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RESULTS AND BENEFITS OF THE ADOPTION OF PULSE-CHLORINATION® FOR INDUSTRIAL COOLING SEAWATER ANTIFOULING AT QATARGAS, RAS LAFFAN INDUSTRIAL CITY, QATAR

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Introduction

To maintain a reliable and efficient operation of seawater cooling systems, a biocide must be added to prevent settlement and growth of marine fouling species, both macro- and microfouling. Worldwide, the typical industry practice in coastal areas includes continuous chlorination of the seawater with periodic shock dosing. However, this practice is not based on ecotoxicological data of targeted species, but is generally based on a post-hoc observation of antifouling efficiency or performed as an attempt to meet the discharge limits of residual biocide concentrations. Shock dosing is applied in the erroneous notion that it prevents fouling species from adapting to continuous chlorination. Such typical dosing procedures are practiced not only in the Persian Gulf, but also at numerous locations elsewhere in the world. Therefore, opportunities exist for science-based decisions to optimize site-specific biocide dosing regimes, that enable cost-efficient and reliable fouling control while complying to stringent regulatory discharge limits.

Qatargas Operating Company Limited (Qatargas) was established in 1984 and pioneered the Liquefied Natural Gas (LNG) industry in Qatar, with Qatargas 1 (which now includes Trains 1-3) commencing operations in 1996. Today, Qatargas is the largest LNG producing company in the world, with a total LNG production capacity of 42 million tonnes per year (MTA).

The Qatargas plant is located within Ras Laffan Industrial City (RLIC) and the LNG is exported from Ras Laffan Port (RLP), which is a purpose built facility[1].
As part of the liquefaction process, seawater is applied as a cooling medium for a variety of heat exchangers (freshwater plate/tube and shell). Currently, the three production trains associated with Qatargas 1 (including sulphur recovery units and utilities of power generation

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[1]The RLP also exports other gas derived hydrocarbon products and sulphur)

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and desalination) utilize approximately 113,000 m^3/hr for the cooling demands required by the plant to produce approximately 10 million tonnes per annum of LNG. The total length of its seawater distribution network is approximately 6 km. Sodium hypochlorite (commonly termed 'chlorine') is the only biocide added to the seawater to prevent fouling and is produced on-site by Qatargas by means of an Electro Chlorination Plant (ECP).

During inspections previous to the implementation of Pulse-Chlorination fouling was observed. Figure 1 shows a strainer containing recently dead oysters, their shells all brownish coloured which is their natural colour. The left photograph shows significant amounts of adult shells at the base of the removed strainer and the close up picture at the right side demonstrates the ability of juvenile oysters to create an increased pressure differential by completely blocking a strainer mesh.

Figure 1 Fouling by oyster shells at a strainer in the year 2007 before P-C was implemented, in front of a heat exchanger at Qatargas

The environmental effects from residual biocide (Chlorination By Products, CBP) after the addition of chlorine is typically local, but since chlorine dosing is widespread throughout the region at most of the numerous cooling seawater users, the total discharge of 'residual chlorine' is considered by regulators on a wide scale. The issue of chlorination of seawater cooling water systems has attracted significant attention from environmentally concerned stakeholders, including regulators. The resultant environmental effect of the chlorination of cooling seawater can vary considerably as it is dependent on operational practices at

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individual facilities. One of the environmental issues is the formation of Chlorination By-Products (CBPs) and the discharge of associated residual oxidants.

Environmental regulatory background

The Qatar Ministry of the Environment (MoE) had required a free residual chlorine limit in cooling seawater discharges of 0.1 mg/L, that was lowered to 0.05 mg/L in the Executive By-Laws of 2005 of the Environment Law 2002. The MoE was concerned about the environmental effect from cooling seawater chlorination on the local marine environment. In addition, the formation of CBPs through the excessive use of sodium hypochlorite has been cited as a cause for concern. The residual biocidal effects of 0.05 mg/L is known to be tolerable to many fouling species and therefore plant operations run the risk of decreased effectiveness of their seawater cooling water management systems' availability for cooling purposes. In addition, the in-field practical quantification limits of equipment utilized for analyzing residual oxidants have been recommended to only consider readings at or above 0.1 mg/L. Furthermore, the actual environmental impact to the marine environment of an efficiently operated cooling seawater system antifouling strategy has been reviewed in the literature as minimal.

Residual biocide concentration regulations should be based on science and include the consultation and engagement of industries relating to engineering - and science - based processes involved in the management of once through seawater cooling water systems. Since 2007, Qatargas' antifouling strategy has operated at the highest level of operational and environmental performance by application of Pulse-Chlorination® (P - C). P - C combines optimal fouling control with minimal chlorine discharge, while retaining safe plant operations. P-C is the EU Best Available Technology (BAT) for industrial cooling seawater system fouling protection by chlorination (BREF, 2001[2]). It has successfully been implemented through on-site field tests worldwide such as Europe, Middle East, Asia and Australia in industries ranging from oil and gas, nuclear to other conventional power industries.

Material and methods

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[2] BREF (2001) Reference Document on the Application of Best Available Techniques to Industrial Cooling Systems. European Commission Integrated Pollution Prevention and Control (IPPC) Bureau, Seville, Spain. Available at http://eippcb.jrc.es/

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To investigate the technical possibilities of using P-C for antifouling optimisation, Qatargas retained the services of DNV KEMA to perform a study to determine the optimal dosing regime according to the P-C methodology. The complete study consisted of 3 phases / reports to achieve a best practice cooling seawater chlorination regime at Qatargas.

This process is summarised as follows:

- Phase 1: description of current and historic fouling scenario, review of current seawater system practices, a literature review of local fouling species and an assessment of whether P-C is practically possible and beneficial to the Qatargas operating conditions.
- Phase 2: on-site research of fouling organism sodium hypochlorite tolerance by ecotoxicological testing with a valve movement monitor within a mobile laboratory, including a short-term (few hours) full scale P-C plant based test.

Based on the tests, measurements and inspections performed on-site during Phases 1 and 2, the optimum hypochlorite injection requirements and monitoring instructions were established. During this time between Phases 2 and 3 Qatargas ran a medium term (10 days) trial to ensure equipment suitability to the required modifications to run P-C.

- Phase 3: covered the final assessment of P-C after implementation on a long-term operational basis (10-12 months) over the period July 2007 to July 2008. During this period Qatargas evaluated whether P-C could provide a permanent optimization of the cooling seawater systems antifouling strategy and also generated a range of further improvements to the management of the system.

Brief description of Pulse-Chlorination® and its benefits

Following exposure to chlorine, bivalves (e.g., mussels, oysters and clams), normally require time to recover before they can open again fully and restart filtration. P-C is based on this biological observation that bivalves show a distinct recovery period after exposure to chlorinated seawater for a certain time period. Only after this recovery period, they open their valves fully before restarting filtering water for oxygen and nutrients. P-C enhances a cyclic mode of hypochlorite dosing (on / off dosing regime), based on the behavioural response of the specific bivalve to chlorine dosing, thereby taking advantage of this recovery period to delay the restart of P-C. By applying P-C, bivalves are forced to switch their metabolic mode continuously between aerobic (when open) and anaerobic (when closed). In this situation the target organisms rapidly use their own energy reserves (*i.e.*, glycogen and muscles). In adult specimens this leads to physiological exhaustion and subsequently death. Thus, the effect of

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P-C upon the target organisms is based on the repetitive too short recovery period after exposure to short successive periods of chlorination.

P-C results in a more rapid effect, *i.e.* mortality of the pearl oyster (Pinctada radiate) which is the target organism at Qatargas, compared to the conventional continuous chlorination method. For better understanding of P-C, an example of the valve movement behaviour which shows the reaction pattern of bivalves in general during P-C is given in Figure 2. Typical behaviour of a bivalve in seawater would be represented by valves being fully open >99% of the time.

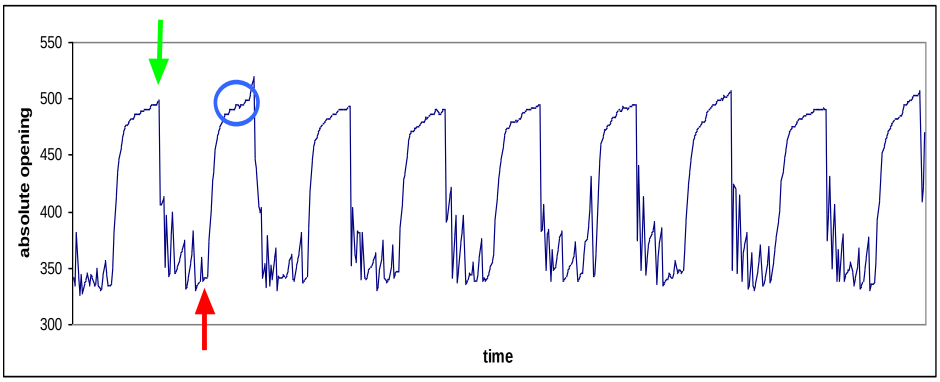

Figure 2. Movement behaviour (opening and closing of the valves) of fouling bivalves detected by a valve movement monitor during a P-C regime. Top arrow (green) indicates the start ('on'), the bottom arrow (red) the timing of stop ('off') of chlorination. The circle indicates the recovery period during which the bivalve slowly opens. Normal behaviour would reflect a continuously open valve position allowing respiration and feeding to occur.

The required effective initial dosage of hypochlorite concentration depends on:

1. the target organism's behaviour, and
2. the seawater quality parameters at the intake.

Qatargas' most significant parameter is temperature as this fluctuates significantly (typically between 17°C - 35°C) and a mere 5°C increase in temperature effectively doubles the chlorine decay rate. The chlorine concentration expressed as Total Residual Oxidant (TRO) has to be measured directly in front of the last point of required protection (*i.e.*, heat exchangers). The initial hypochlorite dosing concentration at the intake to achieve the desired TRO concentration in front of the heat exchangers is largely influenced by the chlorine demand of the intake seawater.

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It is evident from previous studies that P-C leads to an improved method for the control of macro- fouling in once through seawater cooling systems. This is concluded after years of undisturbed operation of power and (petro)chemical plants in the Netherlands and elsewhere, *e.g.*, South Korea and Australia. The application of P-C has proved to provide both economical and environmental advantages. In the case of ECP installations, for the production of sodium hypochlorite, their production requirements are lowered, which allows less and quicker maintenance requirements and significantly reduced power consumption. The environmental benefit is obvious, less chlorine in the discharge cooling seawater and subsequently less production of the unwanted CBPs.

Chlorination chemistry in seawater

In chlorination chemistry a distinction is normally made between free (active/available) chlorine and combined chlorine. Free Oxidant (FO) is present as an equilibrium mixture $HOCl \rightarrow OCl^- + H^+$ (hypochlorous acid and hypochlorite). Combined chlorine is available in chloramines or other compounds having oxidising properties. Total Residual Oxidant (TRO) is defined as the total oxidising capacity (free and combined) which is available after chlorination. Chlorine demand is defined as the difference between the amount of chlorine added and the FO concentration remaining at the end of a specified contact period.

When chlorine is added to sea water, naturally containing 68 mg/L bromide at full salinity, bromide is oxidized and the hypochlorite is displaced by hypobromous acid (HOBr). This reaction is rapid, with 99% conversion within 10 seconds at full salinity and within 15 seconds even at half salinity. Within the Persian Gulf, where salinities are above the normal 35 ‰, typically varying in-between 39 – 42 ‰ depending upon season in well mixed deep locations, this would further increase the conversion rate. However, since hypochlorite is produced and stored on-site (in a 10 m^3 tank at approximately 500 – 2000 mg/L) prior to dosage there is the opportunity for chlorine dominated chemistry to produce various by-products.

Hypo-chlorite and -bromite immediately react with suspended and dissolved organic matter within seawater, especially the N-containing compounds. This process is called “chlorine (bromine) demand”. Reactions between N-containing compounds and chlorine produce halogenated amines are referred to as “bound oxidants”. During chlorination in sea- or brackish water, these oxidants provide an extra toxic effect on bivalves by the reaction product bromamines. Bromamines are, in contrast with chloramines, acutely toxic for bivavles. Brominated amines are, more or less, as toxic as hypobromous acid. The production of these chlorinated by-products accounts for using the term TRO in seawater.

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In summary, the effective part of the hypochlorite dosing in seawater is the total toxicity of free (bromine) oxidants (FO) and bound (bromine) oxidants (the latter defined as total residual oxidants or TRO). For this reason the chlorine concentration is generally defined by the amount of FO when used in freshwater and TRO when used for either seawater or brackish water.

Results Phase 3

The results of the on-line residual chlorine measurements during P-C® implementation at Qatargas, showing the mean concentrations per month during July 2007 – July 2008, are presented in Figure 3. These readings do not represent discharge to sea concentrations, but within plant concentrations and are subjected to aeration and UV degradation prior to discharge to the sea. Data before P-C (2002 – 2007) are presented to show the achieved decrease in concentrations and show that a significant reduction of 36% has been achieved. For some of December and all of January and February concentrations were uncharacteristically high. This was due to a separate operational requirement at the seawater intake structure.

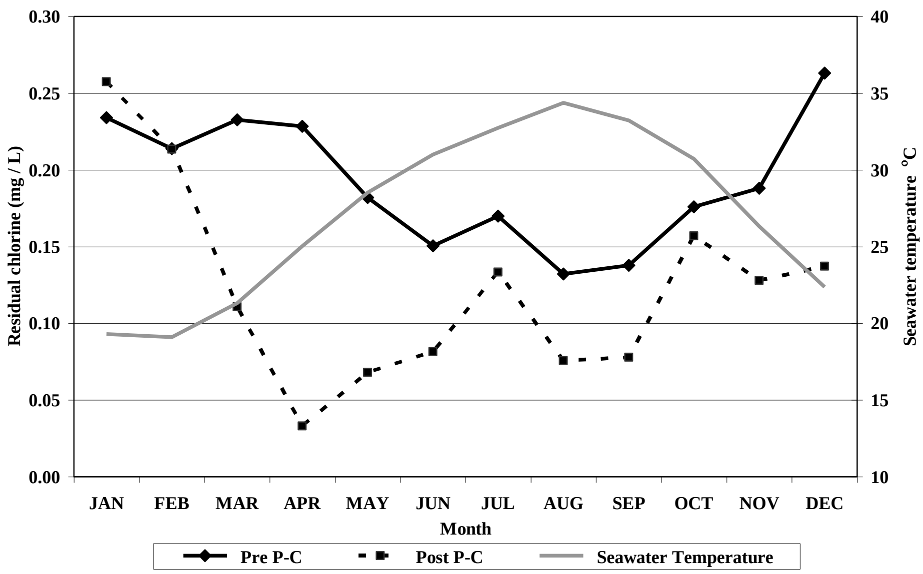

Figure 3. Monthly average data from on-line analysis of residual chlorine in the cooling seawater prior to release through back pressure weir into open channel leading to the sea. Data represents Pre P-C (2002-2007) versus post P-C (July 4th 2007 to 2008). Seawater temperature taken from seawater intake within RLP displayed.

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During an inspection in April 2008 the results on cleanliness of the condensers and strainers were extremely good showing only dead shell fragments from the time before P-C was applied. Figure 4 shows on the left a Condenser endplate (which is nearly clean). A few tubes showed to be clogged by anorganic material and shell remnants. Also a few rope like sealing pieces were found in the tubes. On the right a tube endplate is shown. Figure 5 shows the condition of two different strainers during the inspections in April 2008.

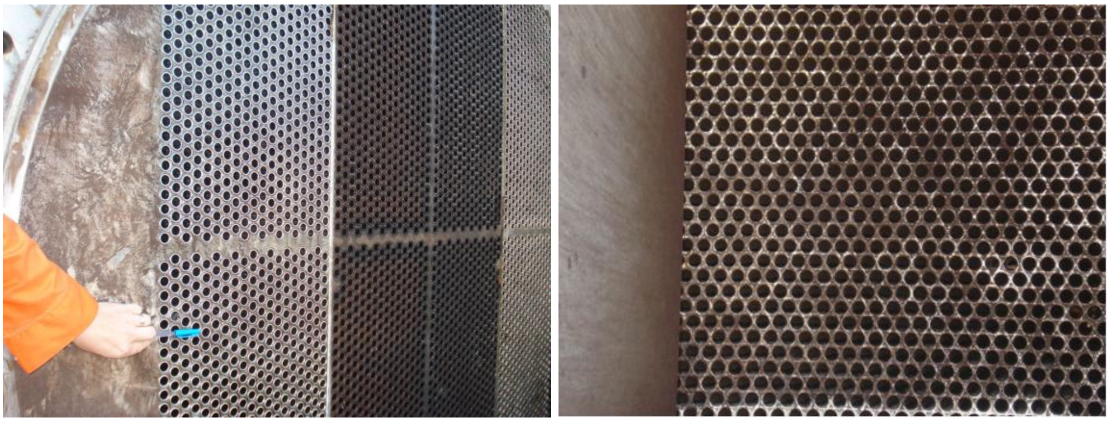

Figure 4 Condenser (left) and Tube (right) endplate after implementation of P-C.

Figure 5 Two strainers after implementation of P-C.

From 2008 onwards P-C did not result in any seawater cooling water system fouling issues of concern at Qatargas.

The implementation of Pulse-Chlorination at Qatargas has been successful with significant improvements observed in both fouling mitigation and significant reductions in the discharge of TRO with no associated problems in production.

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With the implementation of P-C the objectives set for achieving “chlorine” discharges of as low as reasonably practical have been met. However, further reduction in hypochlorite dosing is perhaps possible taking into account well defined breeding periods for the fouling organisms. Qatargas will continue to manage and maintain the P-C system and will review the possibility of refinement as and when needed.

Recognition of Pulse-Chlorination

Besides the acknowledgment as BAT-technology in Europe, Pulse-Chlorination is also seen as a valuable environmentally accepted method to control macrofouling in seawater cooling systems throughout the Middle-East region.

As a result of the successful implementation of the KEMA technology Pulse-Chlorination at Qatargas, the Qatar Ministry of Environment has concurred with Qatargas to acknowledge the KEMA technology as a method to control biological fouling in it’s sea water cooling system and satisfying regulatory concerns over the use of hypochlorite in once through seawater cooling water systems. This acknowledgement supports Pulse-Chlorination as an accepted dosing method to meet the strict chlorine discharge regulations in Qatar. The implementation at Qatargas was also recognized in respect to the environmental benefits and it was awarded with the ‘Excellence in Environmental Technology’ category at the RESCO Offshore Arabia 2009 Conference.

In the UAE a study was carried out in order of the Regulation and Supervision Bureau (RSB) to evaluate the best available options for fouling control in intake systems of power plants and desalination plants in the UAE. As an outcome of this study it was also concluded that Pulse-Chlorination proved to be the Best Available Technology in terms of both cost-benefits and environmental acceptance.

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