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

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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 1998. 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 leakage's of heat exchangers tubes caused by mussels, the amount of biological growth (macrofouling attachment) in KEMA Biofouling Monitors®, and the behaviour of oysters (valve movements) placed in MosselMonitors®. 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 Cl_2) 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®.

Key words: Cooling water, Fouling, Mussels, Antifouling substances, Optimisation, Pulse-Chlorination, Chlorination byproducts (CBPs), Environmental impact, IPPC, Best Available Technique

1 INTRODUCTION

At Terneuzen, Dow Benelux operates a large once-through cooling water system. It comprises 200, mostly copper/nickel 90/10 heat exchangers, connected by 4 km of main conduits. Cooling water is obtained from the Western-Scheldt and during summer months, the flow is 11 m^3/s. A once through cooling system can suffer from abrupt process leakages. Main sources of all troubles are managed nowadays by applying a sophisticated ‘care-system’. This ‘care-system’ consist of several different components all implemented at the existing cooling water system, resulting in a sharp decrease in leakage incidents of copper nickel and coated carbon steel heat exchangers. However, Dow Benelux states that further optimisation of their cooling water system is possible by integration of process technology and biology.

Biological macro- and microfouling (oysters, mussels, microbial slime) thrives on the system surfaces causing leakage, blockage, energy loss (heat flux), and corrosion (see photo’s annex). Biological growth in the cooling water system is therefore a constant threat to the operation efficiency. Additionally, it imposes a significant environmental risk: in 1994, 37 spills at a total of 1.100 kg hydrocarbons, caused by heat exchangers tube leakage’s were recorded, of which 70% were caused by mussel shells.

Biological growth in the system is controlled by using sodium hypochlorite dosed in the cooling water intake, and especially through “target” chlorination near the heat exchangers. Dow Benelux has been consented to use hypochlorite at the intake with a matching outfall concentration of 0,1 mg/L as Cl_2, measured as Free Oxidant (FO). Hypochlorite reacts immediately with all kinds of compounds, forming a largely, undefined mixture of halogenated organic chemicals, so-called chlorination by-products (CBP’s). Dosing hypochlorite in cooling water is therefore considered to be of serious environmental concern.

Beginning 1995, Dow Benelux had evidence to suggest that the number of leakages in heat exchanger tubes could be significantly reduced by an elevated hypochlorite-dosing scheme. It was proposed to increase the concentration FO at the outfall from 0,1 to 0,2 mg/L as Cl_2. The hypothesis was that increase of the hypochlorite concentration will provide better control mussel growth in those zones of the cooling water system with low water flows. A temporary consent was given by Rijkswaterstaat (the Directorate-General for Public Works and Water Management) to carry out an experiment to verify this hypothesis. This was done under the condition that Dow Benelux would evaluate the environmental impact, as well as the impact on the number of spills from heat exchangers in the once-through system. The other aim was to find ways for further decreasing the yearly amount of hypochlorite after the planned experimental period.

At the same time Dow Benelux contracted KEMA to evaluate the effectiveness of increased hypochlorite dosing, and to measure the biological and chemical consequences of that new chlorination regime.

For this study, three hypochlorite-dosing regimes were compared:

- Regime A: a dosing at the intake matching a “free oxidant” level (FO) at the outfall of 0,1 mg/L as Cl_2
- Regime B: an elevated dosing at the intake matching a FO level in the outfall of 0,2 mg/l as Cl_2
- Regime C: a short period of alternating high-level chlorination at both hydrocarbon crackers (LHC’s) of 4/3 chlorine dosage per water unit.

In the early nineties, a platform concerning water issues was created by the Dutch industry for collaborative research and information dissemination. In the mid nineties, a concerted action was undertaken between this industrial “Water-platform” and water authorities i.e. RIZA (Institute for Inland Water Management and Waste Water Treatment) for a Best Available Technique (BAT) study on biofouling control and cooling water systems, carried out by KEMA (Bloemkolk, 1995; KEMA/RIZA, 1996).

2 RESULTS OF THE STUDY

2.1 1995 (KEMA report 64259)

In the project carried out in 1995 two hypochlorite dosing regimes were compared in both field and laboratory: one with a dosage producing a “free oxidant” level (FO) at the outfall of 0,1 mg/L as Cl_2 (regime A), and one with an elevated dosage producing a FO level in the outfall of 0,2 mg/l as Cl_2 (regime B).

Eight field sampling visits were conducted from April 1995 to November 1995. In addition, six chlorination simulation experiments on intake water from Dow Benelux were carried out in the KEMA laboratory. The observations from the field study showed good agreement with the results of the studies carried out in the laboratory. Doubling the FO concentration at the outfall (from 0,1 to 0,2 mg /L as Cl_2) was reached by increasing the hypochlorite dose with 20%. Bromoform is the most important CBP in quantitative terms. The average bromoform concentrations in the outfall water amounted to 84 µg/L (regime A: hypochlorite dosage of 2,1 mg/L as Cl_2). The average bromoform values found at a European coastal power station amounts to 23 µg/L bromoform, during a hypochlorite dosage of 0,8 mg/L as Cl_2. At Dow Benelux the potential toxicity of the intake water is significantly higher compared to the values found at European coastal power stations (Jenner et al., 1997). The increase of potential toxicity (pT) caused by hypochlorite dosing at Dow Benelux amounts to a factor 2,1 to 2,4, compared to a factor 5,2 for European coastal power stations. Switching from regime A to B, the concentrations of CBP’s (like bromoform and dibromoacetonitril) showed an increase of 30% to 60%, and a non-significant increase of the potential toxicity was found (see annex 1.3).

In 1995 at Dow Benelux, no significant effect of elevated hypochlorite dosing on the number of heat exchanger tube leakage’s caused by mussels could be demonstrated. To get a better evaluation, a whole season of elevated hypochlorite dosing was required. It was demonstrated that the elevated hypochlorite dosing at Dow Benelux applied in 1995 removes macrofouling almost completely from the KEMA Biofouling Monitors® located at LHC1 and LHC2. This had not been observed previous years. Hypochlorite dosing causes a significant reduction ($p<0,05$) in average valve opening of oysters at both LHC1, and at the outfall (surge tower). Increasing the hypochlorite dosing level from A to B leads to a significant reduction ($p<0,10$) of average valve opening of oysters at LHC1 (see annex 1.4). At the outfall no significant effect of the elevated hypochlorite dosing could be detected.

Besides the direct erosion-corrosion effect caused by shells in heat exchanger tubes several other failure categories can be pointed for damaging tubes. In table 1 the most important failure categories are presented. Independent of type of failure, nearly all of them in an once-through system will cause an unwanted environmental effect in the outlet area. It is evident that managing the failure categories with the highest impact have high priority in the 'responsible care program'.

Table 1. Failure categories sea water heat exchangers last decade.

Failure categories		**Solution**
erosion corrosion (= shells)	**43 %**	this presentation
vibration	19 %	replacement
coating damaged	15 %	selection/renewal
inlet erosion-corrosion	11 %	"brush-inserts"
pipe – pipe-plate joints/welding	1 %	
coating end of life time	1 %	
corrosion	< 1 %	
under deposit corrosion	< 1 %	
other damage categories	9 %	

2.2 1996 (KEMA report 64683)

In 1996 the sampling program of 1995 was repeated. Further research was carried out into the variation of the potential toxicity of the Western-Scheldt water, the cause of the observed high hypochlorite demand of the Western-Scheldt water, and into CBP formation and "free oxidant" decrease after mixing of the chlorinated outfall water with receiving Western-Scheldt water.

Doubling the FO concentration at the outfall (from 0,1 to 0,2 mg /L as Cl_2) was reached by increasing the hypochlorite dose with 40%. The amount of hypochlorite needed to reach the required FO levels at the outfall, was about 15 - 20% lower in 1996 compared to 1995. This difference can be related to lower water temperatures in 1996. The remaining FO at the outfall does not seem to cause any additional CBP formation (bromoform) when the outfall water is mixed with the receiving Western-Scheldt water. On the contrary, there is some evidence to suggest that mixing with Western-Scheldt water actually reduces the total amount of CBP's formed.

The average bromoform levels in the outfall water were 41µg/L and 67µg/L for respectively regime A and B. This is about 50% lower than those measured in the 1995 project. This reduction between the two years was also present for the other CBP's. These differences are largely explained by the lower hypochlorite dosages used in 1996. The relative increase in

CBP production going from level A to B amounted to 60% to 90%. This is about two times higher than the increase measured in 1995. For both 1995 and 1996 this relative increase in CBP production lies between the increase in hypochlorite dosing (20% - 40%) and the increase in FO concentration at the outfall (100%).

There is no evidence to suggest that the effects of hypochlorite dosing on the potential toxicity tend to be obscured by a high diurnal variability of potential toxicity of the intake (Western-Scheldt) water (as proposed in the 1995 project). The increase in potential toxicity (see annex 1.3) caused by hypochlorite dosing at Dow Benelux amounts to a factor 2,9 (regime A). This compares well the results from the 1995 project. The potential toxicity of the outfall water did not significantly increase going from regime A to B. In 1995 also no significant difference between A and B could be detected.

Results showed evidence to suggest that the elevated hypochlorite dosing - regime B - reduced the number of heat exchanger leakages caused by mussels by 50%. This regime B also removed macrofouling almost completely from the KEMA Biofouling Monitors® located at the LHC's in 1995 (start of regime B) and 1996. This had not been observed in previous years.

The additional plant chlorination (regime C) that was applied at LHC2 from April 1996 and onwards seems to effectively prevent all tube leakage caused by mussel shells. The KEMA Biofouling Monitor® located at LHC2 was also completely cleaned from any macrofouling.

At the end of 1996 temperature measurements were carried out in the outfall plume of Dow Benelux in the Western-Scheldt to get an idea of the structure of the plume. It appeared that there was a distinct layer of outfall water with a depth of 1 meter which was candlelight shaped to about 100 meters out of the coast. Beneath the water layer of 1 meter (containing "warm" outfall water) there is a transition layer of 0,5 meter. Under the transition layer the receiving Western-Scheldt water is present. This confirms the idea that there is only a slight mixing in the outfall water plume and the warmer water is floating on the colder Western-Scheldt water.

2.3 1997 (KEMA report 97565058)

In 1997, the additional plant chlorination (regime C) was applied at both LHC1 and LHC2. In 1997 a “worst case” study on the formation of chlorination by-products in time, and a study on the biological activity, and N compounds (N Kjeldahl; NH_4; NO_2+NO_3) versus the chlorine demand of Western-Scheldt water were carried out.

Effectiveness for both cracker units LHC1 and LHC2 show that regime C has proven to prevent all - but two - tube leakage’s caused by mussel shells. The KEMA Biofouling Monitors® at both LHC1 and LHC2 were also completely cleaned from any macrofouling. Table 2 gives an overview of the heat exchanger tube leakage’s caused by mussel shells that were reported during the twelve-month periods May to April 1993 – 1998.

Dow Benelux 1993 – 1998. Heat exchanger tube leakage’s caused by mussel shells in one year periods (May-April) at different chlorination regimes and the amount of hypochlorite on yearly basis for both LHC’s. Up to the mid nineties the goal was to reduce leakages first and at the same time to increase the efficiency the hypochlorite dosing. A new hypochlorite saving program is started with the application of Pulse-Chlorination®, keeping intact, of course the former low leakage incidences (see §3.5 ‘further optimisation’).

Table 2. Overview of the heat exchanger tube leakage’s caused by mussel shells.

Period	**Regime**	**Number of leakage’s caused by mussels**		**Hypochlorite 10^3 L/y**
		LHC1	**LHC2**	
May 1993 to April 1994	A	28	4	1220
May 1994 to April 1995	A	28	12	2100
May 1995 to April 1996	A and B	32	10	2820
May 1996 to April 1997	B	16	1 [a)]	2480
May 1997 to April 1998	C	0	2	1990
May 1998 to Jan. 1999	C	0	0	1500 (9 months)

[a)] regime C at LHC2 started in April 1996, one leakage in May 1996.

Regarding the formation of CBP’s (see annex 1.2) the hypothesis - formation of CBP’s or potential toxicity (see annex 1.3) continues in the outfall water after discharge in a non-mixing situation - could not be confirmed neither rejected. More than the two experiments carried out in this research are needed to investigate this “worst case” plume situation.

No correlation was found regarding the biological activity, and N-compounds versus the chlorine demand of Western-Scheldt water. This was investigated by measuring the Adenosine Tri-Phosphate (ATP) levels in the intake water and correlate them with the amount of hypochlorite dosed. Therefore, the hypothesis that biological activity and N-compounds in the Western-Scheldt water play a dominant role in the chlorine demand could not be verified.

An anticipated investigation into the effects of the hypochlorite dosing regime C at Dow on the valve movements of oysters was cancelled as a result of a unexpected early shut down of LHC1 in October 1997.

3 GENERAL CONCLUSIONS

3.1 Biofouling control

- Macrofouling in the cooling water system of Dow Benelux was suppressed for more then 99% in the new elevated hypochlorite dosing regime (B). An alternating regime (B+C) is the most effective one and has at the same time the lowest environmental impact.

- The elevated hypochlorite dosing regime (B and C) resulted in a drastic reduction (to almost zero) in condenser tube leakage's caused by erosion by mussel shells at the hydrocarbon cracker units.

3.2 Chlorination by-products and toxic effects

- To establish an increase FO levels of 0,1 to 0,2 mg/L as Cl_2 at the outfall (from regime A to B), the initial amount of hypochlorite to be dosed at the intake was to be increased with 20% to 40%, depending on the chlorine demand. Concentrations of CBP's and Extractable Organic Halogens (EOX) show an increase of 30% to 90% going from regime A to B. The potential toxicity of the outfall water does not significantly increase changing from regime A to B.

- The observations from the field study at Dow Benelux show good agreement with the results of simulation studies carried out at KEMA laboratories in 1995.

- Bromoform is the most important CBP in quantitative terms. The average bromoform concentrations in the outfall water amounted to 84 µg/L (regime A: hypochlorite dosage of 2,1 mg/L as Cl_2). The average bromoform values found at a European coastal power station amounts to 23 µg/L bromoform, during a hypochlorite dosage of 0,8 mg/L as Cl_2.

- The increase of potential toxicity caused by hypochlorite dosing at Dow Benelux amounts to a factor 2,1 to 2,4 compared to a factor 5,2 for a European coastal power station. This is due to the relative high initial potential toxicity of the intake water compared to the values found at European coastal power stations.

- Hypochlorite dosing causes a significant reduction ($p<0,05$) in average valve opening of oysters at both LHC1 and outfall. Increasing the hypochlorite level from A to B results in a significant reduction ($p<0,10$) of average valve opening of oysters at the LHC1. At the outfall no significant effect of the elevated hypochlorite dosing could be detected.

3.3 Temperature

- The structure of the outfall plume at Dow Benelux appeared to be a distinct layer of outfall water with a depth of 1 meter which was candle-light shaped to about 100 meters out of the coast. This means that only a small amount of the outfall cooling water mixes with the receiving Western-Scheldt water.

- An once-through cooling water system is an acceptable option provided thermal pollution and the potential of sudden process leakage's to the receiving biota can be managed to appropriate proportions.

3.4 'Responsible care program' (see annex 2 and 3)

- A once through cooling water system makes an additional 'care-system' necessary. This includes standardised heat exchanger inspection and repairing, standardised chemical on-line and off-line chemical analyses, as well as automation of the conditioning regime itself.

- Heat exchangers can potentially suffer from a dozen different failure modes. For instance, oil is hardly detectable in the cooling water effluent, so the best solution for oil heat exchangers is titanium heat exchangers.

- The improvements implemented at the Dow Benelux cooling water system contributes to the goals of Dow's 'responsible care program'.

3.5 Further optimisation

Further reduction in the amount of hypochlorite is possible using a new regime called Pulse-Chlorination® (P-C). P-C is based on the principle that mussels have a recovery period of about 10 to 30 minutes after exposure to a chlorination period. P-C takes advantage of this recovery time by using short successive periods of chlorination, alternating with periods without chlorine. Next to the effect of the chlorine, the bivalves are physically stressed as they are forced to open and close continuously. This has a maximal stress effect on the mussels and clams and appears even to have a larger impact than the effect of continuous dosing. To determine exactly the behaviour of the mussel, i.e. the valve movements and recovery period, is accurately monitored with the MosselMonitor®.

In 1998 KEMA has demonstrated the P-C regime for the freshwater mussel *Dreissena polymorpha* (KEMA Rhine laboratory), the marine mussel *Mytilus edulis* (EZH power station Maasvlakte, Rotterdam) and the brackish water mussel *Mytilopsis leucophaeata* (UNA power station Hemweg, Amsterdam). Results of the experiments at both stations and laboratory show a saving in chlorine amounts of no less than 50%, although a conservative chlorination regime was applied for both power stations. So even larger savings are possible in the future. Summarised it may be stated that Pulse-Chlorination® can be a major step forward in saving costs and subsequently environmental impact.

REFERENCES

Bloemkolk J.W. (1995) RIZA report 95.050 Industriële koelwaterlozingen; koelsystemen en emissies. ISBN: 9036945445; 102 pp.

Jenner H.A., C.J.L. Taylor, M. van Donk and M. Khalanski (1997) Chlorination by-products in chlorinated cooling water of some European coastal power stations. Mar Environ Res 43:279-293.

KEMA-report 64259-KES/WBR 96-3114 (research project 1995) Effectiveness and environmental impact of elevated hypochlorite dosing at Dow Terneuzen; 94 pp.

KEMA report 64683-KES/WBR 97-3121 (research project 1996) Effectiveness and environmental impact of elevated hypochlorite dosing at Dow Terneuzen 1996; 93 pp.

KEMA report 97565058-KPG/CET 99-4403 (research project 1997) Effectiveness and environmental impact of elevated hypochlorite dosing at DOW Terneuzen in 1997; 49 pp.

KEMA/RIZA report 64387-KES/WBR 96-3113 (1996) Optimisation of biofouling control in industrial cooling water systems with respect to the environment; 98 pp.

ANNEXES

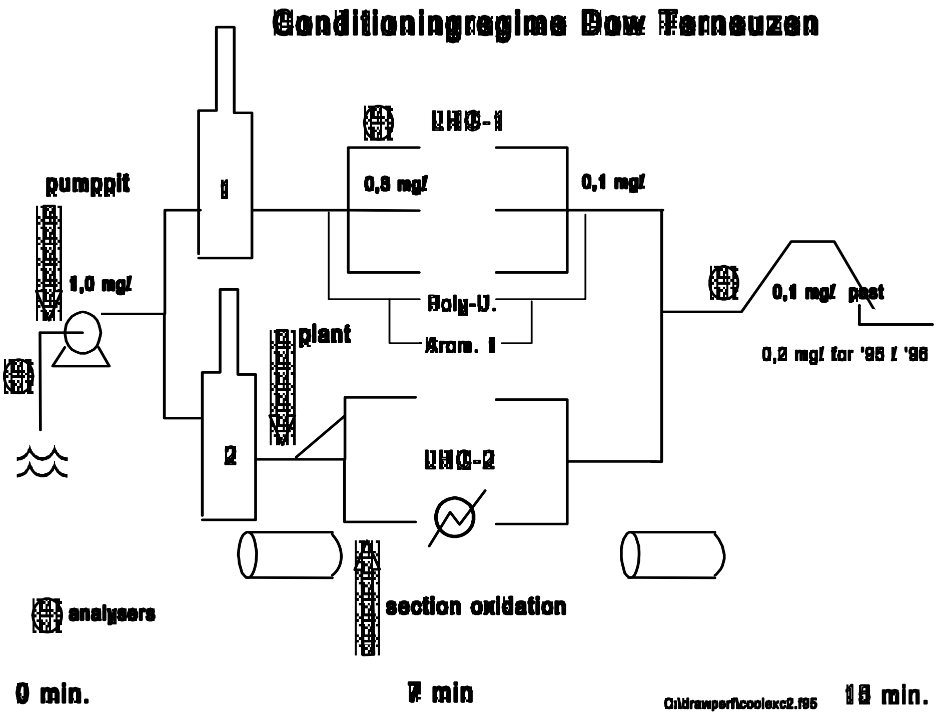
1 METHODOLOGY

1.1 Hypochlorite dosing

The adjustment of the amount of hypochlorite dosed at the intake was carried out by Dow Benelux. During each sampling visit water samples were collected at a hypochlorite dosing regime defined by the amount of FO at the outfall measured with a colorimetric method using DPD (ISO 7393/2). The FO level was to be 0,1 mg Cl_2 L-1 (regime A) and 0,2 mg Cl_2 L-1 (regime B). The third hypochlorite dosing regime was defined as a short period of high level chlorination at the LHC's (regime C). For regime C 2/3 of the amount of hypochlorite used for regime B is dosed just before one of the LHC's, normally in ½ the amount of cooling water which is taken in at the intake.

1.1.1 Outline of the hypochlorite dosing at Dow Benelux

The once-through cooling water system at Dow Benelux delivers water from the Western-Scheldt to several plants. Before the water enters the pump pit it passes band filters (mesh size 6 mm) which primarily serve to protect the pumps.



From the pump pit the cooling water is discharged to one main header which feeds two surge towers on shore. One conduit extends from surge tower 1 to the Light Hydro Carbon plant 1 (LHC1). Near LHC1, three main conduits deliver the cooling water to the heat exchangers, and two smaller conduits are connected to the coolers located at Aromatic-I (Arom1), and Poly-Urethanes (Poly-U). From surge tower 2, two main conduits are connected to LHC2. Within LHC1 and LHC2 most heat exchangers receive primary cooling water. Their effluent is reused by other heat exchangers which are located in a secondary circuit. Each LHC has its own effluent piping (a few hundred meters) back to Western-Scheldt. Near the dike, all cooling water is combined in one common conduit before it is discharged.

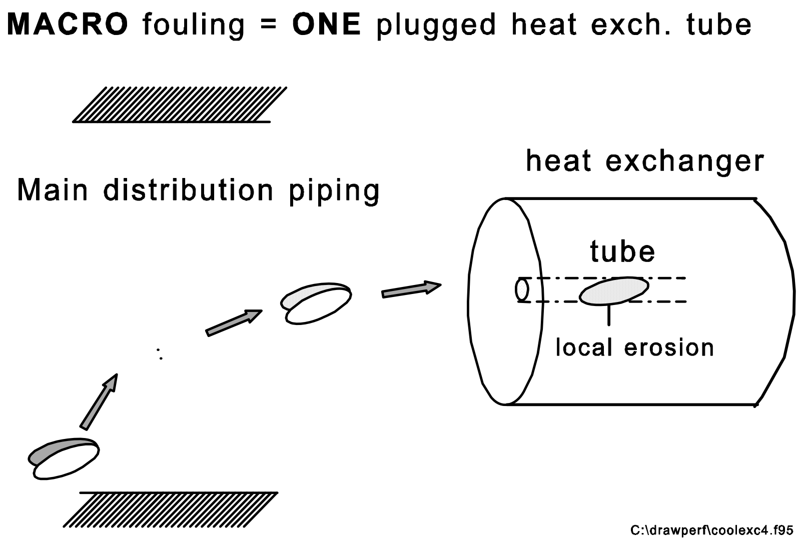
The heat exchangers can suffer from both macro- and microfouling. Macrofouling (shells of bivalves, e.g. mussels) which detaches from the main distribution conduits will plug the heat exchanger tubes. Due to the high number of heat exchanger tubes, the potential settlement area for mussels and oysters is enormous. During the fouling season, every heat exchanger tube can receive a few hundred mussels that have grown in the main system.

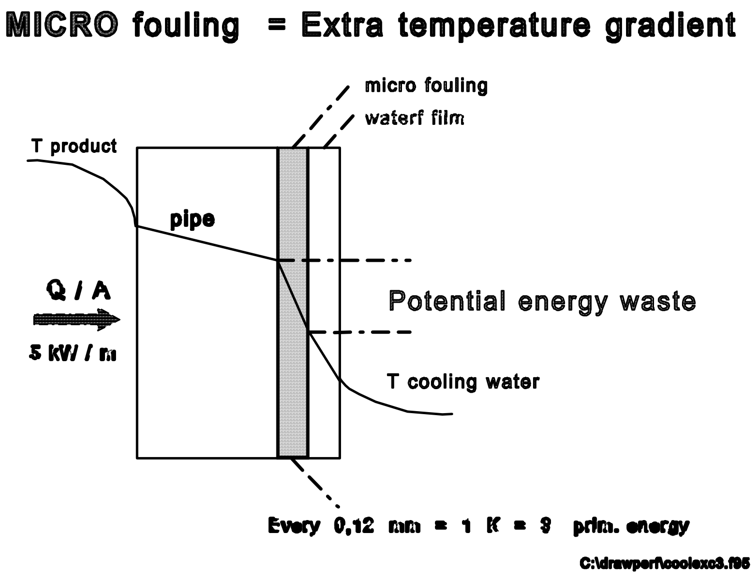
The conditioning regime with hypochlorite aims to prevent the settlement and growth of bivalves in the distribution conduits by maintaining low oxidant concentrations during longer periods. Injections can be continuously directly into the pump pit, as well as alternating directly after the surge towers. The latter will create an excess of oxidants which can penetrate into stagnant zones in the main conduit system before the heat exchangers. A dosage in the main distribution headers directly after the surge towers is called “plant chlorination”.

Micro-organisms attached to the heat exchanger tubes create a matrix of organic material in which suspended material is collected. This reduces the heat transfer capacity, which in turn increases the energy consumption of the plant. Microfouling is controlled by short term alternating dosage of sodium hypochlorite into several sections near the heat exchangers. This results in temporarily high concentrations at these specific locations. These high concentrations disappear after dilution with cooling water from other sections in the effluent pipes. A dosage near a group of heat exchangers is called a “section chlorination”.

The average residence time of the water in the cooling water system is about 15 minutes. However, the residence time of the cooling water varies per route. The LHC2 is located closer to the pump pit, and to the combined cooling water outlet, compared to LHC1. This results in a different average residence time amounting to 2 minutes between both plants. In addition, within each LHC some exchangers are located more close to the influent and effluent ducts of the plant then others.

This can results in average residence time differences up to 4 minutes within the same plant. The applied conditioning regime takes these time differences into account. It takes full advantage of the "neutralisation" reactions that take place in the cooling water system when chlorinated cooling water from one LHC is mixed with non-chlorinated cooling water from the other LHC.





The oxidant demand of the Western-Scheldt water is generally far above 1 mg/L. The cooling water is heated up in two steps which increases the local biological summer period within the system. Besides the difference in residence time of cooling water within the same system, the water velocities varies also greatly. The water velocity is 3,5 4 m/s in the conduits from the pump pit to the surge towers on shore; no fouling is encountered in this area. Behind the surge towers the water velocities are decreased by half which favours greatly the settlement and growth of mussel- and oysterspat. Many stagnant zones (like manholes, pipe elbows and T branches, heat exchanger inlet and outlet heads), are also encountered in this part of the cooling water system, making over-stoichiometric dosage necessary.

1.2 Chemical analyses

Seawater contains approximately 65mg/l bromide, and the applied dose of sodium hypochlorite oxidises the bromide to bromine, leading to the formation of organo bromine compounds. Halogenated by-products such as these can have undesirable ecotoxicological properties, as while the toxicity of the applied oxidant is known to decline rapidly with dilution due to compounding seawater demand the same cannot necessarily be said of the more chemically stable by-products.

The CBPs can be subdivided into four classes, as:

1. Free halogens. The hydrolysis of chlorine dissolved in water produces hypochlorous acid (HOCl) dissociated in hypochlorite ion (OCl) depending on the pH: at pH 7 and 20 oC, the equilibrium is approximately 75% HClO and 25% ClO-. Hypochlorous acid and OCl- constitute "free chlorine". In seawater, free chlorine react with bromide ion and release "free bromine" composed of hypobromous acid and hypobromite ion.
2. Haloamines. In presence of ammonia or organic amines, free halogens give chloroamines (NH2CL, NHCl2) and bromamines (NH2Br, NHBr2).
   Free halogens and haloamines are oxidizing compounds. Free halogens react with organic matters present in water to form organohalogenated compounds (OX) which have no or hardly any oxidizing properties. Organic substrates and amines compete for halogens; OX production yield depends on ammonia concentration. OX constitutes the last two classes.
3. Trihalomethanes (THM's) are the most volatile organic compounds generated by chlorination of natural waters, in chlorinated seawaters they are mainly composed of Bromoform (CHBr3) and bromochloromethanes.
4. Among the remainder of OX three catagories are frequently detected in chlorinated natural waters: halogenated phenols, halo-acetonitriles and haloacetic acids.

Analyses of CBP's measured at the Dow Benelux investigation

HALOFORMS

standard method	NEN 6401 and draft NEN 6407
sample volume	50 mL
extraction	purge and trap
analysis	GC with ECD/FID
compounds	chloroform
	bromoform
	dibromochloromethane (DBCM)
	bromodichloromethane (BDCM)
detection limit	0,1 µg/L

HALOACETIC ACIDS

standard method	-
sample volume	50 mL
extraction	ethyl acetate after acidification of the sample
analysis	derivation with dicyclohexylcarbodimide (DCC) and 2,4-difluoroanaline (DFA), followed by GC with ECD
compounds	monochloroacetic acid MCAA
	dichloroacetic acid DCAA
	trichloroacetic acid TCAA
	monobromoacetic acid MBAA
	dibromoacetic acid DBAA
detection limit	1 to 5 µg/L

DIBROMOACETONITRILE

standard method	-
sample volume	50 mL
extraction	n-hexane
analysis	GC with ECD
detection limit	0,1 µg/L

HALOPHENOLS

standard method	-	
sample volume	100 mL	
extraction	SPE after derivation with acid anhydride	
analysis	GC with ECD	detection limit
compounds	2,4-dichlorophenol 2,4-DCP	0,4 µg/L
	2,4,6-trichlorophenol 2,4,6-TCP	0,06 µg/L
	2,4-dibromophenol 2,4-DBP	0,02 µg/L
	2,6dibromophenol 2,6-DBP	0,1 µg/L
	2,4,6-tribromophenol 2,4,6-TBP	0,05 µg/L
	pentachlorophenol PCP	0,05 µg/L

EXTRACTABLE ORGANIC HALOGENS (EOX)

standard method	NEN 6402
sample volume	1000 mL
extraction	PE under respectively acidic and alkaline conditions
analysis	concentration to small volume and analysis with micro coulometry
detection limit	0,1 µg/L

1.3 Potential toxicity measurement

A technical problem in toxicity testing is that concentrations of toxic compounds in the environment often are too low to produce acute effects. Since the effective concentration levels are inversely related exposure time, this problem can be solved by increasing the concentration. Several methods are available to concentrate toxic substances from water samples. There is, however, no procedure which results in a concentrate that has a chemical composition comprehensively representative of the original material. Despite its high selectivity, adsorption of organic pollutants on organic polymers - e.g. on XAD® resins - and subsequent desorption with an organic solvent, offers the most advantages. The adsorption on XAD® resins shows a relatively high specificity for organic compounds with a mainly apolar or weak polar lipophilic nature. These are compounds capable of passing biological membranes. The technique is compatible with chemical analytical procedures (GC/MS) and is characterised by simplicity, speed and reproducibility.

Microtox® is used to test the toxicity of aqueous XAD-concentrates (Microtox model 500, Microbics corporation, Carlsbad, Ca, USA) conform NVN 6516 (NNI, 1993). The Microtox® test is a rapid acute toxicity test based on the measurement of the inhibition of bioluminescence of the marine bacterium Vibrio fischeri (or: Photobacterium phosphoreum). The result is expressed as a T value which indicates the number of times a sample needs to be concentrated to produce 20% effect in the Microtox® test (a higher T value means a higher potential toxicity). The system measures disruption in the Krebs cycle. The test gives a good estimate of the so-called total aspecific "minimum toxicity", and correlates well with the results of acute toxicity tests with higher organisms (e.g. fish-species). The tests are evaluated after 5 and 15 minutes exposure time resulting in a T5 minutes and a T15 minutes. The T value (or ECF20) is expressed as the concentration factor causing 20% reduction of bacterial luminescence as compared to a control.

1.4 MosselMonitor®

The MosselMonitor® is at present one of the most validated “biological early warning systems” (BEWS) for marine waters. It combines a high sensitivity for chemical pollution, with low maintenance demands. The MosselMonitor® (commercially available by Delta Consult bv, Kapelle) is a biological early warning system (BEWS), that uses the behaviour valve movement response of fresh water , brackish water or marine bivalves (e.g. mussels or oysters). Bivalves in "clean" water show a characteristic valve movement pattern in which they are open most of the time, that is showing filtering activity. A bivalve exposed to contaminated water will show a different behaviour, in most cases resulting in more closing. By using a microprocessor to continuously register the valve movement pattern of eight bivalves, a sensitive, fast reacting, BEWS is obtained. The valve movement patterns that are on-line recorded can be represented as graphs and alarm thresholds can be set.

At Dow Benelux, two MosselMonitors® have been installed and are in use since several years. They are used for two different applications:

- intake-outfall comparison: comparison of the biological quality of intake to outfall water is a helpful tool for detection of on-site born contamination. An increased response of the Mosselmonitor® at the outfall can be caused by hypochlorite dosing, process fluids leakage’s, and temperature differences. It should be noted that when hypochlorite is dosed other contaminations cannot easily be detected.
- Optimisation of hypochlorite dosing by using the Mosselmonitor® at the LHC and outfall. Hypochlorite dosing will provoke a reduction of valve opening time. Hypochlorite dosing can be optimised by determing the dose that will produce sufficient reduction of valve opening. Secondly, the Mosselmonitor® can be used for determination of the time interval that bivalves need to return to their normal behaviour after a hypochlorite dosing. This is useful for choosing the optimal time interval between dosages.

2 RESPONSIBLE CARE PROGRAM

To tackle the spill problem a so-called ‘care system’ was introduced. The following items were investigated:

- thorough review of the cooling water sampling systems (location, representativity, analyses (calibration, detection limit et cetera), fouling sensibility, data storage and presentation). The oil monitor for instance could not get a representative sample which made it necessary to redesign the few oil coolers
- cooling water flow in KEMA Biofouling Monitors® which is essential during the summer months for reliable data on settlement and growth of fouling organisms
- The continuous free oxidant analyser at the outfall near the discharge point has to be flushed during a minute with sweet water including the whole sampling system in reverse flow every 4 hours to measure the cooling water effluent to meet at the same time the goal that no acute toxic water was send back to the Western-Scheldt river

To minimise the time for leakage detection Dow Benelux defined procedures what and how to be done for their technical and analytical operators. For instance the inspection of heat exchangers had to be done in a consisted and representative method. The criteria for a failure mode were defined, as well as its implementation during inspection and preferably independent of human factors. In fact every heat exchanger became its own “finger-print” identification to be used for its maintenance.

The ‘care program’ has become essential to once through cooling water systems for the following items:

⇒ on-line & off-line sampling analyses
⇒ mitigation leakages & quantification of spills
⇒ inspection, i.e. eddy-current
⇒ categorising different installation damages
⇒ applied conditioning
⇒ operator discipline
⇒ maintenance procedures
⇒ testing local filtration systems in front of heat exchangers
⇒ cost efficiency.

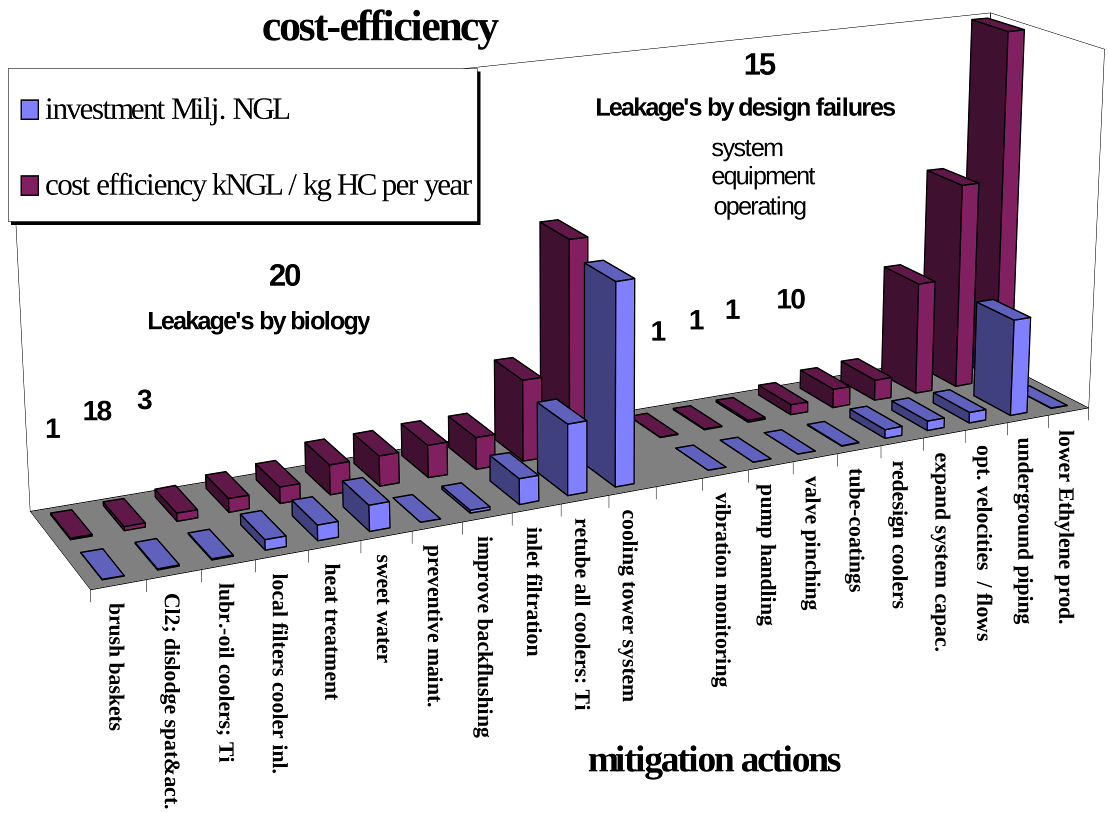
3 FAILURE INCIDENTS, MITIGATION ACTIONS, LEAKAGE VOLUME DETERMINATION AND COST-EFFICIENCY

Every failure mode has its historical known contribution towards hydrocarbon leakage's. Through the years many alternatives were developed to reduce the number of heat exchanger failures. The capital costs as well as the operating cost including capital depreciation have been estimated for each alternative. Any individual improvement action can however not contribute simultaneously towards the managing of all failure modes. In general in the mid nineties 35 incidents happened yearly of which 20 of them were due to the biology of the system; the other 15 failures were due to the other remaining dozen failure modes.

The outcome of this cost efficiency study was that the placement of "brush-baskets" in combination with a efficient conditioning regime was the most effective approach to reduce the hydrocarbon leakage's concerning the fouling of the system. The replacement of a few oil coolers became necessary, since the sampling system could not guarantee a reliable outcome as far as fine oil-droplets in a large water volume are concerned. If these three actions are totally implemented, it is expected that the biological fouling failure rate will drop with 95 %, and by that two third of all incidents.

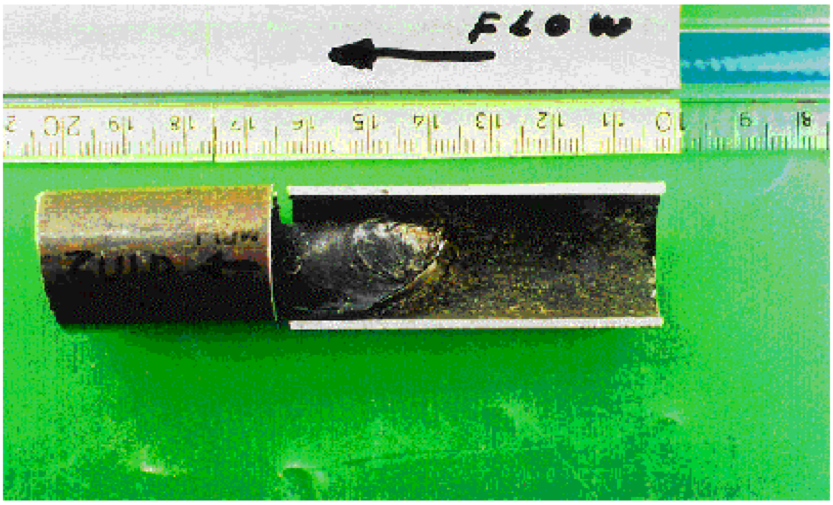
The other alternatives to improve the anti-fouling of the existing once-through cooling water system like local filters for each heat exchanger, increase of inlet water temperature during winter, alternating mixing with fresh water source, huge influent filtration or replacement of all heat exchangers by titanium and or replacement of the system itself in existing plants by a cooling tower are many times less cost effective expressed in amount of hydrocarbon leakage reduction per $.

The other remaining 15 yearly incidents, are due to the other failure modes. Operating care have the highest cost efficiency like vibration monitoring of some specific heat exchangers, pump handling improvements and to be alert on flow pinching by valves of heat exchangers during the cold season. Although their cost effectiveness is high, these direct operating actions could only reduce the number of incidents by two a year. On the second rank came a new coating for specific heat exchangers. The major contribution of failure control will come in redesigning a few specific gas coolers, although their cost efficiency is remarkably lower compared to the first two. But this action is necessary to achieve a total of 90 % failure reduction for the remaining root causes (see histogram below).



Histogram presenting the two main sources of leakage's (biology and design) and the mitigation actions. See text above for explanation.

Of each heat exchanger its unity of seawater flow is known, since all heat exchangers operate in a standard manner within the whole system. When the continuous hydrocarbon analyser at the collective effluent site detects a leakage, a search is started to find the heat exchanger in question. The time needed to locate this exchanger, including the shutdown time, is used to calculate the leakage volume.



› 2:Clamping musselshells were observed inside the tube. Hole is localised under the musselshells.

Condenser tube with jammed mussel. The hole in the tube wall is seen on the right side of the mussel which was shifted to the left for better observation.

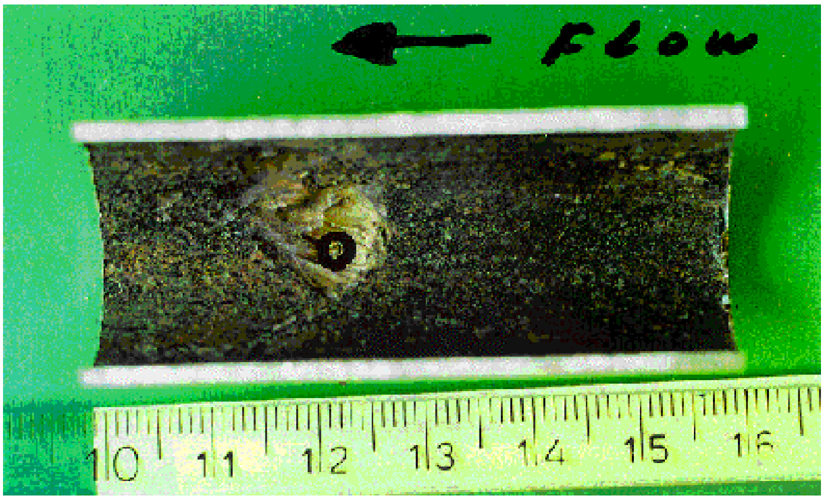


Photo 5: The hole is located in the drawned circle

In August 1995 plastic brush baskets were installed on the inlet of the cleaned tubes to prevent the entrance of mussel shells. Plastic brush baskets were not installed on the outlets of the tubes. In January 1996 a leakage occurred in this tube due to trapped mussel shells during back flushing.

HUIDIGE STATUS (2007) VAN PULSE-CHLORINATION®

Wereldwijd is chloreren de meest toegepaste methode ter bestrijding van micro- en macrofouling in koelwatersystemen. Soorten die bestreden moeten worden zijn zee-, brak- en zoetwater-mosselen, oesters, hydroïden en zeepokken. Vooral mosselen veroorzaken grote problemen.

KEMA heeft in 1998 een nieuwe manier van chloordosering ontwikkeld, Pulse-Chlorination®, waarbij een optimale aangroeibestrijding wordt bereikt met een minimale hoeveelheid chloor. In 1999 is de methodiek, na enkele jaren succesvolle tests, geïmplementeerd bij Dow Benelux (Terneuzen). In 2000 werd Pulse-Chlorination tijdens een Integrated Pollution Prevention and Control (IPPC) bijeenkomst in Sevilla, uitgeroepen tot BAT (Best Available Technology) met de case bij Dow als voorbeeld.

De projecten van 1998 tot en met 2006 hebben geleid tot besparingen op het chloorverbruik tot 50% ten opzichte van continu chlorering. Het is ook gebleken dat Pulse-Chlorination een sterk verbeterde methode is om macrofouling te bestrijden. Het resultaat is een beter functionerend koelwatersysteem waar minder onderhoud voor nodig is. Dit leidt tot langere perioden tussen geplande revisies, waardoor de kosten voor centrales kunnen worden teruggebracht tot € 50,000 per dag gespreid over 3 jaar in plaats van 2 jaar. Voor industriële installaties geldt een reductie van € 25,000 per te openen warmtewisselaar. Ongewenste uitvallen kunnen worden teruggebracht tot de geplande, ongeveer 8-jaarlijkse revisies. Bijvoorbeeld, bij Dow Benelux traden de decennia daarvoor ongeveer tientallen condensorpijp lekkages per jaar op verspreid over gemiddeld 20 koelers per jaar. Na implementatie van Pulse-Chlorination bleek het mogelijk om, tot op de dag van vandaag, een continue bedrijfsvoering te handhaven zonder ongewenste uitval van warmtewisselaars. Daarbij is er een duidelijke reductie in chloorverbruik, waardoor minder chloreringsbijproducten (CBP's) worden geloosd en de impact op het milieu lager is. Tot het succes droeg ook de aangepaste preventieve onderhoudsprogramma's bij.

Implementatie van de Pulse-Chlorination methode geeft een duidelijke verbetering in de optimalisatie van de aangroei bestrijdingsstrategie, kostenreductie en reductie van de bijbehorende impact op het milieu. De belangrijkste voordelen zijn:

- Structurele duurzame betrouwbaarheidsverbetering van het koelwatersysteem als zodanig en daarmee van de gehele fabriek.
- Blijvende energiebesparing dankzij schone goed dorstromende koelers.
- kostenreductie door vermindert chloorverbruik
- beperking van de milieu-impact van hypochloriet
- vermindering van de negatieve effecten van chloor op de installatie
- significante kostenreductie voor onderhoud van het koelwatersysteem en van de Electro Chlorination Plants (ECP)

Inmiddels wordt Pulse-Chlorination succesvol toegepast bij elektriciteitscentrales, afvalverbrandingsinstallaties, (petro)chemische industrieën en LNG productie installaties op 4 continenten (Europa, Australië, Midden-Oosten en Azië).

Ecological conditioning and optimisation of a once-through cooling water system. In Proceedings of Watersymposium 1999, p.327 – 355 (Breda (NL), 1999).

CURRENT STATUS (2009) OF PULSE-CHLORINATION®

World wide, chlorination is still the most commonly applied method to mitigate macro- and microfouling in cooling water systems. Species to mitigate are marine, brackish, and freshwater mussels, oysters, hydroids and barnacles. Especially mussels cause severe problems.

In 1998 KEMA developed a new regime of chlorine dosing called Pulse-Chlorination®, combining optimal antifouling results with the lowest amount of Na-hypochlorite. In 1999, the method was implemented at Dow Benelux (Terneuzen, the Netherlands) after many years of successful tests. In 2000, Pulse-Chlorination was declared BAT (Best Available Technology) during the Integrated Pollution Prevention and Control (IPPC) meeting in Sevilla (Spain), with the case at Dow as example.

The projects performed between 1998 and 2006 resulted in a saving of chlorine use up to 50% on a yearly basis, compared to the regimes applied in earlier years. It was also evident that Pulse-Chlorination proved to be a highly improved method to control macrofouling. The result is a better overall performance of the cooling water system and therefore less maintenance is necessary. This in turn allows longer intervals between planned overhauls, bringing Down the costs for power plants of approximately € 50,000 per day spread out over three years rather than two years. For industrial installations, it means savings of € 25,000 for each heat exchanger that needs to be opened. Unwanted outages can be reduced to the planned, approximate 8-yearly overhauls. For example, Dow Benelux suffered during decades before about a dozen condenser tube leakages per year spread over an average of 20 exchangers per year. After implementation of Pulse-Chlorination, the company was able to maintain to date, a trouble free operation (zero leakages) without unwanted outages. Also, as a result of the decreased chlorine usage, fewer chlorination by-products (CBP's) are emitted in the outfall, reducing the impact on the environment. The changed preventive maintenance program also contributed to the success.

Implementation of the Pulse-Chlorination method is a step forward in optimisation of the fouling mitigation strategy, saving costs and subsequent environmental impact. Substantial benefits are:

- structural improved cooling water system reliability, so also for the whole plant.
- sustainable energy conservation due to clean "goed"doorstomende" heat exchangers.
- reduction of operational costs by using less chlorine
- reduction of the impact of chlorine on the environment
- reduction of the negative effects of chlorine in the process installation
- significant cost savings for maintenance of the cooling water system components and Electro Chlorination Plants (ECP).

To date, Pulse-Chlorination has been implemented successfully at power plants, waste incinerators, (petro)chemical industries and LNG production installations at 4 continents (Europe, Middle East, Asia and Australia).

FURTHER READING

Jenner H.A., C.J.L. Taylor, M. van Donk & M. Khalanski, 1997. Chlorination By-Products in Chlorinated Cooling Water of some European Coastal Power Stations. Marine Environmental Research, Vol. 43, No. 4, pp. 279-293, 1997.

EC, 2001. Integrated Pollution Prevention and Control (IPPC) Reference Document on the application of Best Available Techniques to Industrial Cooling Systems. December 2001.

Polman H.J.G. & Jenner H.A., 2002. Pulse-Chlorination®, the Best Available Technique in Macrofouling Mitigation Using Chlorine. PowerPlant Chemistry 2002, 4(2), 93-97.

Jenner H.A., H.J.G. Polman & R. van Wijck, 2003. Four years experience with a new chlorine dosing regime against macrofouling. Presented at VGB meeting 22/23 October 2003 at Essen, Germany.

Taylor C.J.L., 2006. The effects of biological fouling control at coastal and estuarine power stations. Marine Pollution Bulletin 53 (2006) 30–48.

Polman H.J.G., I.A. Macdonald, M.C.M. Bruijs, H.A. Jenner, 2006. Reducing chlorine discharged to sea: optimising cooling seawater antifouling strategy through pulse-chlorination and the associated benefits to an operating facility from adopting an environmentally friendly / BAT technology. EnviroArabia 2007. *In prep*.