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Towards a Holistic Approach to the Sustainable Use of Seawater for Process Cooling

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Abstract

Industrial cooling using seawater is a critical technology that results in one of the most profound environmental impacts on water quality and public health in Qatar and throughout the Arabian Gulf. The usage of chemical biocides to control growth of unwanted organisms leads to the discharge of enormous quantities of toxic and carcinogenic pollutants. These have a direct impact on aquatic life in the region which leads to subsequent impacts on the food chain. Additionally, there is a serious risk to human health, because the discharges are made to the same body of water used as a source of drinking water. This paper will report on progress in the development and application of a holistic approach to developing optimal strategies for addressing the environmental, technical, and economic issues of seawater cooling systems. Sponsored by the Qatar National Research Fund under the National Research Program scheme, the research initiative aims to provide the world with the implementation tools needed to address this problem.
Keywords: Process cooling, environmental impact, energy management.

1. Introduction

The use of seawater in industrial cooling is a common practice in many parts of the world that have limited fresh-water resources. In Qatar, huge volumes of seawater are used for cooling every day and discharged back to the Arabian Gulf. Biocide (chlorine) is added to the seawater to control biofouling of the cooling system. The added chlorine reacts with bromide and other compounds in the water to produce a wide range of chemical oxidants. Some of these oxidants remain in the cooling water after it is discharged and they pose a major environmental burden. Regrettably, reactions between the residual oxidants and natural organic matter in the water lead to formation of toxic halogenated organic compounds that have detrimental effects on the environment when they are discharged into the Gulf. There is also a potential risk that the toxic and carcinogenic chemicals present in the seawater discharge reach the intakes of desalination systems used to produce drinking water.

New regulations have recently been established in Qatar which specify that the concentration of residual chlorine in the discharged cooling water should not exceed 0.05 mg/L. Industries in Qatar find it difficult to meet these new residual chlorine standards. Therefore, both the regulators and industries in Qatar are looking for ways to minimize environmental pollution while achieving high performance of the cooling system with reasonable cost.

This research will apply a holistic approach to the problem that leads to a better scientific understanding of the effects of polluted seawater discharge as well to development of technologies for the design of cost-efficient cooling water systems with low environmental impact.

2. Background

2.1. Biocides and Chemical Pollution

One of the primary operational problems of using seawater in cooling is biofouling. Biofouling can result from growth of microorganisms on surfaces where they form biofilms or from the growth of macro-organism such as clams. Biofilms tend to stick to heat-exchange surfaces, thereby significantly reducing heat-transfer coefficients (Goodman, 1987). In some cases, excessive bio-fouling can lead to plugging of heat exchangers. There are several techniques for preventing biofouling of both types, but application of chlorine-based biocide is most common. Others include application of ozone, ultraviolet radiation, surfactants, mechanical cleaning with rotating brushes or sponge balls (Langford, 1977), light intensity (Yang et al., 2000), or controlling pH (Yukselen et al., 2003) or the temperature of the cooling water.

Application of biocides (primarily chlorine) is the most widely-used approach to control biofouling. This is attributed to its industrial reliability, large-scale applicability, effectiveness in disinfecting various forms of micro-organisms in seawater, and cost effectiveness. However, optimal operation of these systems is complicated by a web of reactions that occurs after chlorine is added. These include conversion of bromide ion to hypobromous acid and other reactive forms of bromine. These brominated products are the active forms of biocide in seawater systems and their relative concentrations change on time scales from fractions of seconds to days. Understanding their behavior is critical to insuring effective control of biofouling within the plant and minimizing environmental impacts outside the plant. Additionally, the brominated residual biocide also can react with natural organic matter in the seawater to form a number of highly toxic halogenated organic compounds.

Of particular note is the fact that brominated forms of biocide are much more effective in producing halogenated organics than chlorine, but have not been studied as extensively. Understanding the reaction scheme of chlorine, brominated products and natural organic matter is critical to optimizing performance of biofouling control systems while minimizing impacts to the aquatic environment and to human health. Studies by Shams et al. (1991) on Umm Al Nar seawater desalination plant in Abu Dhabi showed that bromoform represented 95% of the trihalomethanes (THM) that were formed. Ali and Riley (1986) reported that THM concentrations as high as 90 µg/L were observed in the vicinity of discharges from combined power/desalination plants in Kuwait. Many other reports are available on the production of halogenated organics in freshwater systems such as water treatment plants and water distribution systems. However, limited data are available on biocides chemistry and their reaction by-products in seawater.

2.2. Kinetic Modeling of Biocides

A wide range of reactions occur when biocides such as chlorine are added to seawater. Kinetic models have been developed to integrate all of these reactions (Haag and Lietzke, 1981; Johnson et al, 1982), but they are more than 20 years old so they do not incorporate current knowledge of biocide chemistry.

Batchelor (1989) has developed a kinetic model for formation of halogenated byproducts (HBP) that was applied to fresh waters. This model describes formation of HBP and decay of biocide in terms of a series of reactions for which defined rate equations are provided. The model assumes that the natural organic matter (NOM) contained in water contains some compounds that are precursors to formation of HBP. The precursors are present initially in 'inactive" forms that must react with biocide to become "active". This step is equivalent to forming chlorinated groups on the large molecular weight compounds that comprise NOM. The active precursor material then reacts further to form the HBP. The yields of HBP are different for different products and are affected by the pH of the water. The model was able to describe formation of both chlorinated and brominated HBP. Figure 1 shows a comparison of model predictions with measured concentrations for 10 different HBP species found in water samples from the Ohio River that had been chlorinated. The axes are logarithmic in order to show concentrations that range over two orders of magnitude, but this results in magnifying the apparent errors at lower concentrations. The ability of the model to describe the effect of bromide ion on the distribution of HBP between chlorinated, mixed, and brominated species is shown in Figure 2. The symbols in Figure 2 represent measured concentrations and the lines represent model predictions.

One of the most important areas of recent research has been on the formation of halogenated organics by reaction of biocides and natural organic matter. Interest in these reactions in drinking water has lead to a variety of kinetic models that describe factors affecting their formation (Gopal et al, 2007, Nokes et al, 1999, Rossman et al., 2001, Sohn et al., 2004). However, all but one of the models is an empirical model that predicts concentrations that would be measured in a batch system as affected by variables such as time, pH and TOC. Such models could not be combined with a hydrodynamic model to predict concentrations as the seawater moves from the discharge point because of the effects of dilution on such empirical models. Also, the characteristics of the seawater are different than that of drinking water and thus the kinetic models developed for drinking water might not work for seawater. Furthermore, these models are developed for temperatures that are much lower than typically seen in the Arabian Gulf. Therefore, a true kinetic model that describes the rate of formation of specific halogenated organics as a function of concentrations of reactants is required. Such a model could be used to optimize conditions so that biocide concentrations are maintained at sufficient levels in the cooling water system to control biofouling while minimizing amounts of biocides and halogenated byproducts that are discharged. Furthermore, such a model can be combined with hydrodynamic models to accurately predict concentrations of halogenated compounds as the seawater moves from the discharge points.

2.3. Environmental impact assessment of seawater discharge

Considerable work has been done in the area of discharge modeling for environmental impact assessment. A number of widely accepted commercial tools (e.g. GEMSS (Kalluru, 2003), CORMIX (Jirka et al., 2006)) are available to simulate the transport of pollutants emitted from industrial processes into the sea. In a recent study, the GEMSS system has been applied to simulate the dispersion of pollution from cooling water discharge into the Arabian Gulf at Ras Laffan (Kolluru et al., 2003). However, the accuracy of such studies is questionable as the simulation tools only account for hydrodynamic effects and ignore the effects of biocide reactions in the seawater. Unfortunately, there is currently no hydrodynamic model available that can account for biocide reactions. In the absence of such a tool, accurate environmental impact assessment remains impossible.

2.4. Process Integration of Seawater Cooling

In a pioneering paper, Bin Mahfouz et al. (2006) developed a simple process integration approach as a first attempt to address the pollution problem associated with seawater cooling. The main focus of the approach was on the reduction of cooling duties of the process which results in a lower usage and discharge of seawater. Consequently, the discharge of biocide will be reduced. An added advantage of reducing the cooling duties is that the utility cost is reduced leading to economic savings while preventing pollution. The approach also considered more effective heat transfer arrangement in order to reduce the flow rate of cooling seawater and, therefore, lower the discharge of biocide. The approach identified the importance of optimal biocide dosage policies; however, techniques to identify such policies systematically were not proposed. The paper stressed that, due to their high cost, the use of biocide removal units should be reconciled with the other alternatives such as reduction of cooling duties, reduction of seawater flow rate, and optimization of biocide dosage. It is worth noting that this approach did not include information on biocides chemistry, reactive transport modeling, or process optimization.

2.5. Process optimization

Previous work in the development of reactor network optimization and synthesis tools are of direct relevance for the optimization of the seawater cooling system (e.g. Rigopoulos and Linke, 2002; Linke and Kokossis, 2003; Ashley and Linke, 2004). Such tools are based on superstructure formulations and enable the identification of reaction systems in terms of mixing, feeding, and recycling strategies that maximize performance criteria associated with the reaction system. The concepts behind those tools are directly relevant to the design of the seawater cooling system as they would provide a basis for the identification of optimal biocide injection policies and optimal biocide feed locations that minimize biocide usage as well as flow and mixing retrofit options that would allow the full exploitation of the biocide chemistry to realize seawater discharge compositions of minimum toxicity.

3. Technical Approach

This research aims at delivering a unified approach to the problem that enables the operation, retrofit and design of a sustainable seawater cooling system for an industrial process that causes minimum damage to the environment. The environmental impact of such a cooling system is directly related to three factors:

1. The amount of cooling water that needs to be used and hence injected with biocide. This is directly linked to the amount of heat that needs to be removed from the industrial process, i.e. its energy efficiency.
2. The efficiency of biocide usage in the process. This depends strongly on biocide injection policies and locations and the design of the cooling water system from seawater intake to discharge.
3. The availability and performance of clean-up operations to remove biocides from seawater prior to discharge. Such operations are extremely costly and detrimental to process economics. Current seawater cooling systems in Qatar operate without clean-up.

In order to reduce environmental impact whilst maintaining or enhancing process profitability, it is important to improve on factors 1. and 2. so as to avoid or at least minimize clean-up costs.

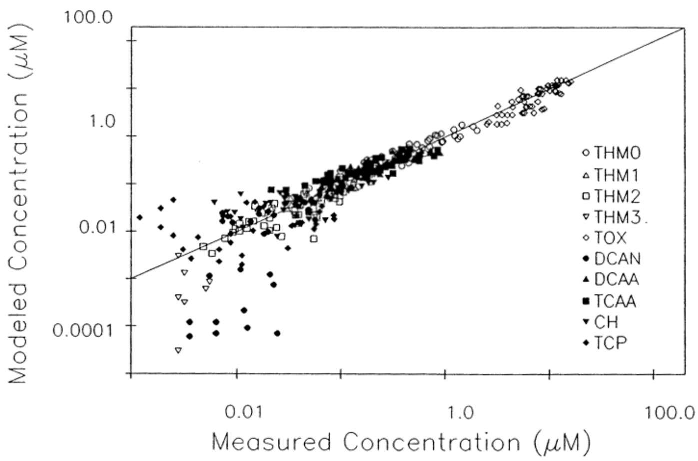

Figure 1. Comparison of Concentrations of Halogenated By-products Predicted by Model with Those Measured. (Batchelor, 1989)
(THM0=chloroform, THM1=bromodichloromethane, THM2=chlorodibromomethane, THM3=bromoform, TOX=total organic halide, DCAN=dichloroacetonitrile, DCAA=dichloroacetic acid, TCAA=trichloroacetic acid, CH=chloral hydrate, TCP=1,1,1-trichloropropanone).

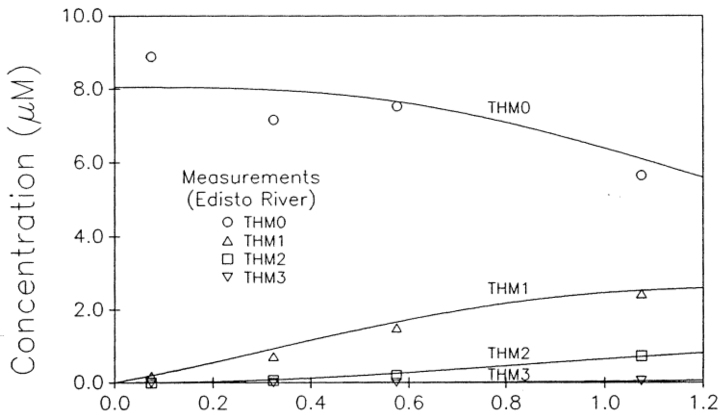

Figure 2. Effect of Bromide Concentration on Distribution of Halogenated Byproducts. (Batchelor, 1989)
(THM0=chloroform, THM1=bromodichloromethane, THM2=chlorodibromomethane, THM3=bromoform)

It is important to note that the environmental impact of seawater cooling is currently assessed by biocide concentrations in the seawater prior to discharge. However, there is consensus amongst industry and government that the environmental impact assessment should be based on the specific biocide discharge and dispersion characteristics of a specific process system. Unfortunately, a tool that can accurately predict such information is currently unavailable although in dire need.

This **holistic approach** is designed to achieve all of the above. It will consist of the coordinated application of a number of technologies in the form of software tools to maximize the efficiency of the system at minimum cost and to assess the environmental impact of biocide discharge. These tools are:

Process integration tools. These tools enable the minimization of the process energy demand which determines the minimum flow rate of seawater required for process cooling. The tools also enable the synthesis of low-cost clean-up systems if clean-up is required.

Process optimization tools. These tools will be designed to maximize the efficiency of biocide utilization inside the process system in order to minimize biocide discharge. The tools will enable the determination of optimal biocide injection policies as well as retrofit options for the seawater cooling system in terms of biocide injection points and changes to the flow and mixing patterns of the system in order to better exploit biocide chemistry and achieve less toxic discharge.

Environmental impact assessment tool. The tool will enable the simulation of biocide dispersion and reactions after seawater discharge to establish the true environmental impact of seawater cooling associated with the specific process system.

The focus of this project is on the development, testing, application and validation of these tools. Whilst the relevant process integration tools are already available and only need to be adapted to the specific problem under investigation, no applicable process optimization and environmental impact assessment tools are currently available. The original research contributions of this project will be associated with the development of these tools.

Accurate knowledge of biocide chemistry inside the process system and after discharge will be the key to the development of accurate tools for process optimization and environmental assessment. Therefore, the chemical, physical, and biological processes associated with the use of different biocides in cooling water systems will be investigated theoretically as well as experimentally. These efforts will culminate in a full kinetic model to describe the biocide chemistry in seawater. The next research stage will address the integration of the kinetic model into flow models so that the effects of biocide chemistry can be fully described throughout the process system as well as after discharge into the sea. The resulting reactive flow models will form the basis of the process optimization tools and the environmental impact assessment tool.

Figure 4 illustrates the individual research and development activities of this project in the context of the steps that constitute the holistic approach towards identification of the most sustainable way of using seawater for process cooling. The individual **research and development activities** are grouped into four themes.

Theme 1: The study of biocide chemistry in seawater. This theme will consist of theoretical and experimental work program to investigate the reaction system and deliver a full kinetic model that accurately describes the biocide reactions in seawater. This model will enable the developments in Themes 2, 3 and 4.

Theme 2: Reactive transport modeling and simulation. This theme will develop reactive flow models that incorporate the kinetic model from Theme1 to simulate (a)

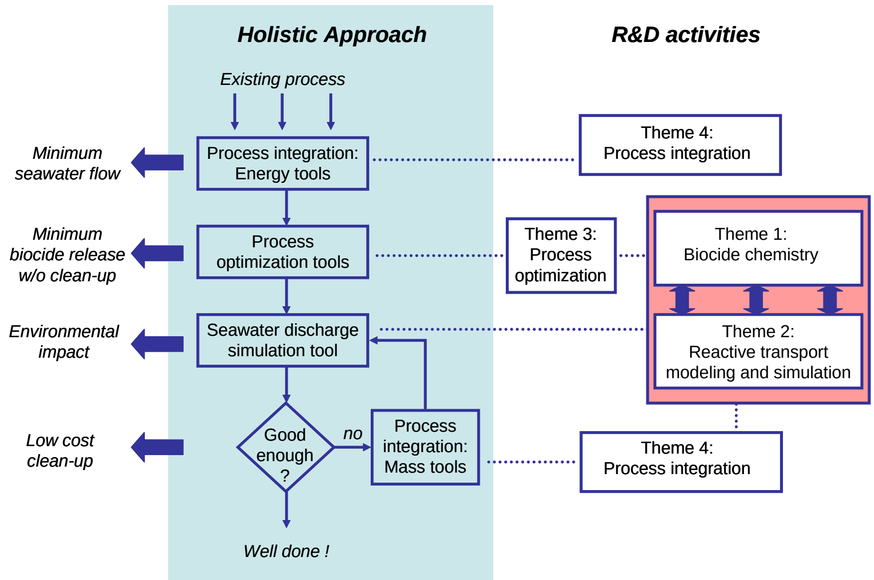

Figure 4. R&D activities in view of the holistic approach.

process internal reactive flows (to be used in Theme 3), and (b) biocide dispersion after discharge (to perform environmental impact assessment).

Theme 3: Process optimization. This theme builds upon the process internal reactive flow models from Theme 2 to develop optimization tools that enable the full exploitation of the biocide chemistry and lead to the identification of optimal operation strategies and retrofit design options for the biocide injection system.

Theme 4: Process integration. Here we adapt modern process integration techniques: (1) energy integration tools to minimize process cooling requirements and thus determine minimum seawater demand, and (2) mass integration tools furnished with knowledge from Themes 1 and 2 to identify efficient clean-up options.

The themes are explained in detail in the following section. With the proposed R&D approach, techniques and tools will be developed that are fundamentally sound and allow the development of optimal strategies for addressing the environmental and economic issues of seawater cooling systems through our holistic approach. The simulation and optimization problems posed in this research are highly complex. In order to develop precise models that can be implemented and solved efficiently, it is particularly important to ensure close collaboration between the kinetic model development, reactive flow modeling, simulation, and optimization research stages. This will allow exploiting insights in terms of kinetic effects and flow characteristics to generate tailored numerical solution schemes that are reliable and fast and deliver the solutions of the required accuracy. The research output will enable industry and regulators in Qatar, the region, and worldwide to address the problem of seawater cooling systematically.

4. Conclusions

The use of seawater for industrial cooling is a vital technology that poses some of the most profound environmental impact on the water quality in Qatar and the Arabian Gulf. This research project will address a significant and worsening environmental problem that poses a substantial threat to the environment. This research will provide both industry and regulators with tools to evaluate the extent of the problem and suggest efficient avenues towards its solution. Its findings will impact operations of numerous industries in Qatar and the world.

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