

Chlorine dioxide in seawater for fouling control and post-disinfection in potable waterworks

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Abstract

Bio-fouling refers to the undesirable accumulation of a biotic deposit on a surface. This consists of an organic film composed by micro-organisms embedded in a polymeric matrix of their own making. Complex fouling deposits, like those found in industrial environments, often consist of bio-films in intimate association with inorganic particles, corrosion products and macro-fouling organisms. The article focuses on the possibility to minimize the problems related to micro and macro-fouling in once-through cooling systems and desalination plant by shot or continuous injection of chlorine dioxide into the seawater at the intake. A special on line monitoring instrument, installed after chlorine dioxide injection point, permits to check the fouling growth due to marine micro-organism and, in the meantime, the residual of chlorine dioxide.

Chlorine dioxide has proved to be an efficient antifouling agent used 1 h/da maintaining residual of ClO₂ in the range of 0.05 to 0.1 mg/L during the dosing shots or 10–12 h/da without any residual at several power station and petrochemical plant in Mediterranean sea, which use seawater both in condenser and evaporators to produce demineralised water. Beside a description of chlorine dioxide chemistry, the article reports 4 power station dosage programmes (one using also river water cooling tower during the summer) and 1 petrochemical plant application. Three different technologies for on site generation of chlorine dioxide have been reported. A full case history selected among the 4 power station is also reported.

Keywords: Chlorine dioxide, seawater, biofouling control, post-disinfection, potable water

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1. Introduction

The cooling systems usually have the following three basic designs: once-through, open recirculation and closed recirculation.

In once-through systems the cooling water, taken from a reservoir, passes through heat exchangers absorbing heat only once and then it is discharged back into the original water source. This process creates a high water withdrawal rate and it is usual where large and cheap volumes of water are available, as near sea coast, great lakes or big rivers. In Mediterranean area, these systems are found in refineries, petrochemical or steel plants as in power stations.

The efficiency of the cooling water systems is usually affected by three main factors: corrosion, scale and fouling or any combination of them. Here we focus on the aspects connected with fouling.

The first stage of fouling formation is an uncontrolled growth of microbial organisms on surfaces, with a preliminary formation of slime, which gives a bio-film, produced by the living cells and their metabolic by-products. The formation of bio-film can be resumed in three stages:

- a preliminary coverage of the surface by primary colonising bacteria and other organisms from water;
- a transition stage with multi-layers of cells which become embedded in their own polymer material;
- a final development of mature bio-film in which the population density is high. At the base of these mature bio-films conditions are completely anaerobic and favour the activity of fermentative and sulphate reducing bacteria (SRBs). The activity of SRBs in bio-films on metallic surfaces are responsible for the corrosion phenomena.

Bio-film is the substrate where other biological and inorganic materials can settle and

adhere, increasing the thickness of material attached to the inside walls of the pipes and therefore changing the ideal operating conditions of the system.

The term fouling refers to the final deposit, resulting from the mixture of bio-film (microbial masses and their extra-cellular polymeric substances (EPS), suspended solids, corrosion products and macro-organisms finally adhering and growing on the surface.

The fouling layer reaches the maximum development with the adhesion of marine animals such as Crustacea (Barnacles), Molluscs (Mussels and Clams), Anellids (Serpulids) and Coelenterates (Hydroids). The most important crustaceous fouling species is *balanus*, that has a planktonic larva that can produce a strong extracellular material at the surface called cement, and adheres strongly to many materials. Mussels are considered the most characteristic macro-fouling species. They are a bivalva species, have two shells and form big colonies on a great number of materials and are the main species responsible for clogging of industrial pipes. It is very difficult to destroy and detach mussel shells from pipe walls due to their strong adhesion.

The general effects of fouling are the following:

- increase of the frictional resistance and of the heat transfer resistance;
- increased maintenance costs (e.g. replacement of equipment);
- shutdowns to clean equipment with consequent loss of production.

When seawater is used, the following peculiar parameters can have a role in the fouling formation:

- water temperature: the relevant seasonal fluctuation can promote microbial growth;
- dissolved gases: the content of oxygen has a strong influence on several species of the aquatic population;

- nutrients content: the most common elements required for biosynthesis are present;
- dissolved solids and turbidity;
- pH and alkalinity.

1.1 Monitoring fouling

If research tests allow better control of the physical, chemical and biological factors and provide a framework for evaluating the fouling phenomena, measurements at the process site are necessary to evaluate the potential for fouling as well as the effectiveness of antifouling treatment programs. Direct and indirect measurements of deposit quantity and composition can be carried out in order to monitor the progress of the fouling.

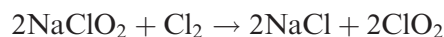
Direct measurements (deposit mass, thickness and composition, chemical and biological characteristics of the supplied water) are usually carried out. Indirect measurements (fluid frictional resistance, heat transfer resistance) can complete the possible available information. Also visual inspection of surfaces (especially crevices, valves, fittings) can give immediately some indications for deposit nature and structure.

On-line and side-stream fouling monitors, visual inspection, samples for destructive analyses and monitoring microbial quality of the feed-water can help in the identification of fouling and in finding the best way to control it.

2. Chlorine dioxide

2.1 General features

Chlorine dioxide (ClO_2) is a greenish-yellow gas, highly soluble in water. It is generated “on site”, mainly according to the following process with sodium chlorite as reagent:



or



ClO_2 is not a chlorinating but a very strong oxidising agent, having usually chloride (Cl^-) and chlorite (ClO_2^-) ions as final products according to the following reactions:



The main features of chlorine dioxide are the following:

- it does not react with bromides to form hypobromites which could contribute to the formation of organo-bromine compounds;
- it does not react with ammonia;
- it has high reactivity with regard to a number of structures including secondary and tertiary amines, organo-sulphur compounds and activated aromatic rings;
- it is not a chlorinating agent and does not lead to a significant formation of halogenated organic compounds;
- it is efficient over a wide range of pH (5–9.5).

Thanks to mentioned characteristics, chlorine dioxide is also largely applied in potable water in order to minimize formation of trichloromethanes, which are considered cancer promoter in humans.

2.2 Chlorine dioxide as antifouling agent

It has been demonstrated [1,2] that chlorine dioxide has a strong antivegetative effect being able to lessen the development of the primary slime, to reduce the biomass weakening the polymeric matrix and the number and type of “pioneer”

species (Diatoms, Cyanophyceae, Silicoflagellatae) which have a marked tendency to colonise the surfaces promoting bio-fouling.

According to seasonal and/or daily parameters (temperature, organisms population, light), to operational parameters (water velocity, water source position etc.), ClO₂ can be dosed in a continuous or in an intermittent way providing always a good mix with the feed water.

To maintain the best control of bio-fouling process and to reduce after growth phenomena, shock dosages (higher dosages for shorter time at fixed intervals of time) or a continuous/intermittent treatment programme can be carried out. Shock dosages can be extremely effective and provide a high inactivation rate of the organisms.

In the “shock programme” the ClO₂ dose must satisfy the “ClO₂ feed water demand” at the forecast contact time and a ClO₂ residual of about 0.1 mg/L should be present. This is the usual treatment procedure in special cases where bio-fouling has already reached the maximum development and it is necessary a strong cleaning action often in conjunction with physical methods.

In the continuous or intermittent procedure, ClO₂ dosage is basically determined on the basis of the “ClO₂ feed water demand” taking into account the transportation of the disinfectant to the interface, the contact time, the structure and type of surfaces.

The dose that varies according to conditions of the water source is a fraction of the ClO₂ demand (usually between 5 and 25%) and therefore, generally speaking, is between 0.05 and 0.25 mg/L on average. In reality, ClO₂ is generally added in higher concentration (i.e. 0.4 and 0.5 mg/L) but only for some hours a day (intermittent treatment).

ClO₂ reacts quickly with feed water and bio-film biological and chemical components

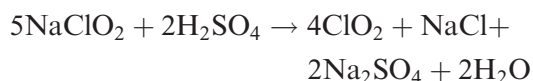
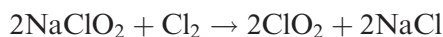
exploiting its oxidising power. No residual ClO₂ is found at the outfall.

In a field test carried out in a nuclear power station in Spain it was found, matching the results obtained treating the sea feed water with 0.2 mg/L of ClO₂ and 1.1 mg/L of active Chlorine from a hypochlorite solution, that lower doses of ClO₂ and shorter contact times were necessary to obtain a 100% mortality of mussels of different size [3].

3. Chlorine dioxide application

In the present article five dosage programmes have been reported. Three methods of chlorine dioxide generation have been applied in power stations and petrochemical plant, which use Mediterranean seawater to feed their once through cooling systems. In all the cases on line monitoring system for micro-fouling and probe for macro-fouling have been installed.

3.1 Generation of chlorine dioxide



The first reaction has been used in an American power station located Alexandria (Egypt), the second in two power stations and a petrochemical plant located near Venice (Italy) and the third one in a power station located in Malta. A complete technology of generation has been developed in order to produce chlorine dioxide in any situation present in a power station by using one of the following chemicals: chlorine gas, sodium hypochlorite from electrochlorinator, concentrated sodium hypochlorite, hydrochloric acid or sulphuric acid and sodium chlorite.

3.2 Type of chlorine dioxide generators

The type of generators used work either under vacuum or by pumps. In the first case, chlorine dioxide is generated by injection of sodium chlorite into the chlorinated water (0.5% Cl_2) coming from the existing chlorinator. In the second case typical under vacuum generators are used and, in the third case a very special generator, which works under water (submerged) installed at the seawater intake is used. This kind of equipment is very safe because the reaction takes place 5 metre under the sea and the reaction chamber is very small, therefore in case of any kind of inconvenient eventual trace of chlorine dioxide that could escape the generator is dissolved in the seawater without any problem. In a different version, submerged generator can be installed inside the main water line or in a by-pass.

3.3 Treatment programmes

All the programmes have been studied according to seawater quality, temperature, cooling system and residence time of the plant and adjusted after on line fouling control: the monitoring equipment is really the driver of the treatment, in fact it allows to know whether fouling is growing inside the condenser and, consequently drive the dosage modality.

- In the first case (power station in Egypt), using 98,000 m^3/h of seawater, after one year treatment, the programme is the following:
1/2 hour shot injection in the morning and 1/2 hour in the evening during the winter time (total 60 minutes/day);
3 similar shot during the summer time (total 90 minutes/day) the residual of chlorine dioxide at the discharge point is max. 0.1 ppm.

- In public power station near Venice, using 100,000 m^3/h of seawater, after 3 year treatment the programme is the following: Only during summer (from March to October) 1 shot per day at concentration of 1 ppm as long as 1:30 hours. There is no residual of chlorine dioxide at the discharge point.
- In a private power station near Venice, using 48,000 m^3/h of seawater after 3 year treatment the programme is the following:
From April to October 0.2 ppm continuously + 1 shot per day at concentration of 1 ppm as long as 1 hour,
From November to March, 2 shot per day at concentration of 1 ppm as long as 2 hours. There is no residual of chlorine dioxide at the discharge point.
- In the petrochemical plant near Venice, using 50,000 m^3/h of seawater after 5 year treatment the programme is the following:
In winter time continuous dosage at concentration of 0.1 ppm, in summer time 0.5 ppm. There is no residual of chlorine dioxide at the discharge point.
- In public power station in Malta, using 48,000 m^3/h of seawater, after 5 months treatment the programme is:
1/2 hour shot injection in the morning and 1/2 hour in the evening during the winter time (total 60 minutes/day);
3 similar shot during the summer time (total 90 minutes/day) the residual of chlorine dioxide at the discharge point is max. 0.1 ppm.

4. A case history

We report a full case history related to a power plant located in Sidi Krir (Egypt) where chlorine dioxide was applied. A special monitoring system named BIOCAFTM CTR

was also installed to control the performance of the treatment.

4.1 Description of the facility and cooling water

Sidi Krir 3 and 4 is the first privately owned power plant in Egypt. It is owned 61% by Intergen, a company based in the US, and 39% by Edison, a company based in Italy. The plant is often referred to as Egypt BOOT #1. The plant owners have built the plant, they own it and they operate it. In 20 years they will transfer the ownership of the plant over to the Egyptian Electric Authority. The plant went into commercial operation in January 2002.

The power plant is a conventional gas fired steam generating electric station located on the north coast of Egypt about 30 km west of Alexandria, Egypt. The generating units are rated at 2×340 MW (net electrical). The typical high load plant net heat rate is about 8900 BTU/kWh. The majority of the plant's rejected heat is discharged to the Mediterranean Sea.

The plant cooling system consists of two identical systems (one for each unit) that pump about 98,000 metric tons of seawater per hour. At full load this water undergoes a temperature rise of about 9°C between the seawater inlet and discharge. The seawater inlet temperature varies from a low of about 16°C in winter to a high of about 31°C in summer. The time weighted average temperature is about 25°C. Seawater is drawn in via an intake structure intended to result in low water velocities located about 350 meters off the shoreline of the power plant in about 8 meters of water. The discharge is via a discharge cap located at a similar distance from shore and depth as the intake structure.

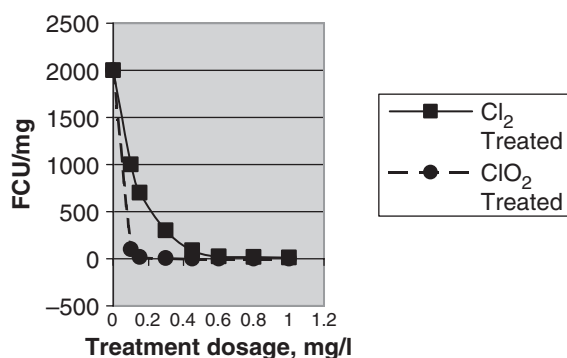
All of the cooling water pipes are cement or cement lined, the condenser water box is

rubber lined and the condenser tubes and tube sheets are titanium.

4.2 Original biocide concepts

The designer's original concept to control biological growth was chlorination via a chlorinator fed from one-ton liquid chlorine cylinders. No studies were conducted of the biological activity in the local waters and no serious consideration was given to the ability of the chlorinated water to be adequately

Microbiological Activity After Treatment



toxic for the organisms present and simultaneously comply with the environmental limits established for the cooling water discharge.

Simple studies by the owner of the effectiveness of chlorine to kill organisms as found near the power plant indicated that high dosages of chlorine would be required and the residual chlorine value in the water discharge would exceed the environmental permit level. The results of these simple tests are shown in the following graph:

A small dosage of chlorine dioxide was much more effective than chlorine to reduce the number of living organisms.

Other tests showed that the chlorine demand of the water a short time after shocking with chlorine significantly increased while

the demand for chlorine dioxide remained constant for the same period. That is to say much of the chlorine injected into the water simply reacted with the water and thus became unavailable to affect the organisms.

4.3 Installation of the chlorine dioxide system

Inadequate consideration was also given to minimizing the risks associated with handling as many as 40 one-ton liquid chlorine cylinders on the site. No consideration was given to the potential dangers of shipping in excess of 400 tons of liquid chlorine on the highways of Egypt. The concept of “safe driving practices” has a unique meaning in Egypt. Accidents and inadequate insurance coverage are all too commonplace there.

Due to the concerns of the owners with respect to on-site and off-site safety relative to chlorine and evidence at other power plants in the region that biological growth could not be prevented or controlled while maintaining the level of residual chlorine in the discharge water below 0.2 ppm the owners decided to consider technologies other than chlorination for biocide treatment of the water.

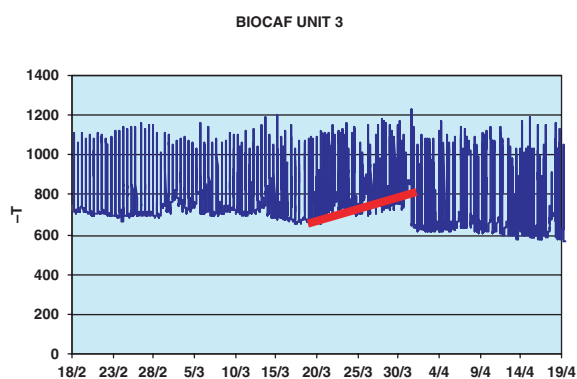
Because of the investment structure of the project and various uncertainties as the first private power developer in Egypt capital intensive alternatives were not considered favorably. The owners were very pleased to work with Caffaro Company of Milano, Italy, a company well known by the partner Edison, to purchase a very inexpensive sodium chlorite injection system that would allow the owners to fully utilize the already existing chlorination system. In fact, the cost of the sodium chlorite injection system was almost significantly offset by the decision to purchase only 10 one ton chlorine cylinders instead of the originally planned 40 cylinders.

4.4 Operating experience with chlorine dioxide

Because Sid Krir 3 and 4 is a new power plant we cannot provide comparisons of biocide results using just chlorine versus using sodium chlorite. Chlorination was utilized for about 4 months of cooling water system service before there was a significant heat load on the condenser. There was no evidence biological fouling during that time period that was from late summer to the end of the fall in 2001.

Full utilization of the chlorine dioxide technology began in November 2001 and is ongoing. The power plant has run well up through the end of June—available about 90% since commercial operation of January 27, 2002.

Based on 6 months of commercial operation we can compare chlorine dioxide system performance to our expectations.



4.5 Two day graph of biofilm activity

As winter turned to spring we tried to economize too much as the water and air became warmer and we did experience the growth of some mussels in April. At the same time the BIOCAF^{CTR} unit was clearly telling us that there was an environment existing to allow such growth to happen. The graph below shows the relevant time period and the clear increase in background

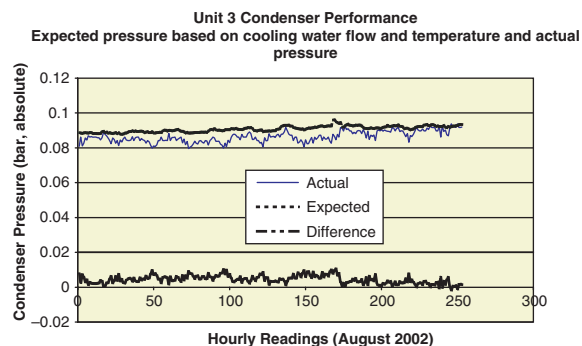
conductivity. With only 2 or 3 one-hour shock treatments of chlorine dioxide the mussels were killed and, since then, there has been no evidence of any additional bio-growth.

4.6 Use of the BIOCAFTM CTR monitor

The BIOCAF^{CTR} Monitor has become a valuable tool at Sidi Krir to monitor biological growth and to help us maintain effective water treatment at the lowest cost. The monitoring system basically consists of a probe which detects electrochemical kinetic process on its metal surface and relays that biological growth activity as a milli-volt signal displayed on a monitor. Also, the signal history is stored in memory for download to a laptop or PC. The signal increases gradually as a result of biological activity and, when the chlorine dioxide biocide is introduced, the sensor sees a very rapid increase in cathodic efficiency. After the biocide has washed through the sensor the indicated electrochemical activity is noticeably less than before the treatment.

4.7 Condenser performance

As mentioned previously there is no comparison available for condenser performance before starting the use of chlorine dioxide. We can only compare actual condenser performance to expected performance.



In making this comparison we must make some assumptions regarding cooling water flow—it presents the greatest source of inaccuracy in the results. With the assumption that the cooling water flow is in accordance with the pump test curve we are able to show that actual condenser performance is better than expected—as displayed on the data curve below. The expected performance is based upon a 90% cleanliness factor so we can conclude that the actual condenser cleanliness is better than 90%. The photographs seem to bear this out.

5. Results

For the waters being used by Sidi Krir power plant to cool their condensers there is no way that chlorination, only, of the water could have been effective to prevent biological growth and allowed the plant to operate within its environmental permit conditions. The use of chlorine dioxide has allowed the plant to very effectively prevent growth and the plant is in compliance with all permits. Additional benefit has been realized in annual cost and safety.

The use of the BIOCAF^{CTR} monitor is a major improvement over the use of chlorine monitors to detect residual chlorine. The BIOCAF^{CTR} unit allows the plant to optimize and minimize their dosing program based on real and immediately available results.

6. Conclusions

We underline the following advantages:

- Chlorine dioxide has allowed to minimize the growing of both micro and macro-fouling inside cooling systems of power stations and petrochemical plant at very low dosage rate,
- Monitoring system has demonstrated to be the “Brain” of the treatment programme. It has permitted to inject chlorine dioxide in a proper quantity and in the right

moment, saving material and protecting the environment.

References

- [1] L. Bartole and G. Bressan, 1993. Effects of chlorine compounds on Peryphyton (Primary slime): a preliminary report. *ICHEM, Biodegradation and Biodeterioration* 9: 123–127.
- [2] L. Bartole, G. Bressan, A. Francesconi, F. Dorè, Fouling control systems using chemicals inside industrial pipings: a laboratory simulation, *Oebalia* 19 (1993) suppl: 375–382.
- [3] M. Bielza, E. Morera, E.F. Lillo, J. Cuadrado, J. Castellnou, Tratamiento con hipoclorito y dióxido de cloro del agua de mar de refrigeración en centrales térmicas y term nucleares, 1991.

