposit formulating on metal surfaces of the two alloys 316 and 904L , which are superior in microbiological corrosion situation(they did not show a notified weight loss).

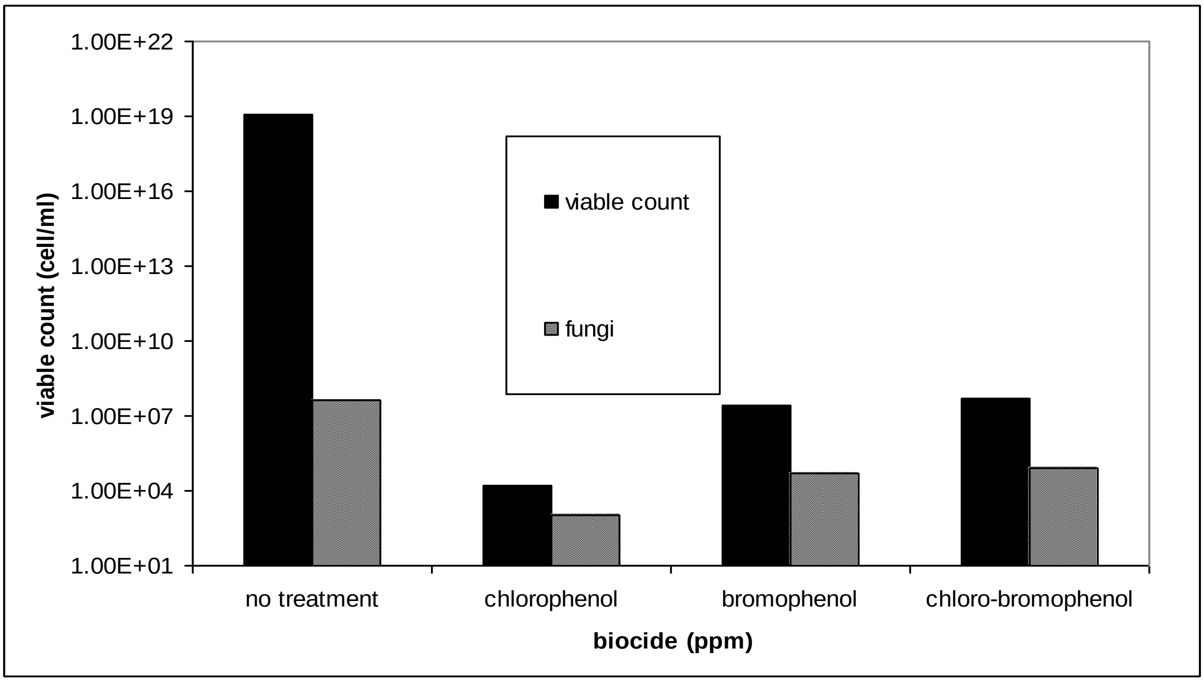


Fig. 3: Microbial Populations of cooling tower biofilms treated with biocides.

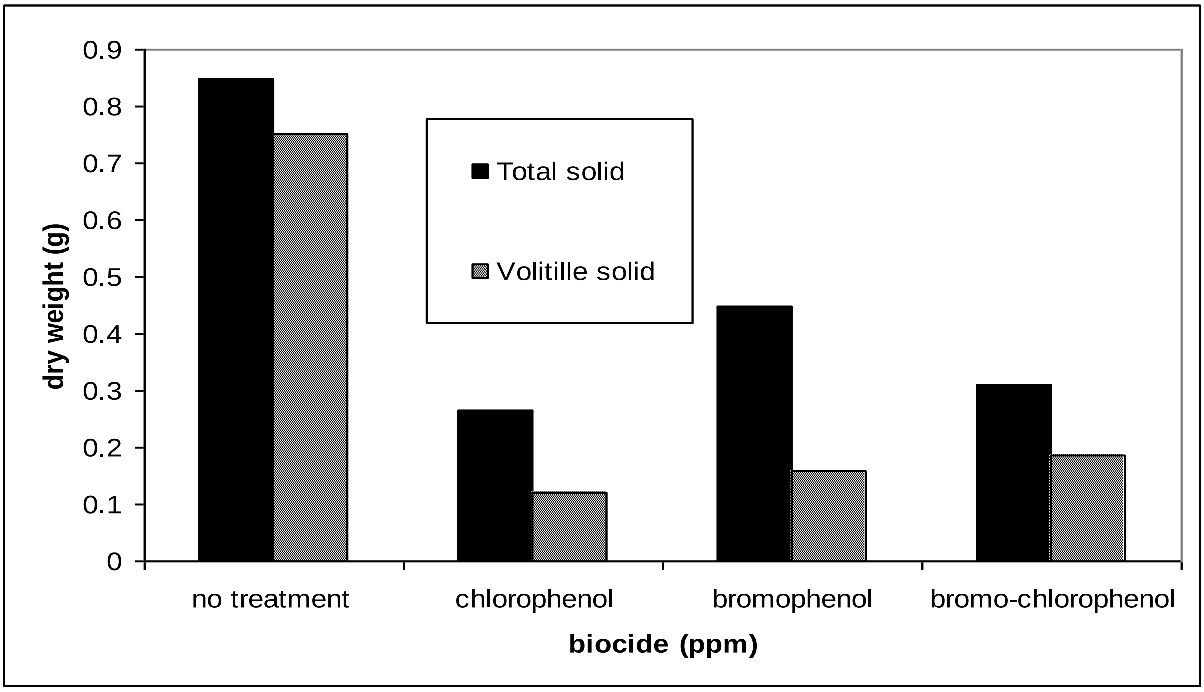


Fig. 4: Dry Weight content of cooling tower biofilms treated with biocides

Theoretically speaking, as water flow through the system, corrosion products sometimes are protective as oxides try to expel, and spill away revealing new surfaces to corrode, unless a corrosion inhibiter to stifle the process should be added. While biocides are more effective in killing suspended cells and preventing any growth of the microorganisms and scaling agents were performed into the system, hence no crystal growth modification observed. On the other hand, algae growth was at appreciable amount as already obvious from the histogram chart.

Conclusion:

1. In order to get a trouble-free cooling water system in service, the design criteria, water quality, size of equipment, temperature, make-up water and evaporation rate should be taken into consideration when a treatment procedure is suggested.
2. Chlorophenols and derivatives are cell killer but algae growth promoters.
3. An integrated system of complete formulation of corrosion inhibitors, biocides, anti-scaling, and anti-fouling agents are preferable.

REFRENCES:

- Characklis WG (1990) "*Microbial biofouling control*". In: characklis WG and Marshall KC (Eds) Biofilms (pp 585-633). John Wiley and Sons, New York.

- Characklis WG and Cooksey KE (1983) "*Biofilm and microbial fouling*". Adv.Appl. Microbial.

- Cloete TE, Brozel VS, and Van Holy A (1992) "*Practical aspects of biofouling control in industrial water system*". Int. Biodeterioration and Biodegradation 29:299-341.

- Favstritsky et al (1992). "*Method for the control of biofouling in recirculation water system*". United state patent, patent number 4,935,153.

- Fletcher M. (1992), "*Bacterial Metabolism in biofilm, Science and technology*" (pp 113-124).

- Goddard, P.A. and McCue, K.A. (2001), "*Phenolic compound. In Disinfection, Sterilization and Preservation"*, 5th edn, (Block, S.S, Ed) pp255-281. Lippincott Williams and Wilkins, Philadelphia, PA, USA.

- Hugo, W.B. (1999), "*Disinfection mechanisms. In principle and practice of disinfection, Preservation and Sterilization*", 3rd edn (pp258-283), Blackwell science, Oxford, UK.

- John Aviles , James K. Rice, Mary E.S.Raivel (1997), "Biocides usage in cooling tower in the electric power plant and petroleum refining industries", US department of energy.

- McDonnell, G. and Russell, A.D. (1999), "*Antiseptics and disinfectants: activity, action and resistance* ", Clinical Microbiology Reviews. 12, 147-79.
- Melo, L.F. and Bott, T.R., (1997), "*biofouling in water system*", Experimental Thermal and fluid science; 14:375-381.
- Michael, L., (2003), "*control and monitoring of biofilm in industrial application*", Int. Biodeterioration and Biodegradation 51:255-363.
- Michael, L. (2004), "*Biocorrosion towards understanding interaction between biofilms and metal*". Curr. Opin. Biotechn. 15,181-186.
- Russell, A.D. (1990),"*The bacterial spore and chemical sporicidal agents*", Clinical Microbiology Reviews, 3, 99-119.
- Russell, A.D. and Furr, J.R. (1996), "Biocides: mechanisms of antifungal action and fungal resistance ", Science progress, 79, 27-48.
- Russell, A.D, (2003), "Similarities and differences in the response of microorganisms to biocides", Journal of Antimicrobial Chemotherapy, 6:750-763.
- Tanji Y., Nakano T., Hori K., Miganaga K., Unno H., (2002) ,"*anti bacterial activity of biocide on biofilm*". Corrosion Eng.51:777-785.