Paper No.
492

CORROSION96
The NACE International Annual Conference and Expositi

OZONE TOXICOLOGY AND GUIDELINES FOR SAFE USE IN COOLING WATER OZONATION SYSTEMS

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ABSTRACT

Ozone, like all oxidizing gases, is potentially harmful if human exposures occur at a significant concentration for a sufficient duration. This paper discusses the physical properties of ozone, current exposure standards, toxicology of ozone, and recommended safety practices for safe operations in cooling water treatment applications.

INTRODUCTION

Ozone is a gas which is used in many industrial and municipal water treatment applications due to its high oxidation potential and disinfecting capabilities, its relatively short half-life, and the fact that it decomposes into simple diatomic oxygen. In addition to cooling water treatment, common applications include:

1. Potable Drinking Water Disinfection & Flocculation
2. Municipal Waste Disinfection & Odor Control
3. Swimming Pool Disinfection
4. Industrial/Hazardous Waste Decontamination
5. Bottled and Beverage Process Water & Container Wash Water Disinfection
6. Fish Hatcheries, Aquaculture & Aquaria Disinfection
7. Food Processing Disinfection
8. Ultrapure Water Disinfection & Organic Oxidation
9. Industrial Sanitation & Oxidation
10. Pulp & Paper Bleaching
11. Chemical Manufacturing
12. Medical Disinfection

PHYSICAL FEATURES OF OZONE

Ozone (O_3) is an unstable , bluish gas which has a molecular weight of 48.0, a gas density of 2.144 grams/liter at 0^{o} Centigrade and atmospheric pressure, and a boiling point of minus 112^{o} Centigrade at atmospheric pressure (1). It is partially soluble in water (more than oxygen - see Table 1) and has a characteristic pungent odor detectable at concentrations as low as 0.01 - 0.05 ppm in ambient air (2).

Ozone is a powerful oxidant, having an oxidation potential of 2.07 volts in alkaline solutions. It is therefore capable of oxidizing many types of organic and inorganic material. By comparison, it is 52% greater than the oxidation potential of chlorine which is 1.35 volts.

Low concentrations of ozone gas are produced for industrial or municipal applications by corona discharge ozone generators, generally at concentrations of 1-3% (w/w) from air and 2-12% (w/w) from oxygen. Ozone can be explosive if produced in concentrations in excess of 15%. This high of a concentration, however, cannot be produced with commercially available ozonation equipment.

Ozone has a relatively unstable in aqueous solutions. It has a half-life in distilled water of 20-30 minutes at 20^{o} Centigrade before reverting back to simple diatomic oxygen (O_2). If oxidant-demanding materials are in the water, the half-life is substantially less and is generally measured in minutes in typical cooling water.

AMBIENT EXPOSURE LEVELS OF OZONE

Ozone is ubiquitous to the environment and is found in varying concentrations throughout the atmosphere. It is formed naturally in the upper atmosphere from oxygen by ultraviolet light and by atmospheric electrical discharges such as or lightning or the aurora borealis. Ozone is also found in lower levels of the atmosphere primarily due to photochemical oxidation of hydrocarbons from automobile and industrial emissions. It is also coincidentally produced by a number of man made methods such as by photocopy instruments, electrical transformers, or other electrical devices. Human exposure to ozone thus occurs at some concentrations on a continuous day to day basis (3).

Congested roadways and industrial areas have been typically associated with comparatively higher levels of ozone in the lower atmosphere. Levels up to 1.0 ppm have been found in some areas of Los Angeles in the past (4). Levels even exceeding these have been found in passenger cabins of some commercial aircraft (5). Workplace exposures of up to 9.0 ppm have been found in some gas shielded arc welding applications (6). Measurable and sometimes excessive levels have also been found in many office environments containing electrical equipment such as X-ray apparatus, neon lamps, and copy machines or laser printers (7) prompting promulgation of recent ventilation standards for such work environments. As discussed further below, some workers can be even exposed to ozone concentrations in excess of the recommended TLV-TWA and TLV-STEL in the absence of any commercial generation and use of ozone at the site because of high background ambient ozone levels.

EXPOSURE THRESHOLD LIMIT STANDARDS FOR OZONE

The current Threshold Limit Value - Time Weighted Average (TLV-TWA) for ozone exposure in the workplace environment is 0.1 ppm (8) as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) and allowed by the U.S. Occupational Safety and Health Administration (OSHA). This is the concentration to which healthy, nonsusceptible individuals can be repeatedly exposed for a normal 8 hour day / 40 hour work week without adverse effects. The current Threshold Limit Value - Short Term Exposure Limit (TLV-STEL) is 0.3 ppm (8). This is the level to which healthy, nonsusceptible individuals can be exposed for a short term period of time without suffering from irritation or other acute effects providing that the TLV-TWA is not exceeded. A TLV-STEL is defined as a 15 minute time-weighted average exposure which should not be exceeded at any time during the workday even if the 8 hour time weighted average does not exceed the TLV-TWA. Exposures at the TLV-STEL should not be longer than 15 minutes and should not be repeated more then 4 times per day. There should be at least 1 hour between successive exposures at the TLV-STEL.

TOXICOLOGY OF OZONE

The acute and chronic effects of excessive exposure to ozone have been well investigated. Exposures to concentrations of ozone in excess of several tenths of a ppm sometimes cause reports of discomfort in a small susceptible portion of the population. This can be in the form of headaches or dryness of the throat and mucous membranes of the eyes and nose following exposures of short duration (9,10). Repeated exposure to ozone at such concentrations at 24 hour intervals, however, caused no further increase in airway irritability. In fact, after the first exposures, additional exposures to ozone had progressively lesser effects suggesting that tolerance may develop to these effects of ozone (4).

Ozone has been shown to be more injurious at concentrations exceeding 2.0 ppm over several hours (11); such as experienced by gas shielded arc welders. The primary site of acute effects is the lung which is characterized by pulmonary congestion. This acute impact subsided in welders when exposures were reduced to less than 0.2 ppm (12). Based on animal studies, exposures over 10-20 ppm for an hour or less are believed to be lethal in humans although there has never been a single recorded fatality attributed to ozone overexposure in the greater than 100 years history of commercial use.

With respect to long term or chronic toxicity, ozone is a radiomimetic agent. That is, the effects of prolonged exposure to excessive ozone exhibits the same effects as excessive exposure to sunlight. These effects are drying of the dermal surfaces and general aging of exposed tissue. According to the ACGIH (8), ozone is not a confirmed nor suspected human carcinogen. Nor does it exhibit teratogenic or mutagenic properties.

COMPARATIVE SAFETY ASPECTS

In many industrial applications, ozone is the gaseous oxidant of choice. This is due to the following properties of ozone or its manufacture:

1. Ozone has the highest oxidation potential of commercially available oxidizing agents. A chemical with an increased oxidation potential has faster reaction kinetics. This will require either less of the chemical or reduced contact times to complete the desired oxidation reactions compared to weaker oxidizing agents.

2. Ozone is manufactured onsite, at relatively low concentrations and pressures (less than 15 psig), and is immediately consumed in the treatment process. It is not stored as a compressed gas. An uncontrolled, widespread, and immediate release of large quantities of ozone is thus not possible to the extent that the sudden releases of the entire contents of containers of other bulk stored, concentrated chemicals can occur upon an industrial accident or natural disaster.

3. Ozone has a comparatively short half-life; generally measured in minutes in the aqueous phase to hours in the gas phase. Any accidental releases of ozone will not persist in the environment as long compared to if more stable oxidizing agents were released.

4. Ozone decomposes into simple diatomic oxygen upon breakdown. It will not form environmentally harmful or persistent compounds upon reaction with common hydrocarbons nor will it result in the formation of chlorinated hydrocarbons.

5. Ozone has a characteristically strong odor that is detected at concentrations as low as 0.01; or one-tenth of the allowable TLV-TWA. It is thus readily detected by an individual at concentrations well below where harmful concentrations are reached. Further, the pungent smell is so powerful at concentrations above 0.5 ppm that normal individuals will quickly remove themselves from such an excessive exposure well before significant exposures are recorded unless incapacitated or exits or egress is otherwise blocked.

6. Ozone is considered to be freely dispersed in the atmosphere. It will not sink to low level and concentrate near the ground where human exposure potential is the greatest.

COMPARATIVE SAFETY STANDARDS

As a result of these properties, ozone is not regulated nor subjected to the same strict safety standards governing the use of other site-stored, compressed oxidizing gases. Following is a summary of safety standards mandated for the safe use of ozone.

Uniform Fire Code Regulations for Ozone Manufacture and Use - Regulations pertaining to the transportation, storage, handling, and use other such gases (such as chlorine) are embodied in Article 80 of the Uniform Fire Code (UFC). Use of ozone in the United States is exempted from these provisions. In recognition of the potential for excessive exposure, albeit reduced, which always exists when ozone is being generated and used in an industrial or public environment, the Executive Committee of the National Uniform Fire Code (UFC) approved a new standard for the safe use of commercial and industrial ozonation systems (4). The new regulations are far reaching in their scope and represent a significant consideration in the development of new ozonation projects and the maintenance or upgrading of older systems. Many aspects of the code changes employ certain standard safety precautions that are currently in widespread use with other compressed toxic gases. Many of these safety precautions have also been routinely employed in the past by most large vendors of ozonation systems and include external interlocks, exhaust treatment of ventilated cabinets, and secondary containment. The new requirements, presented in Appendix A in their entirety, are generally discussed below and elsewhere (5).

For all non-residential ozone generators which have a maximum daily output capacity of greater than 0.5 lbs. per day, the proposed code changes specify that generators must be either in: 1) unoccupied, ventilated rooms labeled with appropriate warnings and continuously monitored for ozone with an alarm and safety shutoff system; or, 2) approved cabinets with ventilation. The cabinets must meet standards appropriate for their use and N.E.M.A standard 250 is noted as an approved design guide. One exception to this requirement is if the "generator is in an approved pressure vessel". In committee developmental discussions, this was presumed and specifically required to be an A.S.M.E approved vessel. The final code language, however, was modified on the floor at the fire code hearings and now seemingly provides more design options compared to A.S.M.E certification of pressure vessels. It is likely, though, that any such pressure vessel approval within any jurisdiction would, in the absence of more definitive standards, require A.S.M.E. compliance. Generators must also be appropriately labeled with specified warning stickers and the generators must be seismically anchored per Uniform Building Code requirements.

Ventilation exhaust from either a room or cabinet must be directed to a treatment system designed to reduce the discharge concentration of the exhausted gas to 5 ppm. This is 1/2 of the level determined to be "immediately dangerous to life and health" (IDLH = 10 ppm). If cabinet ventilation is employed, air intake into the ozone generator must be at a velocity greater than 200 fpm to ensure no fugitive emissions escape from the generator. A high ambient ozone concentration monitor interlock on the ozone generator may be used in lieu of ventilation exhaust treatment when ozone generators are in rooms.

Secondary containment of all valves, fittings, gages, and piping carrying ozone gas must be installed except where welded stainless steel pipe is employed. This secondary containment must also be vented to an appropriate exhaust treatment system.

All materials which come into contact with the ozone gas must be completely ozone compatible to prevent ozone leaks. Acceptable materials include 304 Stainless Steel, PVC, glass, Hypalon, Teflon, etc.

An external interlock must also be provided for the ozone generator to ensure shutdown of the generator in the event of an external system failure or shutdown The external interlocks must include at minimum a failure of the ventilation treatment system, a failure of the ambient ozone concentration monitor(if being used in a room), and a failure of the process being treated (generally indicated by a pump on/off condition and a high ORP interlock).

Emergency shut off switches must be on the generator and within 10 feet of the primary exit if the generator is in a room.

<u>British Columbia Workman's Compensation Board Standards</u> - The only other set of comprehensive standards governing the safe use of ozone is issued by the Workman's Compensation Board of the Province of British Columbia (6). Functionally, these standards are similar in objective and scope compared to the Uniform Fire Code. The primary

differences are that there is not an option for cabinet ventilation allowed in the B.C. -W.C.B. Standards. The B.C..-W.C.B. Standards also do not require secondary containment of ozone carrying process piping if it is not welded stainless steel. Periodic process measurements are also required of the ozone treated water and room ventilation to ensure the absence of ozone in these flows.

Standards for Use of Oxygen as a Feed Gas - Due to the risk of fire, the use of oxygen as a feed gas for ozone generators is also subject to recommended standards and/or those promulgated by the Uniform Fire Code. In general, safe use of oxygen can only be guaranteed if a basic safety tenet of oxygen use has been followed - that being that the oxygen must **never** come into contact with **any** organic material due to the extreme flammability of oxygen and the potential for violent explosions and/or very aggressive fires upon ignition or self combustion. This prevents the use of **any** organic elastomers or materials (even Teflon) in the oxygen manufacture or delivery systems, the ozone generator, or any downstream equipment which may be exposed to the oxygen or ozone-containing oxygen gas. From a practical point of view, this means that only metal, glass, or ceramic components or inorganic elastomers (generally synthetic silicon based). A particular note of caution is warranted strongly advising against the use of carbon filters to convert any outgassed ozone back into oxygen before release into the environment. This is because the use of oxygen in conjunction with activated carbon in the offgas catalytic converter is a serious hazard to human health and safety due to the risk of explosion of the carbon canister if it is ignited while having oxygen passing through it.

Further, as a result of the potential for fire in any application involving highly purified oxygen gas (including both compressed oxygen gas and oxygen produced from oxygen generators), specific safety criteria have been embodied in the Uniform Fire Code (16) pertaining to the proper and safe use of oxygen. The regulations include, among numerous additional requirements, specifications for the type and gauge of gas delivery lines, acceptable solders and brazing materials, pipe and equipment cleaning procedures, material compatibility, etc.

Although not specifically required in any regulations, the use of automatic, temperature actuated halon fire extinguishers mounted internal to the ozone generator cabinet is also very strongly recommended in those cooling tower ozonation applications employing oxygen as a feed gas.

CONCLUSIONS

Ozone, like all oxidizing gases, is potentially harmful if human exposures occur at a significant concentration for a sufficient duration. Exposures to concentrations of ozone in excess of several tenths of a ppm sometimes cause reports of discomfort. This can be in the form of headaches or dryness of the throat and mucous membranes of the eyes and nose following exposures of short duration (9,10). Ozone has been shown to be more injurious at concentrations exceeding 2.0 ppm over several hours (11). The primary site of acute effects is the lung which is characterized by pulmonary congestion. There has never been a single recorded fatality attributed to ozone overexposure in the greater than 100 years history of commercial use.

The current Threshold Limit Value - Time Weighted Average (TLV-TWA) for ozone exposure in the workplace environment is 0.1 ppm as allowed by the U.S. Occupational Safety and Health Administration (OSHA). The Executive Committee of the National Uniform Fire Code (UFC) has recently approved a new standard for the safe use of commercial ozonation systems and these standards should be incorporated in any new industrial applications.

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TABLE 1 - SOLUBILITY OF OZONE AND OXYGEN IN WATER

Temperature (Degrees C)	Ozone Solubility in mg/l with 3% O_3 Gas Concentration	Oxygen (from air) Solubility in mg/l
0	20	6.9
20	8.9	4.3