# AN INTRODUCTION TO INNOVATIVE CHEMICAL OXIDATION TECHNIQUES FOR TREATMENT OF CONTAMINATED WATERS

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#### INTRODUCTION

The contamination generated by industrial development and preparations for national defense over the past 100 years has resulted in an appreciable threat to one of our nation's most valuable resource; groundwater. Total treated volumes in excess of a half of billion gallons is not uncommon for groundwater remediation systems. Additionally, most industrial entities are required to treat wastewater generated from processing operations. Flowrates from these industrial facilities are typically within the 30 - 500 gpm range. Obviously, vast quantities of waters are being treated to meet today's regulatory drivers.

Among the many contaminants threatening groundwater resources or within industrial wastewaters are chlorinated solvents, phenolics, pesticides, chemical weapons, explosives, and fuel derived aromatics. Treatment processes that have been used in the past for remediation of these groundwaters are activated carbon and air stripping. Unfortunately, both processes rely on a solution phase change mechanisms (i.e. transport of the contaminant from water to gas [stripping] or solid [carbon]) and not on the on-site destruction of the contaminants. Additionally, with an increased awareness of air pollution, air stripping is now rarely implemented without some form of air stream treatment, such as activated carbon adsorption, which greatly impacts the economics of this process. As water standards are lowered, both of these technologies become much less efficient in terms of cost and treatment effectiveness (Zappi 1998). Therefore, the development and evaluation of potentially more cost effective and improved performing processes, such as chemical oxidation, is advantageous to interested parties facing either site remediation or wastewater treatment.

## CHEMICAL OXIDATION

Chemical oxidation processes are a group of treatment

technologies that use powerful chemical oxidizers to destroy organic contaminants. Oxidizers used in traditional chemical oxidation processes include ozone, chlorine, hydrogen peroxide, and potassium permanganate (James Montgomery Engineers Inc. 1985; Metcalf and Eddy Inc. 1991). The chemical reaction products associated with organic contaminants during oxidation are usually simple organic compounds, such as carboxylic acids, and/or inorganic compounds, such as carboxylic acids, water, and various anions depending if a substitutional group is present (i.e. chloride for chlorinated species [trichloroethylene] and nitrates for nitrated species [trinitrotoluene]) (Zappi 1995).

The technology has historically been used as treatment technology for municipal drinking water (Metcalf and Eddy Inc. 1991; Langlais et al. 1991) and industrial water treatment (Rice 1981; Echols and Mayne 1990; Kuo et al. 1996). Chlorination has been used almost extensively in the United States for disinfection of municipal drinking water (James Montgomery Engineers Inc. 1985). The Europeans have utilized both chlorine and ozone for water treatment (AWWA 1990).

Peroxidation. Hydrogen peroxide is a clear, colorless, slightly viscous liquid that is completely miscible with water at any proportion. Since it is a liquid, it has some transport properties that are superior to ozone (which is a gas). Hydrogen peroxide is often used in the chemical manufacturing industry as an oxidizer and reducer depending on process requirements (Zappi 1995). Hydrogen peroxide is easily transported and very stable. Oxidation of organic substrates with hydrogen peroxide is referred to as peroxidation. Rice (1981) lists hydrogen peroxide as having a lower oxidation potential (1.77 v) than ozone (2.07 v) and the hydroxyl radical (2.80 v). Water treatment for removal of complex organics using hydrogen peroxide alone is generally considered not feasible because of slow oxidation kinetics. Hydrogen peroxide without some

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form of catalyzation to hydroxyl radicals has been used for water treatment on a very limited basis, with the majority of application used for phenol, cyanide, or hydrogen sulfide oxidation (Sims 1981; Millero et al. 1989; Elizardo 1991).

Hydrogen peroxide usage in terms of water treatment is more often associated with radical production due to Fenton's Reagent reactions (Zepp et al. 1992). Fenton's reagent involves the reaction of hydrogen peroxide with iron to produce the hydroxyl radical as presented below:

 $\begin{array}{l} {\rm H_2O_2 + Fe^{2+} --> 2OH + Fe^{3+}} \\ {\rm 2Fe^{3+} + H_2O_2 \ -> Fe^{2+} + 2H^+ + O_2} \end{array}$ 

Fenton's Reaction has been successfully used to treat various waters that were not amenable to treatment using hydrogen peroxide alone (Murphy et al. 1989; Sediak and Andren 1991). In general, the process is applied by mixing a ferrous salt solution with hydrogen peroxide (usually at an applied concentration of <5%) to initiate the above listed reaction within the influent matrix. The hydroxyl radicals produced actually are the primary destruction agent making this process an advanced oxidation process (see subsequent discussions). Recently, the discovery of a photolytic enhancement to the traditional Fenton's Reaction has been found (Zepp et al. 1992; Pignatello 1992). This enhancement involves recycling of ferric iron into the much more reactive ferrous form which is then available for increased radical production. It can be noted from the reaction scheme above that ferric iron can be converted to the reduced ferrous form without UV irradiation; however, this reaction is kinetically slow compared to the ferrous oxidation step.

**Ozonation.** Ozone has found significant usage for oxidation of complex organic compounds (Staehelin and Hoigne 1982; Sotelo et al. 1991; Hoigne and Bader 1976; Hoigne and Bader 1983; Yao and Haag 1991; Zheng and Kuo 1992; Kuo et al. 1996; Kuo and Chen 1997). Examples include ammonia, phenolics, TOC, and aromatics. Rice (1981) evaluated the oxidation kinetics of a wide variety of organic compounds with ozone based on exhaustive review of the literature. His conclusions indicate that many organic pollutants may be treated using ozone without any form of catalyzation.

Ozone is a gaseous allotope of oxygen which boils at -112°C and is approximately 20 times more soluble than oxygen (Sierka 1982). Ozone is typically generated on-site using ozone generators. The two most common types of ozone generators are corona discharge and electrolytic generation (Langlais et al. 1991). Commercial generators produce air or oxygen

streams containing ozone typically within the 2 - 10 percent (by wt.) range. Oxygen-fed generators usually produce approximately two times as much ozone per scfm as do air-fed units. Since ozone is introduced via diluted carrier gases, the solubility of ozone using these streams is controlled by phase equilibrium between stripping and solubilization. Ozone solubility using typical ozonated feed gases into sparged contactors range from 5 mg/l to 30 mg/l (Langlais et al. 1991). Currently, various groups are attempting the development of an ozone generator with capability of producing ozone compositions in excess of 20% on a commercial scale. This effort will increase liquid phase ozone levels obtainable within ozonated reactors which will in turn increase the rate of contaminant removal during treatment.

In general, ozone is introduced into the influent using a sparge chamber which is designed with extensive buffling to reduce short-circuiting. Bubble rise heights are typically within the 15 - 20 foot range, with the latter being the most commonly used dimension. Design information is well presented by Langlais et al. (1991). Treatment cost using ozone can be below \$0.05 per thousand gallons treated if conditions are optimal (i.e. low levels of pollutants that are oxidizable within a low-scavenger matrix). Other more innovative designs are available that may be more condusive to limited spacing foot-prints found at many industrials settings. These include in-line injectors, U-tube contactors, and counter-current towers. However, the standard sparge tank offers the comfort of a wellproven design and simplicity of operation.

Staehelin and Hoigne (1982) evaluated the role of hydroxide ions (OH) and hydrogen peroxide ( $H_2O_2$ ) on ozone decomposition. The use of hydrogen peroxide for ozone decomposition into hydroxyl radicals is actually the genesis for development of an innovative oxidation process referred to herein as peroxone (which is discussed in significant detail later in this paper). Staehelin and Hoigne determined that the pseudo-first order reaction rate constant increases an order of magnitude for each unit pH increase. Ozone decomposition reaction with OH is described by Staehelin and Hoigne as first order with respect to both ozone and OH. They also proposed the following OH based ozone decomposition mechanism,

 $\begin{array}{l} O_{3} + OH & \rightarrow > O_{2} + HO_{2} \\ HO_{2} < \rightarrow > HO_{2} + H^{+} & pK_{a} = 11.6 \\ O_{3} + HO_{2} \rightarrow > OH + O_{2} + O_{2} \\ O_{3} + O_{2} \rightarrow > O_{3} + O_{2} \\ O_{3} + H_{2}O \rightarrow > HO_{2} + O_{2} \end{array}$ 

They also propose that the mechanism for decomposition of ozone in the presence of hydrogen

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peroxide is based firstly on the dissociation of hydrogen peroxide as follows,

$$H_2O_2 \iff HO_2^+ H^+$$

Once dissociated, the HO2 reacts with ozone to form a variety of other products including the hydroxyl radical. The reaction rate constant for O3 reacting with HO2 was calculated by Staehelin and Hoigne to be 2.8 (+/- 0.5) X 10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup> when it is assumed that two ozone molecules are eliminated with each primary event. From this study, the rate of ozone decomposition with respect to hydrogen peroxide presence is much more dominant than decomposition initiated by pH (i.e. OHpresence). Hoigne and Bader (1983) have evaluated the rate constants of ozone reacting with various organic compounds. They eliminate enhanced organic compound oxidation via secondary oxidizing species such as the hydroxyl radical through the addition of radical scavenging chemicals such as simple alcohols such as t-butyl alcohol and propanol. They also suggest that the rate laws for the ozone-organic compounds are first order with respect to each reactant (i.e. second order for the overall reaction). Ozonation (use of ozone alone) has potential for treating phenolic type compounds, such as pritric acid which is an initiator used by DoD for explosive weapons or dichlorophenol, which is used as a building block chemical for wood preservation formulations. With adjustment of the reactor water pH is values in excess of 9, Zappi (1995) observed significant removal of 2,4,6-trinitrotoluene (TNT). Formation of hydroxyl radicals via OH based ozone decomposition was postulated to be the primary mechanism of TNT removal.

Advanced Oxidation Processes. In terms of contaminated groundwater and industrial wastewater treatment, hydrogen peroxide and ozone have been by far the oxidizers of choice. In this application, these oxidizers have primarily been used in conjunction with ultraviolet (UV) photolysis (Sundstrum et al. 1986; Zappi et al. 1991). Chemical oxidation processes that result in the generation of the hydroxyl radical (OH) have been referred to as advanced oxidation processes (AOPs) by the American Water Works Association (Langlais et al. 1991).

Commercial application of AOPs for contaminated groundwater treatment in the United States has traditionally involved UV irradiation of hydrogen peroxide, ozone, or a combination of both. AOPs tend to be much more aggressive than ozonation alone due to the high reactivity of the hydroxyl radical toward complex organics (Sundstrom et al. 1986), hence their widespread usage for groundwater and wastewater treatment. The addition of UV light to an aqueous solution of hydrogen peroxide or ozone results in the generation of hydroxyl radicals. Mayer et al. (1990) concluded that AOPs are very competitive with both air stripping and activated carbon adsorption for treating volatile organic compound (VOCs) in contaminated groundwaters.

UV Based AOPS. The UV light absorption spectra for both hydrogen peroxide and ozone are very different (Zappi et al. 1993). Ozone absorption of UV light occurs primarily at 253.9 nm (2,539 angstrom units), while hydrogen peroxide absorbs wavelengths of approximately 230 nm and lower. Low pressure mercury UV lamps, commonly used in water treatment for disinfection, emit the vast majority of its radiation spectrum at the 253.9 nm wavelength. Medium pressure UV lamps emit the majority of its radiation spectrum over a wide band from approximately 190 nm to 600 nm, with a large portion of energy centered around the 200 - 300 nm range. Chemical oxidation systems utilizing ozone are better served using low pressure UV lamps. These lamps are more efficient and produce the exact UV spectrum that its readily utilizable by ozone for production of OH<sup>-</sup> radicals.

Medium pressure UV lamps are much more energy intensive than low pressure UV lamps. Much of the electrical energy utilized by medium pressure UV lamp is wasted as heat radiation. However, chemical oxidation systems using hydrogen peroxide are better served with medium pressure UV lamps that emit more UV energy in the absorbance band of the hydrogen peroxide; thereby, resulting in optimal OH radical production. Although medium pressure UV lamps are more energy intensive, some benefit may be derived by using a medium pressure UV lamp for treatment of some organic contaminants because of direct photolysis of the contaminants by UV absorbance. Many organic compounds absorb at lower UV wavelengths (i.e.<230 nm), making the direct absorbance of UV energy from a low pressure UV lamp of little benefit toward direct photolysis. However, in UV-based chemical oxidation systems, it is usually more advantageous to convert the parent chemical oxidizers (O3 and H2O2) into hydroxyl radicals with the UV energy unless the rate of contaminant degradation under direct photolysis is rapid. An optimal UV/chemical oxidizer system should be selected and designed on the basis of the photochemical properties of the contaminant(s) and oxidizer and the physical, chemical, and optical properties of the influent water. For example, Fleming et al. (1995) found that both UV irradiation and oxidation were effective removal mechanisms for RDX (an explosive) using an ozonated photolytic reactor.

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The stoichiometric mechanism responsible for generation of hydroxyl radicals in UV/hydrogen peroxide systems as proposed by Sundstrom et al. (1986) is presented below:

$$H_2O_2 \rightarrow 20H$$

Oxidation of liquid phase contaminants using UV and hydrogen peroxide is commonly referred to as UV/peroxidation. This technology has been successfully used for treatment of several contaminated waters containing a variety of organic contaminants (Sundstrom et al. 1986; Zappi et al. 1989; Froelich 1991; Zappi et al. 1992). Hager et al. (1987) present several case studies where a commercial UV/hydrogen peroxide-based system successfully treated a variety of contaminants. They suggest the costs for treatment would range from \$1.37 to \$58.51 per 1,000 gallons treated.

A typical design for a UV/peroxidation unit involves batch-added hydrogen peroxide applied at the head of the plant, prior to entering the UV chamber. Since most UV/peroxidation units utilize medium pressure mercury (Hg) vapor UV lamps, heat generation within the reactor is a concern because sufficient heating of the reactor contents occurs if the system residence times are too excessive, resulting in the boiling of the reactor contents. Usually, overheating of the reactor contents is prevented via the rapid throughput of the influent and/or periodic recycling of the reactor contents through a water chiller, if longer residence times are required. Since the medium pressure Hg vapor UV lamp produces such extensive light intensities, then only a few lamps are required (i.e. <8 lamps in most applications). The UV lamps are immersed into the radiation chamber by housing the lamps within quartz tubes that are installed perpendicular or parallel to flow. Scumming of the quartz tubes have historically been problematic with the medium pressure Hg vapor UV lamps. Current units often use lamp cleaning systems to allow for sufficient UV irradiation doses. Note that scumming of lamp housing tubes is also problematic with the low pressure Hg vapor UV lamps; however, the scumming problems are much less frequent than those encountered with medium pressure Hg vapor UV lamps. An optimized hydrogen peroxide dose is applied so that the residual hydrogen peroxide concentrations in the effluent are less than 50 mg/l. This prevents excessive losses of the expensive hydrogen peroxide within the reactor effluents. Using this approach, most UV/peroxidation units are designed under a plug flow regime.

Peyton et al. (1987) presents a mechanism for OH generation during UV irradiation of ozone (UV/ozonation). As mentioned above, typically these

units utilize a low pressure Hg vapor UV lamp because of quantum efficiencies associated with ozone and this lamp type. The hydroxyl radical formation mechanism for UV/ozonation is summarized below:

$$O_3 + H_2O + UV --> O_2 + H_2O_2$$
  
 $H_2O_2 + H_2O <--> H_3O^+ + HO_2^-$   
 $O_3 + HO_2 <--> O_2 + O_2^- + OH$   
 $O_3 + O_2^- + H_2O --> 2O_2 + OH + OH$ 

Ozonation under photolysis has been successfully used for treatment of a wide variety of contaminated waters (Jody et al. 1989). Barich and Zeff (1989) list a variety of contaminated groundwaters and wastewaters that were successfully treated using a commercially available UV/ozone system. They indicate that treatment costs range from \$0.15 to \$86.00 per 1,000 gallons treated. Typical UV/ozone systems are designed to allow free ozonated carrier gas rising while floating upward within field of UV irradiation provided by numerous vertically placed lamps. As was the case with the UV/hydrogen peroxide systems, the UV lamps are encased within quartz tubes to prevent shortcircuiting of the lamp ballast. Since ozone is a regulated pollutant, untransferred ozone remaining within the exiting gas stream from the reactor must be destroyed using a variety of destruction chambers. Care must be taken when treating volatile pollutants to ensure that the pollutants are oxidized and not simply stripped via the gas sparging within the reactor.

Burrows (1983) evaluated the use of low pressure mercury vapor UV lamps with ozonation for removing a variety of explosives including TNT (>18,000 ug/l) from wastewater. His experiments indicate that ozonation alone was a poor means for TNT removal. The addition of UV to the ozonation reactor yielded removals in excess of 90 percent within 30 minutes of batch treatment. He presents a first order rate constant of 0.051 min<sup>-1</sup> for TNT. DeBerry et al. (1984) evaluated a host of AOPs for oxidation of TNT (pink water) and trinitrobenzene (TNB), a well-known intermediate of TNT oxidation. It was concluded that the two UV based AOPs were effective. They also stated that Fenton's Reagent and peroxone indicated promise for treating low level contaminated waters and suggested that additional investigation into the peroxone process is required to establish further process feasibility.

Zappi et al. (1993) evaluated a variety of AOPs for treatment of explosives contaminated groundwaters. AOPs evaluated included ozonation with low pressure mercury vapor UV lamp based photolysis, medium pressure mercury vapor UV lamp based photolysis with hydrogen peroxide dosing, low pressure mercury vapor UV lamp based photolysis with hydrogen peroxide dosing, ozonation with medium pressure mercury

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vapor UV lamp based photolysis and hydrogen peroxide dosing, and peroxone. The groundwater contained approximately 30,000 ug/l TNT, 32,000 ug/l RDX, 2,000 ug/I HMX, and 1,500 ug/I TNB. Their results indicate that only the UV/ozone based AOPs were capable of removing all of the explosives and TNB to the current treatment goal of 2 ug/l for TNT, RDX, and TNB and 400 ug/l for HMX. Peroxone did result in explosives removals in excess of 90 percent, yet it was not successful in meeting the 2 ug/l TNB standard after 60 minutes of batch treatment. The UV based hydrogen peroxide dosed systems had mixed results. The medium pressure lamps with hydrogen peroxide removed all of the explosives, but was unsuccessful in meeting the TNB standard. The low pressure mercury UV based system with hydrogen peroxide addition was the least aggressive of all those tested

Peroxone. Peroxone is an AOP that utilizes the combination of hydrogen peroxide and ozone to form the hydroxyl radical without utilization of UV light (McGuire and Davis 1988). The results reported by Glaze et al. (1988) indicated that peroxone could effectively remove chlorinated solvents from the groundwater. Since peroxone does not require the addition of high concentrations of chemical oxidizers and UV light, it is estimated that reductions in treatment costs as high as 50 percent may be realized. Langlais et al. (1991) present the following mechanism for the formation of the hydroxyl radical during peroxone treatment:

Discussions with French researchers indicate that some water utilities in France are currently using peroxone to treat millions of gallons per day of pesticide contaminated groundwater (Personal communication with Dr. Marcel Dore, University of Poitiers 1992). The French researchers claim that treatment costs are on the order of \$0.05 per 1,000 gallons treated.

Glaze et al. (1988) performed laboratory scale studies on the ability of peroxone to remove TCE and tetrachloroethylene (PCE) from a contaminated groundwater. The results proved positive enough to warrant subsequent pilot-scale evaluations (Aieta et al. 1988). Both the bench and pilot studies concluded that the reaction rate of TCE and PCE was increased by factors of 1.8 to 2.8 and 2.0 to 6.5, respectively, as opposed to those achieved by ozonation alone. Apparently, TCE was reactive toward ozone alone as well as the hydroxyl radicals formed; PCE was only reactive toward the radical species. Both studies indicated that a hydrogen peroxide-to-ozone ratio between 0.25 and 0.5 was optimal for removing TCE and PCE from the groundwater studied.

Peroxone reactors are designed very similarly to ozonation chambers except that the provision of hydrogen peroxide must be included within the design. Optimal designs incorporate continual hydrogen peroxide dosing instead of batch addition. This approach increases hydroxyl radical formation due to the establishment of a highly efficient hydrogen peroxide to ozone concentration ration of approximately 0.25 which was found by Glaze et al. (1988) to be optimal. This ratio exists because both hydrogen peroxide and ozone can serve as significant radical scavengers (Hong et al. 1996; Kuo et al. 1997). Therefore, careful operation and design of peroxone systems must be undertaken to ensure maximum reaction rates and to minimize costs. Zappi et al. (1994) designed a peroxone pilot scale reactor that utilized traditional ozonation bubble columns along with a hydrogen peroxide injector system. They successfully treated low levels of pesticides and various military pollutants from a shallow aquifer. Additional work on this pilot unit resulted in the incorporation of a semicontinuous hydrogen peroxide injection system which greatly increased treatment effectiveness.

**Sonolytic Oxidation.** Sonolysis is the irradiation of a medium with ultrasound. Ultrasound is soundwaves produced within the 18 kHz to 100 MHz range (Mason 1991). Ultrasound waves are typically divided into two implementational categories; power and diagnostic ultrasound. Power ultrasound represents wavelengths ranging from 20 to 100 kHz and are most often associated with chemical and cleaning operations. Diagnostics ultrasound falls within the 1 to 10 MHz range and is typically used in the medical industry for non-invasive assessments of patients.

Power ultrasound has been in a wide variety of industrial operations ranging from enhancing sludge dewatering potential (Hall 1982) to inactivation of bacteria (Burleson and Pollard 1975). The most widespread usage of power ultrasound has been cleaning of hard reach areas of metallic instrumentation and jewelry (Mason 1991). The use of sonolysis for enhancing chemical reactions is growing (Grinthal and Ondrey 1992). On-going research efforts are assessing if ultrasound can significantly enhance or actually initiate chemical reactions used in the decontamination of both soils and waters (Grinthal and Ondrey 1992; Zappi 1995).

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The primary mechanism for enhancing chemical reactions using ultrasound is cavitation. Cavitation is a physical effect in which tiny microbubbles are produced through the oscillation of the water molecules as powerful sound waves promulgate through the water. Three discrete mechanisms associated with cavitation have been identified (Suslick 1990): nucleation, bubble growth, and implosive bubble collapse. The stretching effect causes the formation of the microbubbles (nucleation [Mason 1991]) as the stretched water molecules retract; thereby, forming intense vacuum pressures. Negative pressures as high as 500 atmospheres have been reported (Suslick 1990). Microbubbles are formed at "weak spots" in the aqueous matrix of the liquid occupied by dissolved gases. During the collapse of the microbubbles, the violent fractional forces exerted on the water molecules result in tremendous heat generation as high as 5,000°C (Suslick 1990).

A variety of beneficial reactions are possible through the sonolysis of aqueous media. Of primary interest are the formation of hydroxyl radicals using the mechanism proposed by Riesz et al. (1990):

 $\begin{array}{l} H_2O \dashrightarrow H + OH \\ H + OH \dashrightarrow H_2O \\ H + OH \dashrightarrow H_2O \\ H + H \dashrightarrow H_2 \\ OH + OH \dashrightarrow H_2O_2 \\ H + O_2 \dashrightarrow HO_2 \\ H + HO_2 \dashrightarrow H_2O_2 \\ H - HO_2 \dashrightarrow H_2O_2 \\ HO_2 + HO_2 \dashrightarrow H_2O_2 + O_2 \\ H_2O + OH \dashrightarrow H_2O_2 + H \end{array}$ 

Power ultrasound has also been investigated for use in the water treatment industry by a variety of researchers (Calabrese and Kostecki 1989; Kotronarou at al. 1992; Dahi and Lund 1980; Chen 1972; Tumeo et al. 1991). Sierka (1976) evaluated removal of a variety of simple organic compounds using ozonation coupled with sonolysis. They also investigated the impact of sonolysis on ozone mass transfer. His results indicated that sonolysis reduced the aqueous phase equilibrium concentrations due to degradation of the ozone into radical species. He also concluded that the use of ozone and sonolysis resulted in an effective treatment system for the majority of the compounds evaluated.

Heckroth (1974) provides cost data for the sonolytically enhanced ozonation. Heckroth terms the combination of sonolysis and ozonation for water treatment as sonozone and estimates treatment costs to fall within the \$0.10 to \$0.25 per 1,000 gallons treated range. These costs represent results from several large scale pilot evaluations of sonozone for treatment of municipal drinking water where removal of gross pollutants such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and various atheistic parameters, not the removal of complex organic compounds that are usually of concern for industrial entities and groundwater remediation systems.

In 1985, Sierka et al. began experimenting with using ultrasound and oxidation catalysts as a potential treatment option. These efforts focused on the evaluation of the feasibility of two oxidation processes, sonozone and Raney-nickel (Ra-Ni) catalyzed oxidation, for treatment of a synthetic 100,000 ug/l explosive contaminated wastewater composed of 70 percent TNT and 30 percent cyclotrimethy cyclotrimethylenetrinitramine (RDX). This wastewater was formulated at these levels to simulate pink water. Process parameters investigated included sonolysis power level (5W to 50W) using sonolytic frequencies within the 800 kHz to 900 kHz range, pH, initial explosives levels, and reaction temperature. Their results indicate that increasing system pH from 5.43 to 10.0 during ozonation (100 mg O<sub>3</sub>/min) improved TNT percent removal from 83 percent to 97 percent after 15 minutes of batch treatment. Use of sonolysis under the same conditions yielded increased percent removals of 7% and 9% for pHs of 5.43 and 10.0, respectively. However, at best, these experiments only achieved final TNT concentrations of 52,700 ug/l after 15 minutes of treatment. Sonolysis alone did not yield appreciable TNT removal. Increasing sonolytic power during ozonation from 5W to 50W increased TNT removal from 50% to 82% after 60 minutes of treatment. They did not observe significant differences in ultrasound performance between sonic frequencies of 60.0 kHz, 859 kHz, and 1,007 kHz. He did not observe a strong dependency of removal kinetics on initial TNT concentration (i.e. zero order kinetics). Sierka and company also noted an approximate fourfold increase in percent removal of TNT over a 60 minute period by increasing system temperature from 25°C to 59°C. The authors conclude that a system utilizing high pH and temperature ozonation is a technically and economically attractive option to UV based oxidation systems.

The benefits of adding ultrasound to ozonation and peroxone systems have been investigated (Zappi 1995). It was found that the addition of only 48 watts of 20,000 hz ultrasonic power was able to remove TNT and 1,3,5-trinitrobenzene (TNB) at rates two orders more rapid than without ultrasonic irradiation. It was also discovered that sonic irradiation did not enhance peroxone, but initiated a secondary hydroxyl radical generation mechanism (i.e. sonozone) which did result in improved TNT removal over ozonation. For both sonozone and sono-peroxone, reactor residence times of 30 minutes were sufficient to remove 1,000 ug/l of TNT in the influent to levels below the analytical

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detection limit (<2 ug/l). Of the two systems, the sonozone system appeared to out-perform the sono-peroxone system.

Although, sonolytically enhanced oxidation appears very promising, little effort has been expanded toward development of a pilot scale reactor. Several units incorporating venturi meter induced cavitation have been marketed, but no vendor group has developed a sonolytically powered system capable of full scale operation. In fact, most of the research and development efforts continue to focus on process chemistry. Our group is currently involved in activities that are focused on issues pertaining to scale-up of sonolytic based AOPs from the bench scale to pilot scale dimensions. Additionally, a research team housed at the DOE's Argonne National Laboratory is currently developing an in situ groundwater treatment system to be housed within well bores (personal communication with Dr. Bob Peters, ANL). It is hoped that a commercial unit will be used at a field setting within a few years.

#### SUMMARY

Chemical oxidation processes appear to offer a very flexible and economic option for cleanup of contaminated aquifer systems and treatment of industrial wastewaters. Care must be taken with the selection of a proper chemical oxidation process that balances treatment efficiency with reduced costs. Many organic pollutants, that are refractory to other competing treatment technologies, can be treated using chemical oxidation. A strategy for selection of an appropriate oxidation technology must be designed and proper evaluations (bench-scale tests) performed to ensure an effective oxidation process is selected (Zappi et al. 1994). Design engineers having experience with the application of AOPs for water treatment suggest that the various candidate processes be evaluated based on a design life basis (personal communication with Mr. Ted Streckfuss, US Army Corps of Engineers-Omaha District). Also, as a rule of thumb, UV/peroxidation systems often present higher O&M costs over the UV/ozone system; however, the capital costs associated with the UV/ozonation system much higher than those associated with is UV/peroxidation systems. Clearly, total system evaluation and related costs are in order for the proper estimation of process economics.

Continued research by our group will focus on further process development and refinement. Although not a panacea, usage of AOPs by interested parties is sure to increase as regulatory drivers require improved treatment and the US prepares to continue its international leadership role in environmental restoration and preservation. Expanding the utility and reducing limitations, both in terms of cost and performance, is paramount to site managers and industrial environmental groups. Of particular interest are those AOPs that do not require UV light for hydroxyl radical production. Advantages of an AOP that does not need UV is that influent UV transmissivity is not a concern. Therefore, Fenton's Reagent, sonolytical oxidation, and peroxone are considered prime development targets. In fact, our group is currently expanding applications of these "dark" AOPs into intriguing areas such as soil remediation and air phase treatment.

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