Ozone: Science & Engineering
Thirty Three Years and Growing

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Abstract

The first issue of Ozone: Science & Engineering was published in early 1979 with Dr. L. J. Bollyky as the Editor-in-Chief. This was a milestone for the International Ozone Association enabling professional recognition of the advances in ozone technology.

Since this first issue, 33 volumes of Ozone: Science & Engineering have been published containing 168 individual issues, 1128 technical articles and nearly 16,000 pages. Dr. Rip Rice became Editor-in-Chief in 1985 and continued this position until 1998. Under the leadership of these gentlemen, OS&E expanded from about 70 pages per issue four times per year to 100 pages, then to six issues per year, at about 100 pages. In 2001 the dimensions of the journal were increased to accommodate even more manuscripts.

Early articles in Ozone: Science & Engineering focused heavily on aquaculture applications, municipal wastewater treatment and industrial applications. In 1980 the application of ozone to trihalomethane control was developed and a shift to papers on drinking water treatment occurred. Early papers also introduced the use of ozone for pulp bleaching, odor control, bottled water treatment, swimming pool treatment, cooling tower treatment, the use of UV, advanced oxidation, and ozone measurement. As the journal and ozone science matured, papers began to cover more in-depth studies on disinfection removal of specific pollutants and to focus on current environmental problems such as inactivation of Cryptosporidium. Current issues are covering new applications for ozone such as agri-food applications and emerging contaminants (endocrine disruptors).

In 1989, the Harvey M. Rosen Memorial Award was established to recognize the “best paper” published in Ozone: Science & Engineering during the two-year period between World Congresses. The selection of award is determined by the Editorial Board of Ozone: Science & Engineering. To date, eleven papers have received this prestigious award.

This paper reviews the first 33 years of Ozone: Science & Engineering and offers a glimpse into the future of the journal. Emphasis is placed on the contributions to the Journal from France.

Keywords
Ozone; Ozone Applications; Ozone: Science & Engineering;

Introduction

The first issue of Ozone: Science and Engineering was published in early 1979 with Dr. L. Joseph Bollyky as Editor-in-Chief. Dr. Bollyky had been requested by Drs. Morton Klein and Harvey Rosen to prepare a technical journal for the International Ozone Institute. This issue consisted of 7 papers and 88 pages.
The first Editorial Board of OS&E was:

Dr. Walter J. Blogoslawski, National Marine Fisheries Service, USA
Mr. J. K. Carswell, EPA Municipal Environmental Research Laboratories, USA
Dr. Jürg Hoigné, EAWAG, Swiss Federal Institute for Water Resources and Water Pollution Control, Switzerland
Dr. Wolfgang Kühn, Engler Bunte Institute, Univ. of Karlsruhe, German Federal Republic
Dr. Jean Pierre Legeron, Trailigaz, France
Dr. Norman Liebergott, Paper Pulp Research Institute of Canada, Canada
Dr. Willy J. Masschelein, Compagnie Intercommunale, Bruxelloise des Eaux, Belgium
Mr. C. Michael Robson, City of Indianapolis, Indiana, USA
Dr. Harvey M. Rosen, Union Carbide Corp., USA

This first issue started off with a Dedication by Morton J. Klein, President of the International Ozone Association. A few of his comments are excerpted below.

"On December 2-5, 1973, 400 scientists from 15 nations gathered in Washington, D. C. for the First International Symposium on Ozone for Water and Wastewater treatment. At that time, the International Ozone Institute was formally established. This organization, now reincorporated as the International Ozone Association, was formed to collect and disseminate information on all aspects of ozone technology. Toward this end, we conduct biennial 'World Ozone Congresses', which are truly international meetings in which leaders in ozone technology present a broad spectrum of technical papers."

"Now, with a worldwide membership and with our plans for future Congresses and meetings in place, we launch a new endeavor Ozone: Science and Engineering, The Journal of the International Ozone Association. Such an undertaking is not easy, but with the dedication and efforts of Dr. L. J. Bollyky, his Editorial Board, and many others, it has come to pass. Our membership has indicated that we should have a journal. It now remains for them to support it with high quality papers and to promote its utilization."

Dr. Bollyky in his first Editorial stated:

"The scientific and engineering fields involved in ozone related projects have traditionally attracted a group of bright, enthusiastic, dedicated people. However, much of their work, reported at the congresses and symposia of the International Ozone Association did not reach the scientific and engineering community at large. This journal is intended to provide a means of communicating with the outside world and a forum for all researchers, engineers and other interested persons to speak out on any ozone and environment-related problems.

The editorial philosophy is to publish any scientifically and technically oriented paper which deals with new information on ozone, its reactions, applications, engineering design data, plant operations, and experiences. All papers presented at the meetings, symposia, and world congresses of the International Ozone Association will automatically be given consideration for publication. To assure the highest possible standards, the papers will be reviewed prior to acceptance for publication."

The editorial philosophy established in this first issue of OS&E remains in effect today.

The first article published in OS&E was titled "Ozonation as a Critical Component of Closed Marine System Design" by Kenneth V. Honn, Wayne State University, Detroit, MI. (1) This paper describes the use of ozone as an oxidative supplement to biological filtration. Ozone maintained filter bed effluent levels of total ammonia, unionized ammonia and nitrite within acceptable levels.
This issue featured three other articles on marine applications, “Ozone Reactivity with Seawater Components” by Kosak-Channing and Helz (2); “Toxicity and Effects of Bromoform on five Marine Species” by Gibson, et. al. (3) ; and “Ozone-UV Water Treatment System for Shellfish Quarantine” by Blogoslawski and Alleman (4). These four papers had been initially presented at the second “Aquatic Applications of Ozone” workshop held in Orlando, 1979.

This issue also featured the first of several papers by Professor Jürg Hoigné, “Ozonation of Water: Selectivity and Rate of Oxidation of Solutes” (5). In this paper the hydroxyl free radical mechanisms were outlined for the first time in OS&E.

Since its inception, OS&E has published 1128 papers from more than 1900 authors or contributing authors in 168 issues comprising nearly 16,000 pages of text covering an extensive range of ozone-related topics. These will be summarized throughout this paper.

Dr. Bollyky continued as Editor-in-Chief until 1985. At that time Dr. Rip Rice, who had been an editorial board member since 1980 took over as Editor and continued in this position until 1998. Barry Loeb has since held the position of Editor.

Under Dr. Rice’s tutelage the journal continued to grow in size in stature. In 1991, it became necessary to increase number of issues per year from four to six, reflecting the increased number of submittals. The annual number of pages also peaked in 1991 at 744 due to a large number of papers from the 9th Ozone World Congress (New York). In 2000 the total pages again approached 700 and the size of the journal was increased to 8.5 x 11 inches with a new cover design.

To reflect the increasing workload in coordinating peer review of papers, Professor Marcel Doré of Université de Poitiers (France) was appointed Editor-for-Europe in 1985. Professor Nigel Graham of Imperial College (London) was appointed Assistant Editor in 1991 upon the retirement of Professor Doré. In 1993 Professor David Reckhow joined Dr. Graham as Assistant Editor reflecting the increasing number of manuscripts to be reviewed. Dr. Reckhow assumed responsibility for papers generated in the Americas with Dr. Graham covering the rest of the world. In 1998 Dr. Reckhow retired and Dr. Gordon Finch of the University of Alberta assumed the position until his untimely death in 2000. The contributions of the University of Alberta continued with Professor Daniel Smith assuming the position of Associate Editor along with Dr. Graham. In 2002, Professor Hiroshi Tsuno of Kyoto University was appointed Associate Editor, Japan to reflect the increasing number of manuscripts generated from this region.

The Early Years

Pergamon Press published OS&E until 1985 when Lewis Publishers became the journal’s publisher. Lewis Publishers was acquired by CRC Press in the early 1990s, but continued to publish OS&E as the Lewis Publishers division of CRC Press. In 2003, CRC Press was acquired by Taylor & Francis who now publishes OS&E.

Ozone: Science & Engineering was initiated before computer generated manuscripts and the first few issues were prepared by typewriter, a very time-consuming task. One of the first milestones was to have OS&E accepted by Chemical Abstracts as a journal for their referencing. The rigorous peer review process that had been implemented was a key to being accepted by Chemical Abstracts.

The early issues of OS&E are full of articles that still retain interest. In the second issue of OS&E, medium frequency ozone generation was compared with low frequency with the conclusion that medium frequency led to lower operating costs (6).

Although the term “Advanced Oxidation” was not coined for several years, Nakayama et al. introduced the term “catalytic ozonation” to describe the treatment of effluent from an electrodeposition process via ozonation in the presence of hydrogen peroxide (H$_2$O$_2$) (7). This was the
first OS&E published information on “advanced oxidation” involving ozone/H\textsubscript{2}O\textsubscript{2} oxidation of refractory organics.

In the first of only two articles published in OS&E on this topic, the ozonation of a radioactive wastewater was described by Lutton, Bollyky et al. (8). Ozonation was used to remove EDTA and other complexing agents so that the remaining radionuclides could be processed via ion exchange. In a more recent study, Vilve et al. studied ozonation for the degradation of organic compounds from nuclear laundry water (140).

The first of many articles on aquaculture were published, including one describing the use of ozone for shellfish depuration (9), one describing the use of ozone for salmonid fish rearing (10), and a paper describing the use of ozone for purification of fish hatchery waters (13).

Industrial applications were featured in the early years of OS&E. Work was presented showing the use of ozone for shrinkproofing of wool (11), for use of ozone in the photoprocessing industry (12) and one of the first applications in use of ozone for removal of cyanides (14).

The first of many papers on Trihalomethane (THM) formation and control via ozonation was published by Dr. Rice (15). This paper described the mechanisms for forming THM and the role of ozone in this process.

The concept of mass transfer in ozone contacting systems was introduced and discussed in detail by Roustan et al. (16) and later by Bollyky (17). This latter paper outlines a number of industrial applications for ozone mass transfer.

The first (and unfortunately one of the very few) papers on ozone safety and handling was published by Damez and Vigouret (18) with a companion paper on ozone destruction via a thermal catalytic method by Shalekamp (19).

This is by no means an inclusive list of all the early papers but it does show the broad scope of ozone applications that OS&E was covering. It also indicates that many of these papers remain relevant today as they established several fundamental concepts for the understanding and use of ozone.

**Highlights of OS&E**

From the early years, OS&E has grown and continued to be the source of ozone information for scientists and engineers. The journal is frequently cited in other well-known technical journals and we continue to receive papers of very high quality. The journal impact factor has been steadily rising and is currently 1.515. The journal is rated 24/42 in Environmental Engineering and 113/180 in Environmental Sciences.

In this section, a brief summary of major ozone topics is presented indicating how OS&E has been a leader in presenting these topics to the ozone industry. Again this list is not inclusive; the reader is directed to the author and key word indices which appeared in Volume 31 No 2. There is also a CD ROM available which contains all issues of the first 25 years. All issues of OS&E are available to IOA members on the Taylor & Francis website.

**Drinking Water Treatment**

Ozone was used for drinking water treatment long prior to the establishment of OS&E so the initial papers were actually already reporting on advances in the technology. By far, drinking water treatment features the largest number of articles published in OS&E starting with the first major article published in 1979 “Ozonation of Water: Selectivity and Rate of Oxidation of Solute” by Hoigné and Bader (5). Since the first paper, more than one hundred papers investigating various
phases of drinking water treatment have been published. Some examples of drinking water treatment papers are shown in Table 1.

**Table 1.** Ozone: *Science & Engineering* articles featuring drinking water treatment

<table>
<thead>
<tr>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction of hydroxyl radical concept</td>
<td>5</td>
</tr>
<tr>
<td>“CT” concept for drinking water disinfection</td>
<td>20, 21, 22, 24, 25, 26, 115</td>
</tr>
<tr>
<td>Bromate formation and control</td>
<td>27, 28, 29, 30, 31, 32, 33, 113, 114, 126, 142</td>
</tr>
<tr>
<td>Trihalomethane formation and control</td>
<td>2, 38, 39, 40</td>
</tr>
<tr>
<td>Color removal (humic acids)</td>
<td>34, 35, 36, 37</td>
</tr>
<tr>
<td>Biological Activated Carbon with Ozone</td>
<td>41, 42, 43, 44</td>
</tr>
<tr>
<td><em>Cryptosporidium</em> Inactivation</td>
<td>47, 48, 49, 51, 51, 52, 116, 125</td>
</tr>
<tr>
<td>Advanced Oxidation</td>
<td>57, 58, 59, 60, 61, 141</td>
</tr>
<tr>
<td>Ozone Flotation for algae control</td>
<td>45, 46</td>
</tr>
<tr>
<td>Individual Plant Experiences</td>
<td>23, 54, 55, 56</td>
</tr>
</tbody>
</table>

OS&E followed closely the development of the “CT” concept for drinking water disinfection with numerous papers submitted. Several of these are listed in Table 1 starting with the initial concept suggested by Wickramanayake and Sproul (20) and leading to the design of large ozone contactors by Rakness et al. (25). A novel approach to reaction kinetics, the $R_{ct}$ concept was developed by Elovitz et al. (115).

Bromate formation and control has received much attention from the journal. An introduction to bromate chemistry was presented in 1985 by Cooper et al. (27). Gary Amy of the University of Colorado and his colleagues presented a number of works covering models for bromate control and bromate control options (28, 31, 32). Other excellent papers were presented by Somiya (29), Croué (30) and Welté (33) to name a few. Recent surveys have been made on bromates in French (113) and Swiss (114) drinking waters. F. Berne et al. investigated the effect of addition of ammonia on bromate formation during ozonation (126). Jarvis (142) attempted to model bromate formation during ozonation.

**Advanced Oxidation**

The term “Advanced Oxidation” was first advanced by W.H. Glaze et al. in their Harvey Rosen Award winning paper “The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation” (57). This paper outlined the synergy between ozone, hydrogen peroxide and UV. Since then, many papers have discussed advanced oxidation as a standard process for water treatment. A selection of other references for advanced oxidation is listed in Table 1. A paper by Sánchez Polo et al. (141) investigated the combination of ozone with activated carbon as an alternative to conventional advanced oxidation processes.

**Inactivation of Cryptosporidium parvum**

Although the serious nature of *Cryptosporidium* was not fully recognized until the late 1990s when outbreaks were documented in Canada, the United States and Great Britain, the subject was first addressed in OS&E in 1991. E. Nieminski (47) studied the effect of ozone on *Cryptosporidium* in Colorado River Water delivered to the Phoenix Water Treatment Plant. The effect of ozone for *Cryptosporidium* inactivation in a lime softening plant was studied by Crozes et al. (48).

Liyanage, Finch and Belosevic then authored the Harvey Rosen Award winning paper “Sequential Disinfection of Cryptosporidium parvum by Ozone and Chlorine Dioxide” (49). Several excellent papers followed, including a paper sponsored by industry “Design Criteria for Inactivation of Cryptosporidium by Ozone in Drinking Water” by Finch et al. (52). Do-Quang et al. investigated the mathematical modeling of theoretical *Cryptosporidium* inactivation in full-scale ozone reactors.
Owens et al. investigated the pilot-scale inactivation of Cryptosporidium (51); and Levin, Craik, Li and Smith investigated the sequential inactivation of Cryptosporidium using ozone followed by free chlorine (53). Craik et al. investigated the use of a static mixer contactor for Cryptosporidium inactivation (116).

The impacts of CT requirements on design of ozone systems for Cryptosporidium inactivation were outlined by Schulz et al. (125)

Wastewater Treatment

Municipal Wastewater

Much of the work on ozone disinfection of municipal wastewater occurred early in the years of OS&E. Particularly in the United States, ozone was promoted and favored for wastewater treatment with 50-60 plants being built (77, 78).

Early work by Netzer et al. (73) reported on pilot plant studies in Brampton, Ontario, Canada to establish the optimum criteria for the ozone disinfection of effluents under various conditions of wastewater treatment plant operations. Richard and Conan (74) invested the importance of interfacial action on ozone disinfection and wastewater treatment.

In more recent work Finch and Smith (75) investigated the pilot-scale evaluation of ozone disinfection of Escherichia coli in a semi-batch stirred tank reactor. Liberti et al. (76) reported on the use of ozone for disinfection of municipal wastewater for reuse in agriculture.

Most recently, van Leeuwen et al. investigated the integration of ozone into an activated sludge process with encouraging results (165). Ried et al. (166) summarized potential options for applying ozone for the improvement of effluents from wastewater treatment plants, with focus on the technical aspects of integrating ozone in either new or existing plants.

Industrial Wastewater

For an immediate overview of industrial wastewater applications, the reader is directed to the survey paper by Rice (68), that presents a detailed review of published applications (in OS&E and elsewhere) of ozone for treating many types of industrial wastewaters. Applications of ozone technologies to control pollution in full-scale industrial wastewater treatment in the areas of recycling marine aquaria, electroplating wastes, electronic chip manufacture, textiles and petroleum refineries, are discussed. The rising acceptance of ozone as a replacement bleaching agent for paper pulp to eliminate the discharge of halogenated effluents form pulp bleaching also is traced. Newer applications for ozone in treating rubber additive wastewaters, landfill leachates, and detergents in municipal wastewaters are summarized briefly. The combination of ozone oxidation followed by biological treatment has been installed full-scale at a large German industrial chemical complex. Ozone coupled with ultraviolet radiation and/or hydrogen peroxide (advanced oxidation) is being utilized to destroy organic contaminants in groundwaters at munitions manufacturing plants and at Superfund sites (hazardous wastes). Ozone followed by activated carbon adsorption removes color and organics cost-effectively from North African phosphoric acid.

Recent papers on industrial wastewater treatment have covered the removal of chlorophenol (69, 70), the ozonation of phenolic compounds present in wastewater from food processing industries (71), and removal of 3-methyl pyridine (72). Qui et al. reported on ozonation kinetics of six dichlorophenol isomers (117). Ozone has been used for treatment of lye-wastewaters from the table olives industry (118). Ramseier and von Gunten (167) studied the mechanics of phenol ozonation and the resultant reaction products.
Wang et al. (127) reported on oxidation of landfill leachate with ozone and with ozone/peroxide. For the leachate studied, ozone alone was sufficient.

In a comprehensive survey article, Ikehata et al. summarized degradation of recalcitrant surfactants in wastewater using ozone and advance oxidation processes (130).

Ozone Generation and Contacting

Ozone generator manufacturers made many of the advancements in ozone generation and as a result much technology was kept proprietary in the early days of the IOA. However, an increasing number of significant papers concerning ozone generation and ozone generator design have been published in OS&E.

An early work by Louboutin (62) analyzed the appearance of spark phenomena in ozone generators and proposed modifications for its reduction.

In one of the first of many papers authored by scientists from Brown Boveri (Switzerland), Kogelschatz and Baessler (63) reviewed the formation of nitrous oxide and dinitrogen pentoxide from air-fed ozone generators. This article should be reviewed by anyone using air-fed generators and, in particular, those using oxygen generated from on-site air separation (PSA, VSA, VPSA) plants.

Eliasson and Kogelschatz (65) studied ozone formation in oxygen at atmospheric pressure following the photodissociation of oxygen molecules in the vacuum UV range. This process involved xenon excimer radiation from a dielectric barrier discharge. There have been many follow-up papers on this work by several authors.

New ozone generator concepts have been proposed in OS&E. One example is the development of a corona wire-to-cylinder ozone generator by R. Peyrous et al. (66).

The choice of feed gas for ozone generators has shifted from air to oxygen over the years and authors have made economic comparisons of the two feed gases. Horn et al. (67) outlined the criteria for the selection of the feed gas for ozone generation. This work was based on experience at the UK Purton Water Works (Bristol Water Plc).

Ozone Contacting/Solubility

Ozone contacting is a critical component of any operating ozone facility and OS&E has given this extensive coverage. M. Roustan and his associates published a number of papers on the design and modeling of conventional ozone bubble column reactors with one reference listed here (160). Jakubowski et al. analyzed ozone mass transfer in a plunging liquid jet contactor (161). Baawain et al. investigated the modeling of an impinging-jet ozone bubble column reactor (162, 168). Rakness outlined ozone side stream design options and operating conditions (163). A survey of static mixer efficiency and energy consumption was made by Munter (169).

Ozone Analysis
The analysis of ozone is critical to the determination of the efficiency and safety of ozone processes and OS&E has reported on the work in this field with several significant papers published.

In an early paper, Bader and Hoigné (84) proposed a standard method for the determination of ozone in water by the indigo trisulfonate method. Issues with use of the Indigo sensitivity coefficient method for residual ozone measurement were reviewed by Gordon and Bubnis (122).

Grunwell et al. (85) prepared a detailed comparison of analytical methods for residual ozone measurement. G. Gordon et al. (86) presented the chemical reactions of ozone and their role in developing improved analytical methods. Y. Richard (87) presented a classic work outlining an ozone water demand test.

The International Ozone association has been active in developing guidelines or codes of good practice for measuring ozone concentration. In November 1995 a meeting to discuss the formulation of a single guideline was held in Oxford, Ohio USA. At this meeting, members of the quality assurance committees of the Pan American Group (PAG), the European-African-Australasian Group (EA3G) and the Nippon Island Group (NIG) proposed revisions to guidance documents and published the new documents in OS&E (112).

A major event requiring ozone analysis is the measurement of the gas phase ozone composition from an ozone generator. This measurement is critical for determining the economical performance of the generator. The concentration can be measured by either wet chemistry methods or by a commercial UV gas phase ozone analyzer. Rakness et al. and the IOA Quality Assurance Committees prepared two excellent papers proposing guidelines for measurement of ozone concentration in the process gas (88,89).

W. J. Masschelein also compared the measurement of high ozone concentrations in gases by KI titration and UV-absorption (90).

Recently, Rakness et al. (170) reviewed and developed methods for operator-friendly use of the indigo colorimetric measurement of ozone residual.

**Specific Compound Removal**

Ozone research reported in OS&E has focused on the reduction/elimination of many specific compounds. A sampling of these is listed in Table 2. A complete list of the compounds investigated is available in the 30-year keyword index for OS&E. Note the reference on Anthrax (119) which references other work on use of ozone to remove this toxic material.

A very complete two-part survey of aqueous pesticide degradation was completed by Ikehata et al. (128, 129).

**Emerging Contaminants**

Emerging contaminants, i.e. pharmaceuticals, endocrine disrupting chemicals (EDCs), are becoming of increasing concern both in drinking water and wastewater supplies. Ozone has been identified by researchers as one technique which appears to inactivate these chemicals. Ikehata et al. (143) developed a comprehensive review article on the degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes. Extensive information on the degradation of EDCs by ozone was presented by Snyder et al. (144) and Ning, Graham, Gamal el Din et al (145). Yargeau and Leclair (147) reviewed the impact of operating conditions on decomposition of antibiotics during ozonation. Gagnon et al (148) studied the degradation of pharmaceutical products in primary-treated wastewater.
Rahman et al. prepared a major study on the effect of ozone advanced oxidation on removal of pharmaceuticals and EDCs from Lake Huron water, and the effect on turbidity, particles and organics removal (171,172).

**Table 2. Ozone Reduction of Specific Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthrax</td>
<td>119</td>
</tr>
<tr>
<td>Atrazine</td>
<td>91</td>
</tr>
<tr>
<td>Cinnamic Acid</td>
<td>92</td>
</tr>
<tr>
<td>Crotonic Acid</td>
<td>124</td>
</tr>
<tr>
<td>Cyanides</td>
<td>14, 93</td>
</tr>
<tr>
<td>Glycerol</td>
<td>94</td>
</tr>
<tr>
<td>Fatty Acids</td>
<td>95</td>
</tr>
<tr>
<td>Pesticides</td>
<td>96, 97, 128, 129</td>
</tr>
<tr>
<td>Emerging Contaminants</td>
<td>143, 144, 145, 146, 147, 148, 171,172</td>
</tr>
</tbody>
</table>

**Miscellaneous (and unusual) Applications of Ozone**

There are a number of ozone applications that, due to space limitations of this paper, have not yet been addressed. These range from the large number of papers presented on cooling tower control to odor control to the treatment of swine manure. A listing of a few applications is shown in Table 3. This list again is a sampling; many more applications are referenced in OS&E.

A very comprehensive analysis of materials of construction applicable to the design of ozone systems was presented by Sleeper and Henry (121).

An introduction to the use of ozone in the laundry industry and some operating data on commercial systems is presented by a series of papers by Rice et al. (176,177,178).

Ozone is used in a number of industrial applications as an oxidant of organic chemicals. Leitzke and von Sonntag have investigated the ozone oxidation of a number of unsaturated carboxylic acids in aqueous solution (179).

**Table 3. Miscellaneous Applications of Ozone**

<table>
<thead>
<tr>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Tower Water Treatment</td>
<td>98, 99, 100</td>
</tr>
<tr>
<td>Odor Control and Removal</td>
<td>101,102,103,104</td>
</tr>
<tr>
<td>Boiler Feed Water</td>
<td>105</td>
</tr>
<tr>
<td>Microelectronics Industry</td>
<td>120</td>
</tr>
<tr>
<td>Plating Wastes</td>
<td>14</td>
</tr>
<tr>
<td>Silver Recovery</td>
<td>12</td>
</tr>
<tr>
<td>Swimming Pools</td>
<td>107,108,109,110,111</td>
</tr>
<tr>
<td>Whirlpools</td>
<td>106</td>
</tr>
<tr>
<td>Photoprocessing Wastes</td>
<td>12</td>
</tr>
<tr>
<td>Swine Manure Treatment</td>
<td>104</td>
</tr>
<tr>
<td>Laundry</td>
<td>150, 176,177,178</td>
</tr>
</tbody>
</table>

**Agri-Food Applications**

In 2001, the U. S. FDA approved the petition to consider ozone as generally recognized as safe (GRAS) for the treatment and approved it as an antimicrobial agent. These since has been considerable research on the use of ozone for food processing and several commercial installations exist.
An introduction of the use of ozone for agri-food applications can be found in the survey paper by Rice (151). Fujiwara et al. (154) studied ozonated water as an alternate to soil disinfectants. Vijayanandraj et al. showed the effect of ozone on preventing Black Rot disease in onion (155).

Experience from a commercial field trial is presented by Steffen and Rice (156, 157). This process used ozone, UV, advanced oxidation and other techniques for a complete crop protection system.

A good summary of the contribution of ozone to food processing in Japan is presented by Naito and Takahara (152). Wei et al. (159) reported on the effect of ozone treatment on fresh strawberry and shredded lettuce food quality.

Sopher et al. outlined the applications of ozone in catfish processing (158). The use of ozone significantly reduced the microbial loads in a commercial plant.

Strickland et al. (173) reviewed the six year experience of ozone processing of fresh cut salad mixes. In additional to longer shelf-life, the factory experiences less frequent changes of flume water, lower maintenance costs, reduced wastewater disposal costs and reduced chlorine odor in the plant environment.

Ozone is finding increasing application in the wine industry and its use in a clean-in-place system (CFIP) is summarized by Guillen et al. (174)

Medical and Dental Applications

The use of ozone in medicine and dentistry has been and remains controversial, primarily due to federal restrictions on its use in the United States. A number of IOA members have medical background and have studied its use and OS&E has reported on their work. The interest in the use of ozone for medical applications appears to be increasing and IOA technical conferences occasionally include separate medical sessions.

An early review on the clinical applications of ozone therapy was prepared by Rilling (79). Viebahn et al. reported on the influence of ozone on tumor tissue (80). Bocci et al. prepared a comprehensive summary of the uses of ozone in medicine. (83). Menéndez et al. summarized the use of ozone in cancer therapy (153).

Ozonated olive oil is used in many parts of the world to treat various skin diseases. Kataoka et al. (175) studied the effects of this oil on mice with both positive and negative results.

Dr. A. Filippi has extensively studied and reported on the use of ozone in oral surgery (81) and the use of ozone to treat water in dentists’ offices (82).

Contributions from Regional Groups

Figure 1 shows the contribution by regional group to OS&E. By far the largest contribution throughout the history of OS&E has come from the EA3G region.

France has contributed approximately 120 papers to OS&E, about 11% of the total. The first contribution was in the first year of publication where Fauvel et al. (9) discussed seawater ozonation and shellfish depuration. The conclusions reached in this paper are still valid today.
Contributions from France were strong from 1978-2000, peaking in about 1995. Since year 2000, fewer papers have been received.

France produced a number of significant papers relating to drinking water disinfection, mass transfer and ozone analysis. Of particular note were the contributions by J-P Duguet (22,38,50,58), B. Legube (30,113,126), Y. Richard (45,74,87,88) and M. Roustan (22,50,160).

The first contribution from Japan occurred in Issue 2 of the first year of OS&E, “Improved Ozonation in Ozonation Systems by S. Nakayama, K. Esaki, K. Namba, Y. Taniguchi and N. Tabata of Mitsubishi Electric Corporation (7). This early paper described a method of catalytic ozonation using hydrogen peroxide as a catalyst. The process was demonstrated on wastewater from an electro-deposition process. This same paper showed how an oxygen recycling process could be incorporated into the ozonation process. Catalytic ozonation and recycling were advanced topics at this time attesting to the quality of the research being conducted in Japan.

Japan has contributed approximately 73 papers to OS&E, about 7% of the total (Figure 1).

![Regional Contributions to OS&E](image)

**Figure 1.** Regional Contributions to OS&E

Figure 2 shows the distribution of papers contributed from Japan to OS&E. The highest percentage of the papers focused on wastewater treatment, compared to EA3G and PAG where the highest concentration was on drinking water treatment.

In addition to the work by Nakayama mentioned above, there have been several significant contributions reporting on wastewater treatment with ozone. Takahashi et al. (131) have reported on the practical application of ozonation to dyeing wastewater along with many other specific studies (132). Tsuno et al. (133) outlined a new advanced treatment system, which consists of a biological nutrient removal process combined with reduction of excess sludge by ozonation. This process reduced endocrine disrupting chemicals (EDCs) to near undetectable levels.

Mizuno et al. (137) used pre-coagulation, ozonation and ozone/hydrogen peroxide for removal of organic pollutants from municipal sewage. The use of initial ozone allows a smaller dosage of hydrogen peroxide for the final stage of treatment.
Figure 2. Distribution of OS&E Papers from Japan

Unique to Japan is the reporting on the use of ozone to treat night soil. “Night Soil” is human solid waste from communities without a central sewage treatment plant which is removed, usually at night, and transported to a central treating location. A good introduction to night soil treatment is presented by Matsumoto and Watanabe (134). Ono et al. (135) investigated the use of ozonation to reduce the genotoxic potency of substances contained in night soil. Kishimoto et al. (136) investigated ozonation combined with electrolysis followed by biological nitrification-denitrification.

A number of novel approaches to ozone generation have been developed in Japan. An approach to ozone storage and concentration was outlined by A. Murai et al (138). These same researchers (139) also proposed ozone clusters (O₆ and O₉).

Bromate research is also being conducted in Japan with the latest publication by Mizuno et al (164) proposing a simple model to predict formation of bromate ion during ozonation of drinking water.

Harvey M. Rosen Memorial Award

In 1989 the IOA and OS&E Editors decided that an award was appropriate to recognize accomplishments in OS&E. The Harvey M. Rosen Memorial Award was established to recognize the “best paper” published in OS&E during the two-year period between World Congresses. Dr. Harvey M. Rosen was a prime mover behind the establishment of the International Ozone Association and of OS&E, the Journal of the Association. It was Harvey Rosen who recognized early in the 1970s the need for the establishment of an ozone association, and then pressured for the creation (in 1979) of a peer-reviewed technical journal dealing with all aspects of ozone technologies. Recipients of the Rosen Award are determined by consensus polling of the members of the Editorial Board of OS&E every two years.

Recipients of the Rosen Award to date are:

This work first introduced the term “Advanced Oxidation” and reviewed the theoretical and practical yield of OH· from O₃ at high pH and O₃/H₂O₂, O₃/UV and H₂O₂/UV systems. The paper summarized the chemistry of several water treatment processes involving combinations of ozone, hydrogen peroxide and ultraviolet radiation. The purpose was to show that these processes have much in common mechanistically, but there are enough significant differences to make one or the other more practical depending on water quality and water treatment goals.


This study investigated the ozonation of an aquatic fulvic acid extracted from a forest pond near Poitiers, France. By ozonation of a bromide-containing solution of fulvic acid, some brominated organics were formed. Increased GAC filtration efficiency following ozonation was found to be the result of a biodegradability enhancement of fulvic acid by ozone.

1993  In 1993 there were two winning papers
a. Susan J. Masten (USA) and Jürg Hoigné (Switzerland) “Comparison of Ozone and Hydroxyl Radical-Induced Oxidation of Chlorinated Hydrocarbons in Water”, OS&E, 14: 197-214 (1992)

This study investigated the efficiency of ozonation and advanced oxidation processes for chlorinated hydrocarbons using a closed batch-type system. The paper very effectively demonstrated the different results than can be obtained depending on whether ozonation or advanced oxidation with O₃/H₂O₂ or O₃/UV was practiced. The work was directed towards contaminated waters and leachates from landfills.


This paper reviewed current work on ozone treatment of cooling towers and quoted work with supporting data. The paper proposed a scientific basis for evaluating cooling tower performance during ozone treatment. It also expanded on a German approach in which bromide ion is added to recirculating cooling tower water. Ozone quickly produces hypobromous acid, which is a much more stable biocide than is molecular ozone.


This work isolated Natural Organic Matter (NOM) from surface water and subjected it to ozonation. Fulvic acids and humic acids were the most reactive. Although hydrophilic base neutrals were of low to moderate reactivity, they showed the greatest promise for improved coagulation following preozonation.

A finite element analysis computer program was used to model the hydraulic characteristics and to predict the corresponding residence time distribution curves for four full-scale ozone contactors with hydraulic capacities ranging from 14.5 to 394 m³/min (5.5 to 150 mgd). Model predictions were within 7.9% of test values. This program was used by the Metropolitan Water District of Southern California to optimize the hydraulics of their future ozone contactors.


A two-step disinfection approach was evaluated for control of Cryptosporidium parvum using bench-scale experiments in 0.05 M phosphate buffer at pH 8 and 22°C. The sequential treatment of oocysts by ozone followed by chlorine dioxide resulted in additional inactivation of C. parvum due to the synergism of the two disinfectants. The preliminary findings indicated that sequential disinfection with ozone followed by chlorine dioxide may have potential in controlling waterborne parasites. This was the first of a series of papers addressing the inactivation of Cryptosporidium.


The ozonation of model systems and several natural waters was examined in bench-scale batch experiments. In addition to measuring the concentration of ozone, 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. A new parameter Rct representing the ratio of the ·OH exposure to the O₃-exposure was calculated as a function of reaction time. For most waters tested, Rct was a constant for the majority of the reaction. For a given water source, the degradation of a micropollutant (e.g., Atrazine) via O₃ and ·OH reaction pathways can be predicted by the O₃ reaction kinetics and Rct.


This major work which is highly referenced, evaluated several kinetic models for the ozone inactivation of Cryptosporidium. The work pointed out the difficulty in using a single model for the inactivation. It also pointed out the potentially large impact of water temperature on inactivation kinetics and the CT requirements.

2005 Stephen A. Craik, Daniel W. Smith, Miodrag Belosevic (Canada) and Mysore S. Chandrakanth (USA) “Efficient Inactivation of Cryptosporidium Parvum in a Static Mixer Ozone Contactor”. OS&E 25: 295-306

This work showed that efficient and predictable inactivation of C. parvum in drinking water may be achieved by employing a static mixer, and followed by a liquid phase contactor.

2007 Marc-Olivier Buffle (Switzerland), Jochen Schumacher (Germany), Sébastien Meylan (Switzerland), Martin Jekel (Germany)and Urs von Gunten (Switzerland) “Ozonation and Advanced Oxidation of Wastewater: Effect of O₃ Dose, pH, DOM and HO’-scavengers on Ozone Decomposition and HO’ Generation”, OS&E 28:247-260(2006)
This paper investigates the effect of ozone dose, pre-ozonation, pH and DOM on the kinetics of ozone decomposition and HO formation in wastewater, starting 350 milliseconds after ozone addition.


In this study, an ozone self-decomposition model that is meaningful for environmental engineering design under practically encountered pH conditions in the time scale of water treatment is proposed.

The Future of Ozone: Science & Engineering

OS&E has followed the advances in ozone science since its inception and modified its focus as the needs of the industry have evolved. Exciting changes in the industry are occurring, for example, the acceptance of ozone in food processing. Papers on this topic are being presented at technical conferences and are now appearing in OS&E. A recent example was a survey on ozonated water to improve the shelf-life of citrus fruit (123). The use of ozone in aquaculture may similarly expand as outlined in (157).

The use of ozone in laundry applications is seeing a resurgence in interest and steps are being undertaken to apply science to this field instead of anecdotal reporting. A good background in laundry applications was prepared by Cardis et al. (150).

Also, OS&E is seeing an increased interest in publishing peer-reviewed papers on medical applications of ozone, as were in the early issues of the journal. These papers would complement the recent general survey articles and the articles on practical application of ozone to water in dentist offices. The IOA Board must determine the applicability and desirability of these papers in OS&E.

The most significant change in emphasis for OS&E may very well be renewed interest in the use of ozone to treat municipal wastewater. The issue of emerging contaminants and micropollutants has reached a critical level and researchers are starting to conclude that they must be controlled before reaching receiving streams. There are many chemicals for ozone to attack, but byproducts are formed – these must also be investigated. OS&E is ready to report good peer-reviewed research on these topics.

Finally, we have expanded our editorial reach to permit papers on alternate oxidation technologies such as UV in the Journal. We have started to publish a few and expect increasing numbers as we have added several members to the Editorial Board with UV experience.

With our new Publisher, Taylor & Francis, OS&E is now available on the Taylor & Francis website and is available to IOA members. This should greatly increase the exposure of OS&E to non-IOA members and can only benefit the association.

Summary

This paper attempted to show the broad nature of topics covered in OS&E, along with the high quality of the papers presented. It is impossible to give sufficient coverage to any topic due to the vast amount of information available in OS&E. The IOA has made OS&E available on a two-CD ROM set including all issues of Volumes 1-25 along with searchable author and keyword indices. The CD ROM set is available for sale to IOA members and others. If is not anticipated that this CD will be expanded to additional years. IOA members now have access to all 33 volumes and all articles on the Taylor & Francis website by entering their user number and password. It is possible to perform key word searches directly on the website and be directed to the issues and then articles of interest.
References


