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International Ozone Association

Ozone in the United States of America -- State-Of-The-Art

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Abstract

Applications for ozone in the United States have evolved through a lengthy maturation process, which began with drinking water treatment (taste/odor/color removal) in the early 1900s, and grew slowly until acceleration began in the mid-1980s. Although deodorization became a stable market in the 1960s-1970s, these applications were small, for the most part. One of the largest uses for ozone is oxidation of process chemicals in the chemical industry, which began in the USA about the 1940s, and subsequently has spread worldwide. Today, thanks primarily to environmental regulatory pressures which began to impact ozone in the mid-1980s, ozone now is used increasingly in the USA for drinking water treatment and for some municipal and industrial wastewater applications. The U.S. Environmental Protection Agency (EPA) has recognized the growing importance of ozone (> 200 drinking water plants use ozone today), and has appointed IOA representatives to two of its regulatory development committees as stakeholders. Several U.S. cities have installed or are installing wastewater treatment processes for potable reuse purposes, which include the use of ozone. Three full-scale U.S. pulp bleaching plants use tons/day quantities of ozone. Smaller applications for ozone include water treatment for cooling tower waters (biofouling control), swimming pools and spas, marine aquaria, bottled water disinfection and maintenance of high purity waters in the pharmaceuticals and electronics industries. A new application for ozone is in commercial laundries to reduce energy costs and replace chemicals. In mid-1997, a public declaration was made by an expert panel that ozone is Generally Recognized As Safe (GRAS) for contact with foods. This declaration opens the door for ozone to be used in U.S. food processing industries. U.S. research scientists and engineers are at the forefront in studies which define the technical aspects of ozone technologies in a variety of applications employing

advanced oxidation, including the treatment of hazardous wastes, groundwater remediation, and process water recovery and reuse in the semi-conductor industry.

Drinking Water Treatment

MUNICIPAL DRINKING WATER

The first continuous process for the disinfection of drinking water in the United States may well have been ozonation, as described by Vosmaer, with respect to several plants that he installed in Philadelphia (Pennsylvania) in 1900-1905. The largest was able to handle 3.1 m^3/min of rough-strained water from the Schuylkill River (1). Military sanitarians were among those with a keen interest in the developing technology of disinfection (by all methods available). Annual reports of the U.S. War Department's Surgeon General chronicle U.S. efforts to improve troop water supplies. In 1909 the application of ozone was investigated for use at Fort Niagara, NY, using an experimental apparatus installed at the Army Medical Museum. However, ozonation was not adopted by the military for drinking water disinfection, probably because of the many logistical advantages of hypochlorite, iodine and other more easily carried and applied water disinfectants (1).

During the period 1908 through the late 1930s, several water treatment plants installed ozonation in the Great Lakes area that achieved various levels of successful treatment, but one by one, for a number of reasons, they withered and died. Nonetheless, regardless of how efficient or inefficient, reliable or mechanically unreliable, virtually all seemed connected by a common thread -- nearly all had achieved treatment objectives with ozone unattainable by any other method. Indeed, ozone science seemed a giant step ahead of ozone engineering in those days. In fact, some of the great scientists of the nineteenth century such as Pasteur and Bunsen, and Fremy, to mention a few, recognized this. Bunsen once stated that, *"When ozone can be produced commercially, hundreds of uses will be found for it."* Indeed, the use of ozone in the United States appeared to be retarded by the lack of efficient, reliable, and cost-effective equipment. This began to change by the early 1940s (2).

In 1940 a 7-mgd (26,495 m^3/d) water treatment plant went into operation in Whiting, Indiana, which employed ozone for control of tastes and odors. This plant is still using ozone today, and in that respect, Whiting is the "Nice, France" plant of the USA. Five 10-lb (4.54 kg)/day ozone generators were installed initially and, after World War II, these were modified to produce a total of 75 lbs (34 kg)/day at up to 1% concentration in air using only three of the original machines. These ozone generators have been in daily service for more than 57 years and, even at this moment, continue to provide dependable service.

In 1973, the small (< 0.1 mgd = <378 m^3/d) water treatment plant at Strasburg, PA became only the second U.S. water plant to place ozone into continuous operation. Strasburg's clean mountain spring water normally does not need any treatment. However, the State of Pennsylvania passed a law requiring that all water produced in the state be disinfected -- meaning, at that time, that it must be chlorinated. But Strasburg is in Amish country, and the Amish people objected to adding "a poison" (chlorine) to their water. The town obtained a special dispensation from the State to test ozonation, which was conducted successfully.

By 1979, three more U.S. water treatment plants had installed ozone (Monroe and Bay City, Michigan, and Saratoga, Wyoming), primarily for taste and odor control, but also for color removal as well. In the early 1980s, the City of Los Angeles, California began studying the use of ozone for coagulation assistance and to increase the rate of water flow through the plant filters. The world's largest potable water plant (600 mgd = 95,000 m^3/h) went on line in 1987 in Los Angeles having installed the capability to produce 10,000 lbs/day of ozone from oxygen. Los Angeles thereby became the first potable water plant to install its own cryogenic source of oxygen.

In 1986, the U.S. Congress passed the Safe Drinking Water Act Amendments of 1986. A portion of this new legislation required the U.S. EPA to set regulations for several "new" (to the water industry) microorganisms, namely *Giardia* cysts, enteric viruses, and *Legionella* bacteria. At the same time the "CT" principle was adopted and guidance was developed for utilities that would be impacted by the new regulations to attain the new mandated levels of disinfection. The "CT" concept sets specific numerical levels for the product of concentration of disinfectant (C - in mg/L) times contact time (T - in minutes) for each type of regulated microorganism at the water temperature ranges encountered by most treatment plants. CT product values are related to numbers of log-inactivations of the microorganisms involved. Because of ozone's powerful disinfecting capabilities, its CT values are the lowest of the other three disinfectants specified as appropriate by the EPA (chlorine, chlorine dioxide and monochloramine). Consequently, ozone is able to provide the required levels of disinfection in minimal time, and simultaneously reduce the chlorine demand of the water, thereby reducing the formation of halogenated byproducts which would have resulted from chlorine-only treatment.

From the Safe Drinking Water Act Amendments of 1986 (and now the Amendments of 1996) have evolved several new drinking water regulations:

- o The Surface Water Treatment Rule (SWTR - promulgated in 1989)
- o The Disinfectants/Disinfection ByProducts Rule (D/DBP) (Stage 1 - Nov.

1998)

- o The Interim Enhanced Surface Water Treatment Rule (IESWTR - Nov. 1998)
- o The Ground Water Disinfection Rule (GWDR - 1999)
- o The Disinfectants/Disinfection ByProducts Rule (D/DBP - Stage 2 - 2002)
- o The Final Enhanced Surface Water Treatment Rule (FESWTR - 2002).

Ozone has an essential role to play in each of these rules, and recognition of this fact has stimulated the installation of ozone in many U.S. water treatment plants. Figure 1 shows the growth in numbers of plants using ozone in the USA since 1982. As of mid-1997, more than 200 plants had been identified. Several of these plants use advanced oxidation (combinations of ozone + UV radiation or ozone + H_2O_2) to oxidize refractory organics in raw waters. One of the latest U.S. drinking water plants uses two stages of advanced oxidation (O_3 + H_2O_2) to cope with high levels of organics in a particularly polluted lake water (3).

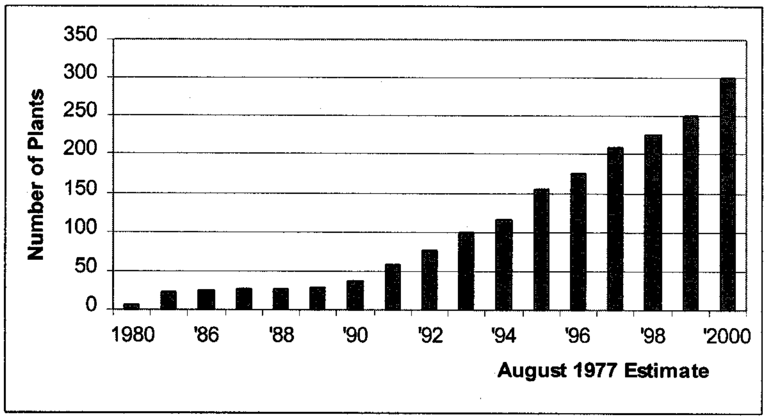

Figure 1. Listing of U.S. drinking water treatment plants, in operation, using ozone as of August 1997.

Figure 2 shows the breakdown by size of these plants. Note that 90 of the 201 listed plants are small -- that is, they produce less than 1 mgd (< 3785 m^3/d).

Today, ozone engineering is on a par with ozone science, and both continue to advance by leaps and bounds. Ozonation for THM control, enhanced coagulation, pesticide removal, oxidation of TOC, TCE, and PCE is becoming as familiar as the time-tested applications for oxidation of iron and manganese, taste and odor control and color reduction. Today, we see retrofitting with ozone for the inactivation of *Giardia* and *Cryptosporidium* cysts following North American outbreaks of giardiasis and cryptosporidiosis. A new technology also has been developed using ozone to control macrofouling by *Dreissena polymorpha*, the rapidly spreading zebra mussel (4). Many drinking water plants use two stages of ozonation (pre- and intermediate = prefiltration) to treat unusually contaminated raw waters. Following ozonation with biofiltration allows biodegradation of organic ozone byproducts in the water plant, so as to minimize bacterial regrowths in distribution systems. These are but some of the objectives of ozone treatment of drinking water in the United States which by late 1995 had the capacity to treat over 2.7 billion gallons (102 million m^3) per day with an ozone production capability of nearly 88,000 pounds 33,916 kg) per day; that equates to just over one lb (0.454 kg)/second (2).

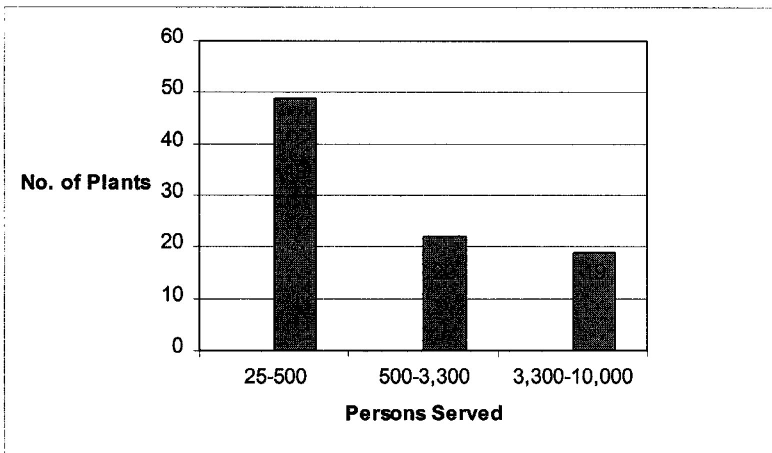

Figure 2. Breakdown by size of 90 U.S. water plants serving less than 10,000 persons.

A truly significant ozone milestone event occurred in March of 1997. In gearing up to promulgate stage 1 of the D/DBP and the IESWT rules, the U.S. EPA recognized that it had overlooked the rapid growth of ozone and ozone + biofiltration in American water treatment plants in recent years. Consequently, when EPA established the M/DBP Expedited Rule Advisory Committee (5) it formally recognized the International Ozone Association as a stakeholder in the rule-making process, and appointed IOA representatives to full voting membership on this advisory committee. The IOA was asked to provide information pertinent to microbial and disinfection byproducts issues, including efficacy, performance, and cost data from operational plants. EPA next established a Small Systems Committee, again appointed IOA as a stakeholder representative, and listed ozone as a technology which can be used by small water treatment systems (those serving fewer than 10,000 persons). Truly a milestone event in the history of ozone in the USA.

BOTTLED WATER TREATMENT

In the United States, sources of bottled water include, primarily, groundwaters or municipal tap water. In the latter case, treatment includes dechlorination, deionization, addition of minerals according to an U.S. FDA-approved formulation, and bottling. Groundwaters sometimes are bottled directly, but sometimes are subjected to additional purification technologies to cope with specific pollutants, e.g., iron/manganese, then bottled. It is during the bottling process that ozone is applied to nearly all U.S. bottled waters to provide final disinfection of the water and to control any air-borne microorganisms that may enter the bottle as it is being filled. Ozone is added to attain a residual of 0.3 mg/L which is held over four minutes. The water, still containing residual ozone, is bottled and sealed; the sealed bottles sometimes are held at the plant for upwards of 24-hours to allow the residual ozone to decay. The process of ozone disinfection of bottled water, as well as the use of ozone to sanitize bottled water plant lines, is approved by the U.S. FDA as GRAS (Generally Recognized As Safe), and is in use at nearly all of the U.S. (and many Canadian) water bottling plants

Wastewater Treatment

MUNICIPAL WASTEWATER TREATMENT WITH OZONE

In municipal wastewater treatment, ozone has been used primarily for disinfection (following primary or secondary treatment). Most of the disinfection work was pioneered in the United States during the early 1970s, where it was developed to the point of full-scale commercial use. However, ozone has several other wastewater applications as well, including: suspended solids removal; biological activated carbon; and sludge conditioning. The Chino Basin, CA plant installed ozone for microflocculation of suspended solids; Marion, NY applies ozone for flotation of suspended solids; Auburndale, FL applies ozone for additional organics oxidation and solids removal following nitrification and partial denitrification in an oxidation ditch; and the Cleveland, OH Westerly plant previously used ozone to oxidize organic material prior to filtration and granular activated carbon adsorption. West New York, NY and Hoboken, NJ have used ozone to stabilize and condition sewage sludge to a material acceptable, after dewatering, for sanitary landfill disposal (6).

Up until 1976, all U.S. municipal wastewaters were required to disinfect their effluents continuously prior to discharge. When disinfection was obtained through chlorination (most plants), many fish kills were experienced in the chlorinated effluent-receiving waters. As a result, the search began for disinfection agents that could attain a high level of bacteria kills while minimizing its detrimental effects on receiving bodies of water. Many studies were conducted on dechlorination approaches. In this context, the use of ozone became very promising, since ozone was (a) a better disinfectant, (b) did not leave a residual in the effluent being discharged, and (c) actually added dissolved oxygen to the effluent. During this time period (up until 1976), ozone appeared to be the ideal "alternative disinfectant" to chlorine for sewage effluent disinfection.

Unfortunately for ozone, in 1976, the EPA changed its disinfection policy, and this had a drastic impact on ozonation. Subsequent to 1976, U.S. sewage treatment plants were not required to disinfect their effluents, unless the receiving waters were to be used for (a) potable water intake, (b) aquaculture, or (c) human contact with the waters. In most northern U.S. areas, human contact does not occur during winter months -- consequently, these plants are required to disinfect only during warm months (May through September). From a capital cost amortization point of view, it is simply not cost-effective to have high capital cost equipment standing idle for many months of the year. Consequently, beginning in the mid-late 1980s, ozone use began to decline significantly in the USA for this application.

At the same time, UV radiation evolved as a technology which disinfects sewage treatment plant effluents at reasonable cost. As a result, today there are far fewer sewage treatment plants using ozone than the peak number of 45 plants reached in the early 1980s.

Municipal Wastewater Reuse for Potable Water Supplies

At Denver, Colorado (7)

The City of Denver concluded that its expanded water needs in the year 2,000 will be sufficiently large that water reuse must play a significant role, and facilities to double Denver's 500 mgd (1,893,939 m^3/day) capacity are planned. At the same time, Denver's sewage treatment facilities also are being enlarged. The expanded oxygen activated sludge plant now treats a wastewater flow of 170 mgd (643,939 m^3/day). Adjacent to this central wastewater treatment plant, a 1-mgd (3,788 m^3/day) pilot plant was installed for treating Denver's secondary effluent by advanced techniques to produce a final effluent which equals or exceeds the quality of Denver's drinking water. The secondary effluent was treated from 1984 through the early 1990s by lime flocculation and sedimentation, filtration, selective ion exchange for ammonia removal, two-stage granular activated carbon (with intermediate ozonation), reverse osmosis, air stripping, and chlorine dioxide disinfection. Having concluded that potable water can indeed be produced through the combined treatment processes, the City of Denver closed down the pilot plant to await the time when wastewater reuse actually will be required.

At El Paso, Texas (8)

In June of 1985, the city of El Paso, Texas began operating the 10 mgd (37,879 m^3/day) Hueco Bolson Aquifer Recharge Project. This involves advanced treatment of sewage effluent for direct injection recharge of a fresh water aquifer for supplying 65% of El Paso's water supplies. In mid-1988, the plant was operating at 4 mgd (15,140 m^3/day). The plant treatment scheme involves two equal 5-mgd (18,940 m^3/day) lines. Equalization is followed by two-stage biological/physical PACT® (Powdered Activated Carbon Treatment), which removes carbonaceous materials, nitrifies ammonia, and removes many organic materials in the first stage. Waste sludge is processed and powdered activated carbon is regenerated by wet air oxidation (236°C; 56.2 kg/cm^2). In the second PACT stage, treatment for 1.25 h by anoxic detention, followed by 0.9 h aerobic detention provides denitrification and more organic removal. Methanol is fed to the second stage to be used as a carbon source by the denitrifying bacteria.

Lime treatment follows PACT treatment to a pH of 11.1 (virus and metal removals), then recarbonation with liquid CO_2, sand filtration and ozone disinfection in two 7.7 minute detention time stages, followed by an additional 7.7 minutes detention to allow completion of ozone reactions prior to filtration through granular activated carbon (GAC). GAC filtration is the final, polishing step prior to recharge. Pilot plant testing indicated the primary GAC reactivation criterion to be trihalomethane formation potential. It is estimated that the GAC filter will last for two years prior to reactivation being required. Just prior to storage in one of three 3.3 million-gallon (12,500 m^3) reservoirs for a minimum of 8-h, the water is treated with 0.25 mg/L chlorine to minimize biological growths in the pipelines on the way to the reservoirs. The 8-h storage allows sufficient time for the many water quality analyses to be conducted, prior to injection of the treated water into the aquifer recharge wells.

Anaerobic digestion is used as the sludge stabilization process (single, high rate, complete mix with dewatering on sand beds), with dried sludge sold as a soil conditioner. Methane gas produced is utilized as an energy source in the plant.

At San Diego, California

In 1995, the San Diego Utilities Commission announced that it will construct a new treatment system for producing potable water from its municipal sewage. Effluent from a secondary treatment plant will be subjected to a multiple step treatment sequence, which will include ion exchange, ozone, reverse osmosis, and other process steps. Treated wastewater then will be added to one end of a large lake which serves as one of San Diego's potable raw water sources. Residence of the treated municipal wastewater in the lake reservoir is well over 30 days, during which time mixing of the treated wastewater with lake inlet water is extensive.

One reason for anion exchange being included in this treatment process is to remove bromide ion from the water prior to ozonation. This will ensure the absence of bromate ion, no matter what the ozonation conditions are during actual plant operation. This wastewater reuse treatment plant has evolved following an extensive pilot plant study, and is scheduled to come on-line in the year 2000.

INDUSTRIAL WASTEWATER TREATMENT

Destruction of Cyanide Ion

Ozone was installed in the 1950s to destroy cyanide ion in electroplating wastes at the Boeing Aircraft plant in Wichita, KS (9). Later, the combination of ozone + UV radiation treatment (an AOP) was installed at the U.S. Air Force's Tinker Air Force Base in Florida to destroy ozone-stable iron-complexed cyanides (10). In the early 1980s, the Cadillac Division of General Motors installed ozone to destroy cyanide in electroplating wastewaters (11). On the other hand, adoption of ozone for this application in the U.S. has not been extensive, probably due to higher costs than those for alkaline chlorination.

Marine Aquaria Water Recycle and Reuse

In the early 1970s, Sea World of Florida (Orlando) installed ozonation followed by biofiltration to treat recycling brine at their dolphin exhibit. Ozone was used to oxidize excess BOD_5, COD, and to disinfect pathogenic microorganisms. During biofiltration, additional BOD_5 was removed along with ammonia (nitrification) (12). In the ensuing years, this application of ozone has grown considerably, to apply not only to dolphin exhibits, but also those of beluga and orca whales, sea lions, shark exhibits, etc. By 1993, it was estimated that at least 35 U.S. marine aquaria had installed ozonation (13). In 1995, Sea World (which by this time had installed ozone at many of its aquaria exhibits throughout the country) installed additional ozone at its Orlando facilities, thus applying ozone to all of its recirculating artificial brines exhibits (artificial brine is man-made to eliminate bromide ion in the waters). Sea World refers to ozone as its "life support" system for its marine mammals (14).

Many U.S. zoos also have installed ozone in various animal exhibits (e.g., hippos, seals, polar bears, and the like, and the acceptance of ozone in aquaria and zoos is growing steadily (13; 15).

Ozone Treatment of Electronic Chip Manufacture Wastewaters

In the manufacture and processing of integrated circuits, very high purity water is a necessity. Impurities in the water lower the electrical yields of these circuits, as well as cause failures that may not appear until the circuits are in use. At many electronic chip manufacturing plants, many million gallons of water per day are treated, and ozone is a recognized oxidizing/disinfecting agent for these purposes.

At Bell Telephone Laboratories, Murray Hill, New Jersey

Zmolek (16) described a water treatment system developed and installed at Bell Telephone Laboratories in 1973, which incorporates the use of ozone for bacterial control. Bacteria can plug the 0.2 micron filters easily, and can cause failure of circuit elements should they arrive at the point of use and stick to any of the active surfaces during wash and rinse cycles. In the Bell system, three tanks are equipped with ozone contactors. Ozonation is conducted for 15 minutes, then the tank is allowed to stand several hours to allow residual ozone to decay. Each tank is ozonized individually and the process is repeated about twice per week. Bacterial monitoring sometimes reveals no colonies, but in most cases the numbers are five to 20 per mL.

At IBM Corporation

Hango et al. (17) described a pilot plant study leading to a full-scale installation at IBM Corporation to recycle spent deionized water from an integrated circuit manufacturing operation by oxidizing trace organic materials (isopropyl alcohol, acetone, photographic stabilizers, chlorinated organic solvents) and ammonia with the combination of ozone/hydrogen peroxide (advanced oxidation at a 5:1 O_3/H_2O_2 wt ratio). When this treatment was followed by reverse osmosis and ion exchange, the treated effluent met all required deionized water quality standards and was suitable for recycling to the integrated circuit manufacturing process. These water quality requirements include: TOC of 2 mg/L or less, resistivity of 18 megohms/cm, and filtration through a 0.45 micron filter. About 90% of the organic contamination in this processing water is isopropyl alcohol and its initial oxidation product acetone. Neither ozone by itself nor ozone combined with ultraviolet radiation were as cost-effective in purifying the process waters.

In pilot plant studies all of the TOC removal could be effected by the ozone/hydrogen peroxide process. If the wastewater treatment system is operated in this mode, subsequent reverse osmosis and ion exchange treatment steps are not necessary, and they can serve as backup. On the other hand, the organics can be partially removed by the ozone/hydrogen peroxide process; then RO and ion exchange steps must be incorporated. In this case, however, TOC oxidation must be carried to the point at which all organics are converted to carboxylic acids, which are easily removed by reverse osmosis and ion exchange. The process has been installed full-scale at IBM, and at many other electronic chip manufacturing plants throughout the United States and Japan.

At Other Plants

Nebel and Nezgod (18) reviewed the preparation of high purity water systems which are in use at many plants manufacturing electronic integrated circuit components and also pharmaceuticals. Organic materials in plant influent water are adsorbed on GAC (which also reduces residual chlorine to chloride ion), and inorganic ions are removed by deionization techniques (ion exchange). Since both GAC and ion exchange resins provide breeding areas for microorganisms, ozone then is applied for disinfection as treated water is recirculated in the high purity water storage tank(s). When process water is drawn from the storage tank, residual ozone then is destroyed by exposure to ultraviolet radiation, without addition of any chemicals. By this process, when an ozone residual of 2.5 mg/L is maintained in the recirculating water, TOC levels can be maintained below 0.1 mg/L.

Oily Wastewaters at Petroleum Storage Facilities (19)

ARCO Products Company treats ca 1 million gallons (3785 m^3) of oily wastewater annually at its Richmond, CA (USA) petroleum product storage and transportation facility. After much testing, the combination of ozonation followed by granular activated carbon (GAC) adsorption was selected. By this combined treatment, hydrocarbons and other organic contaminants are removed from the wastewater to levels below 0.1 mg/L, which is the discharge requirement of the State of California for this type of wastewater. Although the removal of organics can be accomplished by the GAC alone, the beds [2 x 10,000 lbs (9072 kg)] in series] would have to be regenerated rather frequently, at a cost of $20,000 per regeneration. With ozonation prior to GAC adsorption, the life of the GAC is extended by 10-50%, thus providing considerable cost advantage. The ozone-assisted GAC system was installed in 1991 for ca $500,000, which included the ozone generator, two 10,000 lb GAC beds, associated equipment and pumps, engineering costs and labor. Results at this facility have been so successful that the company had installed four additional ozone/GAC facilities by 1993.

Industrial Applications For Ozone

CHEMICAL OXIDATION

Shortly after World War II, the specialty chemical company, Emery Industries, in

Cincinnati, Ohio, developed a process for the ozone oxidation of oleic acid to produce high yields of azelaic acid, the basic monomer for the production of Nylon-6. Emery constructed a manufacturing plant that contained the capability to generate some 40,000 to 50,000 lbs of ozone per day (20) Over the years, Emery developed other chemical oxidation uses for ozone, and built manufacturing plants in various countries outside of the United States, also involving ozone oxidation.

Information on other chemical oxidation technologies involving ozone are difficult to come by, since this type of information usually is held proprietary by the firms involved. It is known, however, that ozone oxidations hold a unique position in the synthesis of some pharmaceutical intermediate compounds. In some syntheses it is necessary to convert a 3-hydroxy-steroid compound to a 3-keto compound without affecting other functional groups in the compound. This conversion classically has been accomplished with ozonation.

OZONE BLEACHING OF PAPER PULPS

There are many reasons for the recent moves toward totally chlorine-free (TCF) bleaching of paper pulps (21,22). The AOX (adsorbable organic halogen) issue has led to changes in the bleaching process. Chlorine dioxide has been substituted at least partially for chlorine in many mills, and this has resulted in a dramatic decrease of the level of AOX formed, from 5 to 6 kg per ton of pulp, down to 1 to 2 kg per ton of pulp. The next step forward is TCF bleaching, not because of the AOX problem, but because it represents the easiest route to the effluent-free mill, in which all process waters can be recycled. Having no chloride ion in the bleaching effluent makes the effluent easier to handle in the recovery system. This is the major justification for going to TCF bleaching, in which ozone and hydrogen peroxide, in combination, offer such excellent promise.

In 1992, the world's first two full-scale commercial ozone pulp bleaching plants went into operation, one of which is the Union Camp facility in Franklin, Virginia (23). Today, 19 commercial ozone pulp bleaching mills are in operation in various countries throughout the world, and three of these are in the USA. In addition to the Union Camp facility, a second plant is located in Memphis, Tennessee, and the third, located in Wisconsin, is the world's first recycle fiber plant to install ozone bleaching.

COOLING WATER TREATMENT

Until the late 1980s, cooling tower water treatment for biofouling control in the U.S. usually involved chromium-containing chemicals -- which provided excellent control.

However, in the mid-late 1980s, the U.S. EPA warned the industry that the use of chromates in that application would be banned in the future. From that point the search was on for other candidates to substitute for chromates, and ozone became one of the more promising candidates. Today, the U.S. cooling water market for ozone in comfort cooling towers (air conditioning cooling towers) is one of steady growth. About 500 cooling towers are estimated to have installed ozone. Its use is recommended at low dosages (ca 0.1 mg/L) for new towers. For towers which have been using chemicals to control biofouling, it is recommended that ozone be dosed at about 0.3 mg/L until the biofilm has been loosened and removed, after which ozone dosages should be decreased to 0.1 mg/L.

SWIMMING POOL WATER TREATMENT

This author is only interested in dipping his body into water that is treated by a German DIN Standard (19 643) process. In such treatment, water is flocculated, filtered, ozonated, passed through granular activated carbon (to destroy excess ozone), then a small residual of chlorine is developed (minimum 0.2 mg/L, maximum 0.4 mg/L), and the water, now of potable quality, is returned to the pool or spa. In addition, the ozone applied must meet certain rigid minimum standards with respect to both dosage and concentration in the gas phase (min 1.5% wt in air). This means that ozone generated by UV radiation is not allowed by the Germans -- because the maximum ozone concentration exiting UV generators of ozone usually is less than 0.1% by weight.

In the United States, the primary consideration in public and municipal water treatment is only the assurance that microorganisms are absent; little or no attention is paid to chemical contamination, and little is understood about the organic materials that enter the pool as a result of the presence of bathers, and even less appears to be known about the reactions of any oxidizing agent with these organic contaminants. However, it is appreciated in the USA that the necessity to add chlorine or bromine in sufficient quantities to control microorganisms usually leaves objectionable odors in the water and the air of enclosed pool halls.

Starting in the mid-1970s, those who make ultraviolet units capable of generating minuscule quantities of ozone leaped into this market waiting to happen and found immediate success. But their marketing claims about UV-generated ozone were based on fantasy and not fact. Their primary claim was that ozone is ozone, and even small amounts of ozone will do as much as large amounts. And besides, UV-ozone units were available at about one-tenth the cost of CD-ozone units. As a result, in the intervening years, it has been estimated that as many as 500,000 "UV-ozone" generators have been sold in the USA for residential pool and spa treatment. By contrast, less than 100 CD-ozone generators have been installed, and only five U.S. facilities are known which employ the full German DIN Standard approach to ozone. As long as Americans (a) do not care what quality of water they put their bodies into, or (b) continue to believe what they are told about their pool/spa water quality, e.g., "we have the best pool water quality in the world", little change is expected. U.S. consumers will only insist on higher quality water when they know that it is available. The competitive nature of swimming pool equipment in the United States has prevented the investment in equipment and processes to produce the highest water quality.

This situation is exemplified by the recent coupling of ozone with bromide ion for pool water treatment in the United States. The technology, originally developed in Germany, is based on the fact that bromide ion is rapidly oxidized by ozone to produce hypobromite ion which rapidly equilibrates with hypobromous acid (HOBr), which is an excellent biocide. Thus, the German concept is to add sodium bromide ion to the recirculating pool water and add ozone according to DIN 19 643 teachings. This allows ozone to perform its chemical oxidation functions, produce HOBr, and the excess bromide ion (over ozone applied) then destroys any excess ozone, producing more microbiocide. As the HOBr does its work, some bromide ion is reformed, and is reoxidized to HOBr when it next passes through the ozone reaction chamber.

In the USA, however, only one company markets a bromine-containing compound, bromo-chloro-dimethylhydantoin (BCDMH), which is approved by the U.S. EPA for treating pool/spa waters. When BCDMH is added to pool waters (no ozone is involved for this argument), bromide ion is formed which then is oxidized to HOBr by the free chlorine, also liberated when BCDMH is dissolved in the water. But now when the bromide ion is reformed, the only way to reoxidize it is by adding more chlorine (meaning the addition of more BCDMH).

Now enter ozone into this picture. The company marketing BCDMH jumped onto the ozone bandwagon by coupling ozone with their BCDMH product. Their initial claims were that the use of ozone would save the pool owners considerable cost (in BCDMH). True enough -- except that the firm was recommending the addition of only small quantities of ozone -- just sufficient to produce more HOBr and ***not*** sufficient to allow ozone to do its (desired) chemical oxidation as in the ozone/NaBr case.

This situation will last for years in the USA, because only a few vendors pay attention to the chemistries occurring during pool/spa water treatment.

COMMERCIAL LAUNDRIES

Beginning in the early 1990s, ozone has found a niche in commercial laundries. The claims for ozone range from the logical to the ridiculous, but both seem to win sales. It is logical that ozone can replace bleach and can do the bleaching at room temperature, thus saving bleach costs and energy costs to heat water. On the not-so-logical side are claims that ozone reacts with organic materials which are the causes of soiled clothing, thereby producing detergents. Thus, ozone is claimed to be a replacement for detergents as well. Other issues that must be exhaustively studied are the compatibility of ozone with the materials of construction of commercial laundering equipment and the effect of ozone on fabric sizings and the fabric itself. Ozone leakage from the laundry equipment into the workplace is also an issue. Peer-reviewed studies on these issues are needed and encouraged.

Some major U.S. hotel chains and many hospitals have installed ozonation systems in their laundries during the past 5-6 years. It remains to be seen whether this application for ozone is truly viable, although increasing efforts are being applied to marketing this concept.

Ozone Advanced Oxidation

The term "Advanced Oxidation Processes" (AOP) involves techniques for formation of the very reactive hydroxyl free radical (^{o}OH), which is short-lived (microseconds) free radical with oxidation power stronger than that of ozone itself. Hydroxyl free radical can be produced by many techniques, not all requiring the use of ozone. Those AOPs involving ozone usually couple ozonation with simultaneous addition of UV_{254} radiation, hydrogen peroxide, or elevation of pH (ca 7.5 - 9), but ultrasound also will decompose ozone to form the hydroxyl free radical. Ozone AOPs are useful when ozone itself cannot perform the oxidation(s) required. On the other hand, because of the very short half-life of the hydroxyl free radical, it is not a suitable disinfectant. Although AOP technologies are relatively new, already several commercial applications have been developed. Those that are in use in the USA are described in a paper presented at the Kyoto World Congress (24) and include the following:

- Groundwater treatment to destroy TCE, PCE, and pentachlorophenol
- Groundwater remediation at Superfund sites to destroy volatile organic compounds and benzidines
- At U.S. Army ammunition plants to destroy explosives

Applications of Ozone in the Food Industry

Uses of ozone are not currently widespread in the United States, because in the past it has been very difficult to secure approval of regulatory agencies. However, in July 1997, a panel of experts in various aspects of food technology declared ozone to be

Generally Recognized As Safe (GRAS) for the treatment and processing of foods, as long as its use was in line with Good Manufacturing Practices (25). This means that attention must be paid to the protection of food processing plant workers, but in addition, conditions must be developed so that levels of ozone applied will accomplish the intended treatment objective(s) without causing damage to the food itself.

There are many potential applications for ozone in the food industry, including disinfection, mold control, treatment of process waters for recycle and reuse, cleansing of cold storage rooms, extension of storage life of fruits, vegetables, fish, etc., none of which have been legal in the USA until the July 1997 GRAS declaration. This subject is discussed in more detail by the author in a presentation at the Kyoto Ozone World congress (26). It is projected that many studies will be initiated shortly which will result in considerable use of ozone throughout the United States food industries.

Conclusions

The state-of-the-art of ozone in the United States is as follows:

1. Rapid growth in drinking water treatment, stimulated by recent EPA Regulations. More than 200 U.S. plants now are using ozone, and at least 90 of these are small plants, producing less than 1 mgd (< 3785 m^3/d).
2. Disinfection of nearly all U.S. (and Canadian) bottled waters -- a mature market for ozone.
3. Declining use of ozone in municipal wastewater, due to EPA's changed disinfection policy requiring disinfection only at certain periods of the year.
4. Increasing use of ozone in reuse of municipal wastewaters for potable purposes.
5. Slowly growing uses in industrial wastewaters for cyanide destruction, reuse of electronic chip washwaters, and treatment of petroleum wastewaters.
6. Rapidly increasing use of ozone in marine aquaria and zoos.
7. Acceptance of ozone in the electronics and pharmaceuticals industries for maintaining cleanliness of stored process waters.
8. Tons per day uses of ozone for industrial chemical oxidations.
9. Three full-scale U.S. plants bleach paper pulps with ozone.
10. More than 500 comfort cooling towers use ozone for biofouling control.
11. More than 500,000 pools and spas have installed UV-generated ozone units; but only a few dozen use CD-generated ozone, and even fewer treat pool/spa water according to German DIN Standard 19 643.
12. Ozone is being installed increasingly in commercial laundries, but additional studies with regard to safety, effects on materials of construction, or on the fabrics themselves need to be made.
13. Several commercial applications of ozone-advanced oxidation have been installed, in both potable water and industrial wastewater areas.

14. Ozone has just been declared Generally Recognized As Safe for contact with foods (June 1997) in the USA. This will result in much activity in the very near future.

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Key Words

Ozone; State-of-the-Art; Drinking Water Treatment; Municipal Wastewater Treatment; Industrial Wastewater Treatment; Municipal Wastewater Reuse; History of Ozone; Disinfection; Bottled Water; Cyanide Destruction; Marine Aquaria Water; Semiconductor Manufacture; Industrial Applications; Chemical Oxidation; Pulp Bleaching; Cooling Water Treatment; Swimming Pools; Laundries; Advanced Oxidation; Food Processing;

Résumé

Les applications de l'ozone aux USA ont connu une lente maturation, qui a commencé avec l'eau potable (élimination du goût, de la couleur et de l'odeur) dans les années 1900, jusqûà une accélèration dans le milieu des années 1980. Un des emplois les plus important est l'oxydation dans l'industrie chimique, qui a commencé dans les années 1940. Aujourd'hui, sous la pression de la législation relative a l'environnment (dans les années 1980) l'ozone est de plus en plus utilisé pour le traitement de l'eau potable et pour quelques traitement. d'eaux résiduaires municipale ou industrielles. L'EPA a reconnu l'importance croissante de l'ozone (plus de 200 usines en eau potable) et a accrédité deux représentants de l'IOA au sein de ses comités d'étude sur la réglementation. Plusieurs villes des USA ont construit des installation pour la réutilisation des eaux résiduaires, incluam une ozonation. Trios usines de blanchiment de la pâte à papier utilisent plusiers tonnes d'ozone par jour. De plus petites installations incluent l'ozone pour le traitement de l'eau des tours de refroidissement, des piscines, des stations thermals, des aquariums, des eaux én bouteille, de l'eau ultra-pure pour les industries pharmaceutiques ou electronique. Une nouvelle application est pour les laveries commerciales afin de réduire la consommation d'energie et de products chimique au milieu de l'année 1997, un expert a fait une déclaration publique disant que l'ozone est généralement reconnu comme sans danger pour l'industrie alimentaire. Les chercheurs et les ingenieurs US sont a la pointe des recherches pour definir les techniques d'utilisation de l'ozone dans de nombreuses applications telles que traitement des résidus dangereux pour la santé, restauration des sols, réutilisation d'eaux de procéd.

Zusammenfassung

Die Ozonanwendung in den U.S.A. war ein langwieriger Entwicklungsprozess, der anfangs 1900 mit der Trinkwasserbehandlung (Geruch, Geschmack, Entfaerbung) begann und langsam zunahm, bis zum Aufschwung Mitte der achtziger Jahre. Obwohl die Entfernung von Geruchstoffen bereits in den sechziger und siebziger Jahren einen stabilen Markt bildete, waren diese Anwendungen relativ klein. Die groesste Ozonanwendung war die Oxidation in der chemischen Industrie, die ungefaehr 1940 begann und sich weltweit verbreitet hat. Heute wird Dank der Umweltgesetzgebung, die die Anwendung von Ozon ab Mitte der achtziger Jahre unterstuetzte, Ozon verstaerkt bei der Trinkwasseraufbereitung und der Behandlung haeuslicher und industrieller Abwaesser eingesetzt. Die U.S. EPA (Environmental protection agency) hat die zunehmende Bedeutung von Ozon erkannt (mehr als 200 Trinkwasserwerke setzen Ozon ein) und hat Vertreter der IOA in zwei seiner Gesetzgebungskomitees berufen. Mehrere Staedte setzen Ozon zur Abwasserbehandlung mit dem Ziel der spaeteren Wiederverwendung ein. Drei Zellstoffbleichereien verbrauchen taeglich Tonnen an Ozon. Kleinere Anwendungsgebiete sind die Behandlung von Waessern in Kuehltuermen (Verhinderung von Faulprozessen), Schwimmbaedern, marinen Aquarien, Flaschenwasserbehandlung und die Behandlung hochreiner Waesser in der

pharmazeutischen und elektronischen Industrie. Eine neue Ozonanwendung ist der Einsatz in Grosswaeschereien, um Energie und Waschmittel einzusparen. Mitte 1997 wurde eine oeffentliche Erklaerung abgegeben, dass Ozon im Kontakt mit Lebensmitteln sicher ist. Diese Erklaerung oeffnet die Tuer fuer die Behandlung von Lebensmitteln mit Ozon. U.S. Forscher und Ingenieure sind fuehrend in Studien, die die technischen Aspekte der weiterfuehrenden Ozonbehandlung (advanced oxidation) in verschiedenen Anwendungsgebieten untersuchen, z. B. die Behandlung gefaehrlicher Abwaesser, Grundwassersanierung, Prozesswasserbehandlung und Rueckfuehrung in der Halbleiterindustrie.