USE OF OZONE EQUIPMENT IN WATER TREATMENT

INCLUDING HEALTH AND SAFETY GUIDANCE

Important Safety Information – Please Read Carefully

Contents:-

1. What is Ozone?

Physical Properties

A colourless gas (O_3). Sometimes also called trioxygen. Made by passing oxygen (either as air or as pure oxygen) through an electric discharge. Very strong oxidising agent, highly toxic to all forms of life and corrosive to many materials. Boiling point -111.9°C, melting point -192.7°C. Liquid ozone is dark blue in colour. Can be measured directly (with ozone probes) but such equipment is very expensive and the Redox potential, or level (which changes with the amount of ozone in the water) is commonly used instead.

Control is essential, as over-dosing can result in concentrations which will harm the fish, and also the off-gassing of ozone in to the air, which in an enclosed area can cause long term harm to humans.

Uses of Ozone in Water Treatment
Mostly commonly used in sterilising systems, where relatively small quantities of water need to be sterilised (such as inlets to hatcheries etc.), and in recirculating systems where the ozone has several beneficial effects such as the breakdown (through oxidisation) of long chain molecules into simpler forms which can then be broken down further in the biological filter. It is through this process that ozone eliminates the yellow/brown colourations, that build up in recirculation systems.

Effects on Humans
Ozone is one of the most powerful disinfecting and oxidising agents known for use in water treatment. For this reason it is also highly toxic to man. Possible ill-effects of over-exposure to ozone are membrane irritation (lungs, eyes, nose, throat etc), headaches and nausea, dermatitis and eczema. Research also indicates possible links between ozone and skin damage, premature ageing and reproductive damage.

2. Ozone in the Working Environment

Materials of Construction.
Materials which are likely to come into contact with the air/ozone mixture, or the ozone solution in the water, must be resistant to electrolytic corrosion and chemical attack. Some of the materials used successfully in the UK are listed below:

- Mild steel Hypalon or Ikosit coated
- Polyethylene – medium and high density
- Polypropylene
- PTFE
- UPVC or CPVC
- Stainless steel grade 316 (low carbon) to BS 970 and BS 1449.

Care must be taken to ensure that all joining materials are also resistant to chemicals.

Any specification should state the limits of water quality required to give a performance guarantee for all materials which come into contact with the ozonated water. In general, operating temperature is critical to the performance of a material exposed to ozone and this should be taken into account. Generally resistive materials are less resistant at higher process temperatures.

Correct Siting of Ozone Equipment
The harzardous and corrosive nature of Ozone gas must be fully considered when designing facilities that may be used for siting equipment that produces, requires or may otherwise come into contact with ozone.

All equipment generating ozone or to which ozone is directed by pipework must be sited in a well ventilated area. Failure to operate ozone generating equipment in a properly designed and correctly ventilated facility risks a harzardous build-up of ozone gas or even an explosion.

It is important that if ozone is permitted to pass into operator working areas of an installation that safe Occupational Exposure Limits (OEL) are not exceeded – see below.
If there is a risk that ozone may accumulate, above these limits, in filter plant rooms or other installation operating areas, TMC strongly recommends the use of ambient air ozone monitors/detectors/alarms and an efficient fume extractor system to provide a well ventilated operating area. Ozone gas is heavier than air and it should therefore be noted that it can accumulate in void spaces. In such cases, the use of circulatory fans should also be considered. If in any doubt as to the presence of ozone, respiratory equipment should be available and used and the area checked with suitable monitors.

Being heavier than air, ozone lies on the surface of water as it comes out of solution and at this point is readily inhaled. If any amount of residual ozone is expected to be discharged from any part of the process above the safe limit of exposure to humans, it must be treated effectively using appropriate approved methods (granulated activated carbon filters, or alternatives - please see table 1.)

Recommended Safe Environmental Exposure Limits (OEL'S).
Exposure to ozone gas at workplaces in the UK is strictly controlled by COSHH Regulations. The Health and Safety Executive has set OELs (occupational exposure limits) for ozone of 0.1ppm (8 hours time-weighted average concentration) and 0.2ppm (15 minutes time-weighted average concentration).

Only air sampling tests can determine whether the OEL is being exceeded. This can be arranged by your company's Safety Adviser if necessary, using suitable ozone monitoring equipment.

It is sometimes possible to smell ozone, even when the OEL is not exceeded. This can occur when there is a build up during heavy and prolonged periods of use in poorly ventilated sites. It can be affected by temperature and climate changes also. There is some dispute about whether the odour alone is a nuisance rather than a hazard. However it possibly indicates that the OEL may be exceeded. Action should be taken promptly, retire to fresh air, ventilate the area, etc. Seek your Health and Safety Adviser's advice if there is a continuing problem.

Further Health and Safety Issues
- Equipment MUST only be installed, operated and maintained by sufficiently qualified or trained personnel.
- All installations must be operated in well ventilated conditions. Ambient Ozone detection equipment may be required if there is a risk that safe OEL's will be exceeded.
- All ozone tubing connections must be secure and joints kept to a minimum.
- Ozone carrying pipework and tubing to be clearly marked to indicate hazard and gas flows, clearly warning against operator intervention with pipework.
- Off-gassing from the process plant must be adequately vented or efficient extraction equipment must be installed. An inline off-gas destructor may be required on the ventilation outlet.
- No smoking to be allowed in the proximity of equipment or process.

3. Application of Ozone in Water Treatment Systems

Ozone Contact times and Dose Rates

After the ozone has been mixed with the water and caused to go into solution, it is necessary to keep the water in contact with the ozone for sufficient time to enable the disinfection and oxidation process to be completed. Typical contact times vary from 30 secs to 10 minutes depending on application. Most water treatments to condition but not sterilise water with ozone operate on contact times of 1 –2 minutes. Sterilisation with ozone may require contact times of up to 10 minutes and even 30 minutes for effective treatment of some viruses. Contact times can be reduced by applying higher concentrations of ozone to the process water.

TMC recommends that ozone should be applied at a concentration of between 5-15mg/hour per 100 litres of volume. In commercial applications, 0.05mg ozone per litre of flow is sufficient to achieve a recommended redox potential of 300 – 400 mV. This will remove yellowing effects of organic build up in the form of phenols etc. A much higher dose rate of 0.2 – 0.5mg ozone per litre of flow is required to achieve redox potentials of 700-800mV, at which the water can be considered sterilised but unfit for livestock without further treatment.

Factors which adversely affect the contacting efficiency are:-

1. Too low a concentration of ozone gas introduced into the water.
2. A higher than average water temperature.
3. The microbial and reducing loads in the water.

Further Guidelines for Use of Ozone in Water Treatment

- Ozone should never be introduced directly into a livestock tank and a suitable reactor/vessel should always be used.
- Ozone should be introduced slowly into the system and monitored carefully to ensure that no negative effects occur.
- A Redox controller should be used which will automatically adjust the ozone generator to changing conditions.
- Off-gas from reactors should be directed outdoors or through a suitable ozone destructor device, such as UV light or granular activated carbon (see table 1).
- Ozone is very unstable and can normally be removed from solution by aeration and a suitable standing period or residence time in an intermediate holding tank before use.
- High residual levels of Ozone in the water may only be removed quickly by further treatment. Activated carbon or UV treatment are accepted methods of removing excess Ozone from water. It should be noted that high levels of ozone treatment may result in the formation of stable secondary oxidation products which themselves maybe harmful to livestock and need to be removed or treated before use on livestock.

Ozone/Water Mixing Systems

Modern ozone generators which operate on dried air give a yield of 18-25 grams Ozone per cubic metre under normal atmospheric pressure and temperature (1 bar, 20ºC). Ozone is more soluble in water than oxygen or nitrogen. Normal air comprises 80% nitrogen and 20% oxygen. Higher concentrations of ozone can be generated when using pure oxygen as the gas source for the ozone generator and the extra output should be considered in terms of extra safety required for risk presented (see below). Most reactors supplied by TMC introduce ozone to the process water by means of a venturi.

Systems are described below which allow the ozone generator to operate in vacuum mode. In each case, isolating valves should be fitted for shut down and maintenance purposes.

Use of Venturi Injectors
A proportion of the water to be treated should be drawn off by a suitable booster pump and fed under pressure to the nozzle of the venturi unit. The entering jet of water causes a vacuum inside the venturi which, in turn, draws air through the ozone generator where it is entrained in the flow of water. The resultant gas/water mixture is then fed into a suitable mixing/contact vessel, for example, a TMC protein skimmer, to further enhance the dissolving of the ozone.

It is strongly recommended that the following design features are employed in any installation:-

- The venturi should be mounted in such a way that it can be readily removed for maintenance purposes.
- Pressure gauges can be fitted upstream and downstream of the venturi for both commissioning and to check for satisfactory operation.
- The booster pump should be selected to enable the venturi to draw the rated gas flow through the ozone generator under all normal conditions of flow and back pressure in the treatment water line.
- A flow-regulating valve should be fitted upstream of the venturi to enable adjustment of correct flow through the venturi.
- A shut-off valve should be fitted in the gas line feeding to the venturi from the ozone generator.
- Check valves should be fitted on both sides of the shut-off valve in the gas line.
- A water trap may be included in the gas line from the ozone generator in case of venturi and/or check valve failure and also to reduce the effects of condensation.
- The booster pumps wetted parts should be manufactured from ozone resistant materials. If this is not possible, the plant must be designed to ensure ozonated water is not introduced into the suction side of the booster pump.
- All pipework carrying ozone gas or ozone in solution should be clearly marked preferably in accordance with the latest British Standard or equivalent.

4. Commissioning, Operation and Maintenance of Ozone Equipment

Ozone Generators
It is most important that commercial ozone generating equipment and any plant connected to it is only installed and operated by a qualified or adequately trained person and in strict compliance with the manufacturer's instructions and recommendations. The equipment must be checked, and serviced at regular intervals according to the manufacturer's recommendation.

Modification of the plant without recourse to the manufacturer or failure to maintain according to the manufacturer's recommendation risks malfunction, harzardous release of gas or even an explosion.

There is a significantly greater risk of hazardous exposure from leaks from larger generators, producing 2 gms or more Ozone per hour. Adequate health and safety data including emergency procedures, in the event of human exposure above safe OEL's, should be displayed near the generating equipment and any plant or equipment supplied by it.

Ozone Detection and Monitoring Equipment
It is most important that ozone detection equipment and any plant connected to it is only installed by a qualified or adequately trained person and in strict compliance with the manufacturer's instructions and recommendations. The equipment must be checked, and serviced at regular intervals according to the manufacturer's recommendation. Ozone probes normally need replacing or factory recalibration at intervals not greater than 6 months. It is important that standby equipment is available when off site servicing is required.

Improper installation or failure to maintain monitoring equipment according to the manufacturer's recommendation risks non-detection of a harzardous release of gas that may cause human injury through inhalation or even an explosion.

Recommended Operating and Maintenance Procedure forUse of High Levels of Ozone (greater than 0.1mg per litre of flow) with Tropical Marine Centre Protein Skimmers.

- **We do not recommend the use of any Ozone Generators larger than 10 gm Ozone/hr to be used with any single TMC Protein skimmer without consulting TMC. Application of ozone at concentrations of higher than 0.5 mg/litre water may require modification of the equipment to ensure the integrity and safe operation of the equipment under these conditions. No modification of equipment should be undertaken without recourse to TMC**

- There is a significant risk that safe OEL's will be exceeded if larger ozone equipment is operated in a confined space and special care and attention should be given to ensuring that the equipment is installed in a properly designed facility with adequate ventilation in the form of both air extraction and mixing. The user may have to consult with a qualified ventilation expert before installing any equipment operating with ozone. It must be remembered that ozone is a corrosive gas and any building material, plant or equipment likely to come in contact with the gas must be enclosed or made of a suitably resistant material.

- A full risk assessment should be carried out on any proposed installation and a sample of a suitable checklist for this is attached to this document (appendix 1). In the event of any failure of air extraction and mixing equipment it is important that leaked or accumulated ozone is detected and a warning given to any person working in or near to the installation. A suitable ambient ozone detection system may be need to be interlocked with:-
  a) the ozone generator and reactor to ensure shut down of ozone production before OELs are exceeded and/or
  b) standby air handling equipment to ensure removal of ozone before OELs are exceeded.

- The integrity of all pipework carrying ozone gas and ozone saturated water must be checked on a DAILY basis for deterioration and all mechanical joints checked for tightness to ensure there are no leaks. All gas line joints on the contact vessel/skimmer and ozone generator, both solid pipework and tubing, MUST be checked on a DAILY basis prior to operation of the unit. All unions must be firmly tightened by hand and if necessary with a strap wrench to ensure a tight seal. It is also recommended that all glued joints be inspected for movement to confirm there is no breakdown in the adhesive. It may be necessary to manually pressurise pipework and connections, after shutting valves at the furthest point of isolation to check for leaks – any loss of pressure as measured on a suitable manometer should be investigated and rectified.

Operating protein skimmer venturis, once filled with liquid but prior to adding ozone with the venturi valves almost shut, would also alert the operator to any noise, suggesting air is being drawn into the pipework under vacuum through a leaking joint.

- Following purging of the unit and commencement of ozone flow, all joints should be run over with a hand held ozone monitor to confirm integrity when in operation.

- It is further recommended that operators carrying out these checks be protected by suitable respiratory equipment to prevent inadvertent inhalation of leaked gas.

- Once process is in full operation, further ozone checks should be carried out periodically around the equipment, including receiving tanks, to ensure there is not a local build up of ozone as a result of the process, i.e. escaping from the discharge pipes, collection vessels etc.

- On a WEEKLY basis, all mechanical joints and unions exposed to ozone gas should be opened and the rubber seals inspected to determine if perishing or any form of wearing and deformation is occurring, in which case these seals should be replaced before operating the equipment again.

- Ozone monitors must be calibrated on a six monthly basis or disposable probes renewed. It is recommended that a backup unit be available so that safety checks can continue to be made of the process equipment if off–site servicing needs to be carried out.

- Ozone generators and contact vessels must be maintained and serviced according to the manufacturer's guidelines

- If significant levels of residual ozone is detected in off–gas or processed liquid from the protein skimmer and any receptacle served by it, then further ozone destruction may need to be applied as suggested in table 1.

- **Table 1.**

Ozone Destruction Methods

Method	Design Criteria	Phase of Destruction	Advantages/ Disadvantages
Degassing	**Cross sectional area of degasser:** **$2 \times (0.0001 \times lpm) / 3.14))^{-2}$** Height 1.5m The air suction rate through the degasser should be at least 20% of the water flow rate.	Liquid	Off gas requires to be either vented away from staffed areas or should be treated. Can result in high pumping costs. Can be used as an integral part of trickle filter or carbon dioxide degasser if used within a system. Will increase oxygen concentrations to approx 85 - 95% saturated
Chemical Dosing	Dosing with sodium thiosulphate at 2mg/l to reduce each 1 mg/l ozone. This is very dependent however on oxygen content of water as the thiosulphate will also be used up reducing this.	Liquid	Costly to install and operate correctly. May result in removal of some oxygen from water Unknown effects of excessive thiosulphate on fish stocks
Activated Carbon	1g of carbon will remove 6g ozone, however allowance must be made for the carbon being used up with other chemicals that it will remove. Attention to water quality is therefore important.	Liquid or Gas	Expensive systems not really suited to aquaculture Costly replacement of carbon High operating costs through pumping through carbon beds.
Ultra Violet Light	150,000 mW cm^2 for 13 seconds to reduce 0.5 - 1.5 mg/l O_3 to safe levels	Liquid	Very dependent on constant water clarity/quality for effectiveness. Expensive to install but relatively cheap to run thereafter. Added benefits of disinfection of the water.

HEALTH & SAFETY PRODUCT DATA SHEET

PRODUCT:	Ozone (colourless gas) Very toxic by inhalation Skin & eye irritant
FIRE & EXPLOSION HAZARDS:	Unstable Solid and liquid gases are highly explosive
HEALTH HAZARDS:	Gas strongly irritates the upper respiratory tract and may cause headaches. High concentrations cause lung congestion Harmful by skin contact
PERSONAL PROTECTION:	Safety glass and good ventilation

In severe cases, seek medical attention.

Guidance notes

Exposure Tme Frame	**Concentration of Ozone ppm**
Up to a maximum of 8hrs in any one day	0.067
Maximum exposure for up to 5hrs per day	0.1
Maximum exposure for up to 15minutes	0.3

Note
0.1ppm is approx equal to 0.2mg of ozone per cubic metre of air

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