



Ozonated Water Removal of Photoresist: Literature Review

SEMATECH and the **SEMATECH logo** are registered service marks of SEMATECH, Inc.
International SEMATECH and the **International SEMATECH logo** are registered service marks
of International SEMATECH, Inc., a wholly-owned subsidiary of SEMATECH, Inc.

Product names and company names used in this publication are for identification purposes only
and may be trademarks or service marks of their respective companies.

Ozonated Water Removal of Photoresist: Literature Review

Technology Transfer # 00023899A-TR

International SEMATECH

February 29, 2000

Abstract: This report is a literature review of papers on ozonated water pre-diffusion cleaning, its application to photoresist removal, ozone decomposition, chemistry of ozone with organic species, and simulation of ozone decomposition.

Keywords: Ozone, Photoresists, Wet Cleaning

Authors: SangWoo Lim and Christopher Chidsey (Stanford University)

Approvals: Glenn Gale, Project Manager, FEPS009
Mike Jackson, Program Manager, Surface Preparation
Steve Burnett, Project Manager, ESHB010
Phyllis Pei, Program Manager, ESH
Bob Duffin, Director, ESH
Laurie Modrey, Technical Information Transfer Team Leader

Table of Contents

1	EXECUTIVE SUMMARY	1
2	REVIEW RESULTS	1
2.1	Ozonated Water Pre-diffusion Cleaning	1
2.2	Application to Photoresist Removal	2
2.3	O ₃ Decomposition in Aqueous Solutions	5
2.4	Reaction of O ₃ with Organics	8
2.4.1	Reactions of Ozone with Aliphatic	8
2.4.2	Reactions of Ozone with Aromatics	8
2.4.3	Reactions of Ozone with Phenol	9
2.5	Comparison of Oxidation by Ozone and Hydroxyl Radical	9
2.6	Numerical Simulation of O ₃ Decomposition	10
3	CONCLUSION	11

1 EXECUTIVE SUMMARY

The oxidation and removal of photoresist residues is an essential step in manufacturing semiconductor devices. Aqueous ozone is an attractive oxidant for this purpose. In particular, aqueous ozone promises to be significantly more environmentally benign than the mixtures of sulfuric acid and hydrogen peroxide. Though several highly effective tools are based on strategies to minimize mass transport of the relatively low concentrations of ozone and the time that the ozone has to decompose in aqueous solution before contacting the photoresist residues, a fundamental understanding of the mechanisms of ozone action will both improve the processes in the current generation of ozone-based tools and also lead to a broader range of tools and resist residues for which ozone chemistries can be effectively deployed.

Strong literature precedent exists for fundamental approaches to this problem. In this literature review, the papers on the ozonated water pre-diffusion cleaning, application to photoresist removal, ozone decomposition, chemistry of ozone with organic species, and simulation of ozone decomposition have been systematically categorized and elucidated.

2 REVIEW RESULTS

The following references and abstracts were searched through SciSearch from Los Alamos National Laboratories and INSPEC at Stanford University, which are also sources of the paper abstracts as presented in this report.

2.1 Ozonated Water Pre-Diffusion Cleaning

A series of papers have been published on the pre-diffusion cleaning using ozonated aqueous solutions. This technology was to replace Piranha cleaning in pre-diffusion processes because ozone can reduce the cost of ownership and is environmentally friendly. Pre-diffusion clean sequences that included ozonated aqueous solutions in place of Piranha steps showed high cleaning efficiency for metals, organics, and particles.

- Ohmi, T., Isagawa, T., Kogure, M. and Imaoka, T., "Native Oxide Growth and Organic Impurity Removal On Si Surface With Ozone Injected Ultrapure Water," *Journal of the Electrochemical Society*, 140, 804–810 (1993).
- Morita, H., Kim, J. S. and Ohmi, T., "Adsorption and Desorption Properties Of Cu and Ag Contaminants On Si Substrate," *Applied Surface Science*, 117, 99–102 (1997).
- Park, J. G., "The Hydrophilization of Process Wafers in Dilute Hydrogen Peroxide Solutions and Ozonated Deionized Water and Its Effects on Defects and Gate Oxide Integrity," *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers*, 36, 5416–5420 (1997).
- Hattori, T., Osaka, T., Okamoto, A., Saga, K. and Kuniyasu, H., "Contamination Removal by Single Wafer Spin Cleaning With Repetitive Use of Ozonized Water and Dilute HF," *Journal of the Electrochemical Society*, 145, 3278–3284 (1998).
- Alessandri, M., Bellandi, E., Pipia, F., Cazzaniga, F., Wolke, K. and Schenkl, M., "Particle Removal Efficiency and Silicon Roughness in HF-DIW/O-3/Megasonics Cleaning," *Solid State Phenomena*, 65–6, 27–30 (1999).
- Hattori, T., "Environmentally Friendly Single-Wafer Spin Cleaning," *Solid State Technology*, 42, 73–& (1999).

- Jeon, J. S., Ogle, B., Baeyens, M. and Mertens, P., "Evaluation of Cleaning Recipes Based on Ozonated Water for Pre-Gate Oxide Cleaning," *Solid State Phenomena*, 65–6, 119–122 (1999).
- Kwakman, L. F. T., Geomini, M., Levy, D. and Malgouyres, D., "Industrial Trends in Wet Processing Technology," *Solid State Phenomena*, 65–6, 31–34 (1999).
- Nakamura, O., Yoshida, M., Shirai, Y., Nagase, M., Kitano, M., Gozyuki, M., Hashimoto, Y. and Ohmi, T., "Construction of the Distribution System for Ozonated Water Used in the Wet Cleaning of Si Wafer Surface," *Solid State Phenomena*, 65–6, 161–164 (1999).
- Pipia, F., Bellandi, E., Crivelli, B. and Alessandri, M., "Fe and Cu Removal Efficiency in HF-DIW/O-3 Cleaning Sequence," *Solid State Phenomena*, 65–6, 109–112 (1999).
- Tardif, F., Lardin, T., Abolafia, Y., Danel, A., Boelen, P., Cowache, C., Kashkoush, I. and Novak, R., "New Aspects of the Diluted Dynamic Clean Process," *Solid State Phenomena*, 65–6, 19–22 (1999).
- Heyns, M. M., et al., "Cost-Effective Cleaning and High-Quality Thin Gate Oxides," *IBM Journal of Research and Development*, 43, 339–350 (1999).

2.2 Application to Photoresist Removal

The first attempt to use ozonated water for photoresist removal was reported by Kashkoush et al. According to their report, the photoresist stripping rate is enhanced by increasing the dissolved O₃ concentration and decreasing the process temperature. They also showed that the O₃ solubility increases with the concentration of O₃ in the gaseous source, but decreases with the temperature of aqueous solution.

- Kashkoush, I.I., Matthews, R. and Novak, R.E., "Photoresist Stripping Using Ozone/Deionized Water Chemistry," *Proceedings of the Fifth International Symposium on Cleaning Technology in Semiconductor Device Manufacturing*, p. 471–479, Paris, France 31 Aug.–5 Sept. 1997.

Abstract: Sulfuric acid is combined with hydrogen peroxide to oxidize stripped photoresist material, though the use of sparged ozone in sulfuric solution is also used to remove resist residues on wafers following the ashing process. Although these mixtures have been used for many years, sulfuric acid processes also have proven to be costly. This is due to the need for frequent bath changes and the use of high temperature which impose safety and environmental concerns. As a result of these and other considerations, the use of mixtures of ozone and deionized (DI) water for photoresist stripping has been investigated. Results show that the technique effectively removes hard-baked resist (ashed and unashed) from bare silicon and patterned wafers and produces cleaner surfaces (i.e., particles and metals) when compared to outcomes from typical SPM processes.

- Kashkoush, I., Novak, R. and Matthews, R., "A Novel Method for Photoresist Stripping Using Ozone/Deionized Water Chemistry," *1997 IEEE International Symposium on Semiconductor Manufacturing Conference Proceedings*, p. 81–85, San Francisco, CA, USA, 6–8 Oct. 1997.

Abstract: The mixture of sulfuric acid and hydrogen peroxide (SPM) that is used to strip photoresist from silicon wafers is a widely employed technique in the semiconductor manufacturing. Although these sulfuric acid processes have been used for many years, they also have proven to be costly. This cost is primarily due to the need for frequent bath change-

outs and the use of high process temperatures which impose safety and environmental concerns. In response to these drawbacks, the use of a ozone and DI water mixture for photoresist stripping has been investigated. Results show that this technique effectively removes hard-baked resist (ashed and unashed) from bare silicon and patterned wafers and produces surfaces with less particles and metals when compared to typical SPM and SOM processes.

- Kashkoush, I., Matthews, R., Novak, R., Brause, E., Carrillo, F. and Rajaram, B., “Photoresist Stripping Using Ozone/Deionized Water Chemistry,” *Science and Technology of Semiconductor Surface Preparation. Symposium*, p. 173–178, San Francisco, CA, USA 1–3 April 1997.

Abstract: The use of sulphuric acid to strip photoresist from silicon wafers is a widely employed technique in the semiconductor manufacturing community. In most cases, the acid is combined with hydrogen peroxide to oxidize stripped photoresist material, though the use of sparged ozone in sulfuric solution is also used to remove resist residues on wafers following the ashing process. Although they have been used for many years, sulfuric acid processes also have proven to be costly. This is due to the need for frequent bath change-outs and the use of high temperatures which impose safety and environmental concerns. As a result of these and other considerations, the use of mixtures of ozone and deionized water for photoresist stripping has been investigated. Results show that the technique effectively removes hard-baked resist (ashed and unashed) from bare silicon and patterned wafers and produces cleaner surfaces (i.e., particles and metals), compared to outcomes from SPM processes.

However, according to the report by DeGendt et al., the photoresist stripping efficiency at a given O₃ concentration is higher at higher temperatures. Therefore, to maximize the photoresist removal rate, the process temperature has to be optimized. In addition, they reported that one method to enhance the photoresist stripping rate is to minimize the thickness of the boundary layer of stagnant O₃ solution at the wafer surface, because it is known that the rate-limiting step of photoresist removal is mass transfer of aqueous ozone to the wafer surface. They thus obtained an increase in cleaning efficiency. They also investigated the effect of radical scavengers and promoters on the photoresist strip rate. Their results show a drastic reduction in photoresist removal when a radical promoter species (H₂O₂) is added and a slight acceleration of stripping rate when a radical scavenger species (acetic acid) is added.

Nelson also found that the addition of a radical scavenger (i.e., NH₄HCO₃) accelerated the rate of photoresist removal. From this observation, Nelson concluded that direct oxidation of photoresist by ozone is the main removal mechanism rather than a mechanism involving OH radicals formed from ozone.

- DeGendt, S., Wauters, J. and Heyns, M., “A Novel Resist and Post-Etch Residue Removal Process Using Ozonated Chemistry,” *Solid State Technology*, 41, 57–60 (1998).

Abstract: A novel, environmentally friendly process has successfully removed photoresist and organic post-etch residues from silicon surfaces. The moist ozone gas phase process described here greatly increases organic removal efficiency and is expected to replace most sulfuric-based process steps in IC production.

- DeGendt, S., Snee, P., Cornelissen, I., Lux, M., Vos, R., Mertens, P. W., Knotter, D. M., Meuris, M. M. and Heyns, M., “A Novel Resist and Post-Etch Residue Removal Process Using Ozonated Chemistry,” *Solid State Phenomena*, 65–6, 165–168 (1999).

Abstract: A novel, environmentally friendly process is successfully applied for the removal of photoresist and organic post-etch residues from silicon surfaces. The improved performance of the moist ozone gas phase process over traditional immersion based ozone processes is due to boundary control processing (i.e., enhanced reactive ozone availability near the wafer surface). Additionally, OH radical scavengers chemically enhance the process efficiency even further.

- Nelson, S. L. and Carter, L. E., “A Process Using Ozonated Water Solutions to Remove Photoresist After Metallization,” *Solid State Phenomena*, 65–6, 287–290 (1999).

Abstract: We show that compared to photoresist on a silicon (Si) substrate, the presence of exposed aluminum (Al) on a wafer surface greatly reduces the photoresist removal effectiveness of solutions containing only ozone in DI water (DI:O₃). We have found that the addition of ammonium bicarbonate (NH₄HCO₃) maintains the effectiveness of O₃ for photoresist removal even in the presence of exposed Al. The relevant chemical reactions to explain these results and the optimal process conditions for the O₃ and NH₄HCO₃ solution are discussed.

- Nelson, S., “Ozonated Water for Photoresist Removal,” *Solid State Technology*, 42, 107–& (1999).

Abstract: Processes using ozonated DI water for resist stripping and surface cleaning can reduce conventional chemical usage and operating costs, and improve process performance and yield. Improvements in ozone-generation equipment have made it possible to prepare supersaturated DIO₃, maximizing stripping efficiency. In addition, ozonated water additives can prevent unwanted radical reactions that lead to the decomposition of the ozone; this step is essential for stripping metallized wafers.

- Narayanswami, N. and Nelson, S., “Dynamics of Mass Transfer on a Wafer Surface in Ozonated Water Processing for Photoresist Removal,” *Solid State Phenomena*, 65–6, 157–160 (1999).

Abstract: The paper presents a theoretical analysis of mass transfer rates on a wafer subjected to liquid phase processing. Expressions are derived for surface mass transfer as a function of process parameters. The predictions show overall agreement with experimentally observed trends for photoresist removal using ozonated water in a spray system.

- Kleemeier, W., Leon, V. and Graham, S., “Plasma Etch Residue and Photoresist Removal Utilizing Environmentally Benign Process Chemicals,” *Solid State Phenomena*, 65–66, 143–152 (1999).

Abstract: An aqueous residue remover, Olin Microstrip 5002, is integrated with an ozonated DI water rinse in a single process for the removal of etch residues, often referred to as etch polymers, and residual resist following dry resist strip. The integrated process is implemented on a Semitool Class 1 Spray Solvent Tool and consists of an etch residue removal step using Microstrip 5002 followed by a rinse in ozonated DI water. The integrated process is tested on post-via and post-metal etch samples. Microstrip 5002 is shown to be an effective cleaning chemistry for etch residues at these levels but is ineffective at removing residual resist. The ozone/DI portion of the integrated process is effective at removing resist exposed to etch and

ash conditions and can be integrated into the residue strip process without impacting throughput. The overall integrated process effectively removes all residues and is shown to have no impact on wafer yield when used at either the via etch or metal etch levels. It is also shown to have no impact on via resistance. The integrated process slightly decreases metal critical dimension (CD); it is shown that the ozone/DI portion of the process, as tested at 95°C, causes the CD loss. The advantages of the integrated process include cost savings and throughput improvement from elimination of the intermediate rinse required with organic solvent strippers. Other advantages include cost savings and reduced environmental impact from the complete elimination of solvent waste and its special disposal requirements from the residue cleaning operation. A final advantage of the integrated process may be enhanced process margin against incomplete resist strip.

2.3 O₃ Decomposition in Aqueous Solutions

Maximizing the ozone concentration in aqueous solutions is quite important to enhancing the photoresist striping rate as well as mass transfer. Ozone decomposes in aqueous solutions, and the decomposition rate is a function of the process conditions: pH, concentration of various additives, and temperature. Ozone can decompose by chain reactions in aqueous solutions. All of these effects are important in determining the ozone concentration.

- Taube, H and Bray, W. C., “Chain Reactions in Aqueous Solutions Containing Ozone, Hydrogen Peroxide, and Acid,” *Journal of American Chemical Society*, 62, 3357–3373 (1940).

Kinetic models of ozone decomposition have been extensively studied. An ozone decomposition model proposed by Hoigne, Staehelin, and Bader (the HSB model) has the reaction between O₃ and OH⁻ as an initiation step of a chain reaction involving various radical species such as O₂⁻, O₃, HO₃, and HO₄. The initiation step constitutes the rate-limiting step in the ozone decomposition sequence, and the formation of superoxide anion, O₂⁻, is a key factor to terminate/enhance the chain reaction. Though the HSB model includes two intermediate species that have not been directly measured, it is known to work in neutral and low pH aqueous solutions. The ozone decomposition rate is determined mainly by pH and the concentration of radical scavengers and promoters. The roles of scavengers and promoters of chain reactions have been chemically and kinetically investigated by Staehelin and Hoigne also. In the presence of radical scavengers such as carbonate, bicarbonate, *tert*-butylalcohol, and alkyl groups that do not produce the superoxide anion, O₂⁻, the lifetime of ozone in an aqueous solution is enhanced. On the other hand, promoters that generate the superoxide anion accelerate ozone decomposition in aqueous solutions.

- Bader, H. and Hoigne, J., “Determination of Ozone in Water by the Indigo Method,” *Water Research*, 15, 449–456 (1981).
- Bader, H. and Hoigne, J., “Determination of Ozone in Water by the Indigo Method: A Submitted Standard Method,” *Ozone-Science & Engineering*, 4, 169–176 (1982).
- Hoigne, J. and Bader, H., “Ozone Initiated Oxidations of Solutes in Wastewater: Reaction Kinetic Approach,” *Progress In Water Technology*, 10, 657–671 (1978).
- Hoigne, J. and Bader, H., “Ozonation of Water: Kinetics of Oxidation of Ammonia by Ozone and Hydroxyl Radicals,” *Environmental Science & Technology*, 12, 79–84 (1978).
- Hoigne, J. and Bader, H., “Ozonation of Water: Selectivity and Rate of Oxidation of Solutes,” *Ozone-Science & Engineering*, 1, 73–85 (1979).

- Hoigne, J. and Bader, H., "Ozonation of Water: Oxidation Competition Values of Different Types of Waters Used in Switzerland," *Ozone-Science & Engineering*, 1, 357–372 (1979).
- Hoigne, J., "Chemical Society of Zurich: May 12 ; 1982: Ozonation of Water: Water Quality and the Kinetics of the Oxidation of Organic Materials," *Chimia*, 36, 400–400 (1982).
- Hoigne, J., "Organic Micropollutants and Treatment Processes: Kinetics and Final Effects of Ozone and Chlorine Dioxide," *Science of the Total Environment*, 47, 169–185 (1985).
- Hoigne, J., Bader, H., Haag, W. R. and Staehelin, J., "Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water.3. Inorganic Compounds and Radicals," *Water Research*, 19, 993–1004 (1985).
- Hoigne, J. and Bader, H., "The Formation of Trichloronitromethane (Chloropicrin) and Chloroform in a Combined Ozonation Chlorination Treatment of Drinking Water," *Water Research*, 22, 313–319 (1988).
- Hoigne, J., "Characterization of Water Quality Criteria for Ozonation Processes.1. Minimal Set of Analytical Data," *Ozone-Science & Engineering*, 16, 113–120 (1994).
- Hoigne, J. and Bader, H., "Characterization of Water Quality Criteria for Ozonation Processes.2. Lifetime of Added Ozone," *Ozone-Science & Engineering*, 16, 121–134 (1994).
- Hoigne, J. and Bader, H., "Kinetics of Reactions of Chlorine Dioxide (Oclo) in Water.1. Rate Constants for Inorganic and Organic Compounds," *Water Research*, 28, 45–55 (1994).
- Staehelin, J. and Hoigne, J., "Decomposition of Ozone in Water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide," *Environmental Science & Technology*, 16, 676–681 (1982).

Abstract: The initiation of ozone decomposition in "pure water" is first order in O_3 and OH^- concentration and k_{O_3, OH^-} becomes $70 \pm 7 \text{ M}^{-1}\text{s}^{-1}$ when a sequence of reactions is assumed by which three molecules of O_3 are eliminated per primary event. The difference between this value and higher values reported in the earlier literature may be explained by interferences by radical chain reaction which have not been totally inhibited in those studies. H_2O_2 also reacts with O_3 when present as an anion, HO_2^- . k_{O_3, HO_2^-} is $(2.8 \pm 0.5) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ when it is assumed that two molecules of O_3 are eliminated per primary event. Therefore, whenever $[H_2O_2] > 10^{-7} \text{ M}$ ($\text{pH} < 12$), HO_2^- has a greater effect than OH^- on the decomposition rate of O_3 in water. The high reactivity of HO_2^- explains that H_2O_2 is observed as a significant intermediate in the ozonated water only if the pH is low (e.g., < 6).

- Staehelin, J., Buhler, R. E. and Hoigne, J., "Ozone Decomposition in Water Studied by Pulse Radiolysis. 2. OH and HO_4 as Chain Intermediates," *Journal of Physical Chemistry*, 88, 5999–6004 (1984).
- Staehelin, J. and Hoigne, J., "Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions," *Environmental Science & Technology*, 19, 1206–1213 (1985)

Abstract: The decomposition of aqueous ozone is generally due to a chain reaction involving OH radicals. Many organic solutes (impurities) can react with OH to yield O_2^- upon addition of O_2 . O_2^- transfers its electron to a further ozone molecule in a rather selective reaction. The ozonide anion (O_3^-) formed immediately decomposes into a further OH radical. Compounds that convert OH radicals into ozone-selective O_2^- , therefore, act as promoters of the chain reaction. The efficiencies of different OH to O_2^- converters (e.g., fomic acid, primary and secondary alcohols (including sugars), glyoxylic acid, and humic acids) are tested in the

presence of other OH radical scavengers that do not primarily produce O₂⁻ (carbonate, aliphatic alkyl compounds, and tert-butyl alcohol). The derived reaction kinetics allows on the qualitatively interpret the variation of the lifetime of O₃ found in model solutions and even in natural waters and during drinking water treatment.

Tomiyasu, Fukutomi, and Gordon suggested a modified ozone decomposition model (the TFG model) in a basic aqueous solution. The initiation step in this model is an oxygen atom transfer from O₃ to OH⁻, while in HSB model, it is described as an oxygen cation transfer. The TFG model also does not include HO₃ and HO₄. It has been verified at high pH levels.

- Tomiyasu, H., Fukutomi, H. and Gordon, G., “Kinetics and Mechanism of Ozone Decomposition in Basic Aqueous Solution,” *Inorganic Chemistry*, 24, 2962–2966 (1985).

Abstract: The kinetics of the decomposition of ozone have been studied in aqueous alkaline solutions by means of an accumulated stopped-flow method. In slightly basic solution ([OH⁻] ~ 0.01 M; 1M=1 moldm⁻³), the reaction can be described by the following rate law involving first- and second-order terms in ozone: $-d[O_3]/dt = k_1[O_3] + k_2[O_3]^2$. The second-order terms is not observed if a radical scavenger (Na₂CO₃) is present in the solution. In solutions of high [OH⁻], the rate law changes markedly. The addition of Na₂CO₃ retards the reaction only in the latter stages, and the rate law becomes nearly first order in ozone as the concentration of added Na₂CO₃ is increased. The results provide kinetic evidence for the initiation step $O_3 + OH^- \rightarrow HO_2^- + O_2$, which corresponds to a two-electron-transfer process or an oxygen atom transfer for ozone to hydroxide ion.

Other examples of papers in this area are listed below:

- Forni, L., Bahnemann, D. and Hart, E. J., “Mechanism of the Hydroxide Ion Initiated Decomposition of Ozone in Aqueous Solution,” *Journal of Physical Chemistry*, 86, 255–259 (1982).
- Reckhow, D. A., Legube, B. and Singer, P. C., “The Ozonation of Organic Halide Precursors: Effect of Bicarbonate,” *Water Research*, 20, 987–998 (1986).
- Sehested, K., Holcman, J. and Hart, E. J., “Rate Constants and Products of the Reactions of Ea⁻; O₂⁻; and H With Ozone in Aqueous Solutions,” *Journal of Physical Chemistry*, 87, 1951–1954 (1983).
- Yurteri, C. and Gurol, M. D., “Removal of Dissolved Organic Contaminants by Ozonation,” *Environmental Progress*, 6, 240–245 (1987).
- Yurteri, C. and Gurol, M. D., “Ozone Consumption in Natural Waters: Effects of Background Organic Matter ; Ph and Carbonate Species,” *Ozone-Science & Engineering*, 10, 277–290 (1988).
- Yurteri, C. and Gurol, M. D., “Evaluation of Kinetic Parameters for the Ozonation of Organic Micropollutants,” *Water Science and Technology*, 21, 465–476 (1989).
- Yurteri, C. and Gurol, M. D., “Ozonation of Trace Organic Compounds: Model Predictions vs. Experimental Data,” *Ozone-Science & Engineering*, 12, 217–229 (1990).
- Vongunten, U. and Hoigne, J., “Ozonation Processes: Molecular Kinetics and Full-Scale Drinking Water Treatment,” *Abstracts of Papers of the American Chemical Society*, 210, 74–ENVR (1995).

2.4 Reaction of O₃ with Organics

In aqueous solution, ozone may directly oxidize organics. Additionally radical species, such as hydroxyl radical, produced by ozone decomposition may oxidize the organics. The direct reactions with ozone can be divided into two mechanisms: cyclo addition (Criegee mechanism) and electrophilic reaction. The cyclo reaction is selective to unsaturated carbon-carbon double bonds and forms carbonyl compounds (aldehydes or ketones). The reactivity of ozone is strongly related to electron density at the reaction site. For example, the reactions of ozone with aromatics substituted with electron donor groups such as OH, CH₃, and NH₂ are enhanced. Therefore, phenol and aniline show very high reactivity with ozone. However, the aromatics substituted with electron withdrawing groups such as COOH, and NO₂ are retarded.

2.4.1 Reactions of Ozone with Aliphatic

- Decoret, C., Royer, J., Legube, B. and Dore, M., “Experimental and Theoretical Studies of the Mechanism of the Initial Attack of Ozone on Some Aromatics in Aqueous Medium,” *Environmental Technology Letters*, 5, 207–218 (1984).
- Hoigne, J. and Bader, H., “Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water. 2. Dissociating Organic Compounds,” *Water Research*, 17, 185–194 (1983).
- Hoigne, J. and Bader, H., “Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water. 1. Non-Dissociating Organic Compounds,” *Water Research*, 17, 173–183 (1983).
- Fronk, C. A., “Destruction of Volatile Organic Contaminants in Drinking Water by Ozone Treatment,” *Ozone-Science & Engineering*, 9, 265–287 (1987).

2.4.2 Reactions of Ozone with Aromatics

- Dore, M., Langlais, B. and Legube, B., “Mechanism of the Reaction of Ozone With Soluble Aromatic Pollutants,” *Ozone-Science & Engineering*, 2, 39–54 (1980).
- Legube, B., Langlais, B., Sohm, B. and Dore, M., “Identification of Ozonation Products of Aromatic Hydrocarbon Micropollutants: Effect on Chlorination and Biological Filtration,” *Ozone-Science & Engineering*, 3, 33–48 (1981).
- Legube, B., Langlais, B. and Dore, M., “Reactions of Ozone With Aromatics in Dilute Aqueous Solution: Reactivity and Biodegradability of Oxidation Products,” *Water Science and Technology*, 13, 553–570 (1981).
- Legube, B., Guyon, S., Sugimitsu, H. and Dore, M., “Ozonation of Some Aromatic Compounds in Aqueous Solution: Styrene; Benzaldehyde; Naphthalene; Diethylphthalate; Ethyl and Chloro Benzenes,” *Ozone-Science & Engineering*, 5, 151–170 (1983).
- Schalekamp, M., Dietlicher, K., Valenta, J. and Gould, J. P., “Ozonation of Aromatic Compounds pH Dependence: Discussion,” *Water Science and Technology*, 14, 1042–1043 (1982).

Here also, the results showed that aromatic compounds with electron-withdrawing groups are less reactive with aqueous ozone.

2.4.3 Reactions of Ozone with Phenol

- Gurol, M. D. and Singer, P. C., “Dynamics of the Ozonation of Phenol. 2. Mathematical Simulation,” *Water Research*, 17, 1173–1181 (1983).
- Gurol, M. D. and Vatistas, R., “Photolytic Ozonation of Phenols,” *Water Science and Technology*, 19, 1177–1180 (1987).
- Singer, P. C. and Gurol, M. D., “Dynamics of the Ozonation of Phenol. 1. Experimental Observations,” *Water Research*, 17, 1163–1171 (1983).
- Gould, J. P., “Correlations Between Chemical Structure and Ozonation Kinetics: Preliminary Observations,” *Ozone-Science & Engineering*, 9, 207–216 (1987).

2.5 Comparison of Oxidation by Ozone and Hydroxyl Radical

On the other hand, the reactions of hydroxyl radical with organics are not selective. Therefore, compounds that are less reactive with aqueous ozone may be attacked by OH radicals and be rapidly oxidized in basic solutions. The importance of this advanced oxidation by hydroxyl radical compared to direct oxidation has been elucidated.

- Masten, S. J. and Hoigne, J., “Comparison of Ozone and Hydroxyl Radical Induced Oxidation of Chlorinated Hydrocarbons in Water,” *Ozone-Science & Engineering*, 14, 197–214 (1992).

Abstract: The efficiency of ozonation and advanced oxidation processes such as ozone/UV, ozone/H₂O₂ and H₂O₂/UV was assessed for chlorinated hydrocarbons using a closed batch-type system. 1,1-Dichloropropene (DCPE), trichloroethylene (TCE), 1-chloropentane (CPA), and 1,2-dichloroethane (DCA) were used as model compounds. The direct reaction between substrates and ozone predominated at lower pH, which resulted in the efficient oxidation of the olefin, DCPE. At higher pH, ozonation resulted in more efficient oxidation of the chlorinated alkanes, with a corresponding decrease in the efficiency of DCPE oxidation. Consistent results were observed for ozone/H₂O₂ and ozone/UV treatment. Due to slow UV-induced decomposition of H₂O₂, the process using H₂O₂/UV (254 nm) resulted in very slow oxidation of all four compounds. The total ozone requirement to achieve a given degree of elimination (to 37% of the original concentration), $\Delta-0.37$, was used to assess the combined effects of the direct and indirect reactions for different types of waters.

- Hoigne, J., “Inter-Calibration of OH Radical Sources and Water Quality Parameters,” *Water Science and Technology*, 35, 1–8 (1997).

Abstract: OH radicals are the key oxidants that control most advanced oxidation processes (AOPs) currently applied in water technology and that also occur in some natural systems such as cloud waters. The efficiencies of the various OH radical sources can be experimentally quantified and compared when they are calibrated by following the oxidation of inter-calibrated reference compounds that react during the process only with OH radicals. To apply and generalize the results, however, water quality parameters controlling the lifetime of OH radicals via OH-scavenging reactions by pollutants and further solutes must also be quantified by methods that allow for calibrations.

- Beltran, F. J., “Estimation of the Relative Importance of Free Radical Oxidation and Direct Ozonation UV Radiation Rates of Micropollutants in Water,” *Ozone-Science & Engineering*, 21, 207–228 (1999).

Abstract: The relative importance of free radical and direct ozonation/photolysis oxidation of micropollutants in water can be estimated from simple kinetics of aqueous ozonation reactions provided these reactions develop in the slow kinetic regime of absorption. Knowledge of kinetic expressions of free radical initiation reactions and direct ozone-micropollutant or UV radiation-micropollutant reactions (and corresponding parameters: reaction rate constants, quantum yields, etc.) allows an estimation of the reaction rate ratios for any micropollutant in the ozone alone and combined with hydrogen peroxide and/or UV radiation oxidation systems.

- Elovitz, M. S. and vonGunten, U., “Hydroxyl Radical Ozone Ratios During Ozonation Processes. I-The R-ct Concept,” *Ozone-Science & Engineering*, 21, 239–260 (1999).

Abstract: The ozonation of model systems and several natural waters was examined in bench-scale batch experiments. In addition to measuring the concentration of ozone (O_3), the rate of depletion of an *in situ* hydroxyl radical probe compound was monitored, thus providing information on the transient steady-state concentration of hydroxyl radicals ($\cdot OH$). A new parameter, R_{ct} , representing the ratio of the $\cdot OH$ -exposure to the O_3 -exposure was calculated as a function of reaction time. For most waters tested, including pH-buffered model systems and natural waters, R_{ct} was a constant value for the majority of the reaction. Therefore, R_{ct} corresponds to the ratio of the $\cdot OH$ concentration to the O_3 concentration in a given water (i.e., $R_{ct} = [\cdot OH]/[O_3]$). For a given water source, the degradation of a micropollutant (e.g., atrazine) via O_3 and $\cdot OH$ reaction pathways can be predicted by the O_3 reaction kinetics and R_{ct} .

2.6 Numerical Simulation of O_3 Decomposition

The decay in ozone concentration in aqueous solution and the concentration changes in various species can be numerically simulated. The simulations easily show how the ozone consumption and radical species concentration are changed by modification of the concentrations of initiators and inhibitors. Particularly, the addition of hydroxyl radical scavengers or promoters strongly affects the ozone concentration in aqueous solutions.

- Chelkowska, K., Grasso, D., Fabian, I. and Gordon, G., “Numerical Simulations of Aqueous Ozone Decomposition,” *Ozone-Science & Engineering*, 14, 33–49 (1992).

Abstract: The decomposition of ozone in basic aqueous solutions was simulated on the basis of two previously reported detailed mechanisms. According to the calculations, the mechanism given by Tomiyasu, Fukutomi and Gordon 5 is an appropriate model for the ozone decomposition, both in the presence and the absence of hydrogen peroxide and/or carbonate ion in basic solution. On the basis of this mechanism the main chain carrier is the ozonide ion radical (O_3^-).

- Westerhoff, P., Song, R., Amy, G. and Minear, R., “Applications of Ozone Decomposition Models,” *Ozone-Science & Engineering*, 19, 55–73 (1997).

Abstract: Simulated ozone decomposition profiles in “pure” water were made using two analytical kinetic ozone decomposition models and contrasted with experimental and literature data. Fundamental and applied applications of ozone consumption models are presented, demonstrating the importance of both direct and indirect oxidation of inorganic

and organic species. A novel approach to simulating ozone decomposition in the presence of natural organic matter (NOM) is presented, concluding that NOM predominantly behaves as a direct consumer of ozone and promoter of ozone decomposition.

3 CONCLUSION

This literature review provides a springboard for planned work to simulate the chemistry of ozone in aqueous solutions. Based on this review, chemical-kinetic simulation will be conducted to investigate the factor to affect the lifetime of ozone and to understand the relative importance and role of direct oxidation by aqueous ozone and advanced oxidation by hydroxyl radical formed by ozone decomposition. In the future, chemical kinetics and mass transport will be combined to simultaneously account for the chemistry and the mass transport effects. This capability will allow specific geometrical aspects of tools to be designed and optimized for cost-effectiveness and minimal environmental impact.

**International SEMATECH Technology Transfer
2706 Montopolis Drive
Austin, TX 78741**

**<http://www.sematech.org>
e-mail: info@sematech.org**