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1. Ballast water treatment by De-oxygenation with elevated CO2 for a shipboard installation - a potentially affordable solution

2. Paper author/s - M. Husain, MH Systems, Inc.
H. Felbeck, Scripps Institution of Oceanography, University of California - San Diego
R. Apple, MH Systems, Inc,
D. Altshuller, MH Systems, Inc.
C. Quirmbach, MH Systems, Inc.

3. Contact details - MH Systems, Inc.
10951 Sorrento Valley Road, Suite 2F
San Diego, CA 92121 USA
T: 858-452-1280 F: 858-452-6035
husainm@mhsystemscorp.com

4. Treatment options being researched

It is estimated that 21 billion gallons of ballast taken on in foreign ports are discharged by commercial vessels annually in the waters of the United States (Carlton et al. 1993). Specifically, ballast water transport is a major vector for the introduction of potentially invasive aquatic species.

The concept to combat Aquatic Nuisance Species (ANS) invasion resulting from ballast water discharge, described in this paper, is a technical extension of MH Systems' American Underpressure System (AUPS). The AUPS utilises a slight negative pressure in the tank's ullage space, in an inert environment, to prevent or minimize oil spillage from tankers (Husain et al. 2001).

The ballast water treatment method consists of bubbling the inert gas via a row of pipes (orifices at the bottom of the pipes) located at the bottom of the tank, while maintaining a negative pressures of -2 psi at the ullage space. The inert gas from a standard shipboard inert gas generator is composed of 84% Nitrogen, 12-14% CO2 and 2% Oxygen. The ballast water will be equilibrated with gas from an inert gas generator. As a result, the water will become hypoxic, will contain CO2 levels much higher than normal, and the pH will drop from the normal pH of seawater (pH8) to approximately pH6.

4.1 Ballast Water Treatment Standards

Standards for treatment of ballast water are still in a state of flux. Efforts to define standards are ongoing in the US Congress, International Maritime Organisation (IMO), and other individual maritime nations. The US Congress (NAISA 2002) proposes an Act that will, among other considerations, set the interim standards for ballast water treatment (BWT). It states, "The interim standard for BWT shall be a biological effectiveness of 95% reduction in aquatic vertebrates, invertebrates, phytoplankton and macroalgae." There are discussions about setting micron standards, i.e., x microns cut-off for living organisms.

Currently, a fifty (50) micron standard is being discussed in various circles, including IMO and US Coast Guard. The default standard appears to be the Ballast Water Exchange (BWE), or something close to it. Cangelosi (2002) states "… the Coast Guard has set forth a "do-it-yourself" approach, directing interested ship owners to conduct complex shipboard experiments (post-installation) to undertake direct and real-time comparisons between BWE and treatment. If the comparison is favourable and defensible, the Coast Guard will approve the treatment. ….."

4.2 Current Investigative Efforts Of Alternative Technologies

Glosten (2002) provides a review of the numerous treatment systems options being investigated. These include heat, cyclonic separation, filtration, chemical biocides, ultraviolet light radiation, ultrasound, and magnetic/electric field. The methods not mentioned in this reference are hypoxia, carbonation, and their combination. In studies of 18 months duration on a coal/ore vessel (Tamburri et al. 2002), the ballast water dissolved O2 level was reduced and held to concentrations at or below 0.8 mg/l by bubbling essentially pure nitrogen. The experiments resulted in a treatment "that can dramatically reduce the survivorship of most organisms found in the ballast water…"

In extensive experiments with gas of varying percent CO2, N2 and O2 (McMahon 1995), the "…results indicate that CO2 injection may be an easily applied, cost-effective, environmentally acceptable molluscicide for mitigation and control a raw water system macrofouling by Asian clams and zebra mussels".

4.3 Corrosion Considerations Of Various Treatment Systems

Shipboard corrosion mitigation is always a priority consideration. It requires the continual attention of the crew and, if not carefully controlled, can actually compromise the strength of the ship. Any installed ballast water treatment system must not under any circumstances increase the potential for corrosion and, if possible, should decrease the potential. The system discussed in this proposal has considered the corrosion issue. As reported in literature (Tamburri et al., 2002), corrosion might even be mitigated by deoxygenation. Perry et al. (1984) states that unless pH level drops below 4, concerns about corrosion are unfounded.

5. Timeframe of the project

We present initial proof of concept results, which have been conducted during 2002-2003.

6. Aims and objectives of the project

Except for ballast water exchange, essentially all treatment concepts involve the chemical change of the water to cause an environment lethal for ANS. The chemical changes described by Tamburri et al. (2002) and McMahon (1995) offer promising results, i.e., reduce the dissolved O2 in the one case, and carbonate and reduce the pH in the other case. In both cases the process involves the exchange of gases, the extraction of the dissolved O2 and the introduction of CO2. Surface contact area and partial pressure differentials permit the gas exchanges to occur. The deoxygenation of the ballast water is based on Henry's Law of gas solubility: The relative proportion of any dissolved gas including oxygen in the ballast water is a function of the concentration, equivalent to partial pressure of the gas (e.g. oxygen), within the mixed gases over the ballast water. The depletion of oxygen in the ballast water is primarily a function of the shared surfaces and concentrations at the interfaces of the inert gases and water.

The pH of the ballast water is lowered by the chemical reaction:

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

All systems described thus far in the literature, including ballast transfer, has left untreated the sediment buildup in the bottom of the tanks. If the orifices in the lattice work of piping pointed down, then the sediment could be stirred up facilitating the kill of the embedded ANS.

The purpose of the preliminary experiments described here was to obtain initial data on the effects of "inert gas" on marine organisms. "Inert gas", hereinafter called trimix, a commercially available gas mixture of 2% oxygen, 12% CO2 and 84% nitrogen resembles the gas generated by commercially used marine "inert gas generators". Adult or young adult animals were chosen for two reasons a) to make the size of specimens amenable for the experimental setup and b) to raise the significance of possible effects since adults of a species are typically more tolerant of environmental changes than juveniles or larvae. All animals were collected fresh from the coastal waters off La Jolla, CA and used immediately. The plankton sample was collected with a plankton net from a small boat.

7. Research methods, test protocols and experimental design

The schematic of the experimental setup is shown in Figure 1. Three parallel incubations were done for each experiment. Several organisms were incubated in 1.5L of seawater at 22℃ in large Erlenmeyer flasks. Each incub ation was equilibrated with the respective gas using aquarium stones before any organisms were introduced. The aerobic control was bubbled from an aquarium pump for approximately 15 min and left open to the atmosphere after addition of specimens. An anaerobic incubation was bubbled with 99.998% nitrogen for 15 min. After introduction of the organisms, the bubbling was continued for another 10 min and then the container was closed with a rubber stopper or the bubbling was continued. The incubation in trimix was treated similarly except that the gas mix was used instead of nitrogen. The oxygen concentrations were measured after the initial bubbling period using a Strathkelvin oxygen electrode with a Cameron instruments OM-200 oxygen analyser. Ph values were determined using a combination electrode and a Radiometer pH meter.

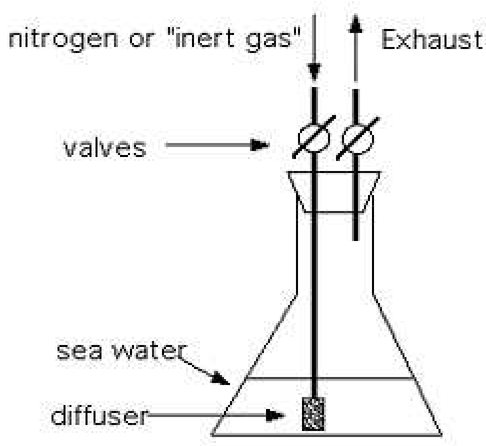


Figure 1. Schematic of the Experimental Setup

Survival of the specimens was determined visually by checking for motile responses to tactile stimulus (e.g. mussels do not close their shells, barnacles to not withdraw their feet, shrimp do not move their mouthparts, worms appear limp and motionless). After each testing of the animals, the incubation flasks were bubbled for 10 min to reestablish original conditions. To verify survival of the specimens, they were relocated to aerobic conditions and checked again after 30 min. If they still did not respond, they were considered dead. The survival of the bacterium Vibrio cholerae strain N16961 was monitored by repeated plating on Luria-Bertani Agar with Rifampicin (100 µg/mL).

This setup allowed us to compare responses to nitrogen and "trimix" while making sure that test specimens were not gravely affected by other experimental parameters. Incubation in pure nitrogen allow for a comparison with published results by others.

8. Results

8.1 Experimental results and discussion.

The oxygen concentrations were measured at "non-detectable" for the nitrogen incubations and 10% air saturation (=16Torr partial pressure) for the "trimix". The pH value of the water bubbled with trimix reached 5.5 after the initial 10 min of vigorous bubbling. The aerobic and nitrogen bubbled seawater maintained their pH at 8. The incubations showed clearly that "trimix" kills organisms considerably faster than incubations in pure nitrogen Table 1. All organisms except of Vibrio cholerae showed no mortality in aerobic conditions. The shrimp and crabs incubated in "trimix" were dead after 15 min and 75 min, respectively. Even a transfer into aerated water did not result in any movement. The brittle stars incubated under nitrogen started to move again after transferred into aerated water. All the mussels incubated in nitrogen and "trimix" were open after 95 min but only the ones in nitrogen still responded to tactile stimuli by closing their shells. The barnacles were judged dead after incubation in "trimix" when they did not withdraw their feet when disturbed, the ones incubated in nitrogen still behaved normally. The plankton sample mainly contained copepods. They stopped moving after 15 min and could not be revived in nitrogen and "trimix" incubations. The results are summarised in Table 1.

Species		Number/ incubation	Nitrogen	Trimix	Comments
Mimulus foliatus	Crab	7/inc	Normal	Dead after 75 min	
Mytilus californianus	Mussel	10/inc	Open but responding	6 dead after 95 min	
Pollicipes polymerus	Barnacle	10/inc	Normal	Dead after 60 min	
Megabalanus californicus	Barnacle	5	Dead after 84 h	Dead after 48 h	
Sebastes diplopora	Rockfish	2	Dead after 19 min	Dead after 7 min	
Ophionereis annulata	Brittle star	5-10	Most survive up to 3 h, most dead after 26 h	Most survive up to 3 h, several dead after 26 h	Mean of 4 experiments
Ophioderma panamanse	Brittle star	8/inc	Not moving but revivable by air	Dead after 50 min	
Unidentified	Caridean shrimp	6	Affected but alive after 30 min	Dead after 25 min	
Unidentified	Caridean shrimp	6	2 dead after 30 min	5 dead after 45 min	
Mysolopsis californica	Mysid shrimp	25	Dead after 15 min	Dead after 15 min	
Lysmata californica	Shrimp	10/inc	Normal	Dead after 20 min	
Plankton mix	Var. copepods	lots	Dead	Dead after 15 min	
Tigriopus californicus	Copepod	8 - 10	Dead after 2 h	Many dead after 2 h	Mean of 3 experiments
Vibrio cholerae	Bacterium	2.5×10^6/ml	>>99% dead after 24 h	>>99% dead after 24 h	Aerobic: 30% dead after 24 h

*Trimix (2% oxygen, 12% CO_2 and 86% nitrogen)

Table 1. Effects of Trimix on Marine Species

Low oxygen concentrations in water are a common natural phenomenon and their effects on live organisms have been widely discussed in the past. Oxygen may not be available to an organism because no water for respiratory purposes is present, e.g., during low tide in the intertidal zone.

Oxygen may also be removed in stagnant waters due to bacterial or other "life based" actions, e.g., in ocean basins, fjords, tide pools, or in waters with high organic content and consequently high bacterial counts, e.g., in sewage, mangrove swamps, paper mill effluent. In addition, oxygen can also be removed by chemical reactions, e.g., in hot springs, industrial effluents. The manuscript by Tamburri et al. (2000) summarises survival of a variety of larvae and adults of organisms including some which may be significant as "nuisance species" under hypoxic conditions. The publication supports extensively that most organisms only survive strongly hypoxic conditions for a few hours and only a few adults for several days. The authors suggest that 72 h of hypoxia will be sufficient to kill most eucaryotic organisms, adults or larvae in ballast water.

The effects of high CO2 on organisms in natural waters have become a research focus because of proposals to dispose atmospheric CO2 in the deep ocean (Haugan 1997, Omori et al. 1998, Seibel and Walsh 2001). Two effects have to be distinguished when looking at "trimix" incubations in seawater: a) the lowering of the pH from pH 8 to about 5.5 and b) the raised CO2 concentrations in the water. While the pH change caused by the incubations in "trimix" are in the range of published experiments, the CO2 concentration in "trimix" (about 14%) is much higher than those investigated in the published literature (0.1% to 1%). Therefore, the effects of "trimix" incubations should be much stronger than those published previously.

Several publications have shown the detrimental effect of lower pH values and high CO2 levels on aquatic life. In a recent publication, Yamada and Ikeda (1999) tested ten oceanic zooplankton species for their pH tolerance. They found that the LC50 (=pH causing 50% mortality) after incubations of 96 hours was between pH 5.8 and 6.6 and after 48h it was between pH 5.0 and 6.4. Therefore, the pH value caused by incubations with "trimix" is well within the lethal range for this zooplankton. Huesemann et al. (2002) demonstrate that marine nitrification is completely inhibited at a pH of 6. Larger organisms were also investigated, a drop in seawater pH by only 0.5 diminishes the effectiveness of oxygen uptake in the midwater shrimp Gnathophausia ingens (Mickel and Childress 1978) and Deep sea fish hemoglobin may even be more sensitive to pH changes (Noble et al. 1986). It appears that a common metabolic response to raised

CO_2 levels and concomitant lowered pH is a metabolic suppression (Barnhart and McMahon 1988, Rees and Hand 1990). Most recently, first papers were published investigating the effects of environmental hypercapnia in detail (Poertner et al. 1998, Langenbuch and Poertner 2002). The effects of pH changes on phytoplankton growth has been reviewed by Hinga (2002). The review summarises data from 22 studies. Many of the cited studies use elevated levels of CO_2 to adjust pH. In almost all cases, the growth of unicellular phytoplankton and diatom species was severely affected by low pH below pH 6.5, only the species Nitzchia closterium showed significant growth at pH 5.5. Since all of the studies cited were done at high light levels and in aerobic conditions, it can be safely assumed that the conditions in an hypoxic dark environment as is found inside of an inert gas treated ballast tank is even more detrimental to phytoplankton growth.

The trimix combines both of these effects on organisms - hypoxia and hypercapnia. Preliminary results demonstrate the effectiveness of this combination in quickly killing a variety of sample organisms. Contrary to methods using additions of biocides or any chemicals in general, nothing is added to the ballast water and, therefore, nothing will be released into the environment when it is released again. Methods using radiation, heating, or filtering ballast water before or during a ship's trip, are much more expensive. The equipment needed to establish a rapid gassing of ballast water is available off the shelf and has been used in the marine environment. The plumbing and gas release equipment has been optimised and has been used in application such as aquaculture, sewage treatment and industrial uses. Extensive supporting literature and research about the design and optimisation of equipment for the aeration of water is available from public resources. Inert gas generators are available for fire prevention purposes on ships and other structures and are already installed on many ships, mainly tankers. They can use a variety of fuels including marine diesel to generate the inert gas. Several topics have to be further investigated before a conclusive recommendation about the treatment of ballast water with "inert gas" can be made: a) how are larvae, eggs, and plankton effected and b) what is the affect of trimix type inert gas in fresh water? If ballast water is taken up through a screen, larger animals will not be included. The initial tests were made with adults because of easy access to them. However, if adults of a species are effected by "inert gas" it is most likely that their larvae will also be effected probably even more so.

Future tests will be conducted with specimens from plankton and larval cultures and with incubations of mixed plankton collected from the ocean. Determinations of viability will be made by microscopic observations (e.g. movement of mouthparts, swimming behaviour), ATP measurements (the ATP levels rapidly decreases after death of an organism), and the ability to bioluminesce (many planktonic organisms emit light, an ability which ceases after death). Fresh water organisms will be of interest because the pH change is not as much as in seawater. Freshwater in its natural environment can have pH values around 5.5. It has to be proven that raised CO_2 concentrations in combination with hypoxia will also affect these species. Only then can the method be used for both, fresh and salt water ballast.

8.2 Analysis and Design Equations

A. Assumptions

In this section, we present mathematical descriptions of the deoxygenation process and of the transfer of carbon dioxide into the ballast water, which, in turn, leads to lowering of the pH to the levels lethal to most ANS. We obtain closed-form mathematical models, usable in design of a shipboard system from any set of given specifications. The list of symbols used in the equations is given at the end of the paper.

The system being analysed places a mixture of nitrogen and carbon dioxide with a relatively small fraction of oxygen in contact with ballast water. The oxygen level in the ballast water is assumed to have reached equilibrium with air as a result of prolonged contact, and therefore would contain a concentration of oxygen sufficient to support a wide spectrum of life forms. The objective is to reduce the oxygen content to a low level by interchange with the gas mixture. The gas is bubbled through the ballast water, which assures uniform distribution of dissolved gas throughout the ballast tank. Thus, diffusion within the tank can be neglected. Bubbles are assumed to be small and variation of hydrostatic pressure over the vertical dimension of a bubble is neglected.

We do not discuss here the size of bubbles and the frequency of their generation. These two issues are addressed in existing reference literature (see, for example, Perry et al. 1984).

We assume that deoxygenation process follows Henry's Law with equilibrium achieved within the residence time of each bubble. The composition of the mixture in the bubble changes primarily due to transfer of carbon dioxide, a dynamic chemical process assumed to obey the mass action kinetics.

B. Deoxygenation Process

As trimix gas is flushed through the system, the total weight of oxygen in the ballast water will be reduced. For the purpose of analysing the deoxygenation process we neglect the presence of carbon dioxide in the trimix.

When a small quantity of gas, dQ, is admitted, it contains an oxygen molar fraction y0. By the time this quantity of gas leaves the system it contains, according to Henry's Law, the molar fraction Y/k_H.

Therefore, we obtain the following differential equation:

$$\frac{dY}{dQ} = y^0 - \frac{1}{k_H}Y$$

Integration of this equation yields:

$$Q = k_H \ln \frac{y^0 - Y/k_H}{y^0 - Y_0/k_H}$$

From this equation it follows that pumping 5,200 m3 of gas into a 32,200 m3 tank reduces oxygen concentration to 0.83 ppm. This level of hypoxia is lethal to many ANS. With the flow rate of 38.2 m3/min this can be achieved in 135 min. The relationship between the size of the tank and the time required to deoxygenate it is linear. Therefore, these results can be scaled to any tank size.

C. Underpressure in Ullage Space of Ballast Water Tank

Deoxygenation is enhanced by the under-pressure, as can be seen from the following simple argument. Let p be pressure of water at a given depth in the absence of underpressure. Let pu be the absolute value of the negative pressure at the top. Let Y be the weight fraction of oxygen in the water without underpressure and Yu - the same weight fraction with underpressure. Then by Henry's Law:

$$\frac{Y - Y_u}{Y} = \frac{k_H yp - k_H y(p - p_u)}{k_H yp} = \frac{p_u}{p}$$

From this equation we conclude that solubility of oxygen is reduced by underpressure. This factor becomes even more significant as a bubble rises to the surface, and the pressure inside decreases.

For example, if p=14.7 psi (the usual value at the surface of the tank) and the absolute value of the underpressure is 2 psi, then the solubility of oxygen is reduced by approximately 14%.

The maintenance of underpressure is not mandatory. The underpressure helps accelerate the de-oxygenation process because, by reducing the oxygen solubility, it also reduces the amount of inert gas needed. For example, 2 psig underpressure will speed up the de-oxygenation by 14%; 0.5 psig underpressure will speed it up by 3.5%. Slight underpressure is also helpful in eliminating the contaminated gas from the ullage space.

D. Carbon Dioxide Transfer

Since we assumed that the pressure inside the bubble depends only on the pressure of the liquid surrounding it, we can write:

$$\frac{dp}{dt} = -\rho g u, \quad p = p^0 - \rho g u t \qquad (1)$$

By definition we have $n_{CO2} = xn$. Differentiating this equation we obtain:

$$\frac{dn_{CO2}}{dt} = x\frac{dn}{dt} + n\frac{dx}{dt}. \qquad (2)$$

However, since the reaction of carbon dioxide with water is the dominant cause of change in the chemical composition, we can write:

$$\frac{dn}{dt} = \frac{dn_{CO2}}{dt}.$$

Combining this with the Equation (2) yields the following equation:

$$n\frac{dx}{dt} = (1-x)\frac{dn_{CO2}}{dt}. \qquad (3)$$

In addition, we can solve for $n = xn+n_N$ to obtain

$$n = \frac{n_N}{1-x}. \qquad (4)$$

From the Law of Mass Action kinetics we have:

$$\frac{dn_{CO2}}{dt} = -kp_{CO2} \qquad (5)$$

For the partial pressure of carbon dioxide we have, according to Dalton's Law $p_{CO2} = xp$.

Combining the equations (1), (3), (4), and (5) yields:

$$\frac{dx}{dt} = -\frac{k}{n_N}x(1-x)^2(p^0 - \rho gut).$$

This equation can be integrated to obtain:

$$I(x) - I(x^0) = -\frac{kt}{2n_N}(2p^0 - \rho gut), \qquad (6)$$

where

$$I(x) = \frac{1}{1-x} + \ln\frac{x}{1-x}.$$

This equation can be used to calculate parameters of the systems, including the residence time of a bubble, required to achieve the desired molar fraction of carbon dioxide in the bubble. The latter quantity is related to the pH and the concentration of carbon dioxide in the water, as we shall see in the next subsection.

E. Concentration of Carbon Dioxide in Water and pH Calculation

Concentration of carbon dioxide in water can be determined as the ratio of the number of moles transferred from the bubble to the volume of the tank. The number of moles transferred from each bubble can be determined from the value of x as follows. By definition, we have:

$$x = \frac{n_{CO2}}{n_{CO2} + n_N}$$

Solving for n_{CO2} we find:

$$n_{CO2} = \frac{x n_N}{1 - x},$$

which gives the following answer for the concentration of carbon dioxide in water:

$$c = \frac{N}{V_t}\left(n_{CO2}^0 - \frac{x n_N}{1 - x} \right). \qquad (7)$$

The concentration of the hydrogen ions in the water can be calculated from *c* by solving the following equation for *h*:

$$\frac{h^2}{c - h} = K \qquad (8)$$

The pH can be then found by taking the -log *h*.

We can also solve the Equation (8) for c and substitute the result into the Equation (7). This yields after some tedious, but straightforward algebra the following relationship between the desired molar fraction of carbon dioxide in the bubble and the desired concentration of hydrogen ions in the water:

$$x = 1 - \frac{KNn_{CO2}^0}{KN(n_{CO2}^0 + n_N) + (K - h)hV_t}. \qquad (9)$$

The equations (6) and (9) constitute a closed-form mathematical model of carbon dioxide transfer usable for design of the treatment system.

8.3 The MH Systems' Ballast Water Treatment System Description

(Note: The Authors are cognizant that a large tanker of the size as 300,000 DWT may not be an ideal candidate for ballast water treatment features. However, this hypothetical design study can be easily modified for smaller tankers.)

The MH Systems Ballast Water Treatment System is a combination of two other effective treatment systems, i.e. deoxygenation and carbonation. It also is an extension of the MH Systems American Underpressure System - AUPS (Husain et al. 2001). The inert gas, supplied by the standard marine gas generator, is 84% nitrogen, 12-14% carbon dioxide and about 2% oxygen. This inert gas has all the ingredients necessary to combine the two very effective treatments of hypoxia and carbonation at a very reasonable cost. The laboratory tests at Scripps, described previously, show that this gas needs very little contact time to be effective. The analyses described earlier established the flow rates and control time for hypoxia carbonated conditions.

Each ballast tank has rows of pipe at the tank floor with downward pointing nozzles. The pressurized inert gas is jetted downward out of the piping. The jets stir up the sediment for contact with the inert gas bubbles. The bubbles then rise through the ballast water to the space above the water surface, which has previously been underpressurized to -2 psi. For the purposes of this paper, a 300,000 DWT single hull tanker was used for design studies of this system to test practicality and affordability. Applicability to a 300,000 DWT double hull tanker was also examined. Figure 2 shows inboard profile, deck plan view, piping layout, nozzle detail and section through ballast tank. Figure 3 shows schematic of the system and Figure 4 shows isometric of one tank. A 300,000 DWT double hull tanker has somewhat less installation costs since the tank bottom is smooth as shown in Figure 4.

For the 300,000 DWT tanker, there are 8 ballast tanks as follows in Table 2:

Table 2. Ballast Water Tank Capacity

Location	Size M^3	Ft^3
Fore Peak	8,265	291,875
B3S	32,200	1,137,000
B3P	32,200	1,137,000
B6S	16,048	567,000
B6P	16,048	567,000
B Engine Room S	1,645	58,000
B Engine Room P	1,086	74,000
Aft Peak	2,331	82,300
Totals	110,823	3,914,175

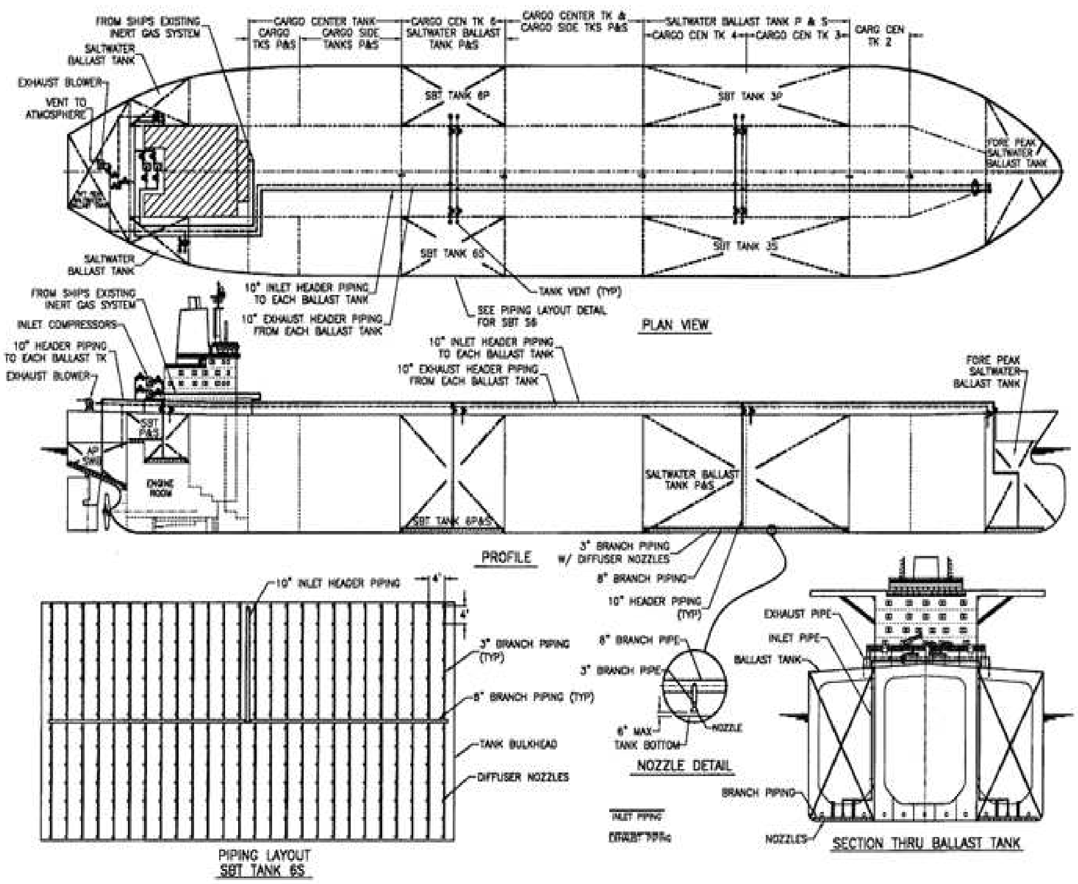


Figure 2

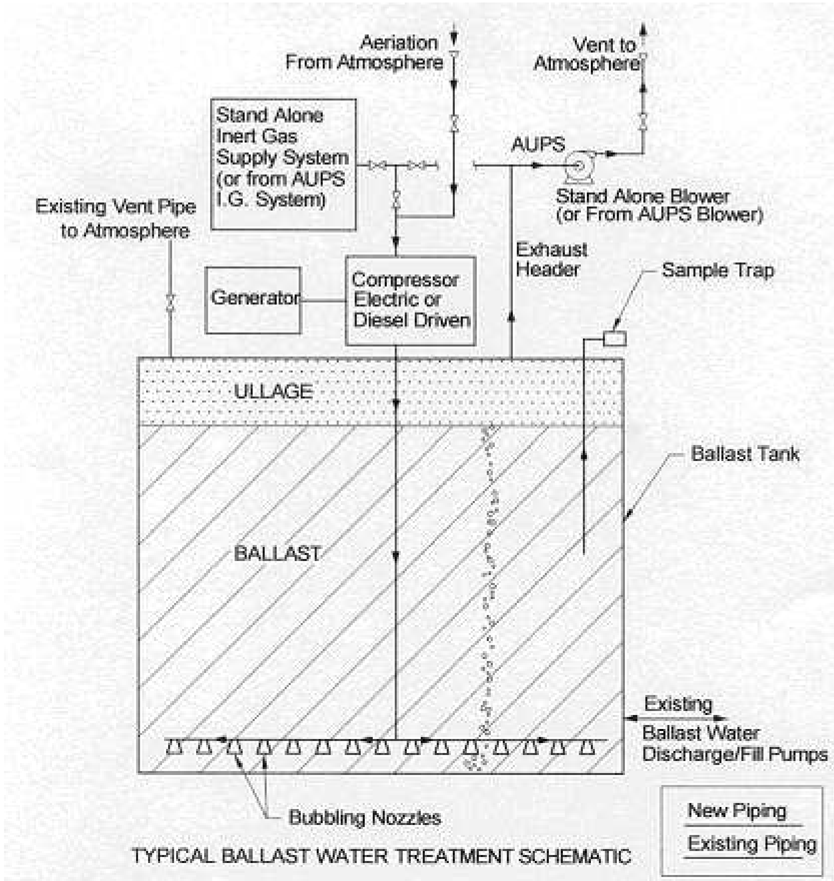
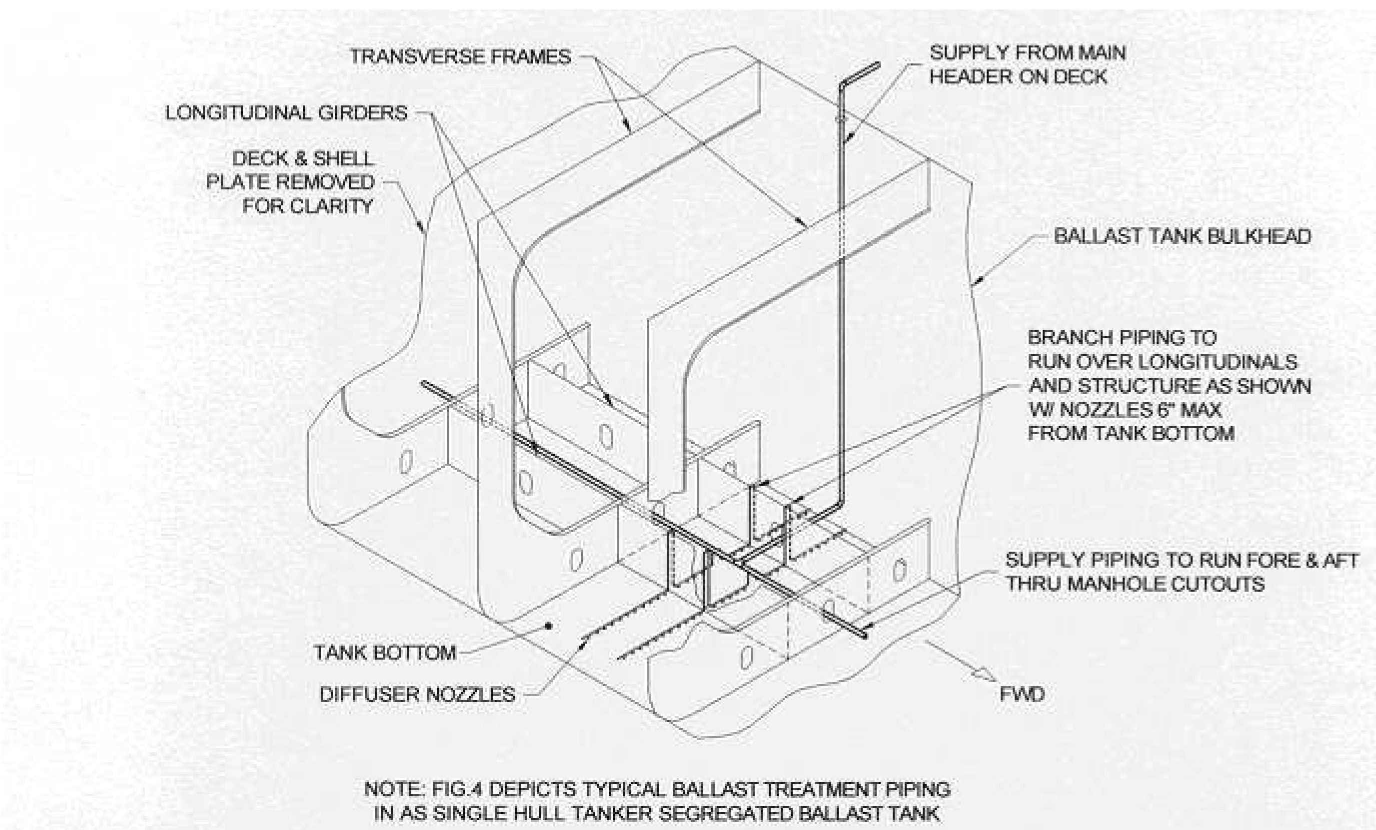


Figure 3



IN A DOUBLE HULL VESSEL THE PIPING SYSTEM IS SIMPLIFIED BY INSTALLING THE NOZZLE GRID ON THE TANK BOTTOM WITHOUT ANY STRUCTURAL INTERFERENCE.

Figure 4

From analyses and experience (Tamburri et al. 2002), it is estimated the hypoxia and pH conditions can be set in at least 8 hours, even in the largest tanks, B3 Port and Starboard. The flow rate is 1350 cfm for each of these tanks. With one 1500 cfm marine gas generator, and treating each tank sequentially, it is estimated that all 8 tanks can be in a hypoxia, low-pH (5.5 - 6) condition in less than 48 hours. Contact time for essentially total lethality may not require more than another 24 hours although the remainder of the 2 to 3 week voyage is available.

The space above the liquid in each tank is underpressurized to about -2 psi and maintained throughout the voyage. As the gas bubbles rise up to the surface, they are evacuated by a blower to maintain the underpressure of the inert gas blanket at the surface. The underpressure further facilitates the solubility of the oxygen (see analysis) and tends to compensate for the oxygen captured in the bubbles as they rise.

Since the ballast tanks are treated sequentially, only two 700 cfm compressors are required to compress the gas. The gas is compressed enough to offset the hydrostatic head plus an additional 25% psi to provide a jet force for stirring the sediment. Two compressors are provided for redundancy. If there are some concerns with the dumping of hypoxia and carbonated treated water, it is easily countered with the system discussed in this paper. The compressors will shift over from the gas generator to atmospheric and the ballast water will be oxygenated within just a few hours. In this same period of time the CO2 is readily washed out since the air contains no CO2 component.

Sensors are needed to monitor the pH to ensure that it never goes below about 5.5. Sensors will measure dissolved oxygen content to ensure that adequate deoxygenation is established. Sensors will also monitor the underpressure. The control system will remotely start and stop the gas generator, the compressor and the blower. The control system also remotely controls the valves off of the inert gas manifold to each ballast tank and the valving for the underpressure manifold.

It is expected that system will be controlled by a suitably designed arrangement of programmable logic controllers (PLCs). These devices are commercially available. They are also easy to program and maintain.

A control console with displays will integrate the functions of the inert gas generator and the AUPS ballast water treatment system as well as provide for monitoring, status displays and manual override, if required.

Tests were conducted with the AUPS System installed on a naval reserve fleet tanker. They verified the structural capability of tanks to withstand the pressure of -3 psi and the controls needed to maintain the required underpressure. These findings are applicable to the equipment and controls that will be used for the ballast water treatment system.

The following are the design features of the shipboard system:

- Dry docking is not required for the installation of the system. The system can be retrofitted at pier side
- The system includes mainly off-the-shelf components.
- The system is fully automated. Data can be transmitted in real time to a shore-side facility, if desired.
- Sensors are installed at different locations inside the tank to determine pH and oxygen levels.
- The system requires low maintenance.

8.4 Economic Evaluation of MH Systems' Ballast Water Treatment System for a 300,000 DWT Tanker

In making an economic evaluation, the analysis methodology described in Mackey et al. (2000) was used. This method states, "a logical basis for economic comparisons would be a change in Required Freight Rate (RFR)." Since there would be no change in cargo capacity, then:

$$\Delta RFR = \frac{[CRF(i,n) * \Delta P + \Delta Y]}{C}$$

where

$CRF(i,n)$ is Capital Recovery Factor for an interest rate i and n for economic payback years,

ΔP is change in Capital Cost, and

ΔY is net change in annual operating cost and revenue.

Mackey et al. (2000) stated that the economic payback period for conversions is typically 5 years.

The Authors selected a 300,000 DWT tanker for analysis. As stated earlier, a ballast water treatment system applicable for ships must have the capacity for treating huge quantities of ballast water. If a system is practical and economical for treating a ship with 8 ballast tanks of 110,823 cubic meters, then it is practical for all ship types. The economics would have to be assessed for ships of other, smaller ballast capacity, as the economics might not scale. But obviously, the effectiveness as well as the practicality of the system would be established.

Table 3 lists the principal parts and materials in the ballast water treatment system together with estimated prices and labour costs.

The total cost is approximately $3,057,100. All tankers already have some type of inert gas generating capability. The newer tankers have generators with a gas mixture discharge similar to the mix used in the experiments at Scripps. Nevertheless, for conservatism, the generator has been included in the cost. Similarly tankers probably have sufficient excess electrical capacity to supply the load of this equipment - the compressors and blower. This is especially true since this is on the return trip in ballast and the machinery will only run about 48 hours each trip. Nevertheless, again for extreme conservation, a 300 KW generator has been included.

To make a usefully indicative estimate of operating costs, the following assumptions were made:

- The tanker will operate to 360 days per year.
- Six (6) voyages per year between Persian Gulf and USA.
- Half of the voyages are return trips in ballast, or 6 trips a year.
- Assume the 2 compressors and blower must operate 48 hours to obtain hypoxia and carbonation in all 8 tanks (note that actually the cfm of both compressors is only required for tanks B3 port and starboard and B6 port and starboard.
- Operating costs are primarily the fuel costs for the inert gas generator and the 300 KW generator.
- n is 5 years (economic payback period) and i (interest rate) is 8%.

PRELIMINARY COST ESTIMATE FOR BALLAST WATER TREATMENT SYSTEM
Note: Labor Cost is Based on US Repair Shipyard Estimates

Parts and Materials	Capacities or Type	Quantity/ Unit	Price/Unit	Material Cost	Labor Cost	Material & Labor
Blower (Exhaust)	2000 CFM-100HP	1	$ 10,000	$ 10,000	$ 75,000	$ 85,000
Reciproacting Compressor	Electric-700 CFM-100HP	2	$ 40,000	$ 80,000	$ 50,000	$ 130,000
Inert Gas Generator -	1500 CFM - 50HP	1	$ 175,000	$ 175,000	$ 150,000	$ 325,000
Row of Pipes at Tank Bottom PVC	3" SCH 80; Length in Ft.	15000	$ 2	$ 30,000	$ 52,500	$ 82,500
Header Branch Piping - PVC	8" SCH 80 "	1000	$ 5	$ 5,000	$ 105,000	$ 110,000
Header Piping - PVC	10" SCH 80 "	1800	$ 7	$ 12,600	$ 252,000	$ 264,600
Header Piping - Steel	10SCH 40 (Steel)	2000	$ 22	$ 44,000	$ 650,000	$ 694,000
Brackets	Steel	2000	$ 30	$ 60,000	$ 35,000	$ 95,000
Valves-Electric (Ballast)	10" Butterfly	16	$ 4,500	$ 72,000	$ 7,000	$ 79,000
Valves-Electric (Inert Gas)	10" Butterfly	2	$ 4,500	$ 9,000	$ 1,000	$ 10,000
Diffusers	Coarse Bubbles	2600	$ 50	$ 130,000	$ 10,000	$ 140,000
Fittings (Elbows,Tees, Couplings)	PVC	4000	$ 20	$ 80,000	$ 140,000	$ 220,000
Generator	300 KW	1	$ 60,000	$ 60,000	$ 15,000	$ 75,000
Sub-Total Materials				$ 767,600		
Sub-Total Labor					$ 1,542,500	
Sub-Total -Materials & Labor						$ 2,310,100
Sensors, Controllers & Computer						
pH Gages		16	$ 1,000	$ 16,000		
Pressure Gages for Ullage space		16	$ 500	$ 8,000		
Pressure Controllers for Ullage		16	$ 1,000	$ 16,000		
Controller For Compressor		2	$ 500	$ 1,000		
Oxygen Sensor		16	$ 500	$ 8,000		
Controller For Valves		16	$ 500	$ 8,000		
Electrical		1	$ 40,000	$ 40,000		
Computer Software & Hardware		1	$ 50,000	$ 50,000		
Sub-Total - Material				$ 147,000		
Labor for Installation				$ 250,000		
Sub-Total - Material & Labor						$ 397,000
Other Costs:						
Engineering & Maintenance						$ 350,000
TOTAL BW SYSTEM COST						$ 3,057,100

Table 3. Ballast Water Treatment by De-oxygenation with Elevated CO2 for a Shipboard Installation - An Affordable Solution

If the gas and electric generators operate 48 hours for each of 6 voyages, then the total operating time is 288 hours per year for each generator. About 6,000 gallons of diesel fuel would be consumed by the electric generator and for the gas generator about 16,500 gallons. This is a total of 22,500 gallons. At a cost $1.25 per gallon, the yearly operating cost will be about $28,125. Considering the few hours per year that the machinery operates and the fact that the ship has no cargo and therefore less requirements of the crew, minimal cost has been allocated for maintenance.

Therefore:

$$
\begin{aligned}
CRF(i,n) &= 0.25 \\
\Delta P &= 3{,}057{,}100\ (dollars) \\
\Delta Y &= 28{,}125\ (dollars) \\
C &= 300{,}000\ Tons
\end{aligned}
$$

$$
\begin{aligned}
RFR &= \frac{0.25 \times 3{,}057{,}100 + 28{,}125}{300{,}000 \times 6} \\
&= \$.44 / ton
\end{aligned}
$$

In estimating the cost of treatment per ton of ballast water, the estimated annual operating costs of $28,125 is used. The approximate 4 million cubic feet of ballast is 128,000 tons. Six trips are made in ballast, which is a total of 768,000 tons treated. Therefore, cost of ballast water treatment is 3.7 cents per ton.

This ballast water treatment system is focused on treating the huge amounts of ballast water discharged into US harbours. It has the capacity to readily treat these huge quantities using standard marine components. For tankers that already have the major components on board, it would be very affordable. And for tankers with the AUPS spill containment, the added cost would be even less expensive.

Also, it appears (although not tested) that this system may be adequately effective in treating sediments. Ballast Water Exchange leaves sediment and other residue untreated. In fact, only the filtration concept treats sediment, by eliminating it.

9. Conclusions and recommendations

9.1 Conclusions

Based on the preliminary study, we conclude that a combination of hypoxia and elevated CO2 levels are expected to kill in excess of 95% of marine phytoplankton, zooplankton, macroalgae, and invertebrates as required by the interim standard proposed by the US Congress. The treatment system proposed requires only off-the-shelf components which can be installed at pier side, without dry-docking. The system can be fully automated. Installing pH and oxygen sensors at multiple locations inside the tank can assure continuous remote monitoring of the ballast water.

9.2 Recommendations

It will be necessary to continue the laboratory tests, especially to include experiments on the effects of the system on phytoplankton, cysts and spores. In addition, the practical application of the system should be verified in a large scale effort using land based tanks or ballast water tanks in ships.

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11. Nomenclature

c	concentration of carbon dioxide in the water, including ions produced by electrolytic dissociation.
g	acceleration due to gravity.

h	concentration of hydrogen ions in the water.
K	dissociation constant of carbonic acid (= 4.3 x 10^{-7} mol/liter).
k	reaction rate constant.
k_H	Henry's Law constant for oxygen (= 39.79 x 10^{-6}).
N	total number of bubbles generated.
n	total number of gas moles in the bubble.
n_{CO2}	number of moles of carbon dioxide in the bubble.
n_N	number of moles of nitrogen in the bubble.
p	total pressure inside the bubble.
p_{CO2}	partial pressure of carbon dioxide in the bubble.
Q	gas weight flow rate.
t	time.
u	bubble speed.
V_t	volume of the tank.
x	molar fraction of carbon dioxide in the bubble.
Y	weight fraction of oxygen in the water.
y	molar fraction of oxygen in the bubble.
rho	density of the ballast water.

Superscript 0 refers to quantities in the gas bubble when it is first introduced into the tank.
Subscript 0 refers to quantities in the water at the time t=0.

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