Study of the ozone technology

Public report

ainia

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Introduction

The **Ozonecip Project** is a demonstration project that aims to contribute to the achievement of a reduction in the environmental impact of the sanitation operations carried out in the food industry through an innovative sanitation technique based on the use of ozone as an alternative sanitizing agent to other sanitation products commonly used. The demonstration activities will focus on clean in place (CIP) protocols. The potential environmental benefits will be tested in three sectors: brewery, winery and dairy Three European centres will implement the project: Ainia (Spain) as coordinator, Bionord (Germany) and Gdansk University of Technology (Poland). Three companies will provide their industrial point of view: Allied domecq bodegas (winery), Becks (brewery) and Meiere-Genossenschaft e.G. Langernhorn (dairy)

This document is an output of the Task A Action A.3 “Study of the ozone technology” consisting on an intensive review of the technology and current applications.

This document is a Public Report that shows some of the main information extracted from the corresponding full reports submitted to the European Commission (Deliverables of the Project).

Acknowledgements

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COVERED ISSUES

The different issues covered in the full reports are the following:

1 Physical-Chemical properties of ozone: stability, solubulity in liquids, compatibility with construction materials, selectivity, reactivity
2 Mass transfer aspects
3 Ozone production, equipment
4 Operational conditions: temperaturer, pH, other
5 Combination of ozone with other agents (Uvlight, peroxide…)
6 Undesired reactions
7 Disinfectant properties of ozone and other chemicals used in food processing industries
8 Oxidant capabilities of ozone. Use of ozone for its oxidant properties (watewater, process)
9 Potential hazards (toxicity, TLVs,)
10 Advantages and disadvantages in front of other disinfectants and oxidants
11 Review of current applications of ozone technology within food processing industries for multiple purposes
12 Review of current applications of ozone for sanitation purposes

In the following pages some of the most interesting information area shown. Extended Reports delivered to the Commission

Ozone properties

Ozone molecule

Ozone is a blue gas but at concentrations at which it is normally produced the color is not noticeable. At -112°C, ozone condenses to a dark blue liquid but at room temperature, ozone is a nearly colorless gas. The ozone molecule contains three oxygen atoms (O3) whose **structures** are shown below:

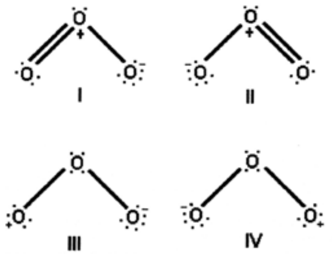
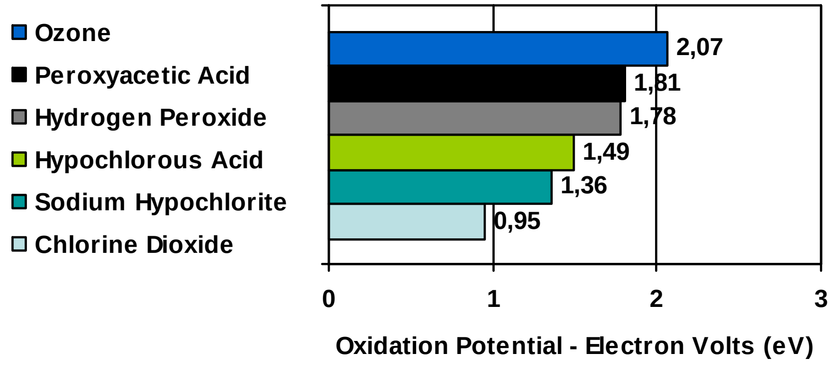


Fig. 1. Resonance structures of ozone molecule (Oehlschlaeger 1978)

The weak bond holding ozone's third oxygen atom is what causes the molecule to be **unstable** and thus, very effective as an **oxidizer**



The potential of the following reaction is:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad 2{,}07\ V$$

As a result of its oxidant properties possible applications of ozone in water solution are:

Oxidation of iron and manganese
Decolouration
Odour elimination
Disinfection
Increase the Biodegradability
Cracking of chelating agents
Mineralisation of contaminants and by products
Oxidation of cyanides, pesticides, hydrocarbons, pharmaceuticals…
Bleaching

Ozone properties

Ozone as a disinfectant

The potential applicability of ozone to the food industry is based on the fact that ozone is stronger than chlorine and has been shown to be effective over a much wider spectrum of microorganisms than chlorine and other disinfectants Based on 99.99% removal of bacterial concentration and considering the required application time ozone is:

10 times more effective than chlorine
25 times more effective than HOCl (Hypochlorous Acid)
2,500 times more effective than OCl- (Hypochlorite)
5,000 times more effective than NH2Cl (Chloramine)

The following table shows some of the most common molds, viruses and bacteria appearing in the food industry and the concentration of ozone and contact time necessary for complete inactivation.

Pathogen	**Dosage**
Aspergillus Niger (Black Mount)	Destroyed by 1.5 to 2 mg/l
Bacillus Bacteria	Destroyed by 0.2 m/l within 30 seconds
Bacillus Anthracis (causes anthrax in sheep, cattle and pigs. Also a human pathogen)	Ozone susceptible
Bacillus cereus	99% destruction after 5-min at 0.12 mg/l in water
B. cereus (spores)	99% destruction after 5-min at 2.3 mg/l in water
Bacillus subtilis	90% reduction at 0.10-PPM for 33 minutes
Bacteriophage f2	99.99% destruction at 0.41 mg/l for 10-seconds in water
Botrytis cinerea	3.8 mg/l for 2 minutes
Candida Bacteria	Ozone susceptible

Clavibacter michiganense	99.99% destruction at 1.1 mg/l for 5 minutes
Cladosporium	90% reduction at 0.10-PPM for 12.1 minutes
Clostridium Bacteria	Ozone susceptible
Clostridium Botulinum Spores. Its toxin paralyses the central nerve system, being a poison multiplying in food and meals.	0.4 to 0.5 mg/l threshold value
Coxsackie Virus A9	95% destruction at 0.035 mg/l for 10-seconds in water
Coxsackie Virus B5	99.99% destruction at 0.4 mg/l for 2.5-minutes in sludge effluent
Diphtheria Pathogen	Destroyed by 1.5 to 2 mg/l
Eberth Bacillus (Typhus abdomanalis). Spreads typically by aqueous infection and causes typhoid.	Destroyed by 1.5 to 2 mg/l
Echo Virus 29: The virus most sensitive to ozone.	After a contact time of 1 minute at 1 mg/l of ozone, 99.999% killed.
Enteric virus	95% destruction at 4.1 mg/l for 29 minutes in raw wastewater
Escherichia Coli Bacteria (from feces)	Destroyed by 0.2 mg/l within 30 seconds in air
E-coli (in clean water)	99.99% destruction at 0.25 mg/l for 1.6 minutes
E-coli (in wastewater)	99.9% destruction at 2.2 mg/l for 19 minutes
Encephalomyocarditis Virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l.
Endamoebic Cysts Bacteria	Ozone susceptible
Enterovirus Virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l.
Fusarium oxysporum f.sp. lycopersici	1.1 mg/l for 10 minutes
Fusarium oxysporum f.sp. melonogea	99.99 % destruction at 1.1 mg/l for 20 minutes
GDVII Virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l.
Hepatitis A virus	99.5% reduction at 0.25 mg/l for 2-seconds in a phosphate buffer
Herpes Virus	Destroyed to zero level in less than 30 seconds wit 0.1 to 0.8 mg/l.
Influenza Virus	0.4 to 0.5 mg/l threshold value
Klebs-Loffler Bacillus	Destroyed by 1.5 to 2 mg/l

Legionella pneumophila	99.99% destruction at 0.32 mg/l for 20 minutes in distilled water
Luminescent Basidiomycetes (species having no melanin pigment).	Destroyed in 10 minutes at 100-PPM
Mucor piriformis	3.8 mg/l for 2 minutes
Mycobacterium avium	99.9% with a CT value of 0.17 in water
Mycobacterium foruitum	90% destruction at 0.25 mg/l for 1.6 minutes in water
Penicillium Bacteria	Ozone susceptible
Phytophthora parasitica	3.8 mg/l for 2 minutes
Poliomyelitis Virus	99.99% kill with 0.3 to 0.4 mg/l in 3-4 minutes
Poliovirus type 1	99.5% destruction at 0.25 mg/l for 1.6 minutes in water
Proteus Bacteria	Very susceptible
Pseudomonas Bacteria	Very susceptible
Rhabdovirus virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l
Salmonella Bacteria	Very susceptible
Salmonella typhimurium	99.99% destruction at 0.25 mg/l for 1.67 minutes in water
Schistosoma Bacteria	Very susceptible
Staph. epidermidis	90% reduction at 0.1-ppm for 1.7 min
Staphylococci	Destroyed by 1.5 to 2.0 mg/l
Stomatitis Virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l
Streptococcus Bacteria	Destroyed by 0.2 mg/l within 30 seconds
Verticillium dahliae	99.99 % destruction at 1.1 mg/l for 20 minutes
Vesicular Virus	Destroyed to zero level in less than 30 seconds with 0.1 to 0.8 mg/l
Virbrio Cholera Bacteria	Very susceptible
Vicia Faba progeny	Ozone causes chromosome aberration and its effect is twice that observed by the action of X-rays

Ozone properties

Stability

Ozone is quite unstable and quickly breaks back down into oxygen. Ozone in pure water rather quickly degrades to oxygen, and even more rapidly in impure solutions (Hill and Rice, 1982). Ozone decomposition is faster at higher water temperatures (Rice et al., 1981). Ozone has a longer half-life in the gaseous state than in aqueous solution (Rice, 1986)

Gaseous	
Temp (C)	**half-life ***
-50	3-months
-35	18-days
-25	8-days
20	3-days
120	1.5-hours
250	1.5- seconds

Dissolved in Water (pH 7)	
Temp (C)	**half-life**
15	30-minutes
20	20-minutes
25	15-minutes
30	12-minutes
35	8-minutes

Thus, ozone will not leave a residual after a short time of use nor will increase the conductivity of the waters when used in water solution.

Ozone properties

Reactivity

The decomposition of O3 may suffer several reactions in which free radicals area produced. The decomposition rate may be increased with temperature and pH and is catalysed by the presence of OH-, organic compounds, alkaline solids, transition metals, metallic oxides, carbon, etc

Ozone reacts with **ORGANIC COMPOUNDS** in two ways:

a) directly, when MOLECULAR OZONE reacts with the compound in question, or

$$O_3 + M \longrightarrow M_{ox}$$

b) indirectly, through the auto-decomposition of the ozone and formation of **HIGHLY REACTIVE FREE RADICALS** such as the hydroxyl or hydroperoxyl radicals

$$O_3 \xrightarrow{OH^-} OH^* \xrightarrow{M} M_{ox}$$

The first type of reaction will occur in acid media and with solutes that will react very fast with ozone, as, e.g. unsaturated organic compounds. The second mechanism may be initiated with species such as OH-, Fe2+

Ozone properties

Solubility

The solubility of gases in liquid media is described by Henry's law. Henry's law states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the liquid. Principally, Henry's law can only be applied on gasses that do not chemically change in water, during transfer. The prediction of ozone solubility is more complicated than for other gasses, because ozone solubility is influenced by several factors. The degree of solubility of ozone gas is dependant on the concentration in gas and thus dependant on the partial pressure. Another important factor influencing the solubility is the temperature. Besides temperature, pH and ion concentration in the solution are the main factors influencing the solubility. Summarized, the solubility of ozone in water can be increased by:

- Increasing the ozone concentration in the feed gas;
- Increasing air pressure;
- Decreasing the water temperature;
- Decreasing the amount of solutes;
- Decreasing the pH

Ozone Solubility Chart

The Chart lists the solubility of 100% ozone in pure water, for the range of 0-60ºC. (Ullmann's, 1991) such values from the Ozone Chart were divided by 40, 20 & 10, respectively to obtain the solubility for 5% & 10% by wt. ozone concentrations.

Temperature (°C)	mg/l (PPM)	mg/l (PPM) (2.5% by wt. O3)	mg/l (PPM) (5% by wt. O3)	mg/l (PPM) (10% by wt. O3)
0	1090	27.25	54.5	109
10	780	19.5	39.0	78
20	570	14.25	28.5	57
30	400	10	20.0	40
40	270	6.75	13.5	27
50	190	4.75	9.5	19
60	140	3.5	7.0	14

Mass transfer gas to liquid

When thinking of ozonated water for sanitation purposes, we'll try to enhance the oxidant available in solution to carry out the job more efficiently and faster. Measures shoul be taken to increase the solubility as staed before, along wiyh other aspects that increase the mass transfer of ozone from the gas phase to the liquid phase:

Gas transfer rates depend on:

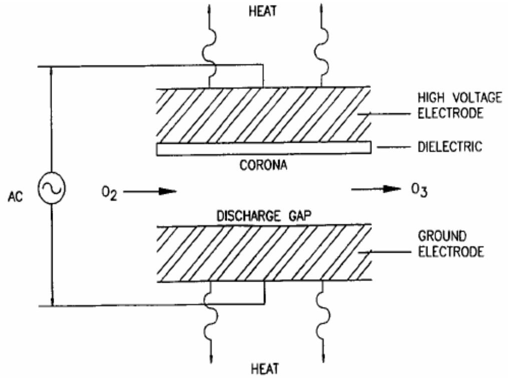
- Gas phase concentration
- Gas to liquid ratio (Vg/Vl)
- Pressure within the contacting system
- Mixing (Gas/Liquid Interface renewal)
- Contact time
- Instantaneous O3 demand

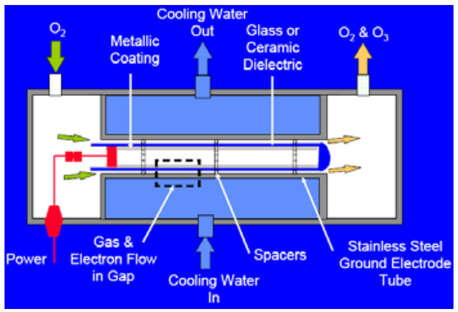
Ozone production

Ozone generator

In order to generate ozone, a diatomic oxygen molecule must first be split. The resulting free radical oxygen is thereby free to react with another diatomic oxygen to form the triatomic ozone molecule. However, in order to break the O–O bond a great deal of energy is required. Ultraviolet radiation (188 nm wavelength) 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. 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). Those are separated by a ceramic dielectric medium and narrow discharge gap should be provided. When the electrons have suffcient 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. **If air is passed through the generator as a feed gas, 1–3% ozone can be produced**, **however, using pure oxygen allows yields to reach up to 6% ozone (Rice et al., 1981).** Consequently, ozone concentration cannot be increased beyond the point that the rates of formation and destruction are equal (Manley & Niegowski, 1967).



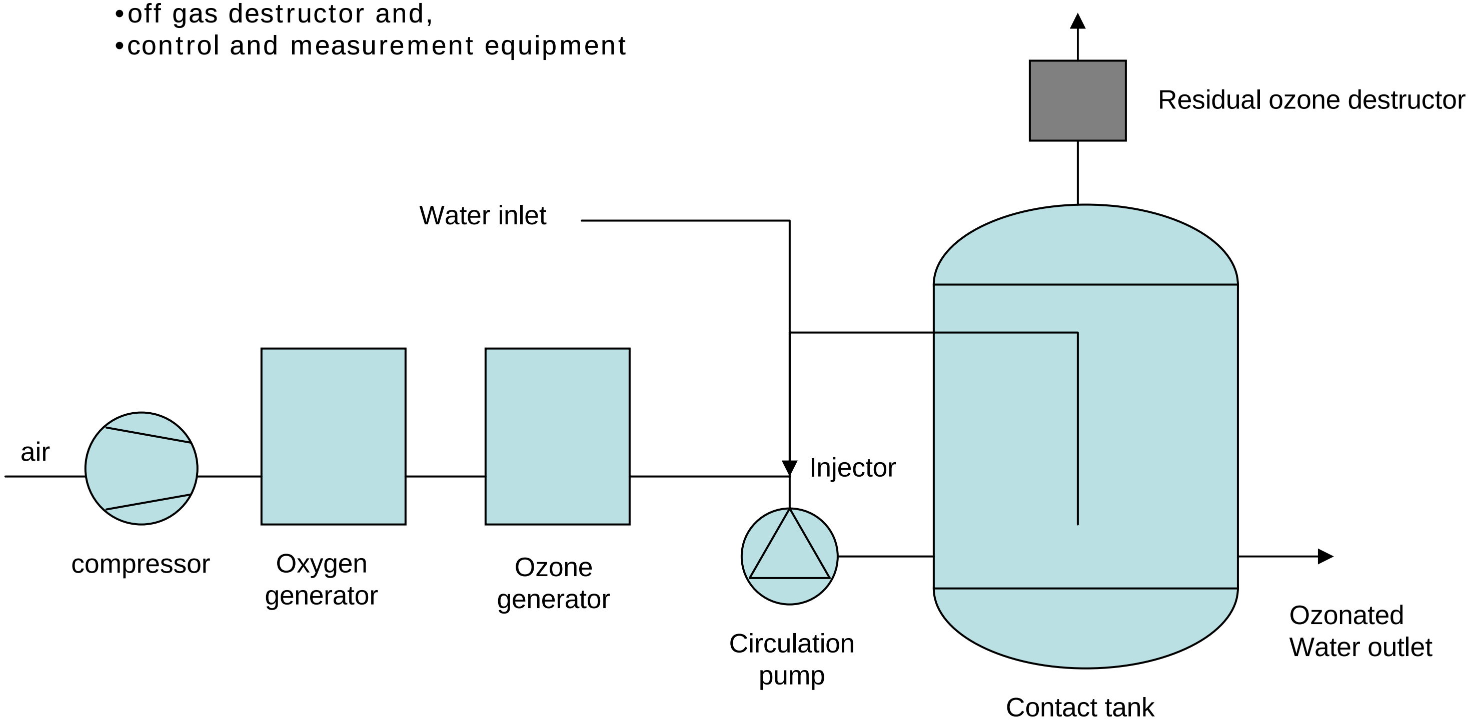


Ozone production

Auxiliary equipment

in addition to the ozone generator an ozonation system, needs auxiliary equipment such as:

- a gas feed preparation system (dry air or oxygen)
- an injector
- a contact tank,
- off gas destructor and,
- control and measurement equipment



Ozone interaction with materials

Material	Rating (Cole Parmer) [Ozone Concentrations not specified]	Material	Rating (Cole Parmer) [Ozone Concentrations not specified]
ABS plastic	B - Good	LDPE	B - Good
Acetal (Delrin®)	C - Fair	Magnesium	D - Poor
Aluminum	B - Good	Monel	C - Fair
Brass	B - Good	Natural rubber	D - Severe Effect
Bronze	B - Good	Neoprene	C - Fair
Buna-N (Nitrile)	D - Severe Effect	NORYL®	N/A
Butyl	A - Excellent	Nylon	D - Severe Effect
Cast iron	C - Fair	PEEK	A - Excellent
Chemraz	A - Excellent	Polyacrylate	B - Good
Copper	B - Good	Polycarbonate	A - Excellent
CPVC	A - Excellent	Polypropylene	C - Fair
Durachlor-51	A - Excellent	Polysulfide	B - Good
Durlon 9000	A - Excellent	Polyurethane, Millable	A - Excellent
EPDM	A - Excellent	PPS (Ryton®)	N/A
EPR	A - Excellent	PTFE (Teflon®)	A - Excellent
Epoxy	N/A	PVC	B - Good
Ethylene-Propylene	A - Excellent	PVDF (Kynar®)	A - Excellent
Fluorosilicone	A - Excellent	Santoprene	A - Excellent
Galvanized Steel	In Water (C - Fair), In Air (A - Excellent)	Silicone	A - Excellent
Glass	A - Excellent	Stainless steel - 304	B - Good/Excellent
Hastelloy-C®	A - Excellent	Stainless steel - 316	A - Excellent
Hypalon®	A - Excellent	Steel (Mild, HSLA)	D - Poor
Hytrel®	C - Fair	Titanium	A - Excellent
Inconel	A - Excellent	Tygon®	B - Good
Kalrez	A - Excellent	Vamac	A - Excellent
Kel-F® (PCTFE)	A - Excellent	Viton®	A - Excellent
		Zinc	D - Poor

Ozone interaction with the equipment and surfaces to be cleaned and disinfected is a key factor that must be taken into consideration, essentially because of the corrosion it may cause but also because the ozone loses its effectiveness. Consequently, it is good practice to identify all the materials on site that could come into contact with the ozone and check their potential resistance in order to avoid unpleasant surprises.

Ratings -- Chemical Effect

A. **Excellent**. -- No effect
B. **Good** -- Minor Effect, slight corrosion or discoloration.
C. **Fair** -- Moderate Effect, not recommended for continuous use. Softening, loss of strength, swelling may occur.
D. **Sever Effect** -- Not recommended for **ANY** use.

N/A = Information Not Available.

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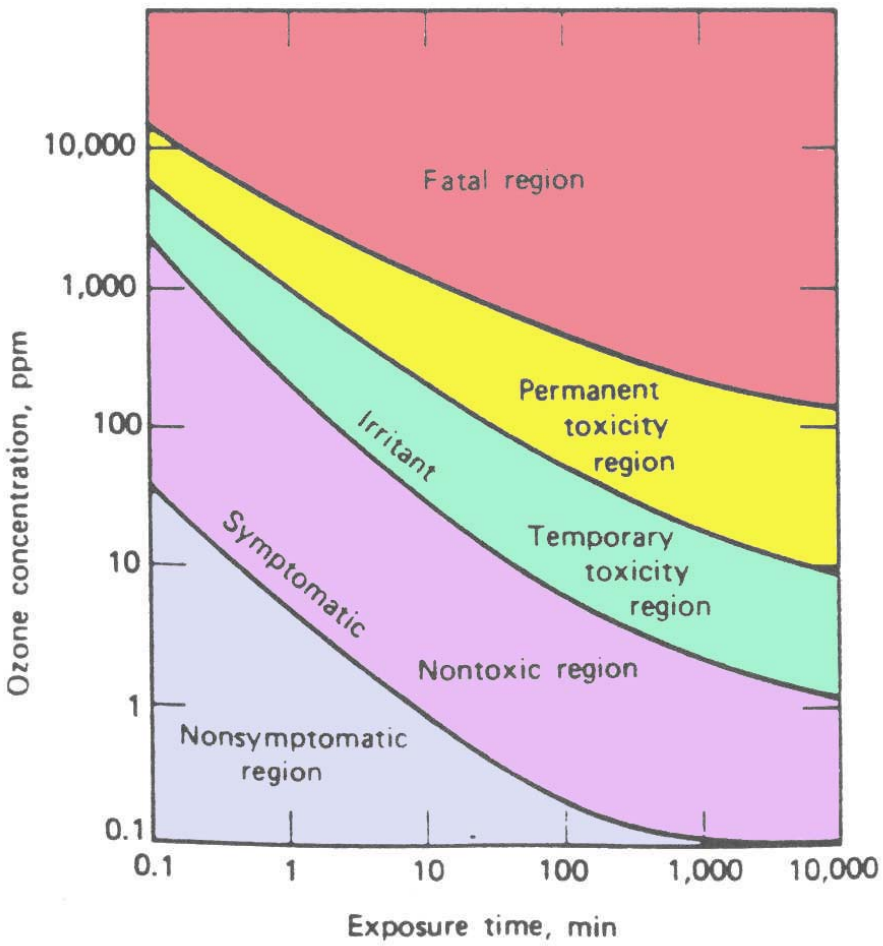
Ozone & hazards

The following table shows the international chemical safety card for ozone. Its aim is to ensure that workers and everyone concerned with their protection, have access to the facts they need to prevent occupational injuries and diseases. Those persons who work with this gas must be aware of its content as it has all the important information concerning ozone exposure.

INTERNATIONAL CHEMICAL SAFETY CARDS			
OZONE		ICSC: 0068	
TYPES OF HAZARD/ EXPOSURE	**ACUTE HAZARDS/ SYMPTOMS**	**PREVENTION**	**FIRST AID/ FIRE FIGHTING**
FIRE	Not combustible but enhances combustion of other substances. Many reactions may cause fire or explosion.	NO open flames, NO sparks, and NO smoking. NO contact with combustibles	In case of fire in the surroundings: use appropriate extinguishing media
EXPLOSION	Risk of fire and explosion when heated or on contact with combustible substances (alkene, ethers).	Closed system, ventilation, explosion-proof electrical equipment and lighting	In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position.
EXPOSURE		STRICT HYGIENE!	
INHALATION	Cough. Headache. Shortness of breath. Sore throat.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
SKIN	ON CONTACT WITH LIQUID: FROSTBITE	Cold-insulating gloves.	ON FROSTBITE: rinse with plenty of water, do NOT remove clothes. Refer for medical attention.
EYES	Redness. Pain. Loss of vision.	Face shield, or eye protection in combination with breathing protection	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.

Ozone & hazards

Toxicity



Ozone is lethal to humans with prolonged exposure at concentrations above 4 ppm. Ozone is readily detectable by human smell at 0.01 to 0.04 ppm concentration in air. It is not listed as a carcinogen. There is a parameter called "Threshold Limit Value" (TLV) which refers to the environmental concentration of a substance to which a worker can be exposed daily without being damaged. Due to individual variation, it has to be considered that some workers may show the symptoms related to some substances at the same or minor concentrations as the TLV. OSHA (Occupational Safety and Health Administration) limits of exposure specify a 0.1ppm threshold for continuous exposure during an 8 hours period and 0.3ppm for a 15 minutes period (both limits are referred to air concentration)

Ozone & hazards

PHYSICAL STATE; APPEARANCE	Colourless or bluish gas, with characteristic odour.
PHYSICAL DANGERS	The gas is heavier than air.
CHEMICAL DANGERS:	The substance decomposes on warming producing oxygen, which increases fire hazard. The substance is a strong oxidant and reacts violently with combustible and reducing materials. Reacts with alkenes, aromatics such as aniline, and ethers, bromine, nitrogen compounds and rubber producing shock-sensitive compounds. Attacks metals except gold and platinum.
OCCUPATIONAL EXPOSURE LIMITS:	TLV: (light work) 0.1 ppm as TWA (Time Weighted Average); TLV: (moderate work) 0.08 ppm as TWA; TLV: (heavy work) 0.05 ppm as TWA; A4 (not classifiable as a human carcinogen); (ACGIH 2004).MAK: Carcinogen category: 3B; (DFG 2004). OSHA PEL (permissible Exposure Limit): TWA 0.1 ppm (0.2 mg/m^3) OSHA STEL (Short Term Exposure Limit) : 0,3 ppm (15 Minutes) NIOSH (National Institute for Occupational Safety and Health) REL (Recommended Exposure Limit): C 0.1 ppm (0.2 mg/m^3) NIOSH IDLH (Immediately Dangerous to Life and Health): 5 ppm
ROUTES OF EXPOSURE:	The substance can be absorbed into the body by inhalation.
INHALATION RISK:	A harmful concentration of this gas in the air will be reached very quickly on loss of containment.
EFFECTS OF SHORT-TERM EXPOSURE:	The substance is irritating to the eyes and the respiratory tract. Inhalation of the gas may cause lung oedema. Inhalation of the gas may cause asthma-like reactions. The liquid may cause frostbite. The substance may cause effects on the central nervous system, resulting in headache and impaired vigilance and performance.
EFFECTS OF LONG-TERM OR REPEATED EXPOSURE	Lungs may be affected by repeated or prolonged exposure to the gas

Ozone safety measures

Some safety measures to allow for are:

- -Correct materials of construction
- -Ventilation
- -Safety monitoring
- -Exposure limits
- -Ozone destruction