Ozone – an Emerging Technology for the Seafood Industry

Alex Augusto Gonçalves*
Center of Water Resources Studies; Department of Civil & Resource Engineering; Dalhousie University; Halifax;
NS; B3J 1Z1; Canada

ABSTRACT

In recent years, increasing attention has been focused on the safety of foods, and in particular on the intervention methods to reduce and eliminate human pathogens from fresh product, especially fresh seafood. Traditional technology utilizes water with or without a sanitizing agent to wash fresh seafood. Chlorine is the most widely used sanitizing agent available for fresh product, but it has a limited effect in killing bacteria on seafood surfaces. An alternative treatment is being sought to improve food safety. Many research and industrial trials are underway to validate the use of ozone in the food industry. This article intends to show a clean technology to be applied in seafood industry and to show that many studies must be done to demonstrate the best concentrations and the best methods of ozone applications in diverse seafood species, so that the governments of all the countries can approve their application in the fishing industry.

Key words: Clean technology, ozone, seafood

INTRODUCTION

Ozonation has been used for years to disinfect water for drinking purposes in Europe. A number of other commercial uses have been found for ozone including disinfection of bottled water, swimming pools, prevention of fouling of cooling towers, and wastewater treatment (Rice, 1997; Silva; Gibbs and Kirby, 1998; Tech Brief, 1999; Duguet, 2004; Guzel-Seydim et al., 2004).

Since the 1920’s scientists have tried to take advantage of long-range disinfection characteristics from ozone, as to slow down the decomposition, as it improve the security of fishing products. The recent advances in electronics and technology of ozone have allowed the development of new line of compact ozone generators (Rice; Farquhar and Bollyky, 1982; Brooks and Pierce, 1990; Wu et al., 2007).

Ozone is one the most powerful antimicrobial substance (natural sanitizing and disinfecting agents) in the world destroying up to 99.9% of pesticides and microorganisms commonly found on food due to its potential oxidizing capacity. Any pathogen or contaminant that can be disinfected, altered or removed via an oxidation process will be affected by ozone. It is the strongest of all molecules available for disinfection in water treatment, and is second only to elemental fluorine in oxidizing power (Rice; Farquhar and Bollyky, 1982; Glaze; Kang and Chapin, 1987; Silva; Gibbs and Kirby, 1998; King, 2001; Duguet, 2004).

Ozone use may have many advantages in the food industry. There are suggested applications of ozone in the food industry such as food surface hygiene, sanitation of food plant equipment, reuse of waste water, lowering biological oxygen.
demand (BOD) and chemical oxygen demand (COD) of food plant waste (Ravesi; Licciardello and Racicot, 1988; Brooks and Pierce, 1990; Rice, 1997; Tech Brief, 1999; King, 2001; Ibanoglu, 2002; Wu et al., 2007).

In the United States, ozone has received in 1997 GRAS (Generally Recognized as Safe) classification, and in 2001 the FDA officially approved media containing ozone for use in the food industry, also for direct contact with food products, including fish, meat and poultry (Mielcke and Ried, 2004; Vaz-Velho et al., 2006; Zentox, 2007).

Multifunctionality of ozone application makes ozone a promising agent. Ozone already has been used in the fishing industry, although of predominantly experimental way and little documented. There are some articles that occasionally have been presented in conferences, and surely are also internal information of the institutes of fishing technology on the subject. Nevertheless, until now, there is little known about that (Seafish, 1997; Ravesi; Licciardello and Racicot, 1988; King, 2001).

This review intends to offer a basic introduction on ozone, mainly its chemical properties, generation, antimicrobial properties, application on food surfaces, application on food plant equipment as an alternative sanitizer, and some of the potential uses that have been investigated until now, as well as the possible risks to the health and the security.

LITERATURE REVIEW

What is ozone?
Ozone (O₃) is an allotropic form of oxygen (O₂), i.e., it is made up of same atoms, but they are combined in different form. The difference is the presence of three oxygen atoms, whereas “common oxygen” has only two. It has low molecular weight (MW = 48) whose three oxygen atoms chemically are arranged in chain. Ozone is then enriched oxygen (O₃) (Seafish, 1997; Tech Brief, 1999; King, 2001; Duguet, 2004; Guzel-Seydim et al., 2004; Chawla, Bell and Marlene, 2007).

How is ozone formed?
The ozone production takes place generally by the ventilation of electrical discharges of high voltage in the air or pure oxygen (Seafish, 1997; Tech Brief, 1999; Guzel-Seydim et al., 2004)

This radiation affects a common oxygen molecule that is found in atmosphere which produces the split of the molecule and separation of free oxygen atom. These atoms collide with other oxygen molecules, forming therefore ozone molecules (Kogelschatz; Eliasson and Hirth, 1988; Duguet, 2004; Chawla, Bell and Marlene, 2007).

- The energy absorbed by an oxygen molecule break it in two oxygen atoms.
  \[ O₂ + hv \rightarrow O + O \]

- Each one of these atoms is joined to an oxygen molecule to give another one of ozone.
  \[ O + O₂ \rightarrow O₃ \]

- Finally, the ozone molecule is destroyed again absorbing more ultraviolet radiation.
  \[ O₃ + hv \rightarrow O + O₂ \]

Ultraviolet energy is absorbed in a closed cycle of formation and destruction of the ozone.

In order to generate ozone, a diatomic oxygen molecule must first be split. The resulting free radical oxygen is thereby free to react with other diatomic oxygen to form the triatomic ozone molecule. However, in order to break the O–O bond, a great deal of energy is required (Kogelschatz; Eliasson and Hirth, 1988; Rice, 1997; Seafish, 1997; Bocci, 2006).

Ultraviolet radiation (188nm wave length) and corona discharge methods can be used to initiate free radical oxygen formation and, thereby generate ozone. In order to generate commercial levels of ozone, the corona discharge method is usually used (Duguet, 2004; Guzel-Seydim et al., 2004; Bocci, 2006; Ozone Solutions, 2007).

Corona discharge method
There are two electrodes in corona discharge, one of which is the high tension electrode and the other is the low tension electrode (ground electrode). These are separated by a ceramic dielectric medium and narrow discharge gap is provided (Fig. 1). When the electrons have sufficient kinetic energy (around 6–7 eV) to dissociate the oxygen molecule, a certain fraction of these collisions occur and a molecule of ozone can be formed from each oxygen atom (Guzel-Seydim et al., 2004; Ozone Solutions, 2007).
Ozone – an Emerging Technology for the Seafood Industry

If air is passed through the generator as a feed gas, a 1-4% of ozone can be produced. However, use of pure oxygen allows yields to reach 6 to 14% ozone. Consequently, ozone concentration cannot be increased beyond the point that the rates of formation and destruction are equal. Ozone gas cannot be stored since ozone spontaneously degrades back to oxygen atoms (Guzel-Seydim et al., 2004).

Advantages of Corona Discharge

- High ozone concentrations;
- Best for water applications;
- Fast organic (odor) removal;
- Equipment can last for years without maintenance.

Ultra-violet lamp

The method is based on conversion of oxygen on ozone molecules by lam of ultraviolet light (wavelength of 188nm, Fig. 2). Nevertheless, the ozone production is of low intensity. At low temperatures, the process of ozone ventilation is made with greater facility. The ozone formed, after certain period of time, is degraded spontaneously in oxygen (Ozone Solutions, 2007).

Advantages of UV Light

- Simple construction
- Lower cost than corona discharge
- Output hardly affected by humidity
- Less by-products vs. corona discharge

Properties of ozone

Ozone is one of the oxidants more powerful than they are known, and for this reason it has a strong capacity of disinfection and sterilization. Their disinfectants properties are superior to those of oxygen (Table 1): it is a powerful germicide which destroys all class of bacteria and fungi, not allowing their development. The high chemical reactivity of ozone is related to its stable electronic configuration which impels to look for electrons from others molecules. During the reaction with other molecules, ozone is destroyed. The final products of organic molecule oxidation with ozone are carbon dioxide and the water (Seafish, 1997; King, 2001; Campos et al., 2005; Campos et al., 2006; Vaz-Velho et al., 2006; Chawla, Bell and Marlene, 2007; Zentox, 2007).

Unlike other biocides agents such as chlorine, the time necessary to make the disinfection is lower. For this reason, it’s very effective in destruction of chlorine resistant microorganisms due to a power of reaction of three thousand times superior to the chlorine, which turns it is a possible biocide agent, as much for the water treatment, like for the treatment of air and closed atmospheres (Brooks and Pierce, 1990; Duguet, 2004; Young and Setlow, 2004).
Figure 2 – Ultra-violet lamp method: Oxygen turns into ozone after it is hit with UV light from a UV generating bulb (Adapted from Ozone Solutions, 2007).

<table>
<thead>
<tr>
<th>Property</th>
<th>Ozone</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>( \text{O}_3 )</td>
<td>( \text{O}_2 )</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>48 g.mol(^{-1})</td>
<td>32 g.mol(^{-1})</td>
</tr>
<tr>
<td>Color</td>
<td>light blue</td>
<td>colorless</td>
</tr>
<tr>
<td>Smell</td>
<td>clothes after being outside on clothesline; photocopy machines; smell after lightning storms.</td>
<td>odorless</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-111.3°C</td>
<td>-183°C</td>
</tr>
<tr>
<td>Density</td>
<td>2.141 kg.m(^{-3})</td>
<td>1.429 kg.m(^{-3})</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>0.64</td>
<td>0.049</td>
</tr>
<tr>
<td>((\text{LO}_3/\text{LH}_2\text{O}))</td>
<td>(190 mg.L(^{-1}))</td>
<td>(14.6 mg.L(^{-1}))</td>
</tr>
</tbody>
</table>

On the other hand, its strong oxidizing capacity (Table 2) makes very appropriate for the water treatment with high organic content. About this form, an ozone treatment in organic wastes can be considered an effective and faster form, that other treatments with chlorine or hydrogen peroxide (Glaze; Kang and Chapin, 1987; King, 2001; Campos et al., 2006).

<table>
<thead>
<tr>
<th>Oxidant agent</th>
<th>Oxidizing Potential (mV)</th>
<th>Reactive power of oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.06</td>
<td>2.25</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
<td>1.52</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>1.77</td>
<td>1.30</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>1.49</td>
<td>1.10</td>
</tr>
<tr>
<td>Chlorine gas</td>
<td>1.36</td>
<td>1.00</td>
</tr>
</tbody>
</table>

In addition, the treatment with ozone is not exclusive and can be combined with the use of hydrogen peroxide or ultraviolet radiation, harnessing therefore the results by a synergic effect (King, 2001; Young and Setlow, 2004). Another property of ozone is the capacity of absorption of flavors and strange smells in the water. This must simply to the fast destruction of organic compounds responsible for the smell. In the same way, ozone has a deodorization role of the air (Rice; Farquhar and Bollyky, 1982). In waters also, it is useful for the elimination from heavy metals like iron and manganese that precipitate quickly in oxide form (Tech Brief, 1999).
In normal conditions of pressure and temperature, ozone is unstable. This instability increases with the temperature and the humidity, arriving to be total over 200°C. On the contrary, its greater degree of stability reaches to – 50°C and 38 mm Hg of pressure, in other words, a twentieth part of the atmospheric pressure. At room temperature, ozone attacks saturated organic compounds slowly. This offensive capability increases at temperatures of and even inferior 78°C (Guzel-Seydim et al., 2004; Bocci, 2006; Ozone Solutions, 2007).

Until now, chlorine has been the sanitizer of choice in the food processing industry (Table 3). But experts share a growing concern about dangerous by-products (such as trihalomethanes or dioxins) that are produced when chlorine reacts with the organic matter found in water. These by-products are known carcinogens and when found in drinking water, their levels are strictly regulated by the U.S. Environmental Protection Agency - EPA (Brooks and Pierce, 1990; Bocci, 2006). The opposite is true for ozone. When ozone reacts with organic matter, it does not form any toxic by-products. In fact, the water in which ozone is delivered can be filtered and even reused. Additionally, chlorinated wash systems require transport and storage of potentially hazardous, toxic chemicals (Brooks and Pierce, 1990; Campos et al., 2006).

<table>
<thead>
<tr>
<th>Table 3 – Ozone vs. Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Action in water</strong></td>
</tr>
<tr>
<td>Oxidation Potential (Volts)</td>
</tr>
<tr>
<td>Disinfection:</td>
</tr>
<tr>
<td>- Bacteria</td>
</tr>
<tr>
<td>- Viruses</td>
</tr>
<tr>
<td>Environmentally Friendly</td>
</tr>
<tr>
<td>Color Removal</td>
</tr>
<tr>
<td>Carcinogen Formation</td>
</tr>
<tr>
<td>Organics Oxidation</td>
</tr>
<tr>
<td>Micro flocculation</td>
</tr>
<tr>
<td>pH Effect</td>
</tr>
<tr>
<td>Water Half-Life</td>
</tr>
<tr>
<td>Operation Hazards:</td>
</tr>
<tr>
<td>- Skin Toxicity</td>
</tr>
<tr>
<td>- Inhalation Toxicity</td>
</tr>
<tr>
<td>Complexity</td>
</tr>
<tr>
<td>Capitol Cost</td>
</tr>
<tr>
<td>Monthly Use Cost</td>
</tr>
<tr>
<td>Air Pre-treatment</td>
</tr>
</tbody>
</table>

Crapo et al. (2004), Guzel-Seydim et al. (2004).

The ozone itself is not toxic in low concentrations. Ozone is an irritating gas with poisonous effects for human. Ozone is toxic by inhalatory via (Table 4), but never noticed an undesired effects if provided correctly by other routes (secondary effects due to errors in the technique of supplying in most of the cases) and in the suitable doses (1-40 mg/ml O₃). The dose does not have to be greater than the capacity to prevent the accumulation of superoxide anion and peroxide of hydrogen on the part of antioxidants enzymes (superoxide dismutase and catalase). Ozone causes the formation of free radicals with pH>8. At lowest pH, the mechanism of ionic reaction predominates (ozonolysis) and generates the peroxide production (Seafish, 1997; Guzel-Seydim et al., 2004; Bocci, 2006).

Ozone technology has several significant advantages over its chemical alternatives i) Ozone can be generated on-site; ii) Ozone is one of the most active, readily available oxidizing agents; iii) Ozone rapidly decomposes to oxygen leaving no traces; iv) Reactions do not produce toxic halogenated compounds; v) Ozone acts more rapidly, and more completely than other common disinfecting agents do; vi) Ozone reacts swiftly and effectively on all strains of viruses (Brooks and Pierce, 1990; Ibanoglu, 2002; Tapp and Sopher, 2002; Young and Setlow, 2004; Chawla, Bell and Marlene, 2007).
Ozone has a longer half-life in the gaseous state than in aqueous solution (Table 5). Ozone in pure water rather quickly degrades to oxygen, and even more rapidly in impure solutions. Ozone solubility in water is 13 times that of oxygen at 0–30°C and it is progressively more soluble in colder water. Ozone decomposition is faster at higher water temperatures (Seafish, 1997; Tapp and Sopher, 2002; Guzel-Seydim et al., 2004).

The solubility of ozone (Table 6) depends on the water temperature and the ozone concentration in the gas phase. The properties of greater interest of ozone are their solubility in water and its liquid and in the middle gaseous stability, since they are those that allow taking ahead their application like disinfectant (Guzel-Seydim et al., 2004). The final ozone concentration in the water is function of the concentration in phase gas, the pressure of the gas and the temperature of the water and the technology of interchange liquid/gas. It depends on the technology used in the generation and the carrying gas (air or oxygen).

Table 4 – Reference Exposure Levels for Ozone

<table>
<thead>
<tr>
<th>Institution</th>
<th>Maximum concentration permitted (ppm) in air</th>
<th>Exposure time for human in ozonated air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food and Drug Administration (FDA)</td>
<td>0.05</td>
<td>8 h</td>
</tr>
<tr>
<td>Occupational Safety and Health Administration (OSHA)</td>
<td>0.10</td>
<td>8 h</td>
</tr>
<tr>
<td>National Institute of Occupational Safety and Health (NIOSH)</td>
<td>0.10</td>
<td>permanent</td>
</tr>
<tr>
<td>Environmental Protection Agency (EPA)</td>
<td>0.08</td>
<td>8 h</td>
</tr>
<tr>
<td>Ministry of Labor and Employment (Brasil) – Portaria 3214/78</td>
<td>0.08</td>
<td>48h/week</td>
</tr>
</tbody>
</table>

Ozone has a longer half-life in the gaseous state than in aqueous solution (Table 5). Ozone in pure water rather quickly degrades to oxygen, and even more rapidly in impure solutions. Ozone solubility in water is 13 times that of oxygen at 0–30°C and it is progressively more soluble in colder water. Ozone decomposition is faster at higher water temperatures (Seafish, 1997; Tapp and Sopher, 2002; Guzel-Seydim et al., 2004).

The solubility of ozone (Table 6) depends on the water temperature and the ozone concentration in the gas phase. The properties of greater interest of ozone are their solubility in water and its liquid and in the middle gaseous stability, since they are those that allow taking ahead their application like disinfectant (Guzel-Seydim et al., 2004).

Table 5 – Typical O₃ half-life vs. Temperature.

<table>
<thead>
<tr>
<th>Gaseous Temp (°C)</th>
<th>half-life *</th>
<th>Temp (°C) Dissolved in water (ph 7)</th>
<th>half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>3-months</td>
<td>15</td>
<td>30-minutes</td>
</tr>
<tr>
<td>-35</td>
<td>18-days</td>
<td>20</td>
<td>20-minutes</td>
</tr>
<tr>
<td>-25</td>
<td>8-days</td>
<td>25</td>
<td>15-minutes</td>
</tr>
<tr>
<td>20</td>
<td>3-days</td>
<td>30</td>
<td>12-minutes</td>
</tr>
<tr>
<td>120</td>
<td>1.5-hours</td>
<td>35</td>
<td>8-minutes</td>
</tr>
<tr>
<td>250</td>
<td>1.5- seconds</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* These values are based on thermal decomposition only. No wall effects, humidity, organic loading or other catalytic effects are considered. Adapted from Guzel-Seydim et al. (2004) and Ozone Solutions (2007).

Table 6 – Ozone Solubility.

<table>
<thead>
<tr>
<th>T°C</th>
<th>Solubility (LO/LH₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.640</td>
</tr>
<tr>
<td>15</td>
<td>0.456</td>
</tr>
<tr>
<td>27</td>
<td>0.270</td>
</tr>
<tr>
<td>40</td>
<td>0.112</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
</tbody>
</table>

Guzel-Seydim et al. (2004).
How ozone works
Ozone acts by direct or indirect oxidation by ozonolysis, and by catalysis. The three major action pathways occur as follows (Brooks and Pierce, 1990; Seafish, 1997; Campos et al., 2006):

- Direct oxidation reactions of ozone, resulting from the action of an atom of oxygen, are typical first order, high redox potential reactions.
- In indirect oxidation reactions of ozone, the ozone molecule decomposes to form free radicals (OR) which react quickly to oxidize organic and inorganic compounds.
- Ozone may also act by ozonolysis, by fixing the complete molecule on double linked atoms, producing two simple molecules with differing properties and molecular characteristics.

Brief history of ozone use for water and food products
- 1906 – Ozone used to provide safe drinking water in Nice, France;
- 1910 – First use of ozone in a German meat packing plant;
- 1918 – Ozone used to sanitize swimming pools in the United States;
- 1936 – Ozone used to treat shellfish in France;
- 1942 – Ozone used in egg storage rooms and in cheese storage facilities in the United States;
- 1972 – Ozone used to purify process water in Germany;
- 1977 – Ozone used to reduce Salmonella in shell eggs in Russia;
- 1982 – Ozone declared GRAS (Generally Recognized as Safe) for bottled water in the United States – Reaffirmed Gras in 1995;
- 1997 – Expert Panel convened by EPRI declared ozone GRAS in food processing in the United States;
- 2000 – Food Additive Petition filed with the FDA, August 15, 2000;
- 2001 – FDA recognizes ozone as a secondary direct food additive to kill foodborne pathogens. This approval opened the floodgates for food processors to begin utilizing ozone in their plants. FDA officially approved media containing ozone for use in the food industry, also for direct contact with food products, including fish, meat and poultry (Federal Register, Vol. 66, no. 123, Tuesday, June 26, 2000. Rules and Regulations);
- 2001: Food Safety and Inspection Service (FSIS) declares acceptable in poultry and meat products.

Today, the use of ozone is steadily replacing conventional sanitation techniques such as chlorine, steam or hot water. It’s gaining momentum in the food processing industry as the safest, most cost-effective and chemical-free way of dealing with food safety management (Vaz-Velho et al., 2006).

The use of ozone in meats and fish
Ozone has been shown to deactivate a large number of organisms, including bacteria, fungi, yeast, parasites and viruses, and can also oxidize natural organic compounds as well as synthetic substances, such as detergents, herbicides and composite pesticides (Graham, 1997; Guzel-Seydim et al., 2004). Ozone has been used in the food processing industry, both as gaseous ozone and dissolved in water to reduce bacteria on a wide range of food products and contact surfaces (Nash, 2002; Capro et al., 2004; Kim, Yousef and Dave, 1999; Guzel-Seydim et al., 2004; Chawla, Bell and Marlene, 2007).

The application of ozone in the food storage has been applied in freezing chambers and warehouses (meats, seafood, fruits, vegetables, cheeses, sausages, etc.). The main objective is to reduce the bacteriological index that occur in the mentioned storage systems, obtain greater durability of foods (in refrigeration, freezing or fresh storage) and eliminating bacteria to not allow to growth in meats or others, formation of moulds, etc. (Rice; Farquhar and Bollyky, 1982; Brooks and Pierce, 1990; Seafish, 1997; Vaz-Velho et al., 2006; Chawla, Bell and Marlene, 2007).

It is well known that molecular ozone and its decomposition products destroy microorganisms due to their effects on microbial intracellular enzymes, nucleic acids and other cell components. In contrast to these positive effects, the possible pro-oxidant effect of ozone on fish constituents has not been extensively studied up to now, although previous reports have shown a potential negative effect on phospholipids, polyunsaturated fatty acids (PUFA’s) and membrane proteins. The reactions of oxidation and inactivation always occur very quickly which shows that ozone acts different to chlorine. The chlorine acts selectively oxidizing certain enzymatic systems whereas
ozone acts like a “general oxidizing agent” (Brooks and Pierce, 1990; Campos et al., 2005). In addition, with ozone product obtained is with better sensory aspect and presentation, preventing the formation of moulds and putrefaction. Also, a deodorization of cameras is obtained, with the consequent advantage for the maintenance. The most advisable concentration is from 2.5 to 3 ppm between 1 to 3°C and with relative humidity of 90%. A higher concentration would oxidize fats, producing disagreeable smells (Rice; Farquhar and Bollyky, 1982; Tapp and Sopher, 2002).

During the freezing process, a concentration from 2 to 3 ppm is recommended, but 1 ppm is sufficient for the freezing maintenance. A very effective method have been obtained is the intermittent ozonization. Excellent results with a concentration of 5 mg O₃.m⁻³ during two hours daily and from 2 to 3 mg O₃.m⁻³ during the rest of the day. From this form, a considerable increase in the time of storage and diminution in the losses weight is obtained. After 4 days at 3°C, with a relative humidity of 65%, a loss of 10% in weight was observed, whereas in an ozonized atmosphere in the same period and humidity from 84 to 90%, the loss was only 4% in the fish (Rice; Farquhar and Bollyky, 1982; Tapp and Sopher, 2002).

In the fresh fish and bivalve mollusk, ozone application suppresses the smell characteristic which sometimes can be disagreeable, giving a healthful aspect to these seafood. It is advisable to consider that ozone, in this case, does not have to be used to mask the low quality avoiding, thus, the economic fraud.

Chilled tilapias were stored at zero and 5°C after short ozone (6 ppm) pretreatment of live fish.

Sensory analysis showed that ozone pretreatment prolonged their storage life by 12 days (40%) and improved their quality characteristics through one month’s storage at 0°C. The combination of ozone pretreatment with storage at 0°C appears to be a feasible means of prolonging the storage life of fish, and extending their marketability and exportation potential (Nash, 2002; Gelman et al., 2005).

The ozonized water for dipping and washing fish or fish fillets (Fig. 3, 4 and 5) showed an effective reduction of microbiological flora and simultaneously had no effect on the product (Ravesi; Licciardello and Racicot, 1988; Brooks and Pierce, 1990; Tapp and Sopher, 2002; Gelman et al., 2005).

The catfish study showed highly statistically significant reductions in plate counts when live fish and fillets were washed in ozonated water. It has been claimed that ozone gassing can be used as a powerful surface disinfectant (Tapp and Sopher, 2002; Campos et al., 2005).

Figure 3 – Tilapia fillets washing with ozonized water.
Ozonated water treatment presents an opportunity to improve the product quality by reducing spoilage bacteria during mechanically peeled shrimp processing operations (Fig. 6). Soaking peeled shrimp meat in ozonated water was found to be more effective than spraying shrimp with ozonated water, and the higher ozone concentrations and longer treatment times studied were more effective for reducing levels of spoilage bacteria levels on the shrimp. The application of ozonated water did not increase lipid oxidation in the shrimp immediately after treatment (Chawla, Bell and Marlene, 2007).

The effects of ozonated water on the quality of ice from ice machines can be very beneficial, especially if ozone generation is being used at the facility and can be employed as a water treatment during periods when ozone is not needed in the plant (Tapp and Sopher, 2002).

A novel refrigeration system that was developed by combining an ozone generator with a slurry ice system, allowed a better maintenance of sensory and microbiological quality, and implied a significant extension of seafood shelf life (Seafish, 1997; Campos et al., 2006).

Biochemical analyses also confirmed that the presence of ozone did not exert any obvious negative effect on fish quality (flat fish species), and even allowed the inhibition of certain mechanisms involved in lipid hydrolysis and oxidation. On the basis of the results, the combined use of ozone and slurry ice may be...
recommended for the refrigerated storage of turbot and other flat fish species (Brooks and Pierce, 1990; Campos et al., 2006).

Ozone has been traditionally used as a disinfectant for fresh water aquaculture systems: in the treatment of fish and egg’s disinfection; sterilization of the water (improve water quality); decomposition of the odorous compounds (geosmin and 2-methylisoborneol, 2-MIB) in natural waters; and its applications for improving the sensory quality and shelf life of fish have been described recently (Brooks and Pierce, 1990; Morioka et al., 1993; Kötters et al., 1997; Kim; Yousef and Dave, 1999; Kim; Silva, Chamul and Chen, 2000; King, 2001; Campos et al., 2005; Campos et al., 2006).

Delivering clean fish with low microbial loads in clean water will be advantageous for maintaining high quality products. An extensive testing in 2002 found that ozone could be applied to aquaculture tanks to reduce foam and slime on fish in the fish tanks. This technology needs to be expanded and tested across the industry (Tapp and Sopher, 2002).

According to Bullock et al. (1997) and Summerfelt et al. (1997), ozone was added to water in a recirculating rainbow trout (Oncorhynchus mykiss) culture system just prior to the culture tanks in order to oxidize nitrite and organic material, improve overall water quality, and assist removal of solids across the microscreen filter.

**Figure 6** – Peeled shrimp washing with ozonized water (Pacific Seafood Group).

**Other applications of ozone (or ozonized water)**

- Air Treatment: to purify the atmospheres contaminated with volatile organic compounds and microorganisms;
- Water Treatment: to reduce in great amount the chlorine use, without form chlorinated organ compound (Rice, 1997; Tech Brief, 1999);
- Medicine/dentistry: like active medicine and dental surgery, presenting and displaying viral inactivation, bactericidal and fungicide effect (Bocci, 2006; Azarpazhooh and Limeback, 2008);
- Industrial Processes: to reduce the use of chemical agents, as chlorine; to reduce the residual pesticides on food (Brooks and Pierce, 1990; Wu et al., 2007).

According to many authors (Brooks and Pierce, 1990; Seafish, 1997; Tech Brief, 1999; King, 2001; Bocci, 2006) ozone also has many advantages:

- It is the strongest oxidant and disinfectant available commercially for the treatment of aqueous solutions and gaseous mixtures contaminated with oxidizable pollutants and/or microorganisms;
- Although only partially soluble in water, it is sufficiently soluble and stable so that its oxidation and/or disinfection properties can be utilized to full advantage;
- As ozone does its oxidation/disinfection work, or when it autodecomposes, the stable end-product from ozone itself is oxygen; and reacts with a large variety of organic compounds, although at varying rates;
Ozone – an Emerging Technology for the Seafood Industry

- Oxidized organic byproducts of ozonation are oxygen-containing. Halogenated organics cannot be produced during ozonation, unless the bromide ion is present. The ability of ozone to produce “free bromine” by oxidation of the bromide ion is an advantage of ozone in treatment of swimming pools and cooling towers;
- Ozone is safe to handle because it cannot be stored, and thus, must be generated and used on-site. Should an ozone leak be detected, ceasing the flow of electrical power to the ozone generator(s) will stop the production of additional ozone.

According to other authors (Crapo et al., 2004; Ozone Solutions, 2007) ozone has also many disadvantages:

- High capital cost compared with other oxidation/disinfection techniques due to the fact that the ozone must be generated on-site, thus eliminating the usual savings from centrally produced chemicals;
- The currently most economical generation of ozone in commercially significant quantities (by corona discharge) is an electrically inefficient process due to the fact that more than 75% of the electrical power sent to a corona discharge generator is converted into heat and light. Therefore, the major operating cost of producing ozone is the electrical energy. Even given this fact, ozone can be and is often more cost-effective than alternative treatment techniques;
- While ozone is a potent oxidant and can reduce bacterial levels in pure culture, the use in food processing operations where bacteria exist within organic material is more difficult;
- Since ozone is the most powerful oxidizing agent available, it is also potentially the most dangerous of oxidants. This danger was recognized in the early stages of ozone research and techniques have been developed to insure the absence of ozone accidents.

**Legislation in different countries**

- In the United States, the FDA has approved the use of ozone like antimicrobial agent for the direct contact with all foods and food products (June 26th, 2001);
- The Ministry of Agriculture of the United States approved it like antimicrobial agent for the direct contact with meats, poultry, fish, mollusks and crustaceans (December, 2001);
- The government of Japan in 1996 admitted its use for the direct contact with all types of food. Ozone appears in a similar list of FDA as “Generally Recognized as Safe” (GRAS). The Japanese boats of fishing use ozonized water routinely to wash the fresh fish, to make the ice with ozonized water and to pack it on board;
- The Canadian Food Inspection Agency (CFIA) has approved the use of ozone for the cleaning of the contact surfaces of food;
- The government of Australia (also in 1996) authorized the use of ozone for the contact with all foods - similar to the Japanese approval;
- The fishing boats German also use ozone in the water and ice;
- In Norway, the farms of aquaculture and the plants of processing use ozone for the preservation of the fish.

**Importance of ozone in the fishing industry**

- the quality and the security are the highest priorities of the fishing sector;
- the control of the deteriorative organisms is a quality goal, whereas the control of the pathogens, like *Listeria monocytogenes* and *Vibrio sp.*, is a food safety goal;
- the FDA declares that ozone was approved like food additive;
- ozone has been demonstrated to produce greater rates of mortality for the microorganisms when compared with chlorine or other chemical agents;
- the advances in the generation of ozone and technologies of the uses have continued making most reliable and economic process;

**Future perspectives**

Quality and safety are the highest priorities of food industry, including fishing industry. Ozone can warrantee the microbiological quality of the fresh fish. However, there are many implied factors that can influence these results, such as method of the use, temperature and pH, besides the quality of used water. Microbial cross-contamination in workplace environment remains a leading cause of food-borne illness. To minimize the spread of harmful bacteria to finished products, better sanitation agents and enhanced sanitation regimens will be needed.

Thus, many studies must be done to demonstrate the best concentrations and the best methods of
ozone applications in diverse seafood species, so that the governments of all the countries can approve their application in the fishing industry.

CONCLUSIONS

All data as summarized in this paper have shown the effectiveness of ozone like a promising broad-spectrum disinfecting agent (significant potential gains in shelf life and ice quality production) that should be considered as part of the any seafood processing sanitation protocol.

Empirical evidence of the data herein offers a multitude of benefits to the industry as a whole. Elimination of chlorine as the prime bactericide is now possible providing the consumer with a product that has added value, as well as essential health rationale.

It is not possible to say that its use would be obligatory because there are other sanitizers agents which are used and in some cases in combination with ozone.

It is a new opportunity to guarantee the quality and shelf life of the seafood and seafood products.

The use of a gaseous ozone system under controlled conditions appears to be a viable option for fisherman to improve catch quality and marketability.

REFERENCES


Crapo, C. et al. (2004), Ozone efficacy as a bactericide in seafood processing. Journal of Aquatic Food Product Technology, 13, 111-123.


Seafish (1997), Use of Ozone in the Fish Industry. Seafish Fish Technology Department, Sea Fish Industry Authority, St. Andrew’s Dock, East Yorkshire Available at <http://www.seafish.org/resources/publications.asp?a=U>


