Information

Oxidation methods in the technology for water and air cleaning (based on the materials of the First international Conference on Advanced Oxidation Technologies for Water and Air Remediation)*

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The term "Advanced Oxidation Technologies," which is generally accepted at present, embraces a rather wide range of technical expedients used predominantly for the removal of impurities whose concentrations are on the order of parts per million or parts per billion from water and air.

The purification of water and air from impurities of pesticides, organochlorine or nitroaromatic compounds and other substances dangerous to human health and to the environment is a rather important and urgent problem. In some cases, the concentrations of these compounds are so low that the adsorption methods widely used in recent years are no longer profitable. The ecological services and the chemical industry expect scientists to find new approaches to the solution of the above-mentioned problem. One of the most promising routes is based on oxidation of this sort of impurity by atmospheric oxygen or using oxidizing agents such as ozone and hydrogen peroxide.

The low concentrations and very low oxidizabilities of hazardous impurities result in that oxidation with oxygen is only efficient when the purification processes are carried out under extreme conditions, *i.e.*, at supercritical pressures and elevated temperatures, under conditions of cavitation, involving the use of ultrasound, or irradiation with light and the use of plasma or γ-radiolysis. Under these conditions, a great number of oxyl radicals are generated, and they efficiently carry out chain free radical oxidation.

Another method for generating oxyl radicals is based on reactions with strong oxidizing agents, hydrogen peroxide and ozone. The Fenton reaction has been used for this purpose for about 100 years:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

To this reaction, the dark reactions (2) and (3) and the photolytic reactions of ozone (4, 4a) and hydrogen peroxide (5) should be added.

$$2O_3 + H_2O \xrightarrow{i} \dot{O}H + O_2 + HO_2 \qquad (2)$$

$$O_3 + H_2O_2 \longrightarrow \dot{O}H + O_2 + HO_2 \qquad (3)$$

$$O_3 + h\nu \longrightarrow O_2 + O(^1D) \qquad (4)$$

$$O(^1D) + H_2O \longrightarrow (2\dot{O}H) \longrightarrow H_2O_2 \qquad (4a)$$

$$H_2O_2 + h\nu \longrightarrow 2\dot{O}H \qquad (5)$$

i. OH^-

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In spite of the substantial expenses of both the production of these oxidizing agents and their photolysis, their use is considered to be quite economically efficient, especially for the treatment of waste water with high background UV absorption. However, the capital investment, the problem of the destruction of unreacted ozone, and the problem of the protection of the personnel can make the use of ozone less attractive.

Virtually all of the approaches used in this field were presented at the First International Conference, organized by Dr. H. Al-Ekabi in Canada:*

1) H_2O_2/O_3 systems including those activated by UV radiation;

2) nonthermal plasma sources;

3) electrohydraulic cavitation and ultrasonic activation;

4) photocatalytic processes involving TiO_2;

5) electron beam- and γ-irradiation;

6) catalytic oxidation;

7) oxidation in supercritical water.

The Conference was attended by more than 350 specialists from Austria, Belgium, Canada, China, Germany, Denmark, Finland, France, Holland, Hong Kong, Iraq, Italy, Japan, Poland, Russia, South Korea, Spain, Switzerland, Taiwan, and the USA. During the Conference, an exhibition took place in which several companies demonstrated products related to the topic of the Conference.

About 200 invited and announced reports and posters were delivered and discussed at the Conference. In addition, three discussions of government ecological programs for the extension of oxidation technologies took place.

Oxidation by hydrogen peroxide and ozone, including processes involving UV initiation

A review of the methods for the catalytic oxidation of volatile organic compounds from stationary sources, including thermal processes, photocatalysis, and UV activation of ozone, were considered in the report by *J. J. Spivey* (USA). Such features as their acceptable activity at relatively low temperatures, the applicability of these methods to a wide range of compounds, the possibility of using poison-tolerant catalysts, and the multifunctional properties of the catalysts, which in some cases not only accelerate oxidation processes, but also hydrolytically decompose impurities, were noted as advantages of catalytic oxidation. Chlorinated hydrocarbons are among the impurities that are most difficult to remove.

In this work, a series of catalysts were tested. Some of these were run for 350 days on a simulated mixture containing 500 ppm of C_1—C_2 chlorohydrocarbons.

Catalytic oxidation is used for purifying breathing air in military vehicles. In these systems, the catalyst, in addition to accelerating oxidation, must also accelerate the hydrolysis of some of the impurities before they arrive at the trapping systems. Purification of air from cyanogen chloride can serve as an example. One typical industrial problem consists of decreasing the initial impurity level, which is a few hundreds parts per million, by a factor of 10 to 15, with a corresponding reduction in the size and cost of the catalytic oxidation unit. This problem can be partly solved by using reactors that operate under non-steady-state conditions and allow one to lower the energy expenses due to the maximum heat recovery.

The report by *J. Hoigné* (Switzerland) dealt with the role of hydroxyl radicals generated from various precursors in the processes of purifying various natural waters and drinking water. From the variety of possible processes, *viz.*, photolyses of solutions of hydrogen peroxide, aqueous solutions of chlorine, nitrates, nitrites, or $Fe(OH)^{2+}$, treatment of water with ionizing radiation or by Fenton reagent, the author has chosen the reactions of ozone with hydroxyl radicals or HO_2^- in water. The lifetime of radicals has always been controlled by the presence of an excess of a radical scavenger. In the framework of this study, the absolute rates of the reactions of hydroxyl radicals with various substrates, including natural organic compounds dissolved in water, were determined. The results obtained allow one to predict the lifetimes of radicals in aqueous solutions with known compositions of dissolved compounds. The greatest deviations from the calculated values have been observed for highly alkaline solutions. All of the pathways for the transformation of ozone into OH radicals known to the author yield approximately the same number of OH radicals per degraded ozone molecule.

The report by *S. J. Buelow* (USA) was devoted to the thermal treatment of hazardous wastes in aqueous solutions. It was shown that hydrothermal processes may result in efficient destruction and removal of such compounds as chlorinated aromatics, nitrates, and ammonia to give water, carbon dioxide, inorganic salts, and traces of carbon oxide and nitrogen oxides as the reaction products.

Hydrothermal processes carried out up to the critical temperature and pressure of water are called Wet Air Oxidation, and those accomplished above the critical point are termed Supercritical Water Oxidation. In these processes, the waste water is pressurized and heated together with an oxidizing or reducing agent. Then the mixture is depressurized, and the gaseous, liquid, and solid components are separated. When the temperature and the pressure are high enough (above 750 K, 25 to 100 MPa), decomposition of a hazardous contaminant yields only carbon dioxide, water, and nitrogen dioxide.

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* This review deals with the information concerning Sessions 1, 3, 6, 7, and, partly, 4. The reports presented at Sessions 2, 4, and 5 are considered in the review by A. K. Pikaev in the journal "Chemistry of High Energies".

The thermal effect of the oxidation is used for heating the reaction mixture. Experiments on the treatment of aqueous radioactive solutions of organic nitrates and nitrites and ferrocyanide at 600—825 K and 25—100 MPa carried out at the Los Alamos National Laboratory showed that the degrees of conversion of undesirable impurities, such as nitrates and nitrites, in reactions with reducing agents, such as ammonia, methanol, urea, or saccharose, at 760 K can be as high as 99 % in seconds to minutes.

The report by *D. F. Ollis* (USA) was concerned with the possibility of using two-step processes comprised of chemical and biological oxidation, in order to decrease the total reactor volume and minimize the consumption of energy and materials.

Oxidation processes as applied to the disinfection of water and the mechanisms of the action of various disinfectants and oxidizing agents in the course of water treatment were discussed in the report by *W. L. Cairns* (Canada).

New reactions of the formation of ozone from hydrogen peroxide

$$3H_2O_2 \rightarrow O_3 + 3H_2O \qquad (6)$$

and a new route for co-oxidation of perfluoroolefins and trifluoroacetic acid

$$\begin{aligned} &R_F{}^1{-}CF{=}CF{-}R_F{}^2 + CF_3COOH + O_3 \rightarrow \\ &\rightarrow R_F{}^1CFO + R_F{}^2CFO + CF_3COOOH \qquad (7) \end{aligned}$$

were discussed in the work of *N. I. Moiseeva*, *A. E. Gekhman*, and *I. I. Moiseev* (Russia).

The rates of the reactions of hydroxyl radicals in the ground state (the Fenton reagent) and in the excited state (photolysis of hydrogen peroxide and the photoassisted Fenton reagent) with benzene derivatives containing both electron-releasing and electron-withdrawing substituents were studied in the work of *E. Lipczynska-Kochany* (Canada). It was found that the electronic structure of the substrate exerts an effect on the reaction rates observed. Moreover, the reactivity of photoexcited *N*,*N*-dimethylaniline with respect to oxidizing agents differs substantially from that observed in the dark reaction.

The potential of the photoassisted Fenton reaction to generate hydroxyl radicals and oxidize chlorohydrocarbons was discussed in the report by *J. Pignatello* (USA). In this system, where catalytic amounts of Fe^{2+} or Fe^{3+} are used, photodecomposition of Fe^{3+} aqua complexes

$$[Fe(H_2O)_6]^{3+} \xrightarrow{h\nu} Fe^{2+} + H^+ + \dot{O}H \qquad (8)$$

and photodecomposition of iron alkane carboxylates

$$RCOOFe^{2+} \xrightarrow{h\nu} CO_2 + \dot{R} + Fe^{2+} \qquad (9)$$

may occur, along with other reactions.

Irradiation with light in the near UV region (300—400 nm) proved to be the most advantageous; monochromatic light at 254 nm actually retards the dark Fenton reaction. The near-UV radiation is less expensive, since it is available from sunlight. Using the $Fe^{3+}/H_2O_2/h\nu$ system, the author managed to completely mineralize a number of compounds including pesticides, chlorinated aliphatic and aromatic hydrocarbons, and phenols. The author believes that this system has a number of advantages over ozone, since hydrogen peroxide is cheaper, less toxic, more stable, more soluble, and more convenient to handle. A drawback of the $Fe^{3+}/H_2O_2/h\nu$ system studied is that it requires a rather narrow pH range (2.5—3). Higher acid concentrations are favorable for scavenging hydroxyl radicals with chloride ions. In addition, some anions may alter the reactivity of iron ions by forming complexes with them.

M. Dore and *N. K. Vel Leitner* (France) investigated the role of initiators, promotors, and inhibitors in the reactions of ozone or ozone and hydrogen peroxide using aliphatic acids as an example. The authors noted that the second-order rate constant for the reaction of ozone with a hydroxyl radical, $k_{O_3/OH} = 70\pm7$ mol^{-1} L s^{-1}, is substantially lower than the corresponding rate constant for the reaction of $HO_2{}^-$ with ozone, $k_{O_3/HO_2^-} = 2.8\pm0.5 \cdot 10^6$ mol^{-1} L s^{-1}. Hence, even low concentrations of $HO^{\bullet}{}_2$ radicals are capable to initiate the decomposition of ozone in water.

It is assumed that the overall reaction leading to the $^{\bullet}OH$ radicals in the O_3/H_2O_2 system involves the consumption of two ozone molecules per molecule of hydrogen peroxide:

$$2O_3 + H_2O_2 \longrightarrow 2\dot{O}H + 3O_2 \qquad (10)$$

Bicarbonate ion, which is known to be hydroxyl-radical scavenger, decrease the efficiency of this system. Fulvic acids act in a similar way.

Oxidation of organic acids yields formic, glycolic, glyoxalic, and other acids that are capable to participate in the conversion of $^{\bullet}OH$ radicals into $HO_2{}^{\bullet}$ superoxide radicals in the presence of dissolved oxygen. Under these conditions, the $^{\bullet}OH$ radicals formed in the reaction with ozone or in the photolytic experiment abstract hydrogen atoms from the substrate and the resulting substrate radicals quickly add oxygen to give peroxyl radicals, which produce $HO_2{}^{\bullet}$ radicals. Recombination of the latter affords hydrogen peroxide.

S. H. R. Davies and co-workers (USA) compared the use of various oxidizing agents, *viz.*, O_3, O_3/H_2O_2, and O_3/UV irradiation for the oxidation of chlorinated benzenes in aqueous systems. Oxidation with the O_3/H_2O_2 system proved to be the most efficient at initial concentrations of hydrogen peroxide and ozone of 10 μmol L^{-1} and 44.5 μmol L^{-1}, respectively. Under these conditions, about 98 % of the tetrachlorobenzene was converted into carbon dioxide and Cl^- ions in a period of 10 min.

For the oxidation of *ortho*-dichlorobenzene and tetrachlorobenzene with ozone or the O_3/H_2O_2 system, a pH of 7—8.5 was found to be the optimal, and in the case of the O_3/UV system, the rates of the disappearance of chlorobenzenes almost do not depend on pH in the pH range 2 to 9. At elevated pH values, the rates of advanced oxidation processes substantially decrease, probably due not only to the scavenging of the $^{\bullet}OH$ radicals by HCO_3^- ions, but also to the reaction of hydroxyl radicals with HO^-_2 ions. Humic acids, which can not only scavenge hydroxyl radicals, but also promote decomposition of ozone, inhibit cleavage of chlorobenzenes in a similar way. Despite the fact that iron ions are able to initiate ozone decomposition, the addition of up to 2 mg L^{-1} of Fe^{2+} did not affect the oxidation of dichlorobenzenes.

The authors concluded that the O_3/H_2O_2 system is the most efficient for removing dichloro- and tetrachlorobenzenes. The steady-state concentration of hydroxyl ions is optimal at pH = 8 for all of the systems studied. It increases on going from O_3 to the O_3/H_2O_2 and O_3/UV systems, and is maximum for the O_3/H_2O_2/UV system. The authors believe that the latter system is more economically efficient and easier to adapt to current water-treatment designs than the other advanced oxidation processes.

The O_3/UV system may be more efficient in removing organic compounds that undergo photolysis when irradiated with UV light. At high pH or in the presence of readily oxidizable organic matter, treatment by ozone may be used, along with the treatment by O_3/H_2O_2 and O_3/UV irradiation systems.

The scavenging of hydroxyl radicals by carbonate or bicarbonate ions, which greatly reduces the efficiency of the systems studied, decreases the possible pH range.

Oxidation of humic acids using H_2O_2/UV and O_3/UV systems has been studied in the work of *M. D. Gurol* (USA). It has been found that the absorption of light by humic acids decreases the rate of the photolysis of hydrogen peroxide; on the other hand, the reaction of humic acids with ozone is a powerful source of H_2O_2.

The report by *Ali S. Amiri*, *J. R. Bolton*, and *S. R. Cater* (Canada) dealt with the role of iron in photoassisted reactions of hydrogen peroxide. The authors have found that the reaction

$$Fe(OH)^{2+} + h\nu \rightarrow Fe(II) + {}^{\bullet}OH \qquad (11)$$

is the prime source of OH radicals in rain water in the daytime. When pH is sufficiently high, the Fe^{2+} ion formed in the photolysis of $Fe(OH)^{2+}$ can react with molecular oxygen to give hydrogen peroxide according to the following scheme:

$$Fe(II) + O_2 \rightarrow Fe(III) + O^{\bullet}{}_2^- \qquad (12)$$

$$O^{\bullet}{}_2^- + H^+ \rightarrow HO^{\bullet}{}_2 \qquad (13)$$

$$HO^{\bullet}{}_2 + Fe(II) + H^+ \rightleftharpoons H_2O_2 + Fe(III) \qquad (14)$$

The resulting hydrogen peroxide again acts as a source of $^{\bullet}OH$ radicals, since it undergoes the Fenton reaction.

The use of these reactions for deactivation of waste water is limited to the cases with low background UV absorption and low concentrations of pollutants. The $Fe(OH)^{2+}$ ion absorbs weakly in the near UV and visible regions and does not absorb beyond 400 nm. The authors pay attention to the photodecomposition of iron(III) carboxylates (12) and discuss, in particular, the photolysis of Fe^{III} oxalates:

$$FeC_2O_4^+ \xrightarrow{h\nu} C_2\dot{O}_4^- + Fe^{2+}, \qquad (15)$$

which involves absorption of light in the 500 nm region. The radicals rising in this reaction and in other reactions of this sort may oxidize Fe^{II}, react with molecular oxygen thus generating OH radicals, or react with organic molecules. It is believed that these processes are responsible for the solar degradation of carboxylates and polycarboxylates in nature. Iron oxalates can be used for practical purposes, since they absorb UV radiation in the region between 250 and 500 nm with high quantum yields that do not depend on the wavelength in this region.

The use of oxidation and microbial mineralization for the purification of pesticide- and herbicide-contaminated waste water was discussed in the report by *C. J. Hapeman* and co-workers (USA). The results obtained by the authors in the laboratory and in field studies imply that the preliminary treatment with ozone of water contaminated with pesticides increases their microbial mineralization, *i.e.*, their breakdown to give CO_2, H_2O, NH_3 or NO_3^-, and inorganic salts. A preliminary evaluation demonstrated the potential usefulness of this approach. Using the most widely applied *s*-triazine derivative, atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), as an example, it has been shown that during ozonation, *N*-alkyl groups are converted to a certain extent into *N*-acetyl groups or even removed, depending on the duration of the process. No dechlorination or ring opening processes were observed. The final product of the ozonation of atrazine was 2-chloro-4,6-diamino-*s*-triazine. The mineralization of this compound through the action of pseudomonades (strain A), which utilize *s*-triazines as the only source of nitrogen, was the most efficient. These bacteria were more efficient than the indigenous soil microflora, though, unfortunately, their action was completely inhibited by farm-generated wastes. Pesticide run-off typically contains surfactants, emulsifiers, lubricants, *etc.* at concentrations of ~200 ppm, along with the main substances. Experiments have shown that ammonia, present at a concentration of ~1 %, is responsible for this inhibition. One more strain of bacteria, *Klebesiella terragena* (strain

DRS-1), was isolated. This also uses triazines as a source of nitrogen and is effective even in the presence of 800 m*M* of ammonia. The growth of DRS-1 cultures and the degradation of *s*-triazine were demonstrated in laboratory experiments. The efficiency of treatment of *s*-triazine by ozonation in a pilot-scale installation with a recirculation-type reactor was shown to be equal to 45 %. The degradation of the ozonation products was carried out in a flow-through reactor with stirring or using celite in a reactor with a fixed contact surface.

E. M. Froelich (USA) noted in his report that the technological improvements made since the first industrial units were installed, including more efficient UV lamps and reactors and the combination of various systems of chemical additives and catalysts, have resulted in a 10-fold decrease in the operating costs of the UV/peroxide treatment of wastes containing chlorinated solvents and most toxic volatile organic compounds. Similar or better results have been achieved with wastes containing fuel, phenolic, or other components. These improvements have given a significant cost advantage of the UV/peroxide treatment over traditional approaches such as absorption with activated carbon or air stripping of ground water.

It has been noted that UV-assisted oxidation is expanding to other fields of application due to perfection of the equipment, the increased flexibility of the technology, its high reliability, and its programmable control, which optimize the process. Specifically, this approach is rather promising for detoxification of radioactive water contaminated with toxic organic compounds, highly corrosive water streams, and highly colored and concentrated industrial wastes.

R. D. S. Stevens (Canada) noted that since the introduction of the first commercial units using UV/H_2O_2, UV/O_3, and O_3/H_2O_2 systems (the late 1970's), the number of these units has increased and now exceeds 150. The author have compared the operating costs for some typical units.

The report by *W. S. Himebaugh* (USA) dealt with the possibility of using UV-assisted oxidation involving ozone and hydrogen peroxide for the treatment of ground water and municipal water systems, for the oxidation of volatile organic compounds both on a laboratory scale and in field tests.

The results of oxidizing model and industrial wastes containing phenols, chlorophenols, dyes, solvents, emulsions, oils, chlorinated aromatic compounds, insecticides, *etc.* with hydrogen peroxide in the presence of homogeneous catalysts (Fe and other transition metals) at 80—130 °C and 1—5 atm were presented in the report by *P. Striolo* (France). When the residence time was less than 1 h, the consumption of hydrogen peroxide was no more than 125—150 % of the stoichiometric amount calculated for total oxidation to CO_2 and water. The technology developed was tested on nature objects near Madrid and Barcelona.

The work of *R. T. Meijers* (the Netherlands) was devoted to the study of the effect of ozone on the treatment of drinking water with hydrogen peroxide. In the Netherlands, the conventional process that combines coagulation and chlorination is no longer acceptable in view of the quality of the drinking water. Therefore, many companies dealing with water supplied from surface sources have their own programs for developing processes aimed at the removal of a wide spectrum of pollutants (colloids, inorganics, microorganisms, and organic micro-pollutants such as pesticides). Within the framework of this new program, ozonation should be the major defense against microorganisms and pesticides. The combination of ozone and hydrogen peroxide is used for degradation of more resistant pesticides and polar pesticides, which cannot be analytically determined at very low concentrations. The laboratory experiments have shown that most of the pesticides normally found in surface water in the Netherlands can be removed by ozonation with an ozone dosage below 2 mg L^{-1}. Of 48 pesticides tested, 30 were 80 % degraded under the experimental conditions (pH 7.5—8; 5—20 °C). More resistant pesticides (atrazine, propazine, simazine, phosphamidon, *etc.*) were degraded more efficiently by the combined action of ozone and hydrogen peroxide.

The ozonation of bromide-containing drinking water may yield bromate ions. Assays of this waters in animals have shown that the bromate ion is a genotoxic carcinogen.

In the Netherlands, drinking water sources normally contain 100 to 400 μg L^{-1} bromide ions. As a rule, the content of bromates does not exceed the detection limit, which is equal to 2 μg L^{-1}. Sometimes, the concentration of bromate was as high as 8 μg L^{-1}. The formation of bromates can be decreased to the level of <2 μg L^{-1} by increasing the H_2O_2/O_3 ratio to more than 2 g/g. No significant formation of bromine-containing organic compounds (brominated trihalomethanes, dibromoacetonitrile, dibromoacetic acid) was observed under the conditions of ozonation of drinking water or its treatment with the H_2O_2/O_3 system. The efficient disinfection and degradation of pesticides without the formation of substantial amounts of bromates can be achieved by the dosage of ozone and hydrogen peroxide.

J. P. Schulz (Germany) reported the results of a study of the effects of various UV sources on the destruction of organic compounds during their oxidation by ozone and hydrogen peroxide. The author studied low-pressure lamps with maxima at 185 nm and 254 nm for the reactions with ozone and hydrogen peroxide. Under these conditions, some OH radicals resulted from the direct photolysis of water. Medium-pressure mercury lamps were used to initiate the reaction in the range between 200 nm and 280 nm. Apart from these lamps, xenon lamps, which have some potential in the pulsed mode, and fluorescent lamps having maxima at 172 nm and 222 nm, were used.

The use of Fe salts for the photocatalytic treatment of industrial waste water oxidized by ozone or hydrogen peroxide was discussed in the report by *G. Ruppert* and *R. Bauer* (Austria). It has been noted that UV assisted oxidation by ozone and hydrogen peroxide is an admissible alternative for detoxification of waste water containing chlorinated phenols and other compounds. The authors compare the results obtained in oxidation by oxygen, ozone, and hydrogen peroxide in the presence of Fe compounds under irradiation with halogen lamps, high-pressure mercury lamps, and sunlight (clear and cloudy days). The complete mineralization of 4-chlorophenol in the Fe/H_2O_2 system irradiated with artificial UV-light (I_{365nm} = 30.1 mWt cm^{-2}) and sunlight (I_{365nm} = 1.8 mWt cm^{-2}) was reached within 60 min.

In the report by *J. W. Bijsterbosch* and *G. H. Harmsen* (the Netherlands), the main items of the government program of the Netherlands for the cleaning of industrial wastes were outlined. In this program, emphasis is given to wet air oxidation, oxidation with ozone and hydrogen peroxide in the presence of catalysts or under UV irradiation, and photocatalytic oxidation. There is a wet air oxidation plant that operates with a productivity of 20 m^3 h^{-1}.

Oxidation with ozone in combination with biological treatment is being used by two tanker cleaning companies. On a smaller scale, oxidation through the action of hydrogen peroxide and ozone is used for disinfection of water. Research aimed at lowering the costs of these methods, which would allow a wider use of advanced oxidation technologies for the remediation of industrial waste water in the Netherlands, is planned for 1994—1998. The program is focused on oxidation with ozone and hydrogen peroxide, since air oxidation has been better studied.

A report by the same authors in collaboration with *G. de Vries* and *J. Botterweg* was devoted to the catalytic oxidation with ozone and detoxification of tanker-cleaning effluents. It was noted that, despite the government support and the use of biological end-of-pipe treatment, the operating plants do not fulfill their task. In the Netherlands there is particular concern associated with the possible damage to the environment caused by discharges of waste water to the surface water. In order to determine the toxicity of tanker-cleaning waste water, research on the acute and chronic toxicity of effluent coming from biological treatment and effluent coming from oxidation with ozone is being carried out. It has been found that the effluents after biological treatment are always toxic. *Daphnia magna* proved to be a suitable microorganism for determining the toxicity of waste water. Treatment with ozone does not increase the toxicity, and in some cases, the toxicity even decreases. By treatment with ozone, the contents of oxidizable compounds can be reduced to the required levels.

The remediation of ground water contaminated with trichloroethylene and perchloroethylene by treatment with O_3/H_2O_2 and UV/H_2O_2 has been investigated in the work of *A. Hirvonen* and coworkers (Finland). The above-mentioned chloroalkenes could be removed with an efficiency of 92—98 % at a contact time of 5 min both in laboratory experiments and at a pilot plant. In the case of photoinduced oxidation, two intermediate compounds, mono- and dichloroacetic acids, were formed. This work was accomplished for the town Oitti in southern Finland with a population of 8,000, where water sources were contaminated by trichloroethylene and perchloroethylene due to the discharge from a dry cleaning laundry. The maximum concentrations of the contaminants were 4000—5000 μg L^{-1}; drinking water contained up to 200 μg L^{-1} of chloroalkenes. At these initial concentrations, more than 96 % of the trichloroethylene and 92 % of the perchloroethylene were removed by treatment with 0.7 % (w/w) of an O_3/H_2O_2 mixture with 5 min contact time. Only a part of these compounds is removed through oxidation; 15—20 % of them are lost by volatilization. Treatment with UV/H_2O_2 at an H_2O_2 concentration of 4 mmol L^{-1} resulted in the removal of 98 % of the trichloroethylene and 93 % of the perchloroethylene, when the initial concentrations of these contaminants were 180 and 200 μg L^{-1}, respectively, and the contact time was 5 min. Without H_2O_2, the efficiency of the removal of the contaminants was only 20—30 %.

Degradation of the organic materials formed by radiolysis of a mixture of tributyl phosphate and kerosene was discussed in the report by *P. H. Jordan* and *G. V. Hutson* (UK). The authors showed that oxidation of these materials with hydrogen peroxide in the presence of a Cr-containing catalyst (an analog of the Fenton system) is an economically acceptable approach.

The photochemical destruction of organic compounds as applied to the purification of air streams has been studied in the work of *J. A. Buckley et al.* (Canada). The authors used a transportable flow-through reactor with a capacity of 100 to 600 scfm produced by the Solair company. The reactor was equipped with a high-power-density lamp (5 kW) with the emission below 240 nm. Oxidation of toluene involves the following reactions, which occur under the conditions of the photolysis of ozone.

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (16)$$

$$O(^1D) + H_2O \rightarrow 2\ {}^\bullet OH \qquad (17)$$

$$O(^1D) + O_2/N_2 \rightarrow O(^3P) + O_2/N_2 \qquad (18)$$

$${}^\bullet OH + C_6H_5CH_3 \rightarrow \text{products} \qquad (19)$$

Under atmospheric conditions, ~90 % of the oxygen atoms formed in reaction (16) are deactivated through reaction (18), however, the authors found that when water vapor is added, the effectiveness of the system increases at least twofold. The EE/Og factor (Electrical Energy per Order for gas-phase systems) for toluene amounted to 0.5 when the toluene concentration was lower than 20 ppm and increased as the toluene concentration increased, which reflects the transition from first-order kinetics to zero-order kinetics.

In the case of trichloroethylene, no ozone was required, since this chloroalkene is efficiently photolyzed. The EE/Og value was 0.05; 33 % of the chlorine present was found as chloride, 8 % appeared as chlorine, and 40 % was in the form of dichloroacetic acid. All of these products were absorbed by caustic scrubbing.

The analysis of the economic factors implied that the removal of 50 ppm of trichloroethylene (without allowance for processing the products absorbed in the scrubber) is $0.015 per 1000 scfm, and in the case of xylene, the cost is $0.080, which is more than twice higher than the cost for incineration. An advantage of the approach developed is that the capital costs are 2—4-fold lower than those in the incineration technique. It was noted that the method being tested would meet with great difficulties in the case of high flow rates.

The kinetics and mechanism of the oxidation of explosives in ground water with hydrogen peroxide and ozone under UV irradiation were studied by *A. Hong* and co-workers (USA). The authors obtained data that describe the kinetics of the degradation of trinitrotoluene and derived a general kinetic model, which makes it possible to optimize the various methods for treating waste water containing this compound. The main pathway of trinitrotoluene degradation under the action of hydroxyl radicals involves oxidation of the methyl groups of the side chain to give trinitrobenzene, subsequent hydroxylation of the aromatic ring or hydroxylation with the removal of the nitro groups, and, finally, cleavage of the ring to give various organic acid derivatives, which are converted into carbon dioxide. The efficiency of the various methods of treatment decreases in the following order: MP-UV/O_3/H_2O_2 or MP-UV/O_3 > products MP-UV/H_2O_2 > LP-UV/O_3/H_2O_2 > H_2O_2/O_3 > LP-UV/H_2O_2, where MP-UV is a medium-pressure mercury lamp and LP-UV is a low-pressure mercury lamp.

Experiments have shown that photolysis of ozone and hydrogen peroxide is a more effective way to generate OH radicals than the dark reaction in which ozone regenerates with an HO_2^- or OH^- ion.

For UV-initiated oxidation, an optimal concentration of H_2O_2 exists, above which the oxidation rate may decrease. Illumination with a low-pressure lamp is more efficient for the reactions involving ozone than for the reactions with hydrogen peroxide, since these lamps emit photons in the 254 nm region, and these photons are intensely absorbed. In the absence of irradiation, the rates of the degradation of trinitrotoluene have a more complex dependence on the concentrations of H_2O_2 and O_3. In this case, the pH value becomes a significant factor; the degradation is faster when the pH is higher, which may be due to the fact that the reaction of OH radicals with HO_2^- proceeds much more rapidly than the reaction with the conjugated acid, H_2O_2. Both in the dark system and in the system involving UV irradiation, the HCO_3^- ions existing in ground water at neutral pH act as powerful scavengers of OH radicals.

The work of *J. De Laat* (France) dealt with the oxidation of chloroalkanes with hydrogen peroxide under UV irradiation. A kinetic model that adequately describes the degradation of chloroalkanes in pure water and the scavenging of OH radicals by bicarbonate and carbonate ions has been obtained.

$$OH^{\bullet} + HCO_3^- \rightarrow HCO_3^{\bullet} + OH^- \qquad (20)$$

$$k_{HCO_3^-} = 8.5 \cdot 10^5 \text{ mol}^{-1} \text{ L s}^{-1}$$

$$OH^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet -} + OH^- \qquad (21)$$

$$k_{CO_3^{2-}} = 3.9 \cdot 10^8 \text{ mol}^{-1} \text{ L s}^{-1}$$

The role of the temperature in the oxidation of trichloroethylene and perchloroethylene with ozone or an O_3/H_2O_2 mixture was discussed in the report by *Joon-Wun Kang* and *Hoon-soo Park* (Korea). The rates of oxidation of both chlorinated olefins with ozone increased linearly as the temperature increased from 10 to 40 °C by a factor of 2 for each 20°. Since perchloroethylene does not react directly with ozone, its degradation results from the interaction with OH radicals. The authors believe that the increase in the reaction rate with the increase in temperature is due to an increase in the rate constant of the interaction of O_3 with the OH^- ions.

The effect of the temperature on the dark reaction involving a mixture of O_3 and H_2O_2 (the PEROXONE system) depends on the amount of carbonates in the water, since in this case, bicarbonate ions are the main scavengers of $^{\bullet}OH$ radicals and compete significantly with the chlorinated alkenes. For the oxidation of the chloroalkenes in ground and surface water, a nonlinear dependence of the reaction rate on the temperature was observed. This led the authors to the conclusion that the action of the PEROXONE system in natural objects has a complex dependence on the temperature.

C. Chen et al. (China) found by ESR that the reaction of cyanine dyes in DMSO with oxygen under UV irradiation affords the superoxide ion, O_2^-. It is believed that this ion results directly from the photoinduced transfer of an electron from the cyanine dye to the dissolved oxygen. The intensity of the ESR signal for the dye being degraded correlates with its redox potential. Since the free energy of the transfer of an electron from an excited state of the dye to oxygen is negative, this process can advantageously compete with other routes for the deactivation of the dye molecule in the excited state. Since the O_2^- ion is unstable in an aqueous solution, its disproportionation into H_2O_2 and O_2 is a rapid process. Hydrogen peroxide, in turn, decomposes catalytically or photochemically to give OH radicals. When solutions of 3,3′-diethylcarbocyanine iodide in aqueous DMSO (1 : 1) saturated with oxygen were irradiated, an unusual reaction, *viz.*, the replacement of a CH_3 group in DMSO by a hydroxyl radical to give a $CH_3^{\bullet}$ radical, was observed.

The use of ozone in the dark reaction or under UV irradiation for the degradation of pesticides in aqueous solutions at various pH was considered in the work of *P. Paton* (Spain). Two reaction zones were found in a flow-through reactor. In one of these, the reaction rate was high and limited by the ozone diffusion, while in the other, the process occurred much more slowly, and its overall rate was limited by the chemical reaction.

The low-temperature oxidation of carbon by OH radicals was studied in the work of *K. Murata* and coworkers (Japan). This work was stimulated by the necessity of decreasing in the yield of soot in the combustion of diesel fuel.

P. Striolo (France) reported the results obtained in the oxidation of a wide range of organic compounds by hydrogen peroxide between 90 °C and 130 °C. The experiments showed that under these conditions 80 % to 90 % of the carbon of the starting compound can be removed by using the Fenton reagent with 1 h contact time and at an oxidant : substrate ratio of 1.1 to 1.5. For example, it was shown that in the oxidation of phenol at 70 °C, phenol rapidly decomposes, but carboxylic acids, which are relatively stable under these conditions, are accumulated. When the temperature is increased to 140 °C, the carboxylic acids resulting from oxidation of the starting compound are completely degraded. In the case of heteroaromatic compounds, ammonia and nitrates were found to be the only detectable products of oxidation. Chlorophenols yield stoichiometric amounts of chlorine. The optimal temperature for this process is 90—140 °C, since above 140 °C, the side decomposition of H_2O_2 prevails and below 90 °C, only partial oxidation occurs; the optimal reaction time is 10—60 min, and the optimal pH is 2.5—4. The system is inefficient when the catalyst content is less than 10 mg L^{-1}. Perchlorohydrocarbons, aliphatic hydrocarbons, and carboxylic acids are the most difficult to degrade.

In the context of the investigation of the activity of chelate metal complexes in photoinitiated oxidation by hydrogen peroxide, *B. N. Diel* (USA) studied the behavior of Ni complexes with EDTA in oxidation processes. It was found that noticeable degradation of complexes only occurs through the combined action of light and an oxidizing agent. The rate of the destruction of the complex increases when an initial excess of H_2O_2 is employed.

Electrohydraulic cavitation and ultrasound

In the overview report by *M. R. Hoffmann*, it was noted that electrohydraulic cavitation initiated by pulsed-power plasma discharge and by a pulsed or continuous ultrasonic radiation may find extensive application for removing hazardous contaminants from water. In all of the cases of plasma discharge, along with hydraulic cavitation and production of a shock wave, high-energy ultrasonic radiation is evolved, and $OH^{\bullet}$ and $H^{\bullet}$ radicals, hydrogen peroxide, and aquated electrons are formed. Chemical compounds dissolved in water are subjected to the action of all of these factors.

For *p*-nitrophenol, the relative efficiency of ultrasound expressed as the total energy consumed for degradation of 1 mole of a compound in 1 L of water was much higher than that achieved in the case of UV photolytic degradation.

It has been noted that sonochemical reactions involving the dissociation of water according to the scheme

$$H_2O \xrightarrow{\Delta} \dot{H} + \dot{O}H \qquad (22)$$

are accompanied by all of the processes typical of supercritical water, direct pyrolysis, and free-radical reactions of the dissolved compound. For example, carbon tetrachloride and hydrogen sulfide undergo decomposition in the collapsing bubbles or on the hot interfaces:

$$CCl_4 \xrightarrow{\Delta} \dot{C}Cl_3 + \dot{C}l \qquad (23)$$

$$H_2S \xrightarrow{\Delta} \dot{H} + H\dot{S} \qquad (24)$$

Under these conditions, combustion and other free-radical reactions of the substrates being removed are possible.

In the case of derivatives of thiophosphoric acid, in addition to pyrolysis and reactions involving attack by $OH^{\bullet}$ radicals, hydrolysis by supercritical water occurs. Ultrasonic treatment accelerates hydrolysis of parathion and *p*-nitrophenyl acetate by two orders of magnitude compared with hydrolysis in unsonicated solutions. It has been noted that hydrolysis in sonicated solutions does not depend on the ionic strength or the pH of the solution. The author believes that this is due to the fact that the interfacial conditions differ considerably from the bulk conditions.*

Methanol decreases the rate of degradation of compounds in solutions under the conditions of ultrasonic treatment. Electrohydraulic shock in an aqueous solution or in water containing suspended matter obtained by discharging electrodes spaced 1—2 cm apart at a high voltage and a high amperage of electrical current with a pulse duration of 20 μs and an energy density between the electrodes of 36 kJ results in the appearance of charged species (H_2O^+, e^-(aq)) and free radicals ($^{\bullet}OH$,

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* In fact, as the direct experiment and calculations indicate, the dielectric constant of supercritical water is more than an order of magnitude lower than that of normal water (Jiali Gao, *J. Am. Chem. Soc.*, 1993, **115**, 6893).

H$^{\bullet}$, *etc.*) with a corresponding increase in the temperature. The plasma produces a shock wave with a very high pressure (above 14,000 atm). Reflection of the shock wave from either a free surface or suspended particles results, in addition, in all of the above-discussed cavitation phenomena. Under these conditions, new reaction pathways arise that involve the rapidly expanding plasma gases and the compounds to be removed.

The report by *C. Pétrier*, *A. Francony*, and *M.-F. Lamy* (France) was concerned with the oxidation of phenol as well as phenol and carbon tetrachloride present simultaneously, 4-chlorophenol, benzene, and chlorobenzene treated with ultrasound in a solution. In all cases, the concentrations of the starting compounds in solutions saturated with air decreased more rapidly at 500 KHz than at 20 kHz. Benzene and chlorobenzene disappeared more rapidly than phenol and 4-chlorophenol.

As shown by the analysis of the gaseous products, benzene and chlorobenzene were converted into carbon monoxide, methane, carbon dioxide, and acetylene; phenol and 4-chlorophenol yielded only CO and CO_2. These data allowed the authors to conclude that polar substrates react in solution with $^{\bullet}$OH radicals, while less polar compounds undergo pyrolysis inside bubbles.

D. J. Casadonte, Jr. and *J. D. Sweet* (USA), who studied transformations of hydrocarbons in aqueous solutions treated with ultrasound found that under the conditions of nearly adiabatic and short-lived (less than 1 μs) cavitation, local temperatures exceed 5000 K and local pressures are above 100 atm. In addition to the gas-phase high-temperature reaction zone, a superheated liquid arises with a temperature of 800 to 2000 K. Under these conditions, aqueous solutions can be successfully purified from aliphatic and aromatic hydrocarbons and their halogen-containing derivatives (0 to 1500 ppm) over a period of 40 to 200 min. The reactivity of a contaminant correlates with its relative vapor pressure and depends on the overall pressure in the system.

G. Mills (USA) studied transformations of dyes in aqueous solutions initiated by ultrasonic treatment. To remove these compounds using conventional free-radical methods, rather large quantities of oxidants are required and, in addition, these processes involve toxic intermediates. The results obtained are consistent with the view that two pathways of the transformation of dyes exist, one of which involves $^{\bullet}$OH radicals, and the other of which is thermal degradation localized on the hot surface of cavitation bubbles.

P. Riesz (USA) noted that the drastic conditions existing in a collapsing gas bubble (a temperature of several thousand K and a pressure of several hundred atmospheres) result in thermal degradation of solvent vapor into radicals, whose formation has been confirmed by ESR spectroscopy and spin trapping. The latter method was advantageously used for the investigation of free-radical reactions in alkanes (C_8—C_{16}), alcohols (C_3—C_8), cyclohexane, toluene, dioxane, and *N*,*N*-dimethylformamide. It has been shown that 2,4,6-tri-*tert*-butylnitrosobenzene is a particularly suitable spin trap for the identification of free radicals in these solutions. By comparing the results obtained for deuterated and non-deuterated solvents, the author showed that the radicals observed do not result from thermal degradation of the trap. For the homologous series of normal alkanes, the yield of trapped radicals increase as the solvent vapor pressure decreases.

The report by *P. F. Barbier* and *C. Pétrier* (France) dealt with the effect of ultrasonic treatment on the oxidation of *p*-nitrophenol and fulvic acids with ozone. It is believed that thermal decomposition of ozone in a cavitation bubble affords hydroxyl radicals, which recombine to give hydrogen peroxide on the bubble surface. Components of waste water may be oxidized under these conditions. At 20 kHz, natural organic materials can be mineralized.

A 500 kHz ultrasonic treatment of water saturated with oxygen is especially efficient. The authors found that the rate of the formation of H_2O_2 in pure water at high frequencies is greater than that at low frequencies (20 kHz) by a factor of approximately 4. Conversely, the rate of ozone decomposition is 60 % lower at high frequencies. The authors believe that the decomposition of ozone during ultrasonic treatment is a thermal process that occurs inside cavitation bubbles and depends on the temperature in the bubbles. The resonating radius of a cavitation bubble is greater at 20 kHz, and, hence, the temperature resulting from collapse is higher at low frequencies. However, the amount of hydrogen peroxide generated from ozone at the high frequency turned out to be 2.5 times greater than that at the low frequency. For a given ultrasonic power (100 Wt L^{-1}), 9 moles of O_3 are required at 20 kHz for the formation of 1 mole of aqueous hydrogen peroxide, while only 4 moles of O_3 are required at 500 Hz. Nevertheless, mineralization of *p*-nitrophenol was 1.5 times more efficient (in terms of the amount of organic carbon removed per 1 mole of ozone involved in the reaction) at 500 kHz than at 20 kHz and at low pH values, when the radical pathways of ozone autodecomposition are suppressed. The reaction of *p*-nitrophenol with ozone is 6.5 times less efficient in the absence of ultrasonic treatment, than at 500 kHz.

At any pH value, the oxidation processes involving ozone and ultrasonic treatment occur more intensely at higher frequencies. However, only 25 % of the ozone consumed yields hydrogen peroxide. In the most favorable cases, this would be equivalent to 2 moles of ozone consumed per 1 mole of OH radicals. Therefore, the process under consideration is less efficient than the typical O_3/H_2O_2 system, where only 1 mole of ozone is needed for the formation of 1 mole of OH radicals.

Since ultrasound-initiated oxidation is based on cavitation, only a small fraction of the intermediates arising during oxidation can diffuse to the bubble surface. At high frequencies this process can be used for the destruction of chlorinated volatile hydrophobic organic compounds such as perchloroethylene and trichloroethylene. These compounds are rather inert with respect to ozone and reach the cavitation zone, where they can participate in wet oxidation, pyrolysis, and combustion.

Disinfection and oxidation *via* hydraulically induced cavitation were discussed in the report by *J. A. Pisani* (USA). The Oxidation Systems Corporation has developed the HYDROX process in which hydraulic cavitation is used to generate OH radicals, which oxidize toxic organic compounds. This process was employed for the reduction of contaminants in sewage, volatile organic compounds in ground water, and for purification of drinking water. The absence of effluents, toxic admixtures, and wastes are advantages of this process.

The use of ultrasonic irradiation for the oxidation of the herbicide simazine (2-chloro-4,6-bisethylamino-*s*-triazine) was investigated in the work of *G. Kleyman* and *J. N. Jensen* (USA). The rate of simazine oxidation obeys first-order kinetics, however, the first-order rate constant depends on the initial concentration of simazine. The authors believe that the reaction rate is limited by the diffusion of OH radicals through the bubble surface. The rate of simazine oxidation depends linearly on the irradiation power and decreases as the pH increases. However, bicarbonate ions, humic acids, or clays have no effect on the rate of simazine removal.

When simazine is irradiated in pure water, nitrites and nitrates are accumulated. Irradiation of solutions of simazine results in the formation of dealkylation and dechlorination products.

The effects of the pressure and the pH on the sonochemical destruction of aqueous carbon tetrachloride was studied in the work of *H. M. Cheung* (USA). As the pressure and the pH are varied, the rate of the decomposition of CCl_4 goes through a maximum.

Catalytic oxidation

A number of works presented at the Conference were directed at the solution of problems associated with the fact that the limits on the amounts of volatile effluents from stationary units and internal combustion engines of automobiles have become more stringent. The main stationary factors that pollute the environment are units for evaporating organic solvents (39 %), chemical plants (24 %), storage and transportation of petroleum (14 %), and the petrochemical industry (11 %). Incineration, catalytic methods, or recoverable adsorbents are used for the removal of volatile organic compounds. The major difficulties are associated with the removal of halogenated hydrocarbons.

In some cases, industry has to discharge gases containing traces of hazardous contaminants (halogens, *viz.*, chlorine and fluorine, volatile organic compounds, sulfur, or phosphorus compounds). Extraction of these impurities through adsorption and their destruction by thermal treatment are not always possible and are associated with substantial power consumption.

The report by *H. Shaw*, *Yi Wang*, *Tai-Chiang Yu*, and *Sanmei Xu* (USA) was devoted to the catalytic oxidation of hydrocarbons contaminated with potential catalyst poisons. The authors found that chlorinated compounds such as dichloromethane and trichloroethylene present at a concentration of 20—60 ppm can be destroyed by high-temperature oxidation in the presence of catalysts containing Pt and Pd and also Fe, Cu, and Mn oxides with a relatively low consumption of fuel. Noble metals are more active than Fe, Cu, or Mn compounds, and platinum is more active than palladium oxide. A catalyst containing 1.5 % Pt on γ-alumina oxidizes H_2S to SO_2 and/or SO_3 depending on the temperature.

It was found that storage of a platinum catalyst in the atmosphere of a gaseous hydrocarbon containing 100 ppm H_2S substantially increases its activity with respect to the oxidation of propane, does not change its activity with respect to the oxidation of methane, and dramatically decreases its activity in the oxidation of CO. It has been suggested that platinum promotes sulfation of the Al_2O_3 surface, which modifies the surface of Pt crystals by changing their surface free energy. It has been shown that the same effects occur when the catalyst is exposed to H_2S-containing nitrogen, *i.e.*, is treated under non-oxidizing conditions.

Palladium oxide, unlike platinum, is deactivated when treated with H_2S, and no promotion is observed in this case.

The use of catalytic oxidation for purification of air was discussed in the report by *D. E. Tevault* (USA). At present, a number of filtration methods are used for the purification of air by the U.S. Army. The author compared the results obtained by using adsorption at various pressures and/or temperatures with the results of catalytic oxidation and also studied combinations of all three of these approaches. The drawbacks of the adsorption technology are associated with the regeneration of the adsorbent and the equipment volume. Catalytic oxidation is simpler in terms of equipment and allows purification of almost 100 % of the stream.

The author found that catalytic oxidation is especially efficient for the purification of air from unburned hydrocarbons and from the products of partial oxidation in the discharge from internal combustion engines.

The new-generation catalysts contain 400 cells per sq. inch. Technology based on catalytic oxidation is especially efficient for the purification of air streams that have constant flow rates and constant concentrations of contaminants. On the other hand, the adsorption approach is characterized by insensitivity to fluctuations in the concentrations of contaminants and can be used, in particular, in combination with catalytic oxidation, as the preliminary step that converts the initial flow into a flow with a low content of a contaminant. Catalytic oxidation, in turn, can be used for purification of effluents that arise during the regeneration of the adsorbent.

The catalytic dechlorination of polychlorinated polyphenyls, which are widely used as heat-transfer agents and high-temperature lubricants, has been studied in the work of *J. Schwartz* and *Yumin Liu* (USA). The authors have found that titanocene dichloride reacts with sodium hydroborate *in situ* to give a catalyst that enables reductive dechlorination of the starting polychlorinated biphenyls to give biphenyls, which can be biologically destroyed. After hydrolysis, the reaction mixture contains biodegradable organics, sodium chloride, titanium dioxide, and sodium borate, which are much less hazardous for the environment than the starting polychlorinated biphenyls, whose oxidation yields dioxins.

The relative rates of the reduction of bromobenzenes catalyzed by the Ti/hydroborate/amine system correlate with their electrochemical reduction potential. This is in agreement with the view that the transfer of an outer-sphere electron is the rate-determining step. In the case of polychlorinated polyphenyls, the introduction of an additional phenyl group into an aryl halide should accelerate the reduction according to the electron transfer mechanism, but not the reduction occurring as nucleophilic addition. A comparison of the $E_{1/2}$ values shows that a *p*-phenyl or *p*-Cl group substitution have similar effects on the reduction potentials of substituted bromobenzenes and, indeed, both substrates are reduced in the Cp_2TiCl_2—$NaBH_4$ system at comparable rates. Similarly, the rates of the reduction of *p*-dichlorobenzene and 4-chlorobiphenyl are comparable. The authors note that in the case of *ortho*-substituted analogs of polychlorobiphenyls, steric factors hamper their microbial degradation, but have little effect on the reduction potentials and, hence, little effect on the rate of their reduction according to the electron transfer mechanism. The advantages of the approach developed were demonstrated using a common mixture of polychlorobiphenyls, which is widely used in industry under the name Arochlor 1248 and consists of tetra-, penta-, and hexafluorobiphenyls. When Arochlor 1248 is treated with the Cp_2TiCl_2—$NaBH_4$ system, it is converted after 12 min into a mixture consisting of 80 % dichlorobiphenyls and 20 % trichlorobiphenyls, and after 2 h, the reaction mixture contains 50 % biphenyl and 50 % monochlorobiphenyl (primarily 3-chlorobiphenyl). After 24 h, complete reduction to biphenyl is observed. The hydrolysis products contain only biodegradable components, sodium chloride, titanium dioxide, and sodium borate. The authors believe that the new process can be used for removal harmful polychlorobiphenyls from soils.

Oxidation of volatile organic compounds for the purification of air from the corresponding contaminants was used in the work of *J. B. Hoke* and co-workers (USA). The authors note that photocatalytic oxidation involving titanium dioxide as the catalyst has technical prospectives.

G. W. Rice et al. (USA) reported a catalyst meant for the remediation of waste gases of diesel engines. The new catalyst removes 70—80 % of soluble organic compounds and allows oxidation of hydrocarbons and CO. Platinum and a basic metal oxide are the active components of the catalyst. The catalyst corresponds to the new US standards for the purification of waste gases of diesel engines.

The work of *R. J. Schwartz and C. J. Pereira* (USA) dealt with oxidation of chlorinated organic compounds. Corroded stainless-steel foil with deposited high-surface-area alumina was used as the catalyst. This monolith catalyst is characterized by rather low aerodynamic resistance. In the 300—500 °C temperature range, up to 95 % of the volatile organic compounds were removed by oxidation. Up to 70 % of the heat evolved was used for heating the stream coming to the oxidation through intense heat exchange.

The destruction of volatile organic compounds using Hopcalite type catalysts has been studied in the work of *N. Singh* (USA). Hopcalite type catalysts are less thermally stable than catalysts containing noble metals. This results in a loss of catalytic activity due to the exothermic nature of catalytic oxidation and due to fluctuations in the contents of organic contaminants oxidized in industrial effluents. The author has suggested a catalyst that contains perovskite type manganese oxide. The catalyst is stable up to 700 °C (MnO_2 is normally stable up to 540 °C). The new catalyst exhibits high efficiency in the degradation of volatile organics and high thermal stability typical of the catalysts based on noble metals. A significant advantage of the catalyst suggested is that it is more stable with respect to halogens than typical metallic catalysts.

Oxidation in supercritical water

Oxidation in water under supercritical conditions is a new direction in the search for ways to remove organic materials from aqueous solutions or suspensions. Under supercritical conditions (at a temperature above 374 °C and a pressure above 22.13 MPa), water is a fluid with rather high density, however its transport properties are close to those of gases, which is favorable for fast chemical reactions. Above the critical temperature and pressure, water, most organic compounds, and most gases (O_2, CO, CO_2) form a single phase. Hydrolytic processes in combination with oxidation processes occurring in the same phase substantially accelerate destruction of a wide range of industrial wastes.

The use of supercritical water has the following advantages: organic compounds are highly soluble in it, the products can be easily separated, the properties of the solvent such as density, diffusion coefficient, and dielectric constant, can be dramatically changed by slight variations of the pressure, and mass exchange is not limited. Supercritical water is a unique solvent in which active oxidation can proceed at a lower temperature than incineration, resulting in a decrease in the formation of both nitrogen oxides and carbon. The heat of a process in a completely closed autoclave is absorbed by the solvent, therefore, one can maintain any required temperature. Oxidation occurs quickly (several seconds to minutes) and affords simple products (ideally, CO_2, H_2O, N_2). The temperature region is 650 to 900 K, and the pressure is above the critical pressure for water, 22.1 MPa. Significant advantages of this approach are high rates of chemical reactions, the absence of nitrogen oxides in the products, and also the fact that at present, the required pressure and temperature ranges are technically achievable.

Oxidation in water under supercritical conditions has been used for the removal of halogenated organic wastes from the biopharmaceutic industry, the production of chemical weapons, hydrolyzed solid rocket fuels, and biological sludges.

The report by *P. E. Savage* (USA) dealt with the macrokinetics of the oxidation of phenol and its derivatives including 2-chlorophenol and *o*-, *m*-, and *p*-cresols. The author found global dependences describing the rates of the consumption of the organic compound and the formation of CO_2. It was noted that both reactions depend on phenol concentration, the density of water, and oxygen concentration. The latter has a more substantial effect on the formation of CO_2 than on the consumption of phenol. The intermediates include carboxylic acids, cyclodiones, phenols, *etc.*

The simplest scheme based on these data includes two parallel pathways for phenol transformation. One of these leads to phenol dimers such as phenoxyphenols, dibenzodioxins, and dibenzodioxanes. The other pathway results in ring-opening products (carboxylic acids and so on).

The kinetics of the oxidation of methane with oxygen in the 10—30 MPa and 650—700 K ranges with a constant reactor volume was studied in the report by *S. F. Rice* and *R. R. Steeper* (USA) using Raman spectroscopy. The rate of methane oxidation decreases as the pressure increases, and the yield of carbon oxide is rather low.

The macrokinetics of the oxidation of hydrolyzed solid rocket fuels in the temperature range of 400 to 475 °C, with a residence time of 5 to 25 s, and at a pressure of 27.6 MPa was studied in the work of *N. Crain, L. Li*, and *E. F. Gloyna* (USA) on the basis of the accumulation of CO_2 and other C_1 compounds, and acetic acid and other C_2 compounds.

The destruction of explosives and rocket fuel components during their oxidation in supercritical water was discussed in the report by *R. B. Dyer* and co-workers (USA). The traditional methods for disposing these compounds are burning or detonation in open systems. The drawbacks of these methods are uncontrolled emissions to the air and soil contamination. A further drawback of the conventional incineration methods for pyrotechnics is the large amount of nitrogen oxides ejected into the air. Soil and ground water have already been contaminated with these materials through ordinary operations during their manufacture and storage at military bases. Incineration can be used for decontamination of these soils, though air pollution during this process cannot be avoided. However, satisfactory and economically acceptable methods for decontamination of ground water are few in number.

Oxidation in supercritical water opens new possibilities in this field. This method also allows one to purify water contaminated with chlorinated aromatic solvents. The main reaction products are water, carbon dioxide, and inorganic salts. Oxygen, air, or hydrogen peroxide are used as oxidizing agents.

The authors studied a number of explosives and rocket fuel elements such as ammonium perchlorate, cyclotrimethylenetrinitramine, nitroguanidine, nitromethane, pentaerythritol tetranitrate, 2,4,6-trinitrotoluene, hydrazine, and asymmetrical dimethylhydrazine in order to optimize the conditions for destroying these contaminants and removing them from water. Under all of the conditions studied, complete oxidation to give carbon dioxide and water with excess oxidant in a flow-through reactor was always achieved at 600 °C at a residence time of 11 s. Balance experiments showed that the above-mentioned conditions ensured complete oxidation, and most of the carbon was converted into CO_2 or carbonic acid. Under milder conditions, for example, when the temperature is not so high and the substrate : oxidant ratio is 1 : 1, complete oxidation requires a longer residence time.

The nitrogen of the starting material is always distributed among a number of products, N_2, NH_3, N_2O, NO_2^-, and NO_3^-, in which the oxidation state of nitrogen varies from 3– to 6+. Balance experiments indicate that molecular nitrogen, whose yield was determined by subtracting the yields of all of the other possible compounds, is the main product. In a number of experiments, the formation of N_2 was confirmed qualitatively by mass spectrometry and GC, and in some cases, quantitative evaluations were made. No correlation exists between the number of nitrogen-containing groups, *e.g.*, NO_2^- or NH_2 groups, and the distribution of nitrogen among the products detected (N_2, N_2O, NO_2^-, and NO_3^-). However, this distribution can be varied by varying the temperature and the oxidant concentration. For example, when trinitrotoluene is oxidized with a large excess of oxidant at 600 °C, a substantial fraction of the initial nitrogen (74 %) is converted into NO_x. This fraction is much lower (12 %) at a fivefold excess of the oxidant, though under these conditions, all of the carbon of the starting substrate is converted into CO_2. Similar phenomena are observed when cyclotrimethylenetrinitramine is oxidized with excess hydrogen peroxide or in the reactions of hydrazines with hydrogen peroxide. This indicates the possibility of controlling the process by varying its parameters.

The report by *E. G. Hauptmann* and co-workers (Canada, USA) was concerned with the purification of effluents from paper plants using supercritical water oxidation. It was noted that this technology allows one to avoid the dewatering of the wastes, in particular, sludges, which requires expensive equipment. One more advantage of this approach is the absence of gaseous emissions. Various strategies for processing streams at different stages of bleach plants have been evaluated. The design parameters for modules capable of treating up to 5 tons of dry solids per day were presented.

The supercritical water oxidation of wastes producing sticky solids was discussed in the report by *P. W. Ordway* and *P. D. Chapman* (USA). The MODAR company in collaboration with Stone & Webster Engineering Corporation developed an industrial-scale demonstration unit to process a wide range of hazardous wastes. This unit allowed the GNI Group, Inc. (Deer Park, TX) to find an ecologically favorable solution for the disposal of their wastes. 4410 kJ kg^{-1} is used to process 795 kg h^{-1} of solid wastes. Air is used as the oxidant and sodium hydroxide is used to neutralize the anions that are produced during the oxidation of wastes containing halogens, sulfur, or phosphorus. The efficiency of the destruction of organic compounds is at least 99.99 %.

R. C. Lyon (USA) reported on testing a unit for supercritical water oxidation of wastes. A pilot plant at the University of Texas in Austin for the purification of municipal waste water decreased the contents of total organic carbon and ammonia to 125 and to below 50 mg L^{-1}, respectively. No air emissions containing nitrogen or sulfur oxides, ammonia, or ozone were detected during the experiments. CO (less than 50 ppm) was virtually the only air contaminant. An evaluation of the operation of the unit showed that the technology suggested is economically acceptable.

Oxidation in supercritical water in those cases where metal salts are formed and deposited on the walls of the reactor, which affects the processing of an organic material, was discussed in the report by *C. A. LaJeunesse and S. F. Rice* (USA). These salts, which result from oxidation of sulfur- and phosphorus-containing organics in the presence of heavy metal compounds, cause corrosion of the reactor. The experiments carried out in the Sandia National Laboratory (Livermore) with a tubular reactor 750 cm in length with two turns showed that under fluid conditions, water containing 0.5 % (w/w) Na_2SO_4 or NaCl yields solid precipitates, which are deposited on the reactor walls. The amount of the precipitate decreases exponentially with the temperature and increases as the pressure increases. When amidonaphthol red G is oxidized with hydrogen peroxide, corrosion of the tube material is observed. Chromium is selectively leached with excess oxygen. Conversely, Ni and Mo are selectively leached in the presence of the dye, but they are not detected when the treatment is carried out with pure water or water containing hydrogen peroxide.

The work of *M. Djafer* and co-workers (France) was devoted to the effect of temperature on the catalytic wet air oxidation of municipal effluents. The purpose of the work was to find oxidation conditions under which a high degree of waste water purification can be achieved with no generation of smoke, fly ash, or nitrogen or sulfur oxides. The addition of Fe, Cu, Ce, and hydrogen peroxide was used in order to decrease the temperature and the pressure of the process. The optimal results were achieved at a pressure of 7 MPa, a temperature of 235 °C, and a residence time of 1 h. Cu^{II} compounds, especially those deposited onto TiO_2, proved to be the most efficient.

The supercritical water oxidation of phenol was studied in the work of *Z. Ding* (USA). The authors used a microreactor made of Hastalloy C-276 placed in a furnace. α-Alumina particles 1.5 mm in diameter were placed into a 25 cm-long reactor 1.25 cm in diameter. Experiments at 390 °C showed that at a 3-4-fold excess of oxygen and initial phenol concentrations of about 0.01 mol L^{-1}, the degree of conversion is 94 to 99 %. When the reaction is carried out under homogeneous conditions, the yield of CO_2 is 17—28 %, and in the presence of catalysts such as MnO_2 or Cr_2O_3, the yield is as high as 65—80 %.

The oxidation of solids of a biological origin in water near the critical point was studied in the work of *F. Luck* and co-workers (France). The authors used a 0.5 L autoclave. The experiments showed that at 383 °C, the materials under study decompose 94 %. Increasing the temperature to 430 °C has a slight effect. Organic acids (acetic, propionic, butyric, and valeric acid) formed in the oxidation of the starting materials are oxidized in supercritical water rather rapidly. Nitrogen-containing compounds decompose to give ammonia, which then reduces nitrates to NO_2 and possibly to NO. However, ammonia is relatively inert in aqueous solutions under supercritical conditions.

The transformations of polyvinyl alcohol during wet air oxidation were studied in the work of *Shyh-Jye Hwang* and *Wen-Chi Yeh* (Taiwan). The authors found that in the 150—240 °C temperature range and 670—2500 psi pressure range, hydrolytic transformations of polyvinyl alcohol are much slower than its oxidation.

The abstracts of the Conference have been published. The next meeting, namely, the World'95 Environmental Congress Promoting Environmental Science, Technology and Business, will be held in London, Ontario, Canada on September 17—22, 1995.

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