Pulse-Chlorination®

Optimising cooling seawater antifouling strategy by adopting an environmentally friendly / BAT technology

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KEMA Technical & Operational Services

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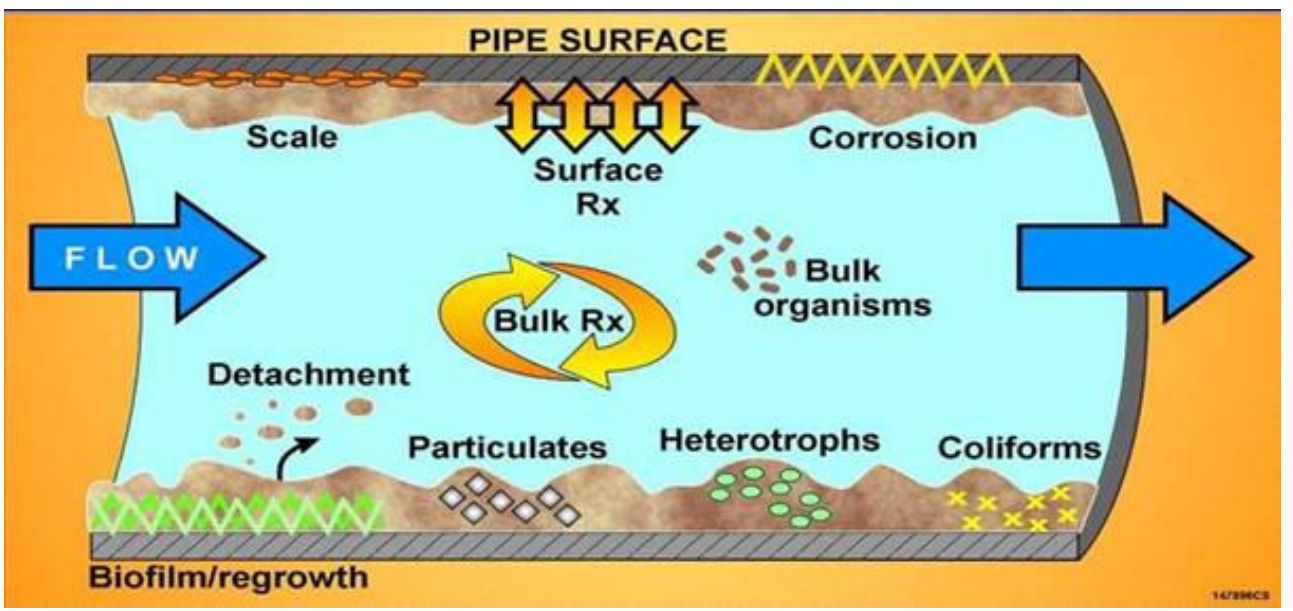
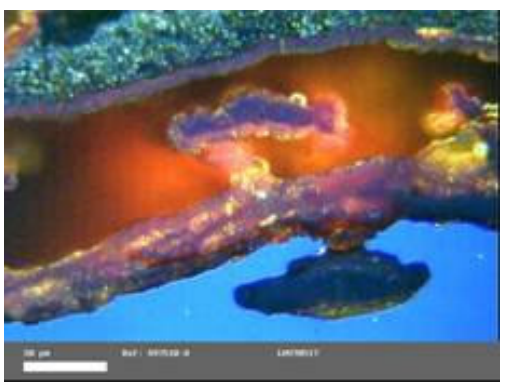
Macrofouling in cooling water systems

- Four phases in biofouling development
  - Biochemical conditioning of substrates
  - Colonization by bacteria
  - Colonization by single-cell organisms
  - Colonization by macrofouling organisms
- Driving force for settlement and growth is water turbulence
- Conditions inside the system are optimal due to:
  - Absence of light and predators
  - Availability of nutrition and oxygen
- Substrate is the limiting factor, not nutrition

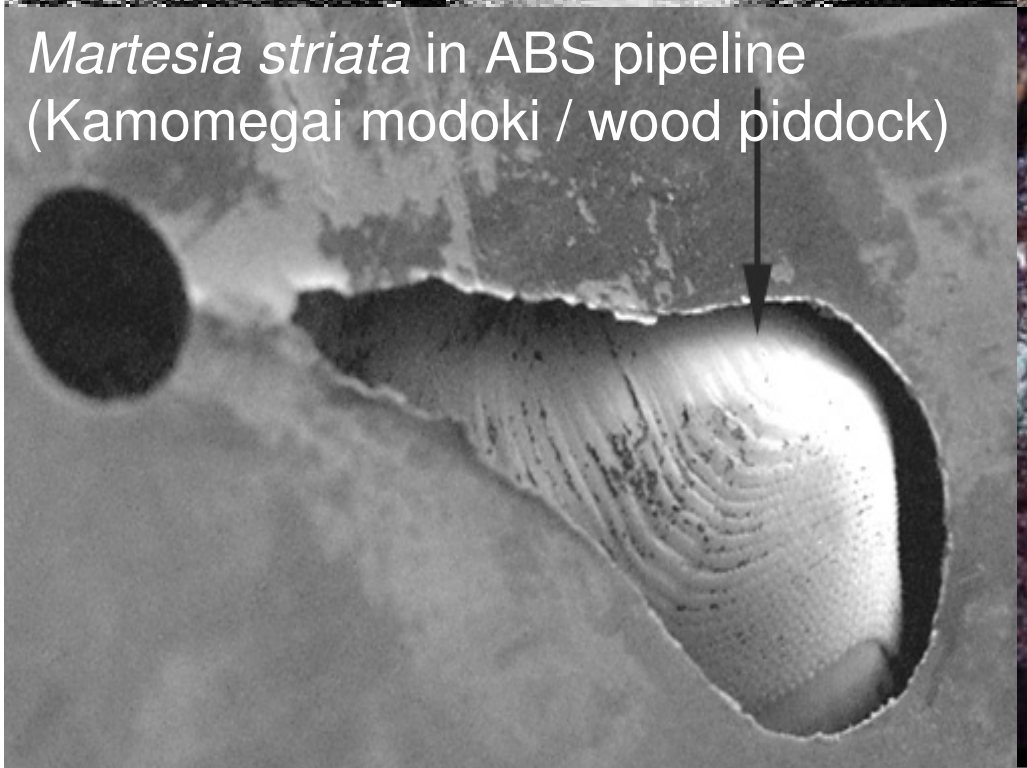
Microfouling

- Biofilm: loss of heat transfer
  - biofilms and deposition of suspended solids
- Microbial Influenced Corrosion (MIC)
- Stimulation of macrofouling settlement
- Increased health risk due to pathogens





Martesia striata in ABS pipeline
(Kamomegai modoki / wood piddock)



Nuisance species in Europe

Marine water

Blue mussel:

Mytilus edulis

Mytilus galloprovincialis

Barnacles:

Balanus crenatus

Elminius modestus (exotic)

Oysters:

Crassostrea gigas (exotic)

Hydroids:

Cordylophora caspia

Tubularia spec.

Bryozoa, sponges, mud shrimps

Brackish water

Brackish water mussel:

Mytilopsis leucophaeata

Barnacles:

Balanus improvisus

Hydroids:

Cordylophora caspia

Chalkworms:

Ficopomatus enigmaticus

Fresh water

Zebra mussel (Zeebs):

Dreissena polymorpha

Dreissena bugensis

'Asiatic' clam:

Corbicula fluminea

C. fluminalis (exotics)

Hydroids

Sponges

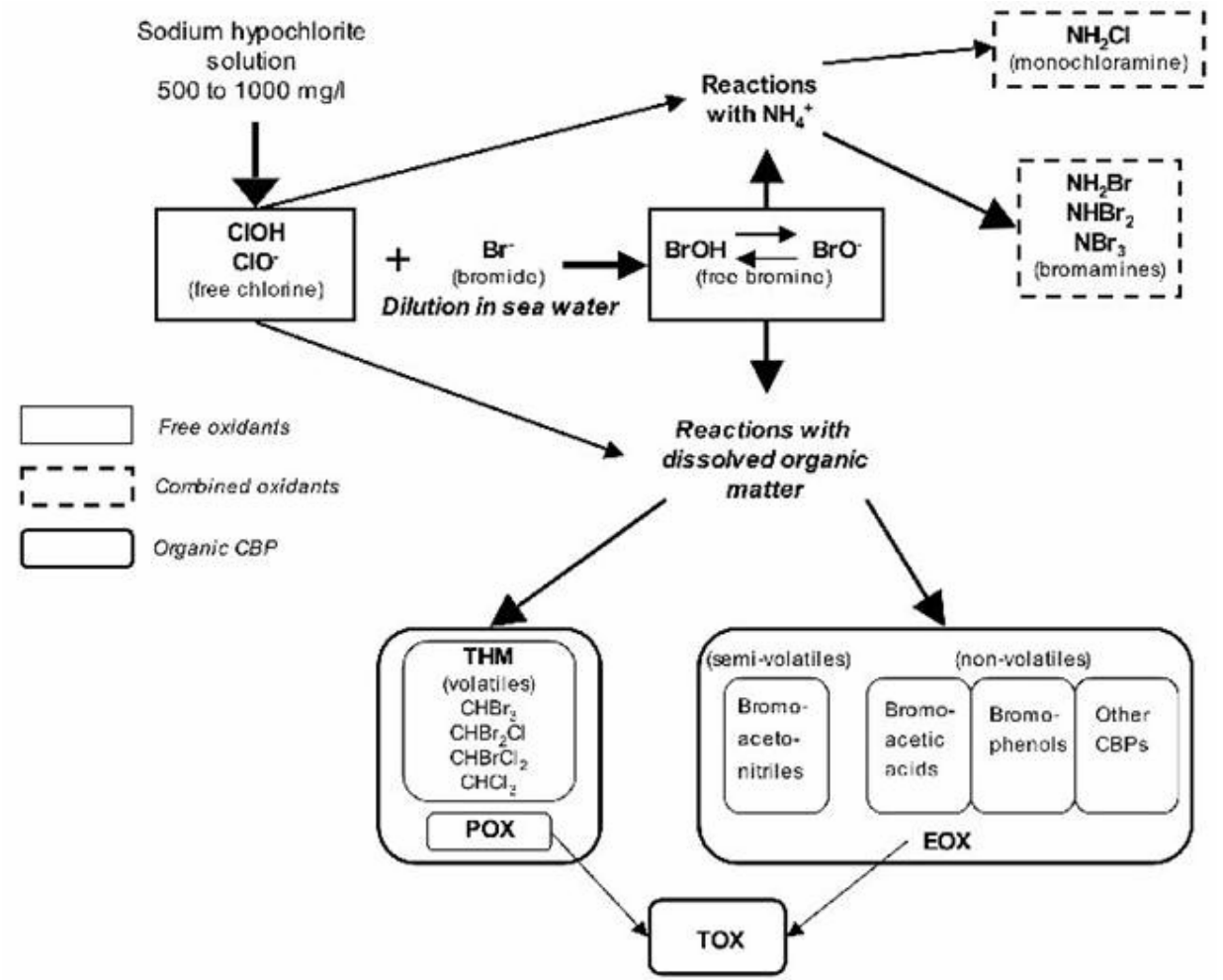
Mud-shrimps

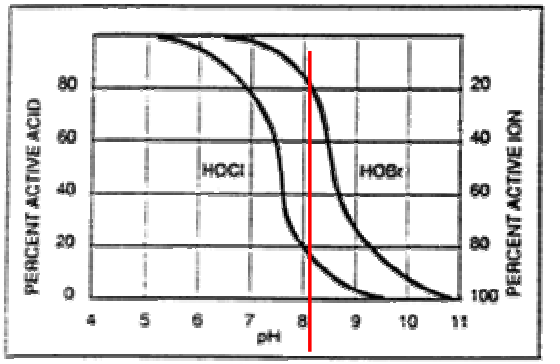
(*several exotic species*)

Chlorination

- Chlorination is worldwide still the most applied method to combat biofouling in once-through cooling water systems
- Proven efficacy
- Relatively low costs (cost-effectiveness)
- Environmental impact low (when applied correctly)

Chlorination chemistry in seawater





Dissociation of hypobromous and hydrochloric acid as a function of pH

Discharge limits (sea water)

- TRO limits in Europe:
  - driving forces: WFD, IPPC, national regulations
  - limit determined by (local) regulator (based on BAT)
  - usually 0.2 – 0.5 mg Cl_2/L TRO maximum limits
- Middle East (Qatar):
  - 0.05 mg Cl_2/L FRC (by SCENR)
  - current discussion for 0.2 mg Cl_2/L FRC
- Australia:
  - 0 (zero discharge) – 0.5 mg Cl_2/L TRO max
- USA:
  - 0 (zero discharge) – 0.2 mg Cl_2/L TRO max

Development of Pulse-Chlorination®

The Dutch Power Industry contracted KEMA (1998) to investigate alternatives in chlorination procedures for reducing the amount of chlorine, without loss of effectiveness in fouling control

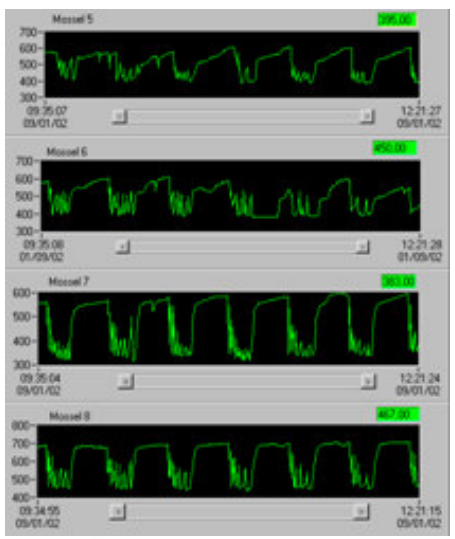
Development requirements

- Reduction chlorine dosing (discharge)
- No loss in effectiveness of fouling control
- Control of macro-fouling AND micro-fouling
- Improved cost benefit
  (ECP maintenance, energy saving)
- Reduced environmental impact

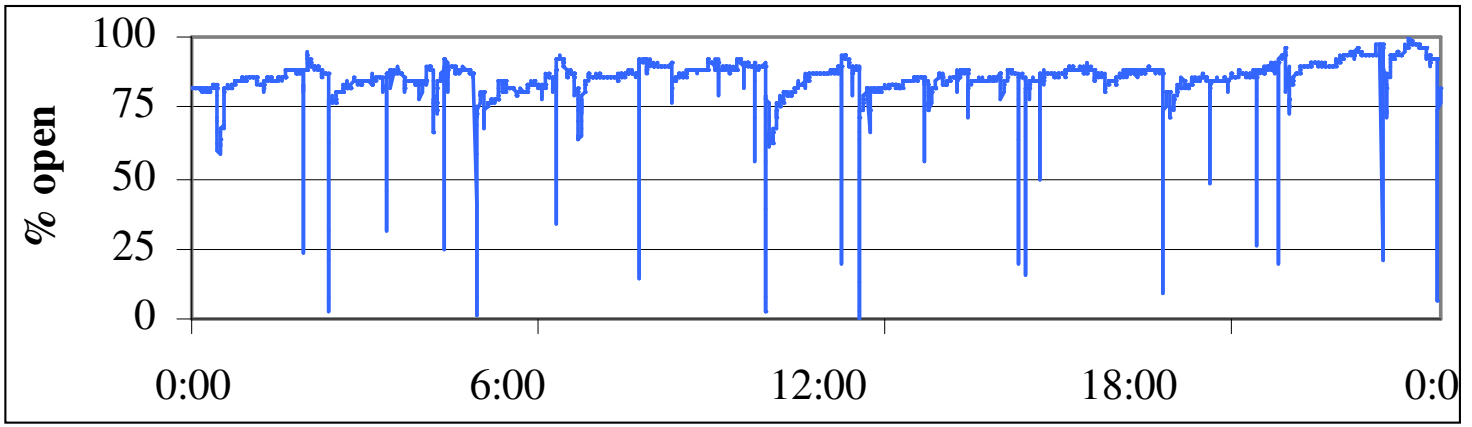
Bivalve reaction patterns to P-C

Mytilus edulis

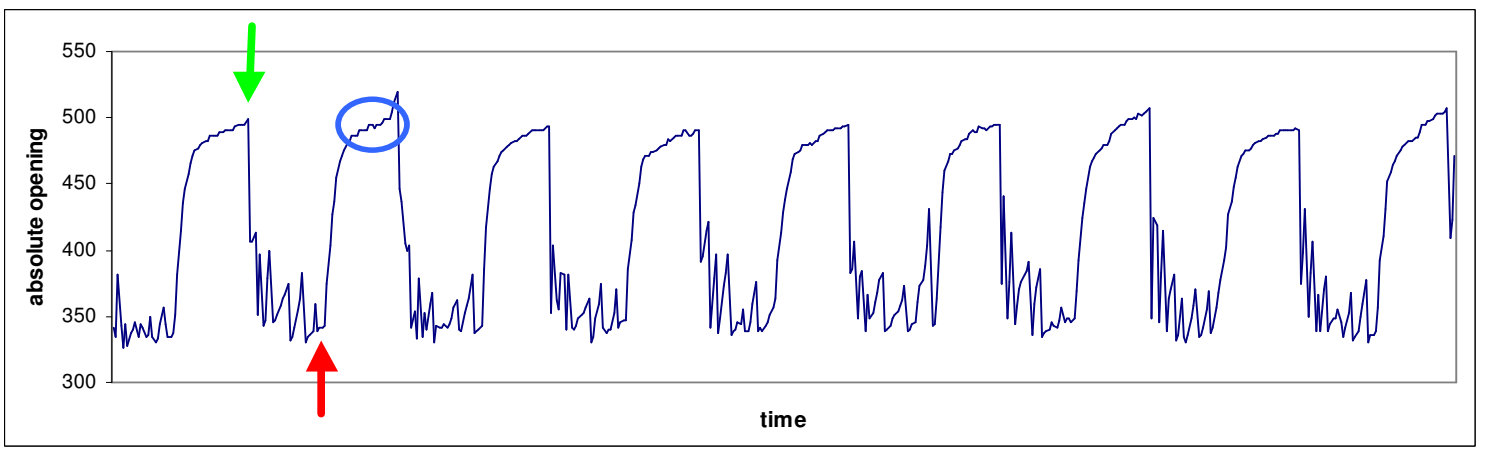
MusselMonitor



Control (natural behaviour mussels)



P-C Regime (mussel behaviour during Pulse-Chlorination)



KEMA

Best Available Technology

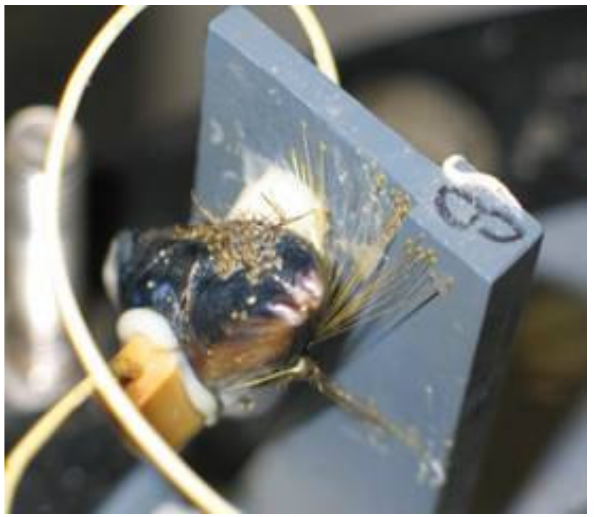
Best **A**vailable **T**echnique (BAT):

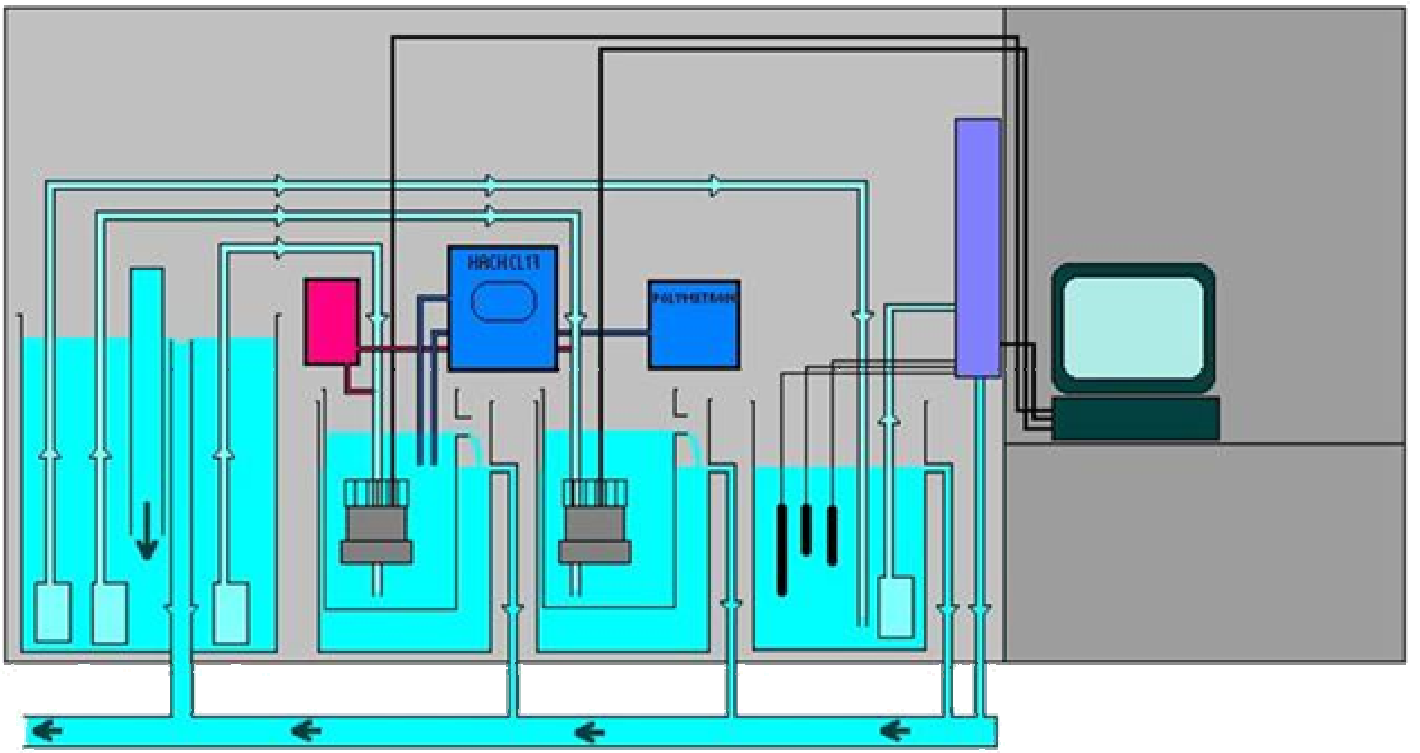
- In once-through cooling water systems
- European Commission (2000):
  - Integrated Pollution Prevention and Control (IPPC)
- BAT Reference Document (BREF Industrial Cooling)

EUROPEAN COMMISSION
DIRECTORATE-GENERAL JRC
JOINT RESEARCH CENTRE
Institute for Prospective Technological Studies (Seville)
Technologies for Sustainable Development
European IPPC Bureau

KEMA

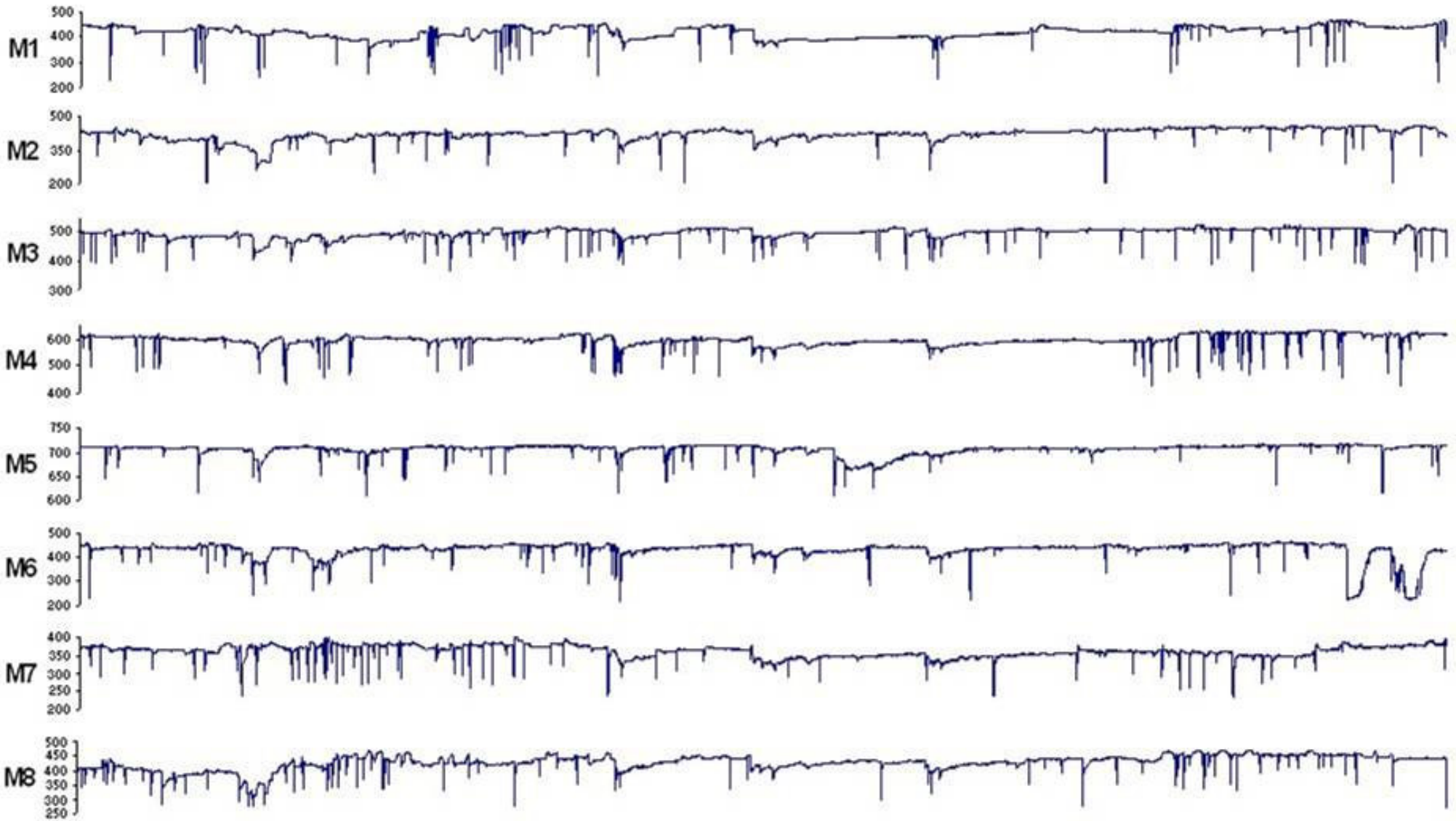
Field tests: KEMA Mobile Laboratory



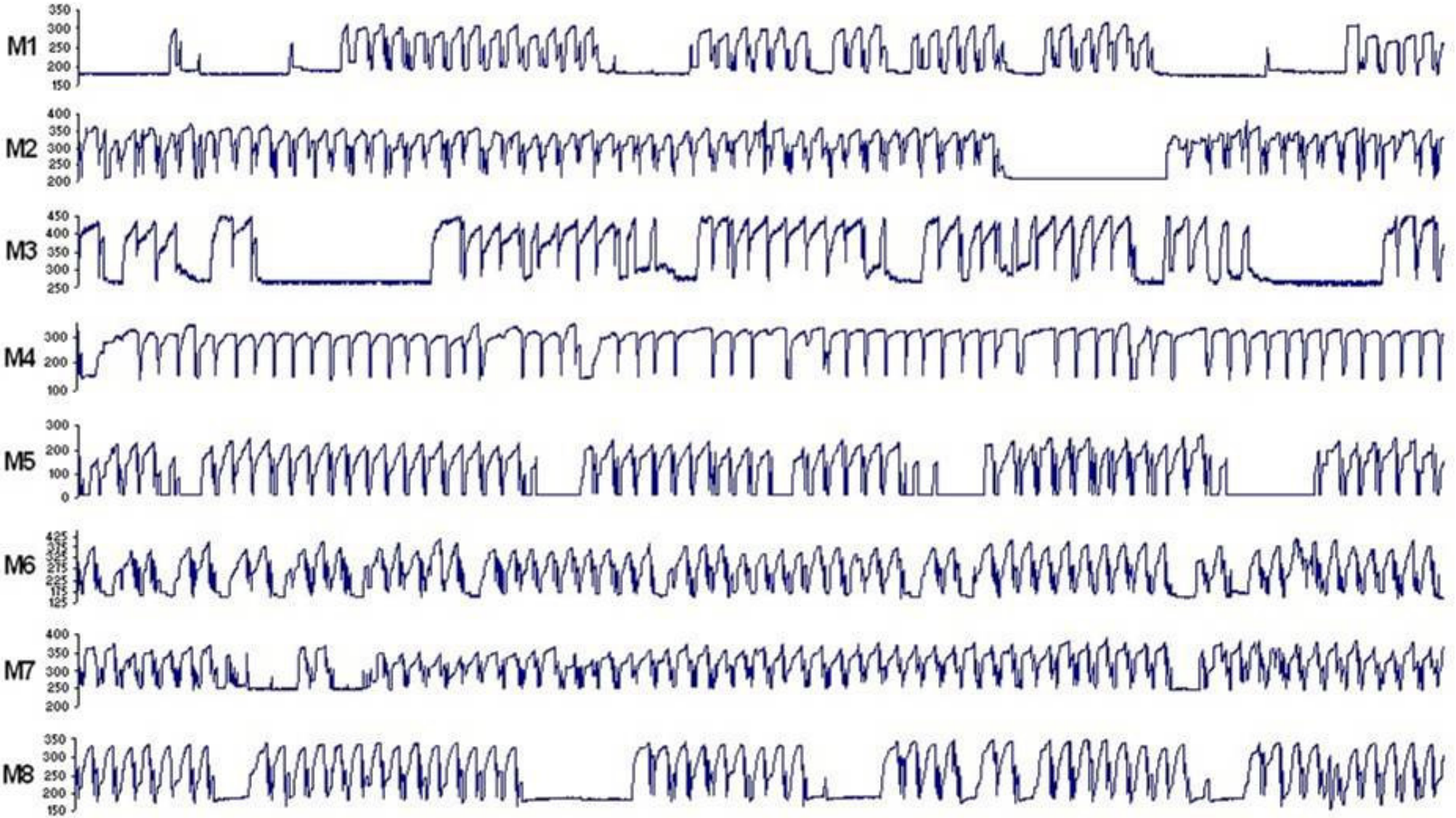


- Step 1: finding out control behavioural pattern of the mussels under ‘natural’ local conditions (without hypochlorite)
- Step 2: finding proper pulsed hypochlorite dosing: concentration and time-intervals

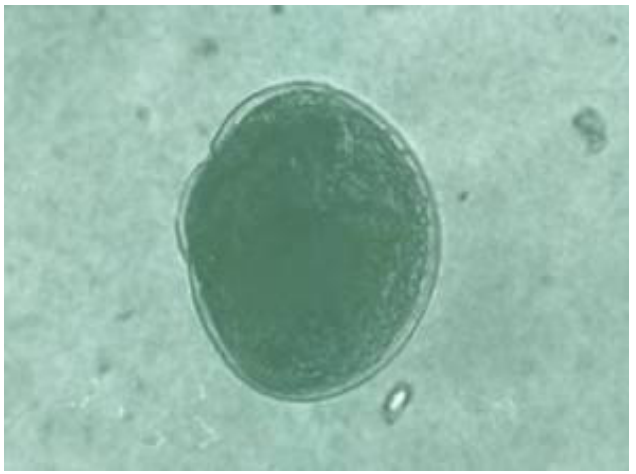
Control behaviour (no dosing)

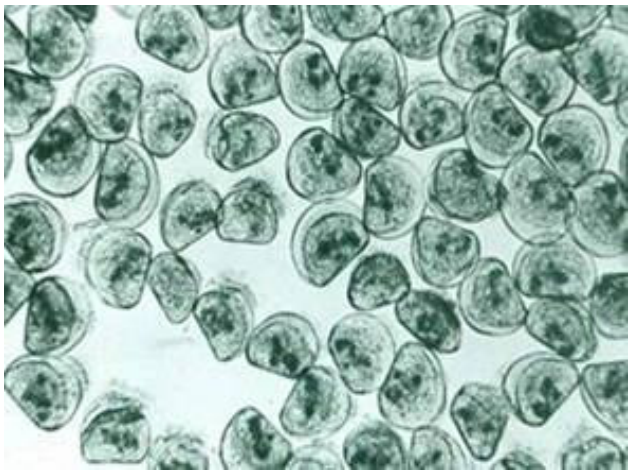


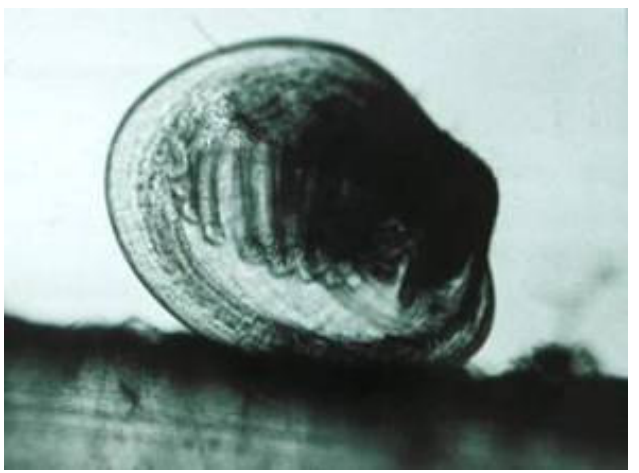
Behaviour during P-C dosing



Settlement of spat







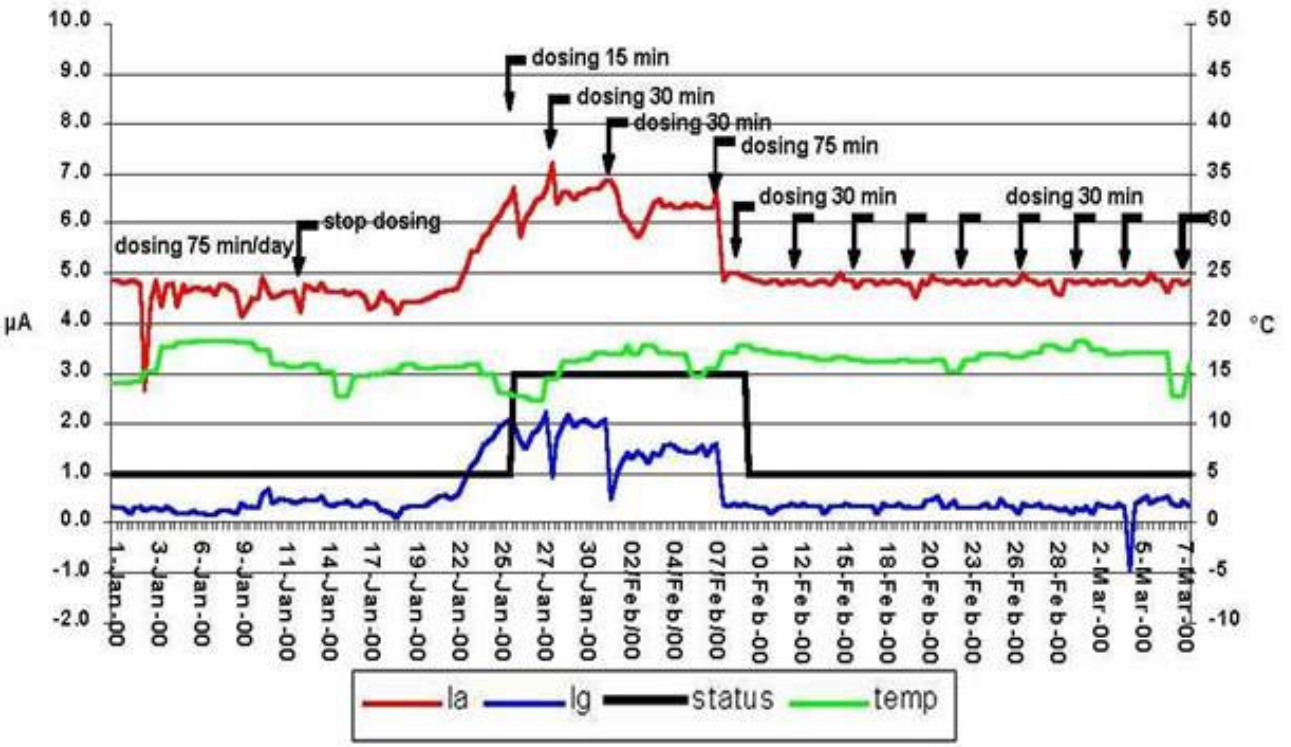
Spat is prevented to settle by P-C, thereby keeping the CWS free from fouling

Monitoring macrofouling: KEMA Biofouling Monitor

- Determining start dosing period
- Monitoring effectiveness chlorination

Monitoring microfouling

- On-line monitoring of microbial (biofilm) activity
- Optimisation water treatment

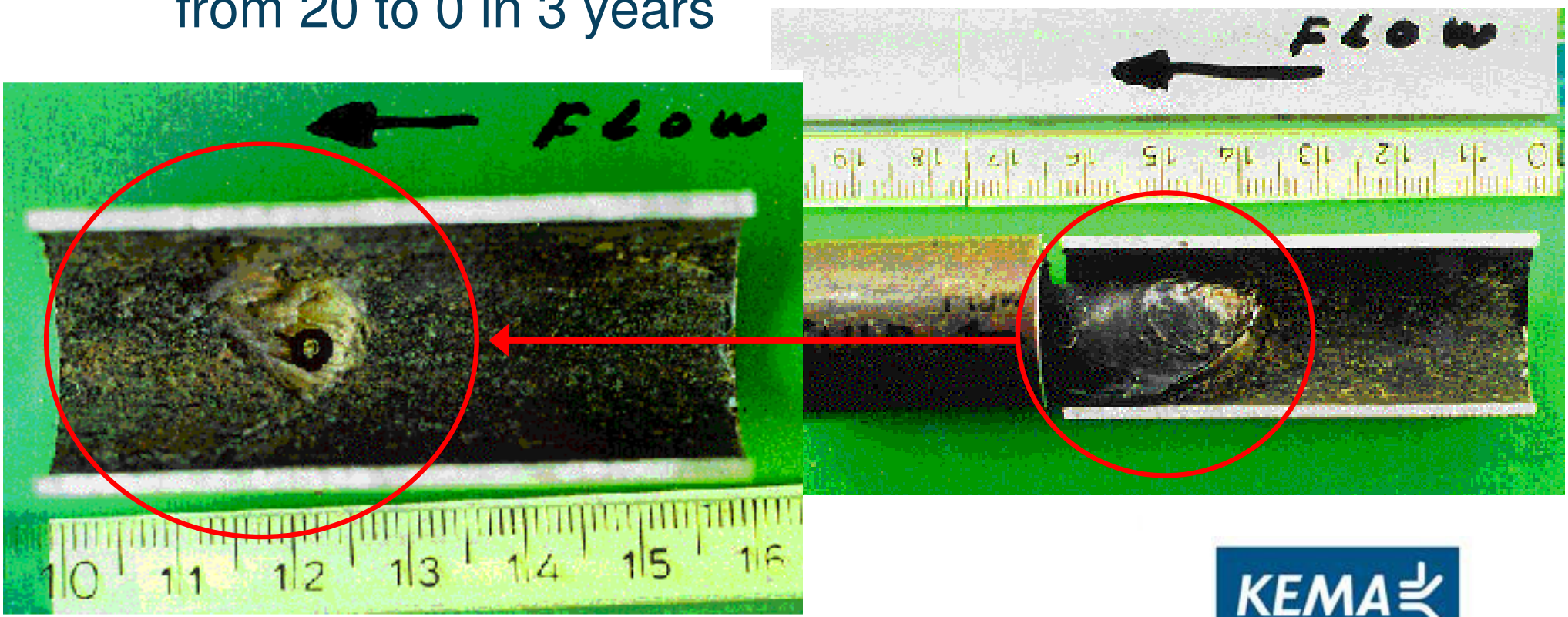


Reference projects

EU	E-ON PP Maasvlakte, Rotterdam (saving 150 kEur/yr)
	Shell Chemical Netherlands, Moerdijk and Pernis R'dam
	DOW Chemical Benelux, Terneuzen (saving 1,000 kEur/yr)
	Reliant Energy Europe PP, Hemweg
	Essent/EPZ PP, Borssele
	ExxonMobil Rotterdam Europort, Rotterdam
	AVR waste incinerator, Rotterdam (saving 30 kEur/yr)
	GDA waste incinerator, Amsterdam
	Yara Fertilizer Plant (Hydro Agri), Sluiskil
ASIA	Wolsong NPP, South Korea (saving 800 kUSD)
ME	Qatar Liquefied Gas Company Ltd., State of Qatar
AUS	Verve Energy Kwinana PP, Western Australia

DOW Chemicals Benelux (Netherlands)

- Seawater cooled: 13 m^3/s in total
- Saving hypochlorite 25.000 USD
- Additional saving due to reduction tube leakages, from 20 to 0 in 3 years



E.ON Maasvlakte PP (Netherlands)

- 2 x 515 MW, sea water cooled, 18 m^3/s per unit
- Saving hypochlorite 50,000 USD
- Additional saving due to prolonged revision intervals

before Pulse-Chlorination

after Pulse-Chlorination

fouling species mitigated:
barnacles, mussels, oysters, hydroids)

KHNP Wolsong NPP (S. Korea)

- 4 x 700 MW, sea water cooled, 27 m^3/s per unit
- Cost saving 800,000 USD, mainly due to reduced maintenance ECP and optimised operation / cleaning

KHNP

한국수력원자력(주)
KOREA HYDRO & NUCLEAR POWER CO.,LTD

Wolsong Nuclear Power Site

KEMA

Qatar Liquefied Gas Co. (Qatar)

Pulse-Chlorination at Verve Energy

- Heat treatment phased out, P-C very effective, clean system

Kwinana and Cockburn power stations, Western Australia

Experiences in EU, ASIA and ME

- P-C applied in fresh, brackish and marine water
- At all locations
  - bivalves show similar behaviour to P-C
  - final P-C regimes are never the same (site specific)
  - P-C effective against all fouling species (macro/micro)
  - strong cost reductions + clean CWS
- Reductions
  - dosing period and amount dosed chlorine
  - CBP discharges (lower environmental impact)
  - Maintenance ECP and CWS (increase redundancy time ECP + improved ECP and CW operations)
- Accepted by regulators as BAT, i.e. beneficial towards discharge allowance

Qatargas gets technology to cut chlorine discharge

Gulf Times 5/9/07 **Business Reporter**

DOHA: Qatargas has adopted 'pulse-chlorination' technology for the seawater cooling system, enabling it to cut chlorine discharge by more than 50%.

The technology has been in place and running successfully for over a month at the Qatargas 1 liquefied natural gas processing plant in Ras Laffan City, a Qatargas spokesman said.

Qatargas has become the first company in the Indian Ocean region to research and use the environment technology that reduces blockages caused by fouling, he added.

The control of biological fouling in the cooling system, by the addition of chlorine, was critical to allow a smooth and trouble-free operation of any industrial plants using seawater for cooling, the spokesman said.

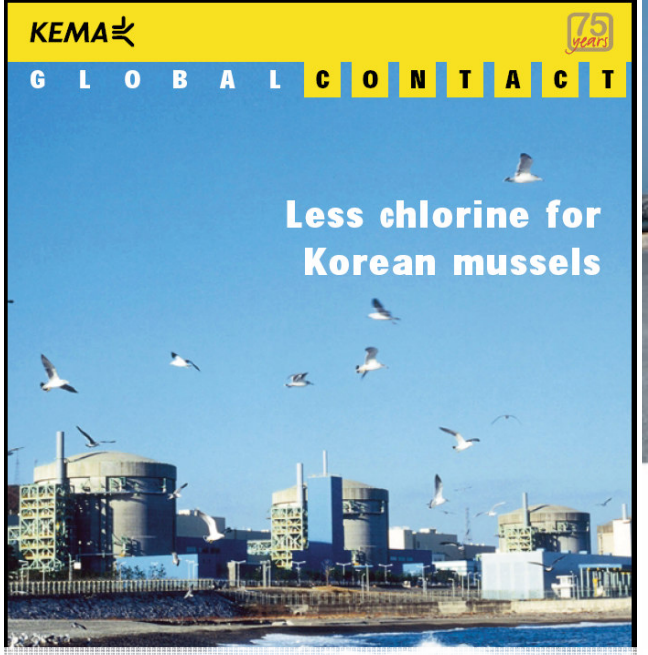
"The environmental and operational benefits gained from pulse-chlorination lead to injecting less chlorine into the cooling seawater system," he added.

By using pulse-chlorination, the chlorine producing equipment operates more efficiently, thus reducing the amount of waste to be disposed, in addition to operational and emissions related performance improvements, he said. "The state environmental regulator has been incrementally reducing the maximum chlorine concentration permitted in discharged cooling seawater from 0.2 to 0.05 milligrams per litre," he said.

A Qatargas official checking the chlorine level.

KEMA 75 years

GLOBAL CONTACT



Less chlorine for Korean mussels

Thank you

How do you reduce chlorine use in cooling seawater systems by three quarters without any adverse operational consequences? That was the question facing liquefied natural gas (LNG) producer Qatargas, located in the hydrocarbon rich Arabian Gulf. The state environmental regulator has been incrementally reducing the maximum chlorine concentration permitted in discharged cooling seawater from 0.2 to 0.05 milligrams per litre. Meeting these stricter regulations sounds like a tall order, but by switching to Pulse-Chlorination Qatargas is predicting compliance with the new regulations on a mass balance basis. Qatargas will be first company in the Indian Ocean region to use this pace-setting technology.

50 percent a year. Less chlorine means reduced environmental impact – and reduced costs too, because it significantly reduces the costs of chlorine production and related equipment maintenance.'

In the summer of 2005, Pulse-Chlorination was tested at the Qatargas plant. Initial findings suggested that the government's new regulation was

KEMA DOW

Ecological Conditioning and Optimisation of a Once-Through Cooling Water System

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Presented at the Watersymposium 1999, Breda (Netherlands)

ABSTRACT

For the coming decade, Dow Benelux will need antifouling treatment for its cooling water system. Hypochlorite dosing is still considered to be the best available technology (BAT). This is based on proven effectiveness, large experience, moderate costs, opportunities to further optimise the chlorination procedure, and by the fact that in earlier studies low-level chlorination has not proven to have major ecological impact.

In an optimisation study for anti-fouling treatment with elevated hypochlorite regimes at Dow Benelux environmental impact and effectiveness were evaluated. The study was carried out from 1995 to 1996. The environmental impact was evaluated by measuring and comparing the amount of chlorination by-products (CBP's) and the potential toxicity formed. The effectiveness was evaluated by looking at: the incidence of blockage's of heat exchangers tubes caused by mussels, the amount of biological growth (macrofouling attachment) in KEMA Biofouling Monitors®, and the behaviour of cyclams (valve movements) placed in MusselMonitors®. Improvements in conditioning regimes were developed, employed and verified.

Results show that it is possible to counteract macro- and microfouling successful, both in the inlet conduits and in water boxes of heat exchangers. The measured CBP's in the outlet increased by 30 to 90% during application of the elevated chlorination level (outlet concentration 0,2 mg/l, instead of 0,1 mg/l, as Cl2) however, no significant increase in potential toxicity was found at the outlet. The incoming water quality (i.e. chlorine demand) plays an important role in the overall needed amount of hypochlorite. The final plant operation result was a drastic reduction in condenser tube leakages caused by erosion by mussel shells at the hydrocarbon cracker units. Further reduction in the use of hypochlorite is foreseen by the application of Pulse-Chlorination®.

KEMA

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

Harry J. G. Polman
Henk A. Jenner

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 hy-

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

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