Ozone – potential application in depuration systems in the UK

Cefas discussion document

Cefas Weymouth Laboratory

June 2010

Glossary

BrO_3	Bromate
COD	Chemical oxygen demand
FBO	Food Business Operator
GAC	Granular activated carbon
HAV	Hepatitis A Virus
HOBr	Hypobromous acid
HOCL	Hypochlorous acid
IFREMER	French institute for exploitation of the sea. Created by decree in 1984, Ifremer is a public institute of industrial and commercial nature. It is placed under the joint supervision of the ministries for Ecology, Energy, Sustainable Development and Town and Country Planning ; for Higher Education and Research ; for Agriculture and Fisheries
INTECMAR -	Instituto tecnologico para el control del medio marino de galicia
LFA	Local Food Authority
NH_2Br	Monobromamine
OBr	Hypobromite
ORP	Oxidation Reduction Potential (ORP) or REDOX Potential
pKa	The symbol for Acid dissociation constant. It is a quantitative measure of the strength of an acid in solution and is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions.
Seafish	A Non Departmental Public Body (NDPB) sponsored by the four UK government fisheries departments and funded by a levy on seafood. Established in 1981.
TRO	Total residual oxidant

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(Cefas discussion document)

Introduction

The compilation of this document has been prompted by industry requests to use ozone as a means of disinfection in depuration systems for use in the UK. To date ozone has not been used in depuration before in the UK, as far as we are aware, as UV disinfection has been the norm. It has been possible to obtain only limited information from colleagues elsewhere in Europe on their use of ozone in this way (details discussed later in this document). This document therefore summarises information found from credible sources via internet searches (and a draft document previously prepared by Seafish), incorporates comments from independent experts (Dr Peter Jarvis, University of Cranfield, Dr Tom Hall, WRc and Mr David Shepherd WRc), and proposes a way forward on this issue. It is intended that this discussion document will assist in interpretation of data that Food Business Operators (FBOs) provide in support of their applications and also inform the regulatory approvals process.

Definition

Ozone (O_3) is a naturally occurring, pale blue gas. The ozone molecule is composed of 3 oxygen atoms. Ozone is an unstable gas that readily decomposes into oxygen and it has a half life of only 20 minutes in room temperature water. It is formed naturally through the electrical discharge produced by lightning or when the sun's ultraviolet rays react with the Earth's stratosphere. It can also be produced commercially by creating an electrical discharge across a flow of either pure oxygen or air. It may also be generated by UV irradiation at 189 nanometres wavelength. Equally it may be destroyed by UV at 254nm by dissociation which occurs when UV energy at 254 nm breaks one of the oxygen bonds in an ozone molecule. As a result of this, each ozone molecule is converted into one oxygen atom and one oxygen molecule. Free oxygen atoms will combine with each other to form oxygen molecules.

Since ozone is highly reactive, and has a short half-life, it cannot be stored as a gas or transported, consequently ozone is always generated on site for immediate use.

Human health concerns associated with ozone

Health Canada conducted a study which showed that both high and low concentrations of ozone can be detrimental to human health (Health Canada 2008). High levels of ozone resulted in immediate oxidizing effects and cellular death, while low levels of ozone resulted in an interference with metabolic processes in the body and eventually caused premature cellular aging. Ozone gas is also an irritant that can cause coughs chest discomfort, and irritation of the nose, throat, and trachea. Whilst this is not a matter that falls within the remit of Cefas/FSA, it is nevertheless a matter that requires careful consideration by the operator to ensure that the application of any ozonation process is carried out safely.

Formation of by-products

As a powerful oxidizing agent, ozone can oxidise bromide, a naturally occurring element found in seawater (and to a lesser extent in freshwater), into bromate, a known carcinogen. This is the ozonation by-product of principal concern. The concentration of bromide in raw water is a major factor in the formation of bromate. Natural seawater of a salinity of 35 g/L contains typically in the region of 50 to 70 mg/L of bromine (as bromide ions). The dominant ozone decay mechanism in seawater differs from that in potable water, which has implications for how disinfection of seawater with ozone should be interpreted. The reason for this difference is the much greater concentration of bromide in seawater relative to freshwater.

Bromate is formed by the stepwise oxidation by ozone of bromide to hypobromite and then to bromate (Von Gunten and Hoigné, 1992):

$$\mathrm{O_3 + Br^- \rightarrow O_2 + OBr^-} \tag{1}$$

$$\mathrm{2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^-} \tag{2}$$

A parallel reaction between hypobromite and ozone consumes ozone:

$$\mathrm{O_3 + OBr^- \rightarrow 2O_2 + Br^-} \tag{3}$$

In aqueous solution, hypobromite exists in equilibrium with hypobromous acid (HOBr),

$$\mathrm{HOBr \leftrightarrow H^+ + OBr^-} \tag{4}$$

Under the mildly alkaline pH of seawater hypobromite (OBr^-) is dominant, and reducing pH reduces the yield of bromate ($Br0_3^-$) (see figure 1).

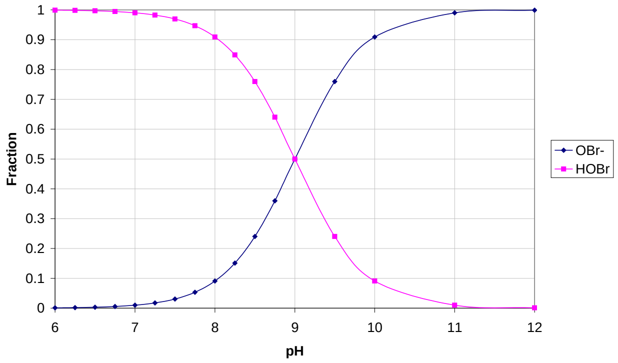


Figure 1 Dissociation of HOBr, pKa = 9.0.

In seawater, the reaction of O_3 with Br^- is of real concern because it is also very fast. It has been estimated that as much as 8% of applied ozone can be consumed by Br^- in the water.

When dissolved in water, ozone may react directly with contaminants/microbes in the water or it may do so through the formation of hydroxyl radicals (HO•). These radicals may in turn react with any impurities in the water. In higher alkalinity waters (such as seawater) the formation of HO• is very fast. When other contaminants are in the water, the reactions of ozone in seawater can be summarised as below in figure 2:

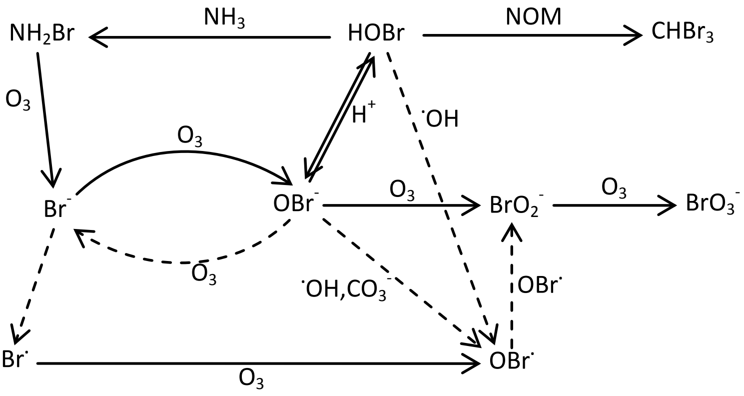


Figure 2 Reaction pathways for decomposition of ozone in seawater (adapted from Herwig et al., 2006).

On a general note, the ozone disinfection requirement is commonly expressed in terms of Ct, the product of disinfectant concentration, C (mg/l) and contact time, t (minutes). In practical terms, C is the residual concentration after contact time t.

It is important to consider that whilst the Ct value will influence bromate formation, the key objective of dosing ozone is to achieve disinfection of the water. It is therefore important to ensure that the Ct is enough to achieve the required disinfection. When talking about ozone concentrations, it is also important to understand how much of the ozone is transferred to the water. This will depend on the contaminants in the water. For example, a water of high turbidity/organic concentration/ammonia concentration will have a high ozone demand before disinfection is achieved.

The ozonation pH is the main factor for bromate formation. As the ozonation pH of the water is increased, the rate of bromate formation increases. In part, this is as a result of the formation of the more unstable and reactive BrO^- compound at high pH. In addition to this, hydroxyl radical formation is promoted at high pH due to the increased concentration of hydroxyl ions present (Song et al., 1997; Siddiqui et al., 1998). Bromate formation has been shown to increase from 10 g/L at pH 6.5 to 50 g/L at pH 8.2 (Legube et al., 2004) whilst Krasner et al. (1994) observed a 60 % decrease in bromate formation for each drop in pH unit. The ozonation pH is widely regarded as being the most effective bromate control strategy at a waste water treatment works and should be considered the best available treatment for bromate control (Ozekin and Amy, 1997). However, this must be balanced by the increased formation of brominated organic compounds as pH is reduced (USEPA, 1999a). Additionally, the cost of pH reduction may be prohibitive for high alkalinity waters due to the volume of acid required (Von Gunten, 2003b).

However, for seawater applications the high buffering capacity of the water will make adjusting pH an expensive option if this is used as a way to control bromate. Re-circulated seawater containing ammonia excreted by the depurating shellfish will help to control bromate production.

Ammonia reacts with hypobromous acid to form monobromamine:

$$\mathrm{HOBr} + \mathrm{NH_3} \rightarrow \mathrm{NH_2Br} + \mathrm{H_2O} \qquad 5$$

Monobromamine then reacts with ozone, relatively slowly:

$$\mathrm{NH_2Br} + 3\mathrm{O_3} \rightarrow 2\mathrm{H^+} + \mathrm{NO_3^-} + \mathrm{Br^-} + 3\mathrm{O_2} \qquad 6$$

The presence of ammonia can therefore reduce the yield of bromate, effectively by holding bromide within the slow-reacting monobromamine while ozone is consumed. The longer a dissolved ozone residual persists, the more bromate will tend to form, so the presence of anything that promotes ozone decay, for example dissolved organic material, tends to restrict bromate formation. This may be an important consideration if a high Ct value is required to achieve disinfection.

The effective outcome of the ozone:bromide reaction scheme changes depending on the relative concentration of the reactants. In potable water treatment, ozone concentration is normally greater than bromide concentration. Conversely, it is normally the case in seawater ozonation that there is a large excess of bromide, and reaction 1 dominates. Haag and Hoigné (1984) derived a half life for ozone in seawater at 20°C of 5.3 s based on a rate constant for reaction 1 of 160 M-1s-1, and regarded this reaction as the dominant mechanism for ozone decay in seawater. The product is $\mathrm{OBr^-}$/HOBr, so one consequence is that a strong disinfectant replaces the short-lived ozone. Comparative oxidation potentials are given in Table 1.

Table 1 Oxidation potentials (USEPA, 1991)

Substance		**Oxidation potential, Volts**
Ozone	O_3	2.07
Hypochlorous acid	HOCl	1.49
Chlorine	Cl_2	1.36
Hypobromous acid[1]	HOBr	1.33
Chlorine dioxide	ClO_2(aq)	0.95

Another consequence of excess bromide is that bromate formation is not favoured. Haag and Hoigné (1984) reported one continuous seawater ozonation system in which no bromate formation had been observed but did note that bromate formation had sometimes occurred in other such systems. They suggested that the conflicting experiences were due to differences in contactor design. If mixing is inadequate near the gas/liquid interface, there may be local depletion of bromide which then allows bromate formation; the contactor design should therefore provide a well-mixed environment at the gas/liquid contact zone. Once the ozone is dissolved, it is desirable (as with any disinfection system) to achieve plug flow to make the most efficient use of the contact time.

Because ozone decays rapidly in seawater, the effective ozone Ct may be low, but disinfection will also be achieved by the more persistent $HOBr/OBr^-$ (Schneider et al, 1990, reported a half life of approximately 4.5 hours). The $HOBr/OBr^-$ is quantified as total residual oxidant (TRO), expressed in units of mg Br_2/l or mg Cl_2/l (Perrins et al, 2006). Overall disinfection is then a combination of the two effects.

In addition to bromate production, there is potential for the formation of brominated organic by-products (e.g. bromoform, bromopicrin dibromoacetonitrile, bromoacetone, bromoacetic acid, bromoalkanes, bromohydrins - von Gunten, 2003) either directly from ozone reactions with organic matter or from HOBr/OBr- reactions. The level of formation of any such by-products will depend on the nature of the organic material present, as well as the oxidant concentration and contact time. The formation of these bromo-organic products is less of a health concern than bromate, however, some of these are regulated in drinking water (e.g. trihalomethanes, such as bromoform, have a maximum permitted level of 100 ug/L) suggesting that maximum levels should be considered in a depuration context. It is understood that GAC and possibly some forms of biological filters can remove such by-products.

Use of artificial seawater with no or negligible bromine content

In the absence of bromide a variety of by-products may be formed from the oxidation of natural organic matter e.g. aldehydes, ketones, keto aldehydes, carboxylic acids, keto acids, hydroxyl acids, alcohols and esters (von Gunten, 2003). Again, it is understood that these are less of a health concern (at the levels at which they are likely to be formed) than bromate.

The Seafish recommended artificial seawater formulation has no bromide/bromine so does not give rise to bromate formation (or other brominated by-product) concerns as the freshwater, from which the surrogate is made, contains considerably lower levels of bromide than seawater. Typically, fresh water sources used for drinking water contain between 30-200 µg/L bromide, with an average of 100 µg/L (Amy et al., 1993), although this can be up to 700 µg/L (Von Gunten, 2003). However, this is 2 to 3 orders of magnitude lower than the concentrations typically found in seawater.

From the by-product formation point of view the use of bromine/bromide-free artificial seawater formulations would appear to be preferable.

Factors affecting formation of by-products

An increase in the following factors in water increases bromate formation: temperature, bromide concentration, pH, ozone concentration, ozone contact time and alkalinity.

An increase in the following factors decreases bromate formation: dissolved organic carbon (also known as natural organic matter) and ammonia.

As discussed above, one of the key chemical components in water which impacts on bromate formation is the ammonia concentration. Tango and Gagnon (2003) reported that bromate was not formed as long as there was ammonia still in the water system. Bromate production may therefore be inhibited in recirculating seawater passing through ozonation systems as active depurating bivalves excrete ammonia as part of their normal metabolic/digestive processes.

An upper level of 0.5 mg/L for a maximum period of 10 minutes has been suggested as a suitable dosing regime to avoid by-product formation in shellfish depuration systems (guidance from FAO 2008).

The use of Ct (ozone concentration x time) has been suggested as being a useful indicator to describe the relative rate of bromate formation because it also gives a simultaneous descriptor for disinfection efficiency (WHO 2004). The rate of formation of bromate ions may increase with temperature and alkalinity (Siddiqui et al., 1995). However, the rate of formation of bromate during ozonation is also affected by ozone characteristics. Thus, a smaller Ct might result because ozone becomes less stable with increasing temperature and/or alkalinity. All factors being equal, initial bromide concentration and ozone dose are the best predictors of bromate formation during ozonation (IPCS, 2000). Ozonation pH is the key factor here.

Human toxicity of bromate

By the oral route, bromate is absorbed from the gastrointestinal tract in both humans and animals.

Bromate has been found to produce tumours in male rats in the kidney, the thyroid gland and the peritoneum (Kurokawa et al., 1986a,b, 1987; DeAngelo et al., 1998). In the female rat, only kidney tumours were found (Kurokawa et al., 1986a). A clear dose–response relationship exists in tumour incidence and the severity/progression of tumours. The weight of evidence from the rat bioassays clearly indicates that bromate has the potential to be a human carcinogen (WHO, 2004).

A maximum guideline permitted value of 10 µg/L is recommended in tap water (WHO 2004). The WHO guideline is based on exposure limits and the risk of ill health. The European Union law specifies that all member states must enforce a maximum bromate concentration in drinking water of 10 µg/L by 2008. In the UK, the legislation enforcing this standard came into effect in 2003.

Effect of ozone on shellfish

Residual levels of ozone may cause shellfish to reduce or stop activity (assuming levels are not so high as to kill the shellfish outright), thus reducing the effectiveness of the depuration process (FAO 2009). Residual ozone must therefore be removed from seawater before it comes into contact with the shellfish.

If ozonation is to be applied to natural seawater (with bromide ions present) then hypobromous acid is likely to be formed and may reach the shellfish, even if any residual ozone has been removed by degassing. It is not clear what effect this compound (also a strong disinfectant) will have on the shellfish. It is understood that it can be removed by a granular activated carbon (GAC) filter and so the installation of such a filter may be advisable post-ozonation.

Haag and Hoigné (1984) noted that for depuration of marine shellfish, ozone had advantages over chlorine: destroying phenolic tastes and odours (phenolic reactions with ozone being of the order of 10^4 times faster than with chlorine; oxygenation of the water; and not imparting a chewy texture to shellfish meats (the latter suggests there was a disinfectant residual in contact with the shellfish in the cited study).

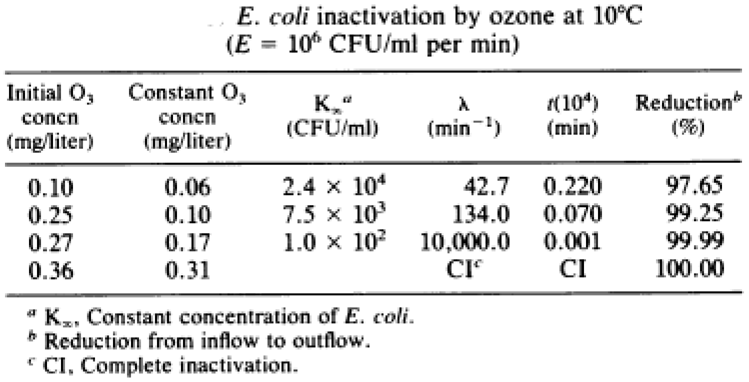
Disinfection capabilities of ozone

The concentrations of ozone used in drinking water disinfection vary between 0.1-1 mg/L. Herbold *et al* (1989) report that a residual ozone concentration of 0.4 mg/L for 4 min is generally thought to be adequate and suggest that their results confirm this: the time taken to achieve a $1x10^4$ reduction in microorganism concentration, $t(10^4)$ or complete inactivation time (CI), at 0.4 mg/L O_3 was calculated to be only a few seconds.

Ozone inactivation of Hepatitis A virus (HAV) and *E. coli* was found to be faster at 10°C than at 20°C (Tables 2 & 3 - Herbold *et al* 1989) i.e. ozone effectiveness diminished as temperature rose (Herbold *et al* 1989).

E. coli was only slightly more sensitive to ozone than HAV. The time required to reduce *E. coli* by a factor of $1x10^4$ at 20°C was 0.6 min at 0.1 mg of 0_3 per litre compared with 0.8 min for HAV. No further surviving *E. coli* cells were detectable at 0.31 mg of 0_3 per litre. Inactivation of *E. coli*, like that of HAV, was much faster at 10°C and was already complete at 0.1 mg of 0^3 per litre (Table 1). At 20°C, 0.25 to 0.38 mg of 0_3 per litre was required for complete inactivation of HAV (Herbold *et al* 1989). Inactivation times, except for those of spores tested, amounted to seconds or a few minutes.

Table 2



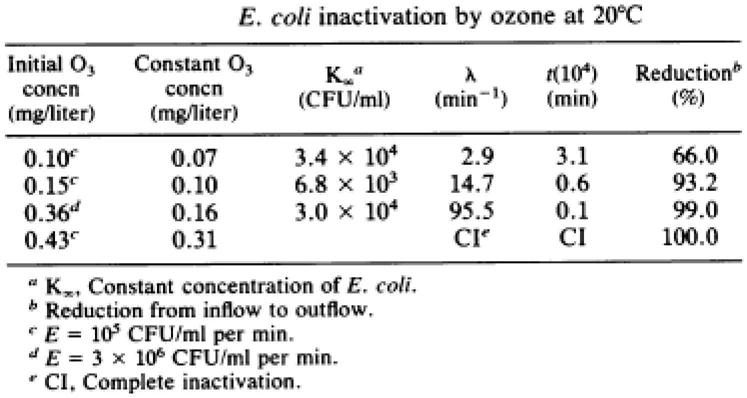
E. coli inactivation by ozone at 10°C ($E = 10^6$ CFU/ml per min)

Initial O_3 concn (mg/liter)	Constant O_3 concn (mg/liter)	K_∞[a] (CFU/ml)	λ (min^{-1})	$t(10^4)$ (min)	Reduction[b] (%)
0.10	0.06	2.4×10^4	42.7	0.220	97.65
0.25	0.10	7.5×10^3	134.0	0.070	99.25
0.27	0.17	1.0×10^2	10,000.0	0.001	99.99
0.36	0.31		CI[c]	CI	100.00

[a] K_∞, Constant concentration of *E. coli*.
[b] Reduction from inflow to outflow.
[c] CI, Complete inactivation.

(From Herbold et al 1989)

Table 3



E. coli inactivation by ozone at 20°C

Initial O_3 concn (mg/liter)	Constant O_3 concn (mg/liter)	K_∞[a] (CFU/ml)	λ (min^{-1})	$t(10^4)$ (min)	Reduction[b] (%)
0.10[c]	0.07	3.4×10^4	2.9	3.1	66.0
0.15[c]	0.10	6.8×10^3	14.7	0.6	93.2
0.36[d]	0.16	3.0×10^4	95.5	0.1	99.0
0.43[c]	0.31		CI[e]	CI	100.0

[a] K_∞, Constant concentration of *E. coli*.
[b] Reduction from inflow to outflow.
[c] $E = 10^5$ CFU/ml per min.
[d] $E = 3 \times 10^6$ CFU/ml per min.
[e] CI, Complete inactivation.

(From Herbold et al 1989)

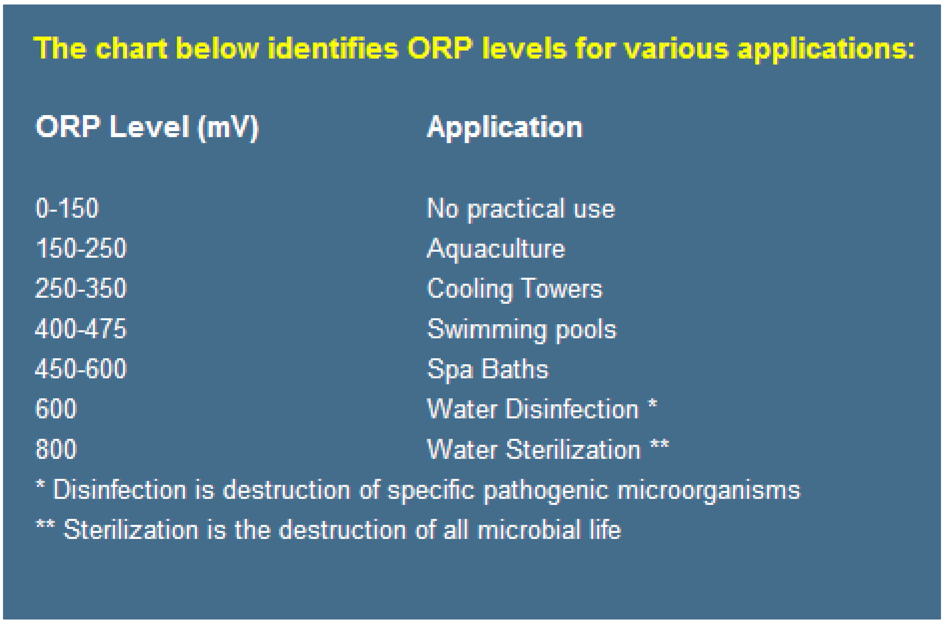
Measurement of ozone & redox potential

There seems to be a general consensus that measuring the concentration of ozone in water is a relatively difficult and/or impractical measurement to make with any degree of accuracy in a commercial setting, especially in seawater or water with a high ionic and organic content. Redox potential is therefore the preferred form of measurement for industrial applications. Ozone is a strong oxidising agent which has a high oxidation potential. When ozone is dissolved in water, the ozone will increase the oxidation capacity of the water. This measurement is referred to as the Oxidation Reduction Potential (ORP) or REDOX Potential. The redox potential is therefore an indirect measurement of the concentration, or activity of ozone in solution.

Oxidation-Reduction Potential has a range of -2,000 to +2,000 and units are in “mV” (millivolts). Since ozone is an oxidizer, we are only concerned with positive ORP levels (above 0 mV).

Ozone has an oxidation reduction potential of +2.07 volts as compared to HOCL (Hypochlorous acid, the active form of Chlorine in aqueous solution) which is +1.49 volts. It is reported to be 3000 times as germicidal as chlorine. It retains this strong oxidizing capability in aqueous solution, a property crucial for water disinfection and sterilization, as well as in high humidity air applications. Table 4 identifies the typical redox potential values used for certain applications. Table 5 illustrates the relationship between the ozone concentration and redox potential (assuming that the water is clean with a low chemical oxygen demand (COD) or organic content).

Table 4



The chart below identifies ORP levels for various applications:

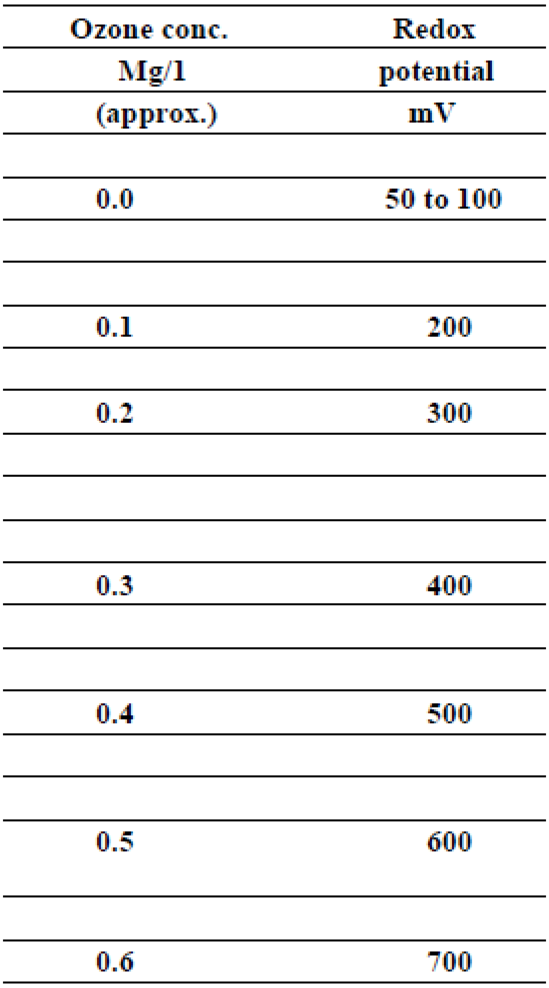
ORP Level (mV)	Application
0-150	No practical use
150-250	Aquaculture
250-350	Cooling Towers
400-475	Swimming pools
450-600	Spa Baths
600	Water Disinfection *
800	Water Sterilization **

* Disinfection is destruction of specific pathogenic microorganisms

** Sterilization is the destruction of all microbial life

Source : http://www.ozonate.co.za/ozinfo.html

Table 5



Ozone conc. Mg/1 (approx.)	Redox potential mV
0.0	50 to 100
0.1	200
0.2	300
0.3	400
0.4	500
0.5	600
0.6	700

Source : http://media.live.harnesslink.com/files/f1038953750.pdf

N.B. The relationship between the ozone concentration and redox potential in the table above assumes that the water is clean with a low COD or organic content.

Experiences of ozone application in depuration systems in France and Spain

The experience of colleagues from IFREMER in France is that the quantity of ozone injected into sea water is regulated according to several parameters, particularly turbidity. They report that it is difficult and expensive to test for bromate ions in the water or in the shellfish and so this analysis is not carried out. Redox potential is used to measure the effectiveness of the disinfection of sea water by ozone. They also confirm that ozone must not be allowed to reach the molluscs and so seawater must be degassed prior to contact with them.

They point out that ozone can be dangerous for operators if the rooms are not sufficiently ventilated. Ozone is a very effective disinfectant, but is expensive to produce, dose and destroy. If it is of consideration, ozone systems have a high carbon footprint.

Colleagues from INTECMAR in Spain also confirm that there is not a standard dose and that final dosing depends on intake water conditions. Ozone concentration is adjusted depending on the salinity, temperature and turbidity of water.

The application of ozone

Considerations relating specifically to the practical application of ozone are included at Appendix 1.

Summary and recommendations

The FSA have produced a recent statement on their position with regard to the use of ozone in depuration systems. The statement is as follows:

'Regulation (EC) 852/2004 defines clean seawater as "natural, artificial or purified seawater or brackish water that does not contain micro-organisms, harmful substances or toxic marine plankton in quantities capable of directly or indirectly affecting the health quality of food." This definition suggests clean seawater could include water that has undergone a treatment so that it meets these requirements.

The question is whether ozone could be considered as a means of treating water. The approval of ozone for water treatment seems to rest on the issue of whether the water so treated is equivalent to 'clean seawater'. In other words, a substance cannot be used to treat water if it can introduce a harmful substance that could directly or indirectly affect the health quality of the water.

In view of this, it is possible that ozone used for water treatment may fall under the definition of processing aid. Processing aids must comply with the requirements of relevant UK and EU legislation on food and must comply with the legal definition for a processing aid, i.e., they should not perform a function in the final product and should leave no residues that present a health risk.

The Agency can provide advice on the statutory restrictions that apply to specific products. However, primary responsibility for food safety rests with the food business operator. Ultimately, it is for the food business operator to demonstrate to the LFAs that any water treatment used is safe and meets the requirement of any relevant food legislation. Also the FBO is best placed to obtain the experimental evidence to demonstrate the safety of the product itself and any by-products formed during water treatment and whether they will introduce substances in quantities capable of affecting the health quality of food. Provided the evidence demonstrates the conditions described above, then the use of ozone to treat water prior to its use in depuration tanks is allowable under the current hygiene regulations.

In addition, the FBO would also have to guarantee that any antimicrobials used for water treatment cannot come into contact with fishery products. According to Regulation 853/2004, antimicrobial treatments cannot be used to remove surface contamination on fish or fishery products.'

Essentially then, ozonation may be used in depuration systems providing ozone does not come into direct contact with the shellfish and does not create harmful by-products that may affect the safety of the shellfish. It is for the food business operator to provide the necessary evidence to demonstrate that these conditions are met.

The minimum level of evidence supplied by the operator needs to be defined. Some data may only be needed at the initial validation stage but a certain amount of ongoing testing should be carried out to confirm key parameters such as ozone dosing and absence of ozone residual post dosing. Given that hypobromous acid, a powerful disinfectant, may be formed if natural seawater with bromide is ozonated then this would also need to be removed prior to contact with the shellfish. Hypobromous acid contributes to the redox potential and so, if not directly tested for, its presence/absence could be assessed by redox measurement. Experience from colleagues at the Centre for Sustainable Aquaculture at the University of Swansea would suggest that ambient seawater (i.e. before any ozonation is applied) would usually have a redox value of around 200mV although the actual value would be dependent upon the content of the seawater with regard to organic material, algae etc.

If, as seems to be the case, that it is necessary to ensure that no ozone residual (or hypobromous acid) reaches the shellfish then it could be specified that the redox value for the treated seawater must match that of the ambient seawater prior to treatment (i.e. as it arrives fresh from the harvesting area or after it has been made up in the case of artificial seawater). There are test kits available that can be used to obtain a direct measure of ozone concentration. Periodic *E. coli* analysis of the treated water would also seem sensible.

Although the emphasis is seen as being placed on the operator to prove that a proposed treatment system is effective, there needs to be some yardstick by which any evidence is assessed. This could be against normally recommended concentration/exposure time regimes, or by reduction of target organism(s).

Given the variation in dose needed depending on turbidity, temperature and salinity it may be difficult/impractical to specify a generic minimum dose from a statutory/Conditions of Approval perspective (as has been set for UV). In general, empirically derived data from experiments are usually required in order to ensure adequate disinfection is achieved.

The FAO guidance (FAO 2008) of a maximum dose of 0.5mg/L for a maximum period of 10 mins (or suitable time/dose equivalent) could, however, be adopted as an absolute limit to avoid by-product formation. Given that practical advice from French colleagues indicates that it is easiest to measure redox potential (as an indirect measure) rather than directly measure ozone levels it will be necessary to identify a redox potential which corresponds to a maximum dose of 0.5mg/L (likely to be in the region of 600mV but this will be dependent on various factors such as organic content).

It could be argued, assuming the FAO guidance time/dose maximum recommendations are followed, that by-product formation would be minimal and so by-product testing may not be necessary (it does not appear to be carried out in France and Spain). However, it would be preferable for some initial testing to be carried out to validate the process to confirm that bromates are not formed to any significant extent where natural seawater (or artificial seawater containing bromide) is to be used.

A level of 10ug/L is the maximum permitted for bromate in drinking water (WHO) and it may be appropriate to adopt this value in ozonated seawater intended for use in depuration. This may, however, be difficult to achieve in seawater. It would be advisable to measure bromate formation rather than assume that guideline Cts will ensure compliance with a maximum bromate concentration.

Some key points

It is difficult to give advice on maximum ozone dose (residual dose) and contact time as universal rules. In general, empirically derived data from experiments are usually required in order to ensure adequate disinfection is achieved. We consider data should be supplied by the FBO as part of the application for approval of a specific plant.

- The FAO guidance (FAO 2008) of a maximum dose of 0.5mg/L (likely to be in the region of 600mV but this will be dependent on various factors such as organic content) for a maximum period of 10 mins (or suitable time/dose equivalent) could be adopted as an absolute limit to avoid by-product formation.

- Ozone decays rapidly in natural seawater by reaction with bromide (Br^-) to produce hypobromite (BrO^-). A half life of 5.3 s for ozone in seawater is quoted in the literature.

- At the mildly alkaline pH of seawater, hypobromite (BrO^-) exists predominantly as hypobromous acid, (HOBr).

- $HOBr/OBr^-$ is an effective disinfectant, and persists for much longer in seawater than ozone (results in the literature suggest a half life of the order of 4 hours). Much of the disinfection observed in ozonated seawater is therefore attributable to the $HOBr/OBr^-$ residual rather than the relatively short-lived ozone residual.

- Bromate formation is possible but reported experience suggests that it is avoidable by ensuring good mixing in the ozone contactor.

- There is potential for formation of brominated organic by-products such as bromoform and mono- and di-bromoacetic acid, the extent of any such formation will depend on the nature of dissolved organic matter.

- A level of 10 ug/L is the maximum permitted for bromate in drinking water and Cefas suggests adoption of this value for ozonated seawater intended for use in depuration.

- A level of 100 ug/L is the maximum permitted for bromoform in drinking water and Cefas suggests adoption of this value in ozonated seawater intended for use in depuration.

- Methods currently used for dechlorination should be applicable for debromination if it is necessary to eliminate the disinfectant residual before the treated seawater contacts the shellfish.

- The use of bromide/bromine-free artificial seawater formulations will avoid the formation of brominated by-products which are of most concern.

Generic requirements that could be applied via Conditions of Approval (CoA)

The target level of ozone should be that which has been shown, by reference to scientific literature, to yield a 4 $\log_{10}$ reduction of *E. coli*. When ozone is being added to a plant already approved for UV, no additional disinfection requirements would be added to the Conditions of Approval with regard to ozone, but the safety considerations (see below) would still apply. Where a new system was being approved for use with UV and ozone, the combination of the two disinfection methods would need to be such as to be expected to achieve the 4 $\log_{10}$ *E. coli* reduction.

- As a maximum dosing level, ozone must not exceed 0.5mg/l for 10 mins (equivalent to approximately 600mV redox) to limit by-product formation.

- Ozone (and hypobromous acid if applicable) must not reach the molluscs i.e. minimal or no residual ozone.

  This can be assessed by measuring the oxidative redox potential (ORP) of the seawater post ozonation before it comes into contact with the shellfish. As suggested by Seafish the ORP baseline figure should be determined from the seawater pre-ozonation. Ozone treated water should match that of the ORP baseline figure +10%.

- Shellfish must not be contaminated with ozonation by-products.

Information and evidence that could be required of FBOs as part of their initial approval assessment

- Proposed ozone dosing arrangements (dosing level and contact time)

- Ozone residual testing (by redox or colorimetric testing) to confirm nil presence of ozone (or hypobromous acid if applicable) prior to contact with shellfish on recirculation

- Challenge testing for *E. coli* in seawater to demonstrate adequate inactivation (to achieve absence per 100ml or 10^4 inactivation)

- Testing of shellfish post depuration (to achieve <230/100g)

Possible ongoing evidence/testing requirements for FBO

Providing the above approval testing arrangements prove satisfactory and that the routine ozone dosing regimes do not change, the following ongoing testing requirements could be applied.

- Ozone dosing regime confirmation and recording (ozone dose level and contact time).

- Ozone residual or redox testing to confirm nil presence of ozone prior to contact with shellfish on recirculation post ozonation.

- Shellfish end product testing.

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Appendix 1

Additional Information

Ozone generation

The established technology for generating ozone is by corona discharge of dry air or oxygen. There are other methods (UV irradiation of oxygen at 140-190 nm; electrolysis) but these have yet to find widespread application for water treatment. The use of oxygen enables ozone to be generated at higher concentrations, which is more energy efficient and beneficial for mass transfer, but carries the additional cost of the oxygen. There are some air-fed installations which have the facility to enrich the feed gas with oxygen, which may be justifiable where there are infrequent short-term peak ozone demands (Langlais et al, 1991).

The main features of an air-fed ozonation plant are illustrated in Figure 3

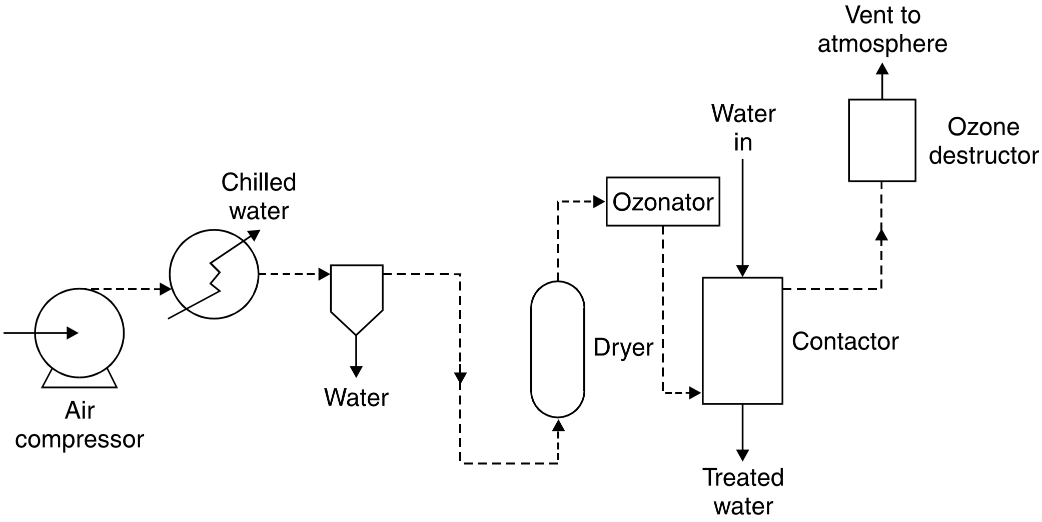

Figure 3. Schematic of air-fed ozonation system

Gas preparation

Air

Air used for ozone generation must be dry, as water vapour causes arcing inside the generator, leading to loss of production and energy waste, and can also result in the formation of nitric acid. The required dryness depends on the generator, but the maximum operating dewpoint is unlikely to be above -60oC and may be lower than -80oC (Langlais et al, 1991). To achieve this level of dryness, desiccant driers are used, with parallel beds that alternate between drying and regenerating modes. Larger systems may also have refrigerant driers upstream of the desiccant driers to reduce the moisture loading, and some further upstream drying may also be achieved by compression. The air must be free from dust particles, which can cause arcing and a loss of efficiency, and hydrocarbons, the presence of which reduces efficiency.

Oxygen

Oxygen can be bought in as liquid (LOX) or produced on site. In the latter case, separation technologies include pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and cryogenic separation. LOX requires relatively little capital investment but has a high unit cost. Cryogenic separation is capital-intensive. PSA and VSA are intermediate in terms of capital investment, PSA being the older, more established technology but VSA potentially being lower cost. The choice depends on a number of factors, but LOX is likely to be favourable for small installations, cryogenic separation for large installations, and PSA or VSA for intermediate installations.

Electrical supply

The most common electrical supply unit provides a low frequency, fixed voltage supply. For larger installations, a medium frequency, variable voltage supply is used to reduce power costs and because it allows for a higher output of ozone. Medium frequency units may require a higher operating pressure (Langlais et al, 1991).

Ozone generator

The corona discharge occurs between two concentric electrodes. In conventional generators, the tubular inner, high tension, electrode is covered in glass, a dielectric material. The inner electrode is mounted inside a stainless steel tube which is the outer ground electrode. The feed gas passes through the gap separating the electrodes. Some 90 - 95% of the energy input heats the dielectric and must be removed by applying cooling water. Greater outputs have been achieved by, among other developments, adjusting the discharge gap and using alternative dielectrics such as alumina.

Ozone contactors

Ozone is generated in the gas phase and must be dissolved. Some form of gas-liquid contactor is therefore necessary. The solubility of ozone is appreciably lower than that of chlorine. The most common form of contactor in potable water treatment is the bubble diffuser, comprising two or more chambers in series separated by vertical baffles. A grid of porous diffusers is mounted near floor level in the first chamber, and possibly in one or more downstream chambers, through which ozonated gas is injected. Water flows down the first chamber, counter-current to the rising gas bubbles, and then alternately up and down through subsequent chambers. The diffusers produce bubbles of 2-3 mm diameter, which provide a high interfacial area. The chambers are typically 5-6 m deep, which, by increasing pressure, assists mass transfer. Having diffuser grids in more than one chamber allows the dose to be divided, which provides dose control flexibility. Generally, no ozone is applied to the last chamber, which serves to provide reaction time; there may also be reaction-only chambers between dosed chambers. Counter-current flow is beneficial for mass transfer. A greater ozone decay rate also benefits mass transfer, but will require a higher dose to achieve a given Ct value. This type of contactor is inherently quite large, which makes it particularly suitable for disinfection applications. The volumetric gas-liquid ratio is important, because there is a reliance on the rising bubbles to provide mixing energy. If the gas-liquid ratio is too low, the bubbles will rise as discrete plumes and the water will tend to channel between the plumes, the result of which will be a decline in transfer efficiency and uneven dosing. This needs to be considered at the design stage, especially if high-concentration oxygen-fed generators are proposed.

There are alternative contactor configurations, most notably turbine mixers and eductors, in which an external source of energy (the mixer or eductor pump) provides a high-shear environment in which the ozonated gas is dispersed as microbubbles, giving a very high interfacial area. Such contactors are much more compact than diffuser chambers, but have higher operating costs. For disinfection applications, there will still be a need to provide appropriate contact time. These types of reactor may be more appropriate for seawater depuration applications if, as reported, intensive mixing is desirable to prevent bromate formation. An eductor system has the advantage of no moving parts (other than the eductor pump). Eductors are mounted in a sidestream, and an important design parameter is the gas:liquid ratio. A lower gas flow requires a lower liquid flow, so eductors are suited for use with oxygen-fed generators (Rakness, 2005).

Off-gas destruction

Complete ozone transfer is not achieved in practice and the off-gas from contact chambers will contain ozone, at a toxic concentration. The off-gas must therefore be processed to destroy remaining ozone before being vented to the atmosphere. Two methods are used: thermal and catalytic. Thermal destructors heat the off-gas to temperatures of up to 400oC, at which ozone decay is virtually instantaneous. Catalytic destructors have a reaction chamber filled with a material which catalyses ozone decay, avoiding the need for high temperature. Some pre-heating is still required to reduce relative humidity and prevent condensation on the catalyst, which would impair performance.

Although there is in principle scope for recycling off-gas, it is not commonly done in practice.

Energy consumption

Total energy consumption for ozone generation from air is typically in the range 20-25 kWh/kg. This range applies to units used for potable water treatment applications. Very small units are likely to exceed this range. For oxygen-fed generators, energy consumption is typically 10-15 kWh/kg, which excludes any energy consumption associated with oxygen production. If the feedstock is LOX there is no additional on site energy consumption but there is the additional cost of the LOX. If oxygen is extracted from air on site (a plausible option at large water treatment works), there will be additional energy consumption.

Contact time

Sufficient contact time will be required to achieve the target Ct. For reasons noted above, in natural seawater or artificial formulations containing bromine/bromide, the Ct should be in terms of HOBr/OBr- rather than ozone, although the ozone will contribute to the overall disinfection. As noted above, TRO is normally expressed in units of Br_2 or Cl_2. The conversion is determined by electrochemical equivalence. One mole of bromine reacts with two electrons:

$$\mathrm{Br_2} + 2\mathrm{e}^- \rightarrow 2\mathrm{Br}^-$$

One mole of hypobromite also reacts with two electrons:

$$\mathrm{OBr}^- + 2\mathrm{e}^- + 2\mathrm{H}^+ \rightarrow \mathrm{Br}^- + \mathrm{H_2O}$$

Hence 1 mole hypobromite is equivalent to 1 mole of elemental bromine. Chlorine and hypochlorite similarly react with two electrons, so the same molar equivalence applies.

Therefore,

1 mole OBr^- is equivalent to 1 mole Br_2 is equivalent to 1 mole Cl_2

1 mg OBr^- is equivalent to 1.67 mg Br_2 is equivalent to 0.74 mg Cl_2

Stoichiometrically, from reaction 1, 1 mole ozone yields 1 mole hypobromite. So if

1 mole O_3 yields 1 mole OBr^- equivalent to 1 mole Br_2 equivalent to 1 mole Cl_2

1 mg O_3 yields 2 mg OBr^- equivalent to 3.33 mg Br_2 equivalent to 1.48 mg Cl_2

Complete conversion of ozone to hypobromite is unlikely but the reported chemistry suggests a high yield can be expected where bromide is in excess. It must be stressed that the above conversions apply only to the units in which concentrations are expressed, and have no relation to the relative disinfection efficacies of ozone, bromine and chlorine.

Whether $HOBr/OBr^-$ Ct data exist for the target pathogens is not known. By way of perspective, the World Health Organisation suggests a minimum Ct for disinfection of potable water with chlorine of 15 mg/l/min, derived from a minimum free chlorine residual of 0.5 mg/l and a minimum contact time of 30 minutes.

Monitoring

Ozonated seawater will initially contain both dissolved ozone and $HOBr/BrO^-$. The ozone will decay relatively quickly, producing more $HOBr/BrO^-$ as it does so. The $HOBr/BrO^-$ will decay more slowly. A standard ORP probe will respond to total oxidant concentration. Current electrochemical ozone sensors are claimed to be ozone-specific, and the indigotrisulphonate analytical method is ozone-specific, so it should be possible, if required, to monitor for dissolved ozone concentration. However, dissolved ozone is likely to interfere with HOBr/OBr$^-$ measurement. The measurement of total residual oxidant (TRO) appears accepted practice in the context of ozonated seawater. All oxidants present will contribute to redox potential.

Eliminating oxidant residual

If the intention is to avoid bringing any dissolved disinfectant into contact with the shellfish then the residual must be eliminated. This could be achieved chemically using sodium sulphite, sodium bisulphite or sulphur dioxide; or catalytically by filtration through granular activated carbon (GAC). GAC would potentially remove brominated organic by-products, although the useful bedlife for some compounds e.g. bromoform may be short. UV can be used for dechlorination, but it is not known if it is effective for debromination.