CHEMICAL BALLAST WATER TREATMENT PROBLEMS

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The need to meet the new regulations on Ballast water treatment and the associated significant expense is a serious concern to modern ship owners.

When evaluating ballast water treatment options a number of general factors must be considered but without doubt, the monetary cost is the deciding factor for the majority of ship owners, especially on ships already built that may have to be retro-fitted with equipment.

Many methods now exist to choose from and more are likely to emerge in the coming years. The common thread in most of these systems is their requirement of expensive equipment and fitting as well as the space for the equipment. Moreover questions remains regarding their effectiveness and impact on operations.

The attractiveness of chemical treatments, especially on ships already built can easily be understood.

Chemical Biocides.

These chemicals act by destroying cell membranes, which leads to cell death. They come in two general types, oxidising and non- oxidising.

With the problems and expense of these various systems, there is evidence that a considerable number of owners are turning to chemical treatment. These biocides are supplied in either liquid or solid form and can easily be stored on board a ship and as they have been widely used ashore, the chemical data sheets for the biocides are easily available and well understood. The machinery required for applying these chemical biocides is reliable and needs little maintenance with the only problem being the size of some of the plants.

It is important to note however that the reactions between biocides and sea water that could produce harmful by products have not been extensively studied. More importantly, there is definite concern now being expressed regarding the release of gases in enclosed and confined spaces, by these agents, especially the oxidising agents of ozone and chlorine.

Ozone

Ozone is an oxidizing biocide that has been used to disinfect water supplies ashore for over one hundred years. It is the major component of smog and is a harmful pollutant. It is also often used as a biocide in water. Ozone is inherently unstable and dangerous to produce, but it is a very powerful oxidizing agent.

The system works by passing water through machinery that releases ozone bubbles into the water. The gas then dissolves in the water and reacts with other chemicals in the water to kill the organisms. As not all the gas dissolves in the water this must be destroyed before it enters the atmosphere, as it is toxic to humans. Further, reaction between the ozone and the components of sea water may also result in toxic chemicals.

Due to the strongly oxidizing properties of ozone, ozone is a primary irritant, affecting especially the eyes and respiratory systems and can be hazardous at even low concentrations. The Canadian Centre for Occupation Safety and Health reports that:

"Even very low concentrations of ozone can be harmful to the upper respiratory tract and the lungs. The severity of injury depends on both by the concentration of ozone and the duration of exposure. Severe and permanent lung injury or death could result from even a very short-term exposure to relatively low concentrations."

To protect workers potentially exposed to ozone, U.S. Occupational Safety and Health Administration has established a permissible exposure limit (PEL) of 0.1 µmol/mol (29 CFR 1910.1000 table Z-1), calculated as an 8 hour time weighted average. Higher concentrations are especially hazardous.

Work environments where ozone is used or where it is likely to be produced should have adequate ventilation and it is prudent to have a monitor for ozone that will alarm if the concentration exceeds the OSHA PEL.

It must also be mentioned that when Ozone is used, if the treated ballast water is pumped out in fresh water, the ozone will remain active for up to 30 minutes, thus having the potential to harm sealife in the area.

Chlorine

Chlorine for ballast water treatment is generated on the ship, from seawater. |It is commonly used to treat drinking water and has been used for such treatment for many years at sea, but recent studies suggest that it may not be as safe to humans as once thought. There is also a possibility that Chlorine may react with sea water to form toxic chemicals.

Chlorine is a greenish-yellow gas, which combines with nearly all elements. It is a respiratory irritant to the mucous membranes and lungs and causes cancer. Chlorinated liquids burn the skin and many fabrics. As little as 3.5 ppm can be detected as an odour. 1000 ppm is likely to be fatal after a few breaths.

Most harmful chlorine exposures are the result of inhalation. Health effects typically begin within seconds to minutes. Following chlorine exposure, the most common symptoms are:

Airway irritation

Wheezing

Difficulty breathing

Sore throat

Cough

Chest tightness

Eye irritation

Skin irritation

The severity of health effects depends upon the route of exposure, the dose and the duration of exposure to chlorine. Breathing high levels of chlorine causes fluid build-up in the lungs, a condition known as pulmonary edema. The development of pulmonary edema may be delayed for several hours after exposure to chlorine. Contact with compressed liquid chlorine may cause frostbite of the skin and eyes. There is no antidote for chlorine poisoning, but chlorine's effects are treatable, and most people recover. People who experience serious health effects (such as severe eye or airway irritation, severe coughing, difficulty breathing, pulmonary edema) may need hospital care.

Chlorine can be detected by its odour below the permissible limit; however, because of olfactory fatigue odour may not always provide adequate warning of the harmful concentrations of this substance.

The recommended exposure rates for chlorine gas are;

TIME-WEIGHTED AVERAGE (TLV-TWA): 0.5 ppm - Carcinogenicity Designation A4

SHORT-TERM EXPOSURE LIMIT (TLV-STEL): 1 ppm - Carcinogenicity Designation A4

Most chlorination systems are applying a dose in the region of 2 mg/l residual chlorine, which has proven to be effective.

Unfortunately, some Ballast water solutions are using Sodium Hypochlorite with a concentration of up to 10 ppm, which can leave a potentially dangerous the gas residue in the tanks after the water is pumped out. Not only that, but the water pumped out with this level of chemical can be harmful to sea life in the local area. This contamination can also occur when a ballast tank or ballast hold is overflowed. Using a ballast pump that can pump 2,000 tons per hour, the overflow rate will be over 33,000 litres per minute.

According to the International Convention for the Control and Management of Ships' Ballast Water and Sediments, regulation D2, vessels are prohibited from pumping out ballast water still containing an active substance and in November 2011, the US environmental protection agency proposed a vessel general permit for discharges incidental to the normal operation of vessels permit that, for the first time would include numeric discharge limits of active ingredients for most vessels.

These limits are as follows;

Table: Maximum Ballast Water Effluent Limits for Residual Biocides	
Biocide or Residual	**Limit** ***(instantaneous maximum)***
Chlorine Dioxide	200 µg/l
Chlorine (expressed as Total Residual Oxidizers (TRO as TRC))	100 µg/l
Ozone (expressed as Total Residual Oxidizers (TRO as TRC))	100 µg/l
Peracetic Acid	500 µg/l
Hydrogen Peroxide (for systems using Peracetic Acid)	1,000 µg/l

Mud and Sediment gas bubble morphology in sediments

In 2005, a micro computed tomographic evaluation completed by a US Navy department showed the feasibility of gas bubble formation in sediment and mud using examples of bay mud.

Even with a forced ventilation system, gas contained in mud may not be entirely released and this is dependent upon the gas composition, mud volume, rheology and ambient temperature.

In other circumstances, a quantity of gas may remain in stable solution in the mud and not be released until changes in the mud chemistry, temperature or other conditions.

This could give rise to a situation where a ship with a depth of mud in a tank could assume that the tank is clear of gas. Then when the tank has been closed for some time, the gas could be released from the mud and now become a potential danger to crew entering the tank later.

Conclusions

As ships may at times fill a ballast tank by overflowing the tank or ballast hold, if the ballast water is treated with these chemicals there will be spillage into the harbour or sea. As all bulk carriers are required by IMO to have a water ingress alarm in the holds, if a Level Gauging system was fitted this would show the water level in the coaming area and thus would prevent the overflow. If the water ingress alarm system had a continuous level sensor that measured up to the coaming area, it would be easy to add an additional high level alarm. Ideally a fixed level gauging system that can be maintained from the tank top should be selected, as this would eliminate the need to enter the tank.

Both Chlorine and zone are heavier than air gases and this means that any ballast tank or hold that has been treated with these chemicals should be uprated in the ship enclosed space management plans to dangerous until they are completely ventilated and tested. Natural ventilation will be inadequate for these spaces and forced ventilation that reaches to the bottom of these tanks will be necessary for complete ventilation.

No one should enter tanks that have contained chlorine or ozone treated ballast water until the tanks can be verified as being clear of the gases. This could be problematic for vessels that need to have tanks surveyed or examined in the port of discharge and without adequate forced ventilation equipment, delays could be experienced.

All ships that use chlorine or ozone treatments should carry ozone and chlorine gas detectors.

Where vessels are using ozone or chlorine ballast water treatment, mud or sediment build up must be avoided and the bottoms of ballast tanks should be water blasted periodically to clear the mud or sediment from the bottom.