Understanding Water Quality and Ballast Water Management System Limitations

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Great Lakes Fresh Water

Yanktze River -Changquing High Turbidity

Arctic Sea Extreme Temperatures

> *"As shipowners investigate potential ballast water management systems for installation on their vessels, they will have to consider trade routes and operating conditions to determine the most effective technology for their vessels."*

Globally, a wide variety of chemical and physical processes are used to disinfect water. As innovators turned to the task of ballast water treatment, common disinfection technologies were adapted for shipboard use. These processes have been studied extensively in land-based applications, and their benefits, drawbacks, and optimal conditions for use have been widely documented.

Each of these technologies are very well-suited for disinfection in certain water conditions. However, disinfection of ballast water presents unique challenges as the quality and characteristics of water found in a ship's ballast will be inconsistent depending on ballasting location. Throughout this paper we will highlight the operating conditions in specific waters that are favorable and unfavorable for each ballast water management system (BWMS) method and discuss the impact of the water treatment on the vessel and crew.

Chemical Disinfection

Chlorination

Chlorination is a good, low-cost disinfection technique; however, the efficiency of its use varies widely depending on water conditions. Disinfection is achieved by adding sodium hypochlorite (bleach) to water. Hypochlorite is one of the two species which is produced when chlorine is added to water. The hypochlorite will revert to form hypochlorous acid, the relative amount depending upon pH. At a pH of about 7.5, equal amounts of hypochlorite and hypochlorite ion will form. Of the two, hypochlorous acid is the better biocide.

Another characteristic of chlorine is that it reacts with both living organisms and organic materials that may be present in the water requiring a high dose of chorine to ensure that there is sufficient disinfectant for all water types. This feature also reduces its effectiveness in "dirty" water which contains high concentrations of organic materials. The reaction with organic matter can also form undesirable by-products, such as chloramines (combined chlorine) and trihalomethanes (THMs), which can pose toxicity risks to both aquatic organisms and human health.

Chlorine bleach is inherently unstable, its stability being impacted by the presence of metal ions, sunlight, and temperature. Consequently, over time, the concentration of bleach stored in tanks will decline if not stored properly, the amount of degradation being a function of the three factors mentioned above.

Residual (or excess) active substance will require neutralization before discharge.

Chlorine Dioxide

Despite chlorination (NaOCl) and chlorine dioxide (ClO_2) having chlorine in the name, there is a vast difference between the two chemicals. Chlorine dioxide is also extremely effective, it reacts mostly with living cells and to a much lesser extent, organic compounds. When chlorine dioxide encounters a living organism, it penetrates the bacterial cell wall and disrupts vital internal processes, inactivating the organism. Chlorine dioxide is unique in that it remains a true gas dissolved in a solution; it does not react with water and retains its biocidal effectiveness over a wide pH range (4-10).

ClO_2 is environmentally friendly and it considered by land-based operations to be the only true "green" biocide. ClO_2 ultimately degrades to sodium chloride (salt), which is very soluble in water. The chlorine dioxide treatment process produces significantly fewer by-products compared to other chemical disinfectants.

Contrasting with other disinfectants, such as ozone and chlorine, chlorine dioxide is a very specific disinfectant due in part to its limited reaction with organic compounds. Thus, the required dose of chlorine dioxide in "dirty" water is much less than that of chlorine or ozone in the same waters. In fact, chlorine dioxide has a long history of working exceptionally well in land-based applications where high levels of organic materials are anticipated to be present.

Another unique property of chlorine dioxide is its superior ability to remove slimy films of bacteria that adhere to surfaces of water storage tanks, known as biofilm. Small cooling towers, frequently contaminated by organic material, have tremendous biofilm forming potential and chlorine dioxide has achieved widespread usage in such systems, due to its excellent biofilm dispersing/bacterial disinfecting properties. Unlike other water treatment technologies, changes in water conditions,

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i.e., salinity, pH, temperature, and turbidity do not affect disinfection efficacy. Chlorine dioxide is effective, particularly in dirty waters and does not require treatment or neutralization at discharge.

The size of the chlorine dioxide generator or chemical dose does not vary based on flow rate and even the largest ships only need one BWMS. As a result, as a ship's size increases, chlorine dioxide becomes more economically viable in treating large volumes of water.

Electrochlorination

Electrochlorination is performed by running an electric current through salt-water to generate the active substance, sodium hypochlorite, which reacts with water to form hypochlorous acid. It should be noted that this is the same active substance that is used when chlorinating water. As addressed in the paragraph on chlorine, it is less effective in dirty water and at high pHs, generates toxic by-products and will require neutralization prior to deballasting.

Under optimal conditions, the generation of the active substance happens rapidly and sufficient disinfectant is generated. However, as conditions such as salinity, water temperature, water hardness, and pH change, both the speed at which the active substance is generated and the quantity of hypochlorous acid generated will decrease. Three of the most important water characteristics affecting this process are water temperature, water hardness, and the amount and purity of the salt in the water. Optimal conditions for electrochlorination are in saline waters with a water temperature range between 15°C and 35°C.

Seawater typically contains 400 – 500 ppm of calcium hardness. This hardness is problematic because in the electrolytic cell, caustic is produced at the cathode. As calcium salts have retrograde solubility, when the pH increases, the driving force for deposition increases dramatically. The high pH produced at the cathode results in the cathode becoming rapidly fouled with calcium salts, thus limiting the life and performance of the electrolytic cell. It may also affect efficiency as the deposition increases. A few electrochlorination treatment systems have the capability to reverse the current on the electrodes, whereas the anode becomes the cathode and the cathode becomes the anode. The deposition on what was the cathode will shed when it operates as the anode, thus eliminating buildup. This operation requires a coating on the electrodes that will not shed when power is reversed, thus making it a self-cleaning electrode. Without this capability, the electrode will need cleaning with acid, usually once a year.

Many electrochlorination BWMS's have incorporate modifications to the electrochlorination process to compensate for operation outside of the optimal conditions as mentioned above. For operation in brackish or freshwater, salt must be added to incoming ballast water. This requires continuous monitoring of the system and storage of a salt solution. An electrochlorination BWMS operating in waters with temperatures below 15°C will see reduced efficiency unless incoming ballast water is heated, this is sometimes accomplished by piping through the engine room but could result in additional power requirements.

Ozone

Ozone (O_3) is an exceptional disinfectant and is the strongest oxidant used commercially. However, similar to chlorine, ozone reacts with both organic and inorganic compounds in the water. Therefore, much more ozone is required in "dirty" waters than in clean waters. Salinity and temperature do not affect the efficiency of a BWMS using ozonation. In fresh water, longer holding times may be required for ozone disintegration, as ozone degrades slower in freshwater than in seawater.

While ozone generation is relatively easy, the properties of ozone make it difficult to remain dissolved in water for sufficient

time to serve as a disinfectant. In fact, the biggest expense for an ozone treatment system is in the manufacturing of the ozone generator, which is used to dissolve ozone in the water. The design of the generator is critical, and may also require extensive space, as ozone will rapidly come out of solution. Consequently, much more ozone than is actually needed must be produced to inactivate the organisms to account for this loss. Finally, ozone has a half-life which is only minutes long. This is a function of pH. If the ozone concentration is not sufficiently high, natural degradation of ozone may prevent the disinfectant from getting to the most remote parts of the ballast tank.

Any ozone not dissolved will need to be neutralized before discharging back to sea. Ozonation produces both THMs and bromate, potentially toxic by-products.

Physical Disinfection

Deoxygenation

Deoxygenation is achieved by using a vacuum to reduce the pressure in the space above water along with inert gas injection. This process removes oxygen from the water, which ultimately asphyxiates the micro-organisms. The elevated level of CO_2 reduces the pH level of the water, which is fatal to aerobic organisms. Deoxygenation will kill organisms with great efficacy in most water conditions, but it requires a hold time of four to five days to allow for full deoxygenation to occur. This is a deterrent to most shipowners.

To achieve deoxygenation, ballast tanks must be vented to ensure they are completely oxygen free. This condition may allow for the growth of anaerobic bacteria (bacteria that thrives in the absence of oxygen). An aerobic bacteria are highly corrosive and the presence of these bacteria could lead to an acceleration of corrosion in the ballast tanks. Deoxygenation is typically used in combination with other treatment technologies.

Ultraviolet (UV)

UV units disinfect by passing water along UV lamps that emit a high dose of short-wave ultraviolet radiation inactivating organisms and thereby rendering them unable to reproduce. UV systems work effectively over a wide range of water types and are not affected by changes in temperature or salinity.

The effectiveness of UV treatment is influenced by exposure time, intensity of the UV light, and water clarity. In order to disinfect, UV light must penetrate the water to reach the invasive species. Anything that comes between the light source and invasive species will absorb UV rays before disinfection can occur and decrease the disinfection effectiveness. Many materials that are dissolved or suspended in water (such as suspended solids, which reduce clarity) and materials that foul the quartz tubes encasing UV lamps prevent the light from reaching organisms. In fact, fouling of quartz tubes can be such a limiting factor that many UV systems are equipped with special wiping equipment, which operates routinely to keep the quartz tubes clean.

In order to improve water clarity during UV treatment, a filter screen of 25-micron or smaller is typically used while other BWMS's tend to use larger screen sizes. If the water is particularly "dirty", the smaller openings in the filter element could cause it to plug up more often, causing additional filter cleaning cycles. Filter screen size will affect the ballasting flow rate. For example, a Filtersafe Model-BS200T filter with a 40-micron screen can filter up to 550 m^3/hr, while the same filter with a 25-micron screen will only have a 370 m^3/hr. Thus, UV systems must either use larger filters, that typically are not required for other BWMS, (using more space and most likely increase the cost) or restrict the ballasting flow rate, which will ultimately extend the ballast time. This may not be an option for some shipowners.

Treatment with UV light at a wavelength of approximately 254 nm is required to inactivate bacteria. Virtually all organic compounds absorb UV in this same range. Therefore, dissolved organics in water will limit the UV light that contacts. and ultimately inactivates. organisms. Consequently, UV systems work best in clear waters with low turbidity and/or low concentrations of dissolved or suspended materials that can absorb UV rays. When operating in waters that don't meet these conditions, the system must increase the UV dose to account for the loss due to absorption by organic compounds. This may result in larger (or multiple) UV systems on board the vessel, which will require additional space and increase power requirements.

Ballast water management with UV typically requires systems to operate during both intake and discharge, but does not create any harmful by-products; neutralization is not required.

Summary

Each water disinfection technology described above has its benefits and drawbacks. Hypochlorous acid (chlorine) and ozone will be most efficient when used in water that does not contain high levels of organic materials. Due to its unique properties, chlorine dioxide is particularly well-suited to treat waters containing organic compounds and/or waters with poor water clarity. Ships that are primarily calling on freshwater or brackish water ports may need to consider the ability and economics of using an electrochlorination system for treatment. Similarly, ships calling on ports near the mouth of rivers (e.g. New Orleans) may need to take into account whether UV treatment will be the most effective technology to use given the turbidity of the water.

As shipowners consider a BWMS for their vessels, they will need to understand the restrictions posed by each type of disinfection technology and how these limitations may affect the operation of the ship in certain types of water. Turbidity, opacity, temperature and salinity level of the intake water are challenges that BWMS are subjected to and the efficacy of the technologies will differ significantly between different waters.

About the Author

Greg D. Simpson has consulted globally on a variety of water issues to a range of industries, including petroleum refining, oil field, aerospace, medical waste sterilization, ballast water, pharmaceutical, chemical, pulp and paper, electronics and semiconductor manufacturing, municipal treatment, environmental, food, and others.

Mr. Simpson was a scientist at a top-secret nuclear weapons facility in his early career. Since 1980, he has been involved in the water treatment industry, serving in an assortment of roles.

He has consulted on a variety of projects including: odor control in a closed paper mill, stress corrosion cracking in a large petrochemical plant, $CaCO_3$ deposition and gravel pack dissolution in an oil-field steam flood, anaerobic digester troubleshooting in a brewery, and a potable water corrosion study where the plant had violated their lead and copper limits.

A recognized expert in the production and use of chlorine dioxide, he has consulted globally on the subject. Most recently he has been extensively involved in the use of ClO_2 for treating flowback water from the hydraulic fracturing process for reuse in several of the shale plays.

His research has resulted in 20 patents, issued and pending. Additionally, he has authored and / or presented well over 100 technical papers. He has written two books about chlorine dioxide and was a major contributor to a third. His fourth book is focused on the use of chlorine dioxide in oil and gas applications.

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