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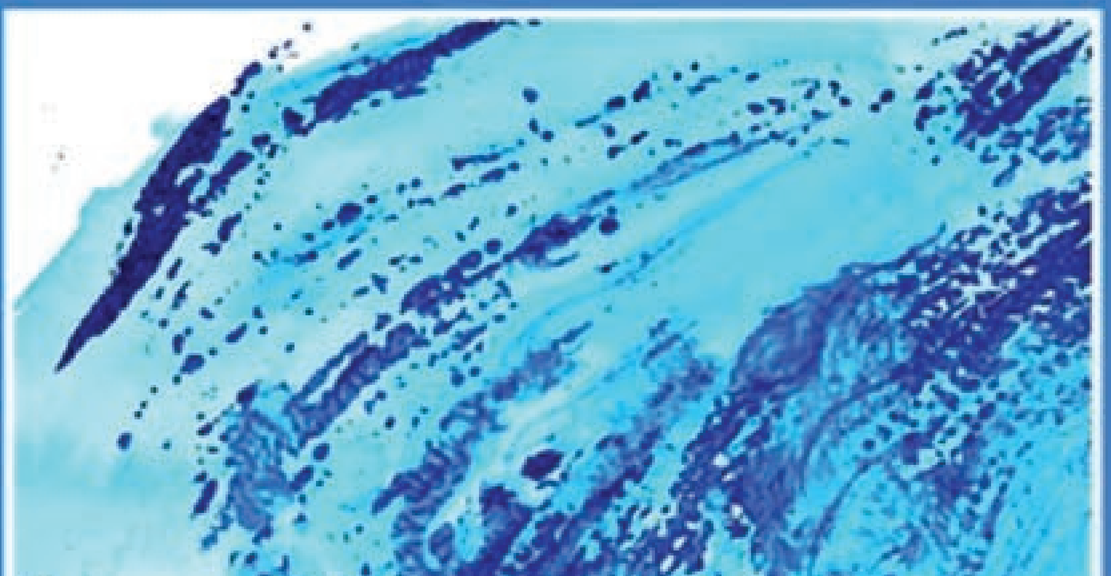
C. Gottschalk, J. A. Libra, A. Saupe

Ozonation of Water and Waste Water

A Practical Guide to Understanding Ozone and its Application



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Preface

The ozonation of compounds in water is a complex process. The mechanisms are very complicated, the parameters are many, but the possibilities of developing cost-effective treatment schemes for drinking water and waste water are large. To take advantage of this potential, it is important to know which parameters contribute to the process, which are important, and how they affect the process.

Because ozonation is so system dependent, most full-scale applications are first tried out bench-scale. That means designers and manufacturers of treatment systems, researchers, as well as potential industrial operators of ozonation must know not only the fundamentals about the mechanisms of ozonation, but also how to set-up experiments so that the results can be interpreted, extrapolated, and applied.

Most books available today concentrate on either drinking water or waste water treatment, seldom dealing with both or explaining the essential differences. And only rare exceptions deal with the how-to of ozone experiments.

This guide fills the gap. It contains the cumulative knowledge gathered by the authors as researchers, teachers and ozone system developers on experimental design, execution, interpretation and application. Drawing on experience gained from hours spent on laboratory research with drinking and waste waters, literature study, intensive discussion with leading experts, perplexed reflection and deep thought, the book offers practical help to avoid common pitfalls and unnecessary work.

This book is aimed at professionals in industry and research currently using ozonation who want to optimize their system, as well as students beginning work with ozonation. Much literature exists today about ozonation, but its practical use for beginners is limited by its specialization, and for the advanced by its magnitude and diversity.

The practical guide presents an overview of current theories and results from the specialized literature in short concise text, tables and figures accompanied with references to important secondary literature. It contains just enough information for beginners to start with, but goes rapidly to the detailed information that advanced readers need.

Structure of the Book

The book consists of two parts: Part A Ozone in Overview and Part B Ozone Applied. The first part is intended to provide a general background on ozonation, briefly reviewing the toxicology of ozone, its reaction mechanisms, and full-scale applications of ozonation. This provides motivation for experimental activity, applying ozone in the laboratory. The second part of the book tries to offer information on just how to go about it. The design of experiments and required equipment as well as analytical methods and data evaluation are first discussed. Then the theoretical background needed to carry out these activities is explored. The goal here is to include the basics necessary for building a solid foundation, and to reference secondary sources, with which the reader can delve deeper into ozonation specifics. Part B is rounded out with a discussion of applications that use ozone in combination with other treatment processes.

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Part A: Ozone in Overview 3

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Introduction

Being poised on the edge of the third millennium in Berlin, the city of Siemens who constructed the first ozone generator almost 150 years ago, and writing a book on ozone applications in water can make one philosophical. Especially when one has been confronted with the puzzlement of most acquaintances about why anyone deliberately produces ozone and what it has to do with water. These two aspects of this book: ozone and water need some clarification.

Ozone can be present as a gas or dissolved in a liquid. The media reports almost exclusively on gaseous ozone. For example, that the beneficial ozone layer in our atmosphere is being depleted, allowing more damaging UV-radiation from the sun to reach us on earth. On the other hand, announcements in the media warn about too high ozone concentrations in our air on sunny days, causing damage to human health and the environment. That ozone can have beneficial and detrimental effects can be confusing if it is not made clear that the effect is dependent on the location of the ozone. Direct exposure is always detrimental.

The other aspect is water itself. A recent survey has shown that pure water contains only 98.1 % H_2O, at least that is the common perception (Malt, 1994). Although water pollution has not caused such an extreme change in the composition of our water resources, we have allowed many substances to enter the natural water cycle with detrimental effects on human health and the natural environment. The result is additional treatment processes are often necessary to prepare drinking water for every day use. And processes are necessary for waste water treatment and groundwater remediation to prevent even larger contamination. Here ozone comes into play. It is capable of oxidizing a large number of pollutants in an environmentally sound way, since normally no harmful end- or byproducts are formed nor are secondary wastes produced. Unfortunately, we cannot make use of the ozone gas sometimes present in unacceptably high concentrations in our breathing air (e.g. $> 240\ \mu g\ m^{-3}$), but we have to produce it in ozone generators from air or from pure oxygen using much energy, to reach concentrations higher by a factor of a million ($240\ g\ m^{-3}$).

That almost 150 years after the production of the first ozone generator a book is still necessary on how to experiment with one, shows that ozonation is a complex subject. Some very good reference books and articles exist that explain the fundamentals of ozonation, the chemical reactions, the effect of some parameters. However, most work concentrates on either drinking water treatment or waste water treatment, seldom dealing with both, reflecting our personal experience that these are two separate "worlds". Since ozone applications in production processes are growing, even more people from various disciplines need access to information on ozone and how to make use of the results from the various applications. We have tried to bridge this information gap with this book, building on our diverse backgrounds in drinking, waste and process water treatment.

Another area rarely dealt with in previous literature is the "how-to" of ozone experiments. This information is usually hard-earned by doctoral candidates and laboratory staff, and either not considered as appropriate information for a scientific treatise or considered as proprietary information that belongs to expertise. This lack of information has motivated us to write a book that contains not only fundamental information about the toxicology of ozone, its reaction mechanisms, and full-scale applications of ozonation (Part A: Ozone in

Overview), but also information on how to set-up experiments so that they produce results that can be interpreted and extrapolated (Part B: Ozone Applied). The experimenter is provided with tools to improve his or her results and interpret results found in the literature. The required theoretical foundation is laid at the beginning of each chapter in Part B, compact and tailored to ozone, followed by practical aspects. References are made to important literature sources to help direct the reader wishing for more in-depth information. A discussion of applications combining ozone with other processes illustrates how the oxidizing potential of ozone can be utilized.

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Part A: Ozone in Overview

1 Toxicology

Toxicology examines the adverse effects of substances on living organisms. The effect on humans has been traditionally the subject of this study. The field of ecotoxicology has been developed to study the wider effects of substances on an ecosystem, not only on individual organisms, but also on the interactions between the elements in ecosystems. Both areas are important when evaluating the toxicology of ozonation applications. The species affected by a substance depends on the application – studies on drinking water concentrate on human toxicology and waste water on aquatic ecotoxicology.

This chapter will give a short overview of the toxicology of ozone. The types of toxicity are briefly reviewed (Section A 1.1), before results from studies made on its application are presented. When talking about the effects of ozone, one has to differentiate between:

- ozone in gas (Section A 1.2),
- ozone in liquid (Section A 1.3) and
- byproducts formed by ozonation (Section A 1.4).

1.1 Background

Acute toxicity describes a fast harmful effect after only a short-term exposure or exposure in limited amounts, e. g. a fast reacting poison. Subchronic reactions from chemicals are mostly determined by biochemical changes as well as changes in growth, behavior and other factors over a time period of several months. For chronic toxicity, the harmful effect to a substance is measured over a much longer time period from years to a lifetime. The harmful effect could be reversible or irreversible and cause benign or malignant tumors, mutagenic or teratogenic effects, bodily injury or death (Wentz, 1998).

In toxicological studies evaluating the effect on human health, experiments are usually made with animals or cultured cells. The test results are usually not directly applicable to human health risk and must be interpreted by professionals. If available, epidemiological studies of humans exposed to a particular environmental situation are preferred because their results are usually directly applicable to human health risk (Langlais et al., 1991).

Aquatic ecotoxicology evaluates the probability of an adverse impact of a substance on the aquatic environment at the present as well as in the future, considering the total flow into the system (Klein, 1999). It encompasses laboratory ecotoxicity tests on appropriate test organisms to explore relationships between exposure and effect under controlled conditions as well as studies of the effects of substances or effluents under a variety of ecological conditions in complex field ecosystems (Chapman, 1995).

Laboratory test organisms should be representative of the four groups: microorganisms, plants, invertebrates, and fish. The results are often reported as a lethal dose or concentration (LD or LC) with LC_{50} the concentration where 50 % of the test organisms survived. The effective dose or concentration (ED or EC) is defined analogously where EC_{50} is used to describe adverse effects in 50 % of the test organisms within the prescribed test period (Novotny and Olem, 1994).

Although many tests have been standardized and much progress has been made in laying a scientific basis for ecotoxicology, there are still many problems associated with predicting effects in such complex systems (Schäfers and Klein, 1998).

1.2 Ozone in Gas

Ozone is a highly toxic, oxidizing gas. The routes of entry are inhalation, skin and eyes.

Inhalation

Acute effects: Ozone concentrations in excess of a few tenths of ppm (1 ppm = 2 mg m^{-3}, 20 °C, 101.3 kPa) cause occasional discomfort to exposed individuals in the form of headache, dryness of throat and mucous membranes, and irritation of the nose following exposures of short duration. The odor threshold is about 0.02 ppm, however, a desensibilization occurs over time. Exposure to higher concentrations can also produce delayed lung edema in addition to lassitude, frontal headache, sensation of substernal pressure, constriction or oppression, acid in mouth, and anorexia. More severe exposures have produced dyspnea, cough, choking sensation, tachycardia, vertigo, lowering of blood pressure, severe cramping chest pain, and generalized body pain. It is estimated that 50 ppm for 30 minutes would be fatal.

Chronic exposures: chronic exposure symptoms are similar to acute exposures with pulmonary lung function decrements depending on concentrations and duration of exposure. Asthma, allergies, other respiratory disorders have been observed. Breathing disorders, tumorgenic, direct and indirect genetic damage have been found in animal and/or human tissue studies.

Carcinogenicity: Justifiably suspected of having carcinogenic potential (group B).

Skin Contact

Contact with ozone may irritate the skin, burns and frostbite can occur.

Eye Contact

Exposed persons may sense eye irritation at or above 0.1 ppm ozone.

Limits

Immediately Dangerous to Life or Health Concentration *IDLH*: 5 ppm

Threshold limit values *TLV* (ACGIH, 1999):

- 0.05 ppm Heavy Work
- 0.08 ppm Moderate Work
- 0.10 ppm Light work

If the working duration is shorter than two hours 0.20 ppm for heavy, moderate, or light work are allowed.

In the soon to be published new MAK-list in Germany (maximal allowable workplace concentration) ozone will be categorized as IIIb which means a substance being justifiably suspected to be carcinogenic. The actual MAK value of 200 µg m^{-3} (= 0.1 ppm) will be suspended until it is known if ozone shows carcinogenic effects (n. n., 1995).

Note: For safety reasons ozone should always be used with an ambient air ozone monitor (measuring ranges 0–1 ppm) with a safety shut down procedure.

1.3 Ozone in Liquid

No health hazard data are available and no limits for workplace exist. Ozonated water in high concentrations can lead to eye and skin irritation. Langlais et al. (1991) summarize some LC_{50}-values (concentration that is lethal to half of the test animals) found in fish tests:

Bluegills (*Lepomis macrochius*) for 24 h:	0.06 mg L^{-1}
Rainbow trout (*Salmo gairdneri*) for 96 h:	0.0093 mg L^{-1}
White perch (*Morone americana*) for 24 h:	0.38 mg L^{-1}

It is important to note that the differentiation between ozone and its byproducts in such tests is often not possible.

Most of the possible toxic effects from ozone in gas can also occur when using liquid ozone, due to the potential risk of it gassing-out. Consequently, liquid ozone has a strong odor and should always be used in closed piping and vessels.

1.4 Byproducts

In order to evaluate the toxicity of ozonation byproducts, the health effects of specific, unidentified substances (byproducts) need to be determined for each target organism (human, animals, fish, etc). The often observed lack of substantial information on toxicity can in part be attributed to the lack of appropriate testing methods. Since identifying all the substances which compose the TOC of a ground-, drinking- or waste water can rarely be achieved, it is almost impossible to determine which substances contribute to the total toxicity of the mixture. Furthermore, toxicity of specific compounds in a complex mixture may also depend on the background matrix and cause synergistic or antagonistic interactions with other substances. Controlled testing with synthetic mixtures of such matrices is almost impossible to achieve.

Methods Used for the Assessment of Byproduct Toxicity

A good overview of the different methods of measuring human toxicological effects can be found in Langlais et al. (1991). They summarize results from many human toxicity studies on ozone and ozonation byproducts. Some results on human toxicity are also presented below.

Standardized ecotoxicity tests (bioassays) have been developed and optimized over the last few years and encompass the effects on bacteria, daphnia and fish (DIN 38 412, parts 30, 31 and 34). These tests are designed to assess the toxicity on aquatic organisms. They are quick to perform, easy to handle and comparatively inexpensive, with the goal of allowing the toxicity of a complex water matrix to be estimated. However, they use pre-concentration steps so that it is possible that not all byproducts are recovered (which itself is hard to prove).

The results are in general matrix-specific and usually give no hint to the compounds responsible for any adverse effects. Their applicability for the testing of differently treated waste waters was discussed by Zander-Hauck et al. (1993) or Dannenberg (1994).

Examples from Drinking Water Ozonation

Bioassay studies involving drinking water disinfection with ozone have not consistently proven mutagenic activity. Most of the screening studies have shown that ozonated water induces less mutagenic activity than chlorinated water does. Though, some cases have been reported where the mutagenic activity was higher than the activity produced by chlorination (Huck et al., 1987). Studies of waters with and without ozonation give no clear picture of ozone's effect on mutagenicity. The reduction as well as the enhancement of mutagenic activity was observed (Kool and Hrubec, 1986). However, it appears that if a sufficient dosage is applied, ozone does not increase the mutagenicity of drinking water (Kool and Hrubec, 1986; Huck et al., 1987). In cases in which the raw water showed mutagenic activity, ozone was able to eliminate this effect.

Summarizing the influence of ozone on toxicity in drinking water applications, Langlais et al. (1991) stated:

> "The chemistry of ozone in aqueous solutions and the health effects are complex. It is clear that ozone reacts with water products in the water supply to form numerous disinfection byproducts. However, the general pattern that emerges from most studies is that the reaction byproducts of ozonation appear to be less toxic than those produced by chlorination. Many reactions with ozone are dose and pH-dependent, and this explains the difference between the results obtained under various conditions."

Examples from Waste Water Ozonation

Ecotoxicity testing is usually carried out on ozonated waste waters to estimate the impact of the effluent on the living organisms in the receiving water. Toxicity testing of combined chemical/biological treatment of waste waters was carried out by Diehl et al. (1995) for landfill leachate and Moerman et al. (1994) for coal carbonization waste water. Both groups pointed out that it is necessary to assess the toxicity before and after each treatment step, thus establishing something similar to a 'toxicity balance' around the whole process. For example in the treatment of the coal carbonization waste water, little COD was eliminated in an activated sludge plant, but the effluent showed no toxicity in the Microtox (bioluminescense) toxicity test (EC_{50} = not detectable) (Moerman et al., 1994). Applying ozonation to this effluent increased the toxicity to a considerably high level, $EC_{50} = 58$. Another (second) biological treatment with an adapted sludge in a trickling filter, however, decreased the toxicity to a non-detectable level again.

Frequently identified byproducts from the ozonation of more or less complex organic substances contained in drinking or waste waters are aldehydes, carboxylic acids and other aliphatic, aromatic or mixed oxidized forms. Such substances are often quite easily biodegradable, and not surprisingly showed no significant toxic effects (Glaze 1987). Care must be taken in executing and interpreting the results of bioluminescense tests, because the availability of non-toxic substrate can also reduce the bioluminescense of the bacteria.

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2 Reaction Mechanism

Two of the strongest chemical oxidants are ozone and hydroxyl radicals. Ozone can react directly with a compound or it can produce hydroxyl radicals which then react with a compound. These two reaction mechanisms are considered in Section A 2.1. Hydroxyl radicals can also be produced in other ways. Advanced oxidation processes are alternative techniques for catalyzing the production of these radicals (Section A 2.2).

2.1 Ozonation

Ozone is an unstable gas which has to be produced at the point of use. A wide variety of gas-liquid contactors has been used to transfer ozone into water where chemical reactions occur simultaneously.

Ozone can react with substances in two different ways, indirect and direct. These different reaction pathways lead to different oxidation products and are controlled by different types of kinetics. Figure 2-1 gives an overview of the indirect and direct pathways, and their interaction.

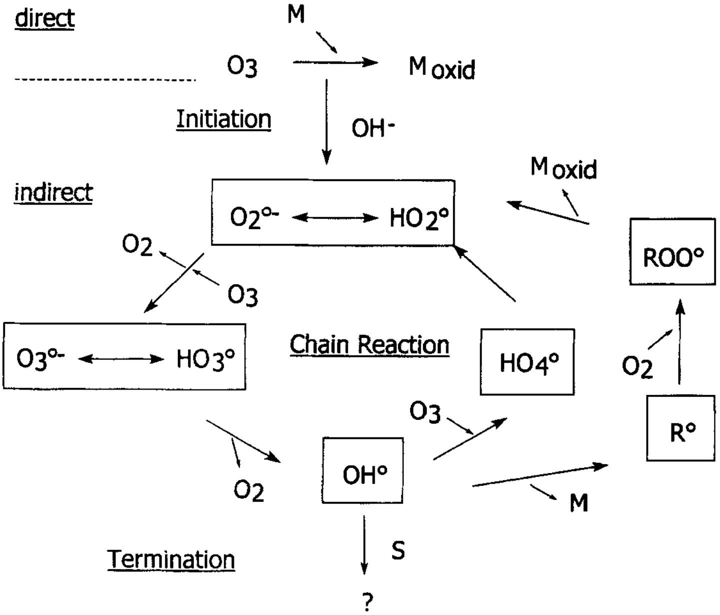

Figure 2-1: Mechanism of the indirect and direct ozonation, S: Scavenger, R: Reaction product, M: Micropollutant (modified from Staehelin and Hoigné, 1983 a, b).

2.1.1 Indirect Reaction

The indirect reaction pathway involves radicals. The first step is the decay of ozone, accelerated by initiators, e. g. OH^-, to form secondary oxidants such as hydroxyl radicals (OH°). They react nonselectively and immediately ($k = 10^8 - 10^{10}\ M^{-1}\ s^{-1}$) with solutes (Hoigné and Bader, 1983 a, b). The radical pathway is very complex and is influenced by many substances. The major reactions and reaction products of the radical pathway based on the two most important models are discussed below (Staehelin and Hoigné, 1983 a, b; Tomiyasu et al., 1985).

The mechanism can be divided in three different parts:

Initiation Step

The reaction between hydroxide ions and ozone leads to the formation of one superoxide anion radical $O_2^{\circ-}$ and one hydroperoxyl radical HO_2°.

$$O_3 + OH^- \rightarrow O_2^{\circ-} + HO_2^\circ \qquad k_1 = 70\ M^{-1}\ s^{-1} \qquad (2\text{-}1)$$

The hydroperoxyl radical is in an acid-base equilibrium.

$$HO_2^\circ \leftrightarrow O_2^{\circ-} + H^+ \qquad pK_a = 4.8 \qquad (2\text{-}2)$$

Radical Chain

The ozonide anion radical ($O_3^{\circ-}$) formed by the reaction between ozone and the superoxide anion radical $O_2^{\circ-}$decomposes immediately into an OH-radical.

$$O_3 + O_2^{\circ-} \rightarrow O_3^{\circ-} + O_2 \qquad k_2 = 1.6\ 10^9\ M^{-1}\ s^{-1} \qquad (2\text{-}3)$$

$$HO_3^\circ \leftrightarrow O_3^{\circ-} + H^+ \qquad pK_a = 6.2 \qquad (2\text{-}4)$$

$$HO_3^\circ \rightarrow OH^\circ + O_2 \qquad k_3 = 1.1\ 10^8\ M^{-1}\ s^{-1} \qquad (2\text{-}5)$$

This OH° can react with ozone in the following way (Hoigné, 1982):

$$OH^\circ + O_3 \rightarrow HO_4^\circ \qquad k_4 = 2.0\ 10^9\ M^{-1}\ s^{-1} \qquad (2\text{-}6)$$

$$HO_4^\circ \rightarrow O_2 + HO_2^\circ \qquad k_5 = 2.8\ 10^4\ s^{-1} \qquad (2\text{-}7)$$

With the decay of HO_4° into oxygen and hydroperoxide radical the chain reaction can start anew (see equation 2-1). Substances which convert OH° into superoxide radicals $O_2^{\circ-}/HO_2^\circ$ promote the chain reaction; they act as chain carriers, the so-called promoters.

Organic molecules, R, can also act as promoters. Some of them contain functional groups which react with OH° and form organic radicals R°.

$$H_2R + OH^\circ \rightarrow HR^\circ + H_2O \qquad (2\text{-}8)$$

If oxygen is present, organic peroxy radicals ROO° can be formed. These can further react, eliminating $O_2^{\circ -}/HO_2^\circ$ and so enter again into the chain reaction.

$$HR^\circ + O_2 \rightarrow HRO_2^\circ \qquad (2\text{-}9)$$

$$HRO_2^\circ \rightarrow R + HO_2^\circ \qquad (2\text{-}10)$$

$$HRO_2^\circ \rightarrow RO + OH^\circ \qquad (2\text{-}11)$$

The experimental proof of the existence of HO_4°, necessary for the verification of this reaction pathway proposed by Hoigné, is missing. These radicals are not found in the radical chain cycles of the model from Tomiyasu et al. (1985). However, the result of both models is the same:

The decay of ozone, which can be initiated by the hydroxide ion, leads to a chain reaction and produces fast-reacting and thus nonselective OH-radicals. This also means that OH-radicals have a very short half-life, e.g. less than 10 μs at an initial concentration of 10^{-4} M.

Due to its electrophilic properties the OH° reacts at the position with the highest electron density of the target molecule. Detailed information can be found in von Sonntag (1996), which gives a good overview of the degradation mechanism of aromatics by OH° in water. Buxton et al. (1988) showed that the reaction rate constants for hydroxyl radicals and aromatic compounds are close to the diffusion limit.

Termination Step

Some organic and inorganic substances react with OH° to form secondary radicals which do not produce $HO_2^\circ/O_2^{\circ -}$. These inhibitors (or scavengers) generally terminate the chain reaction and inhibit ozone decay.

$$OH^\circ + CO_3^{2-} \rightarrow OH^- + CO_3^{\circ -} \qquad k_6 = 4.2\ 10^8\ M^{-1}\ s^{-1} \qquad (2\text{-}12)$$

$$OH^\circ + HCO_3^- \rightarrow OH^- + HCO_3^\circ \qquad k_7 = 1.5\ 10^7\ M^{-1}\ s^{-1} \qquad (2\text{-}13)$$

Another possibility to terminate the chain reaction is the reaction of two radicals:

$$OH^\circ + HO_2^\circ \rightarrow O_2 + H_2O \qquad k_8 = 3.7\ 10^{10}\ M^{-1}\ s^{-1} \qquad (2\text{-}14)$$

The combination of the equations (2-1 through 2-7) shows that three ozone molecules produce two OH°.

$$3\ O_3 + OH^- + H^+ \rightarrow 2\ OH^\circ + 4\ O_2 \qquad (2\text{-}15)$$

Many substances exist that initiate, promote or terminate the chain reaction. Table 2-1 gives some examples.

Table 2-1: Typical initiators, promoters and scavengers for decomposition of ozone in water (Staehelin and Hoigné, 1983; Xiong and Graham, 1992).

Initiator	Promoter	Scavenger
OH^-	humic acid	HCO_3^-/CO_3^{2-}
H_2O_2/HO_2^-	*aryl*-R	PO_3^{4-}
Fe^{2+}	primary and secondary alcohols	humic acid
		alkyl-R
		tert-butyl alcohol (TBA)

Staehelin and Hoigné (1985) found that even phosphate, which is known to react only slowly with OH°, can act as an efficient scavenger when used in concentrations typically found in buffer solutions (50 mM). The action of humic acid is contradictory. It can react as either scavenger or promoter, depending on its concentration (Xiong and Graham, 1992). The classical OH° scavenger *tert*-butyl alcohol is often used to suppress the chain reaction. Even in the presence of formic acid, which is a promoter, TBA (50 μM) was able to reduce the ozone decay rate by a factor of seven (Staehelin and Hoigné, 1985).

Bicarbonate and carbonate play an important role as scavengers of OH-radicals in natural systems. The reaction rate constants are relatively low but the concentration range in natural systems is comparatively high, so that this reaction cannot be ignored. A comparison of the reaction rate constants ($k_6 = 4.2\ 10^8\ M^{-1}s^{-1}$ for CO_3^{2-} and $k_7 = 1.5\ 10^7\ M^{-1}s^{-1}$ for HCO_3^-) shows that carbonate is a stronger scavenger than bicarbonate. This means that the reaction rate with 100 % of the total inorganic carbon being present as bicarbonate is comparable to that with 3.6 % as carbonate. Hoigné and Bader (1977) assumed that the reaction products from bicarbonate and carbonate ions with OH° do not interact further with ozone.

By adding carbonate to ozonated water, the half-life of ozone can be increased. Even some few μmoles decrease the decay rate of ozone by about a factor of ten or more (Hoigné and Bader, 1977). Increasing the concentration of bicarbonate/carbonate up to a concentration of 1.5 mM increases the stability of ozone. Thereafter no further stabilization occurs (Forni et al., 1982).

2.1.2 Direct Reaction

The direct oxidation ($M + O_3$) of organic compounds by ozone is a selective reaction with slow reaction rate constants, typically being in the range of $k_D = 1.0 - 10^3\ M^{-1}\ s^{-1}$. The ozone molecule reacts with the unsaturated bond due to its dipolar structure and leads to a splitting of the bond, which is based on the so-called Criegee mechanism (see Figure 2-2). The Criegee mechanism itself was developed for non-aqueous solutions.

Ozone reacts slowly with many types of water contaminants such as alicyclic taste or odor compounds, e. g. geosmin or THMs and unactivated aromatics such as chlorinated benzenes. Ozone will react faster with certain types of aromatic compounds, e. g. those carrying electron supplying substituents such as the hydroxyl group in phenol. If there is no

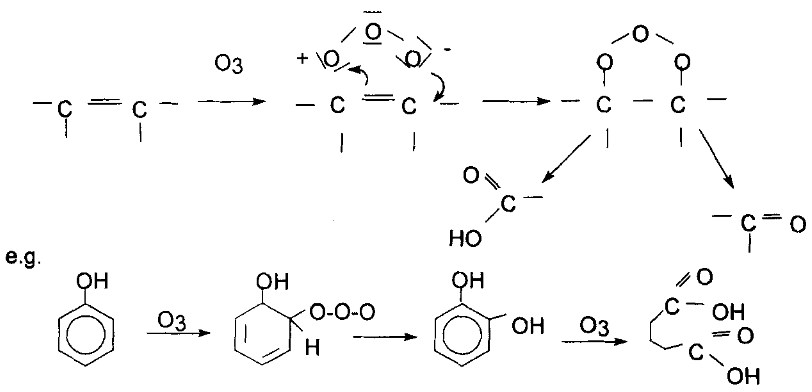

Figure 2-2: Plausible aqueous reactions with ozone.

such substituent the rate of ozonation is much slower. In general the ionized or dissociated form of organic compounds reacts much faster with ozone than the neutral (non-dissociated) form. Olefins are generally more reactive than aromatic compounds with the same substituents.

Further information about the reaction rates as well as the rate constants with ozone and OH° can be found in many publications, e. g. Glaze, 1987; Yao and Haag, 1991; Haag and Yao, 1992; Hoigné and Bader, 1983 a, b as well as Hoigné and Bader, 1985.

Generally speaking, the direct ozonation is important if the radical reactions are inhibited. That means that the water either does not contain compounds that initiate the chain reaction (initiators) or it contains many that terminate the chain reaction very quickly (scavengers). With increasing concentrations of scavengers the mechanism of oxidation tends to the direct pathway. Therefore, both inorganic carbon as well as the organic compounds play an important role.

Normally, under acidic conditions ($pH < 4$) the direct pathway dominates, above $pH = 10$ it changes to the indirect. In ground and surface waters ($pH \cong 7$) both pathways – direct and indirect – can be of importance (Staehelin and Hoigné, 1983 a). In special waste waters even at $pH = 2$ the indirect oxidation can be of importance, depending much on the contaminants present (Beltrán et al., 1994). Both pathways should always be considered when developing a treatment scheme.

2.2 Advanced Oxidation Processes (AOP)

Advanced oxidation processes (AOPs) have been defined by Glaze et al. (1987) as processes which "involve the generation of hydroxyl radicals in sufficient quantity to effect water purification". The most common processes are O_3/H_2O_2, O_3/UV and H_2O_2/UV. The development of the AOPs is an attempt to produce the nonselective and rapid OH° to oxidize pollutants. Each of these processes involves chemistry similar to that discussed above.

Ozone/Hydrogen Peroxide (O_3/H_2O_2)

Hydrogen peroxide reacts with ozone when present as anion, HO_2^-. The reaction rate of the system ozone/hydrogen peroxide is based on the initial concentration of both oxidants:

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad pK_a = 11.8 \qquad (2\text{-}16)$$

$$HO_2^- + O_3 \rightarrow HO_2^\circ + O_3^{\circ-} \qquad k_9 = 2.2\ 10^6\ M^{-1}\ s^{-1} \qquad (2\text{-}17)$$

The reaction of ozone with the undissociated hydrogen peroxide is negligible (Taube and Bray, 1940):

$$H_2O_2 + O_3 \rightarrow H_2O + 2\ O_2 \qquad k_{10} < 10^{-2}\ M^{-1}\ s^{-1} \qquad (2\text{-}18)$$

The reaction continues along the indirect pathway, described previously and OH-radicals are produced (Staehelin and Hoigné, 1982; Bühler et al., 1984).

Comparison of the initial reaction with HO_2^- ($k_9 = 2.2\ 10^6\ M^{-1}\ s^{-1}$) and with OH^- ($k_1 = 70\ M^{-1}\ s^{-1}$) shows that in the O_3/H_2O_2 -system the initiation step by OH^- is negligible. Whenever the concentration of hydrogen peroxide is above 10^{-7} M and the pH-value less than 12, HO_2^- has a greater effect than OH^- has on the decomposition rate of ozone in water.

The combination of the equations (2-2 through 2-7, 2-17 and 2-18) shows that two ozone molecules produce two OH°:

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH^\circ + 3\ O_2 \qquad (2\text{-}19)$$

Ozone/UV-Radiation (O_3/UV)

The advanced oxidation process with ozone and UV-radiation is initiated by the photolysis of ozone. The photodecomposition of ozone leads to hydrogen peroxide (Peyton, 1988). Ultraviolet lamps must have a maximum radiation output at 254 nm for an efficient ozone photolysis.

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \qquad (2\text{-}20)$$

This system contains three components to produce OH° and/or to oxidize the pollutant for subsequent reactions:

- UV-radiation
- ozone
- hydrogen peroxide

Direct photolysis of the pollutant can occur if it absorbs the wavelength used. Direct oxidation by hydrogen peroxide can be neglected under normal conditions (pH between 5 to 10 and ambient temperature). The role of direct and indirect ozonation depends on the conditions already mentioned. Therefore, the reaction mechanism of ozone/hydrogen peroxide is of importance as well as the combination of UV-radiation/hydrogen peroxide. Hereby should be mentioned that the extinction coefficient ε of ozone at the wavelength of 254 nm is much higher ($\varepsilon_{254\,nm} = 3\,300\ M^{-1}\ cm^{-1}$) than that of hydrogen peroxide ($\varepsilon_{254\,nm} = 18.6\ M^{-1}\ cm^{-1}$). The decay rate of ozone is about a factor of 1 000 higher than that of H_2O_2 (Guittonneau et al., 1991).

Hydrogen Peroxide/UV-Radiation (H_2O_2/UV)

The direct photolysis of hydrogen peroxide leads to OH°:

$$H_2O_2 \xrightarrow{hv} 2\ OH^\circ \qquad \varepsilon_{254\,nm} = 18.6\ M^{-1}\ cm^{-1} \tag{2-21}$$

Also HO_2^- which is in an acid-base equilibrium with H_2O_2 (see equation 2-16) absorbs the wavelength 254 nm

$$HO_2^- \xrightarrow{hv} OH^\circ + O^{\circ-} \qquad \varepsilon_{254\,nm} = 240\ M^{-1}\ cm^{-1} \tag{2-22}$$

$$HO_2^- + O^{\circ-} \rightarrow O_2^{\circ-} + OH^- \qquad k_9 = 4.0\ 10^8\ M^{-1}\ s^{-1} \tag{2-23}$$

The following steps in this pathway can be found in Figure 2-1.

Comparison

Figure 2-3 gives an overview about the reactions involved in the AOPs. The reaction rate constants for all these reactions (equations 2-1 through 2-23) have been taken from several references (e. g. Paillard et al., 1988; De Laat et al., 1994; Beltrán et al., 1993) and are

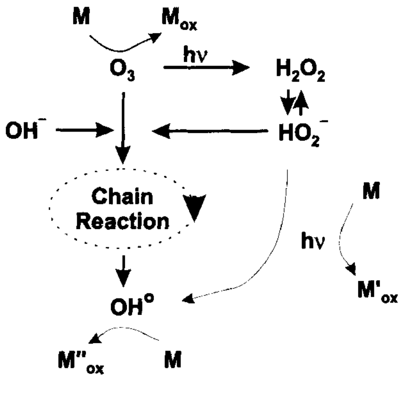

Figure 2-3: Advanced oxidation processes.

Table 2-2: Theoretical amount of oxidants and UV required for the formation of hydroxyl radicals in ozone-peroxide-UV systems (Glaze et al., 1987).

	Moles of oxidants consumed per mole of OH° formed		
System	O_3	UV [a]	H_2O_2
Ozone–hydroxide ion [b]	1.5	–	–
Ozone–UV	1.5	0.5	(0.5) [c]
Ozone–hydrogen peroxide [b]	1.0		0.5
Hydrogen peroxide–UV	–	0.5	0.5

[a] Moles of photons (Einsteins) required for each mole of OH° formed

[b] Assumes that superoxide $O_2^{\circ-}$ is formed which yields one OH° per $O_2^{\circ-}$, may not be the case in certain waters

[c] Hydrogen peroxide formed *in situ*

Table 2-3: Theoretical formation of hydroxyl radicals from the photolysis of ozone and hydrogen peroxide (Glaze et al., 1987).

	$\varepsilon_{254\,nm}$ in M^{-1} cm^{-1}	Stoichiometry	OH° formed per incident photon [a]
H_2O_2	20	$H_2O_2 \rightarrow 2\ OH^\circ$	0.09
O_3	3 300	$O_3 \rightarrow 2\ OH^\circ$	2.00

[a] assumes 10 cm path length; $c(O_3) = c(H_2O_2) = 10^{-4}$ M

presented to illustrate the various orders of magnitude. It is possible to find different values for one reaction, referring the reader to chose the most appropriate.

From the chemical point of view, the effect of O_3/UV is comparable to the system of O_3/H_2O_2 if direct photolysis is negligible (Glaze et al., 1987; Prados et al., 1995). Table 2-2 summarizes the chemistry involved in the generation of hydroxyl radicals from the described four processes.

The stoichiometric yield of OH° is the greatest from the photolysis of hydrogen peroxide. But – as already mentioned – the photolysis of ozone yields more OH° than that from hydrogen peroxide because of the higher molar extinction coefficient of ozone compared to hydrogen peroxide (see Table 2-3).

This comparison is only theoretical. In reality a high production of OH° can lead to a low reaction rate because the radicals recombine and are not useful for the oxidation process. Also not considerd are the effects of different inorganic and/or organic compounds in the water. Various models to calculate the actual OH-radical concentration can be found in the literature, some are described in Chapter B 5. Further information concerning the parameters which influence the concentration of hydroxyl radicals is given in Section B 4.4, as well as a short overview about the application of ozone in AOPs in Section B 6.2.

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3 Full-Scale Applications

Martin Jekel

3.1 Introduction

Ozone application has increased enormously both in number and diversity since the first full scale application of ozone for the disinfection of drinking water in Nice (1906). It is used for the treatment and purification of ground and surface waters, for domestic and industrial waste water as well as in swimming pools and cooling tower systems. It has been integrated into production processes that utilize its oxidizing potential, e. g. bleaching in the pulp and paper industry, metal oxidation in the semiconductor industry. Its effectiveness is based upon the multiple effects produced by the oxidative and disinfective activity of ozone and ozone-derived oxidizing species such as OH-radicals. Typically, ozone is chosen for one or two major purposes, but several side-effects may exist, inducing positive and/or negative effects that need thorough consideration. Changes in the process design or operating conditions may have to be made to reduce or utilize these side-effects.

Another consideration connected with these multiple effects is the optimum placement of the ozonation stages within a whole treatment scheme. The efficiency of every ozonation unit and the ozone demand depend on the water and waste water quality produced by the preceding process units (e. g. particle removal or biodegradation). Ozonation will also have pronounced effects downstream in the treatment sequence, e. g. improved biodegradation of dissolved organics.

Nearly all ozonation effects and their respective extent and kinetic pattern depend on the amount of ozone consumed in the ozone contactor and subsequent reactors. This requires the search for and definition of optimal operational parameters for an ozonation stage, such as a concentration-time-value (*c*-*t*-value) for a given degree of disinfection or the ratio of ozone mass consumed per mass of organic compounds initially present.

This chapter provides an overview and guidance on the various applications of ozone in water and waste water treatment, where full-scale facilities exist and it has been demonstrated that ozonation is effective and economical.

The detection of new kinds of microorganisms, such as the cysts and oocysts of parasites (*Giardia, Cryptosporidium*), the identification of more and more chemical pollutants in waters and increasing quality levels required for drinking and waste waters has induced new interest in ozonation and ozone-based advanced oxidation processes. However, care has to be taken in the application of ozonation, since recent research has indicated that presumably hazardous by-products can be formed, e. g. bromate in the ozonation of waters containing bromide.

The subsequent parts on full-scale applications of ozone for water and waste water treatment are not arranged according to the water source, but describe the different and multiple tasks of ozone with regard to water constituents and treatment goals. Furthermore, attention is given to the appropriate combination of the ozonation process with preceding and subsequent treatment steps.

Generally, the main areas where ozone is used are:

- disinfection,

- oxidation of inorganic compounds,
- oxidation of organic compounds, including taste, odor, color removal and
- particle removal.

3.2 Ozonation in Drinking Water Treatment

Drinking water supplies are based on natural ground waters (the source with highest priority), on artificially recharged ground waters or bank filtered surface waters, on lakes and dam reservoirs and on river waters. Most applications of ozone are found in water treatment systems dealing with polluted surface waters and contaminated underground waters, whereas pure ground waters are either not treated or require only removal of ferrous and manganese ions and/or stabilization.

A recent review on the mechanisms and goals of ozone and associated oxidation processes in drinking water treatment is provided by Camel and Bermond (1998), while extensive coverage of the subject is found in Langlais et al. (1991).

3.2.1 Disinfection

The introduction of ozone in water treatment started about a century ago and was directed at the disinfection of microbiologically polluted water. Later, chlorine and also chlorine dioxide were introduced and have been used successfully to control pathogenic pollution, excluding the parasitic organisms. In view of this problem and the well-known formation of halogenated disinfection by-products (especially *tri*-halomethanes, THMs) by chlorine, there is renewed interest in the use of ozone for disinfection, but in the intermediate stages of treatment, not as the last step. The short life-time of dissolved ozone and the production of biodegradable organics (assimilable organic carbon, AOC) from natural organic matter (NOM) does not favor final ozonation, but its positioning before the rapid filtration/activated carbon filtration/slow sand filtration or underground passage. Ozone is then an essential part of the multiple barrier principle against pathogenic organisms (and organic pollution). It is strongly recommended to remove most particulate material before ozonation to avoid the escape of encapsulated microorganisms from ozone attack and to reduce the ozone demand, which helps in establishing a "free ozone residual", i. e. a residual concentration of dissolved ozone, for a certain time.

In the design of chemical disinfection, the concept of c-t (free disinfectant concentration c multiplied by the available contact time t) is frequently applied, based on the law of Chick/Watson (1908). For a given degree of inactivation, like a two or three log-reduction in the concentration of microorganisms (99 or 99.9 % removal) c-t-values have been reported for various microorganisms, but it is not clear, if they can always be applied for raw waters. A number of older and recent studies confirmed that molecular ozone is a very effective and promising disinfectant, perhaps better than free chlorine, chlorine dioxide, chloramines or hydroxyl radicals. The relative resistance of microorganisms follows roughly the order: bacteria, viruses and parasite cysts. Very often, a c-t-value of 1.6–2 mg L^{-1} min^{-1}

(e. g. 0.4 mg L^{-1} ozone for 5 min) is considered to be sufficient for effective disinfection, after particulate matter is removed down to low turbidities (less than ca. 0.2 NTU). There is some discussion that parasite cysts may require a higher *c-t*-value at low water temperatures (< 10 °C) for a two or three log-removal, but data are not conclusive.

It is worthwhile mentioning that ozone is frequently used for swimming pool water clean-up prior to a chlorine disinfection step. According to Böhme (1999) almost 3600, i. e. more than 50 % of the ozone generators sold by German companies between 1954 and 1997, have been efficiently applied in this field.

3.2.2 Oxidation of Inorganic Compounds

Whereas the use of ozonation to oxidize metal surfaces in the semiconductor industry is growing, ozonation for the oxidative removal or transformation of inorganic constituents of drinking and waste waters is a rather rare application, because other methods exist for most of the target compounds. However, inorganic compounds may be oxidized as a secondary effect of ozonation for other purposes (particle removal, organics oxidation). Table 3-1 provides an overview of the target and product compounds and the rate of oxidation in drinking and waste waters.

Table 3-1: Oxidation of inorganic compounds by ozonation (Langlais et al., 1991; Hoigné and Bader, 1985).

Compound	Products	Rate of Oxidation	Remarks
Fe^{2+}	$Fe(OH)_3$	Fast	Filtration of solids required; application in the beverage industry
Mn^{2+}	$MnO(OH)_2$	Fast	Filtration of solids required; application in the beverage industry
	MnO_4^-	Fast	At higher residual ozone conc., reduction and filtration required
NO_2^-	NO_3^-	Fast	Nitrite is a toxic compound
NH_4^+/NH_3	NO_3^-	Slow at pH < 9 Moderate at pH > 9	Not revelant
CN^-	CO_2, NO_3^-	Fast	Application in waste water
H_2S/S^{2-}	SO_4^{2-}	Fast	Not relevant
As-III	As-V	Fast	Preoxidation for subsequent As-removal
Cl^-	HOCl	Near zero	Not relevant
Br^-	$HOBr/OBr^-$ BrO_3^-	Moderate	Bromination of organic compounds possible Bromate as toxic by-product
I^-	HOI/OI^-, IO_3^-	Fast	Not relevant
$HOCl/OCl^-$	ClO_3^-	Slow	Loss of free chlorine
Chloramines, Bromamines		Moderate	Loss of combined chlorine
ClO_2 ClO_2^-	ClO_3^- ClO_3^-	Fast Fast	Loss of free chlorine dioxide
H_2O_2	OH°	Moderate	Basis of O_3/H_2O_2-process (AOP)

A critical reaction is here the formation of bromate, a potential carcinogen, from bromide in the water source. The WHO standard is set at 25 µg L^{-1}, while the European Union set a new limit value at 10 µg L^{-1}. If bromate formation is a problem, possible measures to limit bromate formation are: adjusting the ozone dosage, or dosing a small amount of ammonia or hydrogen peroxide. Subsequent bromate removal is probably difficult, but could occur in activated carbon filters (Haag and Hoigné, 1983; von Gunten and Hoigné, 1994; Koudjonou et al., 1994).

As shown in Table 3-1, ozone can destroy other disinfectants. This should be avoided by dosing them not ahead of ozonation stages, but rather at the end of the total treatment before the distribution of water to the supply-net. A special case is the reaction of ozone with H_2O_2 (correctly with the species HO_2^-), which is used as an advanced oxidation process (AOP) for intensified formation of hydroxyl radicals and their oxidative attack on persistent organic target compounds (persistent against ozone in the direct reaction mechanism) (see Chapter A 2).

3.2.3 Oxidation of Organic Compounds

Natural Organic Matter (NOM)

All water sources may contain natural organic matter, but concentrations (usually measured as dissolved organic carbon, DOC) differ from 0.2 to more than 10 mg L^{-1}. NOM is a direct quality problem due to its color and odor, but more important are indirect problems, such as the formation of organic disinfection by-products (DBPs, e. g. *tri*-halomethanes (THMs) due to chlorination), support of bacterial regrowth in the distribution system, disturbances of treatment efficiency in particle separation, elevated requirements for coagulants and oxidants or reductions in the removal of trace organics during adsorption and oxidation, etc.

Removal of NOM or its alteration to products less reactive to chlorine is a priority task in modern water treatment, comprising chemical oxidation by ozone, biodegradation, adsorption, enhanced coagulation or even membrane technologies. A DOC-level of approximately 1 mg L^{-1} appears to be the lower limit of ozone applications, but a few cases exist, where waters with lower concentrations of NOM (ground water) have been treated.

The tasks of NOM-ozonation are (Camel and Bermond, 1998):

- Removal of color and UV-absorbance
- Increase in biodegradable organic carbon ahead of biological stages
- Reduction of potential disinfection by-product formation, including *tri*-halomethanes
- Direct reduction of DOC/TOC-levels by mineralization

The first three tasks are much more relevant and applicable to full-scale plants, compared to the last topic. The reason is the high ozone demand for direct chemical mineralization, with typically more than 3 g O_3 g^{-1} DOC initially present needed to achieve a removal efficiency of 20 % or more.

The removal of color and UV-absorbance is one of the easier tasks due to quick reactions and comparatively low required specific ozone consumptions in the range below

1 g O_3 g^{-1} DOC. Thus, this effect is observed in preozonation steps for improved particle separation. Color can be removed by 90 % or more, while UV-absorbance at 254 nm is commonly reduced to 20–50 % of the initial value. The reaction mechanism here is primarily the direct ozone attack on C-double bonds in aromatic and chromophoric molecules leading to the formation of "bleached" products, like aliphatic acids, ketones and aldehydes.

This oxidative reaction with UV/VIS-active substances induces molecular changes, but not mineralization. These changes are also the basis for the production of biodegradable metabolites and the formation of smaller molecules with a higher hydrophilicity that tend to form less DBPs with the chlorine disinfectant.

A decisive operational parameter for organic carbon removal is again the specific ozone consumption. For optimal production of biodegradable DOC (also called AOC) specific O_3-consumptions of about 1–2 g g^{-1} are advised. Higher ratios lead to an enhanced oxidation of intermediates to carbon dioxide (direct mineralization). The AOC/DOC-ratio after oxidation may be 0.1 to 0.6, and is frequently found to be 0.3–0.5. The AOC-formation prohibits the direct supply of ozonated NOM-waters to the distribution system, due to severe bacterial regrowth after ozone decay. It is essential to add a treatment step with high bacterial activity (rapid filters, activated carbon filters, underground passage, slow sand filters) to remove AOC and achieve a microbiologically "stable" water.

The reduction in DBP-formation also depends on the specific ozone consumption. Typical reductions are in the range of 10 to 60 % (compared to non-ozonated water), at specific ozone dosages between 0.5 to 2 g O_3 g^{-1} DOC initially present. If bromide is present, brominated organic DBPs and bromate formation may occur.

The position for NOM-oxidation in water treatment schemes often is an intermediate one, e. g. between settling/flotation and rapid filtration or between rapid filtration and activated carbon filters or other post-treatment units (see Figure 3-1).

If ozone is not only used for NOM-treatment, but also used for disinfection, then the necessary ozone dosage has to be chosen based on either DOC removal or the required *c-t*-value for disinfection. The latter objective may be the dominating one in the case of raw waters with microbiological contamination. Complete mineralization of NOM does not appear to be economical, compared with partial oxidation and biodegradation. Typical intermediate organic metabolites (like oxalic acid) are difficult to oxidize by molecular ozone and nonselective OH-radicals are needed. The AOP-processes are designed for OH-radicals and better mineralization may be achieved through the addition of H_2O_2 or via UV-irradiation.

Oxidation of Organic Micropollutants

Organic micropollutants are found in surface and ground waters, always in conjunction with more or less NOM, but at relatively low concentrations in the range of 0.1 µg L^{-1} to 100 µg L^{-1} (in water sources of sufficient quality for a water supply). Their degradation by ozone to oxidized metabolites or even to mineral products is a complex process, due to the influences of various water quality parameters (pH, inorganic and organic carbon etc.) on the two known major reaction pathways: direct electrophilic ozone reaction and the oxidation via the nonselective, fast reacting OH-radicals.

In practical ozone applications, micropollutant (or trace organic) oxidation has not been a primary task, but was considered to be a positive side effect. However, due to the development of modern analytical tools and the detection of a large number of micropollutants in source waters (some of them being potentially health-hazardous) interest in trace organic oxidation has grown. This was one major reason to introduce and study AOP-techniques to increase the removal efficiencies for trace pollutants, most of which are only poorly accessible to a direct ozone attack. It must be kept in mind that in nearly all cases, the target compounds will not be mineralized, but transformed to metabolites, which are typically more polar in nature and smaller in molecular weight. Quite often some of the products formed do not react further with ozone, so-called dead-end products. A complete removal of organic products does not occur and it is essential to have a subsequent treatment unit, such as biological filtration systems (if the metabolites are degradable) or an adsorption on activated carbon. In the latter case, the oxidized trace pollutant may be less adsorbable, due to the increase in hydrophilicity. If oxidized products are left in the water, their toxicological evaluation is recommended and should be compared to the risk of the original pollutant.

Numerous publications are available on ozonation and ozone-based AOPs for the oxidation of specific organic compounds, either in pure waters, model waters or in full-scale systems (see e. g. Langlais et al., 1991; Camel and Bermond, 1998; Hoigné and Bader, 1983). Kinetic constants k_D and k_R for the direct (molecular) and indirect (radical) oxidation are reported and provide good insight into the range of oxidation rates, however, other water quality parameters exhibit a strong influence, especially on the indirect oxidation by OH-radicals. This may result in considerably differing observed rate constants, which depend on the individual "water matrix".

The subsequent list of organic groups provides a qualitative presentation of expected degrees of removal in full-scale drinking water treatment plants (Table 3-2).

Table 3-2: Degree of removal of trace organics during ozonation in full-scale drinking water treatment plants.

Substances	Degree of Removal, Range in %	Remarks
Taste and odor	20–90	Source specific
Methylisoborneol geosmin	40–95	Improvements by AOPs: O_3/H_2O_2 and O_3/UV
Alkanes	< 10	
Alkenes and chlorinated alkenes	10–100	Chlorine content important, AOP support oxidation
Aromatics and chloroaromatics	30–100	Highly halogenated phenols are more difficult to oxidize
Aldehydes, alcohols, carbonic acids	Low	Typical products of ozonation, easily biodegradable
N-containing aliphatics and aromatics	0–50	AOP may increase oxidation rate
Pesticides	0–80	Very specific to substance, triazines require AOP
Polyaromatic hydrocarbons	high, up to 100	

3.2.4 Particle Removal Processes

All surface waters contain particles of different origin, sizes and materials, which must be removed efficiently before water distribution. There is a renewed interest in improved particle separation due to the hygienic problems with infectious cysts and oocysts of parasites (*Giardia, Cryptosporidium*), which are particles in the size range of 3–12 µm. Depending on the raw water quality, particle separation may be accomplished typically by:

- rapid or slow filtration,
- coagulation/flocculation/deep-bed filtration or coagulation/flocculation/floc separation
- settling or flotation and rapid filtration.

In recent years, membrane processes such as micro- and ultrafiltration have been studied and introduced for near-to-complete particle removal.

It has been observed for more than 30 years that "preozonation" ahead of particle removal units can improve the efficiency significantly, can induce a lower coagulant demand or allow higher flow rates, e. g. in deep-bed filtration. Ozone gas is added either before or together with the coagulant (ferric or aluminum salts or cationic polymers) at rather low dosages of 0.5–2 mg L^{-1}. The terms "microflocculation" or "ozone-induced particle destabilization" are used in practice (Jekel, 1998).

The mechanisms involved appear to be rather complex and several mechanistic models have been described (for a recent review see Jekel, 1998). Results from the references therein as well as from additional pilot and full-scale applications indicate that an optimal ozone dosage exists, typically in the lower range of 0.5–2 mg L^{-1} or, related to the DOC, 0.1–1 mg mg^{-1}. The optimal point must be determined by tests in the combined treatment.

The relative improvements (reference is particle removal without ozone) are quite variable, but were reported to be about 20–90 % lower turbidities and/or lower particle counts in the filtered water. The presence of dissolved organic matter is frequently essential and DOC should be at least 1 mg L^{-1}. The preozonation effects depend strongly on the presence of alkaline earth cations, especially calcium.

Positive effects of preozonation are found in algae removal, usually a difficult task. Preozonation may be combined with flotation, an effective technique for separating coagulated algae. The algae cells are not destroyed at the low dosages required. The preozonation effects are detected in treatment for particle removal with and without coagulants.

Reduced species, like Fe^{2+}, Mn^{2+} or NO_2^- are oxidized quickly and may precipitate ($Fe(OH)_3$, $MnO(OH)_2$), also supporting coagulation. Depending on the amount of oxidizable material present, the preozonation dosage may be insufficient to establish an ozone residual in the water, but in cleaner waters the *c-t*-value necessary to disinfect the water effectively may be met, meaning that the dissolved ozone concentration remains high enough during a certain reaction time.

The ozonation reactors for preozonation have to deal with the particle content of raw waters and are sometimes combined with the coagulant mixing tank. Suitable transfer devices for the ozone containing gas are injector systems, radial diffusers or turbines with blades.

A typical scheme for a surface water treatment including preozonation for particle removal is shown below:

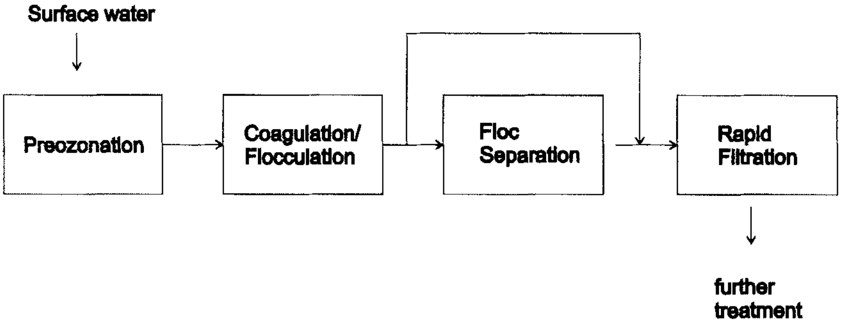

Figure 3-1: Surface water treatment sequence including particle removal.

3.3 Ozonation in Waste Water Treatment

Full-scale waste water ozone treatment facilities may roughly be defined as systems with a ozone generation capacity of more than 0.5 kg per hour. They can be found in various applications in all branches of industry, treating almost all types of waste waters. The operating conditions used in waste water ozonation are dependent on the type of industry and the kind of waste water. They can be grouped according to:

- the overall treatment scheme (only chemical processes; or combinations: chemical/biological and/or/physical)
- the application (inhouse pretreatment for water recycling or indirect discharge to POTWs, end-of-pipe treatment for direct discharge to rivers or bays)
- the removal goal (oxidative transformation of specific compounds due to their toxicity or color, decrease in lumped parameters (DOC or COD), disinfection, or particle removal).

The discussion of full-scale ozonation systems for waste waters in the following sections is grouped according to the main removal goal of the application, analogous to that used in drinking water ozonation systems.

In many full-scale applications the variable costs for energy and oxygen are regarded as economically decisive. Ozone and cost savings have often been achieved by the application of combined ozonation/biodegradation systems. Today, in most cases, ozonation of waste water is embedded into a multi-stage system employing biodegradation at least before and also often after the chemical oxidation step (O_3-Bio-O_3 systems).

The most frequently used contactors in full-scale waste water ozonation systems are bubble column reactors equipped with diffusers or venturi injectors, mostly operated in a reactor-in-series counter-current continuous mode. Many full-scale ozone reactors are operated at elevated pressure (2–6 $\text{bar}_{\text{abs.}}$) in order to achieve a high ozone mass transfer rate, which in turn increases the process efficiency.

3.3.1 Disinfection

Disinfection of waste waters before discharge into receiving waters is sometimes required to meet water quality standards in some countries, e. g. the United States, or desired when treated waste water effluent is directly reused for irrigation or process water applications. Chlorine or chlorine compounds are most often used, but because of the potential DBP production, analogous to the discussion in drinking water treatment, interest in ozonation systems is growing. Masten and Davies (1994) reported the use of ozone in more than 40 municipal waste water treatment plants in the United States. In these applications ozone is primarily used as a disinfectant, but indirect improvements in odor or suspended solids removal were achieved. Since easily biodegradable compounds (or AOC) are produced from the remaining DOC in the effluent, improved performance of granular activated carbon units through biodegradation by immobilized bacteria was also noted. This highlights a potential problem for direct water reuse, bacterial regrowth, especially of pathogenic bacteria must be considered in the process.

3.3.2 Oxidation of Inorganic Compounds

Ozonation of inorganic compounds in waste waters with the aim to destroy toxic substances is mostly restricted to cyanide removal (Böhme, 1999). Cyanide is frequently used in galvanic processes in the metal processing and electronics industry, where it can appear as free cyanide (CN^-) but more often occurs in complexed forms associated with iron or copper. While ozone reacts so fast with free cyanide that the process is likely to be mass transfer controlled at cyanide concentrations above 5 mg L^{-1} (Zeevalkink et al., 1980), complexed cyanides are more stable to the attack of molecular ozone (Gurol et al., 1985). Consequently, the application of nonselective hydroxyl radicals is more promising in this case. The H_2O_2/UV-process was recommended recently as an efficient and easy-to-handle treatment technology for this application (FIGAWA, 1997).

Nitrite (NO_2^-) as well as sulfide (H_2S/S^{2-}) removal from waste waters is sometimes performed by ozonation. Both substances react fast with ozone (see Table 3-1). However, it must be emphasized that there are cost-efficient treatment alternatives, e. g. biological denitrification or sulfide removal.

3.3.3 Oxidation of Organic Compounds

The majority of problematic substances in industrial waste waters are organic compounds. Often a complex mixture, composed of many individual substances present in a wide range of concentrations (from mg to g L^{-1}), has to be treated. The predominant tasks associated with ozone treatment of waste waters are:

- the transformation of toxic compounds (often occurring in comparatively low concentrations in a complex matrix)
- the partial oxidation of the biologically refractory part of the DOC, mostly applied with the aim to improve subsequent biodegradation
- the removal of color.

Similar to the treatment of drinking waters, though, a near-to-complete mineralization of the DOC cannot be achieved economically, and combination of ozonation with other processes is recommended. The success of the treatment scheme should be measured by the over-all DOC-removal.

Full-scale ozonation systems have been used to treat waste waters, such as landfill leachates, as well as waste waters from the textile, pharmaceutical and chemical industries (FIGAWA, 1997; Böhme, 1999). The main pollutants associated with these waters are refractory organics, which can be characterized as (Masten and Davies, 1994):

- humic compounds (brown or yellow colored) and adsorbable organic halogens (AOX) in the landfill leachates,
- colored (poly-)aromatic compounds often incorporating considerable amounts of metal ions (Cu, Ni, Zn, Cr) in textile waste waters,
- toxic or biocidal substances (e. g. pesticides) in the pharmaceutical and chemical industry,
- surfactants from the cosmetic and other industries,
- COD and colored compounds in solutions of the pulp and paper production.

The most frequent operational problems in waste water ozonation systems are foaming and the formation and precipitation of calcium oxalate, calcium carbonates and ferrous hydroxide ($Fe(OH)_3$) which may easily clog the reactor, piping and valves and also damage the pumps.

Goals, technology and results of full-scale applications on some types of waste waters are discussed in more detail in the following sections. An overview of technological features, operating parameters and treatment costs of full-scale plants for waste water ozonation is given in Table 3-3.

Landfill Leachates – Partial Mineralization

According to Böhme (1999) 32 full-scale ozonation systems are located at landfill treatment sites in Germany. However, no such system was sold abroad by German producers. The comparatively widespread application in Germany may be mainly due to the early

Table 3-3: Overview of technological features, operating parameters and treatment costs of full-scale plants for waste water ozonation.

Reference	type of ww	type of treatment system	no. and type of ozone reactors (operating pressure)	ozone production capacity	nominal// real liquid flow-rate	ozone yield coefficient $Y(O_3/M)$ (M = COD)	investment ozonation stage only	specific costs (without annuity)	remarks
				kg O_3 h^{-1}	m^3 d^{-1}	kg O_3 kg^{-1} ΔM	DM	DM m^{-3}	–
Siemers, 1995	landfill leachate	Bio-O_3,UV-Bio (sequential) (UV not used)	1 BC (each, 3 chemical stages in parallel) (5 bar$_{abs.}$)	36	200// 100–400	2.0–3.0	23 Mio.	41.7	pH-control impossible (dirty probe); heavy Ca-oxalate precipitation in reactors, tubes and pumps; foaming polluted off-gas O_3-catalyser
Steegmans et al., 1995	landfill leachate	Bio-O_3,UV-Bio (sequential) (UV not used)	3 BC (1 bar$_{abs.}$)	12	n. d.// 40–108	1.6–2.0	17 Mio.	5.8–9.7 (energy only) 62.5 (total)	controlled Ca-oxalate precipitation and recycling to 1st Bio; only 6 % variable costs, low potential for optimization
Schalk and Wagner, 1995; Kaptijn, 1997	landfill leachate	Bio-NF-O_3-Bio (recycle)	1 BC with fixed bed catalyst (approx. 4 bar$_{abs}$)	6	50 ± 10// n. d.	1.5–1.8 0.8	n. d.	n.d	*Biomembrat*® Plus & ECOCLEAR®; ozone used for NF-concentrate; O_3-transfer at < 2.0 kWh kg^{-1} O_3
Ried and Mielcke, 1999	landfill leachate	Bio-O_3-Bio (integrated)	1 BC	1–8	n. d.// 1.0–20	0.9–1.2	2–4	5–15	*BioQuint*® process, 12 plants in operation since 1995
Barratt et al. 1996; Rüütel et al., 1998	landfill leachate	Bio-O_3-Bio (sequential)	2 or 3 BC + 1 IZR (1 bar$_{abs}$)	12	70–140// ≤ 250	BC: 2.3–3.2 IZR: 1.8–2.5 (depending on HCO_3^- content)	n. d.	BC and IZR: 30–100 (depending on COD laod)	conventional BC-venturi system, reactor made from PVC IZR made from duplex steel (1.4462) for high chloride content; no foaming, O_3-transfer at 2.0 kWh kg^{-1}
Maier and Hartl, 1995	textile	O_3/UV	1 BC (3 bar$_{abs.}$)	1–2	240// 200–400	n. d.	n. d.	3.5	sludge forming; valves stuck
Kaulbach, 1996	textile	Bio-O_3	4 BC (1 bar$_{abs}$)	160	120 000	n. d.	n. d.	0.22	mainly decolourization, oxidation of surfactants to < 1.5 mg L^{-1}, water reuse in textile factories
Leitzke, 1996	textile	Bio-O_3-Bio	1 BC	12	110// 160	0.127$^{\#)}$; 0.343$^{\#)}$ (M = DOC)	n. d.	n. d.	decolourization and removal of polyvinylalcohol (PVA)
BC Berlin Consult, 1996	textile	MT- Bio-O_3	3 BC & 3 Bio in series	5	1750// 500	approx. 1.4	4.5 Mio	approx. 5	decolorization, ozone not used for COD removal
Krost, 1995	industrial	Bio-O_3-Bio	2 BC (1 bar$_{abs}$)	10–15	n. d.// 144–600	approx. 1.5	4.65 Mio$^{\#\#)}$	18	nitrite, nitroaromatics and polyether-alcohols in influent foaming,
Ried and Mielcke, 1999	pulp and paper	Bio-O_3	n. d.	40–100	n. d.// 300–1000	n. d.	3–6 Mio$^{\#\#)}$	0.10–0.50	final polishing: removal of odor, color, AOX and COD

MT = mechanical treatment (filtration, sieving)

1 US \$ ≈ 1.8 DM (1999)

$^{\#)}$ I* = specific ozone input (dosage) given in kg O_3 kg^{-1} M_o

$^{\#\#)}$ cost for equipment, but without costs for construction of reactors legal requirements (AbwVwV-51, 1989), which have promoted efficient treatment for several years. Commonly, the effluent of such plants is directly discharged to the receiving water, which requires the effluent meet limits on COD below 200 mg L^{-1}, an AOX-level below 500 µg L^{-1} and a toxicity factor to fish lower than $G_F = 2$.

Due to the complex nature of the DOC (or COD) the ozonation stage is mostly operated between two biological systems (Bio-O_3-Bio). In the first biological stage almost all easily biodegradable organic compounds are removed. The biological stage can be designed to remove the nitrogen-species as well; nitrification/denitrification can remove ammonium, nitrite and nitrate to low levels. Remaining is often a considerable amount of bio-refractory organic compounds. Here, ozone is used in order to partly oxidize these substances, with the goal of increasing their biodegradability in the subsequent biological treatment stage. An important advantage of this process combination is that no secondary wastes are produced, as would be the case if the O_3-Bio process steps were substituted by an activated carbon treatment.

Under the pressure of the comparatively high treatment costs, the need for adequate treatment of landfill leachates has also initiated important technological developments. New treatment schemes, such as an integrated (cyclic) chemical/biological process (e. g. BioQuint®, or Biomembrat®-Plus systems), as well as advanced reaction systems, e. g. systems employing heterogeneous catalytic ozonation processes (e. g. Ecoclear® or Catazone® systems) or the newly developed impinging zone reactor (IZR; Rüütel et al., 1998), have recently been developed (Table 3-3).

In the integrated chemical/biological processes, the effluent from the biological system is recycled several times to the ozone reactor and vice versa, which reduces the specific ozone absorption due to a higher amount of compounds being biodegraded, instead of mineralized by extended ozonation (e. g. Ried and Mielcke, 1999). Radicals such as $O^{-\circ}$, $O_2^{-\circ}$ and $O_3^{-\circ}$ – but not OH-radicals – are the main oxidizing species in the heterogeneous catalytic processes, where the oxidation of previously adsorbed pollutants develops at the surface of the special grade activated carbon catalyst (Kaptijn, 1997).

All systems proved capable of reaching the required effluents limits at comparatively low specific ozone absorptions, as low as 0.5 to 1.8 g O_3 g^{-1} COD_0 in the influent (for further details see Table 3-3).

Textile Waste Waters – Color Removal

Driven by the recent legislative attempts in Germany to establish effluent standards for color in textile waste waters for direct and indirect discharges, (AbwVwV-38, 1993) and due to the high potential of ozone for color removal, ozone application in the textile processing industry has gained much attention throughout the last decade. Some full-scale plants are already in operation, especially for directly discharged waste water (Table 3-3).

Besides the main goal of removing non-biodegradable (residual) color from often quite large waste streams, removal of surfactants or partial oxidation of DOC for improved bioavailability are secondary goals. Again, the oxidation is normally embedded in a multi-stage biological/chemical/biological system. Simple color removal may be achieved with low specific ozone dosages and low specific operation costs (e. g. 0.22 DM m^{-3}, Kaulbach, 1996; also see Table 3-3). In contrast, color removal and a high degree of total

DOC removal (e. g. > 80 %) can be very costly, especially in smaller applications, e. g. for in-house pretreatment.

Other Applications

One of the few large full-scale applications in the chemical industry in Germany is the plant at BASF Schwarzheide GmbH, Germany, which is equipped with an ozone generator of 15 kg O_3 h^{-1} capacity. A Bio-O_3-Bio system is applied for the treatment of a waste water coming from the manufacture of polyurethane foams. Here, the main aim is the removal of toxic and refractory nitroaromatic compounds, so that the degree of COD removal amounted to only 4 % of the influent loading to the total treatment sequence (Krost, 1995). Ozone consumption for nitrite oxidation due to insufficient biological denitrification and foaming in the ozone reactor caused considerable operational difficulties.

The world's largest industrial ozonation system of 420 kg O_3 h^{-1} production capacity is in operation in a pulp bleaching process in Finland. By using ozonation, chlorine containing chemicals can be fully replaced by a combination of oxygen, hydrogen peroxide and ozone. Thus, the production of high concentrations of AOX is avoided and the plant may be run according to the "Closed Mill" concept. Another advantage is that the remaining oxygen in the off-gas is used for several other oxygen consuming processes in the bleaching sequence (Böhme, 1999).

3.3.4 Particle Removal Processes

As already mentioned in Section A 3.2.4, the ozonation of municipal waste water can also be used to enhance particle removal, although this must be regarded as a side-effect. Further applications of ozonation for particle removal are not reported for waste waters.

3.4 Economical Aspects of Ozonation

Within the last fifteen years the cost-efficiency of the ozone production systems has improved dramatically. According to Kaulbach (1996) the key advances in this technology are:

- higher ozone yield per unit of electrode area due to medium frequency technology
- increased ozone concentration with modern ozone generators, from 6 % to 14 % wt. in oxygen
- increase in the unitary ozone production capacity by a factor of two or three
- 40 % reduction in specific energy consumption (since 1990)
- improved operational reliability.

Considering the investment and operation costs, ozonation still is not a cheap technology. Although safe operation is no longer a problem, ozonation systems require considerable

Table 3-4: Number of ozone production plants built by German industrial companies from 1954–1997 and fields of application (data from Böhme, 1999).

Field of Application	Total no. of Plants	% of Total	Typical Ozone Dosage	Unit of Ozone Dosage
Drinking Water Treatment				
Drinking water	694	10.5	0.5–1.2	g O_3 m^{-3}
Beverage industry	772	12		
Waste Water Treatment				
Process water	660	10	0.5 – > 3.5	g O_3 m^{-3}
Waste water or exhaust air	221	3	2–50 5–20	g O_3 m^{-3} g O_3 m^{-3}
Leachate	32	0.5	0.5–3.0#)	g O_3 g^{-1} Δ COD
Textile industry	6	< 0.1	> 0.13##)	g O_3 g^{-1} Δ COD
Pulp bleaching	9	< 0.1	–	–
Cooling water	47	0.7	–	–
Other Applications				
Swimming pool water	3587	55	1.0 (28 °C) 1.5 (35 °C)	g O_3 m^{-3}
Others	536	8		
Total	**6566**	**100**		

#) dosage from various references (see Table 3-3)

##) dosage from Leitzke (1996)

safety precautions, thus increasing the investment costs. Especially in smaller applications the investment and capital costs cannot be neglected, since they can considerably lengthen the pay-back times.

The number of ozone production plants built by German industrial companies from 1954–1997 as shown in Table 3-4 might be considered as an indicator of the economical importance of the use of ozone in full-scale applications, at least in Germany and some other European countries. Almost 90 % of these systems were set-up during the last 25 years, with an dramatic increase since 1991 (Böhme, 1999). For comparison it is also worth mentioning that in the USA only about 60 water works were using ozone in 1992 (Masschelein, 1994).

In summary, an ozonation system from a customer's viewpoint has to meet the following technical and economical requirements:

- achieve the treatment goal, e. g. reduce the contamination below the legal limits
- use a minimum of ozone (oxygen)
- keep the energy costs low and
- be safe to operate.

The preceding disussion has given an overview of which goals can be achieved with an ozonation system. The following chapters in this book can provide an understanding on how to design and operate an ozonation system to achieve these goals efficiently.

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Part B: Ozone Applied

1 Experimental Design

Much experimental work has been carried out on ozonation in drinking, waste and process water treatment. And since there is still much to be learned about the mechanisms of ozonation, and many possibilities of utilizing its oxidizing potential many experiments will be carried out in the future. Not only researchers but also designers, manufacturers and users of ozonation systems will continue to do bench-scale testing because ozonation is so system dependent. Most full-scale applications have to be tried out bench-scale for each system considered. That means that there is a need for not only fundamental information about the mechanisms of ozonation, but also information on how to set-up experiments so that they produce results that can be interpreted and extrapolated.

To achieve good results experiments should be designed correctly. This seems self-evident, but often in the case of ozone, the complexity of the system is underestimated. The goal of this chapter is to provide an overview of the process of designing experiments, concentrating on practical aspects. It offers a framework for the additional information in this book, which will help in understanding this complex topic. First the basis must be laid, for example, familiarity with which parameters contribute to the process of ozonation is required (B 1.1). Of course, knowledge of their relative importance and how they affect the process is also essential. These topics are found throughout the rest of the book. After the basics, this chapter continues with steps for designing experiments (B 1.2). Checklists are presented, which can be returned to when the practical work is in the planning phase. Similarly, the final Section B 1.3 will be a valuable help as a reference with its tabularized information on ozone throughout an experimenter's career.

Good experimental design can help produce good results with a minimum of effort. There are of course always surprises and unexpected circumstances in the life of an experimenter, however, these can be minimized with good preparation, perhaps even turned to good use.

1.1 Parameters that Influence Ozonation

As we will see, there are a number of steps to be taken before the experimental set-up can be built. Nevertheless, it will consist of the components found in Figure 1-1: an ozone generator, analyzers for process measurement and for safety, a reactor system with a water to be ozonated. Each set-up will be individual, determined by the experimenter's goals and resources.

To begin investigations we need to define the reaction system more exactly. This consists of at least an ozone source, a water to be ozonated with one or more compounds of interest M, and a reaction vessel (a reactor). The reactor could be a stirred tank reactor and could look like Figure 1-2. Some of the parameters necessary to characterize the system are summarized in Table 1-1:

Table 1-1: Main parameters to characterize the reaction system.

Parameters	Symbols
Gas and liquid flow rates	Q_G, Q_L
Reactor volume	V_L
Influent, effluent, and reactor concentrations	
– of ozone in the gas phase	c_{Go}, c_{Ge}, c_G
– of ozone in the liquid phase	c_{Lo}, c_{Le}, c_L
– of M in the liquid phase	$c(M)_o$, $c(M)_e$, $c(M)$
Other relevant water parameters:	
c(initiator), c(scavenger), c(promoter)	$c(I)_i$, $c(S)_i$, $c(P)_i$
Ionic strength	μ
Surface tension	σ
pH	–
State variables:	
Temperature and pressure	T, P
System parameters:	
Mass transfer coefficient	K_La
Reaction rates of ozone in the gas and liquid phase	r_G, r_L
Reaction rate of pollutant in the liquid phase	$r(M)$

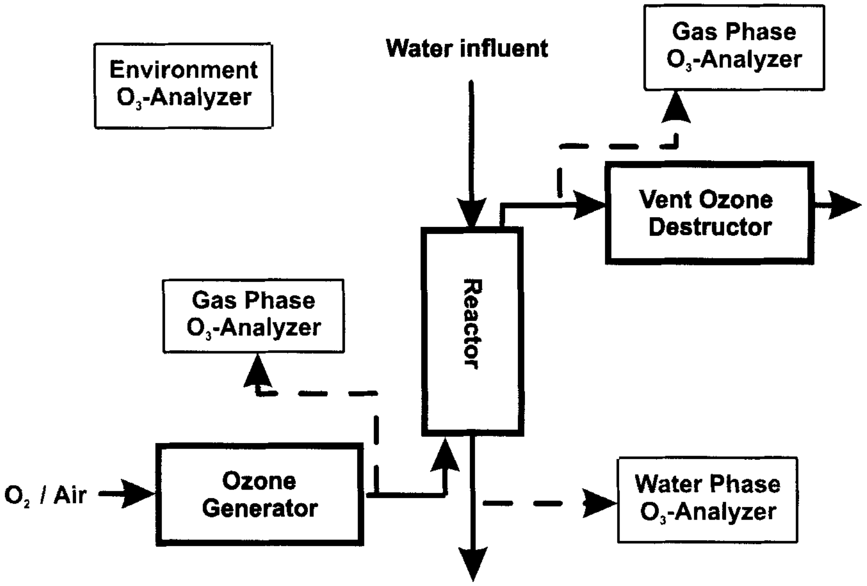

Figure 1-1: Basic elements of any ozonation experimental set-up.

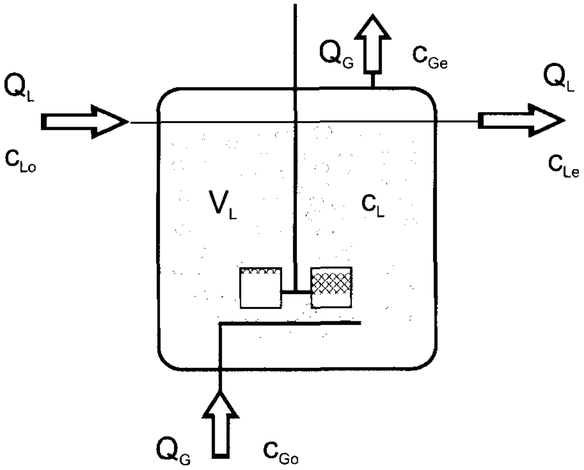

Figure 1-2: Operating parameters necessary for ozone mass balance(s) on a continuous-flow stirred tank reactor (for operation in semi-batch mode: $Q_L = 0$).

With these parameters we can set-up a mass balance on the system, which is the basis for evaluating the experimental results. The mass balance for the absorption (of any gas, e. g. ozone) in a continuous-flow stirred tank reactor (CFSTR) under the assumption that the gas and liquid phases are ideally mixed ($c_L = c_{Le}$, $c_G = c_{Ge}$), are as follows:

liquid phase:

$$V_L \cdot \frac{\mathrm{d}c_L}{\mathrm{d}t} = Q_L\,(c_{Lo} - c_L) + K_La \cdot V_L\,(c_L^* - c_L) - r_L \cdot V_L \tag{1-1}$$

gas phase:

$$V_G \cdot \frac{\mathrm{d}c_G}{\mathrm{d}t} = Q_G\,(c_{Go} - c_G) - K_La \cdot V_L\,(c_L^* - c_L) - r_G \cdot V_G \tag{1-2}$$

total material balance at steady state:

$$Q_G\,(c_{Go} - c_G) - r_G \cdot V_G = Q_L\,(c_{Lo} - c_L) - r_L \cdot V_L \tag{1-3}$$

Assuming that compound M is non-volatile and is not stripped ($c(M) = c(M)_e$), the mass balance for M in the liquid phase is:

$$V_L \cdot \frac{\mathrm{d}c(M)}{\mathrm{d}t} = Q_L\left(c(M)_o - c(M)\right) - r(M) \cdot V_L \tag{1-4}$$

The calculated parameters necessary to evaluate the data and discuss the results are found in Table 1-2.

Table 1-2: Overview of important parameters in ozonation experiments and their equations ($c(O_3)$, $c(M)$ also possible as mol L^{-1}).

Parameter	Unit	Semi-batch system	Continuous-flow system
ozone dose or feed rate $F(O_3)$	mg L^{-1} s^{-1}	$F(O_3) = \frac{Q_G\ c_{Go}}{V_L}$	$F(O_3) = \frac{Q_G\ c_{Go}}{V_L}$
ozone consumption rate[#)] $r(O_3) = r_L$	mg L^{-1} s^{-1}	$r(O_3) = \frac{1}{n}\sum_{i=1}^{n}\overline{r(O_3)(\Delta t_i)};\ \Delta t_i = const.$ $\overline{r(O_3)}(\Delta t_i) = \frac{Q_G\left(c_{Go} - \overline{c_{Ge}}(\Delta t_i)\right)}{V_L} - \frac{\overline{c_L}(\Delta t_i)}{\Delta t_i}$	$r(O_3) = \frac{\frac{Q_G}{Q_L}(c_{Go} - c_{Ge}) - c_{Le}}{t_H}$
ozone absorption rate[#)] $r_A(O_3)$	mg L^{-1} s^{-1}	$r_A(O_3) = \frac{1}{n}\sum_{i=1}^{n}\overline{r_A(O_3)(\Delta t_i)}\ ;\ \Delta t_i = const.$ $\overline{r_A(O_3)}(\Delta t_i) = \frac{Q_G\left(c_{Go} - \overline{c_{Ge}}(\Delta t_i)\right)}{V_L}$	$r_A(O_3) = \frac{\frac{Q_G}{Q_L}(c_{Go} - c_{Ge})}{t_H}$
pollutant removal rate[#)] $r(M)$	mg L^{-1} s^{-1}	$r(M) = \frac{c(M)_o - c(M)_e}{t_e - t_o} = \frac{c(M)_o - c(M)_e}{t_R}$	$r(M) = \frac{c(M)_o - c(M)_e}{t_H}$
specific ozone dose or input[#)] I^*	g O_3 g^{-1} M	$I^* = \frac{m(O_3)_o}{m(M)_o} = \frac{Q_G\ c_{Go}\ t_R}{V_L\ c(M)_o} = \frac{F(O_3)}{c(M)_o}\ t_R = F^*(O_3)\ t_R$	$I^* = \frac{Q(O_3)}{Q(M)_o} = \frac{Q_G\ c_{Go}}{Q_L\ c(M)_o}$
specific ozone absorption A^*	g O_3 g^{-1} M	$A^* = \frac{\Delta m(O_3)}{m(M)_o} = \sum_{i=1}^{n}\frac{Q_G\left(c_{Go} - \overline{c_{Ge}}(\Delta t_i)\right)\Delta t_i}{V_L\ c(M)_o}$	$A^* = \frac{\Delta Q(O_3)}{Q(M)_o} = \frac{Q_G\ (c_{Go} - c_{Ge})}{Q_L\ c(M)_o}$
ozone transfer efficiency $\eta(O_3)$	%	$\eta(O_3) = \frac{A^*}{I^*} = \frac{\Delta m(O_3)}{m(O_3)_o}$	$\eta(O_3) = \frac{A^*}{I^*} = \frac{c_{Go} - c_{Ge}}{c_{Go}}$
degree of pollutant removal $\eta(M)$	%	$\eta(M) = \frac{c(M)_o - c(M)_e}{c(M)_o}$	$\eta(M) = \frac{c(M)_o - c(M)_e}{c(M)_o}$
ozone yield coefficient[#)] $Y(O_3/M)$	g O_3 g^{-1} M	$Y(O_3/M) = \frac{\overline{r(O_3)}}{r(M)} = \frac{\overline{r(O_3)}\ t_R}{c(M)_o - c(M)_e}$	$Y(O_3/M) = \frac{r(O_3)}{r(M)} = \frac{c_{Go} - c_{Ge}}{c(M)_o - c(M)_e}$
Mass transfer enhancement factor, E	–	$E = \frac{r(O_3)}{k_L a\ (c_L^* - c_L)}$	$E = \frac{r(O_3)}{k_L a\ (c_L^* - c_L)}$
[#)] additional calculations for c_{Ge} or c_L (mean values for Δt)	–	$\overline{c_{Ge}}(\Delta t_i) = \frac{\left(c_{Go} + c_{Ge}(\Delta t_i)\right)}{2}\ ;\ \overline{c_L}(\Delta t_i) = \frac{\left(c_{Lo}(\Delta t_i) + c_{Le}(\Delta t_i)\right)}{2}$	$;\ t_R = n\ \Delta t_i = t_e - t_o$

Table 1-3: Parameters to characterize an ozonation experiment.

Required Information	Define System		Experimental Procedure	Assess Results	
–	Reactor	Water	Ozonation (Input)[1]	Amount of Ozone Used[1]	Pollutant Removal[1]
Generally	V_L, h, d	$c(M)_o$	Q_G, Q_L	$\eta(O_3)$	η(M)
	k_La, E	pH	t_R or t_H	$r(O_3)$	$r(M)$
	n_{STR}	$c(TIC)$[2]	c_{Go} (c_L*)	c_L	
	T, P		$F(O_3)$ or I*	A*[3]	
				$Y(O_3/M)$[3]	
	reactor type	buffer type	pH-control	c-t-value[4]	
For kinetic assessment	–	–	–	$k_D(O_3)$[4]	$k_D(M)$, $k_R(M)$

[1] for each stage and pollutant as well as the whole system

[2] sum of concentrations of HCO_3^- and CO_3^{2-}

[3] more important in experiments on waste water ozonation

[4] important in drinking water ozonation.

That seems like a lot of information and the question arises if all of these parameters are necessary to report, and if not all, which ones. Parameters that characterize the experiment can be grouped according to the ones that define the system, describe the experimental procedure, and are used to assess the results (Table 1-3). Some of the calculated parameters are interrelated, as can be seen in Table 1-2. Then a nonredundant set of information containing most of the parameters in Table 1-3 can be reported. For example, besides the operating parameters, information on pollutant removal, i. e. initial pollutant concentration $c(M)_0$, degree of pollutant removal $\eta(M)$, is indispensable, as well as the parameters for ozone, i. e. ozone consumption rate $r(O_3)$, specific ozone dose or input I^*, specific ozone absorption A^*. Combined parameters allow a quick comparison of results, i. e. ozone yield coefficient $Y(O_3/M)$.

The most common shortcoming, though, in published literature is not too much, but rather too little information given. Often the system and the results are not adequately described, so that comparison of results cannot be made.

1.2 Experimental Design Process

Good experimental design involves many preliminary steps before the central experimental work can begin. The steps of experimental design can be roughly grouped under six aspects (Figure 1-3). Perhaps "steps" is a misnomer since they are not meant to be carried out consecutively. An iterative process of identifying possibilities, carrying out initial experiments and then refining methods must be used.

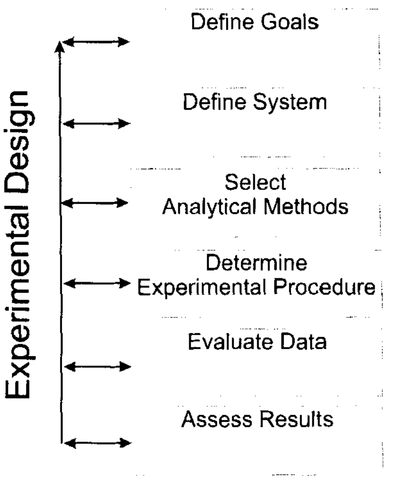

Figure 1-3: Main steps in experimental design.

This process includes determining experimental goals, choosing the equipment, setting it up, and evaluating the reaction system for various operating conditions. The operating conditions should be optimized with respect to the desired goals and the reaction system characterized at these conditions. Still another aspect of the preliminary work is choosing analytical methods and methods for data evaluation, as well as calculating the corresponding error and sensitivity analyses. With these results, the methods can be fine-tuned, so that the experimental goals can be achieved. The next step is to carry out the experiments and evaluate the data. Last but not least in this iterative process is to assess the results. This means to compare the experimental results with others, and check if the desired goals have been reached, for example can the process be modeled or scaled-up on the basis of the experimental results.

Many developments have been made in the use of statistics to aid in experimental design over the last decades. The most important aspect of experimental design methods is that they provide a mathematical framework for changing all pertinent factors simultaneously, and achieve this in a small number of experiments. The description of such methods, though, is beyond the scope of this book and the reader is referred to the literature (Box et al., 1978; Bayne and Rubin, 1986; Haaland, 1989; Morgan, 1991) or to the internet for the latest design software (e. g. StatSoft, 1999).

To help the reader identify the activity associated with each aspect on the more intuitive level, checklists are presented. They are not comprehensive, but can help the beginning experimenter get started. We have placed them at the beginning of Part B to give an overview of the information necessary for successful experimentation. Each reader will spend more or less time initially reading through the checklists. They can be returned to when the practical work is in the planning phase. It is important to use them critically, checking which points apply to the situation at hand and to modify and add appropriate points that have been missed.

Checklists for Experimental Design

1. Define Goals

- Experimental goals could be one or more of the following:
  - determination of process feasibility
  - determination of minimal use of ozone for pollutant required removal efficiency
  - determination of reaction kinetics
  - determination of scale-up procedure
  - determination of best process or combination of processes
  - etc. ...

2. Define System

Water or Waste water

- Define the composition of the (waste) water. Which individual compounds: organic as well as inorganic are present? Can the type of compound at least be determined? How can it be quantified (lumped parameter, individual analysis)?
- Consider using a synthetic (waste) water to test certain hypotheses.
- Check the recent literature on biodegradation in order to determine the conditions under which the compound(s) in question are biodegradable.
- Make a theoretical analysis of the most probable behavior of the individual compounds as well as the complete water matrix during ozonation.
- Determine the most probable oxidation products, and how to measure them.
- Consider that ions contained in the raw water and/or occurring from oxidized substituted organics might act as promoters, inhibitors or scavengers in the radical reaction cycle process (see Chapter A 2) or influence the mass transfer of the system (see Section B 3.3).

Oxidant

- Select the most appropriate type of chemical agent, checking whether there are similar/competitive oxidation processes available (e. g. application of AOPs etc.) which might be more efficient or economical.
- Consider combined treatment, e. g. oxidative and biological processes.
- Respect technical constraints of each treatment step, as well as of combined processes. In general, the feasibility of combined processes (in terms of operating costs) depends on the performance and effectiveness of the oxidation process.
- If choosing ozone as the chemical agent, consider the interdependencies between ozone production by the two most common types of generators and system parameters, e. g. mass transfer (Section B 2.2).

Reaction System (Chemical and Biological)

- Choose between the two operating principles, batch or continuous-flow, and types of reactors.

- Consider possible advantages and disadvantages of each operating principle before setting up the equipment, i. e. volume of influent water required, pumping and storage requirements, length of experimental run.
- Build and operate the reactor system considering all safety precautions.

Total System

- Evaluate the reactor hydrodynamics by determining the retention time distribution (see Levenspiel, 1972, 1999).
- Evaluate the mass transfer by determining the mass transfer coefficient for a range of operating conditions using the same water that will be oxidized later if possible.
- Determine the optimal operating conditions with respect to the experimental goals.
- Characterize the reactor at these operating conditions.

3. Select Analytical Methods

Oxidants

- see Section B 2.5

Pollutants and Water Matrix

- Assess TOC and TIC if possible, consider that TIC values indicate the amount of scavengers.
- DOC is the best parameter for total pollutant removal in (waste)water application, DOC characterizes mineralization uniquely in chemical and biological processes.
- Measure SAC_{254} as indicator of the sum of aromatic compounds or SAC_{436} for humic-like substances.
- Avoid COD because of possible interferences of some inorganics (NO_2^-, H_2O_2 etc.), very different oxidation state of individual substances, and since it does not measure mineralization.
- Use analytical procedures adapted to the individual pollutants (e. g. GC, HPLC, LC, MS, etc.).
- Stop the further oxidation of compounds after sampling by adding Na_2SO_3.
- Ions contained in raw water and/or occurring as oxidation products (e. g. HCO_3^-, CO_3^{2-}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) are best measured with ion chromatography (IC).
- pH: Consider a continuous control of pH since it might change during oxidation due to the production of organic acids.
- Analyze analytical errors and their effect on the results, e. g. a sensitivity analysis with the Gaussian error propagation method.

Toxicity

- see chapter A 1 and Section B 6.4

4. Determine Experimental Procedure

- Decide what information is necessary to achieve the experimental goal(s).

- Generally data are necessary that allow the reaction system to be balanced. If possible an on-line determination is of advantage.
- Decide on and implement a quality control program to assure reproducibility and minimal error.
- Determination in advance:
  - information about the inorganic and organic matrices of the water
- Determination on-line:
  - ozone gas concentration at the inlet
  - ozone gas concentration at the outlet
  - liquid concentration of the oxidants and pollutants
  - information about the inorganic and organic (e. g. SAC_{254}, SAC_{436}) matrices of the water
  - pH-value
  - temperature
- Determination during/after experiment:
  - liquid concentration of the oxidants (if not possible on-line) and pollutants
  - information about the inorganic and organic matrices of the water

  in case of AOP:
  - $F(H_2O_2)/F(O_3)$: specific hydrogen peroxide dose rate
  - O_3/UV: detailed information about the UV-intensity, wave length spectrum, illuminance and penetration
- In general, every experiment should at least be performed twice in order to check whether the same results can be achieved during two independent treatments.

5. Evaluate Data

- Assess the treatment results for each individual process step as well as for the whole system.
- Use DOC as the main parameter if mineralization is required.
- Calculate parameters, e. g. ozone consumption rate $r(O_3)$, ozone yield coefficient $Y(O_3/M)$ (see Table 1-2).
- Make sure the set of parameters reported adequately characterizes the system and results so that they can be of value to other experimenters.

6. Assess Results

- Compare results with those found in the literature.
- Compare results to experimental goals.
- If the goals have been reached, modeling or scaling-up of the results can be undertaken.
- If the experimental goals have not been reached, new experiments must be planned and carried out.

Iterative Process!

1.3 Ozone Data Sheet

gas: blue colored
water: purple blue in concentration higher than 20 mg L^{-1}

Table 1-4: Physical Properties of Ozone.

Property	Value	Unit	Reference
Density (gas, at STP)	2.144	g L^{-1}	Ozonia, 1999
diffusion coefficient	1.26 10^{-9} (20°C)	m^2 s^{-1} (measured)	Matrozov et al., 1978
	1.75 10^{-9} (20°C)	m^2 s^{-1} (calculated)	Wilke & Chang, 1955#)
	1.82 10^{-9} (20°C)	m^2 s^{-1} (calculated)	Scheibel, 1958#)
extinction coefficient	3 300 (λ = 254 nm)	L mol^{-1} cm^{-1}	–
	3 150 (λ = 258 nm)		Hoigné, 1998
boiling point (at 100 kPa)	–112.0	°C	Ozonia, 1999
melting point	–196.0	°C	Ozonia, 1999
	–193.0	°C	Hoigné, 1998
molecular weight	48	g mol^{-1}	
redox potential, E_0^H (in aq. solution for pH = 0 and O_2 / O_3 gas)	+2.07 (25 °C)	V	Hoigné, 1998
vaporization heat	681 at STP	kJ m^{-3}	Ozonia, 1999
viscosity	0.0042 (–195 °C)	Pa s	Ozonia, 1999
	0.00155 (–183 °C)	Pa s	
solubility, *s* ($H_C = s^{-1}$) +) at 101.3 kPa	0.64 (0 °C)	–	Ozonia, 1999
	0.50 (5 °C)	–	
	0.39 (10 °C)	–	
	0.31 (15 °C)	–	
	0.24 (20 °C)	–	
	0.19 (25 °C)	–	
	0.15 (30 °C)	–	
	0.12 (35 °C)	–	

#) cited by Reid et al., 1977
+) see also Section B 3.1.3

Table 1-5: Conversion Table for Ozone Gas Phase Concentrations[+].

Ozone Concentrations			Conversion Formula
$c_G(wt.)$[#]	$c_G(vol.)$	c_G	–
Weight %	Volume %	g m^{-3}	–
1	0.7	14.1	*ideal gas law:*
2	1.3	28.4	$p(O_3) = c_G \dfrac{\Re T}{\mathrm{MW}(\mathrm{O}_3)}$
3	2.0	42.7	
4	2.7	57.2	
5	3.4	71.7	$\Re$ = ideal gas constant (8.314 J mol^{-1} K^{-1})
6	4.1	86.3	MW(O$_3$) = 48 g mol^{-1}
7	4.8	101.0	
8	5.5	115.9	$p(O_3) = y(O_3) \cdot P$
9	6.2	130.8	
10	6.9	145.8	*conversion c_G to $c_G(vol.)$:*
11	7.6	161.0	$c_G(vol.) = \dfrac{c_G \, \mathrm{V}_n}{\mathrm{MW}(\mathrm{O}_3)1000} = y(O_3)$
12	8.3	176.2	
13	9.1	191.6	
14	9.8	207.0	V$_n$ = molar volume (22.4 L mol^{-1})
15	10.5	222.6	$y(O_3)$ = ozone mole fraction in the gas
16	11.3	238.3	(multiply $c_G(vol.)$ by 100 for %-values!)
17	12.0	254.1	
18	12.8	270.0	
19	13.5	286.0	
20	14.3	302.1	

[+] at STP: T = 0 °C, P = 1.013 10^5 Pa

[#] for an ozone/oxygen gas mixture

(1 ppm = 2 mg m^{-3}, 20 °C, 101.3 kPa; 1 ppm = 1 cm^3 m^{-3})

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2 Experimental Equipment and Analytical Methods

Since reaction mechanisms and experimental observations are not independent of the system in which they are made, the experimental set-up and how the experiment is run affect the outcome. That means that it must be clear how equipment and procedures affect the outcome when they are chosen. It also means that experimental set-ups and procedures from drinking water treatment cannot be applied on waste water without appropriate evaluation and vice versa. In general, an experimental set-up consists of an ozone generator, reactor, flow meters and on-line analysis of at least the influent and effluent ozone gas concentrations and ambient air monitor (Figure 2-1). Each set-up will be tailored to the experimental goals and the resources available.

This chapter provides some essentials about the individual components and how they affect ozonation. First the material of the equipment necessary for containing ozone (B 2.1) is examined, followed by the equipment for producing it (B 2.2), and bringing the reactants together (B 2.3). Methods to measure ozone, with their advantages/disadvantages (B 2.4) and the safety aspects to consider (B 2.5) are then discussed. This is rounded off with a list of common questions, problems and pitfalls that we have come across over the years (B 2.6). Perhaps it will be helpful to read before starting your own experiments.

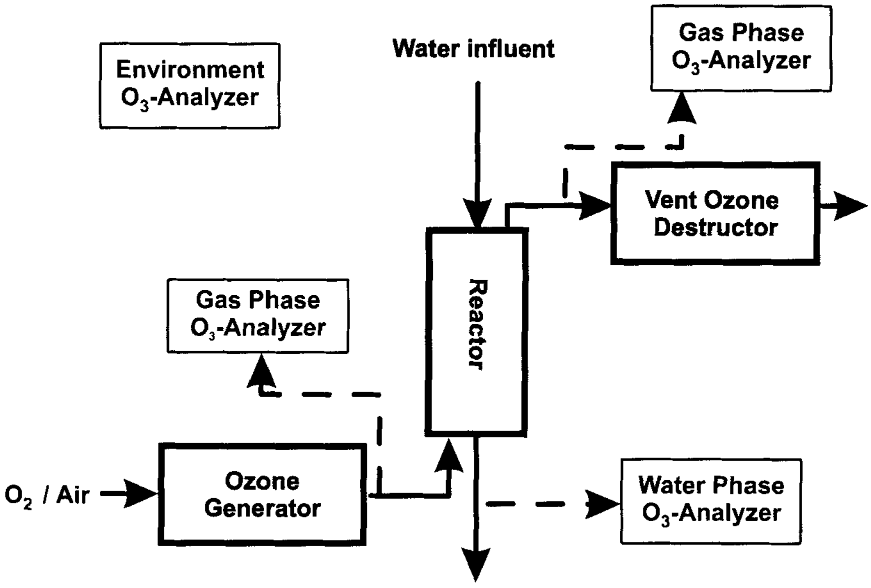

Figure 2-1: Components of an experimental ozonation set-up.

2.1 Materials in Contact with Ozone

Since ozone is a very strong oxidant, all materials in contact with this gas have to be highly corrosion resistant. This has to be considered for all components in the ozone system including the ozone generator as well as all instruments (Figure 2-1, Table 2-1).

Table 2-1: Materials resistant to ozone (Saechting, 1995).

System Components	Preferred Materials	Remarks
Reactor	(Quartz) glass stainless steel (No. 1.4435 or 1.4404) PVC (polyvinylchloride)	
Diffuser	ceramics	
	PTFE (polytetrafluoroethylene)	expensive
Pipes and Valves	glass	glass prone to breakage
	stainless steel	fast corrosion possible with high concentration of salts
	PTFE (polytetrafluoroethylene) PFA (perfluoralkoxy) Kalrez® (Du Pont)	*PTFE, PFA and Kalrez®*: expensive, scarcely oxidizable, stable over time,
	PVC (polyvinylchloride) PVDF (Polyvinylidenfluoride) PVA (polyvinylalkoxy)	*PVC, PVDF, PVA*: less expensive, slowly oxidizable, less stable over time
Seals	PTFE (polytetrafluoroethylene) PFA (perfluoralkoxy) Kalrez® (Du Pont)	

2.1.1 Materials in Pilot- or Full-Scale Applications

In full-scale applications very fast corrosion (formation of holes over the course of weeks, especially at improper welds) has been observed in off-gas piping, even when made from stainless steel. The problem is most evident when aerosols, for example containing chloride, escape from the reactor into the pipes where they form a very corrosive wet film. But corrosion may also occur in stainless steel pilot or full-scale reactors, especially when treating waste waters. Such reactors are best made of stainless steel because of the possibility to operate them at elevated pressures, e. g. 200–600 kPa, which can readily be achieved with commercially available ozone generators (Masschelein, 1994).

PVC is a very inexpensive material that can be used for lab-scale ozone reactors, however, it is slowly but progressively attacked by ozone. Bubble columns or tube reactors can easily be constructed from PVC tubes. Generally, gas tightness is best achieved by welding, but it can only be operated at ambient pressure ($P_{abs} \approx 100$ kPa). Its use in full-scale applications has seldom been reported (see Table A 3-5).

2.1.2 Materials in Lab-Scale Experiments

For the experimenter in the laboratory, not only do materials have to be chosen on the basis of their corrosion-resistance, but also for their effect on ozone decay. Some metals (e. g. silver) or metal seals enhance ozone decay considerably. This can be especially detrimental in drinking water and high purity water (semiconductor) ozone applications, causing contamination of the water as well as additional ozone consumption. Moreover, the latter will cause trouble with a precise balance on the ozone consumption, especially in experiments on micropollutant removal during drinking water ozonation. With view to system cleanliness in laboratory experiments, use of PVC is only advisable in waste water treatment, whereas quartz glass is very appropriate for most laboratory purposes.

Materials in the whole system must be appropriate, that means reactor and piping for ozone gas as well as for ozonated water must be chosen carefully. For example, the material of the reactor and sampling system, especially the seals, has also to be chosen to avoid not only corrosion from ozone, but adsorption of the compound(s) being studied. It is advisable to let the liquid phase contact only glass and stainless steel. In stirred reactors for example, the stirrer seals (unless the stirrer is a magnetic bar) and all connectors for piping are best placed at the top of the reactor, so that the liquid does not come in contact with them.

2.2 Ozone Generation

Since ozone is an unstable molecule, ozone has to be generated on-site. The various methods of ozone production differ in their working principles and ozone sources. The methods and their differences are summarized in Table 2-2.

Table 2-2: Overview of types of ozone generation, working principles and fields of application.

Method of Ozone generation	Working Principle	Ozone Source	Field of Application
Electrical	Electrical discharge (ED)	air or O_2	Common standard from laboratory to full-scale
Electrochemical	Electrolysis (EL)	water (highly purified)	Predominately for pure water applications, laboratory to small industrial scale
Photochemical ($\lambda < 185$ nm)	Irradiation (abstraction of electrons)	O_2 (air), water (drinking water quality or highly purified)	New technology, laboratory to full-scale
Radiation chemistry	X-rays, radioactive γ-rays	water (highly purified)	Very seldom, solely experimental
Thermal	light arc ionization	water	Very seldom, solely experimental

The first two methods of ozone production, electrical discharge and electrolysis, are the only ones of practical importance both in bench- and full-scale applications and are further discussed in the following section.

Ozone production from ambient air or pure oxygen in an electrical discharge chamber is the most widespread technology for ozone generation (Masschelein, 1994). Considering that ozone is a three-oxygen-atom modification of molecular oxygen, its production directly from oxygen seems reasonable. In recent years, electrochemical ozone production by electrolysis of water has gained some importance in special fields of application. This is especially true in areas where highly purified water (e. g. by distillation, nanofiltration or reverse osmosis) is already being produced for the production process or where it at least can be produced easily and cost-efficiently in the quantity needed for ozone production.

2.2.1 Electrical Discharge Ozone Generators (EDOGs)

Electrical discharge, sometimes also called silent discharge ozone generators ionize molecular oxygen by applying high power alternating current to the gas. Air or pure oxygen can be used as feed gas, at either ambient or elevated pressure (P_{abs} = 100–600 kPa). Ozone is formed by recombination of ionized oxygen atoms and unionized molecular oxygen. In this process only 4–12 % of the energy supplied is used for the formation of ozone and the rest is transformed into heat (Ozonek et al., 1994). An efficient cooling system has to be installed, because ozone decays fast at elevated temperatures, with T_G = 50 °C regarded as the critical value. In full-scale systems the gas is cooled to T_G = 5–10 °C (Krost, 1995). Newly developed concepts such as double-side cooling of the electrodes help increase the energy efficiency (ASTeX, 1997).

Various types of discharge chambers are available with plate or tubular geometry. The classical and most frequently used type is the tubular, often also called Van der Made-type or Welsbach-type (Figure 2-2). The central rod electrode technology is a more recent development, especially designed for applications with pure oxygen as feed gas (Masschelein, 1994).

In full-scale electrical discharge ozone generators, ozone is normally produced by medium-frequency (200–650 Hz) high-voltage systems (8 500–10 000 V). One generator contains several thousands of parallel silent discharge electrodes with metallized glass as the dielectric, which can produce up to 100 kg O_3 h^{-1} from pure oxygen. The specific energy consumption for this production rate ranges from 12–18 kWh kg^{-1} O_3.

In contrast, advanced lab-scale generators work at high-frequency (kHz-range) supplied by conventional line voltage of 230 or 380 V at 50 or 60 Hz. In these systems only very few (one or two) electrodes are employed. The electrode geometry, dielectric material and cooling systems vary considerably. Some manufacturers employ ceramic for the dielectric, which is highly efficient in heat transfer (Samoilovitch, 1994). When fed with pure oxygen the ozone production capacity range is 0.001–0.2 kg O_3 h^{-1} and at c_G = 150 g O_3 m^{-3} the specific energy consumption is about 15–18 kWh kg^{-1} O_3 (ASTeX Sorbios, 1996; ASTeX, 1997).

An overview of the main operating parameters and characteristic parameter ranges for lab- and full-scale generators is given in Table 2-3.

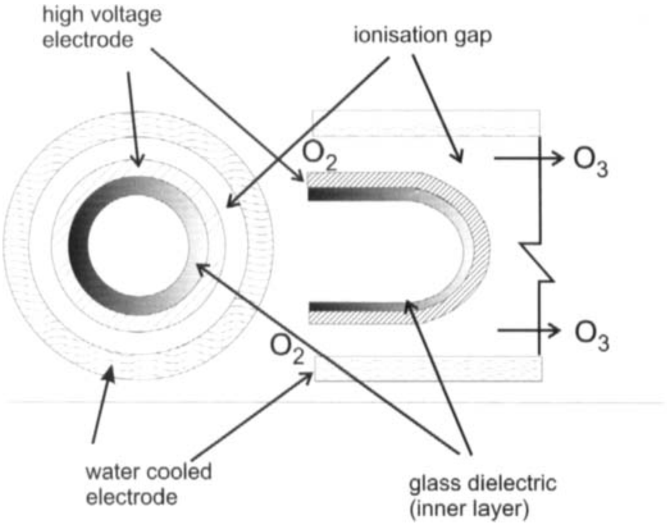

Figure 2-2: Working principle of the tubular Electrical Discharge Ozone Generator (EDOG).

Table 2-3: Characteristic operating parameters of electrical discharge and electrolytic ozone generators.

Parameters	Unit	Type of Ozone Generator		
–	–	Electrical Discharge (ED)		Electrolytic (EL)
Reference		ASTeX Sorbios, 1996	Krost, 1995	Ozonia, 1991
–	–	lab-scale	full-scale	lab-scale
Ozone source	–	air or O_2		high-purity feed-water, conductivity < 20 µS cm^{-1}
Source preparation system	–	gas-compression, cooling, filtering, drying		ion-exchange, ultra- or nanofiltration, reverse osmosis, distillation
P_{abs}	kPa	150–450	200–600 [#)]	600–700
T_G or T_L	°C	4–16	5–10	< 30
Q_G or Q_L	$m^3 h^{-1}$	0.210–1.38 (at STP)	60–150 (at STP)	0.100–0.200
c_G or c_L	$g m^{-3}$	280	100–180	15–30 [##)]
O_3-Production capacity	kg O_3 h^{-1}	0.03–0.20	10–15	0.003–0.012
Required power	kW	0.5–3.0	120–280	0.5–1.0
Specific energy consumption	kWh kg^{-1} O_3	15–(18) 20 (feed-gas O_2)	12–18 (feed-gas O_2)	300
Q_{LC}	$m^3 h^{-1}$	0.125–0.600	air cooling	by ozonated water

[#)] a pressure of 600 kPa is possible in full-scale applications according to Masschelein (1994), but is not applied at BASF-Schwarzheide

[##)] maximum ozone solubility at $T = 30$ °C and $P = 100$ kPa: $c_L^* = 0.23\ c_G$

Type of Feed Gas and its Preparation

The type of feed gas used, air or oxygen, determines the achievable ozone gas concentration and the gas preparation requirements. The higher the oxygen content, the higher the ozone concentration possible. Ambient air contains O_2 in about 21 vol % (at STP) and is thus a cheap and ubiquitous resource for ozone production. Its main use and advantage is in applications where large mass flows are required at comparatively low ozone gas concentrations, e. g. in drinking water ozonation systems.

The major disadvantages of using ambient air as feed gas for ozone generation are:

- a high-quality air preparation system is required, consisting of: compression, cooling, filtering and drying (Horn et al., 1994) and
- nitrogen oxides can be produced (NO, N_2O, NO_2, N_2O_5) (Wronski et al., 1994).

The air has to be dried to a dew-point of –70 °C (at P_{abs} = 1 bar), so that corrosion in the generator and piping to the reactor can be effectively prevented. With pure oxygen, common in lab-scale applications, the gas only to has be dried to a dew-point of –40 °C. The stricter requirements for the drying of air increase the energy consumption. In full-scale applications the specific energy consumption (measured as kWh kg^{-1} O_3 produced) for ozone produced from air is about twice as high compared with that produced from pure oxygen (Horn et al., 1994).

Theoretically, almost fivefold higher ozone concentrations in the gas can be achieved with pure oxygen compared to air. State-of-the-art full-scale EDOGs achieve c_G = 3–4 wt % from air and 10–13.5 wt % from oxygen. Lab-scale systems can produce up to 20 wt % ozone (302 g O_3 m^{-3} at STP) from pure oxygen.

In lab-scale applications O_2 is normally supplied in cylinders. In industrial applications it is either delivered in tanks as liquid oxygen or produced on-site from ambient air, usually with pressure swing or vacuum swing adsorption (Horn et al., 1994).

Use of EDOGs in Laboratory Experiments

Even if pure oxygen from pressurized cylinders is used in lab-scale applications, gas purification is still recommended, especially for experiments in which ozone is used to eliminate trace organic compounds, e. g. preparation of water for semiconductor cleaning applications, drinking or ground water treatment. It is advisable to install the following gas purification system in front of the generator: gas-drying by means of an absorptive material, e. g. silica gel, a molecular sieve (0.4 mm) and a microfilter (4–7 μm) to remove any particles from the gas (Gottschalk, 1997). In semiconductor applications a particle filter (0.003 μm) is also necessary after the ozone generator.

When air is used as the feed gas in lab-scale ozonation equipment, a high-quality air-drying and oil-removal system similar to full-scale applications has to be installed following the compressor. Otherwise the generator may be destroyed from moisture, dust, oil, hydrocarbons and hydrogen.

In lab-scale electrical discharge ozone generators the mass flow rate of ozone produced ($m(O_3)$) mainly depends on the gas flow rate (Q_G) and the power or the voltage applied

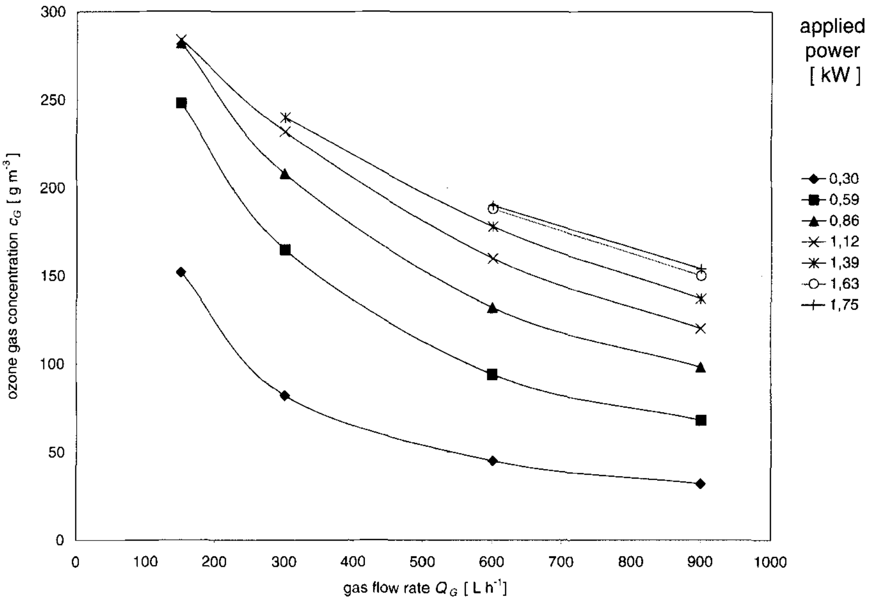

Figure 2-3: Characteristic dependency of the ozone gas concentration on the gas flow rate in an electric discharge ozone generator (from ASTeX Sorbios, 1996).

(power = I · U [VA]). The two parameters are inversely proportional, but linearly. The ozone gas concentration decreases with increasing gas flow rate. The deviation from linearity between the two parameters is largest at lower gas flow rates. Different generators will show different curve types. Figure 2-3 gives an example of an electrical discharge ozone generator with a nominal ozone production capacity of 0.090 kg O_3 h^{-1} (at Q_G = 0.600 m^3 h^{-1} and c_G = 0.150 kg O_3 m^{-3}; ASTeX Sorbios, 1996).

This inverse relationship between Q_G and c_G is important to recognize in planning experiments. For example to increase the k_La-value in bubble columns, the gas flow rate must be increased. Using an electrical discharge ozone generator (EDOG) this will reduce the ozone gas concentration. Careful evaluation of whether the higher k_La-value matches with other goals of the experiment, e. g. the intention to use a high ozone gas concentration or achieve a high ozone transfer efficiency has to be made. Another characteristic of EDOGs of importance for experimental planning is that there is a certain minimum gas flow rate Q_G at which the highest ozone concentration is produced. Below these Q_G-values the ozone production capacity becomes unstable. The highest mass flow rates, on the other hand, can only be achieved at very high power input as well as high gas flow rates.

2.2.2 Electrolytic Ozone Generators (ELOGs)

In the electrolytic ozone generator (ELOG) ozone is produced from the electrolysis of high purity water (Figure 2-4). In the electrolytic cell, water is split into molecular hydrogen H_2

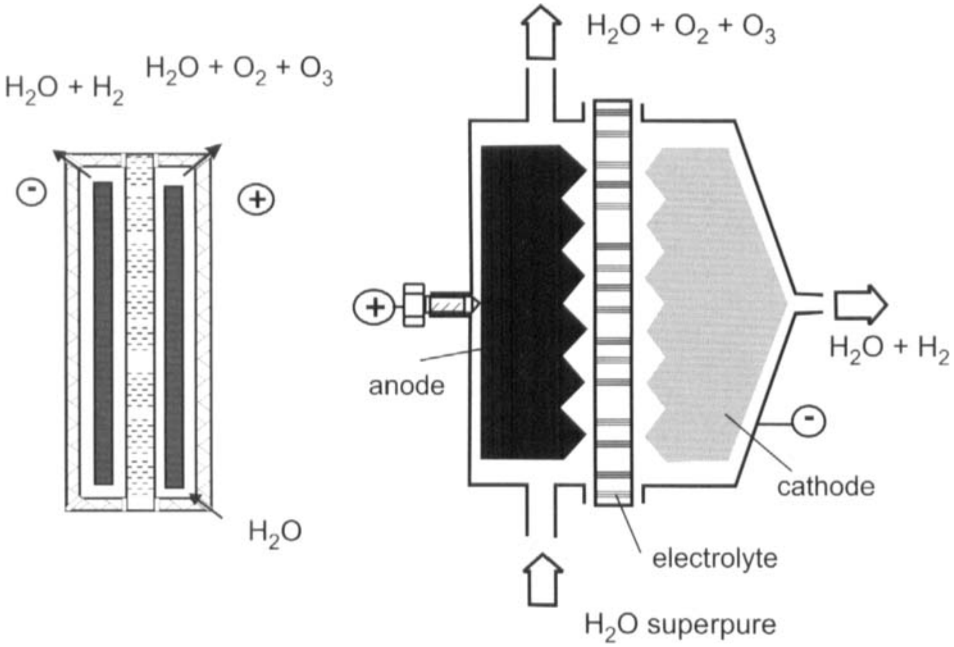

Figure 2-4: Working principle of the Electrolytic Ozone Generator (ELOG) (after Fischer, 1997).

as well as oxygen (O_2) and ozone (O_3) by the action of electrons supplied by the catalytic properties of the electrode material. Water, O_2 and O_3 leave the cell on the anode side, whereas H_2 is produced at the cathode side of the specialized electrolytic cell.

The cell anode and cathode spaces are separated by a solid-state electrolyte membrane. The anode is made of a porous, water-penetrable and current-conductive carrier material coated with an active layer. At the site where the active catalytic layer and the electrolyte membrane touch ozone is produced when a direct current of 3 to 6 V at currents of up to 50 A (corresponding with a current intensity of 0.2 to 3.0 A cm^{-2}) are applied (Fischer, 1997).

Since all materials of the cell have to be electrochemically very stable and have to provide a high conductivity, the cell consists of refined metals or metal-oxides at their highest oxidation level. Also the feed water has to be of high purity, because it has to pass the porous anode and cathode materials without clogging or causing chemical damage. Therefore, ions and other impurities which are contained in normal drinking water have to be removed by ion-exchange, ultra- or nanofiltration, reverse osmosis or distillation.

Electrolytic ozone generators are supplied by several producers. The ozone production capacity of one cell is between 1–4 g O_3 h^{-1}, but several cells can be combined in one generator. The principle dependency of the ozone production capacity (of one cell) on the voltage, the current and temperature is shown in Figure 2-5.

Again, cell temperature strongly influences the ozone production and efficient cooling is necessary. Cooling is mostly achieved by maintaining a high water flow rate (e. g. $Q_L = 100 \pm 50$ L h^{-1}; Ozonia, 1991), however, energy efficient systems with air cooling

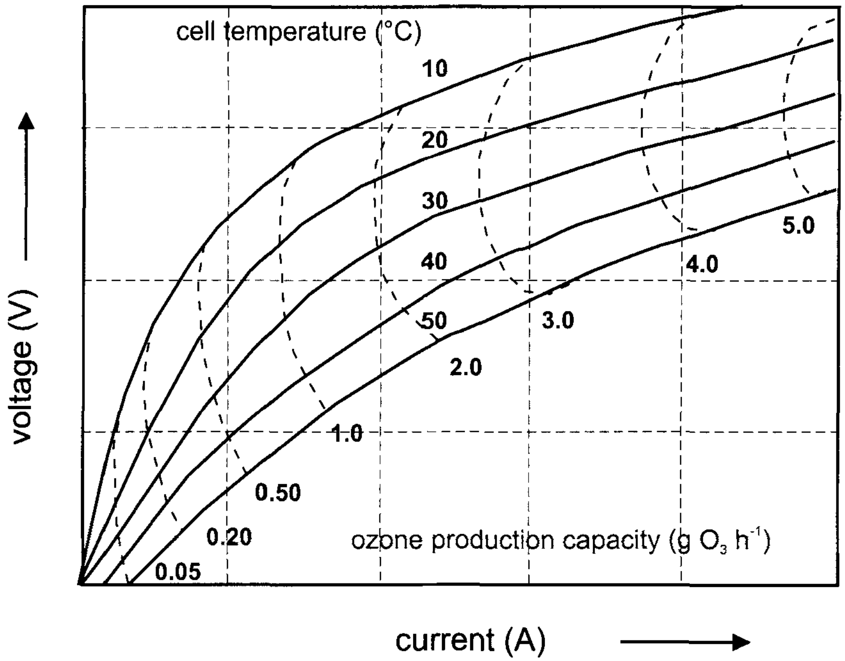

Figure 2-5: Dependency of the ozone production capacity in an electrolytic ozone generator (ELOG) on the applied voltage and current (with cell temperature as a parameter) (from Fischer, 1997).

have also been developed (VTU, 1996). A typical set of characteristic operating parameters is given in Table 2-3. The specific energy consumption is very high 300 kWh kg^{-1} O_3 (about 15 to 20 times the value of the EDOGs). This very high value makes it evident that this type of ozone generator is rarely used in drinking and waste water treatment systems.

Use of ELOGs in Laboratory Experiments

The temperature of the liquid in the system should be kept below T_L = 30 °C because of the possibility of fast ozone decay at higher temperatures. This also requires considerably high flow rates of purified feed water to be directed through the cell, unless the cell is air cooled or the feed water is cooled before entering the ELOG.

The fact that dissolved ozone is produced brings a very important advantage to subsequent ozone applications: mass transfer from the gas to liquid phase is not required. Efficient mixing (e. g. with static mixers) of the ozone-rich pure water stream with the (waste-)water stream to be treated, though, is required. During this *in-situ* ozone production, the liquid ozone concentration (c_L) can easily reach the solubility level (c_L^*), depending on the pressure (P) and temperature (T) in the cell. Oversaturation of the feed-water will immediately occur, when the pressure drops. Due to this potential degassing, vent ozone gas destruction is also required for this system.

2.3 Reactors Used for Ozonation

This section provides a short overview of the types of reactors commonly used for ozonation in lab-scale studies, their hydrodynamic behavior and mass transfer characteristics as well as possible modes of operation. Since ozone is mostly generated as a gas, gas and liquid have to be brought into contact. If ozone is absorbed into a liquid before it is brought into contact with the water to be ozonated, it would be logical to speak of an ozone contactor or absorber, followed by a reactor. If absorption is accompanied by a simultaneous reaction, it would make sense to call the apparatus a reactor. Unfortunately this is not usually true for most literature. The terms are used interchangeably, and the reader must sort out their meaning. Here we will talk about *directly gassed* reactors (Section B 2.3.1) where absorption and reaction occur simultaneously or *indirectly gassed* reactors (Section B 2.3.2), where a contactor is used to absorb the ozone prior to entering the reactor. In both cases an appropriate gas diffuser has to be used (Section B 2.3.3). The mode of operation also must be chosen (Section B 2.3.4). Special consideration is given the practical aspects of design for laboratory experiment, rather than full-scale applications.

Each reactor type has its characteristic hydrodynamic behavior. Knowledge of the hydrodynamic behavior as well as its mass transfer characteristics is important for evaluating experimental results. Table 2-4 summarizes characteristic features of five important reactor types.

Bubble columns (BCs) and stirred tank reactors (STRs) are the most frequently used types of reactors in laboratory ozonation experiments. Bubble columns can be roughly assumed to behave like perfectly mixed reactors with respect to the liquid phase, provided the ratio of height (h) to diameter (d) is small ($h/d \leq 10$).

In small lab-scale STRs almost complete mixing of the gas-phase can also be assumed whereas plug-flow or mixed behavior can be generally assumed for the gas phase in bubble columns (Marinas et. al., 1993; Stockinger, 1995; Huang et al., 1998) and packed towers (Lin and Peng, 1997).

If the liquid as well as the gas phases are ideally mixed (i. e. the reactor behaves like a completely mixed STR, often called CSTR) the degradation processes can easily be calculated from integral mass balances for ozone and the dissolved target substances.

Table 2-4: Characteristic features of gas-liquid contacting systems (Martin et al., 1994).

Type of Reactor or Mass Transfer System	Type of Hydrodynamic Behavior	k_La (s^{-1})	Specific Power Consumption (kW m^{-3})
Bubble columns (BCs)	Non plug-flow for liquid Plug-flow for gas	0.005–0.01	0.01–0.1
Packed tower	Plug-flow for liquid Non-plug-flow for gas	0.005–0.02	0.01–0.2
Plate tower	Disperse flow for liquid Non-plug-flow for gas	0.01–0.05	0.01–0.2
Tube reactors	Plug-flow for liquid Plug-flow for gas	0.01–2	10–500
Stirred tank reactors (STRs)	Completely mixed liquid Non-plug-flow for gas	0.02–2	0.5–10

2.3.1 Directly Gassed Reactors

Water or waste water ozonation – regardless of the scale of equipment – is mostly performed in *directly gassed* systems, where the ozone containing gas is produced by an electrical discharge ozone generator and is introduced into the reactor by some type of gas diffuser. Since two phases, the gas and the liquid, are required for the oxidation reaction to proceed as it does, they are also called *heterogeneous* systems.

Bubble Columns and Similar Reactors

Bubble columns and various modifications such as airlift reactors, impinging-jet-reactors, downflow bubble columns are frequently used in lab-scale ozonation experiments. Moderate k_La-values in the range of 0.005–0.01 s^{-1} can be achieved in simple bubble columns (Martin et al. 1994; Table 2-4:). Due to the ease of operation they are mostly operated in a cocurrent mode. Countercurrent mode of operation, up-flow gas and down-flow liquid, has seldom been reported for lab-scale studies, but can easily be achieved by means of applying an internal recycle-flow of the liquid, pumping it from the bottom to the top of the reactor. The advantage is an increased level of the dissolved ozone concentration c_L in the reactor (effluent), which is especially important in the case of low contaminant concentrations ($c(M)$) and/or low reaction rate constants, i. e. typical drinking water applications

A very simple type of a bubble column, which was not mentioned above is a gas-wash bottle. This very small-scale system (V_L = 0.2–1.0 L) may be used for basic studies, in which general effects (e. g. influence of pH and/or buffer solutions; specific ozone dose) are to be assessed. Its use is not recommended for detailed studies, because the mass-transfer coefficient is often low and its dependency on the gas flow rate is unknown or difficult to measure. Often there is no possibility to insert sensors or establish a reliable measuring system for exact balancing of the ozone consumption. An optimal mode of operation would comprise treatment of the (waste-)water for a certain period of time, preferably without withdrawal of solution during the ozonation. In this way different ozonation conditions can be tested by varying the ozonation time or the ozone gas concentration. A variation of the gas flow rate is not recommended.

Laboratory-scale bubble columns for ozonation preferably have a reactor liquid phase volume of V_L = 2–10 L, with a height-to-diameter-ratio of h/d = 5–10. The ozone/oxygen (ozone/air) gas mixture is supplied through a ceramic or stainless steel porous plate fine pore diffuser (porosity 3, 10–40 μm hole diameter). PTFE-membranes are a comparatively new alternative for the ozone gas-to-water transfer (Gottschalk et al., 1998).

Since mixing is only due to the power dissipated by the gas flow, very small gas flow rates might cause incomplete mixing in the reactor. Tracer studies should be performed to verify the hydrodynamic behavior (Levenspiel, 1972; Marinas et al., 1993; Huang et al., 1998). Experience with single stage lab-scale bubble columns of V_L = 1.5–4.2 L and h/d = 6–35 operated at gas flow rates of Q_G = 20–50 L h^{-1} and liquid retention times of t_H = 0.6–5.0 h has shown that the liquid phase behaved like cascades of perfectly mixed reactors with stage numbers of n = 1.5–4.0, equal to a Bodenstein number of Bo = 0.95–6.4 (Saupe, 1997). Furthermore, at a constant hydraulic retention time t_H, a doubling of the gas flow rate in the range given above had only negligible influence on the theoretical number of stages. The operation of the same reactors as airlift reactors, in which the inner tube was gassed, did not significantly change the hydrodynamic behavior nor the k_La-values.

Stirred Tank Reactors

Stirred tank reactors (STR) are the most frequently used reactors in lab-scale ozonation, partially due to the ease in modeling completely mixed phases, but they are very seldom used in full-scale applications. There are various modifications with regard to the types of gas diffusers or the construction of the stirrers possible. Normally lab-scale reactors are equipped with coarse diffusers, such as a ring pipe with holes of 0.1–1.0 m^3 diameter. The k_La-values are in the range of 0.02 to 2.0 s^{-1} (see Table 2-4:), which are considerably higher than those of bubble columns. From the viewpoint of mass transfer, the main advantage of STRs is that the stirrer speed can be varied, and thus also the ozone mass transfer coefficient, independently of the gas flow rate.

If the experimental goal is to investigate reactions, not develop a new reactor, use of a reactor type for which correlations and experience already exists is preferred. In order to give a general idea of the dimensions of a STR, important features of STRs which have been successfully operated in various fields of water or waste water applications are summarized in Table 2-5. A somewhat extraordinary construction of the stirrer and the baffles was successfully used by Gottschalk (1997) for drinking-water ozonation. A reactor specially designed to measure kinetic parameters is the so-called agitated cell (Figure 2-6, Levenspiel and Godfrey, 1974).

The agitated cell reactor consists of two chambers, one for the liquid phase and another for the gas-phase, which can both be independently mixed by two mixers. In this reactor the mass-transfer area can be varied independently of the gas flow rate by installing various porous plates with a defined number of holes, i. e. a defined contact area gas-liquid, between the two chambers. The value of k_L can then be determined from the measurement of k_La.

Using it in the semi-batch mode of operation this reactor type has been used in the determination of the reaction rate constants of fast direct reactions of ozone with certain waste water pollutants, e. g. phenol or azo-dyes (Beltrán and Alvarez, 1996). Beltrán and coworkers have also successfully studied the reaction kinetics of various fast reacting substances using semi-batch mode STRs (see further references of Beltrán, Benitez or Sotelo et al. in Chapters B 3 and B 4).

In waste water ozonation experiments with high concentrations of (highly reactive) contaminants it is recommended that the ratio of Q_G to V_L not be too low, i. e. the liquid volume not be too large (V_L = 1–5 L) and an appropriate ozone generator be used. This is important because of the high reaction rates which may be achieved and which may cause a total depletion of ozone in the off-gas, causing problems in balancing the ozone consumption in the systems.

2.3.2 Indirectly and Non-Gassed Reactors

In contrast to *heterogeneous* systems, *homogeneous* systems contain only one phase, which in water and waste water applications is the liquid phase. Ozone is either absorbed from the

Table 2-5: Examples of STRs having been succesfully used in lab-scale ozonation studies.

Reference	Gottschalk, 1997	Sotelo et al., 1990; Beltrán et al., 1995	Beltrán and Alvarez, 1996
Water/waste water	Drinking water	Synthetic waste waters	Synthetic waste waters
Pollutants/ model contaminants	Atrazine (micropollutants)	Resorchinol and phloroglucinol; PAHs	Phenol and 4 Azo Dyes
Volume and dimensions	$V_L = 8$ L $h = 260$ mm $h/d = 1.3$	$V_L = 0.5$; 4 L h = n. d. mm h/d = n. d.	$V_L = 0.3$ L $d = 75$ mm $h/d \approx 0.9$
Material	Quartz glass, top and bottom stainless steel, impregnated with PTFE layer	Quartz glass (both)	glass
Stirrer	PTFE plate ($h = 15$ mm, $d = 65$ mm) with six 5 by 5 mm grooves at its bottom	Six-blade rushton-type, stainless steel	n. d.#)
Gas sparger	8 mm o. d. PTFE-tube with 1.0 mm holes at its top	2 mm i. d. bubbler; fine porous diffuser 16–40 μm	none; defined holes in interface plate (agitated cell)
Baffles	3 baffles non-vertical made from PTFE	4 baffles, vertical, stainless steel $h/d =$	n. d.#)
Operating conditions			
T (°C)	20 ± 1	1–20; 10, 20	20 (Phenol), 15 (dyes)
Q_G (L h^{-1})	30 (at STP)	110–70; 25	60
n_{STR} (min^{-1})	1 500	100–700; 1000	75
k_La (h^{-1}) (at Q_G, T)	12	2.8–13.3; 126	0.8
$p(O_3)_o$ (Pa)		12–871; 116–1015	30–2220

#) for constructive details see Levenspiel and Godfrey (1974)

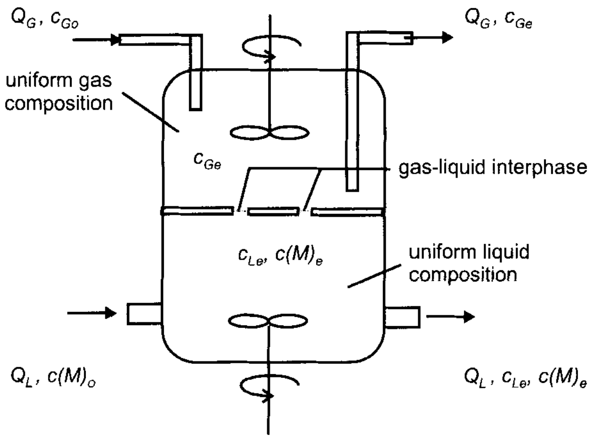

Figure 2-6: Schematic sketch of an agitated cell (from Levenspiel and Godfrey, 1974).

gas phase into water in a separate vessel and the reactor is *indirectly gassed*, or is produced *in-situ* by an electrochemical ozone generator and the ozone reactor is *non-gassed*. In both cases an ozone rich liquid is mixed with the (waste-) water to be treated.

Tube Reactors

Plug-flow with its higher reaction rates compared to completely mixed STRs (Levenspiel, 1972) is difficult to achieve in directly gassed reactors. Non-gassed systems would require the use of an electrolytic ozone generator as well as a highly purified water serving as a carrier for the ozone being produced and dissolved *in-situ*. One trick to achieve plug-flow when using an electrical discharge ozone generator is to use an indirectly gassed system. The practicality of this application depends on the amount of ozone required. In long tube reactors with relatively high ozone consumption, additional ozone as gas or ozonated water must be dosed along the length of the tube reactor.

Sunder and Hempel (1996) oxidized perchloroethylene contained in a simulated (model) contaminated ground water in an indirectly gassed system. The ozone gas was absorbed in a highly efficient ozone absorber, consisting of an injector nozzle and a special absorber chamber, the so-called Aquatector®. In pure water this system produces micro-bubbles of 30 to 50 µm diameter. In this way, dissolved ozone was mixed with the contaminant in the entrance of the tube reactor. This reactor had the following dimensions $Q_L = 220$ L h^{-1}, $l_R = 14.9$ m and $d_R = 18$ mm and was operated at $t_H = 62$ s, Re = 4 300 and Bo = 600. As can be seen from the reactor length and width, the system is comparable to a conventional water pipe. Such systems could be of practical relevance in industrial applications where pipelines of considerable length often exist for waste water transportation.

2.3.3 Types of Gas Diffusers

Contacting ozone gas with water can be achieved with every kind of gas diffuser, which is made of a material resistant to ozone. Ring pipes, porous diffusers and porous membranes, injector nozzles as well as static mixers can be employed. The different types of diffusers are mainly characterized by the diameter of the bubbles produced, e. g. micro ($d_B = 0.01$–0.2 mm), small ($d_B \approx 1.0$ mm) or big ($d_B \approx 2.5$ mm) bubbles (Calderbank, 1970; Hughmark, 1967).

Ring pipes with 0.1–1.0 mm i. d. holes are common types of diffusers in lab-scale stirred tank reactors. Fine *porous plate diffusers* ($d_P = 10$–50 µm) have also often been used, in STRs (e. g. Beltrán et al., 1995) as well as bubble columns (e. g. Stockinger, 1995; Saupe, 1997).

Coarse ($d_P = 50$–100 µm) porous disks are the most frequently applied diffusers in large-scale drinking water treatment systems (Masschelein, 1994). They are seldom used in industrial waste water treatment applications. The reason is that blocking or clogging can easily occur, e. g. by means of precipitation of chemicals, like carbonates, aluminum or ferrous oxides, manganese oxides, calcium oxalate or organic polymers. This is also valid for ceramic filter tubes, which are sometimes used as mass transfer systems in drinking water applications.

PTFE-membranes are now available with very small holes and high pressure resistance. This makes it possible to use them as an efficient gas diffuser. For example the GORE-Tower is such a kind of a membrane contactor (Gottschalk et al., 1998). The liquid phase is directed through a bundle of microporous tubing made from PTFE and housed in an appropriate shell (cylinder). Countercurrent to the liquid the gas is passed through the outer shell where it can diffuse through the porous tube. The achievable ozone concentration in the liquid is a function of the gas concentration, the pressure and the liquid to gas flow rates. Dissolved ozone concentrations in excess of 15 mg L^{-1} at water flow rates of 15 L min^{-1} (P_{gauge} = 280 kPa) are feasible with this system without producing bubbles in the liquid (Gottschalk et al., 1998). The system is especially attractive for semiconductor applications, where the fresh water on the one hand does not contain substances being prone to clogging and on the other hand the ozonated water has to be absolutely free of gas-bubbles.

Two-phase gas/water injector nozzles are mostly used in pilot- or full-scale bubble column applications (Krost, 1995) or in specialized, newly developed reactor types. An example is the Submerged Impinging Zone Reactor (IZR) (Gaddis and Vogelpohl, 1992; Air Products, 1998), which is constructed for very high mass-transfer rates.

Normally, it makes little sense to apply such systems in lab-scale ozonation experiments, since the high mass transfer rates are only achieved at high gas flow rates which because of the typical operation characteristics of EDOGs accordingly means low ozone gas concentrations. An appropriate field of application was, however, presented in the study of Sunder and Hempel (1996) who operated a tube-reactor for the ozonation of small concentrations of perchloroethylene. An injector nozzle coupled with the highly efficient Aquatector® ozone-absorption unit was installed in front of the tube-reactor. Both the gas and liquid were partially recycled in this system. According to the authors more than 90 % of the ozone produced was absorbed in demineralized water and dissolved ozone concentrations ranged up to 100 µmol L^{-1} (c_L = 5 mg L^{-1}, T = 20 °C).

Static mixers can also be applied for gas-liquid mixing. The mixer consists of several mixing elements arranged in series within a pipe. Such systems are small and easy to handle; important advantages are: in-line setting-up in a pipe, compact dimensioning, no mobile part(s) and very little maintenance requirement (if no abrasion occurs!). The main operating characteristics are plug-flow for both phases and radial intensive mixing. The hydrodynamic conditions provide a uniform distribution of dissolved ozone in water and of small bubbles over the whole flow cross-section. Thus the interfacial area is also increased resulting in a high mass transfer rate.

To achieve this high mass transfer rate, though, the specific power consumption is very high since a lot of energy is needed to "push" the liquid through the mixer. A high pressure drop develops in the system. Also, large liquid flow rates are normally necessary for an efficient operation of static mixers. Thus, their predominant field of application will not be in lab-scale but in full-scale application, e. g. in the ozonation of drinking or ground water with the objectives of disinfection and/or removal of micropollutants. Martin et al. (1994) modeled the transfer characteristic of static mixers and compared the efficiency of three commercially available systems.

2.3.4 Mode of Operation

Reactors can be operated either in a batch or continuous-flow mode. The combination, batch with respect to the liquid and continuous-flow with respect to the gas, is called semi-batch. Often this fine distinction is ignored and it is commonly referred to as batch. The majority of ozonation experiments reported in the literature have been performed in one-stage semi-batch *heterogeneous* systems, with liquid phase reactor volumes in the range V_L = 1–10 L. Most full-scale applications are operated in continuous-flow for both phases.

Large differences in reaction rates and products can occur depending on the mode of operation and hydrodynamic behavior of the reactor (Levenspiel, 1972; Levenspiel and Godfrey, 1974). The advantages of continuous-flow operation, e. g. reduced process control and storage requirements, have to be weighed against possible disadvantages, e. g. reduced reaction rates and ozone efficiency.

From the reaction engineering viewpoint, batch processes (even in ideally mixed reactors) behave similarly to those in a continuous-flow tube reactor, in which higher reaction rates are possible than in a continuous-flow ideally mixed system (CFSTR-type) (Levenspiel, 1972; Baerns et al., 1992). In most continuous-flow lab-scale reactor systems where high degrees of pollutant removal, i. e. low effluent concentrations of M, are required, the liquid phase is ideally mixed. A small volume of liquid is treated with comparatively high gas flow rates, providing good mixing and relatively low reaction rates. A lower specific ozone consumption can be achieved with the batch mode of operation as compared to continuous-flow ozonation in such cases (Saupe, 1997; Saupe and Wiesmann, 1998; Sosath, 1999).

Multi-stage STR cascades and plug-flow reactors allow the advantages of continuous-flow to be combined with higher reaction rates (Baerns et al., 1992; Levenspiel, 1972). Few lab-scale experiments have been run in multi-stage STR-cascades or plug-flow reactors (Sunder and Hempel, 1996), however, in principle, the improvements in ozone efficiency and ozone consumption could be dramatic. From a practical point of view, the set-up and handling of multi-stage systems is more complicated than running a one-stage system. The choice of reactor type and number of stages and mode of operation must be made in view of the experimental goals.

Batch Experiments

Batch experiments are comparatively quick and easy to perform. In their simplest form, they can be used to assess the gross effect or the tendency of influence which a certain parameter of interest, e. g. pH, concentration, ozone dose rate, has on the treatment result.

An advantage of batch operation is that normally only a small amount of solution is required. Enough solution, though, must be available to perform all necessary analyses, as well as showing reproducibility. This is especially important to verify for combined chemical/biological processes, where more treatment as well as analyses are carried out.

It is very important to apply the same oxidation conditions in each batch, and vary only one parameter at a time, unless statistical experimental design is being applied. Be especially careful to assure constant liquid ozone concentration c_L as well as constant pH. Both are often observed to vary within the reaction time in waste water ozonation. The liquid ozone concentration shows an increase whereas the pH normally decreases due to the formation of acidic reaction products (organic acids). In drinking water studies, especially when micropollutants are treated, the dissolved ozone concentration may easily be held constant throughout the whole time of experiment. In kinetic studies care has to be taken to establish the steady-state ozone concentration in the liquid before the micropollutants are injected into the water (Gottschalk, 1997).

It is not recommended to withdraw large amounts of liquid from the ozone reactor during the treatment, since the hydrodynamic conditions as well as the ratio of mass of ozone per mass of pollutant remaining may change and thus influence the gas-liquid mass transfer or the oxidation rates. The mass transfer might also be influenced by the oxidation, e. g. when surface active agents are oxidized.

Where necessary and applicable, the specific ozone dose or the specific ozone absorption (best recorded and computed on-line) is recommended as the measure for analyzing process performance. Since in waste water ozonation, the ozone off-gas concentration often increases during the batch-treatment, the specific ozone absorption will not vary linearly with the treatment time.

A procedure for conducting a series of batch ozonations with minimum parameter variation is: fill the reactor to the desired level, ozonate, withdraw the whole solution, fill again to the same level and repeat the oxidation with a new set of ozonation conditions (preferably varying the oxidation time or the specific ozone absorption) in the next run.

Recalling the remarks on reaction engineering (see above, Section 2.3.4) batch ozonation experiments are the best method to minimize the specific ozone consumption (unless simple biodegradation with an adapted biomass is possible).

Continuous-Flow Experiments

The continuous mode of operation causes a comparatively high effort in the laboratory and often the experiments cannot be performed as quickly as in the batch mode.

The size of the system and the desired range of hydraulic retention times determine how much feed water is required. Large reactors or short hydraulic retention times require that a comparatively large amount of feed water has to be prepared and stored in way that guarantees the concentration of the influent remains stable over the necessary period of time. Cool and dark places are often required, but cooling may become problematic if very large volumes are involved. Considering the amount of liquid to be stored, it has to be kept in mind that it takes at least three times the hydraulic retention time before steady-state is achieved in the reactor (Levenspiel, 1972). Extreme situations occur in this regard if a sequential chemical-biological system with two large reactors is operated with the intent to track a possible adaption of the biomass in the biological stage (Saupe, 1997).

Quite a lot of maintenance has to be dedicated to the system to insure stable liquid and gas flow rates. Carbonates can plug up or block a fine porous diffuser for ozone over time, causing the pressure in front of the reactor to increase, the gas-flow rate to sink and the ozone concentration in the influent gas to increase (if an EDOG is used). The experimenter will be severely unsatisfied by this situation although the total ozone mass-flow into the system will be unchanged and the oxidation process might not be affected negatively, if the reaction depends (more) on the total ozone dosage than on the ozone concentration. However, the mass transfer and reaction rates differ.

If a multi-stage system is set up, e. g. a sequential chemical-biological system, care has to be taken, that ozone – either liquid or gaseous – cannot enter the biological stage, since it would kill the biomass due to oxidation. Either the ozone concentration in the off-gas can be controlled at zero (Stockinger, 1995) or the gas phase can be kept separate from the biological stage with a gas trap (Saupe, 1997).

In order to allow flexibility in operation of sequential chemical and biological stages, they do not have to be directly coupled. A storage tank or drain in between allows changes in experimental parameters to be made more independently. An alternative method is outlined in Section B 6.4.

2.4 Ozone Measurement

The following section gives an overview of the different methods available to measure ozone in the gas and liquid phases. For quick reference the methods are summarized in Table 2-7 so that the reader can choose an analytical method that fits his or her system at a glance. All important information e. g. interference, detection limit, as well as the original reference with the detailed description of the method, necessary for its application can be found in this table. The methods are described in ascending order of their purchase costs.

2.4.1 Methods

Iodometric Method (gas and liquid)

This method can be used for the determination of the ozone concentration in the gas and/or liquid phase. The measurement takes place in the liquid phase, though, so that to measure a process gas containing ozone, the gas must first be bubbled through a flask containing potassium iodide KI. For the measurement of the liquid ozone concentration, a water sample is mixed with a KI solution. The iodide I^- is oxidized by ozone. The reaction product iodine I_2 is titrated immediately with sodium thiosulfate $Na_2S_2O_3$ to a pale yellow color. With a starch indicator the endpoint of titration can be intensified (deep blue). The ozone concentration can be calculated by the consumption of $Na_2S_2O_3$.

$$KI + O_3 + H_2O \rightarrow I_2 + O_2 + KOH \tag{2-1}$$

$$3\, I_2 + 6\, S_2O_3^{2-} \rightarrow 6\, I^- + 3\, S_4O_6^{2-} \tag{2-2}$$

advantages:	Purchase price for this method is very low.
disadvantages:	Iodide is oxidized by substances with an electrochemical potential E_0 higher than 0.54 eV. This means nearly no selectivity. (e. g. Cl_2, Br^-, H_2O_2, Mn-components, organic peroxides). The measurement is time-consuming.

UV Absorption (gas and liquid)

The absorption maximum of ozone occurs at 254 nm, which is close to the wavelength of the mercury resonance line at 253.7 nm. The decrease of the UV intensity at $\lambda = 254$ nm is proportional to the concentration of ozone based on the Lambert-Beer's law of absorption:

$$I_l = I_o\, 10^{\varepsilon c(M) l} \tag{2-3}$$

I_l	Intensity passing through the absorption cell containing the sample
I_o	Intensity passing through the absorption cell containing the reference
$c(M)$	concentration in M
l	internal width of the absorption cell in cm
ε	molar extinction coefficient in $M^{-1}\,cm^{-1}$
$\varepsilon_{254\,nm}$	about 3000 $(M\ cm)^{-1}$, depending on the literature source

This method is used for the gas and liquid phase in the same way. The law of Lambert-Beer is valid between $0.1 < \lg I_l/I_o < 1$. So that the concentration range for this method depends on the width of the absorption cell. Systems exist that can measure up to 150 mg L^{-1} in the liquid phase, and up to 600 mg L^{-1} in the gas phase.

In distilled water and tap water without chlorine it is possible to measure the liquid ozone concentration and the unsaturated organic substances by using $Na_2S_2O_3$. The first absorption value at $\lambda = 254$ nm represents the sum of the organic substances and the liquid ozone concentration. After destroying the ozone the residual absorption is correlated to the organic matter (Tsugura et al., 1998).

advantages:	The method is very easy and simple. Continuous measurement is possible.
disadvantages:	Aromatic pollutants in water absorb UV-radiation at $\lambda = 254$ nm and can interfere with the measurement.

Indigo Method (Liquid)

The concentration of aqueous ozone can be determined by the decolorization of indigo trisulfate ($\lambda = 600$ nm). The method is stoichiometric and extremely fast. The indigo molecule contains only one C = C double bond which can be expected to react with ozone directly and with a very high reaction rate (see Figure 2-7).

One mole ozone decolorizes one mole of aqueous indigo trisulfate at a pH less than four. Hydrogen peroxide and organic peroxides react very slowly with the indigo reagent. If ozone is measured in less than six hours after adding the reagents hydrogen peroxide does not interfere.

advantages:	The purchase price for this system is low. The reaction is very fast and selective. Secondary oxidants do not interfere within 4 to 6 h.

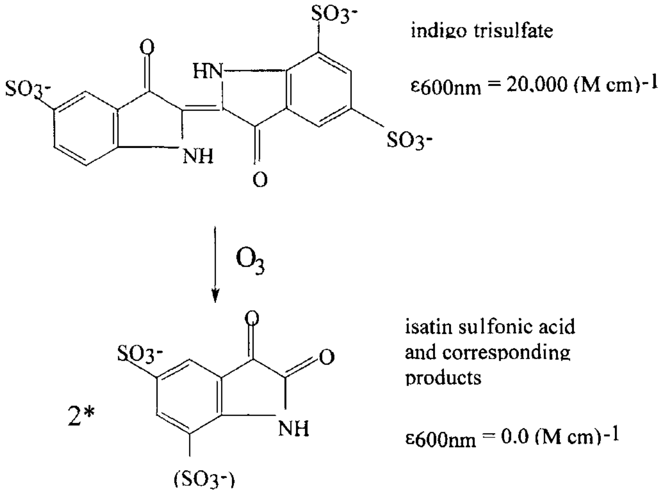

Figure 2-7: Oxidation of indigo trisulfate by ozone.

N,N -diethyl-1,4 phenylenediammonium – DPD (Liquid)

This spectrophotometric method is for determining ozone at low liquid concentrations (0.02–2.5 mg L^{-1} O_3). The direct oxidation of N,N-diethyl-1,4 phenylenediammonium (DPD) by ozone is very slow. Therefore, the concentration of ozone is measured indirectly by the oxidation of iodide with ozone (pH = 6).

$$2\,H^+ + O_3 + 2\,I^- \rightarrow I_2 + O_2 + H_2O \qquad (2\text{-}4)$$

The product iodine forms a radical cation with DPD, which is a red dye (see Figure 2-8). The radical cation DPD ° is stabilized by resonance and forms a fairly stable color with one absorption maximum at 510 nm and one at 551 nm. The concentration of ozone is proportional to the intensity of the dye and can be calculated according to equation (2-3).

advantages: see iodometric method
disadvantages: see iodometric method

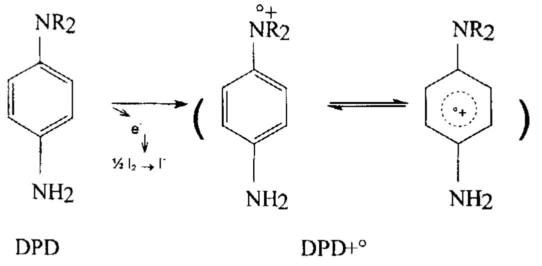

Figure 2-8: Oxidation of N,N -diethyl-1,4 phenylenediammonium -DPD by ozone.

After adding reagents the sample is only stable for 5 min.

Chemiluminenescence – CL (liquid)

The intensity of light from a chemical reaction is measured. The difference between chemiluminescence and photometric absorption is that instead of measuring the decrease in light intensity due to absorption by the compound of interest, the production of light due to a chemical reaction with the compound of interest is measured and proportional to the concentration. Often this method is used with flow injection analysis (FIA). The ozonated water sample is injected into a pure water carrier and mixed with dye reagent in front of the photodetector. The reagents, which are very selective for ozone over other oxidants, undergo a fast reaction with aqueous ozone and produce chemiluminescence. The intensity is proportional to the concentration of ozone. Table 2-6 gives some examples of possible reagents, listed in ascending order according to the intensity of chemiluminescence produced by contact with ozone.

Table 2-6: Reagents for CL-FIA (Chung et al., 1992).

1. Benzoflavin	5. Eosin Y
2. Acridine Yellow	6. Rhodamin B
3. Indigotrisulfate	7. Chromotropic acid
4. Fluorescein	

advantages:	continuous method
disadvantages:	This method is not easy to handle.

Membrane Ozone Electrode (Liquid)

Electrochemical (amperometric) techniques provide the possibility for in situ, continuous and automated measurements of ozone in the liquid. The membrane electrode usually consists of a gold cathode, a silver anode, an electrolyte (e. g. AgBr, K_2SO_4 or KBr) and a teflon membrane. Several companies offer such electrodes in different configurations. The application range and accuracy differs depending on the kind of electrode.

In the presence of ozone in water, ozone diffuses through the membrane into the reaction chamber. The rate of flow is dependent on the partial pressure of ozone. In order to avoid a depletion of ozone molecules at the surface of the membrane, the electrode should be immersed into a continuous flow.

At the gold cathode ozone is reduced into oxygen:

$$\text{cathode:} \quad O_3 + 2\,H^+ + 2\,e^- \rightarrow O_2 + H_2O \tag{2-5}$$

The electrons are produced at the anode by the following process:

$$\text{anode:} \quad 4\,Ag \rightarrow 2\,Ag^+ + 2\,e^- \tag{2-6}$$

Table 2-7: Overview of analytical methods.

Method	Gas	liquid	continuous method	detection limit	interferences	advantages↑/disadvantages↓	literature
Titrimetric							
Iodometric	+	+		100 µg L^{-1}	Cl_2, Br^-, Mn, H_2O_2, all oxidants with $E_o > 0.54$ eV	not expensive↑, no selectivity↓, time consuming↓	DIN 38406-G3-1**) IOA 001/87(F)
Photometric							
UV-Absorption	+	+	+	*)		easy and simple↑, aromatic components can disturb↓	IOA 002/87 (F) IOA 008/89 (F)
Indigo trisulfate		+	(+) FIA	5 µg L^{-1}	Cl_2, ClO_2, Br_2, Br^-	not expensive↑, relatively selective↑, fast reaction↑, stability of the sample after adding reagents < 4–6 h↑, secondary products do not interfere↑, need calibration↓, natural colour of water doesn't disturb↓	Bader and Hoigné, 1981**) DIN 38406-G3-3**) Hoigné and Bader, 1980**) IOA 006/89 (F) Standard methods, 1989
DPD		+	(+) FIA	20 µg L^{-1}	Cl_2, Br^-, Mn, H_2O_2, all oxidants with $E_o > 0{,}54$ eV	not expensive↑, no selectivity↓, stability of the sample after adding reagents < 5 min↓	DIN 38406-G3-2##) Gilbert, 1981**)
CL		+	+	2 µg L^{-1}	Cl_2, $H_2O_2 > 10$ mg/L $MnO_4^- > 2$ mg L^{-1} in the case of Indigo	not easy↓, susceptible↓	Chung et al., 1992
Amperometric				#)			
Electrode		+	+	6 -10 µg L^{-1}		selective↑, expensive↓	IOA 007/89(F) *Smart et al.*, 1979 Stanley and Johnson, 1979

#) detection limit and precision are depending on the systems

##) good description of the procedure

The result is a current conduction which is measured and proportional to the ozone concentration.

advantages:	continuous method
disadvantages:	high purchase price

2.4.2 Practical Aspects of Ozone Measurement

In order to evaluate the results of the experimental work, an ozone balance over the reactor is essential. Measurement of the ozone gas concentration in the in- and outlet of the reactor system as well as the liquid ozone concentration are necessary to complete the balance. This is true for both steady state and non-steady state systems. The monitoring of non-steady state systems, in which the concentrations change over time, requires more measurements.

Continuous analytical methods (amperometric and UV-absorption methods) are advantageous. However, sometimes only discontinuous methods (titrimetric and some photometric methods) are available due to expense. In such cases it is important to measure immediately after sampling to avoid the decay of ozone and in the case of liquid ozone to avoid degassing. Discontinuous photometric methods requiring the addition of chemicals to the sample can be converted to a continuous method by combination with flow injection analysis (FIA). This analytical technique requires instrumentation and is not easy to handle.

2.5 Safety Aspects

2.5.1 Vent Ozone Gas Destruction

Destruction of excess ozone in the vent gas is an essential safety precaution in every ozone system. The following techniques are applied: thermal ($T \geq 300$ °C) or catalytic (manganese or palladium, $T = 40$–80 °C) destruction. In small scale laboratory systems ozone can also be destroyed in packed column filled with granulated activated carbon ($d_P = 1$–2 mm). In large-scale systems with electrical discharge ozone generators the recycling of oxygen is a common standard today; in this case off-gas drying and -compression are additionally required. In lab-scale systems oxygen is normally not recovered.

Even in ELOG applications the evolution of very little but highly concentrated ozone gas is possible. During the *in-situ* ozone production, the liquid ozone concentration (c_L) can easily reach the solubility level, depending on the pressure (P) and temperature (T) in the cell. Out-gassing can easily occur due to oversaturation of the feed-water, especially when the pressure drops suddenly.

Possiblities of explosive gas mixtures exist. In full-scale ground or waste water applications for example, volatile organic compounds could be contained in the off gas. These compounds escape from the reactor due to comparatively high temperatures and condense in the off-gas piping. Care has to be taken to avoid explosive mixtures of these organics and the oxygen/ozone gas. In lab-scale systems, principally the same problem can occur with greasy valves or other equipment bearing organic 'contamination'.

2.5.2 Ambient Air Ozone Monitoring

Ambient air ozone monitoring coupled with an automatic ozone generator shut off device is recommended for every lab-scale application in order to ensure that the laboratory staff will not be harmed in case of leaks in the piping or reactor. Ozone analyzers measuring ozone at $\lambda = 254$ nm in the appropriate range (0.001–1.000 ppm) are supplied by several companies. When installing them, care has to be taken that the input gas-side of the analyzer is properly installed, e. g. the air being free of particles which could form a layer on the inner surface of spectrophotometric cell. Some systems need an ozone-free reference gas for on-line calibrating, which is normally achieved by sucking the ambient air through a small activated carbon filter.

Problems with shutting off the ozone generator at the legislatively required threshold level, e. g. the MAK-value (200 $\mu g\ m^{-3}$), might occur in case of higher ambient ozone concentrations due to summer smog. Sometimes the threshold values for a regular laboratory environment are lower than the actual ambient concentrations.

2.6 Common Questions, Problems and Pitfalls

The following section will be helpful to read before starting your own experiments. Since there is so much information available on ozone applications it is hard for the beginner to sort it into essential and unessential categories. Experience makes everything easier, usually it is paid for with energy and mistakes. Here are some of the things various experimenters would have found helpful to know before they started their work (Table 2-8). Everyone's list is individual depending on his or her background, but perhaps these points will help the beginner to minimize his or her mistakes.

The short answers in this list only provide an overview of the aspects to be considered. Details will be found in the cited Chapters or Sections of this book.

Table 2-8: Common questions, problems and pitfalls.

Problem or question	Aspects to be considered	Section
Define System		
Ozone generator (EDOG): Is it possible to produce every c_{Go} desired at constant Q_G?	No, this depends on the EDOG operation characteristics. Choose an appropriate generator!	B 2.2.1.2 Fig. 2-2
Ozone generator (ELOG): Is it possible to use an Electrolytical Cell Ozone Generator in waste water applications instead of an EDOG so that no mass transfer will be necessary?	No, normally not! The ELOG ozone production rates are rather small, the specific energy consumption is very high and the ELOG requires deionized water for its *in-situ* production of ozone.	B 2.2.2
Ozone reactor: Is it possible to use PVC?	Yes, but it is only recommended for waste water experiments.	B 2.1, B 2.1.2
Ozone reactor off-gas: Can the ozone containing off-gas be handled in a safe way?	Yes, a vent ozone destructor is necessary; several types are available. Beware of explosive mixtures of O_3/O_2-gas and certain organics. Apply a water-filled gas trap after the ozone destructor. This makes it easy to visually control the gas-flow or detect leaks. It furthermore 'smoothes' the gas-flow, due to the back pressure of the liquid (height).	B 2.5
Off-gas ozone destruction: Is it also necessary to have an ozone destructor in the system when using an ELOG?	Yes, ozone can desorb from the water being ozonated due to over-saturation and appear in the reactor off-gas.	B 2.5
Ambient air ozone monitor: Is it necessary to check the ambient air ozone concentration in the lab?	Yes, it is highly recommended to control the lab environment and connect the monitor to the ozone generator so that the ozone production will be shut off in case of leakage in the system	B 2.5
Materials in three-phase systems: Can every solvent or solid be used?	No! Make sure that the solvent is immiscible with water, non-volatile and non-toxic. Solvents as well as solids must be inert against ozone attack, which some are not (e. g. if the material contains C-C-double bonds they will be readily destroyed by ozone)	B 6.3
Select Analytical Method		
Assess correct $c(M)$: How can unwanted reactions in the sample be stopped?	Ozone has to be destroyed (quenched) by using NaS_2O_3.	B 2.4
Assess correct c_L: Can amperometric probes be used in the ozonation of waste water?	Yes, but often a lot of maintenance is required. A comparison of the measured data with data gathered simultaneously with the indigo method is strongly recommended.	B 2-4
	Particles, oil, emulsifiers or colored compounds in the waste water will disturb the measurement.	B 6.3
Determine Procedure		
Ozone generator (EDOG): Can an EDOG be operated at very small gas flow rates Q_G?	No, EDOGs normally need a minimum gas flow rate $Q_{G,min}$, below this, c_{Go} might vary considerably. An experiment with constant operation parameters will be difficult to obtain. It is recommended to avoid this region!	B 2.2.1.2

Table 2-8: continued

Problem or question	Aspects to be considered	Section
Optimization of mass transfer:) Should k_La be optimized by varying Q_G? (especially important in systems where mixing is exclusively provided by the gas flow rate, e. g. bubble columns, where Q_G is the only variable parameter)	No, in systems employing an EDOG (at a constant ozone production rate) two parameters will change at the same time and cause adverse effects on the oxidation-rate: an increase in Q_G normally increases k_La, but decreases c_{G0}	B 2.2.1.2
Use of scavengers: Can *tert*-butyl alcohol (TBA) be applied without constraints in reaction kinetic measurements?	No, TBA influences the k_La-value considerably (*alpha* factor).	B 3.2.2
Ozone decay: Is it necessary to know the ozone decay rate (exactly) in waste water treatment studies?	No, not in every case. Often the reactions of ozone with organic compounds occur in the liquid film (fast reactions), so that c_L is (approx.) zero and ozone decay cannot occur. Generally, measure the dissolved ozone concentration c_L!	B 3.2, B 4
pH control in the ozone reactor: What can be done to prevent a pH-drop (due to the production of organic acids) in the ozonated water?	In batch tests buffers are normally used. They keep the pH very stable, but induce a higher ionic strength in the water compared with no buffer. Remember side-effects when using a buffer solution: buffers contain substances that influence the radical chain reactions (phosphates!) or the k_La (e. g. high concentrations of sulfates); keep their concentration as low as possible! Especially conduct k_La-measurements with the same buffer solution (without compound (M))! In continuous-flow experiments a feasible way is to apply a pH-control unit which continuously doses NaOH. The slight scatter of the pH normally observed will not negative influence on the oxidation results.	A 3, B 3, B 4.4
Stoichiometric factor z: Which method should be applied for determining the stoichiometry of a direct reaction between ozone and compound (M)?	The following method is proposed: dissolve compound M as well as ozone in independent vessels, mix the two solutions making sure that $c(M)_0 \geq 4–10\ c_{L0}$ and let them react until ozone is completely used. Define z as mol O_3 per mol M eliminated; sometimes it is defined inversely!	–
Evaluate Data and Assess Results		
Use of reaction kinetic data from the literature: Are kinetic data (e. g. $k_D(M)$) from the literature useful for comparisons with my own data and may they be used for predictions of my own results?	Yes, if all data necessary to describe the entire process have been assessed and reported; comparisons are only possible on this basis. Consider that mass transfer might influence the (apparent) disappearance kinetics of M in the specific system. Keep in mind, that the k_D (and k_R) values do not take into account the effect of mass transfer enhancement on the removal rate of M ($r(M)$). In general, predictions require good models.	B 1 B 4 B 3.2 B 5

Table 2-8: continued

Problem or question	Aspects to be considered	Section
Explanation of widely varying compound removal rates (*r*(*M*)): What are the reasons for the wide variations in *r*(*M*) frequently being observed in different studies on the (semi-batch) ozonation of one and the same compound?	Mass transfer with simultaneous reactions is a complex matter. Most probably, the results reported were obtained in systems where mass transfer was limiting the oxidation to different extents. Mass transfer might have been enhanced by the reactions and/or the reactions might have occurred in different kinetic regimes.	B 3.2
Calculate mass transfer: Is it advisable to use k_La-values calculated purely from the literature?	No, this is not advisable at all! Use the literature (and this book) to screen the ranges and measure it in the actual system with the actual (waste) water!	B 3.2 B 3.3
Assess mass transfer correctly: Are there any influences on k_La, which are often forgotten before starting the experiments?	Yes, the influence of chemical factors is often forgotten, although it cannot be neglected. A general problem arises from the fact that k_La-measurements are normally performed with "pure" water and not with the actual water under consideration. Be especially aware of the action of	B 3.2.2
	1. surface-active compounds, e. g. phenols, TBA, surfactants etc.	B 3.2.2
	2. 'unimportant' compounds being not oxidizable by molecular ozone, but influencing gas-dispersion in the reactor, e. g. sulfates in buffer solutions which hinder bubble coalescence and increase k_La.	
	The enhancement factor *E* was defined to assess mass transfer enhancement due to (ozone) gas absorption into a liquid accompanied by simultaneous reaction	B 3.2 Fig. B 3-5

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3 Mass Transfer

Ozone, a gas at standard temperature and pressure, is normally generated with electrical power from the oxygen in air or, especially when high concentrations are needed, from pure gaseous oxygen. Consequently, the ozone containing gas has to be brought into contact with the water or waste water to be ozonated. An efficient mass transfer from gas to liquid is required.

This chapter will first provide some basics on ozone mass transfer, including theoretical background on the (two-) film theory of gas absorption and the definition of over-all mass transfer coefficients K_La (Section B 3.1) as well as an overview of the main parameters of influence (Section B 3.2). Empirical correction factors for mass transfer coefficients will also be presented in Section B 3.2. These basics will be followed by a description of the common methods for the determination of ozone mass transfer coefficients (Section B 3.3) including practical advice for the performance of the appropriate experiments. Emphasis is laid on the design of the experiments so that true mass transfer coefficients are obtained.

3.1 Theory of Mass Transfer

When material is transferred from one phase to another across a separating interface, resistance to mass transfer causes a concentration gradient to develop in each phase (Figure 3-1).

Lewis and Whitman (1924) proposed that this resistance to mass transfer across an interface is the sum of the resistances in each phase. They called this concept the two-film theory. As Treybal (1968) pointed out, their two-film theory does not depend on which model is used to describe the mass transfer in each phase, therefore, the "two-resistance" theory would be a more appropriate name. It would also cause less confusion, since the names: *film theory* (mass transfer in one phase) and *two-film theory* (mass transfer between

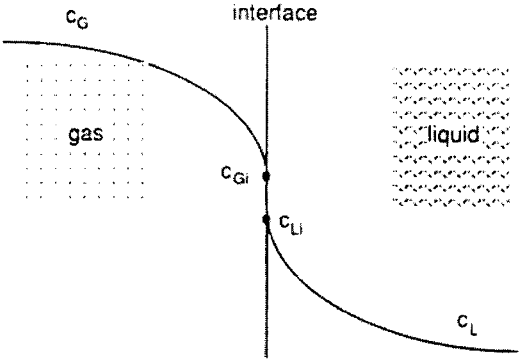

Figure 3-1: Concentration gradients at the interphase between gas and liquid.

two phases) are so similar. The following section first discusses mass transfer in one phase before returning to mass transfer between two phases, i. e. the "two-resistance" theory in (Section B 3.2).

3.1.1 Mass Transfer in One Phase

The resistance in each phase is made up of two parts: the diffusional resistance in the laminar film and the resistance in the bulk fluid. All current theories on mass transfer, i. e. film, penetration, and surface renewal assume that the resistance in the bulk fluid is negligible and the major resistance occurs in the laminar films on either side of the interface (Figure 3-2). Fick's law of diffusion forms the basis for these theories proposed to describe mass transfer through this laminar film to the phase boundary.

The theories vary in the assumptions and boundary conditions used to integrate Fick's law, but all predict the film mass transfer coefficient is proportional to some power of the molecular diffusion coefficient D^n, with n varying from 0.5 to 1. In the film theory, the concentration gradient is assumed to be at steady state and linear, (Figure 3-2) (Nernst, 1904; Lewis and Whitman, 1924). However, the time of exposure of a fluid to mass transfer may be so short that the steady state gradient of the film theory does not have time to develop. The penetration theory was proposed to account for a limited, but constant time that fluid elements are exposed to mass transfer at the surface (Higbie, 1935). The surface renewal theory brings in a modification to allow the time of exposure to vary (Danckwerts, 1951).

Postulating that n is dependent on the turbulence in the system, Dobbins (1956) proposed that under sufficiently turbulent conditions, n approaches 0.5 (surface renewal or penetration theory), while under laminar or less turbulent conditions n approaches 1.0 (film theory). Thus, the selection of the value for n to predict the mass transfer coefficient should depend on the degree of turbulence in the system:

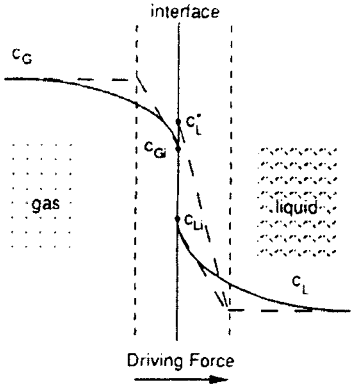

Figure 3-2: Two-film or two-resistance theory with linear concentration gradients (Lewis and Whitman, 1924).

$$k \propto D^n \tag{3-1}$$

k = film mass transfer coefficient
D = molecular diffusion coefficient
n = 0.5–1.0; depending on system turbulence

The mass transfer flux N out of one phase is the product of the film coefficient and the concentration gradient in the film, and is equal to the flux into the second phase:

$$N = k_G\,(c_G - c_{Gi}) = k_L\,(c_{Li} - c_L) \tag{3-2}$$

The concentrations of the diffusing material in the two phases immediately adjacent to the interface c_{Li}, c_{Gi} are generally unequal, but are usually assumed to be related to each other by the laws of thermodynamic equilibrium (see Section B 3.1.3).

In order to calculate the specific mass transfer rate into the liquid, mass per unit time and unit volume, the specific surface area, a, defined as transfer surface area per volume of liquid, is needed in addition to k_L.

$$m = k_L\,a\,(c_{Li} - c_L) \tag{3-3}$$

m = specific mass transfer rate
$a = \dfrac{A}{V_L}$ = volumetric interfacial area.
V_L = volume of liquid

The transfer interface produced by most of the mass transfer apparatus considered in this book is in the form of bubbles. Measuring the surface area of swarms of irregular bubbles is very difficult. This difficulty in determining the interfacial area is overcome by not measuring it separately, but rather lumping it together with the mass transfer coefficient and measuring k_La as one parameter.

3.1.2 Mass Transfer Between Two Phases

The experimental determination of the film coefficients k_L and k_G is very difficult. When the equilibrium distribution between the two phases is linear, over-all coefficients, which are more easily determined by experiment, can be used. Over-all coefficients can be defined from the standpoint of either the liquid phase or gas phase. Each coefficient is based on a calculated over-all driving force Δc, defined as the difference between the bulk concentration of one phase (c_L or c_G) and the equilibrium concentration (c_L^* or c_G^*) corresponding to the bulk concentration of the other phase. When the controlling resistance is in the liquid phase, the over-all mass transfer coefficient K_La is generally used:

$$m = k_Ga\,(c_G - c_{Gi}) = k_La\,(c_{Li} - c_L) = K_La\,(c_L^* - c_L) \tag{3-4}$$

c_L^* = liquid concentration in equilibrium with the bulk gas concentration.

This simplifies the calculation in that the concentration gradients in the film and the resulting concentrations at the interface (c_{Li} or c_{Gi}) need not be known.

3.1.3 Equilibrium Concentration for Ozone

For dilute non-reacting solutions, Henry's Law is used to describe the linear equilibrium distribution of a compound between the bulk liquid and gas phases (Figure 3-3):

$$H_C = \frac{c_G - c_{Gi}}{c_L^* - c_{Li}} = \frac{c_{Gi} - c_G^*}{c_{Li} - c_L} \tag{3-5}$$

H_C = dimensionless Henry's Law constant

if the function passes through the origin, it simplifies to

$$H_C = \frac{c_{Gi}}{c_{Li}} = \frac{c_G^*}{c_L} = \frac{c_G}{c_L^*} \tag{3-6}$$

and the equilibrium concentration c_L^* or c_G^* can be calculated from H_C and the bulk concentration.

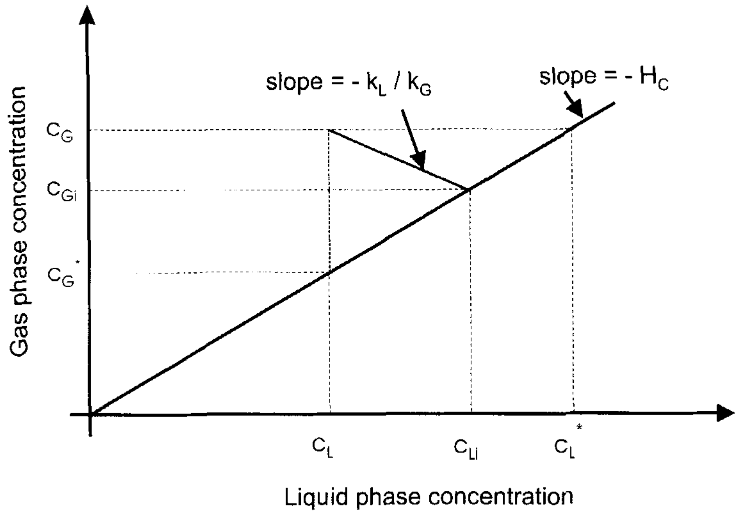

Figure 3-3: Over-all and interfacial concentration differences (after Sherwood et al., 1975).

Table 3-1: Equilibrium distribution of ozone, definitions and calculations.

Parameter	Definition	Equation (T in [K])
Bunsen coefficient β (dimensionless)	Normal Volume of ozone (calculated for STP) dissolved per volume of water at *T*, when the partial pressure of ozone in the gas phase is one standard atmosphere (= 101 325 Pa)*	$\beta = \frac{V_G}{V_L}$ $\beta = \frac{(273.15\ \mathrm{K} / T)}{H_C} = s \cdot (273.15\ \mathrm{K} / T)$
Solubility ratio *s* (dimensionless)	The ratio of the equilibrium liquid concentration to the ozone concentration in the gas (function of *T*)	$s = \frac{c_L^*}{c_G}$ $s = \frac{1}{\mathrm{H_C}} = \frac{c_L^*}{c_G}$
Henry's Law constant $\mathrm{H_c}$ (dimensionless)	The ratio of the ozone concentration in the gas to the equilibrium concentration in the liquid (inverse of the solubility ratio, *s*; function of *T*)	$\mathrm{H_C} = \frac{c_G}{c_L^*}$ $\mathrm{H_C} = \frac{1}{s} = \frac{c_G}{c_L^*}$
Henry's Law constant H (dimensional) [atm (mol fraction)$^{-1}$ or atm L mol^{-1}]	Relation between the ozone partial pressure in the gas and the molar dissolved ozone concentration in equilibrium (also named Henry's Law parameter)	$\mathrm{H} = \frac{p(O_3)}{c_L^*}$ $\mathrm{H} = \frac{p(O_3)\ \mathrm{H_C}}{c_G} = \frac{p(O_3)}{c_L^*\ s}$

* also meaning: the solubility of a gas in a liquid is directly proportional to its partial pressure in the gas above the liquid.

The concept of equilibrium distribution is another area where names can cause much confusion. The equilibrium distribution of a compound between the gas and liquid phase has been expressed in various forms, i. e. Bunsen coefficient β, solubility ratio s, Henry's Law constant expressed dimensionless H_C, or with dimensions H. These are summarized in along with equations showing the relationships between them. Another more general term to describe the equilibrium concentrations between two phases is the partition coefficient, denoted by K. It is often used to describe the partitioning of a compound between two liquid phases.

Not only have various names been used for the same concept, Morris (1988) found a variety of values for the equilibrium concentration of ozone in water reported in the literature. Based on the data from more than nine authors, he suggested that a linear correlation between the solubility ratio of ozone, s (which is the inverse of the dimensionless Henry's Law constant $\mathrm{H_C}$), and the temperature can be used as a first estimate for the solubility of ozone in water:

$$\log_{10} s = -0.25 - 0.013\ T\,[°C] = 3.302 - 0.013\ T\ [K] \tag{3-7}$$

He cautions that the correlation may underestimate the true solubility, since due to ozone decomposition (depending on ionic strength μ as well as the type of ions (see below) and

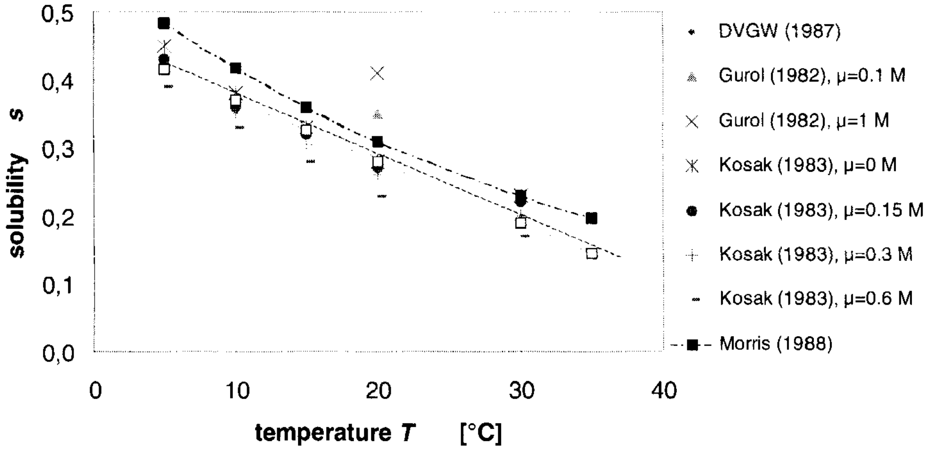

Figure 3-4: Ozone solubility *s* as a function of the fluid temperature (T = 5–35 °C).

temperature) some authors might have failed to achieve true equilibrium or steady state in their work. However, in comparison with other data his correlation obviously generates comparatively high values (Figure 3-4).

At $T = 20$ °C the aqueous solubility of ozone is about one third of the gas-phase concentration seven times higher than that of oxygen! However, we must consider that the gas does not contain pure ozone, but rather approximately 20 % wt O_3 in O_2 (corresponding to $c_G = 320.1$ g m^{-3} at STP, cf. Table B 1-5), which can be achieved with modern electrical discharge ozone generators at standard pressure. Thus, the equilibrium concentration of ozone in the liquid is usually less than $c_L^* = 108$ g m^{-3}.

A more comprehensive analysis of the influences on the ozone solubility was made by Sotelo et al., (1989). The Henry's Law constant H was measured in the presence of several salts, i. e. buffer solutions frequently used in ozonation experiments. Based on an ozone mass balance in a stirred tank reactor and employing the two film theory of gas absorption followed by an irreversible chemical reaction (Charpentier, 1981), equations for the Henry's Law constant as a function of temperature, pH and ionic strength, which agreed with the experimental values within ± 15 % were developed (Table 3-2). In this study, much care was taken to correctly analyse the ozone decomposition due to changes in the pH as well as to achieve the steady state experimental concentration at every temperature in the range considered (0°C $\leq T \leq$ 20 °C). Both values were used to calculate the true equilibrium concentration.

The equations developed by Sotelo et al. (1989) are recommended for general use. As an example, in a sodium phosphate solution of $\mu = 0.15$ mol L^{-1}, at $T = 20$ °C, pH = 7, and $p(O_3) = 0.5$–3.5 kPa, the Henry's Law constant averaged H = 5.577 ± 0.2466 kPa (mol fr.)$^{-1}$ and the ozone decomposition rate was assumed to be of second order ($n = 2$). Sulfate ions were shown to have practically no influence on the ozone solubility. It is, however, important to keep in mind that they may considerably influence the gas/liquid mass transfer of ozone due to the hindrance of bubble coalescence.

Table 3-2: General equations for the dimensional Henry's Law constant H [kPa (mol fr.)$^{-1}$] (after Sotelo et al., 1989).

Type of Salt in Solution	Henry's Law Constant H [kPa (mol fr.)$^{-1}$]	T [°C]	pH [-]	Ionic Strength μ [mol L^{-1}]
Na_3PO_4	$H = 1.03 \cdot 10^9 \, e^{\left(\frac{-2,118}{T}\right)} e^{(0.961 \cdot \mu)} \cdot c_{OH^-}^{0.012}$	0–20	2–8.5	$10^{-3} - 10^{-1}$
Na_3PO_4 and Na_2CO_3	$H = 4.67 \cdot 10^7 \, e^{\left(\frac{-1,364.5}{T}\right)} e^{(2.98 \cdot \mu)}$	0–20	7.0	$10^{-2} - 10^{-1}$
Na_2SO_4	$H = 1.76 \cdot 10^6 \, e^{(0.033 \cdot \mu)} \cdot c_{OH^-}^{0.062}$	20	2–7	$4.9\ 10^{-2} - 4.9\ 10^{-1}$
NaCl	$H = 4.87 \cdot 10^5 \, e^{(0.48 \cdot \mu)} \cdot c_{OH^-}^{0.012}$	20	6.0	$4.0\ 10^{-2} - 4.9\ 10^{-1}$
NaCl and Na_3PO_4	$H = 5.82 \cdot 10^5 \, e^{(0.42 \cdot \mu)}$	20	7.0	$5.0\ 10^{-2} - 5.0\ 10^{-1}$

3.1.4 Two-Film Theory

The connection between the film mass transfer coefficients and the over-all mass transfer coefficients is provided by the two-film theory from Lewis and Whitman (1924): the total resistance to mass transfer is the sum of the resistances in each phase.

$$R_T = R_L + R_G = \frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{H_C \cdot k_G a} \tag{3-8}$$

Rearranging equation 3-8 yields an equation relating the over-all mass transfer coefficient to the individual film coefficients:

$$K_L a = \frac{k_L a}{1 + \dfrac{k_L a}{k_G a \cdot H_C}} = k_L a \, \frac{R_L}{R_T} \tag{3-9}$$

R_T = total resistance
R_L = liquid phase resistance
R_G = gas phase resistance.

In cases where the major resistance is in the liquid phase, the ratio $R_L / R_T \cong 1$ and the simplification can be made that the over-all coefficient is equal to the liquid film coefficient. Which resistance dominates has to be determined from the ratio $k_L a$ / ($k_G a$ H_C) (Table 3-3). For compounds with a low H_C such as semi-volatile organic compounds, both resistances can be important (Libra, 1993). In oxygen transfer the liquid-side resistance dominates and $K_L a = k_L a$. This is also true for most of the cases in ozone mass transfer, unless there is strong mass transfer enhancement by very fast or *instantaneous* reactions of

Table 3-3: Mass Transfer Control.

When ... (ratio of individual mass transfer coefficients and Henry's Law constant)	then ... (over-all mass transfer coefficient defined by)	mass transfer controlled by ...
$k_La << k_Ga\, H_C$	$K_La = k_La$	liquid side resistance only
$k_La \cong k_Ga\, H_C$	$K_La \cong k_La\, R_L / R_T$	liquid and gas phase resistance

ozone with a dissolved compound in the film or at the gas/liquid interface (this question is discussed elsewhere, Section B 3.2). Therefore, normally no information about k_Ga is needed.

3.2 Parameters that Influence Mass Transfer

Many parameters affect the mass transfer between two phases. As we discussed above, the concentration gradient between the two phases is the driving force for the transfer and this, together with the over-all mass transfer coefficient, determines the mass transfer rate. The influence of process parameters (e. g. flow rates, energy input) and physical parameters (e. g. density, viscosity, surface tension) as well as reactor geometry are summed up in the mass transfer coefficient. The important parameters for K_La in stirred tank reactors are:

$$K_La = f\left(\frac{P}{V_L}, v_S; g, v_L, \rho_L, v_G, \rho_G, D_L, \sigma_L, Si, H_C;\ \text{reactor geometry}\right) \quad (3\text{-}10)$$

process parameters
P = power
V_L = reactor volume
v_S = superficial gas velocity
g = gravitational constant

physical parameters
ν = kinematic viscosity
ρ = density
σ = surface tension
Si = coalescence behaviour of the bubbles
D = diffusion coefficient

However, the mass transfer rate can be influenced not only by physical properties, but by chemical reactions as well. Depending on the relative rates of reaction and mass transfer, a chemical reaction can change the ozone concentration gradient that develops in the laminar film, normally increasing the mass transfer coefficient, which in turn increases the mass transfer rate.

3.2.1 Mass Transfer with Simultaneous Chemical Reactions

An enhancement factor E has been defined to describe the increase in mass transfer due to a simultaneous reaction:

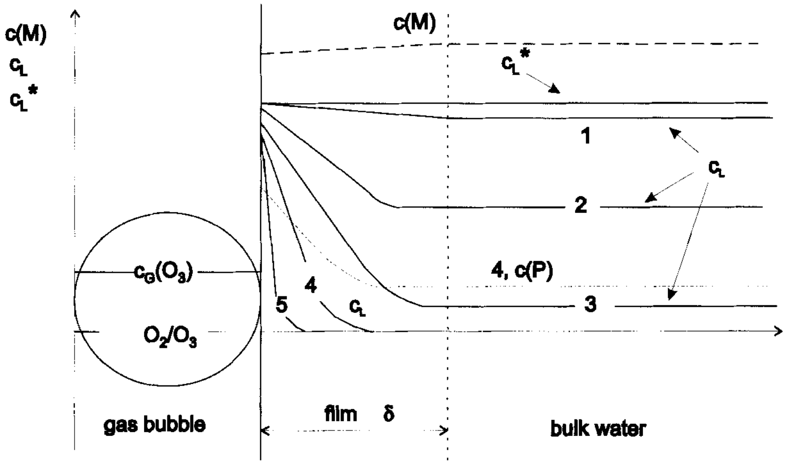

Figure 3-5: The different kinetic regimes for mass transfer with simultaneous reaction (of ozone).

$$E = \left(\frac{\text{rate with reaction}}{\text{rate for mass transfer alone}} \right) = \frac{r(O_3)}{k_L a (c_L^* - c_L)} \tag{3-11}$$

The degree of enhancement depends upon the relative concentration of reacting compounds in each phase, their solubility, and relative resistance of the mass transfer and reaction steps. We can visualize this by considering a reactor with a certain mass transfer rate due to physical absorption, into which we introduce various compounds (Figure 3-5). If we introduce a slow reacting compound where no mass transfer enhancement occurs, a concentration profile similar to (1) will develop in the film and bulk liquid. A compound which reacts more readily with ozone can develop a fast or instantaneous reaction causing gradient (4) or (5) to develop. Oxidation products P are formed in the film and diffuse out into the bulk (4). In between we have the moderate regime (2) and (3). As the kinetic regime goes from slow to moderate, fast or instantaneous, the concentration gradient becomes steeper and the reaction moves further into the film. The kinetic regime (or region) can also be changed by changing the concentration of the reactants. To simplify the discussion, both the concentration of organic pollutants $c(M)$ in the liquid film and ozone in the gas phase are assumed to remain constant for all cases. This is true if the molar $c(M)$ is relatively high compared to the molar c_L. However, in batch reactors for example both concentrations will change with the reaction time, since the pollutant concentration decreases as ozonation continues, while due to a smaller ozone consumption the liquid bulk concentration of ozone will increase.

In the following discussion the four most important regimes are briefly explained in order to outline which step is rate controlling for the removal of the pollutants and which practical situation it represents. An in-depth mathematical description of these situations is beyond the scope of this book, and the reader is referred to further literature. The fundamentals of fast gas-liquid reactions were first described by Hatta (1931). Detailed descriptions were published by Charpentier (1981), Levenspiel (1972), Levenspiel and Godfrey (1974). Beltrán and coworkers were the first to apply this model to the ozonation of waste water (Beltrán et al., 1992 a, b, c; Beltrán et al., 1995) and a comprehensive work was published by Stockinger (1995).

Regime 1 – *(very) slow reactions developing entirely in the liquid bulk*: The mass transfer rate is (very) high and/or ozone reacts (very) slowly with the pollutants. A small difference between the solubility level of ozone c_L^* and the bulk liquid ozone concentration c_L is sufficient for ozone transfer into the liquid along the linear concentration gradient. Besides the general influences of pressure and temperature, the over-all rate of ozone consumption and thus, the reaction rate of the pollutant M, is exclusively influenced by *chemical parameters*, e. g. the concentrations of ozone and pollutants, pH, and the structure of the pollutant molecule. The reaction is controlled by chemical kinetics. This situation is often found in drinking water ozonation, where (very) small concentrations of M react with ozone at considerably slow rates. Even ozone decay, when predominately initiated by a high pH, develops in this region (Metha et al., 1989). Mass transfer is independent of chemical reaction and both k_La and k_D can be determined independently.

Regimes 2 *and* 3 – *moderate reactions in the bulk* (2) *or in the film* (3) *and fast reactions in the bulk* (3): For higher reaction rates and/or lower mass transfer rates, the ozone concentration decreases considerably inside the film. Both chemical kinetics *and* mass transfer are rate controlling. The reaction takes place inside *and* outside the film at a comparatively low rate. The ozone consumption rate within the film is lower than the ozone transfer rate due to convection and diffusion, resulting in the presence of dissolved ozone in the bulk liquid. The enhancement factor E is approximately one. This situation is so "intermediate" that it may occur in almost any application, except those where the concentration of M is in the micropollutant range. No methods exist to determine k_La or k_D in this regime.

Regime 4 – *fast reactions in the film*: In region 4 ozone is entirely consumed inside the liquid film, so that no ozone can escape to the bulk liquid, i. e. $c_L = 0$. Here, the enhancement factor is defined as:

$$E = \frac{r(O_3)}{k_La\ c_L^*} \quad \text{and} \quad 1 < E < 3 \qquad (3\text{-}12)$$

The simplified concentration gradient shown in Figure 3-5 or $c(M)$ is no longer valid. It decreases sharply inside the film, however, it levels off, yielding $\mathrm{d}c(M)/\mathrm{d}x = 0$ at the gas-liquid interphase (Charpentier, 1981). Due to the reactions in the film, oxidation products are formed, which diffuse out of the film along the concentration gradient $c(P)$. If k_La is known and a pseudo-first order reaction can be verified, the reaction rate constant $\mathrm{k_D}$ for the direct reaction of ozone with the pollutant M can be experimentally determined. This procedure has been extensively exploited by Beltrán and co-workers for various fast-reacting organic compounds, such as phenolics or dyes (e. g. Beltrán et al., 1992 c and 1993 or Beltrán and Alvarez, 1996), for which the determination of $\mathrm{k_D}$ is very difficult in *homogenous* systems.

Regime 5 – instantaneous reactions at an reaction plane developing inside the film: For very high reaction rates and/or (very) low mass transfer rates, ozone reacts immediately at the surface of the bubbles. The reaction is no longer dependent on ozone transfer through the liquid film k_L or the reaction constant k_D, but rather on the specific interfacial surface area a and the gas phase concentration. Here the resistance in the gas phase may be important. For lower $c(M)$ the reaction plane is within the liquid film and both film transfer coefficients as well as a can play a role. The enhancement factor can increase to a high value: $E >> 3$.

If a reaction develops in this kinetic regime due to appropriate choice of $c(M)$ and c_G, this situation can be used to determine the k_La-value of the system, or if the specific interfacial surface a in the reactor is known (e. g. from independent measurements) k_L can be determined. This method has been used in combination with fast direct reactions of organic compounds with ozone to determine both k_La and k_D (Beltrán and Alvarez, 1996; Beltrán et al., 1993; see also Section B 3.3).

Mass transfer in most drinking water treatment processes generally occurs in regime 1, with (very) slow reaction rates. The concentration of pollutants and consequently the oxidation rates are very low. The process is completely controlled by chemical kinetics. In waste water treatment, the concentration of pollutants is often higher by a factor of 10 or more. In this case, ozonation takes place in regime 4 or 5, with considerable mass transfer limitation. This has to be considered in the kinetics of waste water ozonation.

A convention used in most literature on ozone mass transfer and in the rest of this book is to define the mass transfer coefficient as the one that describes the mass transfer rate without reaction, and to use the enhancement factor E to describe the increase due to the chemical reaction. Furthermore, the simplification that the major resistance lies in the liquid phase is used throughout the rest of the book. This is also based on the assumption that the mass transfer rate describes physical absorption of ozone or oxygen, since the presence of a chemical reaction can change this. This means that $K_La = k_La$ and the concentration gradient can be described by the difference between the concentration in equilibrium with the bulk gas phase c_L^* and the bulk liquid concentration c_L. So the mass transfer rate is defined as:

$$m = E \cdot k_La\ (c_L^* - c_L) \tag{3-13}$$

3.2.2 Predicting the Mass Transfer Coefficient

Correlations based on dimensional analysis with the above variables in equation 3-10 would allow mass transfer rates to be easily predicted, e. g. in scaling-up lab results to full-scale or for changes in the liquid properties. However, no correlations have been developed with this complexity.

Scale-up factors have been developed for changes in density, viscosity, surface tension and correlations using these factors have been successful for certain reactor geometries, i. e. stirred tank reactors, and well defined systems, i. e. air/water (Zlokarnik, 1978):

$$k_L a\left(\frac{\nu_L}{g^2}\right)^{\frac{1}{3}} = f\left(\left[\frac{P}{V_L\,\rho_L\,(g^4\nu_L)^{\frac{1}{3}}}\right];\left[\frac{v_S}{(g\,\nu_L)^{\frac{1}{3}}}\right];\ \mathrm{Sc};\ \frac{\rho_G}{\rho_L};\ \frac{\nu_G}{\nu_L};\ \sigma^*;\ \mathrm{Si}^*\right) \qquad (3\text{-}14)$$

where:

Sc = Schmidt number, $\frac{\nu}{D}$

σ^* = dimensionless surface tension, $\frac{\sigma}{\rho_L(\nu^4 g)^{\frac{1}{3}}}$

Si^* = coalescence number, not yet defined.

Similar factors have been developed for bubble columns, which includes the concept of gas hold-up ε_G, the fraction of the reactor liquid volume occupied by the gas dispersed in the liquid phase. The number of such factors can be reduced when comparing the mass transfer of just one compound in the same liquid/gas system, e. g. for oxygen or ozone transfer in clean water/air systems the above relationship reduces to the first three terms.

Some useful correlations which can be used for a first approximation of the k_La's or ε_G's in laboratory-scale ozone reactors can be found in Dudley (1995) for bubble columns, and Libra (1993) for STRs. Various correlations found in the literature, empirical as well as those based on theoretical or dimensional analysis, have been compared to results from their own experiments. Dudley concluded that correlations based on theoretical support performed better than those developed by curve-fitting.

Although, constituents in water may not effect a noticeable change in density or viscosity, they may drastically change the mass transfer coefficient due to changes in surface tension or bubble coalescence behavior for which no reliable correlations exist. Empirical correction factors have been introduced to deal with this problem (Stenstrom and Gilbert, 1981), two of which are discussed below in detail. In general, these empirical correction factors are used to "correct" the mass transfer coefficient measured in clean water for temperature changes Θ, or matrix changes α.

The disadvantages of using empirical correction factors, which lump many parameters together, becomes clear when one considers that α and Θ have been found to change depending on not only the concentration and type of contaminants, but also on the hydrodynamics of the system. Clearly, a better understanding of the relationship between physical properties and k_La and the quantification of these physical properties in (waste-)water is necessary, so that correlations based on dimensional analysis can be made. However, from the practical point of view, the empirical correction factors have proven their worth, when measured and used appropriately.

The empirical correction factors are developed from comparing two mass transfer coefficients, thus, it is essential that both are measured correctly. Brown and Baillod (1982) point out that the α value from the ratio of two incorrectly measured mass transfer coefficients, apparent mass transfer coefficients, is different from the α of true mass transfer coefficients.

theta Factor – Temperature Correction Factor

Temperature affects all the physical properties relevant in mass transfer: viscosity, density, surface tension, and diffusivity. The empirical factor most often used to account for temperature changes in all these parameters is the *theta* factor, Θ,

$$k_L a_{20} = k_L a_T \cdot \Theta^{(20-T)} \tag{3-15}$$

$k_L a_{20}$ = $k_L a$ at 20°C
$k_L a_T$ = $k_L a$ at temperature T (°C)
Θ = temperature correction factor.

In reviewing the literature on temperature corrections, Stenstrom and Gilbert (1981) found values for Θ range from 1.008 to 1.047, and suggested $\Theta = 1.024$ should be used, representing an accuracy of ± 5 %.

alpha Factor – (Waste-)Water Composition Correction Factor

Historically, the *alpha* factor, α, was developed from oxygen mass transfer studies in the aerated basins of municipal waste water treatment plants. It thus denotes the ratio of the mass transfer coefficient for oxygen measured in the waste water (WW) to that measured in tap water (TP).

$$\alpha_{O2} = \frac{k_L a_{WW}}{k_L a_{TP}} \tag{3-16}$$

More generally speaking, it denotes the ratio of the $k_L a$ measured in a "dirty" water for certain conditions, i. e. energy input, reactor geometry etc. compared to that found in "clean" water, meaning almost free of any organic or inorganic contamination, under the same conditions. In waste water the constituents in the liquid phase are highly variable depending on its source. Little to no changes in density or viscosity may be measured, but the mass transfer coefficient for oxygen may be drastically changed, e. g. by more than a factor of two to three (Gurol and Nekouinaini, 1985; Stenstrom and Gilbert, 1981). This change may be due to changes in surface tension or bubble coalescence behavior, and may as well – interdependently – influence or be influenced by the hydrodynamic conditions of the system.

3.2.3 Influence of (Waste-)Water Constituents on Mass Transfer

The possible changes in the mass transfer rate due to changes in the composition of the (waste-) water must be considered when performing experiments with the intent to scale-up the results. Examples are given below to illustrate which compounds can affect the mass transfer coefficient and to which degree. The effects can be generally divided into changes in the bubble coalescence or in surface tension. It is important to keep in mind, though, that if the compounds react with ozone, not only are the hydrodynamics of the system dependent on the type of reactor used, but also their concentration in the reactor. The changes in the mass transfer rate in a CFSTR, in which the reactor concentration is equal to the effluent concentration, will be very different from those found in a batch reactor.

Change in Bubble Coalescence

Substituted phenols as well as phenol itself are typical constituents of (bio-)refractory waste waters and can increase $\alpha(O_2) > 3$ (Gurol and Nekouinaini, 1985). They studied the influence of these compounds in oxygen transfer measurements and attributed this effect to the hindrance of bubble coalescence in bubble swarms, which increases the interfacial area *a*. When evaluating the effect of these phenols on the ozone mass transfer rate, it is important to note that these substances react fast with ozone (direct reaction, $k_D = 1.3\ 10^3$ L mol^{-1} s^{-1}, pH = 6–8, T = 20 °C, Hoigné and Bader, 1983 b).

The same effect was also observed for *tertiary* butyl alcohol (TBA), a substance which is frequently used as a radical scavenger in kinetic experiments (see Section B 4.4). Depending on its concentration ($c(TBA)$ = 0–0.6 mM) *alpha* values up to $\alpha(O_2) = 2.5$ were measured (Gurol and Nekouinaini, 1985). Since TBA is hard to oxidize by molecular ozone in contrast to phenols (k_D(TBA) ≈ 3 10^{-3} L mol^{-1} s^{-1}, pH = 7, Hoigné and Bader, 1985), the effect of TBA on k_La can also be studied in mass transfer experiments with ozone.

The hydrodynamic conditions in the reactor system play a large role in coalescence. Bubbles coalesce if the contact time between the bubbles is larger than the coalescence time (Drogaris and Weiland, 1983). Since different reactors have different available contact times, the degree of coalescence inhibition produced by a certain concentration of an organic compound depends on the type of reactor and aerator used. The greater the possibility of coalescence, the greater the effect. Due to a generally higher tendency for bubble coalescence at higher gas flow rates, *alpha* factors in the presence of these compounds have been found to increase with increasing gas flow rates (Gurol and Nekouinaini, 1985).

The importance of a correct evaluation of $k_La(O_3)$ or $k_La(O_2)$ was confirmed in a study on the simulation of (semi-)batch ozonation of phenol (Gurol and Singer, 1983). It was shown that a close match between the measured and the calculated data was only obtained when $k_La(O_2)$ was measured as a function of the residual phenol concentration. The oxygen mass transfer coefficient was observed to change from $k_La(O_2) = 0.049$ s^{-1} at $c(M)$ = 50 mg L^{-1} phenol to $k_La(O_2) = 0.021$ s^{-1} at $c(M)$ = 5.0 mg L^{-1} phenol.

Changes in Surface Tension

Further organic compounds that can severely affect ozone or oxygen mass transfer coefficients are surface active agents or surfactants. Small amounts of surfactants can potentially cause a large change due to their ability to lower the surface tension at relatively low bulk concentrations by adsorbing strongly at the gas-liquid interface. Many studies of the effect of surfactants on mass transfer have found mass transfer to decrease with decreasing surface tension. However, reports of increased mass transfer have also been made. This can be explained by looking at the two ways surfactants can affect mass transfer, by changing the film mass transfer coefficient k_L or the interfacial area *a*.

The decrease in the *alpha* factor to values below $\alpha = 1$ can be due to a decrease in either k_L or a or both. Two theories are commonly used to explain the reduction in k_L: the barrier effect and the hydrodynamic effect. In the barrier theory, the presence of the surfactants at the phase interface creates an additional resistance to mass transfer due to diffusion through the surfactant layer. In the hydrodynamic theory, the layer of surfactant molecules at the gas-liquid interface depresses the hydrodynamic activity (Gurol and Nekouinaini, 1985).

An increase in the *alpha* factor to values above $\alpha = 1$ is most probably due to an increase in the interfacial area a. The reduced surface tension σ can cause smaller primary bubbles to form at the aerator or the layer of surfactant at the interface can inhibit bubble coalescence. Just what effect the surfactant will have depends on the hydrodynamic conditions in the reactor (Mancy and Okun, 1965; Eckenfelder and Ford; 1968, Libra, 1993) and on the surfactant itself (e. g. anionic, nonionic) (Wagner, 1991). In studies with an anionic surfactant in a CFSTR, Libra (1993) found that the oxygen mass transfer coefficient $k_La(O_2)$ was reduced for moderately turbulent regions due to the dampening of interfacial turbulence by the adsorbed layer of surfactant on the bubble/water interface. The lower the surface tension (i. e. the higher the surfactant concentration), the larger the decrease in $k_La(O_2)$. As power increased, $k_La(O_2)$ recovered to the values found in tap water; the increased turbulence caused increased surface renewal at the bubble/water interface, thereby annulling the effect of the surfactant. In the highly turbulent region, $k_La(O_2)$ increased significantly. The inhibition of coalescence by the surfactant increased the interfacial area.

However, not all surfactants inhibit coalescence. Some, especially nonionic surfactants (commonly used as anti-foaming agents), are well-known to increase coalescence, decreasing the interfacial area a (Zlokarnik, 1980; Wagner, 1991). Comparing the effects of two anionic and a nonionic surfactants, Wagner (1991) found that although α decreased as σ decreased for each surfactant, it was not possible to develop a general correlation between α and σ.

The influence of surfactants is predominantly of importance in waste water ozonation studies where often comparatively high concentrations of such compounds occur. However, similar effects can occur in drinking or ground water ozonation applications. This was shown for the decomposition of the organic phosphate pesticide diazinon (phosphorotoic acid *o,o*-diethyl-*o*-[6-methylethyl)-4-pyrimidinyl]ether) in aqueous solution by ozonation. This compound was found to considerably affect the surface tension of the aqueous solution, even at low concentrations ($c(M) \leq 10$ mg L^{-1}) and, thus, also influenced the oxidation mechanism (Ku et al., 1998).

3.3 Determination of Mass Transfer Coefficients

The methods to determine mass transfer coefficients can be grouped according to whether the concentration of the transferred compound changes over time:

- nonsteady state methods
- steady state methods.

Which experimental method should be used depends on the type of reactor and how it will be operated, and if clean or process water is to be used for the measurement. Nonsteady state methods are generally simpler and faster to perform if k_La is to be determined in clean water without reaction. For processes that are operated at steady state with a reaction, determination of k_La using steady state methods are preferred, since continuous-flow processes need not be interrupted and operating conditions similar to the normal process conditions can be used. This is especially important for systems with reactions because the reaction rate is usually dependent on the concentration of the reactants present. They are thus often applied for investigations of the mass transfer coefficient under real process conditions with chemical reactions $k_La(O_3)$ or biological activity $k_La(O_2)$, e. g. in waste water treatment systems.

Experimental determination of the mass transfer coefficient is based on the appropriate mass balance on the specific reactor used (Figure B 1-2). The simpler the reactor system is, the simpler the mass balance model for evaluating the experimental results can be. For example, if mixing in the reactor deviates too far from ideality, k_L is no longer uniform throughout the reactor. Neither method as described below can then be used. Instead a more complicated model of the mixing zones in the reactor would be necessary (Linek, 1987; Stockinger, 1995).

Reactor systems, in which the following general assumptions are valid, are preferable:
- Both gas as well as liquid phase are ideally mixed.
- Negligible ozone transfer occurs at the liquid surface.
- The liquid and gas flow rates to the reactor are constant.

There is no net change in gas flow rate in and out of the reactor, so that $Q_{G\,in} = Q_{G\,out} = Q_G$ (i. e. when nitrogen is used in $k_La(O_2)$ measurements to produce oxygen-free water, the volume of nitrogen desorbed approximately equals the volume of oxygen absorbed.)

The following equations are written for absorption (of any gas) in a continuous-flow stirred tank reactor (CFSTR) under the assumption that the gas and liquid phases are ideally mixed (Figure B 1-2). The assumption of an ideally mixed phase can be checked by determining the residence time distribution in the reactor (e. g. Levenspiel, 1972; Lin and Peng, 1997; Huang et al., 1998).

The general mass balance for each phase at nonsteady state, considering convection, mass transfer and reaction (e. g. ozone decay), can be written:

liquid phase:

$$V_L \cdot \frac{\mathrm{d}\,c_L}{\mathrm{d}\,t} = Q_L\ (c_{Lo} - c_L) + k_La \cdot V_L\ (c_L^* - c_L) - r_L \cdot V_L \qquad (3\text{-}17)$$

gas phase:

$$V_G \cdot \frac{\mathrm{d}\,c_G}{\mathrm{d}\,t} = Q_G\ (c_{Go} - c_G) - k_La \cdot V_L\ (c_L^* - c_L) - r_G \cdot V_G \qquad (3\text{-}18)$$

In case of steady state d*c*/d*t* equals zero, the material balance for each phase can be combined for a total balance on the reactor, which can be used as a check on the system, making sure that what goes in, either reacts or comes out:

$$Q_G\ (c_{Go} - c_G) - r_G \cdot V_G = Q_L\,(c_{Lo} - c_L) - r_L \cdot V_L \tag{3-19}$$

The most common and appropriate methods used to determine the mass transfer coefficient and the problems inherent in each are presented in the following sections. The methods are discussed from a practical viewpoint for the direct determination of the ozone mass transfer coefficient. However, it may be impractical, even impossible to use ozone as the transferred species, because of fast reactions which cause mass transfer enhancement etc. Then the oxygen mass transfer coefficient can be used to indirectly determine the ozone mass transfer coefficient. The procedure is described below and special aspects of oxygen mass transfer experiments are referred to in the following sections whenever necessary or of general importance.

3.3.1 Nonsteady State Methods without Mass Transfer Enhancement

The nonsteady state methods described in this section are all based on no or negligible reactions taking place in the system. If reactions are present, the treatment of the mass balances becomes more complicated since

- the reaction rate is most often a function of the reactant concentrations, which then also changes over time
- or mass transfer enhancement can occur.

Other methods to evaluate the data are then necessary (see Levenspiel, 1972; Levenspiel and Godfrey, 1974).

Batch Model

The most common approach in the laboratory is to use a batch set-up (with respect to the liquid) where ozone-free (clean) water is gassed with the ozone/air or ozone/oxygen mixture. The change in the liquid ozone concentration over time is measured with an ozone probe or an on-line photometer. The mass balance reduces to:

$$\frac{\mathrm{d}\,c_L}{\mathrm{d}\,t} = k_L a \cdot (c_L^* - c_L) - r_L \tag{3-20}$$

It is important to note that even in clean water, ozone decay (which can be considered a special ozone 'reaction') cannot be prevented at pH ≥ 4. In order to achieve a situation where no reactions occur ($r_L = 0$), the ozone mass transfer experiments are mostly conducted at pH = 2. The use of higher pH values in ozone mass transfer experiments require that the ozone decay rate (r_L) has to be known or experimentally assessed (Sotelo et al., 1989; see Section B 4.4).

Fortunately changes in k_La due to mass transfer enhancement from ozone decay can be neglected, as Huang et al. (1998) showed by example of cyanide ozonation in strongly basic solutions (pH = 12–14) in a system where the value of the purely physical liquid side mass transfer coefficient was not too low ($k_{L^\circ} > 0.03$ cm s^{-1}). This is supported further by the results from several ozonation experiments, which showed that no ozone decay occurs in the liquid film at lower pH values (phenol, pH = 10 (Metha et al., 1989); 4-nitrophenol, pH = 8.5 (Beltrán et al., 1992 a)).

Experimental Procedure

In batch nonsteady state experiments the reactor is first filled with the water, in which the gas is to be absorbed. The water is allowed to come to the desired operating temperature. Then the ozone is removed from the water by vacuum degassing or by gassing with N_2 to at least 0.10 mg L^{-1} O_3. Through the use of a three-way valve, the gas is switched to the ozone/air or ozone/oxygen mixture and the change in the dissolved ozone concentration over time is recorded, preferably with a computer. The ozone generator should be started and running before the gas is switched, so that c_{Go} is constant during the experiments.

The mass transfer coefficient can be found using the mass balance given by equation 3-17, simplified for $Q_L = 0$, and, if ozone decay is negligible, $r_L = 0$. The integrated mass balance is then:

$$\ln \frac{c_L^* - c_L}{c_L^* - c_{Lo}} = k_La \cdot t \quad \text{or} \quad \frac{c_L^* - c_L}{c_L^* - c_{Lo}} = e^{k_La \cdot t} \qquad (3\text{-}21)$$

The data can be evaluated using any commonly available non-linear regression program or with a linear regression, in which k_La is the slope from the plot of the natural log of the concentration difference versus time. Linearity of the logarithmic values over one decade is required for the validity of the measurement. Of course the assumptions inherent in the model must apply to the experimental system, especially in respect to completely mixed gas as well as liquid phases and reactions are negligible. Two common problems are discussed below. Other common pitfalls and problems are summarized in Table 3-3.

The initial data with the fastest change in c_L may not be correct because of possible probe lag effects. The degree of deviation depends on the response time of the probe and the magnitude of k_La (Philichi and Stenstrom, 1989). For commonly used laboratory oxygen probes (time constants < 10 s), truncation of the data below 20 % of c_L^* is recommended (ASCE Standard, 1991). This problem can be taken into consideration in both linear and non-linear regression by choosing the appropriate start values for c_{Lo} t_o.

Another problem is the equilibrium concentration c_L^*. Use of the correct value of c_L^* is essential for calculating a correct k_La. The value for c_L^* is derived from the gas phase ozone concentration by applying Henry's Law. It is evident that the value calculated for the effluent gas will be lower than that calculated for the influent gas. In small laboratory scale ozonation reactors, such as STRs, a mean value can be calculated:

$$\bar{c}_L^* = \frac{\mathrm{H_C}}{2} \cdot (c_{Go} - c_G) \tag{3-22}$$

In larger and especially higher reactors, such as bubble columns, a constant value of c_L^* can normally not be assumed. A differential balance over the height of the column is necessary. An approximation for this case for oxygen transfer was recommended by Zlokarnik (1980), the so-called 'logarithmic concentration difference' to be used for (c_L^* - c_L) and defined as:

$$\overline{\Delta c_L} = \frac{c_{Lo}^* - c_{Le}^*}{ln\dfrac{c_{Lo}^* - c_L}{c_{Le}^* - c_L}} \tag{3-23}$$

c_{Lo}^* = equilibrium concentration corresponding to the influent gas and
c_{Le}^* = equilibrium concentration corresponding to the effluent gas.

The other possibility to contend with this problem is to fit the value of c_L^* to the data. This can be done per hand, or may be possible with the program used for non-linear regression.

Continuous-Flow Model

In systems with continuous flow, the nonsteady state approach is a bit more complicated. A perturbation in the dissolved ozone concentration (c_L) is made and the change in c_L over time is measured as the system returns to steady state. In principle, to remove ozone a fast chemical reaction with some substance leaving no oxidation products which can further consume ozone or influence the mass transfer has to be used. For oxygen mass transfer $c_L(O_2)$ can be removed by a chemical reaction with Na_2SO_3 catalyzed with cobalt (Libra, 1993). Although ozone reacts fast with sulfite ($k_D = 0.9\ 10^9\ M^{-1}\ s^{-1}$; calculated for pH = 8; $pK_a\ (HSO_3^-/SO_3^{2-}) = 7.2$, Hoigné et al. 1985) no reports on the application of this method for the assessment of $k_La(O_3)$ have been found in the literature. The data are evaluated using the nonsteady state liquid phase mass balance, equation 3-17. The integrated form of the equation without reaction is:

$$\ln\left[1 - \frac{c_L - c_{Lo}}{c_{L\infty} - c_{Lo}}\right] = -\mathrm{K}_2 \cdot t \tag{3-24}$$

$$\mathrm{K}_2 = \frac{Q_L}{V_L} + k_La \tag{3-25}$$

c_{Lo} = ozone concentration at $t = 0$
$c_{L\infty}$ = ozone concentration at $t = t_\infty$

Experimental Procedure

The continuous-flow nonsteady state measurements can be made after the reactor has reached steady state, which usually takes at least 3 to 5 times the hydraulic retention time under constant conditions. Then an appropriate amount of the compound to be oxidized (e. g. Na_2SO_3) is injected into the reactor. An immediate decrease in the liquid ozone concentration to $c_L \approx 0$ *mg* L^{-1} *indicates that the concentration is correct.* Enough sulfite has to be added to keep $c_L = 0$ for at least one minute so that it is uniformly dispersed throughout the whole reactor. Thus a bit more than one mole of sodium sulfite per mole ozone dissolved is necessary. The subsequent increase in c_L is recorded by a computer or a strip chart. The data are evaluated according to equation 3-24, the slope from the linear regression is $-(Q_L/V_L + K_La(O_3))$.

Common Problems Inherent to the Determination of Mass Transfer Coefficients with the Nonsteady State Method

A variety of problems encountered with the measurement of oxygen mass transfer coefficients by using the nonsteady state method are well known and well understood. Libra (1993) gives a comprehensive discussion based on oxygen mass transfer measurements. The most important problems are found in the following table.

The magnitude of error that can be caused by neglecting these problems depends on the system used. Most of theses problems are not serious in the case of small k_La's, e. g. for the range normally found in waste water treatment plants (0.001–0.005 s^{-1}). For example, Brown

Table 3-4: Problems inherent to the determination of mass transfer coefficients with the nonsteady state method.

Problematic Step of Experimental Procedure	Conflict with Model Assumptions	Explanation	Remark
Degassing the water by *purging with nitrogen* gas (N_2)	c_G and c_L^* = constant *over time*	Dilution of the gas phase by N_2 *just after* the beginning of reaeration	underestimation of k_La's on the order of 40 % (Chapman et al., 1982) or even 50 % (Osorio, 1985) was observed, depending on the magnitude of k_La
Reaeration, especially with low Q_G	Ideally mixed gas phase; c_L^* = spatially constant	Local concentration gradients (of c_G and c_L^*), probable surface aeration	can cause major differences if the gas space above the liquid is large and Q_G small
Addition of sodium sulfite and cobalt catalyst	Low to moderate ionic strength and coalescing system	high ionic strength and non-coalescing system → change in interfacial area	*this method generally yields* incomparable values to low ionic strength waters especially for large k_La's (Libra, 1993)
Oxygen probe	Immediate response to changes in c_L	Oxygen probe lag τ	Various models have been proposed to describe the oxygen probe lag (Dang et al., 1977; Linek et al., 1987) and *can be used for ozone probes*

and Baillod (1982) found that the error caused by neglecting gas phase depletion was less than 10 % for $k_La < 0.0025\ s^{-1}$.

In order to overcome these problems especially for processes with large $k_La(O_2)$ the following recommendations are made (Linek et al., 1987; ASCE Standard, 1991):

- using pure oxygen combined with vacuum degassing of the liquid or
- using an appropriate model for the gas phase oxygen concentration.
- compensate for the oxygen probe time constant with either a model or by truncating the initial data in the reaeration test below 20 % of c_L^*

The first recommendation, to use a one component gas, is not possible to achieve since ozone generators can only achieve approximately 20 % wt, equivalent to 14.3 % vol. It is important to consider the probe dynamics when measuring k_La's in highly efficient transfer devices ($k_La > 0.01\ s^{-1}$), as often found in industrial applications for ozonation.

3.3.2 Steady State Methods without Mass Transfer Enhancement

The steady state method is often used in continuous-flow operation with reaction, which is often the case in full-scale applications. In laboratory-scale investigations, the steady state method can be used with a semi-batch set-up (gas phase continuous) with reaction or a continuous-flow set-up (both gas and liquid phases continuous) with or without reaction.

The advantages of the steady state method are

- little to no changes in the hydrodynamics of an operating system are necessary
- since concentrations do not change, no dynamic effects have to be considered and concentration measurement is simplified
- reaction rates for slow reactions in the liquid phase do not have to be known if using the gas phase balance.

Since we know the mass of ozone transferred has to have reacted or left the system, it is relatively easy to determine the reaction rate for slow reactions, which are controlled by chemical kinetics with this method. For kinetic regimes with mass transfer enhancement, the two rates, mass transfer and reaction rate are interdependent. Whether k_La or k_D can be determined in such a system and how depends on the regime. Possible methods are similar to those described below in Section B 3.3.3 (see Levenspiel and Godfrey, 1974).

The following discussion assumes any reaction present is in the slow kinetic regime. It also combines the batch and continuous-flow models, since there is so little difference between them.

Batch and Continuous-Flow Models

For the calculation of k_La two methods based on the liquid and gas phase mass balances (equations 3-17 and 3-18) are possible. For steady state and the case with reaction only in the liquid phase one obtains:

for the gas phase:

$$k_L\,a = \frac{Q_G}{V_L}\,\frac{(c_{Go} - c_G)}{(c_L^* - c_L)} \tag{3-26}$$

for the liquid phase (batch):

$$k_L\,a = \frac{r_L}{(c_L^* - c_L)} \tag{3-27}$$

for the liquid phase (continuous-flow):

$$k_L\,a = \frac{Q_L}{V_L}\,\frac{(c_L - c_{Lo}) - r_L V_L}{(c_L^* - c_L)} \tag{3-28}$$

The error associated with the steady state method becomes large as the liquid phase concentration approaches the saturation concentration. Care must be taken to avoid this region.

Experimental Procedure

The semi-batch set-up uses a chemical reaction to immediately remove the absorbed gas from the liquid. In oxygen transfer measurements, sulfite (SO_3^{2-}) or hydrazine (N_2H_4) have been used to remove the oxygen transferred (Charpentier, pp. 42–49, 1981). For example, the addition rate of the reactant (SO_3^{2-} or N_2H_4) is adjusted until the system comes to a steady state dissolved oxygen concentration of about 2 mg/L. Then the sulfite addition rate equals the transfer rate. Mass transfer enhancement must be avoided, which is difficult with hydrazine, so that it is rarely used.

The continuous-flow set-up can use either a reaction, similar to semi-batch, to remove the oxygen transferred or two reactors in series. The ozone or oxygen is removed from the liquid in the first reactor by stripping or vacuum degassing and then it flows into the absorber. After having passed through the absorber, the liquid can be recycled or discharged. More information on full-scale application of this method in municipal waste water treatment plants can be found in Redmon (1983) and ASCE (1991).

Steady state can be assumed to have been reached when c_L and c_G are constant for at least 30 minutes. As already mentioned before, the average time required for the reactors to reach steady state is approximately three to five times the hydraulic retention time.

The mass transfer coefficient for ozone can be calculated from both the liquid and gas phase mass balances as described by equations 3-26, 3-27 or 3-28. Difficulties arise with the liquid phase mass balance if a reaction is present. The reaction rate under the operating conditions investigated must be used, considering especially the c_L prevalent in the system. Since this can be very difficult to assess, and use of inaccurate reaction rates leads to inaccurate $k_L a$, application of the gas phase mass balance is an elegant way to avoid this problem.

3.3.3 Methods with Mass Transfer Enhancement

In a *heterogeneous* gas-liquid reactor system, that is where gas absorption precedes a liquid-phase reaction, the mass transfer rate has to at least equal the reaction rate. This principle can be used to determine mass transfer coefficients and/or reaction rate constants for certain kinetic regimes (see Section B 3.2.1). To determine the mass transfer coefficient, the kinetic regime must be instantaneous, and the place of the reaction must be in the film (Charpentier, 1981; Beltrán and Alvarez, 1996). To determine the reaction rate constant, the kinetic regime must be fast and k_La must be known.

An instantaneous reaction is the fastest reaction possible and no gas is transferred into the liquid bulk. This can be utilized to determine k_La, for example with the reaction of ozone with certain fast-reacting organic compounds. The reaction develops in a reaction plane located either

- directly at the gas-liquid interface, if $c(M)_o \geq c_L^*$ (as molar concentrations) holds, or
- in the liquid film, if $c(M)_o << c_L^*$ holds.

The situation is characterized by the fact that both reactants are entirely consumed, so that $c_L = c(M) = 0$ holds in the plane. Only in the latter case can k_La be determined. In the former case there is no transport of ozone into the liquid film, so that the mass transfer rate is only determined by k_Ga (Charpentier, 1981). The reaction rate depends on the mass transfer rate of ozone and pollutant to the reaction plane in the liquid film, but not on the reaction rate constant. Whether the reaction develops instantaneously in the liquid film depends on the experimental conditions, especially on the values of the applied ozone partial pressure $p(O_3)$ and the initial concentration of M $c(M)_o$. For example, the reaction tends toward instantaneous for low $p(O_3)$ and high $c(M)_o$.

Ozonation experiments to determine k_La from such an instantaneous reaction should preferably be conducted in a so-called agitated cell in which both phases are perfectly mixed and the transfer area is determined by the geometry of the constructed interface between the gas and the liquid in the system (see Figure B 2-5; Levenspiel and Godfrey, 1974). The method has also been used in stirred tank reactors (Sotelo et al., 1990; Sotelo et al. 1991; Beltrán and Gonzales 1991), but these reactors have two drawbacks:

- the specific interfacial area is unknown and
- the ozone partial pressure at the reactor outlet changes with time.

If an agitated cell is used, both problems are overcome because the transfer area is known and $p(O_3)$ is practically constant due to continuous dosing and complete mixing of the gas-phase.

For example, Beltrán and Alvarez (1996) successfully applied a semi-batch agitated cell for the determination of k_L, k_La, and the rate constants of synthetic dyes, which react very fast with molecular ozone (direct reaction, $k_D = 5\ 10^5$ to $1\ 10^8$ L mol^{-1} s^{-1}). In conventional stirred tank reactors operated in the semi-batch mode the mass transfer coefficient for ozone $k_La(O_3)$ was determined from an instantaneous reaction of ozone and 4-nitrophenol (Beltrán et al., 1992 a) as well as ozone and resorchinol (1,3-*di*hydroxybenzene) or phloroglucinol

(1,3,5-*tri*hydroxy-benzene) (Beltrán and Gonzales, 1991). In the latter study, comparisons were made with k_La-values from independent measurements using the nonsteady state method for oxygen absorption in high-purity water or the steady state method for oxygen absorption in cuprous chloride. The three different methods showed a high similarity and low standard deviations of the determined k_La–values ($k_La = 0.0018 \pm 8.8\ 10^{-5}\ s^{-1}$) were calculated.

Experimental Procedure

The determination of k_La from an instantaneous reaction is rather complex and the experimental procedure complicated, requiring an extensive knowledge of the theoretical background. Since it is not within the scope of this book to go into the necessary details, the basic experimental procedure is summarized in Figure 3-6, and only a few remarks shall be made here. For complete information the reader is referred to the original literature in which the nonsteady state method has been applied in ozonation experiments (e. g. Beltrán and Gonzalez, 1991; Beltrán et al., 1992 a; Beltrán and Alvarez, 1996) and the basics (e. g. Levenspiel and Godfrey, 1974; Charpentier, 1981).

First k_La is determined from an instantaneous reaction. Then k_D from a fast reaction using the known k_La. In order to avoid the influence of the gas-side resistance the experiments have to be conducted with an initial molar concentration of pollutant M far below the solubility level of ozone (related to the input gas concentration respectively the ozone partial pressure). In the study of Beltrán and Alvarez (1996) an instantaneous reaction of ozone and phenol developed with $c(M)_o < 0.5$ mM and $p(O_3) > 500$ Pa ≈ 6.1 mmol L^{-1} gas ($T = 20$ °C). All parameters were held constant while testing pairs of $c(M)_o$ and $p(O_3)$, for which the concentration change over time was measured. The instantaneous kinetic regime must be verified for each run (Beltrán and Alvarez, 1996).

3.3.4 Indirect Determination of Ozone Mass Transfer Coefficients

Oxygen transfer measurements can be used to obtain $k_La(O_3)$ and sometimes it is the only method available. In such cases, the ratio of the diffusion coefficients from equation 3-29 is employed:

$$k_La_{O3} = \left(\frac{D_{O3}}{D_{O2}}\right)^n \cdot k_La_{O2} = 0.622 \cdot k_La_{O2} \tag{3-29}$$

Using experimentally determined values of the diffusion coefficients for ozone $D(O_3) = 1.26\ 10^{-9}\ m^2\ s^{-1}$ (Matrozov et al., 1978) and oxygen $D(O_2) = 2.025\ 10^{-9}\ m^2\ s^{-1}$ (St. Denis, 1971) results in the above factor of 0.622 for $n = 1$. The power can vary from 0.5 to 1.0 depending on the hydrodynamic conditions in the reactor as discussed in Section 3.2. For ozonation in bubble columns, n is generally assumed to be 1.0. The diffusion coefficients are valid for the system 'gas/(clean) water' at $T = 20$ °C.

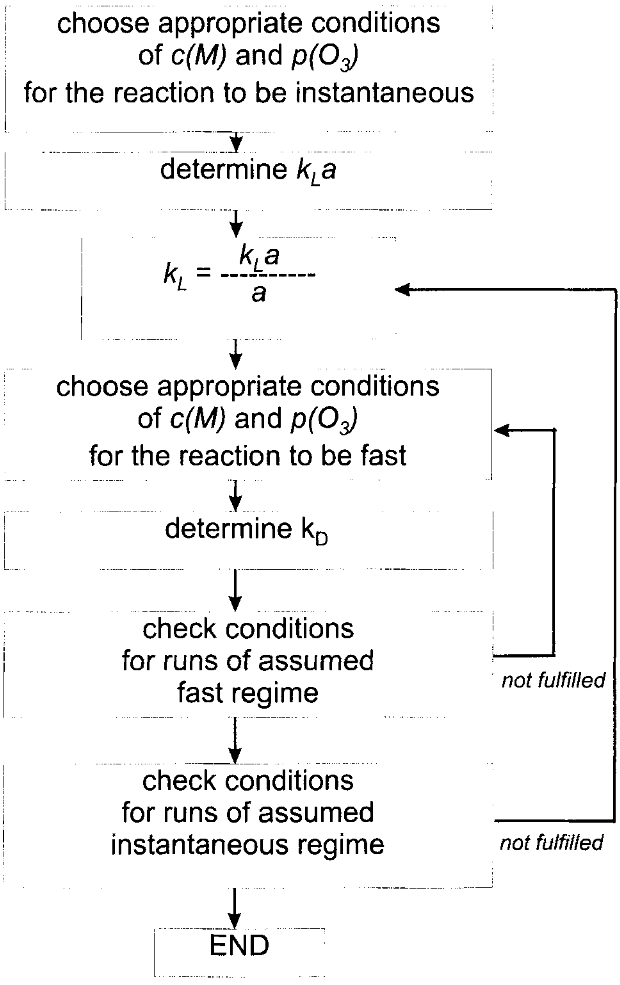

Figure 3-6: Experimental procedure for the determination of k_La and k_D from fast reactions of organic compounds with ozone (after: Beltrán and Alvarez, 1996).

Other values for $D(O_3)$ and $D(O_2)$ can be found in the literature, and depending on which ones are used the factor can vary considerably. For example, using diffusion coefficients for ozone derived from theoretical considerations, e. g. Wilke and Chang (1955) or Scheibel (1958) (cited by Reid et al. (1977), with the same $D(O_2)$ as mentioned above will result in seriously different factors for $D(O_3)/D(O_2)$ (0.864 and 0.899 respectively) and would thus result in different values for $k_La(O_3)$.

Based on these considerations, it is preferable to perform mass transfer measurements using ozone whenever possible. The measurements should be conducted with the same water or waste water and under the same range of operating parameters in which the oxidation reactions will later be performed if possible. However, ozone and OH° reactions can cause complications. A high pH-value for example can cause a fast ozone decay rate. Thus highly reactive hydroxyl radicals can be produced, which in turn may change the composition of the water. It is important to take these changes into account. Unfortunately, even in clean water, a high pH affects ozone mass transfer measurements. Due to ozone decay, the steady state ozone concentration in the liquid is not equal to the c_L^* calculated from Henry's Law for c_{Go} (Sotelo et al., 1989).

Furthermore, it is almost impossible to use ozone for k_La-measurements when organic substances are present that are (easily) oxidized by molecular ozone. Mass transfer enhancement will occur during such measurements, so that the mass transfer coefficient based on only the physical process cannot be determined. In this case, the oxygen mass transfer coefficient $k_La(O_2)$ should be determined to assess the mass transfer rate without reaction. The enhanced mass transfer due to reaction should be considered separately, because it is not only dependent on the parameters listed above in equation 3-10, but also dependent on the concentration of the reactants.

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4 Reaction Kinetics

Reaction kinetics describes what influences the reaction and how fast it takes place. Knowledge of kinetic parameters, such as reaction order *n* and reaction rate constant k, helps us to assess the feasibility of using ozonation to treat waters and to design an appropriate reactor system. It can help us to understand how a reaction can be influenced, so that a treatment process can be optimized. Kinetic parameters are also necessary for use in scientific models, with which we further improve our understanding of the chemical processes we are studying.

First we will review the basic concepts of kinetics (Section B 4.1), discussing in detail reaction order (Section B 4.2) and reaction rate constants (Section B 4.3) with emphasis on the practical aspects of determining them for oxidation processes. This lays the foundation for the discussion of which operating parameters influence the reaction rate and how (Section B 4.4). These influences are illustrated with results from current publications, with special emphasis on analyzing the common and apparently contradictory trends.

4.1 Background

For any given reaction

$$\alpha\,\mathrm{A} + \beta\,\mathrm{B} + \gamma\,\mathrm{C} \rightarrow \delta\,\mathrm{D} + \varepsilon\,\mathrm{E} \tag{4-1}$$

where α, β, γ, δ, ε are the stoichiometric coefficients for the reactants A, B, C and the products D and E,

the following differential rate equation can be used to describe the reaction rate of a non-volatile compound A in an ideally mixed reactor:

$$\frac{dc(\mathrm{A})}{dt} = -k\, \mathrm{c(A)}^{\mathrm{n_A}}\, \mathrm{c(B)}^{\mathrm{n_B}}\, \mathrm{c(C)}^{\mathrm{n_C}} \tag{4-2}$$

$c(A)$, $c(B)$, $c(C)$	concentration of the compound A, B, C
k	reaction rate constant
n	reaction order with respect to compound

The concentration of each compound is raised to a power *n*, which is called the order of the reaction with respect to the considered reactant. The total order of the reaction is the sum of the orders for each reactant.

$$n_\Sigma = n_A + n_B + n_C \tag{4-3}$$

n_A, n_B and n_C are determined empirically from experimental results and are not necessarily related to the stoichiometric coefficients α, β or γ (see equation 4-1). Reactions in which the order of reaction corresponds with the stoichiometry of the reaction, are called elementary reactions. For example:

$$1\ \mathrm{A} + 1\ \mathrm{B} \rightarrow 1\ \mathrm{D} \tag{4-4}$$

$$\frac{dc(A)}{dt} = -\mathrm{k}\ c(A)^1 c(B)^1 \tag{4-5}$$

In nonelementary reactions, the reaction order and stoichiometric coefficients are different. A single reaction is observed, but in reality a sequence of elementary reactions occurs. The amount of intermediates formed is negligible and, therefore, not detectable. One famous example is the reaction between hydrogen and bromine. The overall reaction can be described as:

$$\mathrm{H_2 + Br_2 \rightarrow 2\ HBr} \tag{4-6}$$

which has a rate expression:

$$\frac{dc(HBr)}{dt} = \frac{2\ \mathrm{k_2\ k_3(k_1 / k_5)^{0.5}}\, c(H_2)\ c(Br_2)^{0.5}}{\mathrm{k_3 + k_4}\ c(HBr) / c(Br_2)} \tag{4-7}$$

However, the following chain of reactions occur, which explains the nonelementary reaction:

$$\mathrm{Br_2 \rightarrow 2\ Br^\circ} \qquad \mathrm{k_1} \tag{4-8}$$

$$\mathrm{H_2 + Br^\circ \rightarrow HBr + H^\circ} \qquad \mathrm{k_2} \tag{4-9}$$

$$\mathrm{H^\circ + Br_2 \rightarrow HBr + Br^\circ} \qquad \mathrm{k_3} \tag{4-10}$$

$$\mathrm{H^\circ + HBr \rightarrow H_2 + Br^\circ} \qquad \mathrm{k_4} \tag{4-11}$$

$$\mathrm{2\ Br^\circ \rightarrow Br_2} \qquad \mathrm{k_5} \tag{4-12}$$

Since the order refers to the empirically found rate expression, it need not be an integer. If it is a fraction, the reaction is nonelementary, giving no clue to the stoichiometry of the reaction. If the reaction order is an integer, it may or may not be an elementary reaction.Often it is not necessary to know the stoichiometry of a reaction exactly, or even the reaction order for all compounds. For example if a reactor system is desired where compound A is to be removed by reaction with B and C, the reaction partners should be in surplus in the system to ensure complete removal of A, as may be the case in the oxidation of a micropollutant in the O_3/H_2O_2-process. The concentrations of B and C can be regarded as constant. Only the concentration of compound A changes and the reaction can be regarded as pseudo n_Ath order, equation 4-2 can be simplified to:

$$r(A) = \frac{\mathrm{d}c(A)}{\mathrm{d}t} = -k'\ c(A)^{n_A} \tag{4-13}$$

k': reaction rate coefficient, pseudo-first order when $n_A = 1$

The reaction rate constant, however, also changes. It becomes a pseudo rate coefficient k', where the concentrations and reaction orders of the reactants B and C are lumped together with the reaction rate constant of compound A. Though it is often referred to as a constant in the literature, it is dependent on the concentrations of B and C.

In general the dimensions of the reaction rate constants for nth order reaction are:

$$(\text{concentration})^{1-n}\ (\text{time})^{-1}.$$

If n_A in the above example is equal to one, the reaction is pseudo-first order and the rate constant has the dimension $(\text{time})^{-1}$.

Another important concept is the half-life of the reaction τ (sometimes $t_{1/2}$), the time needed to decrease the concentration to one half of the initial value $c(A)_0$. It is related to the order of reaction and the rate constant through the following equations:

$$n \neq 1: \quad \frac{\mathrm{d}c(A)}{\mathrm{d}t} = -k'\,c(A)^n \quad \Rightarrow \quad \tau = \frac{2^{n-1} - 1}{k'(n-1)\ c(A)_0^{1-n}} \tag{4-14}$$

$$n = 1: \quad \frac{\mathrm{d}c(A)}{\mathrm{d}t} = -k'\,c(A)^n \quad \Rightarrow \quad \tau = \frac{\ln 2}{k'} \tag{4-15}$$

For $n \neq 1$ it is important to keep in mind that the "half-life" is a function of the initial concentration $c(A)_0$. Knowing the order of reaction and the rate constant allows the half-life to be calculated. Or it can be determined experimentally and used to calculate the other parameters, e. g. by the trial and error method.

4.2 Reaction Order

Generally the oxidation of compounds with ozone is considered to be second order, which means first order with respect to the oxidant (O_3 or OH°) and to the pollutant M (Hoigné and Bader, 1983 a, b). A requirement for the experimental determination of the reaction order with respect to the pollutant is that the ozone concentration in the bulk liquid remains constant. A further requirement for determining kinetic parameters in general, is that the reaction rate should be independent of the mass transfer rate. These are easy to achieve for (very) slow reactions by using a continuously sparged semi-batch reactor. Such a reaction regime is often found in drinking water ozonation. In contrast, mass transfer limitations often occur in waste water applications. More effort is necessary to find operating conditions where mass transfer does not affect the reaction rate, or if this is not possible, more complicated methods than the ones presented below must be used to determine the reaction order.

Care must be taken that these requirements are met over the whole experiment. Especially when ozonating waste water in the semi-batch mode, the reaction regime can change over time as the concentration of pollutant changes. Often no dissolved ozone can be measured in the bulk liquid ($c_L \cong 0$) at the beginning of the experiment. The pollutant is normally present at a high concentration, causing (very) fast reactions with molecular ozone, and consequently, the direct reaction may occur inside the liquid film. The reaction rate is then limited by the mass transfer rate (Section B 3.2), and the reaction order and rate constant are dependent on the mass transfer rate. As the semi-batch ozonation continues, and the pollutant concentration decreases, the reaction regime moves from mass transfer to chemical kinetic controlled. The reaction order and rate constant are then independent of the mass transfer rate.

A very prominent, but somewhat confusing, example for the determination of reaction order is the process of ozone decay in "clean water". The large variation in reaction order found for ozone decay by various authors shows that the determination of reaction order can be rather complicated (see Table 4-1). From a chemical point of view, this radical chain process – as shown in detail in Chapter A 2 – is foremost a function of pH, or more accurately the hydroxide ion concentration. The main reason for the different reaction orders

Table 4-1: A comparison of reported reaction orders for the decay rate of ozone in phosphate buffered solutions of demineralized water.

Reference	T in °C	pH	n with respect to O_3
Stumm, 1954[2]	0.2–19.8	7.6–10.4	1
Kilpatrick et al., 1956[2]	25	0–6.8 8–10	1.5 2
Rankas, 1962[1]	5–25	5.4–8.5	1.5
Hewes and Davis, 1971[2]	10–20	2–4 6 8	2 1.5–2 1
Kuo et al., 1977	15–35	2.2–11	1.5
Sullivan, 1979[1]	3.5–60	0.5–10	1
Gurol and Singer, 1982	20	2.2–9.5	2
Staehelin and Hoigné, 1982	20	8–10	1
Sotelo et al., 1987	10–40	2.5–9	1.5–2
Minchews et al., 1987		6.65	2
Grasso and Weber, 1989		5–9	1
Gottschalk, 1997	20	7	1–2

[1] taken from Gurol and Singer, 1982

[2] taken from Minchews, 1987

found, is that ozone decay is part of a chain reaction mechanism involving hydroxyl radicals (OH°), similar to the example of bromide shown above, but much more complex.

A systematic dependence of reaction order on temperature and pH is not visible, *n* varies between one and two. Different experimental conditions and/or missing details about these conditions as well as different analytical methods make a comparison of these results impossible. Staehelin and Hoigné (1985) proposed a possible explanation for the second order reaction ($n = 2$). Since in 'clean' water ozone not only reacts with the hydroxide ions but also with the intermittently produced hydroxyl radicals (see Chapter A 2), it behaves like a promoter and the decay rate increases with the square of the liquid ozone concentration. This is supported by the results obtained by Gottschalk (1997). She found a second order decay rate in deionized water, compared to a first order decay rate in Berlin tap water, which contains about 4 mg L^{-1} DOC and 4 mmol L^{-1} total inorganic carbon. Staehelin and Hoigné (1982) also found first order in complex systems.

Experimental Procedure to Determine the Reaction Order n

The reaction order can be determined in many different ways. All methods require that reaction conditions, i. e. temperature, pH etc., be held constant and intermediates must not influence the reaction. The following three methods are the most commonly used:

Half-life method: Two different initial concentrations of A are used. The decrease in A over time is measured. The half-life $\tau = t_{1/2}$ is defined as the time where $c(A) = c(A)_o/2$. The order can be determined with the following equation: (see Figure 4-1a, b)

$$n = 1 - \frac{\lg \tau_1 - \lg \tau_2}{\lg c(A_1)_o - \lg c(A_2)_o} \tag{4-16}$$

Initial reaction rate method: Again the decrease in the concentration of A over time is measured for two different initial concentrations. The reaction rate *r* for $t \to 0$ is calculated with the help of a tangent at the steepest region of the curve, intersecting c_o at $t = 0$, and the following equation (see Figure 4-1c):

$$r(A)_i = \frac{\Delta c(A)_i}{\Delta t}, t \to 0 \tag{4-17}$$

The order of the reaction can be determined as follows:

$$n = 1 - \frac{\lg r(A_1) - \lg r(A_2)}{\lg c(A_1)_o - \lg c(A_2)_o} \tag{4-18}$$

Trial and error method: A rate equation which describes the experimental points with the best fit is chosen. The differential and integrated rate equations for the various reaction orders are found in Table 4-2. The best fit is easy to find by comparing the linear regression coefficients for the appropriate $x;y$-pairs. The x-axis is always the time t.

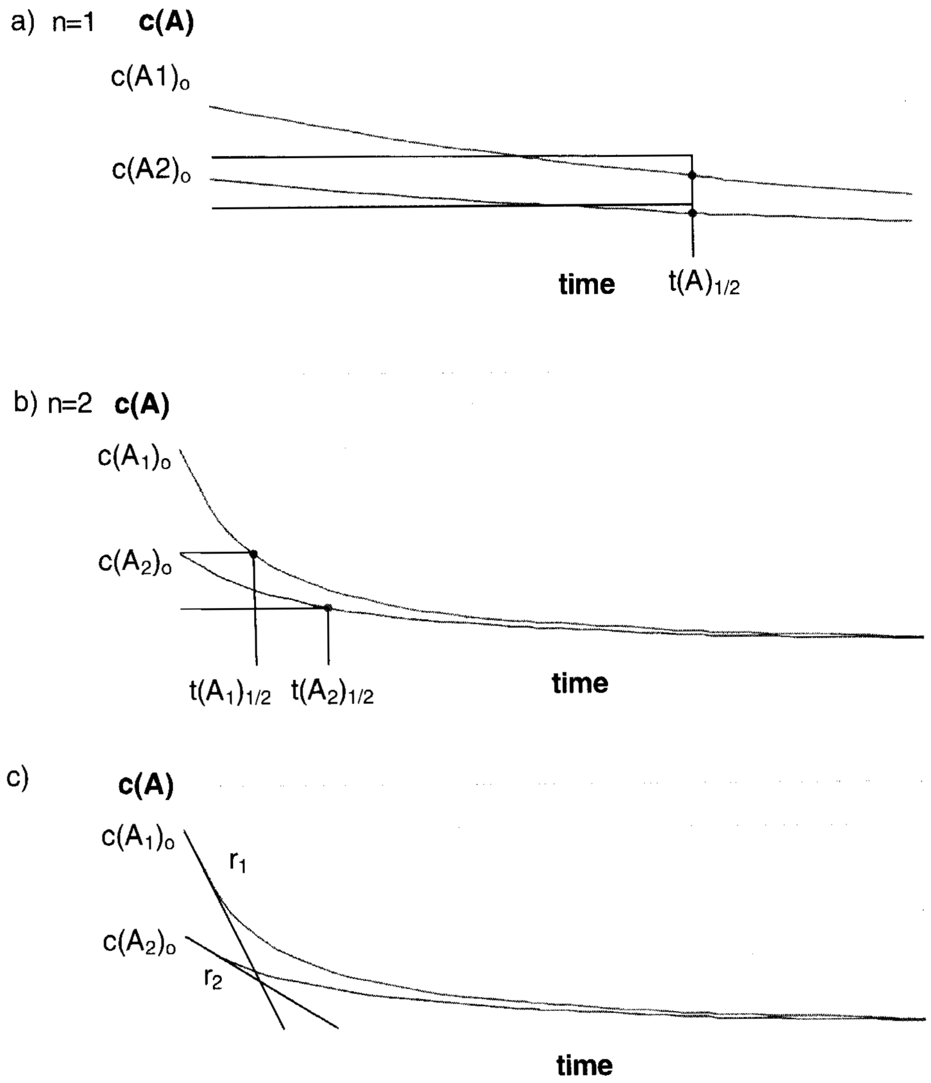

Figure 4-1: Method of half-life (a and b) and initial reaction rate method (c).

Table 4-2: Order of reaction with their differential and integrated equation for concentration over time.

n	Differential Equation	Integrated Equation	Unit of k #)
0	$d\,c(A)/dt = -k$	$k\,t = c(A)_o - c(A)$	$M\,s^{-1}$
0.5	$d\,c(A)/dt = -k\,c(A)^{0.5}$	$k\,t = 2\,(c(A)_o^{0.5} - c(A)^{0.5})$	$M^{0.5}\,s^{-1}$
1	$d\,c(A)/dt = -k\,c(A)$	$k\,t = \ln c(A)_o/c(A)$	s^{-1}
2	$d\,c(A)/dt = -k\,c(A)^2$	$k\,t = \frac{1}{c(A)} - \frac{1}{c(A)_o}$	$M^{-1}\,s^{-1}$
2	$d\,c(A)/dt = -k\,c(A)\,c(B)$	$k\,t = \frac{1}{c(A)_o - c(B)_o}\ln\frac{c(A)\,c(B)_o}{c(B)\,c(A)_o}$	$M^{-1}\,s^{-1}$

#) M = molar = mol L^{-1}

4.3 Reaction Rate Constants

Knowing the kinetics of the aqueous ozonation process can help us assess its feasibility as a treatment process. Hereby it is important to differentiate between the two types of reaction, direct and indirect. Although both types of reaction often occur simultaneously, the reaction rates can vary by orders of magnitude, depending on the reaction rate constants and concentrations of the reactants present. In order to determine reaction rate constants, there should be no mass transfer limitation in the experimental set-up. That means operating conditions should be chosen where the mass transfer rate is faster than the reaction rate. If this is possible depends on the reaction regime. For typical concentrations of pollutants in drinking water ($c(M) < 10^{-4}$ M) – even in the case of AOPs using incident UV-radiation and a hydrogen peroxide concentration lower than 10^{-3} M – the kinetic regime is likely to be slow, so that mass transfer limitations can be avoided. In a fast kinetic regime mass transfer limitations are unavoidable and a more rigorous and complex procedure, which takes the mass transfer limitation into consideration, is necessary (Beltrán, 1997; Section B 3.4).

In general the method of determining the reaction rate constants is based on knowing the reaction order for each reaction. The appropriate equation for the reaction order is chosen (Table 4-2) and the reaction rate constants are calculated from the linearization of the observed concentration decrease over time (usually the slope, see Table 4-2). However, since the reactions are complicated and often occur simultaneously, there are many experimental parameters to be considered. Some of the most important are summarized below.

Determination of Rate Constants for Direct Reactions (k_D)

For the determination of k_D the indirect reactions have to be suppressed. This is generally done by inhibiting any reactions between the hydroxyl radicals and the target substances through the addition of substances, which quickly scavenge the hydroxyl radicals produced and themselves do not or only very slowly react with molecular ozone.

The various methods are: addition of *tert*-butanol (TBA), decrease in the pH (i. e. an addition of H^+ ions), use of n-propanol, methylmercury (pH > 4) or bicarbonate (HCO_3^-, pH > 7). The concentration of these scavengers has to be kept as low as possible, in order to exclude any direct reactions with these substances. For experimental details see Hoigné and Bader (1983 a), Staehelin and Hoigné (1985) and Andreozzi et al. (1991).

To inhibit the indirect reaction, Beltrán et al. (1994) found that it is sometimes not sufficient to use a low pH-value, even as low as pH = 2. Comparing the reaction rate of atrazine with ozone at pH = 2 with and without *tert*-butanol, they observed a decrease in the reaction rate in the presence of TBA. This means that there were radical reactions even at this extremely low pH.

Care has to be taken that the changes to the water matrix, e. g. to inhibit the indirect reaction, do not change the direct reaction rate. The addition of TBA, for example, can change the mass transfer rate (see Section B 3.2). A change in pH can also affect the reaction rate of compounds that can dissociate. Hoigné and Bader measured the direct reaction rate of molecular ozone with organic solutes which do not dissociate (1983 a), which can dissociate (1983 b) and with inorganic compounds (1985). In general the compounds are more reactive in their dissociated form, which was attributed to the electrophilic character of the ozone molecule.

Further results of interest can be found in Yao and Haag (1991), who determined the kinetics of direct ozonation of several organic trace contaminants in deionized water with 50 mM phosphate buffer and 10 mM TBA.

Another aspect to be considered is that ozone also decays during the experiments. To obtain a constant ozone concentration in a system where ozone decay occurs, the reactor can be operated semi-batch. Gaseous ozone is continuously sparged to the reactor and after the ozone concentration reaches steady-state, the investigated compound is injected into the reactor. Another possibility is to measure the ozone decay rate independently and take this into account in the calculations.

Fast reactions with relatively high k_D-values above approximately $10^4\ M^{-1}\ s^{-1}$ can best be measured by the method of competition kinetics that was first described by Hoigné and Bader (1976) for *homogeneous* systems in which an ozone containing fluid is rapidly mixed with the fluid containing the pollutants M_1 and M_2 and the disappearance of both is tracked over time (Hoigné and Bader, 1979; Yao and Haag, 1991). The reaction rate constant of one of them, e. g. M_1 is known, serving as a reference compound, the other one has to be determined. Under the assumption that both components react pseudo-first order in a batch system, the unknown reaction rate constant k_{M2} can be calculated by the following equation:

$$k_{M_2} = \frac{\ln \frac{c(M_2)_t}{c(M_2)_o}}{\ln \frac{c(M_1)_t}{c(M_1)_o}} k_{M_1} \qquad (4\text{-}19)$$

This method can be applied universally for direct and indirect reactions.

A prerequisite for the use of this method in *heterogeneous*, gas-sparged semi-batch systems is that the reaction does not develop in the *instantaneous* regime (Beltrán et al., 1993; Gurol and Nekouinaini, 1984). Phenol has often been used as a reference compound (M_I) yielding a pH and temperature dependent value of $k_D = 1\ 300\ M^{-1}\ s^{-1}$ at pH = 2, $T = 22$ °C (Hoigné and Bader, 1979) and $k_D = 10\ 000\ M^{-1}\ s^{-1}$ at pH = 4, $T = 25$ °C (Li et al., 1979).

Determination of Rate Constants for Indirect Reactions (k_R)

Rate constants for the reaction of hydroxyl radicals with different compounds were determined by Haag and Yao (1992) and Chramosta et al. (1993). In the study of Haag and Yao (1992) all hydroxyl radical rate constants were determined using competition kinetics. The measured rate constants demonstrate that OH° is a relatively nonselective radical towards C–H bonds, but is least reactive with aliphatic polyhalogenated compounds. Olefins and aromatics react with nearly diffusion-controlled rates. Table 4-3 gives some examples comparing direct (k_D) and indirect (k_R) reaction rate constants of important micropollutants in drinking water.

In general the reaction rate constants of the direct reaction are between 1 and $10^3\ L\ mol^{-1}\ s^{-1}$, and the indirect reaction rate constants are between 10^8 and $10^{10}\ L\ mol^{-1}\ s^{-1}$ (Hoigné and Bader, 1983 a, b).

Table 4-3: Examples of reaction rate constants for direct and indirect reaction of well-known drinking water contaminants (micropollutants) (Yao and Haag (1991); Haag and Yao (1992).

Pollutant	Reaction Rate Constant k in $M^{-1}\ s^{-1}$	
	k_D	k_R
Dibromomethane	–	$0.4–1.1\ 10^9$
1,1,2 Trichloroethane	–	$0.13–0.35\ 10^9$
Lindane	< 0.04	$4.2–26\ 10^9$
Phthalates	0.14–0.2	$4\ 10^9$
Simazine	4.8	$2.8\ 10^9$
Atrazine	6–24	$2.6\ 10^9$
2,4-D	2.4	$5\ 10^9$

Calculation of the Reaction Rate

Since the ozonation of a compound M involves both the direct and indirect reaction pathways, the general rate equation 4-2 has to be modified to include both reactions:

$$r(M) = -\frac{\mathrm{d}c(M)}{\mathrm{d}t} = k_D\ c(M)\ c(O_3) + k_R\ c(M)\,c(OH^\circ) \qquad (4\text{-}20)$$

where $c(M)$, $c(O_3)$ and $c(OH^\circ)$ represent the concentration of the pollutant, ozone and the hydroxyl radical, k_D and k_R the reaction rate constants for direct and indirect reaction.

Knowing the reaction rate constants of the direct and indirect reactions and the concentrations, the total reaction rate can be calculated. Unfortunately some data continue to be generated that fail to distinguish between the direct ozone reaction and hydroxyl radical chain reaction. Knowledge of independent rate constants for each pathway is useful to predict competition effects. In drinking water the direct oxidation kinetic is often negligible compared with the indirect, in waste water there is often no clear preference and both pathways can develop simultaneously. This was found for example in the ozonation of 4-nitroaniline at pH = 2, 7 and 11 (T = 20 °C) (Saupe, 1997; Saupe and Wiesmann, 1998).

The pseudo-first order rate constants (resp. coefficients) for the direct reaction of some compounds may almost be in the order of typical hydroxyl rate constants ($k_R \geq 10^8\ M^{-1}\ s^{-1}$), due to high concentrations of the pollutants as well as mass transfer enhancement. For example, Sotelo et al. (1991) measured values of 6.35 10^6 and 2.88 $10^6\ M^{-1}\ s^{-1}$ for the dissociating hydroxylated phenols, resorchinol (1,3-*di*hydroxybenzene) and phloroglucinol (1,3,5-*tri*hydroxybenzene) respectively (pH = 8.5 and T = 20 °C).

4.4 Parameters that Influence the Reaction Rate

4.4.1 Concentration of Oxidants

Direct Reactions

Normally a second order reaction is assumed for all direct reactions of organic compounds (M) with ozone, with the rate dependent on the concentration of ozone, as well as on that of the compound, to the first power.

In general an increase in the ozone concentration in the liquid bulk causes an increase in the oxidation rate of the substrate (Prados et al., 1995; Adams and Randtke, 1992 a; Bellamy et al., 1991; Duguet et al., 1990 a, b). A linear correlation between the oxidation rate and liquid ozone concentration was found by Gottschalk (1997) and Adams and Randtke (1992 a) for the oxidation of atrazine in drinking water ozonation studies.

In special cases, where no liquid ozone can be measured and where the ozone mass transfer rate is equal to the reaction rate (E = 1), the ozone dose rate can be used to describe the amount of ozone available for reaction. Gottschalk (1997) was able to correlate the oxidation rate of an organic substrate (atrazine) with the ozone dose and absorption rates.

Indirect or Hydroxyl Radical Reactions

The same observation was made for hydroxyl radical reactions occurring in advanced oxidation processes involving ozone. Increasing the ozone dose rate will increase the reaction rate (UV/O_3: Beltrán et al., 1994; Paillard, 1987; Glaze et al., 1982; H_2O_2/O_3: Gottschalk, 1997; Bellamy et al., 1991; Prados et al., 1995, Aieta et al., 1988). To be able to make a good comparison in AOPs, the concentration of the second oxidant has to be constant. Furthermore, it is important that there is enough ozone in the liquid and that the reaction is not limited by the ozone transfer from the gas into the liquid phase.

For example, by varying the dose rate of hydrogen peroxide while holding the ozone dose rate constant, the dependency of the oxidation rate on the dose ratio $F(H_2O_2)/F(O_3)$ can be investigated. The optimal dose ratio, i. e. the dose ratio resulting in the fastest reaction rate, has often been found to lie between 0.5 and 1.4 moles H_2O_2/mol O_3 (Aieta et al., 1988; Duguet et al., 1990 a; Glaze and Kang, 1988; Paillard et al., 1988; Gottschalk, 1997). The different values of the optimal dose ratio can be explained by considering the expected stoichiometry for OH° formation from ozone and hydrogen peroxide:

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH^\circ + 3\ O_2 \qquad (4\text{-}21)$$

According to this reaction, a molar ratio of 0.5 or a weight ratio of 0.35 moles H_2O_2 per mole O_3 is necessary. This ratio was found in "clean systems" such as deionized water with a low concentration of buffer. In ground water or water with high scavenger concentrations, the optimal dose ratio was higher. Here the chain reaction is influenced by other compounds.

There are several factors that may influence this stoichiometry:

- H_2O_2 can act as a radical scavenger itself
- O_3 can react directly with OH°, consuming O_3 and OH°
- O_3 and OH° may be consumed by other constituents (scavengers)

In order to measure the optimal dose ratio it is suggested that the concentration of one of the oxidants be held constant while the other is varied. The influence of parameters is only measurable if there is no mass transfer limitation.

4.4.2 Temperature Dependency

For any reaction the rate constant is a temperature-dependent term. The rate constant k has been found to be well represented by Arrhenius' law:

$$k = A' \exp(-E_A/\Re\, T) \qquad (4\text{-}22)$$

A'	frequency factor
E_A	activation energy in J mol^{-1}
$\Re$	ideal gas law constant (8.314 J mol^{-1} K^{-1})
T	temperature in K

If the Arrhenius function is valid, the plot of ln k versus T^{-1} shows a straight line; and the slope is $-E_A/\Re$. When determining the activation energy for an ozone reaction, it is important to keep in mind that by increasing the temperature of the water, the solubility of ozone decreases. The same liquid ozone concentration should be used at the various temperatures, which can be a problem in systems with fast reactions. Simplifying the temperature dependency, one could say that the increase of the temperature by 10 °C will double the reaction rate, the so-called van't Hoff rule (Benefield et al., 1982).

4.4.3 Influence of pH

The relevance of the pH-value was already seen in the chain reaction of ozone, especially in the initiation step. It also plays an important role in all the acid-base equilibrium by influencing the equilibrium concentrations of the dissociated/nondissociated forms. This is especially important for the scavenger reaction with inorganic carbon, which will be discussed further in Section B 4.4.4.

The decomposition of ozone is catalyzed by the hydroxide ion. Ozone dissociates in the presence of OH^- to $HO_2^\circ/O_2^{\circ-}$. Further decomposition via the ozonide anion radical $O_3^{\circ-}/HO_3^\circ$ results in the formation of OH° (see Figure 2-1, Part A, p. 11). They may react with organic compounds, radical scavengers (HCO_3^-, CO_3^{2-}) or ozone itself.

The results reported in the literature for the oxidation of micropollutants show that in synthetic water (deionized water with or without buffer) an increase in the pH-value increases the reaction rate (Adams, 1990; Heil et al., 1991; Gilbert, 1991). Gottschalk (1997) found a direct proportionality between the reaction rate and the OH^- concentration. In deionized water with added scavenger (Masten et al., 1993; Gottschalk, 1997) an optimum in the reaction rate was observed at about $pH = 8$. The positive effect caused by the increased OH^--concentration was counteracted by the strong scavenger potential of carbonate as the pH increased above 8. At higher concentrations of scavenger (> 2–3 mmol L^{-1}) this effect was no longer observed, which was explained by the constant potential of scavenger in this concentration range (Gottschalk, 1997).

For the combined oxidation processes, the effect of pH is even more complex. Experimental results have shown a steady increase in the reaction rate of micropollutants with increasing pH, as well as optima at various pH values.

On the one hand, the equilibrium between H_2O_2/HO_2^-, which plays an important role in all the previously discussed AOPs, shifts towards HO_2^-. The result is that for the O_3/UV and O_3/H_2O_2 processes, a higher amount of initiator is present, leading to an increase in the amount of OH° present. For the UV combined processes it is important that HO_2^- absorbs more UV-light at 254 nm than H_2O_2, again the amount of initiators increases (see Chapter A 2). On the other hand HO_2^- is known to act as a scavenger itself. If inorganic carbon is present in the water, the effect of the stronger scavenger potential of CO_3^{2-} compared to HCO_3^- is added (see Section B 4.4.4)

4.4.4 Influence of Inorganic Carbon

Inorganic carbon can also influence the total reaction rate by acting as a scavenger for hydroxyl radicals, whereas ozone itself does not react with carbonate or bicarbonate (Hoigné, 1984). The reaction of OH° with inorganic carbon proceeds according to the following mechanisms:

$$HCO_3^- + OH^\circ \rightarrow H_2O + CO_3^{-\circ} \tag{4-23}$$

$$CO_3^{2-} + OH^\circ \rightarrow OH^- + CO_3^{-\circ} \tag{4-24}$$

Table 4-4: Reaction rate constants for the reaction of hydroxyl radical with inorganic carbon.

Reference	HCO_3^- k_R (L mol^{-1} s^{-1})	CO_3^{2-} k_R (L mol^{-1} s^{-1})
Hoigné et al., 1976	1.5 10^7	20 10^7
Masten and Hoigné, 1992		42 10^7
Buxton et al., 1988	0.85 10^7	39 10^7

Not much is known about reactions of the carbonate radical with organic compounds; they seem to be almost unreactive. The carbonate radical, though, has been found to react with hydrogen peroxide (Behar et al., 1970):

$$CO_3^{-\circ} + H_2O_2 \rightarrow HCO_3^- + HO_2^\circ \qquad k = 8\ 10^5\ M^{-1}s^{-1} \qquad (4\text{-}25)$$

The reaction rate constants for the inorganic carbon reactions are summarized in Table 4-4. A comparison of both reactions shows that carbonate is a much stronger scavenger than bicarbonate. This indicates that the pH-value, which influences the form and concentration of inorganic carbon present (pK_a (HCO_3^-/CO_3^{2-}) = 10.3), is of major importance in determining the effect inorganic carbon has on the reaction rate.

Although these reaction rate constants are relatively low in comparison with the reaction rate constants of organic compounds with OH° (see Table 4-3), the reaction of inorganic carbon with OH° is not negligible, since it is usually present in drinking water at comparatively high concentrations (Hoigné and Bader, 1976; Gottschalk, 1997).

By increasing the concentration of inorganic carbon, i. e. increasing the concentration of scavengers, the reaction rate of organic target compounds with OH° will be decreased. On the other hand, this also reduces the decay of ozone. Thus, the direct oxidation of the organic substrates becomes more important, with the consequence of a lower total reaction rate. This decrease in reaction rate with increasing inorganic carbon concentration has often been shown in the literature, also for the AOPs (e. g. Hoigné and Bader, 1977; Duguet et al., 1989; Adams and Randtke, 1992; Masten and Hoigné, 1992; Legrini et al. 1993; Beltrán et al., 1994; Gottschalk, 1997).

The effect on the reaction rate is relatively high at low concentrations of inorganic carbon. However, above 2 mmol L^{-1} for ozonation and about 3 mmol L^{-1} for the ozone/hydrogen peroxide process, the decrease in the reaction rate is negligible (Gottschalk, 1997). Forni et al. (1982) found this plateau at 1.5 mmol L^{-1} of inorganic carbon for ozonation.

4.4.5 Influence of Organic Carbon on the Radical Chain Reaction Mechanism

Organic carbon can react as a scavenger and/or a promoter. This depends on the kind of organic carbon and its concentration (Staehelin and Hoigné, 1983; Glaze and Kang, 1990; Xiong and Legube, 1991). Since the carbon concentrations of the target compounds, the micropollutants are in the range of micromoles, even some milligrams of DOC, e. g. from humic acids, can exert strong influence on the indirect reaction mechanism in the treatment of ground or surface waters.

Primary organic radicals are produced according to the following general reaction:

$$2\,R + 2\,OH^{\circ} \rightarrow 2\,HR^{\circ} + O_2 \qquad (4\text{-}26)$$

In many cases the primary radicals react quickly with dissolved oxygen and form peroxyradicals, which initiate further oxidation processes.

$$HR^{\circ} + O_2 \rightarrow HRO_2^{\circ} \qquad (4\text{-}27)$$

For this reaction a surplus of oxygen is necessary (Legrini et al., 1993). Three different pathways exist for further reactions (Peyton and Glaze, 1987):

- the back reaction

$$HRO_2^{\circ} \rightarrow HR^{\circ} + O_2 \qquad (4\text{-}28)$$

- homolysis to a hydroxyl radical and carbonyl rest

$$HRO_2^{\circ} \rightarrow RO + OH^{\circ} \qquad (4\text{-}29)$$

- heterolysis with the formation of an organic cation and a superoxide anion radical

$$HRO_2^{\circ} \rightarrow HR^{+} + O_2^{\circ-} \qquad (4\text{-}30)$$

Especially humic acid in natural waters can react as scavenger or promoter depending on its concentration (Xiong and Graham, 1992; Masten et al., 1993). Xiong and Graham found that the fastest ozonation of atrazine in deionized water buffered at pH = 7.5 (KH_2PO_4/Na_2HPO_4) takes place with a concentration of humic acid of 1 mg L^{-1} (approx. 0.5 mg L^{-1} DOC; Schulten and Schnitzler, 1993). With higher concentrations of humic acid, the oxidation rate was lower. Various authors have studied the oxidation rate of DOC found in natural systems by OH°. Table 4-5 gives some examples of the reaction rate constants determined.

Table 4-5: Reaction rate constants of OH° with DOC in natural water.

Reference	DOC k_R in L mg^{-1} s^{-1}
Liao et al., 1995	1.6 10^4
Novell et al., 1992	1.7 10^4
Haag et al., 1992	2.3 10^4
De Laat et al., 1995	2.5 10^4
Kelly, 1992	10^5

A comparison with other organic compounds gives the impression that the reactivity is relatively low (see Table 4-3). During oxidation, however, the parameters used to characterize the organic carbon, i. e. concentration of the compound, DOC and COD, decrease with different velocity. For example the first oxidation step of an organic compound usually decreases the measured concentration of the compound as well as COD, but not the DOC. The first step usually adds oxygen, thus changing the compound and reducing its COD, but does not mineralize the organic compounds, yielding no reduction in DOC. This is important to keep in mind when using reaction rate constants to design a reactor system. If the treatment goal is mineralization and not just transformation of the organic carbon, then the disappearance of the parent compound or decrease in COD is not sufficient.

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5 Modeling of Ozonation Processes

Kinetic models can be used in the design of treatment plants. With their help it is possible to predict the influence of important parameters on the oxidation process. Knowing the kinetic parameters quantitively allows the size of the reactor system to be calculated. Models are also important research tools, which help us to understand the system being investigated.

Models in general are a mathematical representation of a conceptual picture. Rate equations and mass balances for the oxidants and their reactants are the basic tools for the mathematical description. As Levenspiel (1972, p.359) pointed out "the requirement for a good engineering model is that it be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select a model which closely mirrors reality but is so complicated that we cannot do anything with it." In cases where the complete theoretical description of the system is not desirable or achievable, experiments are used to calculate coefficients to adjust the theory to the observations; this procedure is called semi-empirical modeling.

Every ozonation process where gaseous ozone is transferred into the liquid phase and where it subsequently reacts, involves physical and chemical processes which need to be considered in modeling. Physical processes include mass transfer and hydrodynamic properties of the reaction system, e. g. gas- and liquid-phase mixing. Chemical processes include, ideally, all direct and/or indirect reactions of ozone with water constituents. Of course these processes cannot be seen independently. For example, fast reactions can enhance mass transfer.

The chemical processes in drinking water ozonation are well known. The rate equations including the direct and indirect reaction mechanisms form the basis for the mathematical models that have been developed to describe these processes (Section B 5.1). The models vary in their complexity and usefulness. The main problem is to describe the influence of the initiators and scavengers on the OH° concentration, depending on the water matrix. Examples are given of various approaches that have lead to a sufficient – but not complete – description of experimental results in drinking water (Section B 5.2). In general, waste water has a much more complex matrix and not all reactions are known. So simplified models are generally used in this area, often showing limited validity when the boundary conditions change (Section B 5.3).

Mass transfer is often neglected in drinking water studies, meaning that it is often regarded as a prerequisite that liquid ozone (regardless where it comes from) is available for the reactions, which develop entirely in the liquid bulk. Sometimes this makes the problem of modeling the ozonation process appear solely a chemical model, which indeed it isn't. On the contrary, mass transfer is known to have an important influence on the oxidation of waste water and is seldom neglected in the modeling of waste water ozonation (Section B 5.3, see also Chapter B 3).

Lab-scale systems used for experiments are usually completely mixed, especially with respect to the liquid phase. This has been assumed for the following discussion. It simplifies the description of the system hydrodynamics in the models immensely, but often leads to neglect of the system hydrodynamics in the scale-up of lab-scale results for pilot or full-scale applications, and can lead to different results. Models that are useful for scale-up must take into consideration that the hydrodynamics in larger reactor systems are often more complicated.

5.1 Chemical Model of Oxidation

The oxidation process consists of direct and indirect reactions which can occur at the same time. A second order rate equation is commonly accepted for both reaction pathways. So that the oxidation of the model compound M can be described as the sum of the two reaction pathways as follows:

$$-\frac{\mathrm{d}\,c(M)}{\mathrm{d}\,t} = \left[\mathrm{k_D}\ c(O_3) + \mathrm{k_R}\ c(OH^\circ)\right] \cdot c(M) \tag{5-1}$$

M: model compound
$\mathrm{k_D}$: reaction rate constant for the direct reaction
$\mathrm{k_R}$: reaction rate constant for the indirect reaction

with the assumptions that:
- ozone and hydroxyl radicals are the main oxidants of the pollutant,
- no stripping of the pollutant occurs.

Often the reaction is simplified to pseudo-first order:

$$-\frac{\mathrm{d}\,c(M)}{\mathrm{d}\,t} = k'\ c(M) \tag{5-2}$$

with:
k': reaction rate coefficient, pseudo-first order

and:

$$k' = \underset{\text{direct}}{\mathrm{k_D}\ c(O_3)} + \underset{\text{indirect}}{\mathrm{k_R}\ c(OH^\circ)} \tag{5-3}$$

The reaction rate coefficient k' is dependent on the direct ($\mathrm{k_D}$) and indirect ($\mathrm{k_R}$) oxidation rate constants as well as the ozone and OH° concentrations. However, it is assumed to be constant with respect to time.

Both drinking water and waste water applications often use a pseudo-first order rate equation, though the reasons for this are quite different. This can be quite confusing for the beginning ozone modeler, especially when trying to extrapolate knowledge from the one field to the other. A short summary of what is different is presented here, the discussion of why can be found in the respective sections on drinking water and waste water modeling.

In *drinking water oxidation* it is assumed that

- the concentration of O_3 and OH° are at steady state (von Gunten et al., 1995), as well as that of the intermediates like $O_2^{\circ-}$, $O_3^{\circ-}$, HO_3° and organic radicals (Peyton, 1992)
- the indirect reaction is very important
- whereas the direct reaction is often small to negligible

In *waste water oxidation*, mass transfer is often limiting so that

- the concentration of dissolved ozone is often zero, with the rate as a function of the mass transfer coefficient
- the direct reaction is very important
- whereas the indirect reaction is often small to negligible.

This leads to largely differing areas of interest for the two fields. Models to determine the concentration of the OH° as a function of the water matrix are needed in drinking water applications, while models that incorporate the influence of the hydrodynamics and mass transfer on the reaction rate are necessary for waste water applications.

5.2 Modeling of Drinking Water Oxidation

Modeling in drinking water applications is largely confined to describing chemical processes. The mathematical models used in this area are based on the reaction rate equation to describe the oxidation of the pollutants, combined with material balances on the reaction system to calculate the concentrations of the oxidants as a function of the water matrix. As noted above, the reaction rate equation is usually simplified to pseudo-first order. This is based on the assumption of steady-state concentrations for ozone and the radicals involved in the indirect reaction.

The assumption of a steady-state ozone concentration for the direct reaction is based on the relatively large concentration of ozone compared to the micropollutants, which means the change in the ozone concentration over time is negligible. Several authors have shown that the indirect reaction of OH° with organic compounds is pseudo-first order due to the steady-state concentration of the hydroxyl radicals (e. g. Yao and Haag, 1992; von Gunten et al., 1995). Further assumptions are that the concentrations of the intermediates, e. g. $O_2^{\circ-}$, $O_3^{\circ-}$, HO_3° and organic radicals, are also at steady-state (Peyton, 1992).

The pseudo-first order reaction rate coefficient is then:

$$k' = \mathrm{k_D}\ c(O_3)_{\mathrm{SS}} + \mathrm{k_R}\ c(OH^{\circ})_{\mathrm{SS}} \tag{5-4}$$

ss means steady-state conditions

The concentration of ozone is relatively easy to measure, however, the OH-radical concentration must be calculated. It is for this OH° concentration that a diversity of models has been developed. The concentration is influenced by the water matrix, with its initiators and scavengers. Depending on the amount of kinetic information available for the initiating and scavenging reactions, the OH° concentration can be modeled at different levels of complexity.

The following sections provide examples of the various types of models that have been developed to calculate the OH° concentration. The first example illustrates the use of the rate equation, combined with experimental data and literature values. Then a general model based on the important known reaction mechanisms is presented, followed by models with varying degrees of complexities and simplifications. Further help in choosing an appropriate model can be found in the discussion by Peyton (1992). In his 'Guidelines for the Selection of a Chemical Model for Advanced Oxidation Processes', he gives an overview of the different levels of model complexity and a general idea when to use which level. Glaze et al. (1992) provide further examples for the calculation of the OH° concentration for various AOPs, including ozonation, ozone with hydrogen peroxide and the hydrogen peroxide/ultraviolet combination.

5.2.1 Model Based on the Rate Equation and Experimental Data

An experimentally determined reaction rate coefficient *k*' can be used to calculate the OH° concentration from equation 5-3:

$$c(OH^\circ)_{SS} = \frac{k' - \mathrm{k_D}\; c(O_3)_{SS}}{\mathrm{k_R}} \tag{5-5}$$

The reaction rate coefficient *k*' can be determined from the experimental observation of the elimination of a model compound over time (Chapter B 4). It can be combined with literature values for $\mathrm{k_D}$ and $\mathrm{k_R}$, and the experimentally determined ozone concentration to calculate the amount of OH-radicals which were present during the oxidation process. If indirect oxidation dominates, the term for the direct oxidation ($\mathrm{k_D}\; c(O_3)_{SS}$) can be neglected.

It is possible to use this OH° concentration to predict *k*' for the oxidation of other compounds under the same conditions.Von Gunten et al. (1995) calculated the actual concentration of OH° using this general and easy way for the ozonation of surface water at neutral pH in a two-stage pilot plant. Atrazine was used as the model compound, ozone decay was assumed to be of first order and the reactors completely mixed. Based on this model they were able to precisely predict the formation of bromate (BrO_3^-) by oxidation of bromide (Br^-) for a full-scale water treatment plant. Bromate is a disinfection byproduct (DBP) of the ozonation of bromide-containing waters, and of concern because of its carcinogenic effects in animal experiments (see also Chapter A 3).

5.2.2 Model Based on Reaction Mechanisms

An equation for the steady-state concentration of OH° can be developed from the indirect reaction mechanisms and mass balances on the liquid phase for the system O_3. The same can be done for O_3/H_2O_2. Table 5-1 summarizes all the important mechanisms that have been considered in the following equations.

Table 5-1: Hydroxyl Radical (Indirect) Reactions initiated by OH^- or H_2O_2.

Reaction	Reaction Rate Constant*)
Initiating reaction	
$O_3 + OH^- \rightarrow O_2^{\circ -} + HO_2^{\circ}$	$k_1 = 70\ L\ mol^{-1}\ s^{-1}$
$H_2O_2 \leftrightarrow HO_2^- + H^+$	$pK_a = 11.8$
$HO_2^- + O_3 \rightarrow HO_2^{\circ} + O_3^{\circ -}$	$k_9 = 2.8\ 10^6\ L\ mol^{-1}\ s^{-1}$
$O_3 + I \rightarrow$ products	k_I
Chain reaction	
$O_3 + O_2^{\circ -} \rightarrow O_3^{\circ} + O_2$	$k_2 = 1.6\ 10^6\ L\ mol^{-1}\ s^{-1}$
$HO_3^{\circ} \rightarrow OH^{\circ} + O_2$	$k_3 = 1.1\ 10^5\ s^{-1}$
$HO_4^{\circ} \rightarrow O_2 + HO_2^{\circ}$	$k_5 = 2.8\ 10^4\ s^{-1}$
$OH^{\circ} + O_3 \rightarrow HO_4^{\circ}$	$k_4 = 2.0\ 10^9\ L\ mol^{-1}\ s^{-1}$
Scavenging reaction	
$OH^{\circ} + HO_2^{\circ} \rightarrow O_2 + H_2O$	$k_6 = 3.7\ 10^{10}\ L\ mol^{-1}\ s^{-1}$
$OH^{\circ} + HO_2^- \rightarrow HO_2^{\circ} + OH^-$	$k_{10} = 7.5\ 10^9\ L\ mol^{-1}\ s^{-1}$
$OH^{\circ} + H_2O_2 \rightarrow HO_2^{\circ} + H_2O$	$k_{11} = 2.7\ 10^7\ L\ mol^{-1}\ s^{-1}$
$OH^{\circ} + CO_3^{2-} \rightarrow OH^- + CO_3^{\circ -}$	$k_7 = 4.2\ 10^8\ L\ mol^{-1}\ s^{-1}$
$OH^{\circ} + HCO_3^- \rightarrow OH^- + HCO_3^{\circ}$	$k_8 = 1.5\ 10^7\ L\ mol^{-1}\ s^{-1}$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	$pK_a = 10.25$
$OH^{\circ} + HPO_4^{2-} \rightarrow OH^- + HPO_4^{\circ -}$	$k_{12} = 2.2\ 10^6\ L\ mol^{-1}\ s^{-1}$
$OH^{\circ} + H_2PO_4^- \rightarrow OH^- + H_2PO_4^{\circ}$	$k_{13} < 10^5\ L\ mol^{-1}\ s^{-1}$
$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$	$pK_a = 7.2$
$OH^{\circ} + M \rightarrow$ products	k_R
$OH^{\circ} + S \rightarrow$ products	k_S
Net Equation for the generation of OH° (Stoichiometry)	
$2\ O_3 + H_2O_2 \rightarrow 2\ OH^{\circ} + 3\ O_2$	
$2\ O_3 + OH^- + H^+ \rightarrow 2\ OH^{\circ} + 4\ O_2$	

*) reaction rate constant taken out of literature as examples

for O_3:

$$c(OH^{\circ})_{SS} = \frac{c(O_3)_{SS}\{2k_1 10^{pH-14} + \sum_{i=1}^{m} k_{Ii}\ c(I_i)\}}{k_R c(M) + \sum_{i=1}^{n} k_{Pi}\ c(P_i) + \sum_{i=1}^{o} k_{Si}\ c(S_i)} \tag{5-6}$$

for O_3/H_2O_2:

$$c(OH^\circ)_{SS} = \frac{c(O_3)_{SS}\{2\mathrm{k}_1 10^{\mathrm{pH}-14} + 2\mathrm{k}_9\, 10^{\mathrm{pH}-11.6} c(H_2O_2)_{SS} + \sum_{i=1}^{m} \mathrm{k}_{\mathrm{I}i} c(I_i)\}}{\mathrm{k}_\mathrm{R} c(M) + \sum_{i=1}^{n} \mathrm{k}_{\mathrm{P}i} c(P_i) + \sum_{i=1}^{o} \mathrm{k}_{\mathrm{S}i} c(S_i)} \tag{5-7}$$

The numerator contains all hydroxyl radical forming reactions and all initiating reactions are summarized ($\Sigma \mathrm{k}_{\mathrm{I}i}\, c(I_i)$). The denominator contains all hydroxyl radical consuming reactions. The second term includes all reactions with intermediates ($\Sigma \mathrm{k}_{\mathrm{P}i}\, c(P_i)$), the third the reactions with scavengers($\Sigma \mathrm{k}_{\mathrm{S}i}\, c(S_i)$). Similarly, the steady-state concentrations of ozone and hydrogen peroxide can be calculated from the liquid phase mass balances.

The terms for the initiators $\Sigma\, \mathrm{k}_{\mathrm{I}i}\, c(I_i)$ and scavengers $\Sigma \mathrm{k}_{\mathrm{S}i}\, c(S_i)$ are those with the biggest uncertainty or error. The values of these terms vary depending on the water matrix. Generally, there is not enough kinetic information at hand to use such a complicated model, so that various simplifications have been developed. The following examples illustrate the various approaches that can be taken.

5.2.3 Semi-Empirical Model Based on the Mass Balance

In the following first example the liquid ozone concentration and the OH-radical concentration are calculated with semi-empirical formula from the mass balance for ozone (Laplanche et al., 1993). For ozonation in a bubble column, with or without hydrogen peroxide addition, they developed a computer program to predict the removal of micropollutants. The main influencing parameters, i. e. pH, TOC, UV absorbance at 254 nm (SAC_{254}), inorganic carbon, alkalinity and concentration of the micropollutant M are taken into consideration.

$$c(OH^\circ)_{SS} = \frac{c(O_3)_{SS}\{2\,\mathrm{k}_1 10^{\mathrm{pH}-14} + 3.16\; 10^{-7}\; 10^{0.42\mathrm{pH}} c(TOC) + 2\,\mathrm{k}_9\; 10^{\mathrm{pH}-11.6} c(H_2O_2)\}}{\mathrm{k}_\mathrm{R} c(M) + c(HCO_3^-)\;(\mathrm{k}_7 + \mathrm{k}_8 10^{\mathrm{pH}-10.25})} \tag{5-8}$$

The steady-state liquid ozone concentration is calculated with the help of a mass balance in which for the decay term the following equation was used:

$$-\frac{\mathrm{d}c(O_3)}{\mathrm{d}t} = \mathrm{w}\, c(O_3) \tag{5-9}$$

The OH° concentration is calculated as a function of:

$$c(OH^\circ) = \mathrm{f}\,(c(O_3), \mathrm{pH}, c(TOC), c(H_2O_2), SAC_{254}, c(M), c(HCO_3^-))$$

Based on 56 experiments carried out on natural water the following semi-empirical equation was developed:

$$\lg w = -3.93 + 0.24\ \mathrm{pH} + 0.7537 \lg \mathrm{SAC}_{254} + 1.08 \lg c(TOC) - 0.19 \lg c(Alk) \qquad (5\text{-}10)$$

$c(Alk)$: alkalinity in mg L^{-1} $CaCO_3$

This model was also successfully applied for three different experimental set-ups taken from literature with ozonated spiked tap water or raw water of similar composition. In each case good correlation between the experimental and calculated data was obtained.

5.2.4 Empirical Radical Initiating Rate

The next model (Beltrán et al., 1994 a) started with the attempt to ignore all initiators by setting $\Sigma k_{\mathrm{Ii}}\, c(I_i)$ to zero. The result was that the initiator term was not negligible. The fitting of the experimental data with a hydroxyl radical initiating rate ß was necessary. Beltrán et al. (1994 a) studied the oxidation of atrazine in distilled water with and without scavengers (carbonate, *tert*-butanol) under different conditions of ozone partial pressure, pH, temperature and concentration of the scavengers. The oxidation was modeled considering the above mentioned reaction mechanisms (see Table 5-1) as well as the molar balances for atrazine and ozone. In a first approach they neglected the initiators and assumed that the oxidation term of atrazine and the intermediates are constant.

$$\mathrm{k_R}\, c(M) + \sum_{i=1}^{n} \mathrm{k_{Pi}}\ c(P_i) = \mathrm{k_R}\, c(M)_o \qquad (5\text{-}11)$$

with the explanation that:

- atrazine and the intermediates have nearly the same rate constants due to the unselective character of OH° and the similar structure of the intermediates,
- the mass balance of all micropollutants is constant because of the negligible mineralization.

By a comparison of the calculated values for the OH° concentration according to equation 5-4 and 5-6 in connection with 5-11 it was shown that the initiation term was not negligible and the simplified model not appropriate. Thus, the authors defined a hydroxyl radical initiating rate ß that includes all possible initiating reactions, calculated by the OH° concentration difference between the experiment and the model.

$$c(OH^\circ)_{\mathrm{SS}} = \frac{c(O_3)_{\mathrm{SS}}\, 2\ \mathrm{k_1}\, 10^{\mathrm{pH}-14} + \beta}{\mathrm{k_R}\ c(M)_o + \sum \mathrm{k_{Si}}\ c(S_i)} \qquad (5\text{-}12)$$

ß: hydroxyl radical initiating rate

The scavenger term $\Sigma\, k_{Si}\, c(S_i)$ was calculated by known values. If only carbonates are present it is calculated with

$$\sum_{i=1}^{2} k_{Si}\, c(S_i) = k_9\, c(HCO_3^-) + k_{10}\, c(CO_3^{2-}) \qquad (5\text{-}13)$$

furthermore assuming that the formed carbonate radicals $HCO_3^\circ/CO_3^{\circ-}$ do not promote the radical chain reaction. Note however, that this is not always the case (for further information: Chen and Hoffmann, 1975).

Thus OH° concentration was calculated as a function of:

$$c(OH^\circ) = f\,(c(O_3), \mathrm{pH}, \beta, c(M), c(HCO_3^-))$$

With the help of this correction term the atrazine concentration could be calculated with a precision of ± 15 %. The ß-term showed no trend, no general considerations were possible. The prediction of the dissolved ozone concentration was only possible in the presence of scavengers. The effect of ozone consumption due to direct reactions with the intermediates was estimated.

The same method was used for the combination of ozone with ultraviolet radiation (Beltrán et al., 1994 b). Here the previous model was extended by terms considering the degradation rate due to direct photolysis. Again, the model was able to predict the experimentally observed oxidation time course of atrazine as well as the liquid ozone concentration with a precision of ± 15 %. However, the estimated concentration of hydrogen peroxide, which is formed during the AOP, was much too high. A plausible reason may be that decomposition of hydrogen peroxide by reaction with OH-radicals was not considered in the model.

In general, the model from Beltrán et al. uses ß as a kind of correction factor. Without experimental data from which ß can be calculated, no prediction is possible.

5.2.5 Empirical Selectivity for Scavengers

The following model was developed by Glaze and Kang (1988, 1989 a, b) for the ozone/hydrogen peroxide process in a semi-batch reactor. High organic background was not taken into account, as well as any initiators other than OH^- and H_2O_2. The effect of HCO_3^-/CO_3^{2-} was found to concur with the model prediction. A part of the OH-radicals destroyed by the reaction with the carbonate species will be regenerated by the following reactions:

$$CO_3^{\circ-} + H_2O_2 \rightarrow HO_2^\circ + HCO_3^- \qquad k_{14} = 8\ 10^5\ \mathrm{L\ mol^{-1}\ s^{-1}} \qquad (5\text{-}14)$$

$$HCO_3^\circ + HO_2^- \rightarrow HO_2^\circ + HCO_3^- \qquad k_{15} = 4.3\ 10^5\ \mathrm{L\ mol^{-1}\ s^{-1}} \qquad (5\text{-}15)$$

With the help of a term called selectivity S_{PER} (Glaze and Kang, 1989 a) this part of $CO_3^{\circ-}$, which reacts with hydrogen peroxide as a fraction of all reactions with $CO_3^{\circ-}$ is included in the model:

$$S_{PER} = \frac{k_{14}\, c(CO_3^{o-})\, c(H_2O_2)}{k_{14}\, c(CO_3^{o-})\, c(H_2O_2) + \sum_{j=1}^{n} k_j\, c(CO_3^{o-})\, c(I_j)} \tag{5-16}$$

S_{PER}: selectivity

That means that these reactions increase the steady-state concentration of OH°. The scavenger term of carbonate must be reduced by the selectivity term. The following expression is used in the model:

$$c(OH^{o})_{SS} = \frac{c(O_3)_{SS}\, \{2\, k_1 10^{pH-14} + 2\, k_9 10^{pH-11.6} c(H_2O_2)_{SS}\}}{k_R\, c(M) + (1 - S_{PER})\, \{k_8\, c(HCO_3^-) + k_7\, c(CO_3^{2-})\}} \tag{5-17}$$

Thus OH° concentration was calculated as a function of:

$$c(OH^{o}) = f\,(c(O_3), \mathrm{pH}, c(H_2O_2), c(M), c(HCO_3^-), S_{PER})$$

To determine the reaction rate Glaze and Kang divided the ozone/hydrogen peroxide system into three regions depending on different relationships concerning the molar dose rate $F(O_3)$ of ozone and the molar feed rate $F(H_2O_2)$ of hydrogen peroxide.

Region 1: $F(O_3) > F(H_2O_2)$: Ozone is measurable in the liquid, hydrogen peroxide is consumed as fast as it is added.

Region 2: $F(O_3) = 2\, F(H_2O_2)$: Stoichiometric point where two moles of H_2O_2 and one mole of O_3 are necessary to produce two moles of OH°

Region 3: $F(O_3) < F(H_2O_2)$: Hydrogen peroxide is measurable in the liquid, ozone is consumed as fast as it is added. ($S_{PER} = 1$)

For each region certain assumptions were possible. For further details the reader is referred to the original articles (Glaze and Kang, 1988, 1989 a, b).

The model was tested with distilled water containing carbonate. As a tracer substance PCE was used to predict the rate constant with OH° (Glaze and Kang, 1989 a). Good results where found in the ozone transfer limited region 3, in region 1 and 2 the results were poorer. In region 3 it was also possible to calculate the hydrogen peroxide concentration in very good agreement with the measured values.

Using this approach of a selectivity term S_{PER} Sunder and Hempel (1996) successfully modeled the oxidation of small concentrations of Tri- and Perchloroethylene ($c(M)_o = 300$–$1300\ \mu g\ L^{-1}$) by ozone and hydrogen peroxide in a synthetic ground water (pH = 7.5–8.5; $c(S_i) = 1$–3 mmol $CO_3^{2-}\ L^{-1}$). In this study an innovative reaction system was used; the oxidation was performed in a tube reactor and mass transfer of gaseous ozone to pure water was realized in a separate contactor being located in front of the tube reactor. By this way a *homogeneous* system was achieved. Since the two model compounds react very slowly with molecular ozone ($k_D < 0.1\ L\ mol^{-1}\ s^{-1}$), nearly the complete oxidation was due to the action of hydroxyl radicals, which were produced from the two oxidants (O_3/H_2O_2). With

$S_{PER} = 0.2$ the experimental results could be excellently modeled and S_{PER} did not vary significantly with the variation of the initial oxidant concentrations and the pH.

5.2.6 Summary of Chemical Models for Drinking Water

The following Table 5-2 gives an overview of the discussed chemical models.

Table 5-2: Overview of the discussed chemical models.

Author/ System	Matrix	Promoter considered	Scavenger considered	Specials	Results
Glaze and Kang O_3/H_2O_2	distilled water with carbonate	OH^-, H_2O_2	HCO_3^-, CO_3^{2-}	S_{PER}: selectivity	only good results in region 3
Laplanche O_3/H_2O_2	tap and raw water	OH^-, H_2O_2	HCO_3^-, CO_3^{2-}, TOC	semi-empirical	good correlation
Beltrán O_3, O_3/UV	distilled water with/without scavengers	OH^-, UV	HCO_3^-, CO_3^{2-}, *tert*-butanol	β: hydroxyl radical initiating term	prediction was only possible with β included
Sunder and Hempel O_3/H_2O_2	synthetic ground water	OH^-, H_2O_2	HCO_3^-, CO_3^{2-}	S_{PER}: selectivity	$S_{PER} = 0.2$ excellent correlation

One of the unsolved questions regarding the chemical kinetic model is the influence of scavengers and initiators especially with water containing organic matrix. Further investigations are necessary to solve the question to what amount the organic matrix promotes or terminates the chain reaction. Here models could act as a tool to understand this process in more detail.

5.2.7 Models Including Physical Processes

Modeling of micropollutant removal during drinking or ground water ozonation is often found to be a process without mass transfer enhancement, meaning that all reactions without exception develop in the liquid bulk (slow to moderate kinetic regime, $E \leq 1$) (Marinas et al., 1993). However, in an attempt to develop a more general model, the work of Marinas et al. (1993) was recently extended by the incorporation of fast reactions respectively the consideration of mass transfer enhancement into the model (Huang et al., 1998). The mass transfer and the resulting liquid ozone concentration is calculated via mass balances. Most models are based on the assumption of completely mixed liquid. Examples for more complex hydrodynamic systems useful in scale-up are given by Marinas et al. (1993) as well as Laplanche et al. (1993). They achieved good predictions of the ozone (and hydroxyl radical) residual concentrations in pilot-scale bubble columns. As we already pointed out, for successful modeling in such systems all relevant reactions and the corresponding reaction rate constants have to be known.

5.3 Modeling of Waste Water Oxidation

Models in waste water applications have to describe both chemical and physical processes. The concentration of pollutants is usually much higher than in drinking water, leading to high ozone consumption in the reactor. This in turn requires high mass transfer rates in the reaction system. A possible consequence is that the reaction rate is dependent on the mass transfer rate and vice versa. This can cause concentration gradients to occur in the reaction system, depending on its hydrodynamics. Therefore, the mathematical models used in this area are based on the reaction rate equation to describe the oxidation of the pollutants, combined with equations to describe the mass transfer rate and mixing.

In a first approximation a pseudo-first order reaction rate is often assumed. This must be checked against what really happens in the reactor. In semi-batch or nonsteady state oxidation, the concentration of the pollutants as well as the oxidants can change over time. A common scenario: initially a fast reaction of ozone with the pollutants occurs, the reaction is probably mass transfer limited, the direct reaction in the liquid film dominates, and no dissolved ozone is present in the bulk liquid. As the concentration of the pollutants decreases, the reaction rate decreases, less ozone is consumed, leading to an increase in the dissolved ozone concentration. Metabolites less reactive with ozone are usually produced. This combined with an increase in dissolved ozone, may also shift the removal mechanism from the direct to the indirect if radical chain processes are initiated and promoted (see Chapter A 2). These changes are often not observed in waste water studies, mostly because dissolved ozone is often not measured.

In steady-state experiments, although all concentrations remain constant, the simplification to pseudo-first order should be avoided or used only conditionally. It is important to remember that the pseudo-first order rate coefficient k' is also dependent on the concentrations of the oxidants. For example if the steady-state dissolved ozone concentration changes due to changes in the operating conditions, k' also changes. The same is true for the OH° concentration.

The concentrations of the oxidants involved in the indirect reaction are a function of the inorganic and organic carbon in the water matrix. In principle they can be calculated from the material balances on the reaction system developed for drinking water applications. However, the composition of the organic fraction is much more complex as well as present in higher concentrations in waste water. Usually it is unknown whether a compound acts as a scavenger or initiator, let alone what value its reaction rate constant has. Consequently, this method is impractical for waste water applications. The drinking water models though can be helpful in understanding possible effects and trends.

Modeling of waste water ozonation generally suffers from incomplete information or high complexity of the model. Most of the effort in modeling waste water is devoted to quantifying the influences on mass transfer (e. g. *alpha* factor, Chapter B 3) as well as the interactions of mass transfer and the (direct) reaction rate (mass transfer enhancement, Chapter B 3). The influences on the indirect reaction are usually summarized in a factor involving pH. The following discussion gives examples of some of these models.

5.3.1 Chemical and Physical Models Based on Reaction Mechanisms and Mass Balances

An ambitious example for the modeling of waste water ozonation based on reaction mechanisms and mass balances is found in the work of Stockinger (1995). In a lab-scale bubble column (V_L = 2.4 L) he ozonated a synthetic wastewater containing 11 nitro- and chloroaromatic compounds. His model comprised direct and indirect reactions with the contaminants in the liquid bulk. Reactions occurring in the liquid-side film between ozone and the contaminants were also considered. A compartment model of four CSTRs was used for the gas phase. Although he was able to use k_D and k_R values from the literature, no close match between the measured and the calculated concentration profiles was obtained. Due to the high complexity of the chemical and hydrodynamic models, the limit of the available computer power was reached, which limited the possibilities of fitting the model.

The two following studies are noteworthy as successful examples for the modeling of waste water ozonation, where a close match between the measured and the calculated concentration profiles was achieved. In each case only one organic model compound was initially present. In both studies it was found that the k_La value of the completely-mixed semi-batch reactors was very dependent on the concentration of the original compound, thus exerting considerable influence on the oxidation process. In order to assess and model the changing k_La, two different approaches were made.

1. In a chemical model for the ozonation of 2-hydroxypyridine (HPYR) in a STR ($c(M)_o$ = 0.85–5.15 mmol L^{-1}; n_{STR} = 380 min^{-1}; Andreozzi et al., 1991), the mechanism of the direct reactions of ozone with the initial compound as well as the most important organic intermediates, the ozone decay and the action of hydrogen peroxide were included. Reevaluating these experimental results to improve the model, Tufano et al. (1994) postulated that k_La varied with reaction time. As the reaction time increased, the concentration of HPYR decreased, changing the value of k_La. They integrated k_La as an adjustable parameter into the model. However, no measurements of the varying k_La were made.
2. The ozonation of phenol ($c(M)_o$ = 5–50 mg L^{-1}) in a small bubble column (gas-wash bottle, V_L = 0.5 L) could be modeled when the effect of phenol on the mass transfer rate was considered (Gurol and Singer, 1983). Phenol reacts very fast with ozone, and its effect on the mass transfer rate changes as its concentration changes. The change in $k_La(O_3)$ values (or the *alpha* factor) due to different concentrations of phenol was experimentally assessed, indirectly through oxygen transfer experiments (see Section B 3.3.3). The disappearance of phenol and the concentration profiles of three intermediate products were described well when appropriate $k_La(O_3)$ values were used.

Due to the complexity of most waste waters and unknown oxidation products, differences in lumped parameters such as COD or preferably DOC are used to quantify treatment success. A model to describe the oxidation process, including physical and chemical processes, based on a lumped parameter has been tried (Beltrán et al., 1995). COD was used as a global parameter for all reactions of ozone with organic compounds in the chemical model. The physical model included the Henry's law constant, the k_La, mass transfer enhancement (i. e. the determination of the kinetic regime of ozone absorption) as well as the reactor hydrodynamics. The results from the ozonation of two complex industrial waste waters from a distillery and a tomato processing company were compared to model calculations. Unfortunately, little removal of COD in the bubble column reactors was achieved experimentally: 10 and 35 % in the lab-scale studies with distillery and tomato waste water, respectively, and 5 % in pilot-scale with tomato waste water. The model is interesting in its approach, however, further experimental verification with larger removal efficiencies are necessary. Moreover, it is questionable whether it is possible to lump all reactions in such complex waste waters together.

5.3.2 Empirical Models

The works of Whitlow and Roth (1988) as well as of Beltrán et al. (1990) employed an empirical approach for modeling. This procedure uses a global rate law of n^{th} order for the observed disappearance of all target contaminants

$$-\frac{\mathrm{d}c(M)}{\mathrm{d}t} = k'\, c(M)^n \tag{5-18}$$

and correlates the determined global rate coefficient k' with "significant observable parameters of the system" (Whitlow and Roth, 1988). Thus, all individual reactions of ozone with organics are lumped together and ozone decay is globally incorporated by the effect of varying the pH. The influence of mass transfer as well as mass transfer enhancement is also lumped in observable parameters like, e. g. the ozone dose rate ($Q_G\, c_{Go}\, V_L^{-1}$) or the initial substrate concentration $c(M)_o$. As a result, the coefficients which are e. g. calculated by multi-linear regression, represent the boundary conditions of the individual system but normally cannot be used in another.

5.3.3 Summary

Table 5-3 gives an overview of some important work in the field of waste water modeling. By comparing the 'completeness' of the individual approaches the reader can get an idea of what should be done in his or her own research work. Due to the complexity of the matter it is strongly recommended to study at least the following works Gurol and Singer (1983), Andreozzi et al. (1991), Stockinger (1995) and Tufano et al. (1994) in detail.

Table 5-3: Examples of waste water ozonation modeling (n. d. = not determined).

Process	Chang and Chian, 1981	Whitlow and Roth, 1988	Beltrán et al., 1990	Andreozzi et al., 1991	Tufano et al., 1994	Gurol and Singer, 1983	Stockinger, 1995	Beltrán et al., 1995
type of waste water	synthetic	synthetic, industrial ww	synthetic	synthetic	synthetic	synthetic	Synthetic	industrial ww
contaminants	methanol	phenol, CN^-, NH^+ etc.	o-cresol	2-HPYR	2-HPYR	phenol	nitro-, chloro-aromatics ($\Sigma 11$)	A: distillery ww B: tomato ww
type of reactor	BC	BC, STRs	STR	STR	STR	gas-wash bottle	BC	STR
mixing of liquid	completely	completely	completely	completely	completely	completely	completely	completely
mixing of gas	plug flow	n. d.	n. d.	n. d.	n. d.	n. d.	completely in 4 sections	plug flow
k_La	measured	n. d.	measured	measured, used as parameter	measured, modelled	measured	measured	measured
regime	slow	n. d.	fast	n. d.	moderate	n. d.	n. d. but film reactions modeled	A: moderate to fast B: slow
E	$E \approx 1$		$E = 3$	$E \leq 1.5$ (estimate)	$E = 1.2–1.5$	*alpha* factor!		
pH/T in °C	9/25°C	2–12/ 15–30	2, 7, 8.5/ 10, 20, 30	5 + TBA/20	5 + TBA/20	3/20	2, 12/20	A: 8–8.5/17 B: 7–7.5/18
n of contaminant	2^{nd}	n^{th}	n^{th}	2^{nd}	2^{nd}	2^{nd}	2^{nd}	pseudo 1^{st}
n ozone decay	1^{st}	pH dependent	pH dependent	2^{nd}	2^{nd}	2^{nd}	2^{nd}	2^{nd}
mineralization	yes	no	no	no	no	no	yes	no
H_2O_2 considered	no	no	no	yes	yes	no	yes	no

5.4 Final Comments on Modeling

The utility and validity of models are often overrated. They are usually only valid over a small range and under certain conditions. These have to be checked before using a model. In drinking water applications with significant contribution from indirect reactions to the oxidation rate, the major difficulty is the determination of the OH° concentration. Models with various simplifications to describe the influence of scavengers and initiators on the complex reaction mechanisms have been developed. The search for general models is complicated by the fact that a multitude of compounds, both inorganic and organic carbon, can act as either scavengers or initiators. To model the effect of these compounds on the oxidation rate, rate constants are necessary. The mechanism and rate constants for inorganic carbon are well known. Due to the multitude of possible organic compounds, the lumped parameter DOC is used to describe them. The results of the drinking water modeling efforts reported above have shown that all DOC is not alike, not even in drinking water. Carrying this further to waste water applications we realize that the complexity makes calculation of OH° concentrations from individual parameters almost impossible and that the validity of models using lumped parameters i. e. DOC, COD or pH to describe reaction rates is severely restricted.

Nonetheless, the long term goal is to develop models with a large range of validity. Existing models must be checked, expanded and possibly discarded. New or expanded ones will be developed as our understanding increases, most likely leading to increased complexity. As pointed out in the introduction, however, it is important to keep the models usable.

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6 Application of Ozone in Combined Processes

The previous chapters in Part B have dealt with the basics of the ozonation process. As seen in the discussion of full-scale ozonation applications (Chapter A 3), ozone is rarely used alone. The combination of ozone with other water treatment processes can often greatly increase effectiveness and cost efficiency of ozonation, or the addition of ozonation to an existing production process can increase efficiency in achieving production goals. Process combinations make sense that utilize ozone's effectiveness in:

- disinfection,
- oxidation of inorganic compounds,
- oxidation of organic compounds, including taste, odor, color removal and
- particle removal.

An example where all four areas are utilized in combination with production processes is found in ozone applications in the semiconductor industry (Section B 6.1). Part of ozone's effectiveness in these four areas is derived from its production of OH-radicals. Combined processes, i. e. advanced oxidation processes, represent alternative techniques for catalyzing the production of these radicals and expands the range of compounds treatable with ozone (Section B 6.2).

Treatment combinations often introduce a third phase into the system, either solid or liquid, intentionally (e. g. adsorption onto a solid, absorption into a liquid, biodegradation) or because of contamination (soil, cutting oils). The third phase can have many effects on the ozonation step (Section 6.3). The treatment combination with biodegradation is based on the finding that many oxidation products of biorefractory pollutants are easily biodegradable. Combining chemical oxidation with a biological process can minimize the amount of oxidant needed and thus reduce operating costs (Section 6.4).

6.1 Applications in the Semiconductor Industry

Over the last few years interest in ozone application in the semiconductor industry has increased. Its use in the cleaning process for wafers is well-established. Here its ability to oxidize organic and metallic contaminants in the aqueous phase is utilized. New applications exploiting its ability to oxidize inorganics as well as organics in the solid phase are being investigated, e. g. in fast oxidation of silicon (step 1 below) and photoresist removal (step 4). Another use is the disinfection of deionized water to keep the water system free from microbial contaminants. For better understanding of how ozone is used, the process used for the production of chips from wafers is briefly explained using the simplified process sequence shown in Figure 6-1. Further information on the whole process in the semiconductor industry can be found in Gise and Blanchard (1998), Kern (1993).

Production Sequence

A wafer is a thin slice of a crystal, grown from pure silicium (= silicon) and used to produce electronic components like integrated circuits (IC). Silicium itself does not conduct electricity, additional ions must be introduced into its matrix to make it conductive (ion implantation). These changes in the crystal structure are made in intricate geometrical patterns to achieve the desired conductive properties. The necessary production steps are briefly explained below (Figure 6-1).

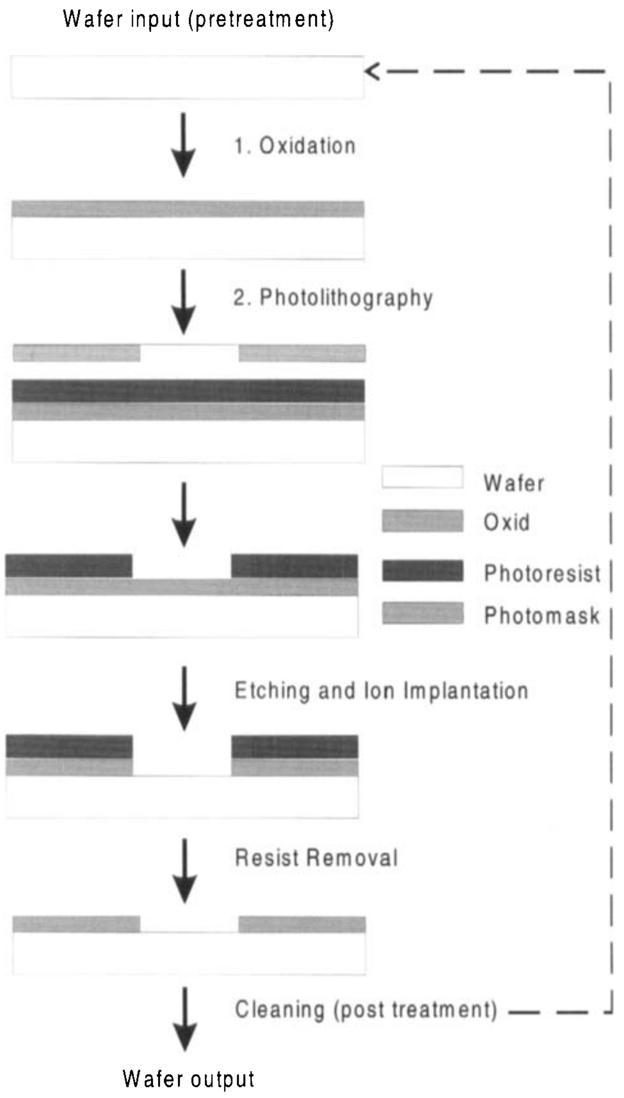

Figure 6-1: Process sequence (simplified).

1. Oxidation
An oxide layer is produced on the surface of the silicium wafer (SiO_2). This layer of silicium dioxide is an isolating layer on the surface, it is usually grown in an atmosphere containing oxygen, water vapor or other oxidants (O_2, O_3, H_2O_2).

2. Photolithography
In the photolithographic process, the geometrical pattern that produces the desired electrical behavior is transferred to the surface of the wafer.
a) The wafer has been coated with photoresist which can be applied as a thin film and acts like the photographic film in a camera. An image can be developed in the photoresist by using a mask. Through a photomask the wafer is exposed using UV radiation. The radiation alters its chemical bonding to make it more soluble where it has been exposed (positive photoresist).
b) After the development of the photoresist and its removal, the positive image stays on the wafer in the resist.

3. Etching and Ion Implantation
In this process step an etchant (gas or liquid) removes the SiO_2 where it is not protected by the photoresist. Ions are implanted into the unprotected silicium. With the implantation of ions the structure of the surface will be changed.

4. Photoresist stripping
The photoresist is removed.

Because the geometrical patterns are so intricate, multiple passes through the sequence may be necessary to obtain the desired structure. Every wafer processing step is a potential source of contamination. Consequently, cleaning of the wafers must take place after each processing step and is so the most frequently repeated step during manufacturing. The following chapter will provide some examples of ozone application, concentrating on the cleaning and oxidation process. The other possible application of photoresist removal is still not widespread.

6.1.1 Principles and Goals

In the semiconductor industry cleanliness is an absolute requirement. Even small traces of contaminants can cause modification of the structure of the wafer surface area. Cleaning processes employing ozone in the chip production have been in use since the late 80's. Interest continues to grow as modifications and new methods are developed.

The requirement for an efficient cleaning process is the removal of all contaminants which would effect the functionality or reliability of elements. Possible contaminants can be divided into the following groups:

- particles: mainly from the ambient environment and from humans (skin, hair, clothes), but solvents and moving parts can also act as a particle source,
- organic impurity: e. g. not completely removed photoresist or solvents,

- ionic contamination: from humans, solvents,
- atomic contamination: elemental metal films from solvents or machines.

Every wafer processing step is a potential source of contamination, each step with its specific type of contaminant. This means that an efficient cleaning process consists of several cleaning steps in order to remove all contamination from the crystal.

6.1.2 Existing Processes for Cleaning

The existing cleaning methods can be divided into wet and dry cleaning. The wet cleaning process uses a combination of solvents, acids, surfactants and deionized (DI) water to spray and dissolve contaminants from the surface area. The DI water is used to rinse after each chemical use. The oxidation of the wafer surface is sometimes integrated into the cleaning steps.

Dry cleaning, also called gas-phase cleaning, is based on excitation energy such as plasma, radiation or thermal excitation. This section will concentrate on the wet processes, the area where ozone is of interest.

To better illustrate the purpose behind the cleaning steps, the conventional RCA cleaning process will first be examined in detail. It was developed for wafer cleaning in 1965, published in 1970 (Kern and Puotinen, 1970) and is still of importance. The following Table 6-1 shows the steps of the preliminary cleaning and the conventional RCA cleaning, as well as the purpose of each step.

The RCA cleaning was developed at a time where the semiconductor industry was much smaller and the environmental restrictions were not as strict as today. Since then the goal in the development of new processes was to reduce the number of necessary cleaning steps, chemical consumption and waste disposal. Recent improvements in wet cleaning have been very successful in further reducing costs, chemical and water usage. Many advances are based on the use of ozonated ultra pure water (UPW) as a replacement for hydrogen peroxide or even sulfuric based mixtures (Heyns et al., 1999).

The so-called IMEC clean (from the Interuniversity Microelectronic Center, set-up in 1984 by the Belgian Government) is one possible improvement. It is a simple two step process with an optional third step (Heyns et al., 1997).

1. Sulfuric acid/ozone mixture (SOM): to remove organic contamination and growth a thin chemical oxide layer. Under optimized conditions ozonated ultra pure water (UPW) can replace the SOM. The SOM step or ozonated UPW step replaces the SPM (sulfuric acid, hydrogen peroxide, DI water mixture) step.
2. **HF/HCl** step to remove particles, metals and oxide, H stabilized surface.
   optional
3. **HCl/O_3** or other ozone or hydrogen peroxide mixtures: re-grow a thin oxide layer, hydrophilic passivation

Comparison of the IMEC process with the RCA cleaning shows a drastic reduction in the number of necessary steps. The RCA with preliminary cleaning includes nine steps, this is

Table 6-1: RCA cleaning (Ohmi, 1998; Kern, 1999).

Process	Procedure	Goals
Preliminary Cleaning		
H_2SO_4/H_2O_2 (4 : 1), 120–150 °C	**SPM** (**S**ulfuric acid, hydrogen **P**eroxide, DI water **M**ixture), often called Piranha	Removal of organic carbon
DI water	**UPW** (**U**ltra **P**ure **W**ater)	Rinse
HF (0.5 %)	**DHF** (**D**iluted **H**ydrofluoric acid)	Removal of oxide
DI water	**UPW**	Rinse
RCA **Standard Clean 1 (SC1)**		
$NH_4OH/H_2O_2/H_2O$ (1 : 1 : 5)*, 70–90 °C	**APM** (**A**mmonium hydroxide, hydrogen **P**eroxide, DI water **M**ixture)	Removal of particles, organics, some metals
DI water	**UPW**	Rinse
Standard Clean 2 (SC2)		
$HCl/H_2O_2/H_2O$ (1 : 1 : 6)*, 70–90 °C	**HPM** (**H**ydrochloric acid, hydrogen **P**eroxide, DI water **M**ixture)	Removal of metals
DI water	**UPW**	Rinse
Oxide Growth (Possible after SC1 or SC2)		
HF (0.5 %)*	**DHF**	Growth of oxide

* various concentrations and mixtures are used

reduced to two/three steps with the IMEC process. The number of chemicals goes from six (RCA) to four (IMEC).

The following sequence reduces the number of necessary chemicals even more. Megasonic (0.8–1.2 MHz) is used to increase the efficiency of particle removal (Kanetaka et al., 1998), the so-called **UCT cleaning** (ultra clean technology).

1. **Ozonated DI Water** (5 mg L^{-1}): step to remove organic carbon and metal
2. **$HF/H_2O_2/H_2O$/Surfactants + Megasonic** (0.5 % : 0.1–1 %): step to remove particle, metal and to grow chemical oxide layer
3. **Ozonated Water + Megasonic** (1 mg L^{-1}): removal of organic carbon and adhered chemicals
4. **DHF/O_3** (0.1 %): growth of chemical oxide
5. **DI Water + H_2 + Megasonic:** rinsing

The whole process is done at room temperature.

The requirements for these applications with respect to ozone concentration and flow rate depend on the application. For the cleaning process a liquid concentration of about 5 to 20 mg L^{-1} is normally mentioned, for photoresist removal much higher concentrations are required (50 mg L^{-1} and higher).

6.1.3 Process and/or Experimental Design

General considerations for the design of ozonation processes, or for experimental work on developing new applications or improving existing methods are contained in the following section.

Define System: The variability in water found in other applications is greatly reduced here since ultra pure water (> 18 MΩ) is used in all applications sometimes in combination with defined chemicals. The industry requirement of "absolutely clean" extends to clean equipment (ozone generator, contact system), which means no particle generation, metal, ion or organic contamination. A whole industry has been developed to supply devices which fulfill these requirements.

Select Analytical Methods: In order to ensure reproducibility process control is required. Especially the liquid ozone concentration must be measured (see Section B 2.5).

Determine Procedure: The basic reactions are the same as in drinking water and waste water treatment. Therefore, knowledge about necessary equipment (Chapter B 2), ozone mass transfer (Chapter B 3) and reaction kinetics (Chapter B 4) including influencing parameters are very helpful for the development of new cleaning methods or recipes.

The absorption of ozone into water and the processes for the wafer (cleaning, photoresist removal etc.) are often two separate systems with distances between them of up to 40 m. Therefore the decay rate of ozone or at least the liquid ozone concentration near the point of use should be measured to insure reproducibility of the process.

Evaluate Data and Assess Results: See Chapter B 1

6.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been defined by Glaze et al. (1987) as water treatment processes that involve the generation of highly reactive radical intermediates, especially OH°. Even ozone alone at high pH-values is one kind of AOP. Because ozone reacts with most organic contaminants in natural waters primarily through the nonselective indirect pathway, AOPs represent alternative techniques for catalyzing the production of these radicals, thereby accelerating the destruction of organic contaminants. Since the radicals are relatively nonselective in their mode of attack, they are capable of oxidizing all reduced material and are not restricted to specific classes of contaminants as is the case with molecular ozone.

The mechanism of these AOPs was already described in Chapter A 2, the importance and influence of various parameters affecting the oxidation process was discussed in Section B 4.4. The goal of the following section is to give some examples of existing processes and some general hints for the application of AOP.

6.2.1 Principles and Goals

Ozone is one of the strongest oxidants in drinking and waste water treatment. Due to the slow reaction rate constants and mostly incomplete mineralization with the direct reaction of ozone, treatment methods with an even stronger oxidant, the OH-radical, were developed such as:

- Ozone/hydrogen peroxide
- Ozone/UV radiation
- UV radiation/hydrogen peroxide

By combining two oxidants, the oxidation potential will increase and the treatment can be more successful than a single oxidant (UV, H_2O_2 or O_3). Much theoretical and practical work has been done in this field. Comprehensive reviews can be found in Peyton (1990), Camel and Bermond (1998).

6.2.2 Existing Processes

Ozone/Hydrogen Peroxide (O_3/H_2O_2)

The O_3/H_2O_2 system is also called PEROXONE. Its oxidation potential is based on the fact that the conjugate base of H_2O_2 can initiate ozone decay, which leads to the formation of OH° (Staehelin and Hoigné, 1982). Brunet et al. (1984) and Duguet et al. (1985) found that the addition of hydrogen peroxide enhanced the efficiency of oxidation of several organic substances. In a bench scale study of TCE and PCE and an associated pilot-scale study of contaminated groundwater with these compounds in Los Angeles, Glaze and Kang (1988) reported the successful application of O_3/H_2O_2.

If compounds already react very fast with ozone, the addition of hydrogen peroxide is nearly ineffective, which was shown by Brunet et al. (1984) in the case of benzaldehyde and phthalic acid. The functional groups on the aromatic ring are relatively reactive towards molecular ozone. The advantage of this process lies in the removal of compounds relatively non-reactive with ozone. It was shown that the oxidation of oxalic acid, which is often an end product in the case of molecular ozone reactions, was significantly accelerated with the addition of hydrogen peroxide.

An optimum dose ratio of H_2O_2/O_3 has often been shown to be in a molar range of 0.5–1 depending on the presence of promoters and scavengers. Peroxide itself can act as a scavenger as well as an initiator, so searching for the optimum dose ratio is important. Enhancement of ozone mass transfer over that during ozonation alone can be expected in many cases.

Ozone/UV Radiation (O_3/UV)

Because of the stronger photolysis of ozone compared to hydrogen peroxide in combination with UV radiation ($\varepsilon_{254\,nm} = 3\,300\ M^{-1}\ cm^{-1}$; compared to $\varepsilon_{254\,nm} = 19\ M^{-1}\ cm^{-1}$ for

H_2O_2) the oxidation potential is higher than in the combination hydrogen peroxide/UV radiation (see below).

Prengle et al. (1975) were the first to see the commercial potential of the O_3/UV system in waste water. They showed that this combination enhances the oxidation of complexed cyanides, chlorinated solvents, pesticides and lumped parameters like COD and BOD (cited by Glaze et al., 1987).

Paillard et al. (1988) summarized that O_3/UV treatment is not suitable for the removal of aliphatic organohalogen compounds because less energy was required to remove them using air stripping. They found that an energy consumption of about 290–380 Wh m^{-3} was required for 90 % removal for unsaturated organohalogen compounds, whereby no optimization was done and could reduce these numbers.

In other studies it was shown that ozone in combination with UV radiation is capable of removing halogenated aromatic compounds and that the oxidation is faster than with ozone alone (Peyton et al., 1982; Glaze et al., 1982). The optimum ozone-UV ratio varies depending on the water and its matrix, no general guidelines can be given. However, ozone must be present in the liquid, which in the case of waste water is not always the fact.

Hydrogen Peroxide/UV Radiation (H_2O_2/UV)

With the addition of hydrogen peroxide to UV radiation, the elimination rate of pollutants can be increased. Hydrogen peroxide is cheaper than ozone production, and the application is less complicated and requires less safety precautions than the more toxic ozone. All this allows hydrogen peroxide/UV radiation to be easily included in a treatment scheme. It has its drawbacks though.

The photolysis of one mole hydrogen peroxide leads to two moles OH°, making it seem that this combination is the ideal treatment when looking only at the theoretical yield of the oxidant (see Chapter A 2). In practice due to the low extinction coefficient, hydrogen peroxide is a poor absorber at 254 nm and the efficiency in producing OH° is low. Because of this low absorption coefficient ($\varepsilon_{254\,nm} = 19\ M^{-1}\ cm^{-1}$) a surplus of H_2O_2 is necessary or a longer UV-exposure-time.

In the case of drinking water treatment, high concentrations of hydrogen peroxide at the outlet of the treatment plant can be a problem. Often a limit exists, in Germany it is 0.1 mg L^{-1}. The treatment of pesticide-containing groundwater with hydrogen peroxide/UV was studied by the research group from Wabner and taken to pilot scale (Pettinger, 1992; Wimmer, 1993). The pesticides could be removed to under the required level (0.1 ng L^{-1}) from 0.25 ng L^{-1} for atrazine and 0.55 ng L^{-1} for desethylatrazine, the problem concerning the remaining concentration of hydrogen peroxide was not solved.

Comparison

If properly used, AOPs generally result in higher oxidation rates than ozone alone, but need to be evaluated for effectiveness, costs and possible side effects (Glaze, 1987). However, for removing taste and odor problems in drinking water, ozone alone is sufficient without the addition of hydrogen peroxide or ultra violet radiation.

For drinking water treatment plants a comparison of the AOPs showed that the combination ozone/hydrogen peroxide is the most efficient and inexpensive combination followed by ozone/UV radiation (Glaze et al., 1987; Prados et al., 1995).

The mechanism in Chapter A 2 showed that O_3/UV and O_3/H_2O_2 are similar, in the first one H_2O_2 is formed *in-situ*, while it is added in the second process. When a substance absorbs strongly in the UV region, the O_3/UV process can be much more effective, which was reported by Peyton et al. (1982) in the case of tetrachloroethylene. For some photolytically labile substances like pesticides the reaction rate is so large that little is to be gained from using ozone. On the other hand when the substances are not photolyzed directly, the use of UV combined with O_3 to generate hydrogen peroxide makes little sense.

An advantage of the O_3/H_2O_2 process is that it does not require maintenance such as cleaning or replacement of a UV lamp, and the power requirements are usually lower. Treatment plants which already use ozone as a treatment step can easily add hydrogen peroxide to increase the reaction rate.

6.2.3 Experimental Design

In addition to the general aspects for experimental design (see Chapter B 1) the following aspects should be considered:

Define System:

- Water: Due to the enormous influence of the water composition always use the same water which is to be treated later.

- Oxidant: Avoid treating water by AOP which can easily be oxidized by ozone or UV itself.
  Use screening methods to find out if you are using the right dose rates.

If the water consumes ozone very fast, in this case faster than transferred, a mass transfer limitation can occur. Ozone could already be consumed before the second oxidant is added. Then one cannot talk about combined processes, a pretreatment with ozone alone could be a possible solution before using combined oxidants. Even if ozone is not consumed before the addition of the second agent the role of transfer limitation should always be considered and investigated.

Reactor: Conceptually the application of O_3/UV and O_3/H_2O_2 is quite simple. In the first case the water is treated by UV lamps while or before ozone/oxygen gas stream is bubbled through the solution. In the second case hydrogen peroxide is added while ozone is bubbling through the solution. In practice however it necessary to pay attention to several details.

For the O_3/UV process Prengle (1975) has recommended the use of stirred photochemical tanks (STPR) to obtain better mass transfer. Simultaneous ozone contacting and irradiation was found to be more successful than in sequence due to the need for good ozone transfer to sustain the OH-radical reaction. A promising alternative to the STPR may be the use of static mixers in conjunction with a bubble column-photochemical reactor and recirculation pump.

For the AOP combinations with ultraviolet lamps, low pressure mercury lamps are often used. Their major output is at 254 nm (85 % of total intensity), which is important for the efficiency of the ozone photolysis. Mercury lamps which have a quartz envelope without TiO_2 doping also emit the 185 nm line which produces ozone and aids in hydrogen peroxide photolysis. For drinking water applications where the hydrogen peroxide concentration is above the legal limits, lamps emitting a large fraction below 254 nm should be considered.

Select Analytical Method: In order to calculate the mass balances necessary for data evaluation, the concentration of the incoming and outgoing ozone gas stream as well as the liquid concentration of ozone and/or hydrogen peroxide must be measured. In case of UV-radiation the amount of photons should be measured by actinometry.

Determine Experimental Procedure: see Section B 1.2

Evaluate Data and Assess Results: see Section B 1.1

6.3 Three-Phase Systems

Anja Kornmüller

Ozone is applied in three-phase systems where a selective ozone reaction, oxidation of residual compounds and/or enhancement of biodegradability is required. It can be used to treat drinking water and waste water, as well as gaseous or solid wastes. Especially in drinking water treatment full-scale applications are common, e. g. for particle removal and disinfection, while in waste water treatment sludge ozonation and the use of catalyst in AOP have been applied occasionally. Current research areas for three-phase ozonation include soil treatment and oxidative regeneration of adsorbers. Ozonation in water-solvent systems is seldom studied on the lab-scale and seems favorable only in special cases. In general, potential still exists for new developments and improvements in ozone applications for gas/water/solvent and gas/water/solid systems.

The principles and goals of ozone application in both types of three-phase systems are discussed in Section B 6.3.1. Since mass transfer may decisively influence the oxidation outcome in these complex systems, their additional resistances and effects on mass transfer is also discussed in detail in this section. In doing so, the gas/water/solvent system is used as an example for both types of system, leaving the reader to adapt the principles to the gas/water/solid systems by him- or herself. Examples of ozone application in both types of three-phase systems are then presented (Section B 6.3.2), with emphasis on their goals, as well as technical advantages and disadvantages, while Section B 6.3.3 provides useful advise for experimentation with three-phase systems.

6.3.1 Principles and Goals

Three-phase systems contain a second fluid or solid phase in addition to the water and gaseous ozone/oxygen or ozone/air phase. They can be classified according to whether the solvent or solid phase is dispersed in water or segregated (Table 6-2). Ozone can be directly or indirectly gassed to the reactor. If it is directly gassed, the chemical reaction in the liquids or in the liquid film around particles occurs simultaneously with the mass transfer. In indirectly gassed reactors, the ozone is absorbed in pure water or the second liquid phase prior to entering the reactor containing the water and/or solid to be treated.

Table 6-2: Three-phase systems classified by the state of the third phase in water.

State of Third Phase in Water/in System ...	
Gas/Water/Solvent	Gas/Water/Solid
• non-dispersed phases/segregated phases (*fluorocarbons in membrane reactors*)	• non-dispersed phases/segregated phases (*fixed bed catalysts, regeneration of adsorbents or in situ treatment of contaminated soil*)
• solvent dispersed in water (*oil droplets in water-oil emulsions, with or without emulsifier*)	• particles dispersed in water (*organic or inorganic, e. g. sludge from biotreatment processes, contaminated soil in reactor*)

The target compounds of ozonation are often found in the water phase, although there are applications in which they are found in the solvent, e. g. highly lipophilic PAHs in dispersed oil droplets, or adsorbed on the solid, e. g. in the regeneration of spent adsorbents or treatment of contaminated soils. Generally, the tendency of a solute to partition between water and solvent or water and solid has to be considered carefully in three-phase systems.

Gas/Water/Solvent Systems

The most frequent goals of ozonation in gas/water/solvent systems are

- to make use of the increased solubility of both ozone and target compound(s) (M) in the solvent and thus
- to establish a selective direct reaction between ozone and target compound(s) (M).

Two processes can occur: a chemical extraction of the organic solute by the solvent followed by ozonation in this phase, and the diffusion of ozone from the solvent into water with subsequent reaction.

The feasibility of a water/solvent-phase ozonation depends mainly on the properties of the solvent. The following properties of the solvent should be met:

- low vapor pressure,
- nontoxic and immiscible with water,
- high ozone solubility,
- inertness against ozone.

The reaction mechanism of ozone with the solute should be known to establish a selective oxidation. Non-targeted compounds contained in the water phase should not have a higher reactivity to ozone. Otherwise ozone might already react to a large extent in the aqueous phase, consuming much of the ozone so that it is not available for the oxidation of the target solute in the solvent phase. The achievable selectivity depends much on the distribution of the solute between the gas, water and solvent phase, which should be checked by partition coefficients from the literature or experimentally determined.

The selectivity of the ozone reaction in pure solvent or water-solvent systems is known from early studies conducted by chemists under analytical and preparative aspects (Bailey, 1958). Inert solvents (e. g. pentane, carbon tetrachloride) provide an opportunity to produce and study oxidation products of the ozonolysis, such as ozonides at low temperatures (Criegee, 1975). Only in the last two decades have ozonation techniques been developed and studied that utilize the higher ozone solubility, enhanced mass transfer rates, higher reaction rates etc. to be found in water-solvent systems.

Gas/Water/Solid Systems

The ozonation of three-phase systems containing solids normally has one or more of the following goals:

- change in the solids (better sedimentation/filtration or reduction of solids mass),
- change in compounds adsorbed on the solids (transformation or mineralization),
- improved oxidation efficiency through catalytic production of radicals.

Ozone applications in gas/water/solid systems cover a wide range of media such as sludges, soils, adsorbents and catalysts. Disinfection, which can be regarded as a three-phase system, is a well-described and established application (see Section A 3.2.1 and 3.3.2). The preozonation for particle removal is discussed frequently, especially in the treatment of surface water, where different organic (e. g. bacteria, viruses, algae, suspended organic matter) and inorganic (e. g. silica, aluminum and iron oxides, clay) particles can be present (see Section A 3.2.4).

Mass Transfer in Three-Phase Systems

Most of the parameters that influence the rates of mass transfer and chemical reaction, and therefore the efficiency of the system, have already been discussed in Chapter B 3, however, in addition to the resistances to mass transfer found in gas/water systems, two more resistances can be found in three-phase systems:

- resistance in the films at the interface water/solvent or resistance in the water film at the interface water/solid,
- diffusional resistance in the second liquid or particle.

The over-all resistance is then the sum of the individual resistances (see equation 3-8) and the over-all mass transfer coefficient $K_L a$ takes all of them into account. In practice, it is often not possible to determine the mass transfer coefficient for a dispersed liquid or solid phase, i. e. the oxygen or ozone concentration cannot be measured in the second liquid or solid phase. In such cases the over-all mass transfer coefficient is defined with respect to the continuous phase. For the case where the second liquid is saturated with ozone, followed by the extraction of pollutants from water into this solvent, two distinct mass transfer coefficients can be defined, one for each step.

Solvents and solids, as well as water constituents, can have varying influences on k_La, depending not only on their properties but also on the hydrodynamics of the system (as discussed in Section B 3.2). Therefore, the k_La and the *alpha*-factor (ratio of k_La in the three-phase-system to the one in water) in the three-phase system under operating conditions similar to the ozonation experiments should always be determined.

The addition of a third phase not only adds resistances to mass transfer but also more possible directions for mass transfer. For example, ozone can be transferred from gas to water or solvent, or from solvent to water, and the solute can be transferred from water to solvent or back again. The third phase also brings complications when considering the chemical reactions. Both aspects are discussed below.

Knowing that a solvent has a higher ozone solubility than water does not allow us to predict what effect the three-phase system will have on the mass transfer coefficient k_La. It might be higher or even lower than that found in water alone. The effect depends on whether the resistance to the mass transfer of ozone at the water/solvent interface is controlled by the water or solvent film. This in turn depends on the relative magnitudes of the film mass transfer coefficients and the partition coefficient, which are based on the diffusion coefficients and solubility of ozone in the solvent (see Section B 3.1.4). Battino (1981) critically reviewed the ozone solubility in water and various non-aqueous liquids. If no ozone solubility data are available for a specific solvent, values for oxygen if available can be used to calculate ones for ozone (e. g. Battino et al., 1983). An experimentally determined diffusion coefficient for ozone is only available in water (see Section B 3.3.4). However, the diffusion coefficients can be calculated for other solvents and water, e. g. with the Wilke-Chang equation (Wilke and Chang, 1955). Then the ratio of the diffusion coefficients in both liquid phases together with the solubility data can be used for estimating the influence on the ozone mass transfer water/solvent.

The driving force for the mass transfer of the solute in the three-phase system can be determined with the solvent/water partition coefficient, just as the partition coefficient for gas/liquid phases, the Henry's Law constant, is used to determine the driving force for the mass transfer of ozone. A solute tends to diffuse from phase to phase until equilibrium is reached between all three phases. This tendency of a solute to partition between water and solvent can be estimated by the hydrophobicity of the solute. The octanol/water partition coefficient K_{ow} is a commonly measured parameter and can be used if the hydrophobicity of the solvent is comparable to that of octanol. How fast the diffusion or transfer will occur depends not only on the mass transfer coefficient in addition to the driving force but also on the rate of the chemical reaction as well.

The mass transfer rate of the solute to the solvent phase has to be considered compared to its reaction rate in the solvent. The system is controlled by the chemical reaction, if the oxidation of the solute in the solvent is slower than the mass transfer rate water/solvent of ozone. This is reversed in the case of a diffusion controlled or mass transfer limited system. The reaction mechanism of the solute with ozone should be considered in order to utilize a selective ozonation at the water/solvent interface or in the solvent. The more hydrophobic oxidation products might stay in the solvent phase but will also diffuse from the solvent to the water phase until reaching equilibrium. So their further oxidation might take place in the aqueous phase.

6.3.2 Existing Processes

Generally, most of the existing processes are examples from lab-scale studies. Only a few full-scale applications are known, e. g. the Ecoclear® process for the treatment of biologically pretreated landfill leachates, in which a special grade activated carbon is used as a submerged solid catalyst, or particle removal processes in drinking water ozonation or ozonation of effluents from the final biological stages of waste water treatment plants. Below, the various approaches are discussed predominately with respect to the system, the type of dispersion of the third phase (solvent or solid) in the aqueous phase as well as the purposes of the treatment.

Gas/Water/Solvent Systems

In most of the gas/water/solvent systems ozonation was applied to model (waste) waters where the target substances were contained in the water phase, though examples of the treatment of pollutants contained in the solvent phase also do exist. The experiments were often conducted to study the working principles of such systems with their general goals (cf. Section B 6.3.1). Also some development of special types of reactors has been made. Table 6-3 gives an overview of the examples discussed.

Nontoxic fluorinated hydrocarbons were probably some of the earliest and are even now the most often used solvents for lab-scale applications, mainly in the ozonation of chlorinated compounds (Stich et al., 1987; Bhattacharyya et al., 1995; Guha et al., 1995; Freshour et al., 1996; Shanbhag et al., 1996).

Table 6-3: Examples of investigated lab-scale gas/water/solvent systems.

Dispersion of Solvent (third phase) in Water/Reactor	Solvent	Solute (M)	References
non-dispersed continuous or dispersed solvent phase/three step system of ozone saturator for solvent, STR for reaction and two-phase separator	fluorinated hydrocarbons (e. g. FC40 or FC77 from 3 M Co.)	phenols and chlorinated organic compounds, e. g. PCP, TCE	Stich et al., 1987; Bhattacharyya et al., 1995; Freshour et al., 1996
non-dispersed, segregated phases/innovative hollow fiber membrane reactor	(FC43 or FC77)	toluene, phenol, acrylonitrile, TCE, nitrobenzene	Guha et al., 1995; Shanbhag et al., 1996
solvent dispersed in water (with or without emulsifier)/standardized STR	oil droplets in oil/water- emulsions	2–5 ring PAHs	Kornmüller et al., 1996, 1997 a, b, and 1999

For example, an inert fluorinated hydrocarbon phase (FC40; from 3M Co.) with a high ozone stability and solubility (saturation concentration of 120 mg L^{-1} at 25 °C, under applied experimental conditions) was first saturated with ozone and then contacted with an aqueous solution containing PCP or various chlorinated organic pollutants (Bhattacharyya et al., 1995; Freshour et al., 1996). In these experiments a high degree of pentachlorophenol (PCP) destruction (95 %) was obtained independently of the partition of PCP in the two liquid phases and it was concluded that ozone mass transfer was not a limiting factor in this system. Compared to an aqueous system, the specific ozone consumption was lower by 1/25, and at pH 10.3 the pseudo-first order reaction rate constant of PCP was three orders of magnitude larger. During dehalogenation of several compounds by ozonation, the chloride anions set free remained in the aqueous phase due to their low affinity to the fluorocarbon (Bhattacharyya et al., 1995).

A new approach in reactor design exploiting the advantages of water-solvent systems was developed by Guha et al. (1995). A membrane reactor made of microporous Teflon hollow fibers was used. The space around the outside of the hollow fibers was filled with an inert fluorocarbon phase. The hollow fibers were divided into two groups: ozonated air was passed through the first group, waste water through the second. The target compounds (e. g. toluene, nitrobenzene etc.) and ozone diffused through the membranes to the outer fluorocarbon phase used as reaction medium. Hydrophilic oxidation products were extracted back into the aqueous effluent. Only 40–80 % of the pollutant was transformed, probably due to the resistance in the aqueous phase film. Therefore, two reactors in series were suggested to increase the degree of removal. This membrane-based reactor was improved by Shanbhag et al. (1996) for the treatment of volatile organic compounds in air. Compared to conventional treatment where the ozone gas is bubbled directly through fluorocarbons, losses by fluorocarbon volatilization could be avoided in membrane aeration systems, however additional boundary layer and membrane resistances existed.

Highly condensed polycyclic aromatic hydrocarbons (PAH, with more than four aromatic rings) have a mutagenic and/or carcinogenic potential and low biodegradability. Due to their lipophilic behavior and low water solubility PAH are often dissolved in the dispersed phase of oil/water-emulsions or in hydrophobic organic material (e. g. crude oil, metal working oils). The higher solubility of both ozone and PAH in oil droplets of homogeneous oil/water-emulsions was used for the oxidation and resulted in fast reaction rates (Kornmüller et al., 1997 a). No reaction of dodecane, used as a model substance for a mineral oil, with ozone could be detected, while some of the emulsifiers stabilizing the emulsions partially reacted with ozone (Kornmüller et al., 1996).

The absorption of ozone from the gas occurred simultaneously with the reaction of the PAH inside the oil droplets. In order to prove that the mass transfer rates of ozone were not limiting in this case, the mass transfer gas/water was optimized and the influence of the mass transfer water/oil was studied by ozonating various oil/water-emulsions with defined oil droplet size distributions. No influence of the mean droplet diameter (1.2 ~ 15 µm) on the reaction rate of PAH was observed, consequently the chemical reaction was not controlled by mass transfer at the water/oil interface or diffusion inside the oil droplets. Therefore, a microkinetic description was possible by a first order reaction with regard to the PAH concentration (Kornmüller et al., 1997 a). The effects of pH variation and addition of scavengers indicated a selective direct reaction mechanism of PAH inside the oil droplets

(Kornmüller et al., 1997 b). For example, in the ozonation of the five ring condensed benzo(e)pyrene this was confirmed by the oxidation products being formed: a secondary ozonide and oxepinone (hydroxytriphenylenol[4,5-cde]oxepin-6(4H)-one), which are specific for an ozonolysis (Kornmüller and Wiesmann, 1999).

Gas/Water/Solid Systems

The discussion of existing processes of gas/water/solid systems is grouped according to the treatment goals. Table 6-4 gives an overview of the various systems studied in lab-scale or even applied in full-scale.

Table 6-4: Examples of gas/water/solid systems.

Dispersion of Solid (third phase) in Water/Reactor	Solid	Solute (M)/ Adsorptive (M)	Main Purpose	References
non-dispersed, segregated phases/fixed bed reactors	octadecyl silica gel (ODS)	PAH (BeP)	regeneration of spent adsorbents	Eichenmüller, 1997
non-dispersed, segregated phases/full-scale fixed bed reactor	special grade AC (Ecoclear® process)	landfill leachate	improved oxidation efficiency	Kaptijn, 1997
solid dispersed in water/shaker flasks, bubble columns, STRs, or full-scale waste water treatment plants	various biosludges		change in solids, particle removal	van Leeuwen, 1992; Collignon et al., 1994; Saayman et al., 1996; Kamiya et al., 1998; Yasui et al., 1996; Sakai et al., 1997; Scheminski et al. 1999
	contaminated soil	NOM	change in compounds adsorbed on the solids	Ohlenbusch et al., 1998
	AC (Filtrasorb 400)	TCE	regeneration of spent adsorbents	Mourand et al., 1995
	highly active granulated iron hydroxide (ß-FeOOH)	fulvic acids	regeneration of spent adsorbents	Teermann et al., 1999
solid with (very) little water/*in situ* soil remediation or lab-scale soil columns	contaminated soil	PAHs (Pyr, BaP)	change in the compounds adsorbed on the solids	Eberius et. al., 1997

Change in the Solids

Ozonation of sludge (biosolids from biotreatment processes) has been studied under aspects of bulking control and improving the settling characteristic (van Leeuwen, 1992; Collignon et al., 1994) or stabilizing the phosphate removal (Saayman et al., 1996). In addition to bulking control, a simultaneous reduction in excess sludge was achieved (Kamiya and Hirotsuji, 1998). In full-scale applications Yasui et al. (1996) and Sakai et al. (1997) completely eliminated excess sludge in a pharmaceutical and municipal waste water plant. While these effects are generally explained by the destruction of bacteria cell membranes, the more detailed work of Scheminski et al. (1999) showed a transformation of digested sludge into soluble substances i. e. protein, lipids and polysaccharides at an ozone consumption of 0.5 g g^{-1} (ozone per organic dry matter).

Results from sludge ozonation studies are difficult to generalize because of the complexity of sludge, numerous parameters influencing the process and different set-ups used. Often the experiments are focused on the ozone dose necessary to achieve the desired effect without adequate consideration of the influencing parameters. The applicability of this process is very site-specific. Each country or region has different boundary conditions, such as prevailing costs and regulations for sludge disposal (esp. organic dry matter content) and availability of alternative disposal options (agricultural use, incineration, landfill).

Change in Compounds Adsorbed on the Solids

Another application in a three-phase system is the ozonation of contaminated soil, both *in situ* or in reactors. The goal is to increase the biodegradability of residual, nonvolatile organic compounds like PAH in contaminated soils. The water is present either as a water film covering the soil particles in the non-saturated water zone (*in situ* treatment) or in the reactor where the soil is suspended in water (mainly on-site treatment). Eberius et al. (1997) studied the ozonation of the radioactively labeled (C^{14}) PAH pyrene (Pyr) and benzo(a)pyrene (BaP) in silica and soil. Considerable percentages of both PAH were oxidized to water soluble, probably biodegradable substances (20–30 %), but 10 % were found in non-extractable and 30 % in bound residues in the soil organic matter. The toxicity and stability of bound residues is still unknown under long-term degradation conditions. The ozonation of the soil organic matter led to a decrease in the humic acid fraction with a reduction in average molecular size. Because of an increase in the building-block and low molecular acid fraction, which are easily biodegraded, Ohlenbusch et al. (1998) expected a fast and high bacteria regrowth after ozonation.

While in lab experiments or on-site the pH can be controlled, in an *in situ* application it will always decrease due to the formation of organic acids. This will effect shifts in the oxidation mechanism toward the direct oxidation pathway and in the chemical equilibrium of the soil. Furthermore, both ozone applications will result in changes in the soil chemical constituents, i. e. the cation exchange layer and the humic fraction. The consequences of these changes are still mostly unknown. A special lag-phase and a selection of bacteria in regrowth might be caused by the ozonation.

An *in situ* soil ozonation is not recommended with the present state of knowledge. The oxidation products of most compounds and their toxic effects are not even known for homogeneous aqueous systems, let alone for the complex ecological system "soil". More work is necessary to evaluate possible effects on the ecological system "soil" as well as safety aspects for a full-scale *in situ* application.

Chemical oxidative regeneration is used for the oxidation of compounds sorbed on adsorbents to regain adsorption capacity. Such regeneration of spent adsorbent can provide advantages (no shipment to regeneration units or disposal of concentrates) over thermal ones. Several adsorbents were tested by Eichenmüller (1997) for the feasibility of regeneration by ozone. Adsorber polymers like Wofatit reacted with ozone and therefore their usage is not advisable, while octadecyl silica gel particles (ODS) hindered an electrophilic attack by ozone on the adsorbent itself due to its chemical structure with alkane side chains. Six cycles of adsorption and oxidative regeneration by ozone dissolved in water could be obtained with ODS loaded with benzo(e)pyrene without a significant loss in adsorption capacity. A direct reaction of ozone with the adsorbed compound was indicated by the two main oxidation products found from the reaction of sorbed benzo(e)pyrene, which were similar to the one mentioned above in the ozonation of homogeneous oil/water-emulsions. In contrast, complete regeneration for a Filtrasorb-400 activated carbon saturated with trichloroethylene (TCE) was not achieved with ozone/hydrogen peroxide (Mourand et al., 1995).

Highly active granulated iron hydroxide (β–FeOOH) loaded with fulvic acids was regenerated using dissolved ozone in water (Teermann and Jekel, 1999). The results indicated that an initial ozone concentration in the suspension higher than 8 mg L^{-1}, which is difficult to reach in lab-scale applications, and an ozone dosage above 1.2 mg mg^{-1} (ozone/adsorbed organic carbon) are necessary for a good regeneration efficiency. Other oxidants may be more efficient than ozone for metal hydroxide adsorbents due to mass transfer limitations of ozone and because of the catalytic activation to OH-radicals by the highly active surfaces, which already favors a indirect reaction.

Improved Oxidation Efficiency through Catalytic Production of Radicals

As already mentioned in the oxidative regeneration of adsorbents, solids can be used to catalyze the oxidation of compounds by ozone. A heterogeneous catalytic oxidation is used in the Ecoclear® process, where ozone gas and water with pollutants are applied co-currently in a fixed-bed reactor and adsorb to special grade activated carbons as catalyst. For protection of the activated carbon it has to be preloaded before the first application of ozone. In contrast to AOP (see Section B 6.2), which produce OH-radicals and are effected by scavengers, oxygen radicals are formed from ozone by the carbon and react with the adsorbed organic compounds. Therefore, the selectivity of the oxidation depends on adsorption characteristics and reactivity of the organic compounds (Kaptijn, 1997). The Ecoclear® process has been successfully applied full scale for the treatment of biologically pretreated landfill leachates since 1992 (see also Table A 3-3).

6.3.3 Experimental Design

Define system: In both gas/water/solvent and gas/water/solid systems, it is important to keep dispersions and suspensions homogeneous during ozonation. A suitable type of reactor and effective mixing has to be provided depending on the properties of the system.

For gas/water/solvent systems, the vapor pressure of the solvent has to be checked before starting any experiment so that stripping of the solvent will be negligible. The solute should also be non-volatile. The solvent should be nontoxic, immiscible with water and provide a high solubility for ozone. The inertness of the solvent against ozone and thus the stability of a three-phase system has to be guaranteed during the whole ozonation. If the solvent cannot be reused, it should be generally treatable and preferably biodegradable. An important safety aspect is that ozone (and pure oxygen) might be explosive on contact with highly reactive lipids, fats and oils.

Generally, the role of mass transfer limitation should always be considered and investigated in the ozonation of three-phase systems. In the case of suspensions the k_La and the *alpha*-factor should be determined as discussed in section B 3-2. Kinetic modeling of the ozone reaction, which even in heterogeneous systems is often described as pseudo-first order, has to be reviewed critically. Often the influences of the ozone mass transfers gas/water and water/solid were not examined. When studying the ozonation of compounds adsorbed onto or inside particles, a limitation of the reaction by the ozone diffusion through the interface water/solid or inside the particles can be expected in most cases. Using a model system with defined particle size and known compounds, the mass transfer water/solid can be studied and a kinetic model of the reaction might be possible, but real systems will be too complex for such an approach.

To achieve successful regeneration of spent adsorbents by ozonation of gas/water/solid systems, the adsorbents used have to be almost completely inert against ozone. Before considering the regeneration of an adsorbent with ozone, the ozone decomposition caused by the adsorbent alone should be tested. Activated carbon is not recommended as adsorbent if regeneration is to be carried out with ozone. Depending on the experimental conditions ozone reacts more or less strongly with its double bonds and/or is decomposed by the activated carbon. For example, activated carbon is often used as a gas phase ozone destructor in lab-scale set-ups, resulting in a consumption of the carbon by slow burning.

In the oxidation of compounds sorbed on adsorbents, the appropriate treatment scheme should be evaluated on the basis of the oxidants used for regeneration. Perhaps the direct ozonation of pollutants in water is more favorable than a two stage process of adsorption followed by oxidative regeneration. However, if the pollutants are present in small concentrations in water, the enrichment by adsorption followed by ozonation in the sorbed state might be advantageous.

Select analytical methods:

- Compounds (M): Known compounds (M) and their oxidation products should be analyzed in both the water and solvent phases separately with methods which allow individual quantification if possible. While the oxidation progress can be described by overall parameters like DOC and COD in the aqueous phase, in the solvent phase these concentrations are normally dominated by the one of the solvent itself. In gas/water/solid systems a method should be developed to measure a compound on the particles, e. g. by extraction or dissolution of the particles, and to describe the oxidation in the solid phase.
- Ozone: Measuring the dissolved ozone concentration may also be more complicated in three-phase systems. The analysis of dissolved ozone by the photometrical indigo method (Hoigné and Bader, 1981) is disturbed by compounds or materials that scatter or absorb

light. Williams and Darby (1992) suggest a procedure for measuring the dissolved ozone concentration in the presence of suspended material by the indigo method. However, a measurement in the presence of other compounds like oil might not be applicable (Kornmüller et al., 1997 b). A correction based on the turbidity of homogeneous oil/water-emulsions did not provide reliable results with the indigo method. Nevertheless, the method has been modified successfully for measuring dissolved ozone in the presence of a fluorocarbon phase (Bhattacharyya et al., 1995).

When using an amperometric electrode as the measuring technique, interference from the solutes and solvent can occur. The solutes and solvent can adsorb to the semipermeable membrane of the electrode, therefore giving an additional resistance to the diffusion of ozone through this membrane to the electrolyte chamber. The use of an amperometric electrode is not recommended for water containing particles. In these cases the ozone consumption can only be calculated from the ozone gas balance.

Determine experimental procedure: Homogeneous sampling is very important in three-phase systems and can be studied by taking samples at different heights of the reactor. The homogeneity has to be guaranteed including analysis, e. g. samples from water/solvent systems have to be stirred during TOC-measurements. If a compound is analyzed in both water and solvent phase, a reproducible and efficient separation process of both phases has to be chosen, while for water/solid systems filtration is a common one. Due to the high ozone solubility in solvents, after sampling the further reaction of ozone has to be stopped (Section B 1.2).

Evaluate data and assess results: Prior to carrying out oxidation experiments, the mass balance of a compound should be examined under the conditions of aeration with oxygen or air, so that other elimination processes can be excluded. For example stripping of a compound can be determined by absorption of the off-gas in water or other appropriate liquid in gas wash bottles.

Before transformation of a compound by ozonation can be reported, the concentrations of the compound in all three phases have to be checked. A decrease in a compound concentration in one phase might not be caused by oxidation but by partitioning into another phase.

6.4 Ozonation and Biodegradation

Biological treatment is often the least expensive and most effective process for eliminating organic pollutants. Many pollutants can be fully biodegraded (mineralized) by the microorganisms in such processes, whereas many physical and chemical processes just concentrate the pollutants or transfer them from one medium to another, leaving their ultimate fate in the environment unclear. Unfortunately, not all compounds are biodegradable. Treatment schemes combining chemical and biological processes are based on the finding that many oxidation products of biorefractory pollutants are easily biodegradable. The goal of combining an unavoidable chemical oxidation with a biological process is to minimize the amount of oxidant needed and thus reduce operating costs.

6.4.1 Principles and Goals

Combination of chemical and biological processes are called for if one process alone cannot achieve the required treatment goals such as

- to transform especially toxic or refractory substances in drinking or waste water,
- to maximize mineralization, that is to reduce the amount of dissolved organic carbon (DOC) as completely as possible or as defined by the legislative requirements

or cannot achieve the goal economically. The coupling of the two processes tries to utilize the strengths of each process: biorefractory but easily ozonated compounds (e. g. aromatics) are partially oxidized producing byproducts which are easily (or at least more) biodegradable than the original mixture, e. g. low molecular weight acids, which themselves are difficult to ozonate.

A typical plot of the change in DOC concentration and biodegradable fraction as a function of the specific ozone dose shows a continuous increase in the biodegradable fraction until a certain maximum is reached. Further ozonation decreases the biodegradable fraction (Figure 6-2). This is an optimization problem: the compounds must be made bioavailable, but mineralization in the chemical stage must be minimized.

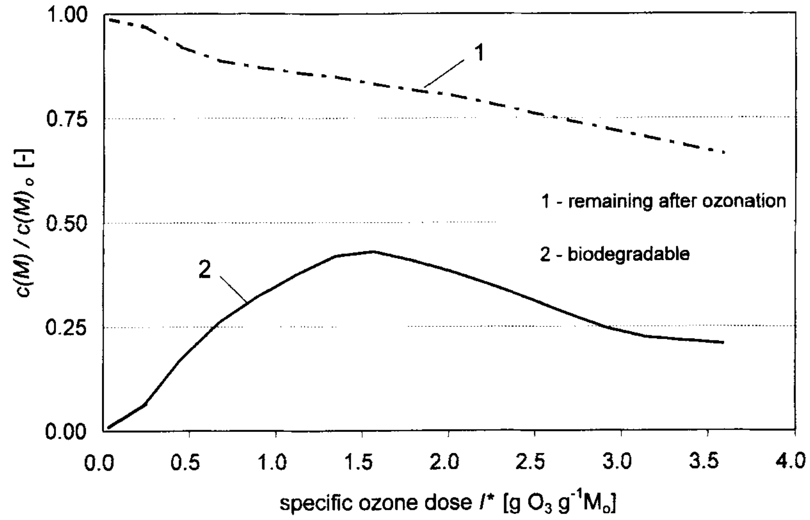

Figure 6-2: Typical change in DOC remaining after ozonation (1) and biodegradable (2) as a function of the specific ozone dose I^* for the ozonation of model pollutant M and subsequent biodegradation of its oxidation products in a batch system.

Operating costs can be reduced by removing the oxidation products using the less expensive biological process instead of further oxidation. A progressive adaptation of the microorganisms in a combined integrated process to the oxidation products can lead to further reduction in the amount of ozone necessary. This has been observed in lab-scale systems (Stern et al., 1995 and 1996).

In drinking water applications, the combined process is normally based on immobilized biofilms in an activated carbon column following ozonation. In this way adsorption is assisted by biodegradation, resulting in extended operation times of the activated carbon between two regeneration cycles, which increases the economical feasibility of the process. Similar treatment schemes can be applied for waste water. Immobilized biofilms have proven to be advantageous for the removal of slowly biodegradable oxidation products. However, reactors treating waste waters must be designed for higher amounts of biomass, whether it is suspended or immobilized.

6.4.2 Existing Processes

Drinking Water Applications

The application of ozone before a biological treatment process originates from studies in drinking water treatment where ozonation units were used for the removal of organic trace compounds. Since ozonation alone did not – in every case – help to meet the low contaminant limits required by legislative regulations, an activated carbon process was often installed behind the ozonation step (Rice, 1981). The resulting operation cycles of the activated carbon filters were very long, enabling considerable cost savings. Detailed examination of the removal processes in a full-scale application confirmed that biodegradation was responsible for the prolonged cycles (Jekel, 1982).

Due to this observation, several hundred chemical/biological processes, often called the (ozone enhanced) biological activated carbon ((OE)BAC)-process, were successfully put in operation in the field of drinking water treatment since the late 1970's (Masschelein, 1994). Nevertheless, even after more than twenty years of research and application, the studies on this process proceed (e. g. Kainulainen et al., 1994).

Waste Water Applications

The idea to use combined chemical/biological processes, which had been successful in drinking water applications, for the treatment of waste waters caught on around the mid-1980's. Increasing awareness about refractory organic substances in the effluents of publicly owned treatment works (POTWs) was accompanied by the definition of a list of priority pollutants, many of which are poorly or scarcely biodegradable in normal activated sludge processes (Pitter, 1976; Tabak et al., 1981). Thus, the requirements for waste water treatment increased and existing technologies had to be applied in new combinations. Ozonation combined with subsequent biodegradation under aerobic conditions was found to be a viable treatment option in such cases.

There are still only a few examples of industrial full-scale application of such systems, e. g. in the treatment of waste dump leachates or waste waters from the textile, pulp bleaching or chemical industry (compare Section A 3.4 and Table A 3-3). Scott and Ollis (1995) have reported comprehensively about the state-of-the-art research on chemical oxidation and subsequent biological treatment of the oxidation products and stated that most of the reported applications have been batch treatments in laboratory scale. This research has covered a wide variety of organic compounds. The comprehensive study of Gilbert (1987) on 28 substituted aromatic compounds showed that 100 % transformation of the aromatic compound corresponded with 55–70 % removal in COD and 30–40 % in DOC due to ozonation and also resulted in good biodegradability. This was defined using the ratio BOD_5 to COD which remained after the chemical treatment step. The biodegradability was rated good for values of 0.4 ± 0.1 g BOD_5 g^{-1} COD or higher.

During the last five years, investigation of the two-step sequential treatment (ozone-bio) has continued parallel to the development of the continuous flow integrated process (ozone-bio + ozone-bio + ...), where the water is cycled between the two process steps several times (Heinzle et al., 1992 and 1995; Stern et al., 1995 and 1996). Furthermore an approximation of the integrated proecss can be made by applying a multi-sequential batch treatment, repeating the chemical and biological treatment for two or three times, in each stage using the treated solution of the former (Jochimsen, 1997; Kaiser, 1996; Karrer et. al., 1997).

In several studies the integrated process has proven to be superior to the sequential process, in terms of much lower ozone consumption per DOC removed. Treating chloro- and nitro-substituted benzenes with both treatment schemes, Stockinger (1995) found the degree of overall DOC removal increased from approximately 50 % to between 75 and 95 % at specific ozone input doses of 3.5–6.0 g O_3 g^{-1} DOC_0 for the integrated process. Similar results were found for several waste dump leachates (Steensen, 1996), with 75 % COD removal achieved with almost 20 % less ozone, applying specific ozone input doses of 1.6–3.0 g O_3 $g^{-1}COD_0$. The recycle ratios were between 1–2 and 3–4, respectively. Higher recycle ratios did not bring any additional benefit. Both types of process are schematically shown in Figure 6-3.

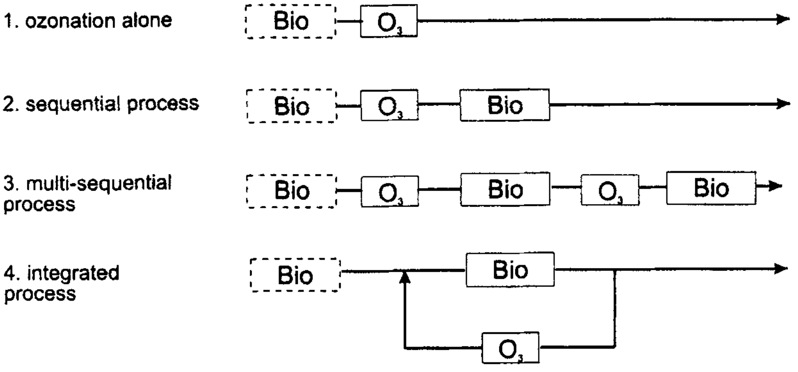

Figure 6-3: Possible treatment schemes of chemical/biological processes after a biological pretreatment step.

In some cases prolonged operation of such systems allowed the biomass in the biological stage to adapt to the problematic compounds in the waste water influent, which were originally classified biorefractory. Thus, the amount of ozone necessary for their complete elimination decreased considerably, or even completely, e. g. in the case of 3-methylpyridine (Stern et al., 1996). However, this effect is very substrate-specific, e. g. no adaptation occurred with 5-ethyl-2-methylpyridine (Stern et al., 1996) and 4-nitroaniline (Langlais et al., 1989; Saupe, 1997) or 2,4-dinitrotoluene (Saupe and Wiesmann, 1996 and 1998).

6.4.3 Experimental Design

Define system:

- Type of water or waste water:
  - check the biodegradability of the original solution in order to treat only the biorefractory and/or toxic part of the (waste-) water constituents,
  - theoretically analyze possible oxidation products of the (main) compounds contained in the (waste-) water, their measurement and biodegradability.

Choice of biomass:

- aerobic or anaerobic process
- mixed or pure bacterial culture
- biomass adapted or non-adapted to the oxidation products

Most often a non-adapted aerobic mixed culture is used for the biodegradation of the oxidation products. The use of an aerobic biological process results in part from the fact that due to the application of an air/ozone or oxygen/ozone mixture in the chemical treatment step the water normally is rich in oxygen. Especially in the case of highly loaded waste waters anaerobic processes can also be applied, since many of the oxidation products will be low molecular weight organic acids being also biodegradable in an oxygen-free environment. Andreozzi et al. (1998) applied such a treatment to highly concentrated olive *o*il *m*ill *e*ffluent (OME, $COD_0 = 50–250$ g L^{-1}). Problems occurred due to a strong inhibition of methanogenic bacteria by ozonated OME and especially by *para*-hydroxybenzoic acid. Since the ozonated mixture was not inhibitory to acidogenic bacteria the authors proposed the applicability of a two-step acidogenic and methanogenic process but did not present results themselves.

Choose an inoculum as appropriate as possible, e. g. if the ozonated solution will be fed to an existing process or if there is a preadapted culture able to consume (some of) the main oxidation products (if known), use this specific inoculum. The reverse is quite often successful, using a highly diverse mixed culture, preferably from a POTW, for developing a culture capable of degrading the oxidation products. Such a culture can be used to test the "general biodegradability" of the oxidation products.

Adaptation of the biomass to the oxidation products is basically possible. Since it is not clear how long the process has to be operated until an adaptation occurs – or if ever – the laboratory effort required may be unsatisfactorily high. In several studies adaptation was reported to cause a dramatic reduction in the amount of expensive ozone needed for the same removal efficiency, or with the same amount of ozone much higher degrees of DOC removal were achieved. Both batch (Jones et al., 1985; Moerman et al., 1994) as well as continuous (Stockinger, 1995; Stern et al., 1996) mode of operation of the combined system was applied.

Choice of (reaction-)system:
- flocs or biofilm immobilized on support material
- if immobilized, suspension or fixed bed reactor
- batch or continuous-flow processes
- sequential or integrated two stage process.

The use of an immobilized biofilm system is recommended, since the oxidation products often are only slowly biodegradable. Biomass, especially slow growing microorganisms, can efficiently be kept in the system using support material. This is especially important in continuously operated systems where the liquid phase is completely mixed. In such a system suspended biomass would be washed out when the hydraulic retention time is less than or equal to the population doubling time (i. e. the reciprocal of the specific growth rate; Grady, 1985). In several studies materials such as polyurethane foams (Moerman et al., 1994; Jochimsen, 1997) or quartz sand particles (Stern et al., 1995 and 1996; Heinzle et al, 1995; Saupe and Wiesmann, 1998) have been used for immobilization.

For lab-scale experiments the use of a continuous-flow miniaturized fixed-bed bioreactor can be advantageous. Such reactors are easy to operate, need only a small volume of ozonated substrate, and allow some important operating characteristics of the biological system to be assessed. For example, a high concentration of biomass can be achieved and a biodegradation rate (r_{DOC}) for the system can be calculated. Miniaturized continuous-flow bioreactors have been successfully applied for the aerobic biological mineralization of several nitroaromatic substances, which have long been considered scarcely biodegradable, e. g. 2,4-dinitrotoluene (DNT), 2,6-DNT, 3- and 4-nitronaniline (NA), 2,4-dinitrophenol (Saupe,1999) and 4,6-dinitro-*ortho*-cresol (DNOC) (Gisi et al., 1997; Saupe, 1999). High biodegradation rates up to 2.0 and 1.6 kg DOC m^{-3} h^{-1} as well as high degrees of total DOC-removal (> 85 %) were achieved for 4-nitroaniline and 2,4-di-nitrophenol, respectively. In all these experiments the mixed-culture biomass had been preadapted in batch-systems before being transferred to the continuous system.

Nevertheless, in laboratory batch tests on the (multi-)sequential chemical/biological treatment suspended biomass is normally used to determine the biological fraction of DOC since the amount of biomass added to each batch is easier to control and measure (and indeed no washout is possible) (Karrer et al., 1997; Jochimsen, 1997). In most cases the operation of a continuous-flow sequential ozonation/biodegradation unit cannot be recommended without having performed batch tests before.

Sometimes batch and continuous flow modes can be used together in two stage processes, each stage can be operated differently. This is easy to carry out for two stage processes operated sequentially using storage tanks. Combinations of flow modes for processes with an integrated recycle are less easy, but modifications are possible.

Select analytical methods:
- Measurement of oxidized compounds (chemical analyses): (see Section B 1.2 and B 2.5)

- Measurement of biodegradation (chemical analyses): A very good overview of biodegradation, its definition and measurement, was given by Grady (1985). Practically, two methods to measure the biodegradability are frequently applied in the treatment of the higher DOC levels found in waste waters:
  - measure the mineralization caused by biological activity, e. g. by assessing the dissolved organic carbon (DOC) removal over a certain length of time, e. g. 5 days (equivalent to BOD_5) 28 days (inherent biodegradability test (Zahn-Wellens-Test; DIN EN 29 888, 1993))
  - assess the biological oxygen demand, i. e. mostly run for five days (BOD_5), but extended test duration may also be applied.

  In both cases non-adapted biomass is employed. In the treatment of drinking water various methods to measure the assimilable organic carbon (AOC) have been developed. Measuring the DOC removal of a biodegradation process has the advantage over BOD_5 that the degradation effect is expressed in the same units as the effect of the chemical oxidation step. Mineralization due to the biological action can be quantified and compared with the mineralization in the chemical step. Nevertheless, BOD_5 measurement was not only used in the early work of Gilbert (1987), but also employed in a recent study of Karrer et al. (1997). In the latter study, with the aim to decide whether waste waters containing biorefractory compounds can be successfully treated in the continuous integrated process, a lab-scale applicability test employing a multi-sequential combined chemical/biological batch treatment was developed.

- Measurement of toxicity (biological analyses): The development of toxicity during chemical/biological treatment of waste waters was seldom assessed. Only in the last few years has the application of toxicity testing been reported more frequently (e. g. Diehl et al., 1995; Moerman et al., 1994; Jochimsen, 1997; Sosath, 1999). Moerman et al. (1994) showed that a 'toxicity balance' around the whole process is important for combined chemical/biological treatment. It is not sufficient to assess the effect of ozonation alone (cf. chapter A 1).

Determine experimental procedure: Both the chemical stage and the biological stage require attention when developing the experimental procedure, not only individually, but also how they fit together. In this section special attention is given to the biological process. Some recommendations to help avoid common pitfalls are given below.

Batch operation of the biological stage requires the consideration of the following aspects:

- Check that the biomass is active and has not suffered from inadequate storage conditions (e. g. at high temperature or due to starving and/or lysis) before the experiments are started.
- Make sure to use one and the same inoculum in each bottle of the biodegradation test following a series of batch ozonations.
- Take care that the concentration of DOC introduced into the bottle with the inoculum is far lower than the DOC of the ozonated solution. Otherwise it will be difficult to differentiate between the origins of the DOC and to track the mineralization of the oxidation products.

- The test duration may be varied with respect to the standardized Zahn-Wellens or BOD_5 tests according to the individual boundary conditions of the experiments. Nevertheless, be careful to work in a way that the results are comparable to others from the literature.

Batch tests are recommended before starting any kind of continuous-flow experiments, especially if the use of an integrated system is intended. For example, Karrer et al. (1997) proposed a batch 'applicability test' for multi-sequential chemical/biological treatment. Such testing is quick and easy to perform, reliable due to the underlying standardized methods of measurement, and can be used to roughly estimate the costs for a combined process. Similar approaches, which take into account the amount of COD which is partially oxidized in the chemical process step and then biodegraded, were proposed by other authors (Jochimsen, 1997; Jochimsen and Jekel, 1996; Kaiser, 1996).

When operating a chemical/biological process in the *continuous-flow* mode it is important to prevent ozone (gaseous as well as liquid) from entering the biological stage in high concentrations. Regardless whether operating a sequential or integrated process, ozone will at least partly kill (oxidize) the biomass. This in turn will cause the biological process to slow down or cease completely. In the integrated system it will also cause additional and completely ineffective ozone consumption due to additional organic carbon (DOC) from destroyed biomass being transported into the chemical system (Stern et al., 1995; Karrer et al., 1997). Thus, it is important to construct the system in such a way which effectively prevents such problems. A pressure equalizer or gas trap to prevent gaseous ozone entering the biological stage was installed and successfully operated in between the two reactors of a sequential system (Saupe and Wiesmann, 1998). Another approach was to automatically control the dissolved ozone concentration at near zero in the integrated system (Stockinger, 1995).

Often the rate-determining step in experiments with a continuous-flow sequential combination is the biological stage. In order to increase flexibility in experiments or shorten total experimentation time, a single batch or continuous-flow ozone reactor may be indirectly coupled with one or more continuous-flow bioreactors. The disadvantages of batch biological testing (changes in substrate concentrations causing transition from substrate degradation to autodigestion, little adaptation of biomass possible) have to be weighed against the possible variability between bioreactors in bacterial cultures over time and amount of biomass.

For either continuous-flow (CF) or batch (B) ozonation, the complete system could be operated as follows:

- run the ozonation stage at the desired operating conditions, until either enough effluent has been collected (CF) or the desired ozone dose (B) has been reached → store effluent in tanks (cool, dark) → feed it to continuous-flow miniaturized fixed-bed bioreactor(s).

This allows the ozone reactor to be operated independently, possibly producing different oxidation products and/or concentrations at a number of operating conditions in one day. The oxidation products of each run can be fed to a different bioreactor over a number of days or weeks. The goal is optimization of the combined overall removal. Another possible use of a number of bioreactors in parallel would be the optimization of the hydraulic retention time for the same influent, with the goal of high biodegradation rates.

The total time of experimentation can be reduced in this way compared to a direct coupling of the stages. However, care must be taken that the oxidation products are not changed during storage, due to chemical, physical or undetected biological processes.

Evaluate data: Experiments on the combined treatment of (waste-) water with ozone and biodegradation mostly aim at a high degree of total DOC removal (e. g. ≥ 85 %). In general, not only the total, but also the degrees of removal in the individual stages are of interest. Here, care has to be taken to exactly indicate the reference value for the calculation of the degree of removal in the individuals stages, either the input concentration to the whole system or to the stage.

All experimental results should best be evaluated as a function of the specific ozone dose and related data such as the specific ozone absorption and/or consumption. Additionally the ozone yield coefficient, denoting the ratio of ozone absorbed in the liquid (i. e. transferred from the gas) to the DOC removed by ozonation or the total system (cf. Chapter B 1), is often of interest.

Assess results: Several methods can be applied to minimize the ozone consumption in combined processes of ozonation and biodegradation. For example, the different operational behavior of batch and continuous-flow systems, with the resulting differences in oxidation products, etc. has to be considered, as well as the fact that multi-stage systems for each treatment process may be of advantage over single stage systems.

- *Method* 1: increase ozone efficiency by increasing the number of stages in continuous-flow ozonation or choose batch ozonation instead.
- *Method* 2: use a continuous-flow tube reactor for ozonation to achieve efficiencies and products similar to batch ozonation.
- *Method* 3: operate the integrated (recycle) process at low specific ozone feed rates ($F(O_3)^*$, the ratio $F(O_3)$ to $c(DOC)_o$),
- *Method* 4: simulate (approximate) the continuous-flow integrated process by a multi-sequential chemical/biological batch treatment or use the sequencing batch reactor (SBR) technology.

In the laboratory batch ozonation is easy to apply, whereas multi-stage continuous-flow systems are difficult to handle (*Method* 1). However, mainly due to large liquid flow rates the inverse situation is valid for many full-scale applications. Often three oxidation reactors in series are found in waste water ozonation (cf. Table A 3-3). The advantage of a multi-stage CFSTR system – or even a batch system – lies in their faster reaction rates compared to a single CSTR due to the reduced axial/longitudinal mixing.

Method 2 basically addresses the same advantages as Method 1, with the additional consideration that the same favorable reaction rates found in batch ozonation systems can be achieved in a continuous-flow tube reactor (Sunder and Hempel, 1996; Levenspiel, 1972). More work is necessary to see how effective such reactors are for higher loaded (waste) waters, where gaseous ozone must be continuously dosed.

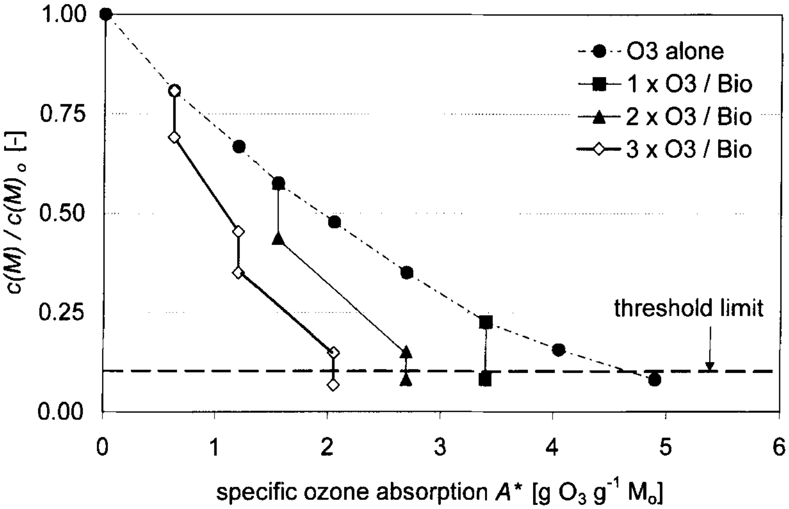

Figure-6-4: Typical degradation profile ($c(DOC)_t/c(DOC)_o$) of a multi-sequential chemical/biological batch treatment process (after Jochimsen, 1997).

Operating the integrated (recycle) process at low specific ozone feed rates (*Method* 3) would mean introducing as little ozone as possible into the (one-stage) ozone reactor, so that almost all gaseous ozone is consumed. The specific ozone absorption would approximate the specific ozone dose yielding a high ozone efficiency of $\eta_{O3} \approx 100\ \%$. Since ozone – in general – reacts slow when low concentrations of pollutants are present (which indeed is true for high degrees of removal), the ozone consumption (oxidation) rates, $r(O_3)$ will be low and thus only comparatively low ozone feed rates will be feasible.

A multi-stage or SBR-technology (*Method* 4) can help minimize the ozone consumption for a given degree of removal. During every pass through the chemical stage, the compounds present will be partially oxidized with little mineralization occurring. The biodegradable oxidation products will be transported into the biological stage before they are chemically mineralized.

In the laboratory, this method has been successfully applied to highly loaded tannery waste water (Jochimsen, 1997). Figure 6-4 shows a qualitative example of how such experiments can be evaluated by assessing the remaining concentration of the DOC (or the degree of DOC removal) as a function of the specific ozone absorption.

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Glossary

Symbols (*variables* and constants)		**units$^{*)}$**
a	specific (volumetric) area	m^{-1} (m^2 m^{-3})
A	total bubble surface area	m^2
A^*	specific ozone absorption	g O_3 g^{-1} DOC
A'	frequency factor	–
$c(A)$	concentration of the compound A	mg L^{-1}
c^*	saturation concentration	mg L^{-1}
c_G	gas concentration (in reactor)	mg L^{-1}
c_{Go}	influent gas concentration	mg L^{-1}
c_{Ge}	effluent gas concentration	mg L^{-1}
c_L	liquid concentration (in reactor)	mg L^{-1}
c_{Lo}	influent liquid concentration	mg L^{-1}
c_{Le}	effluent liquid concentration	mg L^{-1}
d	diameter	m
D	diffusion coefficient	m^2 s^{-1}
d_B	bubble diameter	mm
d_R	reactor diameter	m
E	mass transfer enhancement factor	–
E_o	electrochemical potential under STP	V
E_A	activation energy	J mol^{-1}
F	dose or feed rate	mg L^{-1} s^{-1}
F^*	specific dose or feed rate	mg L^{-1} s^{-1}
$F(H_2O_2)/F(O_3)$	hydrogen peroxide/ozone dose ratio	mg mg^{-1}
g	gravitational constant	m s^{-2}
h	height	m
H	Henry's Law constant, with dimension	atm L mol^{-1}
$\mathrm{H_C}$	Henry's Law constant, dimensionless	–
I^*	specific ozone dose	g O_3 g^{-1} DOC
I_o	intensity before absorption cell	–
I_t	intensity after absorption cell	–
k	film mass transfer coefficient	m s^{-1}
k'	reaction rate coefficient, pseudo first order	s^{-1}
k	reaction rate constant, first order	s^{-1},
k	reaction rate constant, second order	L mol^{-1} s^{-1}
$\mathrm{k_D}$	reaction rate constant for direct reaction of ozone	L mol^{-1} s^{-1}
k_G	gas film mass transfer coefficient	m s^{-1}
$k_G a$	gas phase volumetric mass transfer coefficient	s^{-1}
k_L	liquid film mass transfer coefficient	m s^{-1}
$k_L a$	liquid phase volumetric mass transfer coefficient	s^{-1}
$K_L a$	over-all mass transfer coefficient	s^{-1}

$\mathrm{k_R}$	reaction rate constant for hydroxyl radicals	$\mathrm{L\ mol^{-1}\ s^{-1}}$
l	internal width of the absorption cell	m
l_R	reactor length	m
N	mass transfer flux	$\mathrm{mg\ m^{-2}\ s^{-1}}$
m	specific mass transfer rate or mass flow rate	$\mathrm{mg\ L^{-1}\ s^{-1}}$
$\mathrm{MW(O_3)}$	molecular weight of ozone (48)	$\mathrm{g\ mol^{-1}}$
n	reaction order	–
n_{STR}	stirrer speed	$\mathrm{s^{-1}}$
p	partial pressure	Pa
$P_{abs.}$	pressure, absolute	Pa
P_{gauge}	pressure, gauge	Pa
$\mathrm{pK_a}$	dissociation constant	–
Q_G	gas flow rate	$\mathrm{L\ s^{-1}}$
Q_L	liquid flow rate	$\mathrm{L\ s^{-1}}$
Q_{LC}	cooling water flow rate	$\mathrm{L\ s^{-1}}$
r	reaction rate	$\mathrm{mg\ L^{-1}\ s^{-1}}$
r_G	ozone consumption rate in gas phase	$\mathrm{mg\ L^{-1}\ s^{-1}}$
r_L	ozone consumption rate in liquid phase	$\mathrm{mg\ L^{-1}\ s^{-1}}$
$r(O_3)$	ozone consumption rate in liquid phase	$\mathrm{mg\ L^{-1}\ s^{-1}}$
$r_A(O_3)$	ozone absorption rate in liquid phase	$\mathrm{mg\ L^{-1}\ s^{-1}}$
R_G	gas phase resistance	s
R_L	liquid phase resistance	s
R_T	total resistance	s
$\mathfrak{R}$	ideal gas law constant (8.314)	$\mathrm{J\ mol^{-1}\ K^{-1}}$
s	solubility	–
t	time	s
t_H	hydraulic retention time	s
t_R	reaction time	s
T	temperature	°C or K
T_L	temperature of or in liquid	°C or K
T_{LC}	cooling water temperature	°C or K
V_B	bubble volume	$\mathrm{m^3}$
V_G	gas volume	$\mathrm{m^3}$
V_L	liquid volume	$\mathrm{m^3}$
$\mathrm{V_n}$	molar volume	$\mathrm{L\ mol^{-1}}$
$\mathrm{v_S}$	superficial gas velocity	$\mathrm{m\ s^{-1}}$
y	mole fraction in gas phase	–
$Y(O_3/M)$	ozone yield coefficient	$\mathrm{g\ O_3\ g^{-1}\ \Delta DOC}$

*) mass based units may as well be replaced by molar units

Greek Alphabetic		**unit**
α	*alpha* factor	–
ß	hydroxyl radical initiating rate	–

ε	extinction coefficient	L mol^{-1} cm^{-1}
$\eta(M)$	degree of pollutant removal	–; %
$\eta(O_3)$	ozone transfer efficiency	–; %
wavelength	nm	
μ	ionic strength	$\mu S\ cm^{-1}$
ν	kinematic viscosity	kg m^{-1} s^{-1}
θ	temperature correction factor	–
ρ	density	kg m^{-3}
σ	surface tension	N m^{-1}
τ	half-life of the reaction (sometimes $t_{1/2}$)	s

Dimensionless Numbers

Bo	Bodenstein number
Re	Reynolds number
Sc	Schmidt number
Si*	coalescence number
σ^*	dimensionless surface tension

Abbreviations

Alk	alkalinity
AOP	Advanced Oxidation Processes
APM	ammonium hydroxide, hydrogen peroxide, DI water mixture
BC	bubble column
BOD	biological oxygen demand
CFSTR	continuous-flow stirred tank reactor
CL	chemiluminescence
COD	chemical oxygen demand
CSTR	completely mixed stirred tank reactor
DBP	disinfection byproducts
DHF	diluted hydrofluoric acid
DI	deionized water
DOC	dissolved organic carbon
DPD	N,N-diethyl-1,4 phenyldiammonium
ED	electrical discharge
EL	eletrolysis, electrolytic
EDOG	electrical discharge ozone generator
ELOG	electrolytic ozone generator
FIA	flow injection analysis
HPM	hydrochloric acid, hydrogen peroxide, DI water mixture
HPYR	2-hydroxypyridine
I	initiator, intermediate
IC	integrated circuit
M	micropollutant, compound, substrate

M	molar (mol L^{-1})
NOM	natural organic matter
OEBAC	ozone enhanced biological activated carbon
OME	oil mill effluent
P	promotor, product
PCE	tetrachloroethylene
PFA	perfluoralkoxy
POTW	publicly owned treatment work
PTFE	polytetrafluoroethylene
PVA	polyvinylalkoxy
PVC	polyvinylchloride
PVDF	polyvinylidenfluoride
S	scavenger
SAC	spectral absorption coefficient
SC	standard clean
SOM	sulfuric acid, ozone mixture
S_{PER}	selectivity
SPM	sulfuric acid, hydrogen peroxide, DI water mixture
ss	steady state
STP	standard pressure and temperature
STPR	stirred photochemical reactor
STR	stirred tank reactor
TBA	*tert*-butanol
TCE	trichloroethylene
THM	trihalomethane
TIC	total inorganic carbon
TOC	total organic carbon
TP	tap water
UPW	ultra pure water
UV	ultraviolet
WW	waste water

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