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REMOVAL OF MICRO-POLLUTANTS FROM DRINKING WATER WITH ADVANCED OXIDATION PROCESSES

Thesis
CENTRAL OSTROBOTHNIA UNIVERSITY OF APPLIED SCIENCES
Degree Programme in Chemistry and Environmental Technology
April 2009

ACKNOWLEDGEMENT

THESIS ABSTRACT

Department	Date	Author
Technology and Business, Kokkola, Finland	30.04.2009	Fabian Sander

Degree Programme
Degree Programme for Chemistry and Environmental Technology

Name of Thesis
Removal of micro-pollutants from drinking water with advanced oxidation processes.

Instructor	Pages
Jens Krüger and Dr. Achim Ried	96 + Appendices(2) (57 confidential version)

Supervisor
MSc Jana Holm

This thesis determines the feasibility of ozone gas and ultraviolet (UV) technologies to reduce pollutants from drinking water. The merging of both techniques, ozone and UV, is known as a so called advanced oxidation process (AOP). ITT Wedeco is developing new technologies to meet the growing concern of water works to remove micro-pollutants from their water.

The emphasis of this work was put on the formation of the oxidation by-product bromate and the removal of the solvent 1.4 dioxane from drinking water. Three different ozone gas diffusing technologies were compared and evaluated. An injector was compared to a gas diffuser and micro porous tubing. One part was the reduction of the pollutant, but the principal item of this pilot study was to control the formation of bromate, due to the immediate destruction of ozone gas through ultraviolet light into hydroxyl radicals.

Key words
Advanced oxidation process, drinking water, oxidation byproducts, ozone, UV, micro-pollutants, bromate, 1.4 dioxane.

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AOP	Advanced oxidation process
AOT	Advanced Oxidation Techniques
AOX	Adsorbable Organohalogens
COD	Chemical Oxygen Demand
COD	Catalytic Ozone Destructor
DBD	Dielectric Barrier Discharge
DOC	Dissolved Organic Carbon
EDC	Endocrine Disrupting Compounds
EEO	Electrical Energy per Order
GAC	Granulated Activated Carbon
H_2O_2	Hydrogen Peroxide
LOX	Liquid Oxygen
LP	Low Pressure UV lamp
MCL	Maximum Contaminant Level
MP	Medium Pressure UV lamp
MTBE	Methyltertbutylether
NDMA	N-nitrosodymethylamine
NOM	Natural Organic Matter
NTP	Normal Temperature Pressure
PPM	Parts Per Million
PSA	Pressure Swing Adsorption
RO	Reverse Osmosis
TCE	Trichloroethylene
THM	Trihalomethane
TOC	Total Organic Carbon
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UVT	Ultraviolet Transmission
WHO	World Health Organisation

1 INTRODUCTION

No life on our planet would exist without water. Our planet's surface is covered by 71% with water, which is equal to 1,386,000,000 billion m³. Only a fraction of that amount can be used for consumption, as only 3% is fresh water.
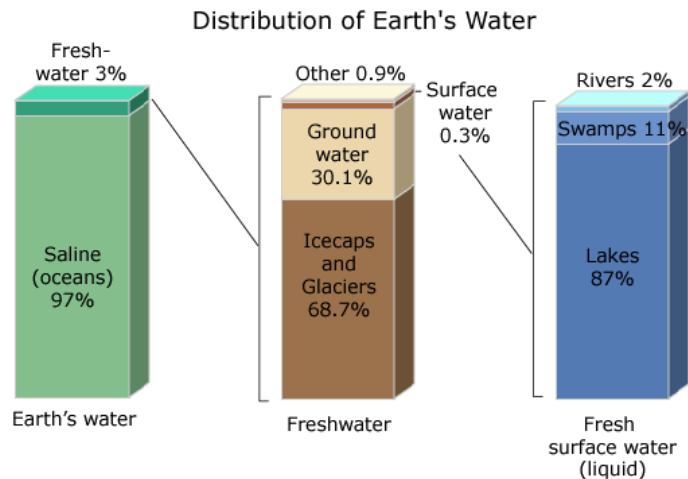
GRAPH 1. The distribution of the world´s water resources (USGS 1996, courtesy of the U.S. Geological Survey)

Fresh water is a carrier for minerals and organic substances which are essential for flora and fauna. These substances such as salts, calcium carbonate, sodium, nitrogen, carbon dioxide, etc. are part of a natural water matrix, but unfortunately water can also carry undesired substances.

Only less than 5% of the commercially distributed water is consumed or used in food preparation. This so called drinking water is of sufficient high quality which can be consumed without risk of immediate or long term harm. Drinking water quality is determined under two categories: physical/chemical and microbiological. Physical/chemical parameters include heavy metals, trace organic compounds, total suspended solids (TSS), and turbidity. Microbiological parameters include Coliform bacteria, E. coli, and specific pathogenic species of bacteria, viruses, and protozoan parasites. The physical/chemical parameters are associated to a more chronic health risk than microbiological. Mostly produced by mankind, these trace

organic compounds such as pesticides, endocrine disrupting compounds (EDC), by-products of industrial productions and other toxic synthetic products cause increasing problems to natural water systems. Once released into the environment, these elements blend into surface water and eventually end up polluting lakes, rivers and ground water reservoirs. The amount of these compounds in water is rather low. Concentrations of micro-pollutants range in milli (m), micro (µ), or even nano (n) grams per liter.

Nevertheless, they are considered pollutants due to the long term toxicity on human and animals. While short term consumption of such polluted water would not be expected to cause problems on human, the long term consumption of polluted drinking water is a contentious issue. The world health organisation (WHO) and national environmental authorities like the United States Environmental Protection Agency (USEPA) have released recommendations such as the maximum contaminant level (MCL) which is the legal threshold limit on the amount of a hazardous substance that is allowed in drinking water. This MCL is applied for pesticides, solvents and disinfection by products and is usually expressed as a concentration in milligrams or micrograms per liter of water.

To achieve such low concentrations in drinking water, water distributors need to treat the product before it is released into the water network. As to the removal of micro pollutants, this treatment step often requires very high efforts, due to the complex molecular structure of most pollutants. In most cases, the typical treatment by bacteria biodegradation is not successful, since absorption by activated carbon does not achieve the desired results either and reverse osmosis (RO) leaves the problem of a concentrate. The destruction of the undesired molecule into less harmful substances would therefore be ideal.

The so called advanced oxidation process (AOP) is capable of breaking the molecular bonds within the pollutant molecule and therefore crack it into smaller, less harmful parts. Ideally, this would be carbon dioxide and water. In most cases the oxidation of undesired molecules will create less harmful substances, but unfortunately this is not always the case.

This work determines the degradation of a solvent called 1.4 dioxane, which is fortunately known to break into less harmful fragments after oxidation. Such advanced oxidation technologies (AOT) are capable of destroying pollutants due to the generation of very reactive radicals. Hydroxyl radicals (•OH) are a connection of oxygen and hydrogen atoms by a covalent bond, and highly reactive with any substance present in water. The generation of such radicals can be initiated through different pathways such as the combination of ultraviolet light (UV) with ozone, UV with hydrogen peroxide (H_2O_2) or hydrogen peroxide and ozone.

(CONFIDENTIAL)

2 THEORY OF ADVANCED OXIDATION PROCESS

2.1 Introduction to water pollutants

Water pollution is estimated to be the leading cause of deaths and diseases worldwide and is expected to account for the deaths of 14,000 people per day. Water is typically referred to be polluted when it is impaired by manmade contaminants and does not support human use or negatively affects its constituent part for animals and plant life. These contaminants can affect human health on a short term basis such as micro organism pollution; but also long term contamination with substances such as heavy metals or chemicals ranging in low concentrations in water. These micro pollutants can cause chronic poisoning or support the chance of cancer if consumed by humans through drinking water. (USEPA 1994.)

This thesis work about the technology of advanced oxidation processes is specialized to pollutions ranging in very low concentrations in water. Since the late eighties of the last century, pesticides are found in raw water sources. The issue has caused increasing attention during the last years, with ongoing debates about maximum contaminant levels in the EU. They were encountered in surface water and bank filtrate, as well as in ground water. This development triggered the water supply companies to search for solutions in the removal / degradation of the pesticides in order to meet the European standard. The Netherlands are affected by this problem in particular, since most of the drinking water is obtained from surface water bank filtrate. Surface water has the highest tendency of being polluted. Some water works have started considering the reduction of micro pollutants for the sake of their customers even without any mandatory reduction level by the authorities.

ITT Wedeco has started pilot plant co-operations with water suppliers in the Netherlands for the reduction of such pollutants by either ozone-hydrogen peroxide, UV-ozone or UV-hydrogen peroxide AOPs. In general, the pesticide concentration can be lowered by oxidation, granulated activated carbon (GAC) and membrane filtration. Disadvantages of oxidation is the formation of smaller degradation products and the relatively high costs if the process is applied for pesticide control only. The advantage of oxidation processes may be the combination of disinfection and degradation of organic micro-pollutants. Optimization of the process conditions with respect to the desired degree of degradation of micropollutants and by-products formation is needed. (Ijpelaar 2001.)

2.1.1 Micro pollutants

As can be referred from the word micro (μ), micro pollutants range in concentrations of parts per million (ppm). Such pollutants are therefore hard to detect, do not cause immediate intoxication, are often difficult to remove and, unfortunately, are expensive to treat. The removal requires very high dosages of treatment material. In the case of ultraviolet radiation with ozone, this would be a high intensity of light flux (J/m²) and ozone gas (g/m³). A 99.99% (4log) deactivation of micro-organisms from water by UV light would typically require a dose of 400 J/m², whereas the 90% (1log) removal of a micro pollutant such as 1.4 dioxane would require 10000 J/m² and a second media such as ozone to achieve a reduction of the desired pollutant. (Wedeco 2008.)

This problem of high treatment dosages is eventually a commercial one. The treatment cost of one cubic meter of water will increase significantly if micro-pollutants are being removed. Municipal water works try to keep the treatment costs as low as possible, meaning that only obliged pollutants are being removed. Graph 2 gives an example of spiking a pollutant into water for degradation tests. To obtain the concentration of 80 μg/l, the content of this pipette, 1.4 dioxane, was diluted with 2000 l of water; this is equal to 1000 beakers in the graph.

GRAPH 2. Spiking of water

The following table provides information about common water impurities, as well as the related effect on humans from ingestion. The threshold value in drinking water is usually expressed as the maximum contaminant level (MCL), with the exception of micro organism control which is expressed in percent removal from the initial concentration.

TABLE 1. Inorganic contaminants and their MCL (USEPA 1995)

Inorganic chemicals	Potential health effects from ingestion of water	MCL (mg/l)	Sources of contaminant
Arsenic	Skin damage, problems with circulatory systems, risk of getting cancer.	0.010	Runoff from factories.
Cadmium	Kidney damage.	0.005	Discharge from metal refineries.
Cyanide	Nerve damage or thyroid problems.	0.2	Discharge from steel, metal, plastic factories.
Mercury	Kidney damage.	0.002	Discharge from refineries and factories, runoff from landfills and croplands.

TABLE 2. Organic contaminants and their MCL (USEPA 1995)

Organic chemicals	Potential health effects from ingestion of water	MCL (mg/l)	Sources of contaminant
Atrazine	Cardiovascular system or reproductive problems.	0.003	Runoff from herbicide used to grow crops.
Benzene	Anemia; decrease in blood platelets; increased risk of cancer.	0.005	Discharge from factories; leaching from gas storage tanks and landfills.
Polychlorinated biphenyls (PCBs)	Skin changes, immune deficiencies; reproductive or nervous system difficulties, risk of cancer.	0.0005	Runoff from landfills; discharge of waste chemicals.
Tetra chloroethylene	Liver problems; increased risk of cancer.	0.005	Discharge from factories and dry cleaners.
Dioxin	Reproductive difficulties; increased risk of cancer.	0.00000003	Emissions from waste incineration and other combustion; discharge from chemical factories.
1,4 dioxane	Damage to liver and kidneys.	No limit	Solvent for manufacture of textile, cosmetics, shampoos, paper and cotton.

2.1.2 Solvent 1.4 dioxane

The solvent 1.4 dioxane is a manmade compound primarily used as an industrial solvent or solvent stabilizer that prevents the breakdown of chlorinated solvents during manufacturing processes. $C_4H_8O_2$, 1.4 dioxane, also called dioxane, dioxan, p-dioxane, diethylene dioxide, diethylene oxide, diethylene ether or glycol ethylene ether, is a colourless, flammable, and oily liquid with the melting point of 11.8°C and boiling point of 101°C. (Heiland 2004.)

One remarkable property is the excellent dissolving power of solvents. Due to these properties, it is commonly used as a solvent stabilizing agent. It is an

ingredient in paints, varnishes, detergents, cements, stains, inks, cosmetics and is a natural component in vine-ripped tomatoes and tomato products, fresh shrimps, brewed coffee and fried chicken. It is also present in ordinary household products like shampoos, liquid/ dishwashing soap, baby lotion, hair lotions, bath foam, and other cosmetic products. (Zenker 2003.)

Other solvent applications include those for dyes, fats, greases, lacquers, mineral oil, paints, resins and waxes. It can be blended with water and most organic solvents in any kind of ratio. On the other hand, dioxane has a high stability and is not reactive in chemical reactions. Therefore it can be used in chemical reactions, in determining the optical activity and for cryoscopy and it is formed as a by-product during the manufacture of polyester and various polyethoxylated compounds. (Heiland 2004.)

Dioxane is commonly used to dissolve acetyl cellulose, cellulose ether and chlorinated rubber. Furthermore it is used for extraction of animal and plant tissue. It can form an addition reaction with several organic and inorganic substances, whereas the bonding is formed through van der Waals forces, donor-acceptor, or hydrogen bonds. In high concentrations, dioxane is narcotic to human and causes severe damage to kidney and liver. In vapour, it irritates eyes and the respiratory tract. In liquid phase, it can be absorbed by human skin. It is expected to be human carcinogen by the USEPA and therefore classified as group B2 (probable human carcinogen). A person must drink 2 liters per day of water over the action level of 3 µg/l for a period of 70 years in order to generate one additional cancer case out of a million people. (Zenker 2003.)

The long term effects on animals were examined in laboratory trials. Rats, which were exposed to 1.4 dioxane in their drinking water, showed damage to liver and kidneys. Short-term inhalation exposure to high levels of 1.4 dioxane has caused vertigo, drowsiness, headache, anorexia and irritation of the eyes, nose, throat, and lungs in humans. It may also irritate the skin. (USEPA 1995.)

Dioxane is highly soluble in groundwater, does not readily bind to soils, and accidental solvent spills have resulted in the contamination of groundwater with 1.4 dioxane. It can remain in groundwater for several years and has caused increasing attention to the public. Dioxane has been detected at concentrations of 1–220,000 µg/l in groundwater, 1-290 µg/l in surface water and 0.1-2,100 µg/l in drinking water. The EPA has not yet established a federal drinking water standard or maximum contaminant level for 1.4 dioxane, but some state level Environmental Protection Agencies in the US have established state drinking water guidelines which vary between 3 µg/l in California and 70 µg/l in Maine. (USEPA 1995.)

To treat waters containing 1.4 dioxane, volatilization and sorption are not significant treatment mechanisms due to 1.4 dioxane's complete miscibility with water. Advanced oxidation processes, and therefore the destruction of molecular bonds, are the only proven technology for 1.4 dioxane treatment at the moment. In North America, there are several known ground water remediation sites using either UV-H_2O_2 or ozone-H_2O_2 to treat 1.4 dioxane. (USEPA 1995.)

TABLE 3. Fact sheet of 1.4 dioxane (USEPA 1995)

Property	Value
Common synonyms	1.4 diethylene oxide
Molecular formula	$C_4 H_8 O_2$
Physical state	Flammable liquid, faint pleasant odor
Molecular weight	88.10 g/mol
Melting point	11.80°C
Boiling point	101.1°C at 760 mm Hg
Density	1.0329 g/ml at 20°C
Henry's law constant	4.88 x 10-6 atm m^3/mol

2.1.3 Transformation and persistence

In soil, the low estimated soil-sorption coefficient will cause that 1.4 dioxane readily leach to ground water. The estimated Henry's Law constant suggests that

volatilization from moist soils will be slow; however, based on its vapor pressure, volatilization from dry soils should be fast. 1.4 dioxane is not expected to biodegrade in soil. (Howard 1989.)

In water, ethers in general have been classified as generally resistant to hydrolysis. Therefore 1.4 dioxane is not expected to hydrolyze significantly. The estimated Henry's Law constant for 1.4 dioxane and its miscibility in water suggest that volatilization will be slow. It is not expected to significantly adsorb to suspended sediments and is not expected to biodegrade in water. (Howard 1989.)

2.2 Ozone

Ozone is a gas consisting of three oxygen atoms which is highly reactive. It is formed naturally in the upper zones of the atmosphere (25 km above sea level) where it surrounds the earth and protects the surface of our planet from UV-B and UV-C radiation which are dangerous to human. In the atmosphere close to the surface, ozone is unfortunately a toxic gas with a maximum contaminant level of 0.1 parts per million (ppm) for an exposure of 8 h. Exposure of 0.1 to 1 ppm produces headaches, burning eyes, and irritation to the respiratory passages. (Carrithers 1997.)

On the other hand, due to the reactive properties of ozone, it became popular for the treatment of water, medicine, organic chemical synthesis, etc. as an environmental friendly treatment technology. The reactivity is due to the structure of the molecule. Each oxygen atom has the following electronic configuration surrounding the nucleus: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. The valence band has two unpaired electrons, each one occupying one 2p orbital. In order to combine three oxygen atoms and yield the ozone molecule, the central oxygen rearranges in a plane sp^2 hybridation from the 2s and two 2p atomic orbitals of the valence band. With this rearrangement the three new sp^2 hybrid orbitals form a triangle. The high

reactivity can be attributed to the electronic configuration of the molecule. (Carrithers 1997.)

Ozone has gained increased attention for the disinfection of water since the discovery of trihalomethanes (THM), due to chlorination of natural substances present in raw water, in the late 1970s. The search began for alternative oxidant disinfectants that could play the role of chlorine without generating the problem of THM formation. (Beltran 2004.)

Studies have shown that organohalogen compounds formed in the treatment of surface waters with chlorine and other chlorine derived oxidant disinfectants cause a higher disinfection by-product risk than ozone. However, chlorine is not the only concern in water quality. Other compounds are often discharged into natural waters or in soils and eventually leach into the aquatic system, resulting in contamination of wells and aquifers. Ozonation or hydroxyl radical oxidant based processes have proven to be efficient technologies for the removal of such pollutants. (Beltran 2004.)

Table 4 illustrates the physical properties of ozone. Under normal conditions, ozone is not present in gases, but might occur from the destruction of oxygen. This topic will be introduced in the following section.

TABLE 4. Physical properties of ozone (Perry 1997)

Property	Value
Melting point, °C	-251
Boiling point, °C	-112
Molar mass	47.998 g/mol
Solubility in water	0.105 g / 100ml (0 °C)
Specific gravity	1.658 higher than air
Density	2.144 g/l (0 °C), gas

2.2.1 Chemistry of oxidation

The term oxidation corresponds to the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant). Both the oxidant and the reductant are chemically transformed. Species with an odd number of valence electrons are produced as well, which are known as radicals. Radicals are highly unstable and highly reactive because one of their electrons is unpaired which is represented by a dot next to the chemical structure, for example the hydroxyl radical ($\bullet OH$). Radicals that were produced in oxidation reactions tend to react further between radical oxidants and other organic and inorganic reactants until thermodynamically stable compounds are formed. The oxidation potential measures the ability of an oxidant to initiate reactions. The end products of complete oxidation (mineralization) of organic compounds such as MTBE or 1.4 dioxane are carbon dioxide (CO_2) and water (H_2O). (Beltran 2004.)

2.2.2 Oxidation potential

The oxidation potential, expressed in electron volts, is an indicator of how strongly a compound is potentially forming a oxidation reaction with other molecules. The higher the E^o value, the more reactive the species, but also the more difficult the handling of such reactions will become. The following table presents the oxidation potential of the most oxidative species known. (Perry 1997.)

Fluorine has the highest oxidation potential, but for commercial applications, this compound is not suitable due to the high reactivity. The next available compound is the hydroxyl radical, which is produced during the reaction of ozone and UV. Ozone alone has a lower potential to oxidize species, but it is still relatively high.

TABLE 5. Standard redox potential of some oxidant species (Perry 1997)

Oxidant species	E^{o}, Volts	Relative potential to ozone
Fluorine	3.06	1.48
Hydroxyl radical	2.80	1.35
Atomic oxygen	2.42	1.17
Ozone	2.07	1.00
Hydrogen peroxide	1.77	0.85
Chlorine dioxide	1.50	0.72
Bromine	1.09	0.53
Oxygen	0.40	0.19

2.2.3 Applications of ozone

Ozone has a wide range of commercial applications. Due to its environmental friendly properties to decompose into oxygen, ozone is widely used for water purifications, as presented in the following table.

TABLE 6. Typical industrial applications of ozone (Wedeco 2008)

Application	Usage
Drinking water	Improvement of flocculation
	Decoloration, taste, odor improvement
	Iron / manganese elimination
	Disinfection
	TOC-elimination
	Elimination of persistent substances
Desodoration	Oxidation of H_2S
Ozonolysis	Synthesis of new products
Synthesis	Modification of synthesis
Surface treatment	Laminating / coating
Bleaching	Pulp
	Kaolin
Wastewater treatment	Elimination of COD
	Elimination of surfactants
	Elimination of phenols
	Decoloration
	Sludge treatment
	Elimination of AOX
	Elimination of endocrine and/or persistent substances
Process water	Cooling water (in power plants)
	Swimming pools
	Rinsing water in beverage industry
Product polishing	Stabilization of still water
	Disinfection of food (salad, fish)

2.2.4 Ozone generation from oxygen

Because of its relatively short half-life, ozone is always generated on-site by an ozone generator. The main principle of ozone generation is based on the dielectric-barrier discharge (DBD). It is the electrical discharge between two electrodes separated by an insulating dielectric barrier. The process uses high voltage alternating current. The gap distance between the electrodes is about 1 mm in ozone generators. A multitude of random arcs form between the two electrodes during operation, as the charges collect on the surface of the dielectric, they discharge in microseconds, leading to their reformation elsewhere on the surface. Oxygen gas is flowing through the electrodes and due to the discharging arcs, the oxygen is split into two single oxygen atoms. The oxygen atoms will eventually recombine to the formation of three oxygen atoms: ozone. (Wedeco 2008.)
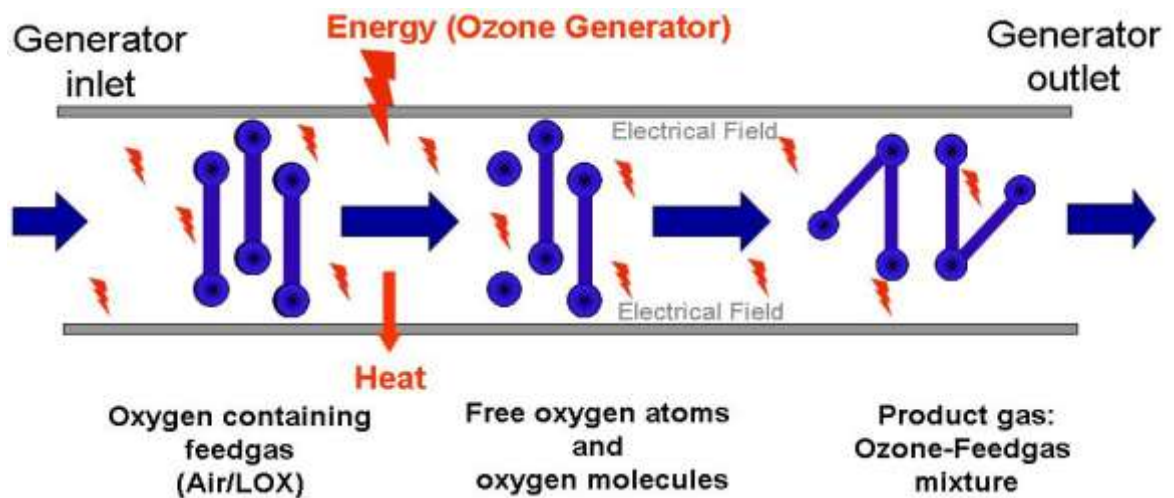
GRAPH 3. Generation of ozone from oxygen feed gas (Wedeco 2008)

For the production of ozone, ambient air can be used as well as pure liquid oxygen (LOX) or on site generated oxygen (PSA). To condition this air, dryers and dust filters must clean the air before usage. Ozone generators require a high current between 6-10 kV and frequencies between 300–600 Hz for operation. Ozone is always present as a gas under normal temperature and pressure (NTP). The applications introduced in Table 6 utilize ozone in gaseous form, it must be

indicated though, that ozone will never be available in pure form. The technical generation of ozone from oxygen is limited to the following concentrations of ozone in oxygen gas. Table 7 indicates the ozone/oxygen ratio for various concentrations of ozone, which were utilized during the performance of this thesis. (Wedeco 2008.)

TABLE 7. Ozone conversion table (Perry 1997)

Ozone concentration g/m³ (NTP)	O_3 to O_2 Wt%	O_3 to O_2 Vol%	kg Oxygen / kg Ozone	m³ Oxygen / kg Ozone
10	0.6	0.4	143.2	100
20	1.3	0.9	71.7	50
50	3.4	2.3	28.9	20
100	6.8	4.6	14.6	10
150	10	6.9	9.8	6.9
200	13	9.2	7.4	5.2

The oxygen/ozone ratio shows the limitations of ozone generation. A typical ozone generator cannot produce a higher ozone ratio due to physical limitations. The highest utilized ozone concentration during the experiments was 200 g/Nm³; which would correspond for about 9% of ozone by volume. The largest part of the utilized gas was therefore still oxygen.

Graph 4 presents a schematic view of a large ozone water purification unit. (Not AOP). The gas supply can consist of liquid oxygen, air or on-site oxygen generation through pressure swing adsorption (PSA). A chiller unit is required for cooling of the ozone generator. The off-gas ozone must be converted back into oxygen before released into the environment; this is done by a catalytic ozone destructor (COD). Ozone is generated from oxygen, based on the dielectric barrier discharge phenomenon, inside the ozone electrodes.
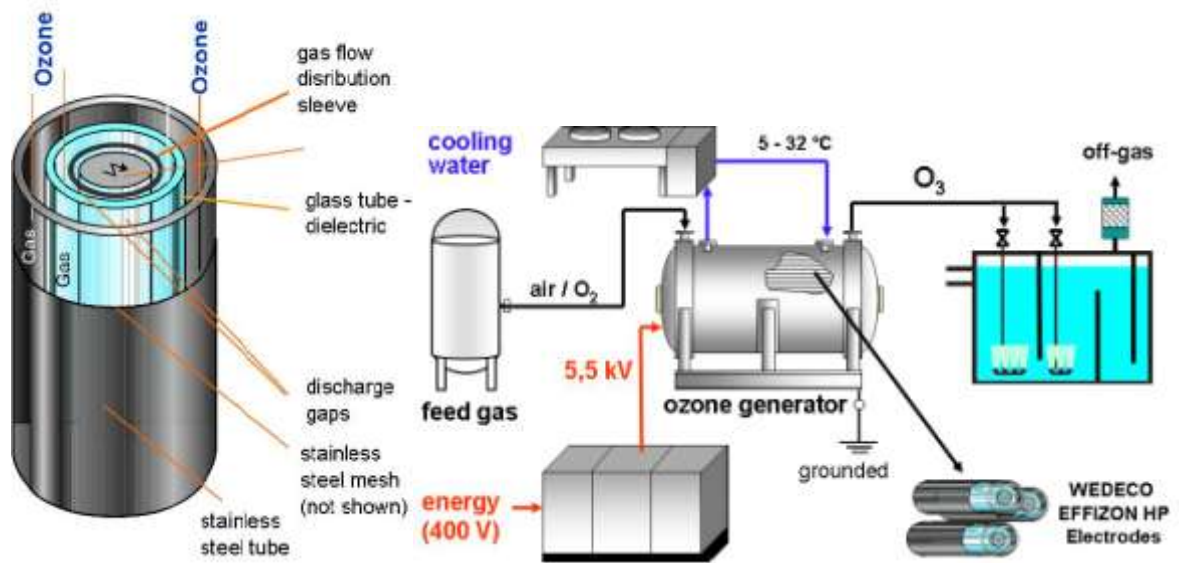
GRAPH 4. Ozone electrode and ozone purification system (Wedeco 2008)

2.2.5 Reaction properties

Due to its electronic configuration, ozone has different reactions in water. The three main categories are: Oxidation-reduction, dipolar cycloaddition and electrophilic substitution reaction. (Beltran 2004.)

In some cases, free radicals are formed from these reactions. These free radicals propagate themselves through mechanisms of elementary steps to yield hydroxyl radicals, which are extremely reactive with any organic matter present in water. For this reason, ozone reactions can be divided into direct and indirect reactions. Direct reactions undergo with any other type of chemical species, like molecular products and free radicals. Indirect reactions are those between the hydroxyl radical, formed from the decomposition of ozone or from other direct ozone reactions, with compounds present in water. The direct ozone reaction is the initiation step towards the indirect reaction. (Beltran 2004.)

Redox reactions are characterized by the transfer of electrons from one species (redactor) to another one (oxidant). The oxidizing or reducing character of any

chemical species is given by the standard redox potential. Ozone has one of the highest redox potentials, lower only than those of fluorine atom, oxygen atom and hydroxyl radical. Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds. (Beltran 2004.)

Addition reactions are those reactions resulting from the combination of two molecules to yield a third one. One of the molecules usually has atoms sharing more than two electrons, unsaturated compounds with carbon double bonds, and the other molecule has an electrophilic character. (Beltran 2004.)

In electrophilic substitution reactions one electrophilic agent (ozone) attacks one nucleophilic position of the organic molecule (e.g. an aromatic compound), resulting in the substitution of one part (e.g. atom, functional group) of the molecule. This type of reaction is the base of the ozonation of aromatic compounds. (Beltran 2004.)

Indirect reactions of ozone are due to the action of free radical species resulting from the decomposition of ozone in water. The free radical species are formed in the initiation or propagation reactions of the mechanisms of advanced oxidation processes. In the ozone decomposition mechanisms, the hydroxyl radical is the main responsible species in the indirect reactions. The reactions of ozone with the hydroxyl radical can be considered the main initiation reactions of the ozone decomposition mechanism in water. (Beltran 2004.)

Other initiation reactions develop when other agents, such as UV radiation are present. The direct photolysis of ozone that yields hydrogen peroxide and then free radicals, or the ozone adsorption and decomposition are also examples of initiation reactions. There are also other reactions that lead to the decomposition or stabilization of ozone in water. These substances are initiators, inhibitors and promoters of the decomposition of ozone. The initiators are the substances that directly react with the ozone to yield the superoxide ion radical, such as the ionic form of hydrogen peroxide. The superoxide ion radical is important for propagating free radical species, because it reacts immediately with ozone to yield the hydroxyl

radical. Promoters are those substances which propagate the radical chain to yield the free radical through their reaction with the hydroxyl radical. Hydrogen peroxide plays an important part in this role, it is in fact the initiating agent, but it also acts as a promoter of ozone decomposition. (Beltran 2004.)

2.2.6 Scavengers of the hydroxyl radical

Inhibitors are also called hydroxyl-free radical scavengers because their presence limits or inhibits the action of these radicals on the target contaminants. The presence of carbonates for example, reduces the efficiency of ozonation to oxidize contaminants in water. Theses carbonates, which also account for the hardness of water, limit the degradation of the desired pollutant significantly. (Beltran 2004.)

Hydrogen carbonate: $HCO_3^- + \bullet OH \rightarrow CO_3^- + H_2O$

Carbonate: $CO_3^{2-} + \bullet OH \rightarrow CO_3^- + HO^-$

Another problem is the presence of bromide ion in ozonated water. Ozone readily oxidizes bromide ion to yield bromate ion, which is considered a highly toxic pollutant. Formation of bromate is highly dependent on the presence of other substances that consume ozone, for instance hydrogen peroxide. The presence of natural organic matter (NOM) is another factor which can affect the decomposition of ozone; it can act as promoter or inhibitor. A fraction of hydroxyl radical yields the superoxide ion radical during reaction with NOM. Therefore, a fraction of NOM is a promoter of the ozone decomposition. (Beltran 2004.)

2.2.7 Ozone decomposition

Once dissolved in water, ozone is unstable and decomposes. This can be considered an advantage, but also a drawback. When ozone decomposes, free radicals are generated and oxidation of compounds occurs. But due to its instability, ozone cannot be used for a final disinfectant of water. There are two

ozone decomposition periods when treating natural waters. The first one, called fast ozone demand, lasts from a few seconds to 1-2 minutes and is due to the presence of substances that readily react with ozone through direct reactions. Once these substances have disappeared or their concentrations decrease, the longer ozone decomposition starts. During this period, instantaneous or very fast consumption takes place. During the second or long ozone decomposition, ozone slowly decomposes until all dissolved ozone has decomposed. (Beltran 2004.)

2.2.8 Diffusion into water

In a gas-liquid reacting system, diffusion convection and chemical reactions proceed simultaneously. In general, when gas and liquid phases are in contact, the components of one phase can transfer to the other phase to reach equilibrium. If component A of a gas phase is transferred to the liquid phase, the rate of mass transfer or absorption rate of A is:

$$N_A = k_G (P_{Ab} - P_i) = k_L (C_A - C_{Ab})$$

k_G = mass transfer coefficient for gas phase

k_L = mass transfer coefficient for liquid phase

P_{Ab} = Partial pressure of A in bulk gas

P_i = Partial pressure of A at the interface

C_A = Concentration of A at the interface

C_{Ab} = Concentration of A in the bulk of liquid

(Beltran 2004.)

The transfer rate is dependent on the physical properties of gas and liquid, the difference in concentration across the surface and turbulence. (Beltran 2004.)

When two phases (gas and water) are in contact, the main resistance to mass transfer is the layer of thickness close to the interface. This so called film layer consists of two films in a gas-liquid system, one for each phase. In most situations the gas is bubbled into the liquid phase, thus the interfacial surface is due to the

external surface of bubbles. Ozone solubility is a fundamental parameter in the absorption rate. Ozone-water systems are characterized by a low concentration of dissolved ozone, ambient pressure and temperature. In order to achieve good degradation of pollutants in water, a high ozone transfer into water phase is desired. (Beltran 2004.)

This absorption process is dependent on pressure and temperature according to Henry's law:

P = He * x

P = partial pressure of gas above the solution (in atm)
x = mole fraction of gas in solution
He = Henry's law constant which accounts pressure and temperature dependency

Henry's law can be described at a constant temperature. The amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. However the Bunsen adsorption coefficient is expressed as a volume of gas at NTP which is dissolved at equilibrium by a unit volume of liquid at a given temperature, when the partial pressure of the gas is the unit atmosphere. The Bunsen coefficient has no dimension. In the coefficient, the gas absorption rate into water decreases with increasing temperature. (Beltran 2004.)

For efficient ozone transfer, it is therefore important to achieve low water temperatures. In practice, this is not always applicable, but it is important to monitor the temperature of water during application of ozone. In real life applications, less gas can be absorbed into a liquid than stated in Henry's law. This is caused by circumstances which the absorption factor takes into consideration.

$A_f = (V_w / V_g) * α * P$

The absorption factor determines the amount of gas absorbed by the solving liquid under known conditions.

V_w= Volume of solving liquid
V_g= Volume of gas
α= Bunsen coefficient
P= Total pressure
(Beltran 2004.)

The efficiency of dissolving ozone into water, which is usually carried out at conditions close to NTP, is not ideal. A higher operating pressure would allow a higher gas to liquid ratio, but this process is virtually impossible during continuous operation of the AOP system. (Beltran 2004.)

As can be inferred from the absorption factor, the solubility of ozone gas is depending on the concentration in gas and partial pressure and temperature, pH and ion concentration in the solution. The solubility can theoretically be enhanced by increasing the ozone concentration in the air (oxygen), increasing air pressure (oxygen), decreasing the water temperature, decreasing the amount of solutes or decreasing the pH. (Beltran 2004.)

In practice, these values are considered as limiting factors, because the only economical reasonable variable is the pH factor and ozone concentration in air, while other factors remain important to be monitored during operation.

2.3   UV radiation

2.3.1   Introduction to ultraviolet radiation

Ultraviolet radiation is energy of electromagnetic waves. Electromagnetic radiation is classified according to the wavelength or frequency of the light wave. This radiation includes radio waves, microwaves, terahertz radiation, infrared radiation,

visible light, ultraviolet (UV) radiation, X-rays and gamma rays. Of these, radio waves have the longest wavelengths and gamma rays the shortest. Ultraviolet radiation is defined as that portion of the electromagnetic spectrum between x rays and visible light, between 40 and 400 nm. (Bolton 2008.)

The ultraviolet radiation spectrum is divided into UV-A (320-400 nm), UV-B (290-320 nm), UV-C (220-290 nm), Far UV (190-220 nm) and Vacuum UV (40-190 nm), whereas the UV-C radiation spectrum is the important frequency range for the technical usage of light. Ultraviolet light, which travels in "packets" of energy known as photons, can exert a variety of beneficial or deleterious effects on plants, animals and materials in the biosphere, including processes responsible for driving atmospheric chemistry. Other photochemical processes, utilizing the absorption of light (either visible or ultraviolet), include photosynthesis in plants, sun tanning/burning, snow blindness, fading of textiles and in contaminated waters the photo degradation of organic pollutants by advanced oxidation processes. UV radiation is also commonly used for disinfection of water or surfaces from micro organism. (Bolton 2008.)

2.3.2 UV spectrum

Graph 5 presents the wavelength spectrum of electromagnetic radiation. Light is the same form of electromagnetic radiation as other non visible wavelengths, yet with a different wavelength. The human eye will interpret wavelengths between 400 and 700 nm as visible light. (Zeman 2008.)
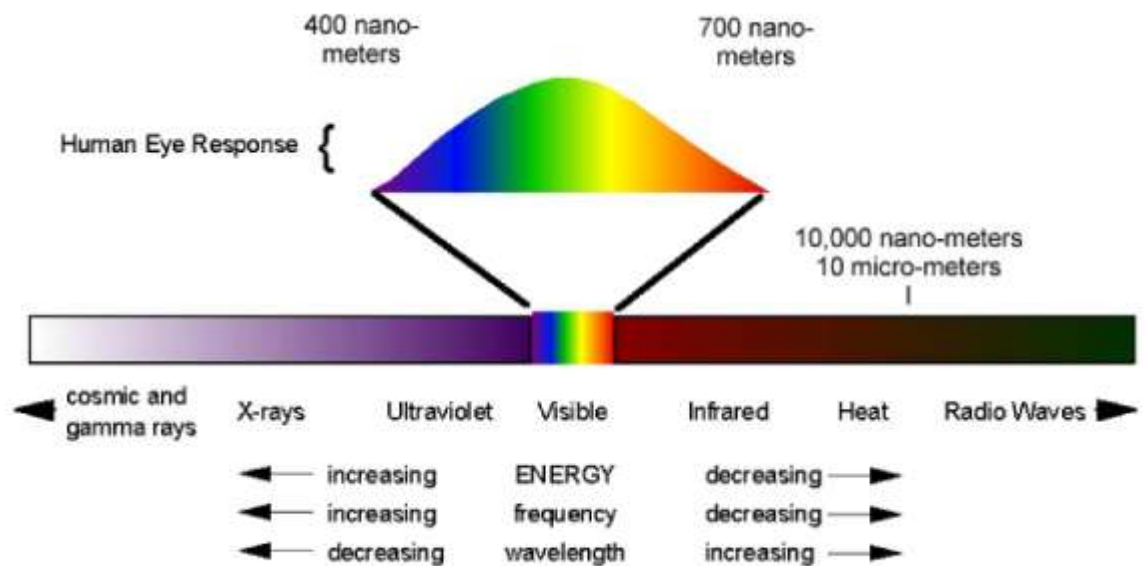
GRAPH 5. The spectrum of electromagnetic radiation (Treiman 2008, courtesy of USRA Lunar and Planetary Institute)

Visible light only accounts for a small fraction of the wavelength range. The ultraviolet spectrum has a shorter wavelength. Therefore a shorter frequency and carries more energy. The shorter the wavelength, the more damage such radiation can cause to human skin. Gamma rays penetrate deep into the human cell tissue and cause severe damage to cells. (Zeman 2008.)
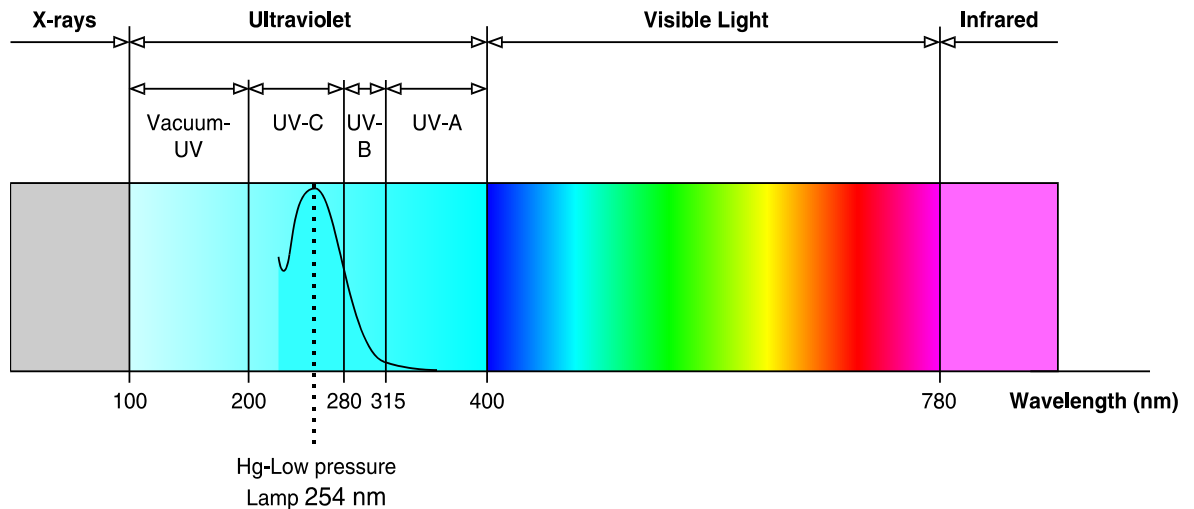
GRAPH 6. Wavelengths between 100 and 780 nm (Wedeco 2008, courtesy of ITT Wedeco Corporation)

Electromagnetic wavelengths between 100 and 780 nm can be considered as light. The ultraviolet spectrum is further divided into fractions, where the UV-C spectrum causes most damage to human skin. The low pressure lamps used in water disinfection have their maximum power output at 254 nm. (Wedeco 2008.)

2.3.3 Effect on micro organism

Certain electromagnetic wavelengths are mutagenic to bacteria, viruses, other micro-organisms and even humans. UVC is almost never observed in nature because it is absorbed completely in the atmosphere, as are far UV and vacuum UV. The wavelength of 254 nm will break the molecular bonds within micro-organism DNA, producing thymine dimmers in their DNA and destroying them, rendering them harmless or prohibiting growth. A similar process can be seen with the UV-B effect on humans, including sunburn. Micro-organisms have less protection from UV than humans and cannot survive prolonged exposure to it. (Infralight 2008.)
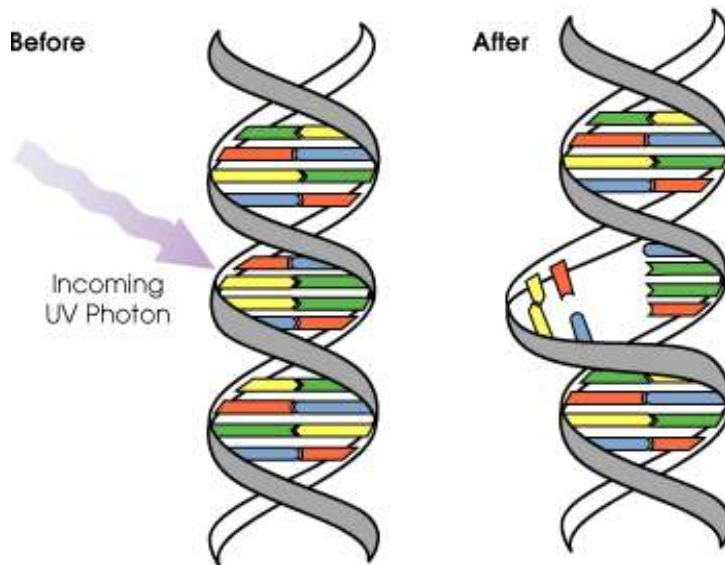
GRAPH 7.Effects of UV on the DNA of micro organism (NASA 2009, courtesy of NASA)

Due to the ability of UV-C light to act germicidal to damage the DNA, this wavelength is commonly used in water purification systems. ITT Wedeco is specialized into this environmental friendly disinfection technology, and is currently the world leader in waste and drinking water disinfection systems.

2.3.4 Dose of ultraviolet light

In waste and drinking water applications, a certain dosage of UV light irradiation is required to achieve a so called 4-log reduction (99.99%) of harmful organism. This dosage is measured in J/m^2, the amount of photons per area. For disinfection of drinking water this dose usually requires about 400 J/m^2. In contrast, the required dose for AOP applications is usually around 10000 J/m². Certain factors, such as the water transmission and turbidity, affect the calculation of such doses. Therefore the UV dose depends greatly on the specific water property. Furthermore the light intensity is also expressed as the amount of light applied per volume of water. This value is expressed as watts per cubic meter of water (W/m^3). This value is used to express a cost based calculation value, since the

energy demand of the light source is expressed as watts. The utilized UV lamp during this performance has the power output of 330 W. (Wedeco 2008.)

The energy of light (and any other electromagnetic energy) is given by Planck's equation:

$$\mathbf{E = h\nu = hc / \lambda}$$

The intensity of UV light at 254nm is expressed as $\mathbf{h\nu}$.

$\mathbf{h}$ is Planck's constant = 6.63 x 10^{-34} J sec

ν has the unit sec^{-1}, also called "Hertz" or Hz

λ is the wavelength, expressed in meter (m) or nm

$\mathbf{c}$ is the speed of light in (m/s)

The energy of the emitted light is inversely proportional to its wavelength ($\lambda\upsilon$) or directly proportional to its frequency (ν) (Bolton 2008).

2.3.5 Ultraviolet lamps

The most important lamps for UV disinfection and therefore AOP as well are gas discharge lamps. These usually have two electrodes, one at each end of a tube containing a gas, which contains metal atoms (mercury). In such lamps, light emission arises from atoms that have been exited to higher energy states by high energy electrons emitted from the electrodes. The lamps used in UV disinfection systems are mercury vapour lamps. In the lamps, electric current that flows through the ionized hot plasma causes the mercury atoms to be raised to higher energy states. When exited states return to their ground state, UV light is emitted with a wavelength inversely proportional to the energy difference between the exited state and the ground state. The lifetime of the exited mercury atoms is limited and in microseconds they decay to lower energy levels with the excess energy emitted as light or heat. The wavelength of the light is determined by the difference in the energy levels. Graph 8 illustrates this process. (Wedeco 2008.)
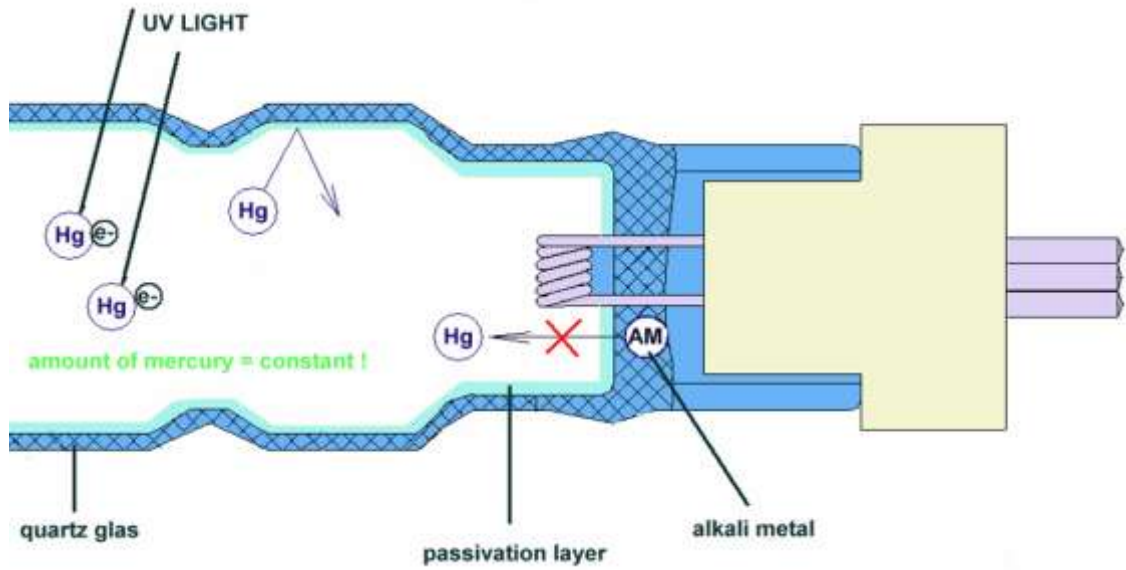
GRAPH 8. Emission of electrons (Wedeco 2008, courtesy of ITT Wedeco Corporation)

Graph 8 illustrates the exiting of mercury atoms in a low pressure lamp. The operation principle is commonly used in luminous tubes, with one difference: UV lamps are filled with a different gas mixture to achieve a lower wavelength output.
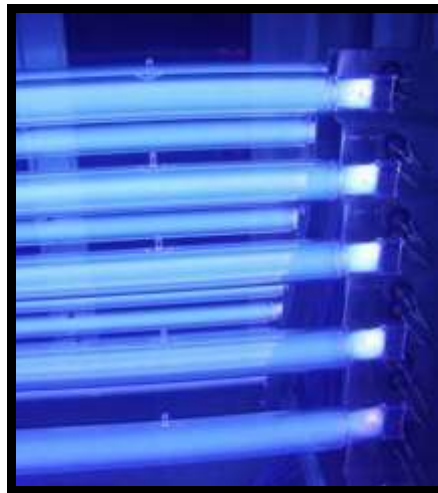
GRAPH 9. UV lamp during operation

Graph 9 illustrates the operation of low pressure high output amalgam UV lamps in water. The radiation of 254 nm is interpreted as blue by human eyes. There are four common types of mercury discharge lamps: low pressure, low pressure high output, low pressure high output amalgam and medium pressure. However, only

the two most competing systems, low pressure high output amalgam and medium pressure are presented here.

2.3.6 Low pressure high output amalgam lamps

Low pressure lamps emit only in narrow lines with no emission between the lines. Graph 10 will show the wavelengths and relative emittances for the lines of a low pressure mercury vapour lamp. As can be seen from the graph, the emission spectrum is rather concentrated to 254 nm. The inner surface of the lamp envelope can be coated with various types of phosphors, which absorb the 245 nm radiation and emit longer wavelengths. This is the basis of the popular fluorescent lamp. The low pressure high output amalgam lamp is a modified version with a 2 to 3 times higher output than a regular low pressure lamp. The lamps have heavy electrodes and contain no free mercury. A solid amalgam (a compound of mercury and another element, such as indium or gallium) spot is placed on the inner wall of the lamp. This spot serves to control the mercury vapour pressure. The XLR 30 low pressure high output amalgam lamp used in the experiments has a length of 143 cm and was capable of 330 W output energy. (Bolton 2008.)

2.3.7 Medium pressure lamps

The emission lines of a mercury lamp are only sharp when the pressure of the gas is low (<100 Pa). If the pressure is increased, the lamp can carry much more power, but the increased collision rate from other gas molecules causes the emission lines to broaden. For the same length of lamp, an MP lamp (pressure of 100 KPa) can carry up to 30000 W instead of 330 W. Medium pressure lamps operate very hot. Thus they are less efficient in comparison to low pressure lamps. The emission spectrum is polychromatic, with several emission peaks between 186 and 600 nm. The operating bulb temperature is ranging between 600 and 900°C. Medium pressure lamps require several times more energy than LP lamps

for the same UV output, but for one MP lamp up to ten low pressure lamps are required to meet the same dose of radiation per area. Generally, the much higher energy efficiency of LP lamps compensates their low power output, but increases their footprint of the system. (Bolton 2008.)

TABLE 8. Comparison of LP and MP lamps (Bolton 2008)

Characteristic	LP high output amalgam	MP
Emission	Monochromatic (254 nm)	Polychromatic (185-600 nm)
Operating bulb temperature	60-100°C	600-900°C
Germicidal efficiency	30-35%	12-16%
Power density (W/cm)	0.6-1.2	125-200

Graph 10 illustrates the emission curves of LP and MP lamps with relative spectral emittance of medium pressure (MP) and low pressure (LP) lamps. The higher gas pressure of MP lamps results in several emission peaks. The desired peak at 254 nm is only partly covered, whereas the undesired peaks between 300 and 600 nm result in higher power consumption than LP lamps for the same light flux. (Bolton 2008.)
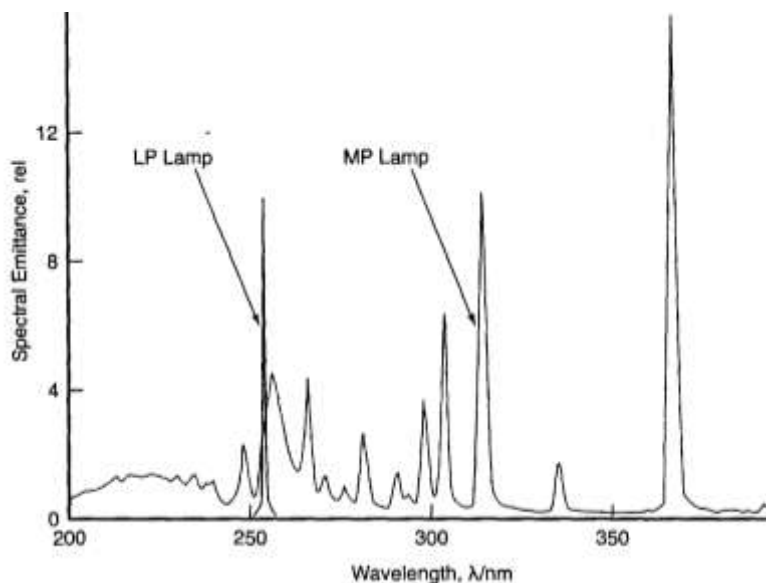
GRAPH 10. Peaks of LP and MP lamps (Bolton 2008, courtesy of AWWA)

A UV lamp must be separated by an air space from flowing water because a UV lamp needs to operate at higher temperatures than water. This separation is accomplished by placing the lamp inside a sleeve, which is usually made of quartz because it permits the passage of UV in the 200-300 nm region. Normal glass does not allow the passage of such frequencies and therefore no harm occurs if UV is blocked by normal glass.

2.3.8 Effects of water quality on UV efficiency

Water quality can have a major effect on the efficiency and performance of a UV reactor. Several water quality factors are important.

UVT (ultraviolet transmission) is the most important parameter because it measures the amount UV light absorbed by the water itself, rendering it unavailable to activate ozone gas. Furthermore, when more UV light is absorbed (by low UVT), more lamps are needed to meet a UV dose than with a higher UVT can be achieved. Typically, UVT at 254 nm is used as the primary water quality design parameter. For UV systems with low pressure (LP) lamps, the most important design parameter is the UVT at 254 nm. (Bolton 2008)

It is essential that the transmittance of the quartz sleeve between the UV lamp and water be as high as possible, so that the maximum amount of the UV light from the lamp can enter the water. However, in some cases the quartz sleeve can become fouled with deposits that reduce the transmittance and adversely affect the performance of the UV reactor. (Bolton 2008.)

Turbidity is caused by suspended particles in the water. These particles can affect the UV light distribution in the water, by scattering the light or by absorption of light by components in the particles. If algae are present in the water, this may reduce the UVT. However, most algae are removed by the conventional coagulation/sedimentation/filtration processes that exist in most water treatment plants. (Bolton 2008.)

2.4   Advanced oxidation processes

The elimination of organic contaminants by advanced oxidation processes is a destructive process. Typically a chemical or photochemical oxidant is used to destroy a contaminant compound directly or indirectly through reaction intermediates. In the case of AOP, this oxidant is either ozone or the hydroxyl radical or ultraviolet radiation. Since the contaminant is physically broken up into its elemental components, the process depends on the efficient transfer of energy to achieve contaminant destruction. If such a process is not 100% efficient, remnants of the contaminant may still remain. These remnants may produce adverse health effects or reform the parent compound.

The hydroxyl radical has a higher oxidation potential and reacts immediately with nearly all organic compounds. This enhanced reaction leads to better treatment results regarding advanced degradation and faster kinetics (shorter contact times). Theoretically, there are several technologies that exist for advanced oxidation, see table 9.

TABLE 9. Advanced oxidation technologies

AOP combinations
Hydrogen peroxide + ultraviolet light
Hydrogen peroxide + ozone
Ultraviolet light + ozone
Ultraviolet light + titanium dioxide
The photo-fenton process
Oxidation in combination with electrolysis
Various catalytic processes (oxidant chemical + catalyst)

Although there are a number of processes which are defined as advanced oxidation processes, the most widely used definition includes techniques that are based on ozone, hydrogen peroxide and ultraviolet light. In the case of ultraviolet

light and ozone, an ozonised gas stream, produced by a dielectric barrier discharge, is introduced into the aqueous medium to be treated. The ultraviolet light radiation has a wavelength of 254 nm and is readily absorbed by ozone, resulting in the formation of highly reactive hydroxyl radicals. These short-lived radicals are more powerful oxidizing agents than ozone and hydrogen peroxide alone and are capable of converting virtually all organic compounds to carbon dioxide, water and similar species. (Sakaji 2002.)

There are a number of alternative reactions that can take place and it is known that high concentrations of both ozone and hydrogen peroxide need to be avoided as hydroxyl radicals are not selective in their reactivity and can react with excess oxidants. The oxidation rates achieved with hydroxyl radicals are much higher than those attainable from conventional oxidants such as ozone. In some cases, reaction rates achieved using hydroxyl radicals are 10^6 to 10^9 times higher than the rates achieved using ozone alone. (Sakaji 2002.)

2.4.1 Ozone destruction by UV

The pilot plant in this work was designed for the purification of water in which an ultraviolet lamp simultaneously irradiates the water and ozone mixture, combining the catalytic effect of ultraviolet radiation and the disinfecting and oxidizing effects of ozone on bacteria, viruses and chemical compounds in the water. Photolysis (direct absorption of UV) and photo-initiated oxidation (activation of ozone by UV to form oxidative hydroxyl radicals) have great potential for the destruction of a wide range of organic contaminants in water. (Taghipour 2004.)

During the advanced oxidation process of ozone with UV, ozone concentrations are expected to decrease inside the reactor. This is due to the ozone decomposition by UV radiation. The concentration of •OH is higher near the UV lamp, where the UV fluence rate is higher. This is expected as •OH formation depends on the fluence rate. The concentration of micro pollutants, such as atrazine or 1.4 dioxane, would be reduced along the reactor due to direct

photolysis and oxidation with •OH radicals. The water pollutant would show lower concentration near the UV lamp, where higher UV fluence rate and •OH radicals are present. It is evident that the pollutant decomposition is influenced by both reactor hydrodynamics and fluence rate. (Taghipour 2004.)

2.4.2 Ozone photo dissociation

The energy of an absorbed photon is strong enough to break molecular bonds and therefore capable of molecular fragments. One example of photo dissociation can be found in the stratospheric ozone. Ozone is produced in the stratosphere from molecular oxygen through the following pair of reactions:

$O_2 + hv \rightarrow O + O$ and $O + O_2 \rightarrow O_3$ where hv represents the energy of a photon of ultraviolet light with a wavelength less than 260 nm. (Taghipour 2004.)

Ozone is also dissociated by short-wavelength ultraviolet light (200-300 nm) through the reaction: $O_3 + hv \rightarrow O_2 + O$. The oxygen atom formed from this reaction may recombine with molecular oxygen to regenerate ozone, thereby completing the ozone cycle. The ozone layer in the stratosphere absorbs the UV-C radiation and "filters" the sunlight radiation before it reaches the earth's surface. The same reaction is used in the advanced oxidation processes, with the difference that the UV light is used to break the ozone into radical fragments. (Taghipour 2004.)

The utilized wavelength for this process is 254 nm, because the highest ozone absorption rate is achieved at exactly this point. The molar extinction coefficient ε, which describes the amount of absorbed photons by the ozone molecule, is 3300 M^{-1} cm^{-1}. The higher the extinction coefficient, the easier it is for ozone to absorb the UV light. The following graph presents the absorption rate of ozone for different wavelengths of light. The highest absorption rate is achieved at exactly 254 nm. This benefits the selection of low pressure lamps in contrast to medium pressure lamps which would work less efficient. (Kenshi 2001.)
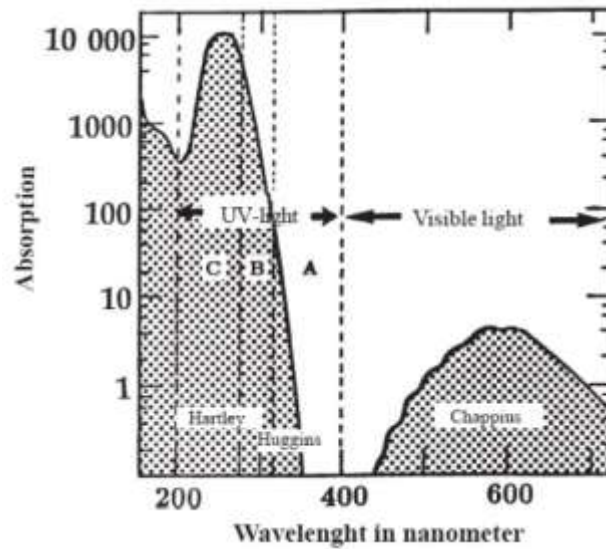
GRAPH 11. The molar extinction coefficient of ozone (Kenshi 2001)

2.4.3 Hydroxyl radical formation

The formation of hydroxyl radicals is based on a multi step mechanism. The introduced ozone is first broken up into one oxygen (O_2) molecule and one oxygen atom (O). This reaction is very efficient at the wavelength of 254 nm with a quantum yield of almost $\Phi=1$. The quantum yield is the number of destroyed molecules divided by the number of photons absorbed by the system. That means almost all photons are absorbed by the ozone. The oxygen atom reacts with water to form hydrogen peroxide. Hydrogen peroxide will partly be destructed directly by the UV irradiation into hydroxyl radicals, but due to the low extinction rate of hydrogen peroxide, most of the formed liquid will react further with ozone and HO_2^- which can be seen in the following equations. There is the significant difference of dissolved ozone and gaseous ozone in water. Ideally, all ozone should dissolve when introduced into the water phase. (Beltran 2004.)

The following reactions indicate the properties of dissolved ozone in water and hydroxyl radical formation with hydrogen peroxide formation. (Beltran 2004.)

$$O_3 \text{ (aqueous)} + h\upsilon \rightarrow 2 \, {}^\bullet OH$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+$$

$$HO_2^- + O_3 \rightarrow O_3^- + HO_2$$

$$HO_2 + h\upsilon \rightarrow {}^\bullet OH + O$$

$$O + H_2O \rightarrow 2 \, OH^{\cdot}$$

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2$$

$$H_2O_2 + h\upsilon \rightarrow 2 \, {}^\bullet OH$$
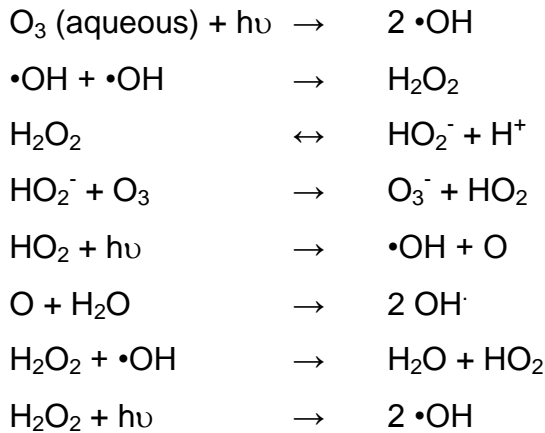
In contrast, the following reactions present the reactions of gaseous ozone in water. However these reactions can only occur on the film layer of gas and water. (Beltran 2004.)

$$O_3 \text{ (gas)} + h\upsilon \rightarrow O_2 + O$$

$$O + O_3 \rightarrow 2 \, O_2$$

$$O + H_2O \rightarrow 2 \, {}^\bullet OH$$

$$O + H_2O \rightarrow H_2O_2$$

$$O_3 + H_2O_2 \rightarrow O_2 + {}^\bullet OH + HO_2^-$$

$$H_2O_2 \leftrightarrow H^+ + HO_2^-$$

$$O_3 + HO_2^- \rightarrow {}^\bullet OH + O_2^- + O_2$$

$$O_3 + O_2^- \rightarrow O_3^- + O_2$$

$$O_3^- + H_2O \rightarrow {}^\bullet OH + HO^- + O_2$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2 + H_2O$$

$$H_2O_2 + h\upsilon \rightarrow 2 {}^\bullet OH$$

$$HO_2 + h\upsilon \rightarrow {}^\bullet OH + O$$
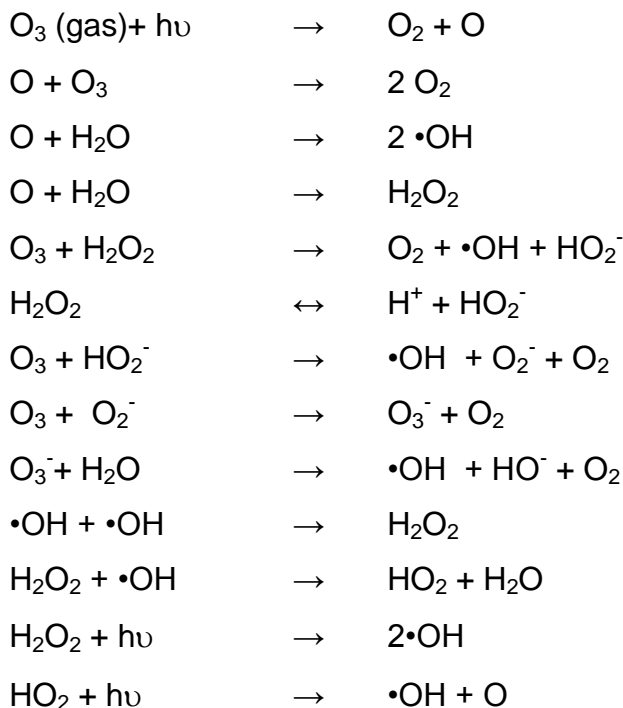
There are further ways for the generation of hydroxyl radicals which are dependent on the generated intermediates such as excited oxygen atoms (O), hydrogen peroxide or the conjugated base of hydrogen peroxide (HO_2^-). (Beltran 2004.)

Graph 12 shows the four main pathways for the generation of hydroxyl radicals in advanced oxidation processes.
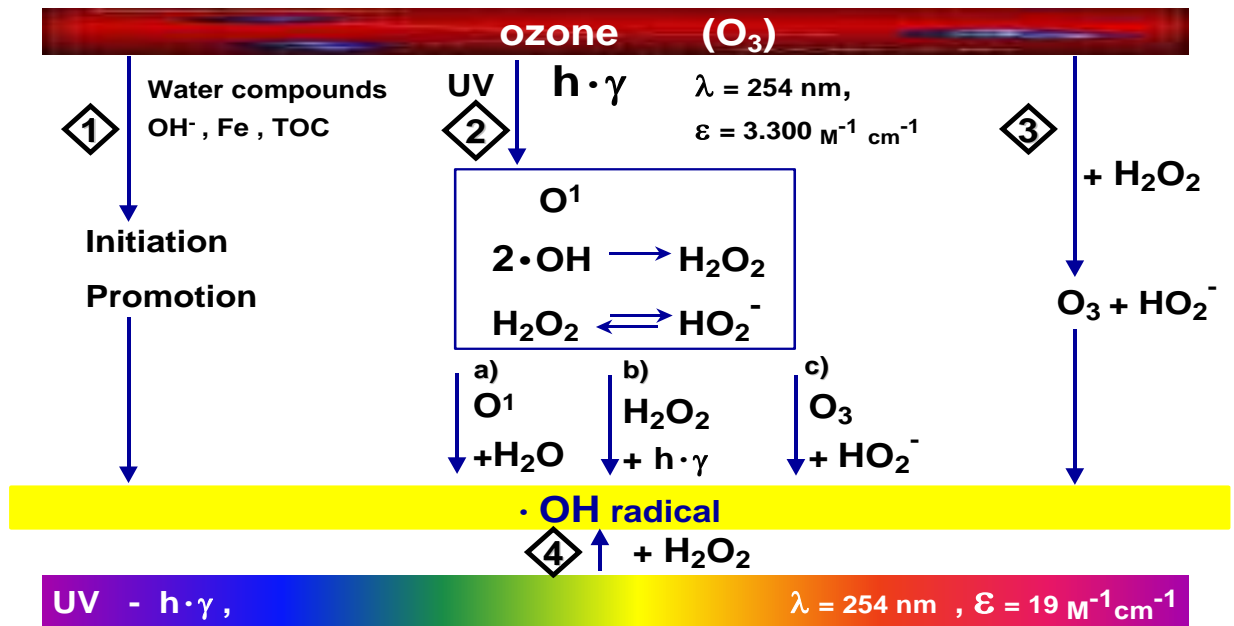
GRAPH 12. Hydroxyl radical pathways (Ried 2005)

1. Ozone alone. Typical water compounds such as hydroxyl anions, iron ions or organic compounds can initiate or promote a decomposition of dissolved ozone and generate hydroxyl radicals. When using ozone for waste water treatment, there is a possibility of generating the hydroxyl radical without the addition of UV or H_2O_2. However, it is difficult to predict the hydroxyl radical formation in this pathway as it is highly specific to water chemistry and the reaction kinetics of the system. It is unlikely that one would use ozone alone as an advanced oxidation process for water, but it is important to note that the impact of ozone alone may achieve the desired result. (Ried 2005.)

2. Ozone in combination with UV. Different oxidized species will be generated during the UV radiation of ozone molecules in water. Depending on the generated intermediates, e.g. excited oxygen atoms (O), hydrogen peroxide or the conjugated base of hydrogen peroxide (HO_2^-), there are different further pathways (a, b, c in the graph) for hydroxyl radical generation. (Ried 2005.)

3. Ozone in combination with hydrogen peroxide. In the presence of hydrogen peroxide, ozone reacts with the conjugated base of hydrogen peroxide (HO_2^-) to form hydroxyl radicals. (Ried 2005.)

4. Ultraviolet light in combination with hydrogen peroxide. The UV radiation of H_2O_2 leads directly to the formation of hydroxyl radicals. From the stoichiometric yield (1 mol $H_2O_2 \rightarrow$ 2 mol •OH radicals) this process is theoretically the most efficient, but the molar extinction coefficient for H_2O_2 (at 254 nm) is only 19 mol^{-1}cm^{-1}. This means that this process is highly dependent on the UV transmittance, when the UVT decreases, the low coefficient results in lower hydroxyl radical yields. For a given UV radiation this low coefficient and low radical yield can be 20 times less than the ozone + UV process. It is possible to work with wavelengths in the range of 180 to 250 nm to improve the molar extinction coefficient. (Ried 2005.)

Since low pressure lamps have a 99% output at 254 nm, a polychromatic, medium pressure (MP) lamp may be more efficient at converting H_2O_2 to the •OH radical. The energy input will be significantly increased in this case due to the use of MP lamps. This may become the limiting factor in comparison to other AOP. In addition, the depth of penetration of lower wavelengths (180–200 nm) is very low so the positive effect on the extinction coefficient at this lower wavelength is highly dependent on UVT. (Ried 2005.)

2.4.4 Comparison of ozone to hydrogen peroxide

While the production of ozone is relatively more expensive than hydrogen peroxide, one major advantage is due to the photochemical properties of ozone. The molar absorption coefficient at 254 nm is much higher for ozone than for hydrogen peroxide with 3300 M^{-1}cm^{-1} in comparison to 19 M^{-1}cm^{-1}, respectively. Therefore a high efficiency of ozone absorption can be achieved at 254 nm, in comparison to the UV-hydrogen peroxide AOP. The problems of ultraviolet - ozone based systems are the high operating costs for both the ozone generation and UV

light radiation. A high intensity of UV flux is required for ozone to break. While this is also the case in UV-hydrogen peroxide AOP, the capital costs are lower due to the easier treatment train. The only energy consumed in these systems is the UV light demanded to break the liquid hydrogen peroxide. In comparison, ozone-UV AOP require the UV light unit, but also the ozone generation unit, which will cause high initial costs and therefore a larger treatment unit in general. (Ijpelaar 2007.)

2.4.5 Low pressure and medium pressure lamp differences

Low pressure and medium pressure lamps are both used for the "destruction" of hydrogen peroxide by UV light. The wavelength of 254 nm, which is used in LP lamps, is excellent for H_2O_2 irradiation compared to the spectrum of MP lamps. The contribution of the 254 nm emission of a typical MP lamp to the total emission is 5-10%. For a LP lamp this is >90%. At the same input level of UV dose, LP lamps perform comparable in high water quality or better in low water quality regarding the fraction of light absorbed by H_2O_2. (Ijpelaar 2007.)

Due to the low molar extinction coefficient of the UV + H_2O_2 process, the percent conversion of H_2O_2 to the hydroxyl radical is low. One way to overcome this fact is to dose a higher amount of peroxide into the water. By overdosing, the required hydroxyl radicals may be produced, but there will also be excess H_2O_2 in the water after the UV process. Especially for drinking water, excess H_2O_2 cannot remain in the system therefore an absorption process (GAC), quenching process (chlorination, sodium bisulphite) or catalytic quenching with metal oxides must be considered downstream of the UV oxidation step. UV + ozone based AOP will also produce hydrogen peroxide during reaction, but the remaining concentrations of peroxide are rather low and therefore do not require further removal. (Ijpelaar 2007.)

2.4.6 UV photolysis

The pathways mentioned in graph 12 are specifically used for the formation of the hydroxyl radical, but certain contaminants can be treated without the generation of radicals. For example, N-nitrosodymethylamine (NDMA) can be destroyed by direct UV photolysis. UV photolysis takes place when UV light is absorbed by the target contaminant and causes it to breakdown. In effect, NDMA absorbs UV light at 228 nm, which results in cleavage of the N-N bond. No hydrogen peroxide is required with UV photolysis since the hydroxyl radical is not needed. The emitted photons from the UV lamp are strong enough to break some molecular bonds and therefore capable of destroying the pollutant. This effect only works for some pollutants, such as NDMA, while most compounds are somewhat resistant to the ultraviolet radiation. (Ijpelaar 2007.)

Another example where the hydroxyl radical is not required is the oxidation of endocrine disrupting compounds (EDCs). Studies have shown that ozone alone can oxidize most EDCs and achieve removal levels greater than 90%. For treatment of EDCs in wastewater, UV based AOP systems may also be adversely affected by the typically low transmission of wastewater, compared to drinking water, whereas UVT has no impact on ozone oxidation. (Ried 2005.)

2.4.7 Example of ozone destruction through ultraviolet light (CONFIDENTAIL)

GRAPH 13. Ozone destruction by UV-C light

2.4.8 Applications for AOP

There are several areas where advanced oxidation processes can be commercially used for the degradation of pollutants from water. Examples include

endocrine disrupting compounds, pharmaceuticals, pesticides (e.g. atrazine), persistent substances, taste and odor causing substances (such as algae during the summer months), 1.4 dioxane, NDMA (N-nitrosodimethylamine), MTBE (methyl-tertiary-butyl-ether), chlorinated hydrocarbons (e.g. TCE).

2.4.9 Advantages and disadvantages of AOPs

The advantage of AOPs is the actual treatment technology. AOP is a destruction process and the final products are only carbon dioxide, water and inert salts. The process residuals do not need any further treatment. If ozone is utilized, the oxidant can replace the disinfection properties of chlorine and therefore reduce the toxic properties of chlorine. Because ozone must be generated on site and used immediately, no storage area is required for the oxidant. A wide variety of contaminants and concentrations can be treated.

Some pollutants (e.g. MTBE) can be removed by air stripping, granulated activated carbon (GAC) adsorption and resin sorption, whereas the actual destruction of the pollutant would require additional processes. In contrast, AOPs destroy primary organic contaminants directly in water. Several AOP technologies involving UV light or ozone would also have the positive side effect of disinfection capability of the source water. Therefore no further disinfection treatment step would be required.

The components utilized in AOP (UV light and ozone) have been used by the water community in commercial water disinfection applications for many years already. Consequently, even conservative treatment plant operators are already familiar with these technologies in contrast to hydrogen peroxide, Fenton´s reaction, TiO_2 or other emerging technologies.

The disadvantage is that the reaction between organic contaminants and the hydroxyl radical is fast, but does not directly result in the mineralization of these contaminants. Instead, organic oxidation by-products are produced which can further react with hydroxyl radicals for complete mineralization.

Ideally, AOP treatment systems are capable to completely mineralize the organic contaminants of concern to carbon dioxide and water. In real life applications this may require high energy and greater chemical doses and can therefore be too costly in certain applications.

In some cases, the actual pollutant cannot be mineralized completely, and the remaining substances might cause higher risks of concern than the initial substance. These oxidation by-products must be fully understood and determined according to the specific water matrix to be treated. Both organic and inorganic oxidation by-products can be formed. When ozone is employed in AOP applications, bromate can be formed from bromide, which is naturally present in the source water. This will be further discussed in the following section.

The effectiveness of AOPs can be limited through the presence of nitrites, TOC and other inorganics. This is due to the scavenging of radicals that would otherwise react with pollutants. Operational costs will increase when concentrations of these scavengers in source water increase. Contact times and chemical dosages will also increase to maintain treatment goal. AOPs are hard to plan due to the sensitivity of operational costs to changing source water.

TABLE 10. Advantages and disadvantages of AOPs

Tech-nology	Advantages	Disadvantages
General AOPs	AOPs are destructive processes. Several AOPs have disinfectant capabilities. Many AOP components have been utilized in the water industry.	Potential for accumulation of oxidation by-products. Radical scavenging by interfering compounds can reduce effectiveness of AOPs.
O_3 - H_2O_2	Efficient in treating waters with high pollution concentrations. Supplemental disinfectant. Established technology for remediation applications.	Potential for bromate formation. May require treatment of excess H_2O_2. May require ozone off-gas treatment and permit.
O_3 - UV	Supplemental disinfectant. More efficient at generating radicals than other processes for equal oxidant concentrations.	Energy and cost intensive process. Potential for bromate formation. Turbidity can interfere with UV light. Ozone diffusion may result in mass transfer limitations. May require ozone off-gas treatment and permit. Interfering compounds can absorb light. Potential increase in THM and HAA formation when combined with pre/post chlorination.
UV – H_2O_2	No potential for bromate formation. UV radiation can serve as disinfectant. No off-gas treatment required. Not limited by mass transfer relative to ozone processes.	Turbidity can interfere with UV light. Less stoichiometrically efficient at generating radicals than O_3 – UV process. Interfering compounds can absorb light. Potential increase in THM and HAA formation when combined with pre chlorination.

2.4.10 Parameters affecting the AOP efficiency

There are several water quality parameters that influence the effectiveness of any AOP. The most important parameters are the following:

Alkalinity: The hydroxyl radical is non selective and can be exhausted by the presence of organic or inorganic compounds other than the contaminants of concern. Both carbonate and bicarbonate will scavenge hydroxyl radicals to create carbonate radicals which react with other organic or inorganic compounds present, but at a much slower rate. Source waters with medium to high alkalinities usually contain carbonate and bicarbonate. High concentrations are likely to react with the hydroxyl radical and therefore scavenge it, which could otherwise react with micro pollutants. (Hoigne 1976.)

TOC and NOM: Organic matter present in water will scavenge and therefore limit the effectiveness of the hydroxyl radical. Total organic carbon (TOC) measurement include all organic compounds in water; with concentrations usually ranging from <1 mg/l to >7 mg/l and include pesticides, oil and gasoline traces and chlorinated compounds. Non organic matter (NOM) accounts macromolecular organic compounds, which also negatively affect the effectiveness of hydroxyl radicals. Furthermore there are concerns about potential negative side effects of UV irradiation in combination with chlorine addition. Such combination might lead to the formation of harmful by-products. (Steward 1993.)

Nitrates and nitrites adsorb ultraviolet light in the range of 230 to 240 nm and 300 to 310 nm and will decrease the formation of radicals. This effect is especially affecting the polychromatic spectral curve of medium pressure lamps, which have several emission peaks in that region. (Steward 1993.)

Phosphates and sulfates are present in low amounts in source waters, but are slow in reacting with hydroxyl radicals. Therefore their influence can be diregarded.

Turbidity and transmission lower the transmittance of the source water for light. The efficiency will decrease with increasing turbidity. (Wedeco 2008.)

2.5 Oxidation by-products

Minimizing the risks of disinfection by-products while maintaining adequate protection from microbial and organic contamination is one of the dilemmas water utilities and regulating agencies are faced with today. Disinfection by-products are formed during water treatment when disinfectants and oxidants react with organic and inorganic matter present in water. Several of these by-products have been associated with various health effects, including cancer risks. The by-product concerning the usage of ozone-UV techniques is called bromate. (Bundy 2002.)

TABLE 11. Description of drinking water disinfection by-products

Disinfection by-products	Potential health effects from ingestion of water	MCL (mg/l)
Bromate	Increased risk of cancer.	0.010
Chlorite	Anemia, nervous system effects.	1.0
Haloacetic acids	Increased risk of cancer.	0.060
Total Trihalomethanes	Liver, kidney or central nervous system problems; increased risk of cancer.	0.080

2.5.1 Bromate

Bromate (BrO_3^-) is an inorganic disinfection by-product of potable water that is potentially carcinogenic and mutagenic (Neal 2006). It is not expected to be present in natural water, but may be formed during treatment by oxidation. Deafness, renal failure, coma and convulsions to humans have been attributed to bromate ingestion (Quick 1975), which results in bromic acid formation in the stomach in the presence hydrochloric acid. (Turkington 1994).

Bromate is considered a potential human carcinogen by the International Agency Research on Cancer and a probable human carcinogen by the disinfection/disinfection by-product rule of the USEPA (USEPA 1994).

Compounds with bromine in formal oxidation state $^{-1}$ are called bromides; therefore bromide is the ion of bromine and is present in natural soft water in concentrations between 30 and 200 µg/l (Haag 1983.)

Bromide can originate from saltwater intrusion, natural fractionation, anthropogenic bromide emissions, water disinfection with chloride, or agricultural applications. Even if bromide ion in drinking water supplies has not been observed to cause direct public health problems, it is a precursor of the formation of bromate ion. (Myllykangas 1999.)

2.5.2 Formation of bromate

Bromate is formed in potable water mostly as a result of ozonation of raw water containing bromide. For those processes using ozone alone the by-product that causes most concern is the bromate ion. EU, Japanese and the US regulations specify a bromate standard of 10 µg/l, the WHO guideline value is 25 µg/l and the Australian regulations limit bromate to 20 µg/l. (Legube 1996.)

The mechanism for bromate formation is rather complicated and includes both molecular ozone and •OH radical reactions. During the chemical oxidation and / or disinfection of natural waters containing bromide with ozone, bromate is formed at concentrations ranging from 0 to 50 µg/l under normal drinking water treatment conditions. Fortunately, the reactions of ozone with bromide and hypobromide ions are relatively slow. Hence, ozonation of waters during a brief period of time will lead to a low oxidation yield of bromide ion to bromate ion. (Legube 1996.)

Bromate ion formation by reaction of hydroxyl radicals on bromide ion is possible only in the presence of hypobromite ion. Moreover, hypobromite ion cannot be formed by reaction of hydroxyl radical with bromide ion. Therefore, hydroxyl radicals alone are not precursors of bromate ion formation. (Legube 1996.)

Several parameters can impact the conversion of bromide to bromate. Parameters such as bromide concentration, dissolved organic carbon (DOC), temperature and pH are important to be determined during performance. The rates of reaction depend especially on pH because ozone reacts predominantly on OBr^-. Therefore acid waters have lower risk of bromate formation. (Neal 2006.)

It is possible to optimize the design and the operation to keep the bromate formation down. Low residual ozone concentrations in water, the addition of hydrogen peroxide, pH control, several injection points instead of one, the reaction time of ozone or the direct irradiation of ozone gas by UV light are some possibilities to use ozone even in the presence of bromide in the source water. Furthermore, UV irradiation in the wavelength range of 180-300 nm provides energy sufficient for producing intermolecular changes of the irradiated molecules. The decomposition of bromate leads to the production of bromite ion. (Neal 2006.)

$$2\ BrO_3^- + h\upsilon \rightarrow 2BrO_2^- + O_2$$
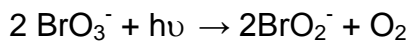
Bromite ion (BrO_2^-) is further decomposed to hypobromite ion (BrO^-) and bromide ion (Br^-) via complex reactions which are initiated by the products generated by the primary reactions of photolysis.

$$2BrO_2^- + h\upsilon \rightarrow 2BrO^- + O_2$$
$$2BrO^- + h\upsilon \rightarrow 2Br^- + O_2$$
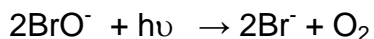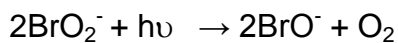
These reactions indicate that the photodecomposition of bromate leads to the production of Br^- and oxygen as end products. However, the required UV irradiation dose cannot be applied for typical AOP applications due to the high energy needed for this process. (Siddiqui 1996.)
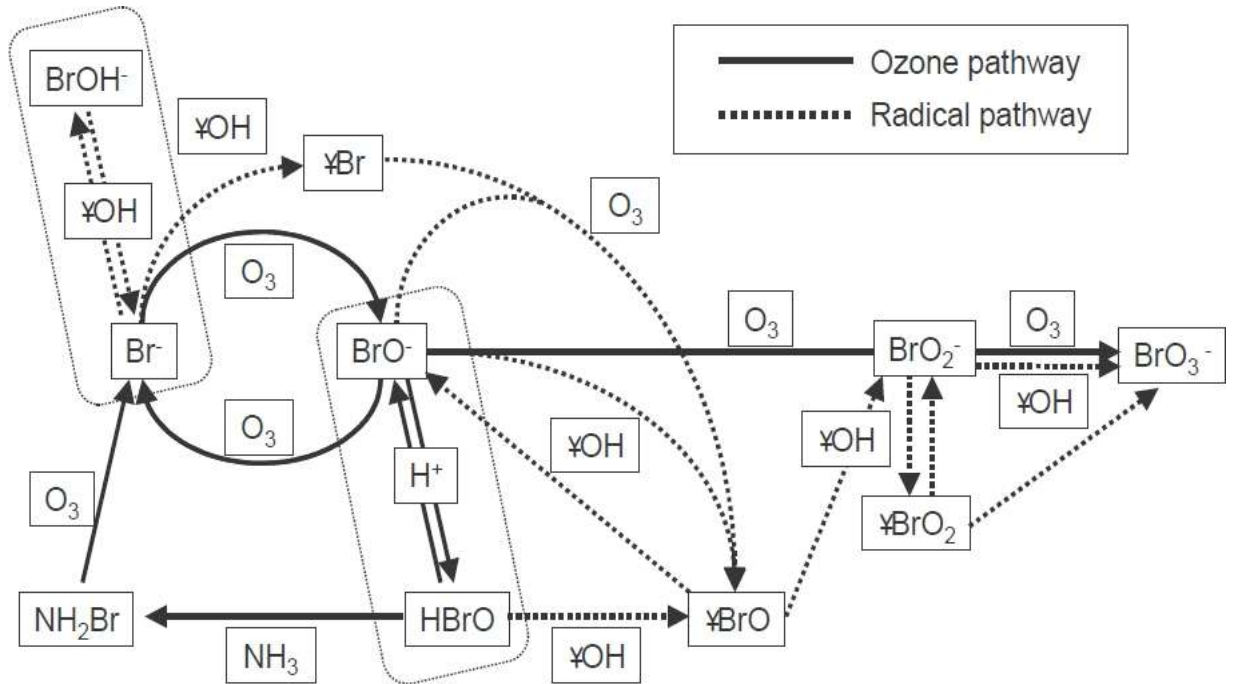
(CONFIDENTIAL)

2.5.3 Formation pathways

Bromate can be produced through different pathways. Ozonation of water forms two powerful oxidants: aqueous molecular (O_3) and hydroxyl radical ($\bullet OH$). Both O_3 and $\bullet OH$ radicals react with organic and inorganic species in water. The three major pathways are as follows:

The first pathway is the direct ozonation pathway, in which O_3 sequentially oxidizes Br^- to aqueous bromine ($HOBr/OBr^-$) and then BrO_3^-. Because OBr^- rather than $HOBr$ can be oxidized to bromite (BrO_2^-) at an appreciable rate, BrO_3^- formation of favored at high pH upon continuous ozonation. A second pathway for BrO_3^- formation is that O_3 oxidizes Br^- to aqueous bromine, followed by $\bullet OH$ oxidation of $HOBr/OBr^-$ to $BrO\bullet$, which disproportionates to BrO_2^-. BrO_2^- is then oxidized by O_3 to form BrO_3^-. The third pathway for BrO_3^- formation is: Br^- is first oxidized by $\bullet OH$ to form $BrO\bullet$. This continues to form bromate through disproportionation to BrO_2^-, followed by O_3 oxidation to BrO_3^-. (Yasunaga 2005.)

About 17% of bromide in solution can be transformed to bromate. Temperature of water plays an important role in bromate formation. Generally, all the rates of reactions involved in formation of bromate are raised with temperature and the value of the dissociation constant of hypobromous acid (Ka of $HOBr/OBr^-$) diminishes as the temperature rises. Consequently, the hypobromite ion concentration increases with the temperature thus increasing the formation of the bromate ions. (Li 2007.)

Graph 14 presents the formation pathway of bromate from the ozonation of bromide in water. The two main pathways are the direct ozone pathways, which is by far more important and the radical pathway which is less likely to occur.

GRAPH 14. The bromate formation pathway (Yasunaga 2005, courtesy of Mitsubishi Electric Corporation)

3 AOP SYSTEM AND PERFORMANCE

3.1 Pre examinations

(CONFIDENTIAL)

3.1.1 The initial design of the reactor

(CONFIDENTIAL)

3.1.2 Conclusions after first test run

(CONFIDENTIAL)

3.1.3 Injector

The injector type of gas injection system works on the principle of the venturi effect. A high pressure is required on the inlet of the nozzle, where pressurized water enters the injector inlet. The water stream is then constricted towards the injection chamber and changes into a high velocity jet stream. The increase in velocity through the injection chamber results in a decrease in pressure, thereby enabling an additive material to be drawn through the suction port and entrained into the motive stream. This media can be liquid or gas, depending on the type of application. In the case of advanced oxidation process, ozone is used as the gas media. As the jet stream is diffused toward the injector outlet, its velocity is reduced and it is reconverted into pressure energy.

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Graph 18 illustrates the venture effect.
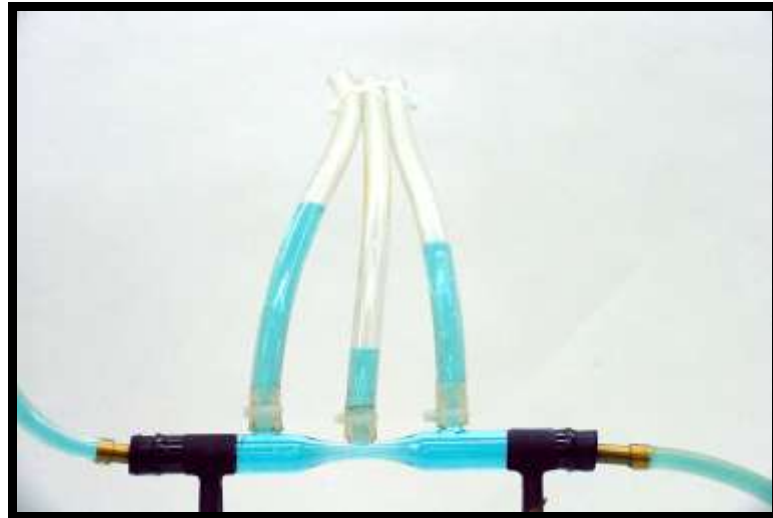
GRAPH 15. Injector venturi effect

The injector working principle is based on the venturi effect. A stream is compressed into a smaller diameter section, whereas the velocity is increased. As a result of the high velocity, the pressure will drop and a second media can be sucked into the stream. Graph 19 illustrates water that is flowing with high velocity through the suction point where the highest velocity is reached. At this point, air is sucked into the system and a high mixing rate is achieved. The left graph shows the injector "Körting 135-5-2556" utilized during the performance, whereas the right graph is for illustration purpose only.

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GRAPH 16. Injector during performance

3.1.4 Diffuser

O.I.Filtration Ltd, of Stoke on Trent, England, supplied the stone diffuser sample with a mean pore size of 30 microns (30 µm) which was small enough to fit into the reactor. In comparison, human hair is 100 µm wide.

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GRAPH 17. Diffuser built into the rector

Graph 20 shows the diffuser built into the reactor bottom part. The small reactor diameter of 80 mm was the limiting factor for most commercial diffusers. The utilized stone diffuser was capable of creating relatively small bubbles.

For processes such as ozonation, aeration of drinking water, waste water, aquariums, fish farms, lakes and ponds, air stripping of volatile organic compounds, iron and sulfide removal by oxidation, the bubble creation is very important. Especially the bubble diameter can critically affect process efficiency, because it determines the surface area of the bubbles. For two different spherical bubble diameters with the same total volume of gas, the ratio of the total surface areas is inversely proportional to the ratio of the diameters. To give an example, if the mean bubble diameter would be decreased from 2.5 mm to 0.5 mm, the interfacial contact area between the air and water would increase by the factor 5 for the same gas flow rate.

A finer pore size is expected to offer the best solution for increasing the ozone transfer efficiency. Ceramic diffusers with very small pores can create fine bubbles, but are not suitable for this type of ozone diffusion due to the high pressure drop. The ozone generator used in this AOP application, "Ozomantic Modular 8HC", is only capable of handling pressure up to 1 bar.

A fine ceramic diffuser with pore size of 2.0 µm (Kerafol, Membrane disc Ø 152 mm) would have delivered very fine bubbles, but the bubble point of air into water had to be larger than 1.6 bar, which would have required a larger ozone generator. In addition to this, the size of the diffusing disk did not fit into the reactor with a diameter of only 80 mm. Graph 21 illustrates the bubble size of the Kerafol disk diffuser. It created very fine bubbles, which would have been ideal for the AOP pilot trials.

GRAPH 18. Fine bubble distribution of ceramic diffuser

Experiments have shown that the diffuser material property that is the primary determinant of bubble size is not only the pore size, but also the free energy at the surface, which is a result of intermolecular attraction. With the small contact angle, water displaces the gas from the high energy diffuser surface pore so that the tension holding the bubble to the surface is minimized. A smaller upward force from the gas balloon is enough to detach it to rise up into the liquid. In contrast, the contact angle for a low surface energy diffuser is greater so that the gas displaces the water. The bubble must increase in dimension before the upward force produced by the density difference between gas and liquid is sufficient to overcome the surface tension of the larger area and rises up into the liquid. The surface energy of materials is the primary factor for the yield of small bubbles. (Burries 1999.)
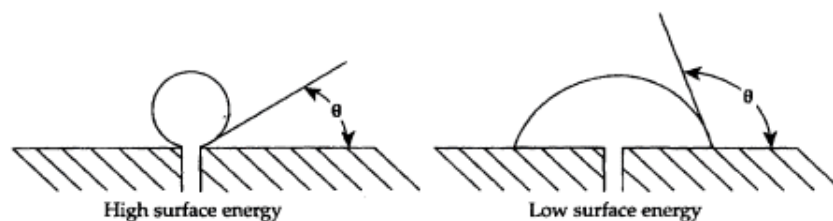
GRAPH 19. Surface energy dependency of bubbles (Burries 1999, courtesy of Alan Burries, Alabdiffusers)

3.1.5 Tubing

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GRAPH 20.Tubing built into reactor

3.1.6 Determining bubble size of injector, diffuser and tubing

The actual size of the gas bubble is the key indicator for efficient transfer of ozone into the water phase. In order to achieve reliable results, the comparison between the compared technologies included the optical determination of average bubble size. This test was once again conducted with a plastic pipe and the size was manually evaluated according to the following graphs. For safety reasons, the test was performed with oxygen gas, not with ozone. The bubble size during ozonation is expected to remain similar. One influencing factor is the water flow rate. During counter current flows, the water will act against the rise of the bubbles. This leads to a flattening of the bubble.

The average bubble size of the injector was determined to be ~2.5 mm in diameter. This value is based on averages taken from several pictures during flow rates of 20, 50 and 80 liters of oxygen gas, respectively.

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GRAPH 21. Diffuser during gas flow rates of 20 l/h

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GRAPH 22. Bubbles during gas flow rates of 20 l/h

TABLE 12. Comparison of gas diffusing technologies

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3.1.7   The first performance test: co-current

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GRAPH 23. Co-current flow injector arrangement

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Graph 28 illustrates the co-current diffuser arrangement.

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GRAPH 24. Co-current flow diffuser arrangement

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3.1.8   The first performance test: counter-current

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GRAPH 25. Counter current arrangement

3.1.9 Bubble contact time with UV radiation

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GRAPH 26. Contact time for co-current and counter-current arrangements

3.1.10 Compounds of the system

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TABLE 13. Determined properties during performance

Analytical determination parts	Description / Type
Conductivity meter	WTWConduktometer LF191
pH meter	Schott Lab 850
Photometer	Dr. Lange CADAS 100
Gas flow meter	ABB FAG6100 140 l/h
Water flow meter	Krohne optiflux 1100 c
Ozone gas concentration	BMT 961 tpc BMT 964 c
Dissolved O_3 concentration, and water temperature	Orbisphere 510

3.1.11 Sampling

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3.2 Results of pre study

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4 DEGRADATION OF 1.4 DIOXANE AND BROMATE CONTROL

(CONFIDENTIAL)

4.1 Final pilot runs

(CONFIDENTIAL)

4.1.1 Sampling amounts and procedure

(CONFIDENTIAL)

4.2 Results

(CONFIDENTIAL)

5 CONCLUSIONS AND RECOMMENDATIONS

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APPENDIX 1

Determined parameters

The following process parameters were measured during the AOP comparison.

TABLE 14. Measured parameters during AOP performance

Parameter	Unit	Description
Gas flow	m^3/h	Volume of oxygen/ozone gas mixture flowing into the reactor.
Water flow	m^3/h	Volume of water flowing into the reactor.
Ozone IN	g/Nm^3	Concentration of ozone in oxygen/ozone gas mixture streaming into the reactor from the generator.
Ozone OUT	g/Nm^3	Concentration of ozone in oxygen/ozone gas mixture streaming out of the reactor after UV. Ideally, no ozone should be detected here anymore.
Ozone OUT (no UV)	g/Nm^3	Concentration of ozone in oxygen/ozone gas mixture streaming out of the reactor, when no UV light was present. This indicates how much ozone is "consumed" by the water matrix even without any UV light present.
Dissolved ozone pre UV	mg/l	Amount of dissolved ozone in water matrix before the UV irradiation. This value shows how much ozone would have been able to be destructed by UV light.
Dissolved ozone after UV	mg/l	Amount of dissolved ozone after the UV irradiation. Ideally no ozone should be detected here anymore, due to the UV destruction.

Parameter	Unit	Description
pH		The pH is one of the most important factors affecting the efficiency of AOPs.
Conductivity	µS/cm	The conductivity should not change significantly during the oxidation process.
Water transmission	%	The transmission is an important factor for UV light efficiency.
Hydrogen peroxide after UV	mg/l	Hydrogen peroxide is formed through the process. This value is determining how much peroxide is still left after the process, i.e. has not been destructed by the UV light.
Water temperature	°C	Ambient water temperature is important for reaction kinetics and how much ozone can be dissolved into water phase.

TABLE 15. Parameters calculated according to the measured values

Parameter	Unit	Description
Ozone dose IN	g/m^3	The dose of ozone applied to the water per hour. It is calculated from (ozone IN*gas flow)*water flow.
Ozone dose OUT	g/m^3	The dose of ozone which has not been activated by the UV. Ideally, this value should be zero. It is calculated from (ozone OUT*gas flow)*water flow.
Reacted ozone TOTAL	g	The amount of ozone reacted inside the system. For both gas and dissolved phases. This value is most important, because it shows how effective ozone has been activated. Ideally, if ozone dose IN is 4 g, 4 g should have also reacted in this value.
Reacted ozone gas phase	%	Amount of ozone which has reacted in the gas phase. The higher the percentage, the better the percentage activation.
Activated dissolved ozone	mg/l	Amount of ozone which has reacted into radicals in dissolved phase. It subtracts dissolved ozone pre UV – dissolved ozone after UV.
Activated dissolved O3	%	Amount of dissolved ozone which has been activated in percent.
Hydrogen peroxide concentration (theoretical)	mg/l	It is calculated how much hydrogen peroxide would theoretically be formed during the process from the reaction theory of ozone.