

Current Perspectives on Ozone Chemistry in Marine Life Support Systems

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Abstract

Ozone (O_3), with a standard redox potential of 2.07 V (1.60 V at pH 8.00), is the current gold standard for disinfection of marine aquaria. This paper addresses the fundamentals of aqueous ozone chemistry with an eye toward marine life support systems (LSS) operations. We begin by addressing ozone and total residual oxidant (TRO) measurement methodologies and a discussion of the role of oxidation reduction potential (ORP) determination. We then focus on the disinfection process and the organic and inorganic reaction chemistry at play. Included here is a discussion of the effect on a bacterial cell wall, its reactivity with dissolved organic carbon (DOC), and bromide ion (Br^-). The dynamic model of hypobromous acid (HOBr) and bromate ion (BrO_3^-) production is addressed. We use this chemistry knowledge in LSS design, and present an ozone reactor sizing scheme. This is extended to an existing foam fractionation design model that incorporates particulate matter (PM) and DOC. Finally, we propose ideas for future research on advancing these existing models.

Introduction

Water is the life blood of an aquarium and its inhabitants. In the words of Jacques Yves Cousteau, “No aquarium, no tank in a marine land, however spacious it may be, can begin to duplicate the conditions of the sea” (Keaffaber et al., 2008). This statement brings front and center the design and operations challenges that we face as life support system (LSS) operators, engineers, and researchers. LSS feature many chemical processes. Almost all of these are oxidation-reduction and acid-base reactions. An understanding of these processes is central to ensuring sound operations and design. Ozone disinfection chemistry is tied to both reaction types.

TRO Measurement

Several well known methods have been used to measure TRO concentration in aquaculture. These techniques include several different variations of iodometric titrations, DPD (*N,N*-diethyl-*p*-phenylenediamine), and ORP. These methods have been designed to measure chlorine-containing oxidants, but they are not specific to chlorine. They also may be used to determine levels of bromine-containing oxidants and ozone. These methods have been compared for seawater (Buchan et al., 2005), and the DPD test was preferred based on convenience and performance. ORP, while not a direct measurement of TRO concentration, was observed to increase rapidly in seawater from a starting value of 350 mV to 700 mV at a relatively low ozone dose of 25 mg/h. At higher doses (100 mg/h), ORP values of near 800 mV were observed (Buchan et al., 2005). This result is consistent with exhaustive ozonation experiments of sodium bromide (NaBr) solutions where ORP values of approximately 800 mV were observed (Grguric et al., 1994). The TRO associated with an ORP of 800 mV was determined to be hypobromous acid (HOBr) and its conjugate base hypobromite ion (BrO^-), not ozone, and we will discuss these experiments later.

ORP Theory and Practice

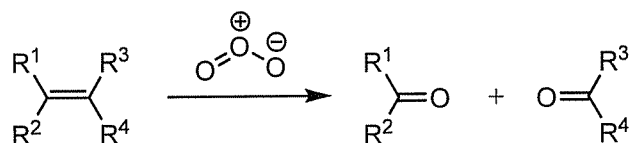
ORP is used to monitor chemical reactions, quantify ion activity, or determine the oxidizing or reducing properties of solutions. In oxidation-reduction reactions, electrons are transferred from one substance to another. In a reduction reaction, a substance gains electrons, and in an oxidation reaction a substance loses electrons. Both reactions are coupled together as a pair until equilibrium is established. The ORP value (mV) represents all redox reaction products taken together. It is important to note that while TRO concentration (ppm or mg/L) can be loosely

correlated to an ORP value or range, there is no absolute correlation. For example 0.05 ppm (mg/L) BrO^- and 0.5 ppm BrO^- would both, most likely, give an ORP around 800 mV.

ORP provides the operator with a quick indication of the disinfection potential of water. For a food produce application, *E. coli* and *Salmonella* are killed in 30 seconds when an ORP of 650-700 mV are maintained (Suslow, 2004). These ORP levels represent typical chlorinated systems where hypochlorous acid (HOCl) and hypochlorite ion (ClO^-) are the dominate oxidants.

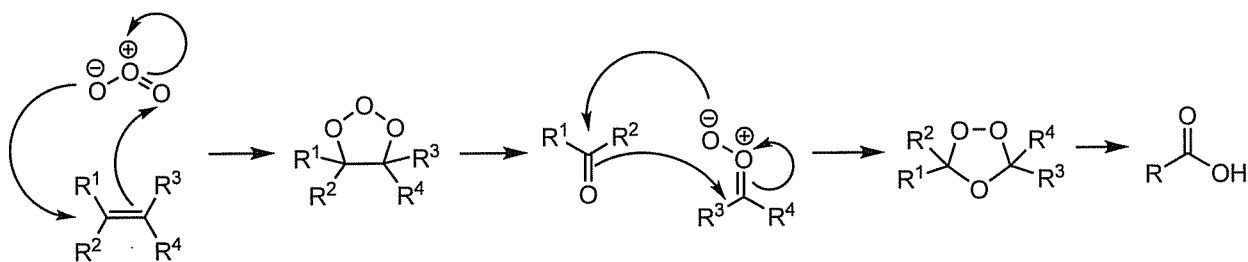
Primary Ozone Disinfection – An Organic Reaction Mechanism

The general idea requires that ozone be generated, transported, mixed, and dissolved in a column of seawater. Once dissolved in the aqueous phase, ozone reacts with electron-rich organic materials. Disinfection occurs when the ozone molecule reacts with a bacterial cell wall. Long organic chains in the cell wall are oxidized and carbon-carbon double bonds begin to break. This causes a hole to form in the cell wall, and the cell contents leak out, killing the organism.



Scheme 1. General reaction of ozone with carbon-carbon double bond in bacterial cell wall.

The reaction proceeds by the Criegee mechanism (Criegee, 1975). Each step of the process involves oxygen-rich ring systems that rearrange to form carboxylic acids (RCO_2H) under oxidative conditions.

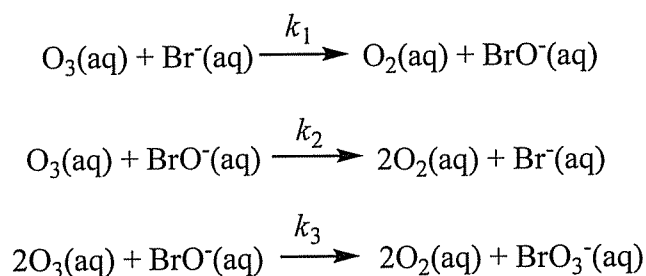


Scheme 2. The Criegee mechanism (of disinfection) detailed.

A secondary process involving the ozone disinfection byproduct, hypobromous acid (HOBr), also causes the cell wall to break. Again the carbon-carbon double bonds are oxidized while the bromine atom inside the hypobromous acid molecule is reduced to bromide ion (Br^-). The neutral (uncharged) hypobromous acid is a more effective disinfectant in comparison to its conjugate base hypobromite ion since it can interact with the non-polar (uncharged) carbon chains of the cell wall. This process is exactly analogous to a chlorinated system where hypochlorous acid (HOCl) is the active disinfection agent.

Secondary Disinfection Byproduct Formation – An Inorganic Reaction Mechanism

A series of inorganic reactions of ozone with bromine species have been shown to form disinfection byproducts (Haag and Hoigne, 1983).



Scheme 3. Formation of hypobromite and bromate ion when ozone reactions with bromide ion.

For the above reactions at 20°C, $k_1 = 160 \text{ L mol}^{-1}\text{s}^{-1}$, $k_2 = 330 \text{ L mol}^{-1}\text{s}^{-1}$, and $k_3 = 100 \text{ L mol}^{-1}\text{s}^{-1}$. Each of these second order rate constants is on the order of 10^2 , and these reactions are considered fast. In Scheme 3, ozone in solution oxidizes bromide ion (Br^-) to hypobromite ion (BrO^-), and then the bromine atom in hypobromite ion can be reduced back to bromide ion or oxidized to bromate ion (BrO_3^-). Taken together, the first two reactions catalytically destroy ozone in the presence of bromide ion. The bromate ion is stable and cannot be oxidized further under aquarium conditions (Grguric, et al., 1994). If oxidized brominated ions persist, they can have a deleterious effect on marine life (Steslow, 1991).

Acid-Base Chemistry of Hypobromous Acid and Hypobromite Ion

When a buffer system of a conjugate acid / base pair is present, the Henderson-Hasselbach equation may be used to calculate the concentration ratio of the base to acid depending on pH.

$$\text{pH} = \text{pKa} + \log \frac{[\text{BrO}^-]}{[\text{HOBr}]} \quad (1)$$

For the acid dissociation reaction: $\text{HOBr(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{BrO}^-(\text{aq})$, the K_a expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HOBr}]} \quad \text{and } \text{pKa} = -\log K_a \quad (2)$$

The pKa of HOBr is 8.55 at 25°C. So at pH 8.00, the BrO^-/HOBr ratio is 0.282. In other words, the mixture is 22% BrO^- and 78% HOBr at this pH. For reference, at pH 7.55, the ratio is 0.100. The ratio at pH 8.55 is exactly 1.00.

Ozonation of Pure Solutions

For most practical natural and artificial seawater applications, aquarium ozone contact times are only seconds to 1-2 minutes per cycle, and almost all of these now use ozone on a side-stream injection process which may incorporate fractionation. During such a short time period, the formation of oxidized bromine species, especially bromate ion, does not proceed to any appreciable extent, making their measurement difficult. To overcome this, we ozonated separate solutions of distilled water, pure sodium chloride (468 mM), and sodium bromide (722 μ M). These concentrations of NaCl and NaBr are those that correspond to seawater with a salinity of 30 g/kg (o/oo). Ozone time varied from 100-300 min to allow ozone concentrations in these solutions to reach steady state. Long duration ozonations were especially helpful to study the formation of bromate ion which increased linearly with time.

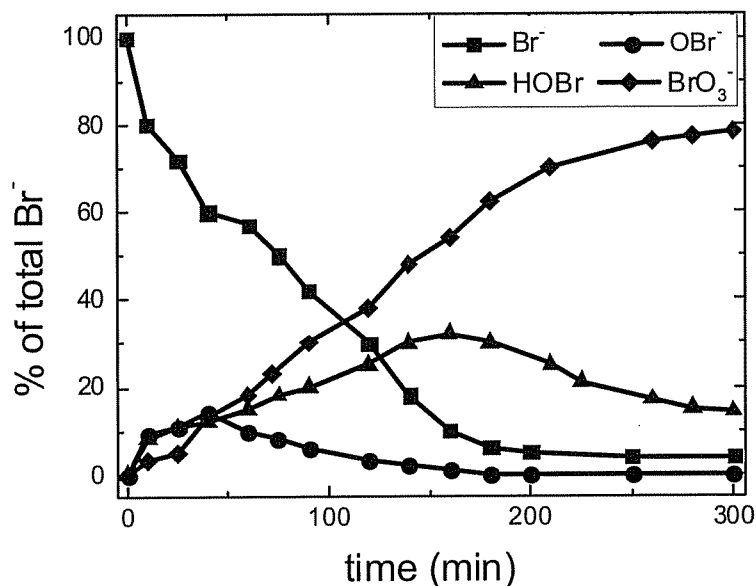


Figure 1. Bromine speciation vs. time during ozonation of 722 μ M NaBr.

After 300 min of continuous ozonation, about 80% of the bromine in the solution had been converted to bromate ion. The solution was unbuffered and the pH was observed to drop from

8.8 to 7.0 during this time period. The change in bromine speciation versus time shows that, during the oxidation of bromide ion to bromate ion, BrO^- acts as an intermediate. This is consistent with the mechanism shown in Scheme 3.

The ORP of all solutions were initially between 350 and 500 mV, and a rapid increase was observed upon ozonation. After just 20 min of ozonation, the distilled water sample and the NaCl solution reached 1050-1150 mV. These values confirmed that dissolved ozone residuals were present in solution. The rate constant for chloride ion oxidation in the presence of ozone is $3.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ (Bousher, et al., 1986). Therefore, in the NaCl solution, the rate of ozone dissolution far exceeded the rate of chloride ion oxidation. However, during the ozonation of NaBr, an ORP plateau of 830 mV was achieved for 160 min. This value was observed while there was no measurable ozone in solution indicating that this is the ORP of oxidized bromine species, primarily the more reactive hypobromite ion. A second plateau was then achieved after a total reaction time of 180 min. At this point the hypobromite ion concentration was effectively zero and the ORP resembled those achieved for distilled water and the NaCl solution.

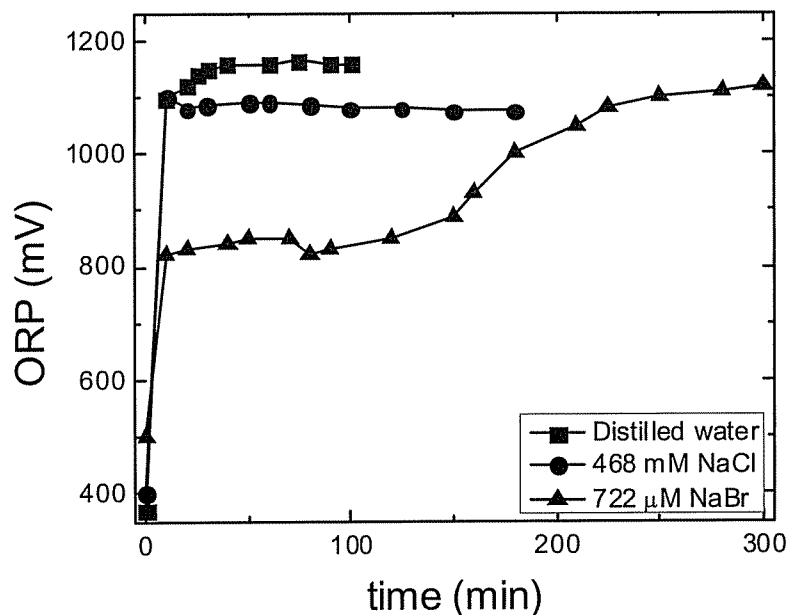
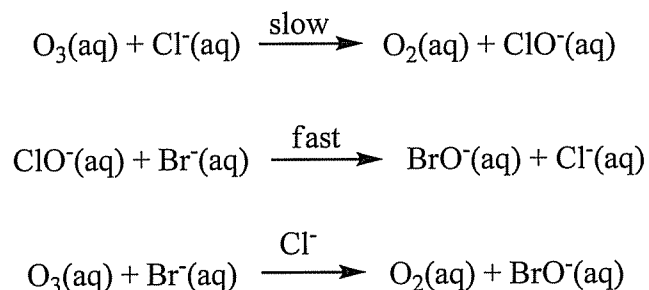


Figure 2. Values for ORP vs. time for ozonation of distilled water, NaCl, and NaBr solutions.

Ozonation of Mixed NaCl / NaBr Systems

Production of bromate ion is enhanced in a mixed NaCl/NaBr solution which can be used as a model of a natural seawater system. Further, no bromate ion is formed during the long term, exhaustive ozonation of pure NaCl solution. In addition to the reactions cited in Scheme 3, the following reactions involving hypochlorite ion occur in mixed solutions:



Scheme 4. Production of hypobromite ion in the presence of chloride ion.

The oxidation of bromide ion by hypochlorite ion in the mixed solution occurs rapidly with a rate constant of $6.77 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ (Bousher et al., 1986). The rate constant ratio for the first two reactions in Scheme 4 above is 4.4×10^{-7} clearly showing that the first step is the rate limiting step. The last reaction in Scheme 4 is the overall reaction. Further, the reaction of hypochlorite ion with bromide ion to produce BrO^- is two orders of magnitude (10^2) faster than reaction of ClO^- with ozone to produce chlorate ion (ClO_3^-). These results allow us to conclude that as long as there is bromide ion present in solution, chloride ion acts as a catalyst to enhance production of hypobromite ion. Hypochlorite ion, to the very small extent that it is produced, is only a transitory species that is consumed rapidly by any measureable bromide ion in solution. Lastly, the slight enhancement in hypobromite ion concentration is also responsible for an increase in bromate ion production.

An Ozone Kinetics Model

A model was developed for ozone contact times of ~2 min to follow reactions of ozone with bromine species in an aquarium LSS. The initial conditions used in the model were those measured in the aquarium. Changes in concentration of dissolved species with time (t) were calculated by numerical integration using time increments that were small enough to avoid significant changes in the concentration of any species in delta t. The time increments selected were 0.01 min over the 0-0.6 min time interval, and 0.1 min during the 0.6-2.1 min time interval. The differential equations 3-5 and included rate constants were based on existing kinetic data (Haag and Hoigne, 1983).

$$-\frac{d[O_3]}{dt} = k_1[Br^-][O_3] + (k_2 + 2k_3)[BrO^-][O_3] \quad (3)$$

$$\frac{d[HOBr]}{dt} = k_1[Br^-][O_3] - (k_2 + k_3)[BrO^-][O_3] \quad (4)$$

$$\frac{d[BrO_3^-]}{dt} = k_3[BrO^-][O_3] \quad (5)$$

The concentration $[BrO^-]$ can be calculated using $[HOBr]_{total}$, pH, and pKa for hypobromous acid using the Henderson-Hasselbach equation (1) above. Equations 3-5 were solved for d[species] (of interest), knowing the initial concentration of species at the start of the time interval.

Several experiments were designed to test the model. In one experiment, distilled-deionized water was ozonated, and then the ozone generator was turned off. At this point pure NaBr was added. Changes in pH were measured continuously and concentrations of ozone, hypobromite

ion, and bromated ion were measured after a 2 min mixing time. Observed and predicted concentrations are given in Table 1 (Grguric, et al., 1994).

Table 1. Observed and predicted concentrations of ozone and bromine species at 2.0 min after addition of pure NaBr to ozonated distilled-deionized water.

Solution	[O ₃]init (uM)	Concentration after 2.0 min (uM)			
		[O ₃]	[BrOH]total	[BrO ₃ ⁻]	[Br ⁻]
722 uM NaBr, obs	194	<10	120	<2	602
722 uM NaBr, model	194	0	136	6	580
144 uM NaBr, obs	241	<10	80	13	51
144 uM NaBr, model	241	25	83	14	47

In all, Table 1 shows fairly good agreement between the observed and the model generated values.

These results indicate that a kinetic model may be used for a self-contained marine system. The Living Seas served as suitable test system. An initial ozone concentration was calculated from the ozonator output and the volume of the pipe where contact occurs. The ozone contact was 2.1 min and the initial concentration was calculated to be 0.766 uM (0.0368 mg/L or ppm). The pH in the model was kept constant at 8.0, a typical average pH. The buffer capacity of the system was approximately 3000 times greater than the amount of ozone delivered so no change in pH occurred. The concentration of total bromine-containing species was 57 uM (4.6 mg/L). All of this bromine was originally bromide ion at the start of operations. Table 2 shows the results of running five variations of the model (Grguric, et al., 1994).

Table 2. A model for concentrations of ozone and ozone byproducts after a reaction time of 2.1 min.

Model	[O ₃] (μM)	[HOBr] _{total} (μM)	[BrO ₃ ⁻] (nM)	[HOCl] _{total} (μM)	[Ox. Organic] (μM)
Initial	0.766	0.00	0.00	0.000	0.000
1	0.238	0.52	0.25	—	—
2	0.231	0.51	0.25	—	—
3	0.197	0.49	0.22	0.065	—
4	0.197	0.55	0.25	0.001	—
5	0.194	0.55	0.25	0.001	0.007

1, Reactions between ozone and bromine species only; 2, reaction of ozone and OH⁻ added; 3, reaction of ozone with 400 mM Cl⁻ added; 4, reaction between ClO⁻ and Br⁻ added; 5, phenol (0.1 μM), an oxidizable organic compound (representing DOC) added to the model.

From the results of this model, it is clear that although the chloride ion concentration is about 10⁴ times greater than the bromide ion concentration, bromide ion is the primary oxidized inorganic species during an ozonation cycle. Of the two principle species formed during the oxidation of bromide ion, hypobromite ion is the more abundant, but less stable species. Bromate ion, on the other hand, is stable under aquarium conditions. Over a six year period the bromate ion concentration can be calculated and it was 4.5 μM (0.58 mg/L). The calculated result is very close to the measured value of 5 ± 1 μM considering the uncertainties in contact time and initial ozone concentration.

A Hypothetical Ozone Reactor Design Model

An ozonation system was designed for a mixture of pathogens where the 99.9% killing concentration-contact time was found to be 0.621 (mg min) / L. The ozone reactor was sized for a one minute contact time by solving the following proposed equations (Sugita et al., 1992).

$$\frac{\pi r^2 h}{Q} = 1 \text{ min} \quad (6)$$

$$h = cr \quad (7)$$

The flow rate through the reactor is Q . The reactor radius and height are r and h respectively, and c is an arbitrary constant that is used to obtain h as a function of r . For a one-tank system with $c = 5$, a 1.0 m diameter tank with a height of 2.5 m will be required. The calculated flow rate through the reactor is $1.96 \text{ m}^3/\text{min}$ (518 gpm). To achieve a concentration-contact time of 0.621 (mg min)/L , $1.23 \text{ g O}_3/\text{min}$ would be required to be injected into the reactor. It should be cautioned that bromide ion present in natural or artificial seawater can result in levels of brominated disinfection byproducts. It is always good practice to monitor ozone doses during the start-up and operation period of the reactor (Richardson, 2005).

A Hypothetical Foam Fractionator Design Model

Foam fractionation is a mixed phase process that relies on the gas bubble surface to provide a site for the accumulation of dissolved organic matter, a mixture of long chain hydrophobic molecules and surfactants. During the process, bubbles of air or ozone-concentrated air are introduced to a column of water. This may be accomplished using positive (high) or negative (low) pressure techniques. Porous stones deliver the gases at higher pressures and venturi injection draws a fine mist of gases into the water using lower pressures. Much of this organic material is oxidized, forming foam waste that is carried to and deposited at the top of the fractionator column.

Foam fractionation has also proven to be a facile method for removing small particles (particulate matter, PM) that could pose health risks to fish (Chen, et al., 1993). Foam fractionation devices, also called protein skimmers, are quite efficient at removing solids, and they complement other well-known filtration techniques, such as high pressure sand and granular activated carbon (GAC) filters. A model of the separation process has been proposed, and it is

quite complex (Timmons, et al., 1995). The rates of dissolved organic carbon and particulate removal are given by

$$-\frac{d[\text{DOC}]}{dt} = \beta_1[\text{DOC}] \quad (8)$$

$$-\frac{d[\text{PM}]}{dt} = \beta_2[\text{PM}] \quad (9)$$

where β_1 and β_2 are complex functions of several parameters, including air flow, bubble size, particle size, and fractionator size. Assuming a single foam fractionator, 1 m tall, with a 0.2 m column diameter ($\sim 0.03 \text{ m}^2$ footprint), 0.333 L/s air flow, and 1 mm mean bubble radius, β_1 and β_2 are determined to be $192/d$ and $255/d$, respectively, using the Timmons model. Equations 10 and 11 below are used to find the respective steady-state concentrations with a single foam fractionator. Assuming a system that has $[\text{DOC}] = 0.30 \text{ ppm}$ and $[\text{PM}] = 0.27 \text{ ppm}$, addition of a second, foam fractionator of equal size will cut these values in half and add redundancy to the LSS.

$$m_{\text{DOC}} = (0.55 - 0.475p)F \quad (10)$$

$$m_{\text{PM}} = 0.45F \quad (11)$$

In equation 10 and 11, the mass (kg) of DOC and PM was determined empirically in aquaculture studies. Here, F is the mass (kg) of food required per day and p is the fraction of protein in the feedstock (El-Shafai, et al., 2004).

Conclusions and Future Work

In our future research, we plan to extend the application of the ozone kinetics model to several other aquarium facilities with natural and artificial seawater life support systems. This will create a bromine species distribution data base that can be shared with aquarium operators. In addition, we intend to investigate the Timmons foam fractionation model in much more detail with an eye toward using ozone enriched air as the fractionator feed gas. Finally, ozone is used widely in our industry, and foam fractionation is ever growing in its popularity. New mathematical models that marry these two processes are vital to advance LSS theory and practice!

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