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# Pulse-Chlorination®, the Best Available Technique in Macrofouling Mitigation Using Chlorine

## ABSTRACT

In 1998, KEMA developed a new chlorination method called Pulse-Chlorination®. It enables optimal antifouling treatment with a minimum use of chlorine. This technology is based on the principle that in general mussels and clams have a recovery period after exposure to chlorination before opening fully and restarting filtration. The method takes advantage of this recovery time by using short successive periods of chlorination, alternating with periods without chlorine. The tests undertaken between 1998 and 2001 resulted in chlorine savings up to 50% on a yearly basis, compared to regimes applied in earlier years. Results on site after one year with Pulse-Chlorination® show improved control of macrofouling and a better overall performance of the cooling water system. This in turn allows longer intervals between planned outages, thus spreading the running costs over three years rather than two years. There are additional advantages for power plants that use electrochlorination plants to produce hypochlorite. As the Pulse-Chlorination® reduces the hypochlorite dosage up to 50%, only part of the installed equipment is used at any one time allowing maintenance of the unused electrochlorination plants. Because less hypochlorite is dosed, there is a reduction in chlorination by-products discharged and thus less environmental impact.

## INTRODUCTION

The majority of the Dutch (power) industry uses chlorination for antifouling treatment in their cooling water systems. This is due to proven efficacy, wide experience, moderate costs, opportunities to optimize the chlorination procedure, and to the fact that low-level chlorination has not proven to have a major ecological impact [2–7].

The Dutch power industry asked KEMA to study alternative methods of chlorination with the aim of reducing the total quantity of hypochlorite used without loss of effective fouling control. Any new system should be applicable in as wide a range of industrial plants as possible. The method described here is called Pulse-Chlorination® and has been declared as a BAT (Best Available Technique) under the terms of the EU Integrated Pollution Prevention and Control (IPPC) reference document for macrofouling mitigation in once-through cooling water systems using chlorine [1].

In the Netherlands, the majority of the macrofouling problems in industrial cooling water systems are caused by three mussel species: the marine mussel *Mytilus edulis*, the brackish water mussel *Mytilopsis leucophaeata*, and the fresh water mussel *Dreissena polymorpha*, known as the Zebra mussel.

Pulse-Chlorination® is based on the principle that in general mussels and clams have a recovery period after exposure to a chlorination period before they open fully and restart filtration for oxygen and food uptake. Pulse-Chlorination® takes advantage of this recovery time by using short successive periods of chlorination, alternating with periods without chlorine. During continuous chlorination the mussels close and switch from aerobic to anaerobic metabolism and can live on

their own reserves for up to 10 weeks. By applying Pulse-Chlorination® the mussels continuously have to switch their metabolism from aerobic to anaerobic, leading to physiological exhaustion. This results in a more rapid antifouling compared to the conventional continuous chlorination. To exactly determine the behavior of the mussel, i.e., the recovery period, the valve movements are monitored in a special device, the MusselMonitor®.

## MATERIALS AND METHODS

### Mobile laboratory

All tests are carried out in the KEMA mobile laboratory on location; see Figure 1. This laboratory is a rebuilt 20-ft sea container consisting of a "wet" laboratory part and a "dry" part for the electronic equipment. The temperature in the laboratory is regulated with air-conditioning. In the laboratory the cooling water system conditions, which are unique for each plant location, are simulated so that the results are directly applicable to the station. The tested cooling water system conditions, which differ for each of the plant sites and which are crucial for the desired regimes, are ambient water composition, residence time of the cooling water (pumps to condensers) and water velocity. If possible, the organisms used as biosensors for the MusselMonitor®, are collected near the test location. For the chlorination experiments, sodium hypochlorite is used from that plant site. Water is usually obtained near the cooling water intake. In the laboratory, the water is collected in a 1 m<sup>3</sup> buffer tank with a water flow of about 500 L min<sup>-1</sup>. Due to the high water flow no sediment precipitation occurs in the buffer tank. With submersible pumps, the water is directed from the buffer tank through a hard PVC tubing system to the test tanks. In this system, the water flow is regulated and measured on-line with a Magno flow meter. For a Pulse-Chlorination® test usually three test units (tanks) are used (Figure 1, right):

- In Unit 1, the natural (= control) valve movement of the mussels is monitored with the MusselMonitor® without chlorination.
- In Unit 2, chlorination takes place. The reaction of the mussels is monitored with a MusselMonitor®. The free oxidant (FO) and/or total residual oxidant (TRO) concentration is measured with a continuous colorimetric measurement using DPD reagent (HACH CL-17). The results gained with Unit 2 are compared with the control Unit 1. If mussels in Unit 1 show abnormal behavior, results of that period from Unit 2 are skipped out for data analyses.
- In Unit 3, continuous on-line measurements are made of the following water parameters: temperature, turbidity, dissolved oxygen, pH, and salinity.

On each visiting day, the FO or TRO concentration is measured with a single spot colorimetric measurement using DPD reagent (HACH DR/2000) and is used for checking the concentrations measured with the HACH CL-17; if necessary, the HACH CL-17 is calibrated. All recorded data from Mus-

selMonitors® and water parameters are stored in a computer and transferred by (cellular) phone to KEMA in Arnhem. A data acquisition and presentation program developed by KEMA called the Tele Diagnostic System (TDS) enables on-line graphical data presentation of the valve movement patterns and storage of all measured water parameters and data in one database.



Figure 1: KEMA mobile laboratory.

After installation of the laboratory on-site, the background (control) behavior of the mussel species is determined, making all test units fully operational. After this, several dosing regimes are applied. Changes to the dosing regime always depend on the conclusions drawn from previous dosing regimes.

#### MusselMonitor®

At present, the MusselMonitor® is one of the most validated "Biological Early Warning Systems" (BEWSs) for surface waters using the valve movement response of bivalves (e.g., mussels or oysters) [9]. In "clean" water, bivalves show a characteristic valve movement pattern in which they are open most of the time, showing filtering activity. Bivalves exposed to contaminated water show strikingly different behavior, in most cases more frequent opening and closing activity resulting in long closed periods.

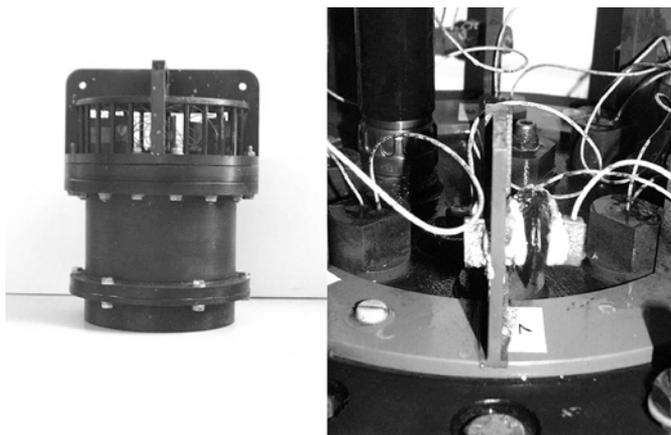


Figure 2: The MusselMonitor®.

Eight mussels are placed on top of the MusselMonitor®. Each mussel is provided with two sensors, one fixed on each of the valves; see [Figure 2](#), right. The principle is

based on the measurement of the inductive distance between the two sensors at 250 kHz, determined by the degree of opening and closing of the valves. By using a microprocessor to continuously register the action of the valve movement pattern of eight bivalves, a sensitive, fast reacting BEWS is obtained. With this monitor changes in valve movement of < 100 µm can be measured.

#### Data analyses

To get an insight into the effect of different dosing regimes on the valve movement of mussels, calculations are performed on the data collected from the MusselMonitor®. For each dosing regime, the absolute maximum and minimum valve position is calculated. These values are compared to the maximum and minimum values obtained during periods without dosing, i.e., no stress (control). From each period, regime or control situation, the average percentage (%) opening value of each mussel is calculated. During a dosing regime, mussels do not always open completely

and therefore produce a lower maximum opening value than they theoretically could reach. To get a realistic average % opening value of each mussel during each dosing regime, the calculation of the average % opening value for each mussel is corrected with the absolute maximum valve opening value obtained in the previous control regime. By comparing several effect parameters, the amount of effect of each dosing regime on the mussels can be determined. The major effect parameters used are:

1. FO or TRO concentration at which the mussels close their valves.
2. Time period that a mussel needs to reach a fully maximum valve opening after a dosing period and the increasing effect perceptible after several dosing periods.
3. Does the mussel reach its maximum valve value during a dosing regime as compared to the previous control regime?
4. Decrease in the % opening during a dosing regime.
5. Decrease in the % opening in time during a dosing regime.
6. Time that a mussel needs to fully recover (normal behavior obtained during previous control regime) from a dosing regime which it experienced for several days.

#### General reaction patterns of mussels

Mussels in "clean" water (uncontaminated) show a characteristic valve movement pattern in which they are open for more than 90% of the time, showing filtering activity for oxygen and food; see [Figure 3](#). A mussel exposed to hypochlorite shows a different behavior pattern, in most cases closing up within seconds. Previous studies using video recordings have shown that a mussel is capable of filtering activity only when it is fully opened [8]. To reduce mussel settlement and growth in a cooling water system, it is important that the hypochlorite dosing regime prevents the mussels from opening fully. When closed, a mussel switches from aerobic to anaerobic metabolism. Closed mussels live on their own reserves and can "survive" over up to 10 weeks, depending on their condition and the water temperature.

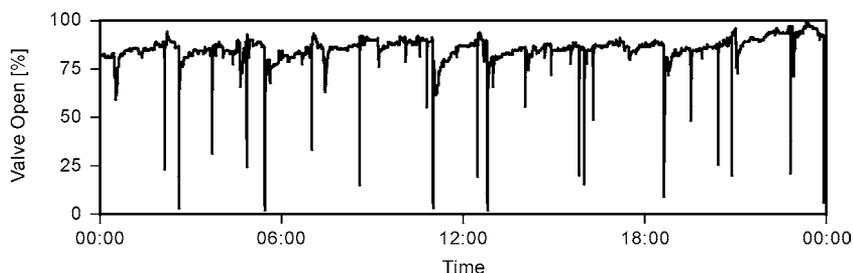


Figure 3: Valve movement of *Mytilus edulis*, control behavior.

After they close, mussels will frequently open a little bit to "taste" if the chlorine is still present. The mussel will repeat this "tasting" as long as dosing continues. When the hypochlorite dosing is stopped, and the TRO concentration has fallen below  $0.1 \text{ mg L}^{-1} \text{ Cl}_2$ , the mussel will open gradually to regain filtering activity. The time it takes a mussel to open fully and restart filtering activity is called the recovery period. The recovery period depends on the chlorine concentration the mussel was exposed to, the length of the dosing period, the number of previous dosing periods and on the water temperature. Mussels are more active and more sensitive to chlorine at higher temperatures. During the experiments, special attention is given to the cumulative effect of repeating dosing periods on the length of the recovery period.

## RESULTS

From 1998 to 2001, KEMA determined the optimum Pulse-Chlorination® regime for several companies in the Netherlands (power plants, chemical plants, waste incinerators). In [Table 1](#) the optimum Pulse-Chlorination® regime of each location is presented.

Water Type	Test Organism	Pulse-Chlorination® regime
Marine	<i>Mytilus edulis</i>	10 min on TRO = $0.3 \text{ mg L}^{-1} \text{ Cl}_2$ , 10 min off
Marine	<i>Mytilus edulis</i>	Combination of a pump pit dosing with a dosage just before Light Hydro Cracker installations [5,11]
Marine	<i>Mytilus edulis</i>	10 min on TRO = $0.3 \text{ mg L}^{-1} \text{ Cl}_2$ , 10 min off
Brackish	<i>Mytilopsis leucophaeata</i>	15 min on TRO = $0.6 \text{ mg L}^{-1} \text{ Cl}_2$ , 15 min off
Brackish	<i>Mytilopsis leucophaeata</i>	15 min on TRO = $0.6 \text{ mg L}^{-1} \text{ Cl}_2$ , 15 min off
Fresh	<i>Dreissena polymorpha</i>	15 min on FO = $0.4 \text{ mg L}^{-1} \text{ Cl}_2$ , 30 min off
Fresh	<i>Dreissena polymorpha</i>	15 min on FO = $0.3 \text{ mg L}^{-1} \text{ Cl}_2$ , 30 min off

Table 1: Optimum Pulse-Chlorination® regimes 1998–2001.

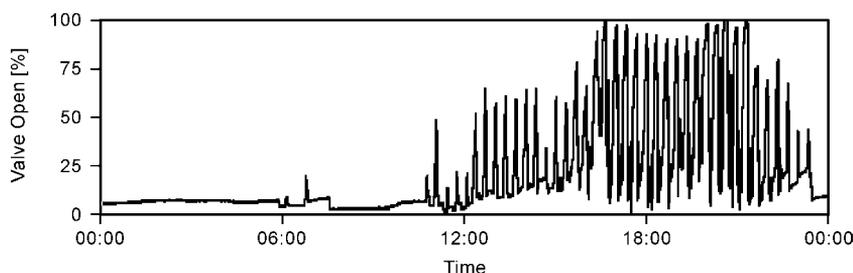


Figure 4: Valve movement of *Mytilus edulis*, chlorination.

From 0:00 to 12:00 – continuous dosing regime, TRO =  $0.45 \text{ mg L}^{-1} \text{ Cl}_2$ ;  
 from 12:00 to 0:00 – Pulse-Chlorination® 10 min on/10 min off, TRO =  $0.45 \text{ mg L}^{-1} \text{ Cl}_2$ .

In Figure 3, the mussels show a characteristic valve movement pattern in non-chlorinated control water in which they are open for more than 90% of the time, showing filtering activity for oxygen and food (control).

In Figure 4 the valve movement of the mussels in chlorinated water is presented. In this figure the mussels are first exposed to a continuous dosing regime with a concentration of  $0.45 \text{ mg L}^{-1} \text{ Cl}_2$ . They are fully closed most of the time but are sometimes open a little bit to "taste" if the chlorine is still present.

After this they are exposed to a Pulse-Chlorination® dosing regime of 10 min on/10 min off with a TRO concentration of  $0.45 \text{ mg L}^{-1} \text{ Cl}_2$ . During this period the mussels try to open during every short time period without dosing to open themselves fully to start filtering activity. The mussels continuously have to switch their metabolism from aerobic to anaerobic, leading to physiological exhaustion. As a result, an optimal effect on mussels is achieved resulting in a reduction in mussel settlement and growth in a cooling water system. In [Table 2](#) the main benefits found in these studies are summarized.

These results show that there is no optimum Pulse-Chlorination® regime efficient for all water types and fouling species. Even at locations close to each other, different optimal dosing regimes were needed. The sensitivity depends largely on the water type and quality in which the organism lives, as these influence the reactions and its chlorination by-products. Therefore, dosing regimes cannot be used without being tested at specific locations to determine the minimum concentration FO/TRO to produce a sufficient effect on mussels. Results show that the time (recuperation) interval is more decisive for the desired antifouling effects than changes in (higher) chlorine concentrations.

An optimal Pulse-Chlorination® regime for a location leaves no room for variation. The time intervals and FO/TRO concentration have to be established at a critical point in the cooling water system, e.g., just before the condenser. This means that a reliable on-line measurement of the FO/TRO concentration is essential for the proper implementation of the Pulse-Chlorination® regime.

## DISCUSSION AND CONCLUSIONS

Pulse-Chlorination® is cost saving. This technology results in less chlorine dosed in the system than conventional chlorination methods. The tests applied between 1998 and 2001 showed savings in chlorine use of up to 50% on a yearly basis compared to the regimes applied in earlier years.

Main benefits
<ul style="list-style-type: none"> <li>• 30 to 50% reduction in chlorine use on yearly basis compared to previous years.</li> <li>• Better mitigation of mussels since Pulse-Chlorination® is applied in conformation with a strict regime.</li> <li>• Postponement of the revision period from every 2 to every 3 years. This leads to an extra reduction in costs in addition to the reduction in chlorine use.</li> <li>• Reduction in the heat exchanger tube leakages caused by erosion corrosion by mussels and oysters from 20 to 0 within two years [5,11].</li> </ul>

Table 2: Main benefits found in Pulse-Chlorination® studies 1998–2001.

It appears that Pulse-Chlorination® leads to an improved antifouling treatment. This was concluded after comparing analyses of mussel settlement and growth using the KEMA Biofouling Monitor® (KBM) before and after Pulse-Chlorination® was applied. As a result of a Pulse-Chlorination® test, an optimal dosing regime is devised and additional recommendations on chlorine monitoring and use of the KBM are given to the company to improve the understanding of antifouling treatment methods. These recommendations lead to better control of fouling.

Pulse-Chlorination® results in a better overall performance of the cooling water system. Therefore, less maintenance of the cooling water system is necessary, leading to longer intervals between standard maintenance outages, thus reducing the annual costs. For power plants that already use electrochlorination plants (ECP) to produce hypochlorite for antifouling treatment, the application of Pulse-Chlorination® can also have additional advantages. Pulse-Chlorination® only needs part of the installed ECP capacity. This results in extra capacity for subsequent maintenance of the ECPs. Another improvement seen at chemical companies was a large decrease in heat exchanger tube leakages caused by erosion corrosion.

As a result of the decreased chlorine amount, there is a reduction in the environmental impact. In addition, less chlorination by-products are emitted in the outfall. The Dutch water authorities stimulate industries to reduce the usage of biocides (e.g., chlorine) to reduce the impact on the environment. By applying Pulse-Chlorination® the companies show their commitment to chlorine reduction. At present, Pulse-Chlorination® is entitled as a BAT for chlorination in once-through cooling water systems using chlorine. The regulating authorities now use this to encourage companies to reduce their chlorine use.

A Pulse-Chlorination® dosing regime can be started when the intake water temperature reaches a fixed temperature level, e.g., 12 °C, and stopped when the water temperature drops below this fixed temperature. An extra reduction in costs and the amount of chlorine is obtained by starting the chlorine dosing with the appearance of the first mussel spat. This can be achieved by using the KEMA Biofouling Monitor®, installed parallel to the cooling water system. By installing two KBMs, even more reliable data on the amount of fouling potential (spat settlement period) and on the effectiveness of the applied dosing regime can be obtained.

In other countries good results have been gained with intermittent chlorination regimes that were not developed ac-

ording to the Pulse-Chlorination® method [10]. These regimes, used by EdF (Flamanville nuclear power station, France) and Ontario Hydro (Canada), were established by monitoring mussel settlement and biomass and comparing results with their traditional, usually continuous, chlorination regimes. However, with implementation of an intermittent chlorination regime without a test phase according to the Pulse-Chlorination® method, no optimal antifouling procedure can be guaranteed.

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