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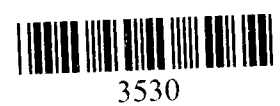
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ASSESSING ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF TRINITROTOLUENE CONTAMINATED GROUNDWATER

by

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ABSTRACT

Advanced oxidation processes (AOPs) are groundwater remediation techniques that use powerful chemical oxidizers under catalyzing conditions to produce hydroxyl radicals which in turn can destroy a wide variety of organic compounds. The USAE Waterways Experiment Station (WES) has been investigating AOPs, traditional and non-traditional, for treatment of trinitrotoluene (TNT) contaminated groundwaters. Processes evaluated include ultraviolet (UV) catalyzed ozone/hydrogen peroxide based AOPs which have been traditionally used for treatment of contaminated wastewaters. WES studies indicate that these processes also show promise for treatment of explosives contaminated groundwaters. Non-traditional AOPs are also currently being evaluated by WES for treatment of TNT contaminated groundwaters. These processes include peroxone and ultrasonically (sonolysis) catalyzed oxidation.

The test influent used in this study was a 1,000 ug/l TNT solution made of partially hydrated TNT and distilled, ionized water. The UV based AOPs had the highest TNT degradation kinetics, while the non-UV based systems proved to be more economical for the same level of treatment. The results of these studies indicate much promise for treating TNT contaminated groundwaters with the non-traditional AOPs at a potential cost savings as high as an order of magnitude over the more traditional AOPs. The addition of sonolytic catalyzation generally increased TNT degradation kinetics.

INTRODUCTION

The US Department of the Army has numerous sites that are contaminated with explosive compounds. These chemicals threaten the overall integrity of one of the country's most valuable resources; groundwater. Unfortunately, extensive groundwater contamination has already occurred at many of these sites, requiring that some form of groundwater remediation be initiated. Existing state-of-the-art technology, activated carbon adsorption, can be cost prohibitive and does not result in the on-site destruction of the contaminants. Activated carbon simply results in the transfer of contaminants from the liquid phase onto the solid phase. Also, some difficulty in the disposal of explosives laden spent carbon has been encountered.

Although activated carbon is a valid option for treating contaminated groundwaters, innovative treatment techniques such as chemical oxidation processes may offer both a cost effective and technically sound alternative. Selected data for 2,4,6-trinitrotoluene (TNT) oxidation in distilled water solutions using both traditional and non-traditional AOPs are presented. These research efforts were performed by the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, within the WES Hazardous Waste Research Center.

ADVANCED OXIDATION PROCESSES

Chemical oxidation processes are a group of treatment technologies that use powerful chemical oxidizers and/or ultraviolet light to destroy organic solutes and pathogenic organisms in water. These processes have traditionally been used by United States municipalities for treatment of drinking water. Over the last twenty years, oxidation processes have been successfully used for cleanup of contaminated groundwaters and wastewaters.

Chemical oxidizers commonly used in oxidation processes for treating contaminated groundwater include ultraviolet photolysis in conjunction with ozone, hydrogen peroxide, and/or potassium permanganate addition. Since the mid-1970's, the WES has been developing and evaluating chemical oxidation processes for treatment of groundwaters contaminated with a wide variety of organic contaminants. The early research efforts at the WES indicated that chemical oxidation processes were technically attractive; however, the economics of the process versus alternative treatment options during that period were not conducive toward widespread application. Today, recent technology developments and stricter environmental regulations have made chemical oxidation processes much more cost competitive. The WES, under the Army's Environmental Quality and Technology Program, is currently performing research in the development and refinement of chemical oxidation processes for use in the remediation of explosives contaminated groundwaters.

Of primary research interest by WES are those chemical oxidation processes that result in the generation of the hydroxyl radical, (OH \cdot). These processes are by definition referred to as advanced oxidation processes (AOPs). The hydroxyl radical is an oxidizer species that is much more powerful than traditional oxidizer species such as ozone (O $_3$) and hydrogen peroxide (H $_2$ O $_2$). Due to its high reactivity, the hydroxyl radical is very unstable requiring that it be produced on-site. There are a variety of chemical oxidation processes that may be used for production of hydroxyl radicals. Examples of such processes include combinations of ultraviolet (UV) light, hydrogen peroxide, and/or ozone.

Degradation of TNT during AOP treatment is accomplished through one or more of the following oxidation mechanisms:

- a. Oxidation by the parent oxidizer (ozone or hydrogen peroxide),
- b. Oxidation by secondary oxidizer species (hydroxyl radicals),
- c. Direct photolysis by UV light,
- d. The synergistic effect of all of the above mechanisms.

The final products of TNT chemical oxidation reactions are usually simple organic acids, carbon dioxide, water, residual levels of oxidizers, and nitrate. None of these compounds pose a threat toward human or environmental health. However, in some cases, chemical oxidation may not be effective in completely oxidizing the TNT into environmentally benign chemical species. Trinitrobenzene (TNB) is a commonly detected oxidation intermediate of incomplete TNT oxidation. Understanding treatment kinetics is crucial to the safe application of oxidation processes for TNT contaminated groundwater remediation. Figure 1 presents a proposed oxidation pathway for TNT. This pathway is currently being validated by WES researchers. A properly designed oxidation process will completely cleave the aromatic ring into the above listed "safe" oxidation products.

TRADITIONAL AOPs

In terms of groundwater remediation, most applications of AOPs involve the addition of ultraviolet (UV) light into ozone or hydrogen peroxide dosed reactors. Ultraviolet light is a relatively short wave radiation that is capable of exciting a wide variety of chemicals including organic compounds and chemical oxidizers. The two most common types of UV sources (lamps) in groundwater treatment are low and medium pressure mercury (Hg) vapor UV lamps. Low pressure mercury vapor lamps emit the majority of its spectra at or near the 254 nm wavelength. Medium pressure mercury vapor UV lamps emit a spectra that is extremely wide in comparison to low pressure UV lamps. Unlike low pressure Hg vapor UV lamps, medium pressure Hg vapor UV lamps produce a significant amount of photons within the 200 nm to 250 nm range which is the band where explosive compounds and hydrogen peroxide absorb UV light. Low pressure Hg vapor UV lamps have a lower energy consumption and are more energy efficient than medium pressure lamps. Improved energy efficiency results in less heat generation which is an inefficient use of expensive electrical power. Although more energy intensive, medium pressure Hg vapor UV lamps produce more UV photons available for contaminant destruction and hydrogen peroxide excitation (i.e. radical production if using hydrogen peroxide). Increased photon production at key wavelengths usually equates to more rapid degradation kinetics through improved quantum yield (the amount of photons within a given wavelength involved in beneficial reactions over the total amount emitted by the lamp).

Ozone based AOPs have traditionally almost exclusively used low pressure Hg vapor UV lamps (LPUV). WES has successfully used UV/ozone systems for treatment of a wide variety of contaminated groundwaters. The major drawback to UV/ozone based systems is the relatively high capital costs associated with the ozone generation equipment. Positive aspects of UV/ozone based systems includes relatively lower operational and maintenance (O&M) costs, little or no heat generation, and a lower potential for fouling of the quartz sleeves housing the UV lamps.

On the other hand, hydrogen peroxide based AOPs have traditionally used medium pressure Hg vapor UV lamps (MPUV). Compounds successfully treated using this technology generally include the same compounds treated by the UV/ozone based systems. UV/hydrogen peroxide based systems usually have higher O&M costs and a higher fouling potential for the quartz lamp housing sleeves. Advantages of UV/hydrogen peroxide processes include increased degradation kinetics, little or no process off-gasses, reduced potential for oxidation intermediates, and lower capital costs.

Costs associated with treatment of TNT contaminated groundwater using traditional UV based AOPs range from approximately \$1.00 to \$5.00 per thousand gallons treated. Commercial vendors of these processes are currently available. WES has experience with most of these vendors and, in general, they all market well designed process equipment that are quite effective for treating organics contaminated groundwaters.

Figure 2 presents treatment data for a 1,000 ug/l TNT dosed distilled water solution using traditional UV based AOPs. These results were generated by WES using one liter, bench scale reactors. As shown in Figure 2, both traditional AOPs, MPUV/hydrogen peroxide and LPUV/ozone sparging, achieved extremely rapid TNT removals. The MPUV/hydrogen peroxide does appear to be more aggressive than the LPUV/ozone sparged system based on complete TNT removal with five minutes of treatment as compared to complete TNT removal achieved by the ozone based system within ten minutes. TNB, the predominant intermediate of TNT oxidation, was not detected in any of the post five minute study effluents.

NON-TRADITIONAL AOPs

Peroxone is one of the most innovative AOPs for treatment of organics contaminated groundwaters. Until recently, application of this process has been limited to drinking water treatment. Bench and pilot studies performed by the WES and other research organizations indicate a high potential for utilization of peroxone for treatment of contaminated groundwaters. Peroxone involves the generation of hydroxyl radicals through reaction of ozone with hydrogen peroxide. Optimal stoichiometric ratios of hydrogen peroxide to ozone are in the 0.25 to 1.5 range. Estimated treatment costs range from \$0.10 to \$1.00 per thousand gallons treated. This represents a potential cost savings of an order of magnitude over the costs of traditional UV based AOPs. Discussions with French researchers indicate that some French municipalities are removing low levels of pesticides from drinking water at a cost of only \$0.02 per thousand gallons at flowrates within the hundreds of millions of gallons per day range. The City of Los Angeles, California, has recently installed a pilot scale peroxone water treatment plant with a few million gallon per day flow capacity. Preliminary results are encouraging and process economics attractive.

Ultrasound are soundwaves produced from 20 khz to 100 khz frequency range by electrical devices. Ultrasound is commonly used for cleaning small objects where extremely clean conditions are required in hard to reach areas. Ultrasound has also been used to catalyze slow chemical reactions. Using a directional 40 watt ultrasonic probe along with one liter, glass reactors, WES has evaluated the feasibility of using ultrasound to increase the reaction rate of TNT during ozonation and peroxone oxidation. Mechanisms responsible for increasing reaction rate are improved mass transfer, production of hydroxyl radicals, and localized pockets of high pressure and temperatures. Unfortunately, there are little or no cost information of ultrasonic reactors. Furthermore, there are no large scale ultrasonic chemical reactors available at this time for evaluation of ultrasonic catalyzed oxidation on the pilot scale.

Figure 3 presents the results of both peroxone and ultrasound catalyzed oxidation. Comparing this figure to Figure 2, it can be seen that the non-traditional AOPs have slower TNT removal kinetics than the more traditional UV based AOPs (approximately four times slower). However, peroxone, a non-traditional AOP, can be implemented at a potentially much lower cost. A 10 mg/l hydrogen peroxide dose in the peroxone system indicates potential to remove all of the TNT within 30 minutes of treatment. Subsequent studies (not shown) indicates that a 100 mg/l dose was able to achieve similar treatment within less than 20 minutes of batch treatment.

The beneficial impact of ultrasound on ozonation and peroxone treatment is evident in Figure 3. The addition of ultrasound to the 10 mg/l hydrogen peroxide dosed peroxone system substantially enhances the rate of TNT removal at both the 20 and 40 watt dose. With increasing ultrasound intensity, from 20 watts to 40 watts, an overall increase in reaction kinetics is achieved. Ozonation in an ultrasonic field appears promising as illustrated in Figure 3. Much like the peroxone data, as the level of ultrasonic power into the ozonation system is increased, so does the overall TNT oxidation rate.

The formation of TNB in the non-traditional AOP systems was noted as presented in Figure 4. The additional 40 watts of ultrasound to the 10 mg/l dosed hydrogen peroxide peroxone system was able to completely remove all of the TNB that was formed during TNT oxidation. The 20 watt peroxone and 40 watt ozonated sonic systems indicated potential for removing the TNB within 30 minutes of treatment. The peroxone system requires treatment times longer than 25 minutes to completely remove TNB from the test solution. Data recently generated by WES indicates that higher hydrogen peroxide to ozone dosing ratios does significantly improve TNB removal. The 20 watt ozonated

sonic system did not indicate a downward trend in TNB removal indicating longer treatment times are probably required to remove the TNB to below detection levels.

ON-GOING WES RESEARCH ACTIVITIES

As knowledge of the mechanisms involved in contaminant destruction improves, it is expected that treatment costs associated with UV based systems will decrease and the range of application will increase. Of significant note, is the definition of oxidation pathways of explosives compounds (TNT, RDX, and HMX) during AOP treatment currently under investigation by the WES under collaboration with Howard University and the University of North Carolina, Chapel Hill.

The WES has performed three pilot studies at Rocky Mountain Arsenal, Commerce City, Colorado during the Fall of 1994, for treatment of three contaminated groundwaters using peroxone. The focal point of these studies was the WES designed and constructed Peroxone Oxidation Pilot System (POPS). This unit has a 0.5 to 15 gpm flowrate and is completely mobile. WES is also developing other UV based AOPs that are non-traditional in nature. The primary system under development are semi-conductor catalyzed photolysis and second generation hydrogen peroxide/UV based AOPs.

CONCLUSIONS

Recent advances in AOP technologies have made these processes cost competitive as compared to traditional groundwater treatment processes such as carbon adsorption. Design engineers currently have a wide variety of AOP configurations at their disposal for use in remediating contaminated aquifers. Traditional AOPs that utilize UV irradiation had the most rapid TNT removal kinetics of all the AOPs studied. Non-traditional AOPs, such as peroxone and ultrasonically enhanced oxidation also had appreciable removal kinetics.

Traditional UV based AOPs costs typically range from \$1.00 to \$5.00 per thousand gallons treated. Peroxone oxidation costs are estimated to range from \$0.10 to \$1.00 per thousand gallons treated. Ultrasonically catalyzed oxidation is still in a state of process conceptualization and development and as such process costs are not yet available. Ongoing research at the WES should further reduce AOP treatment costs and increase the range of applicability of AOPs toward remediation of DoD sites.

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Figure 1.

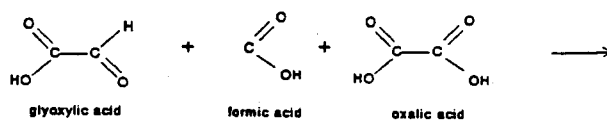
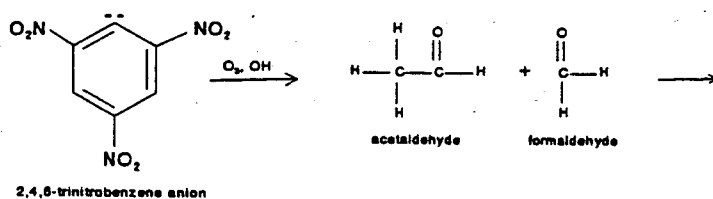
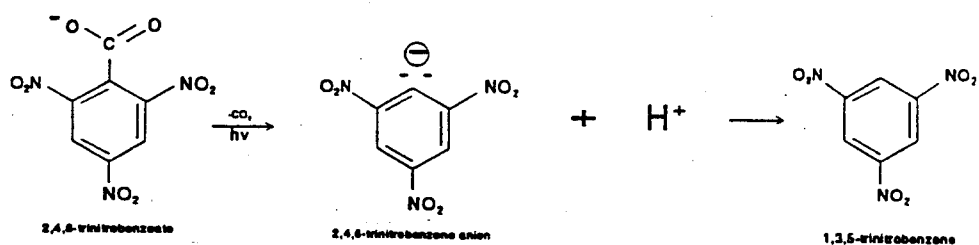
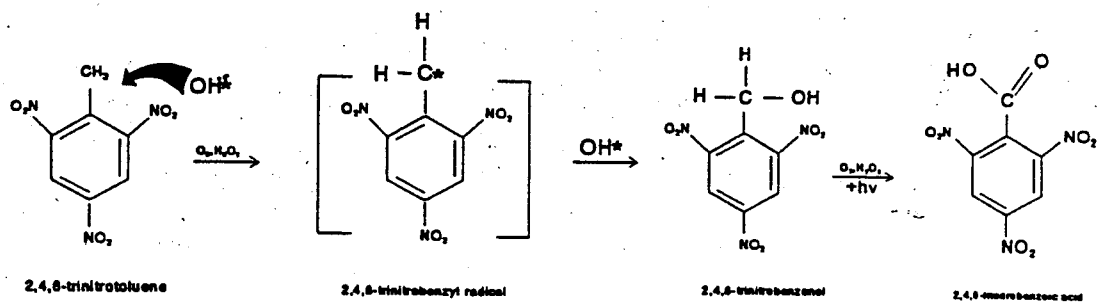


Figure 2. Evaluation of Traditional UV Based AOPs
TNT Oxidation

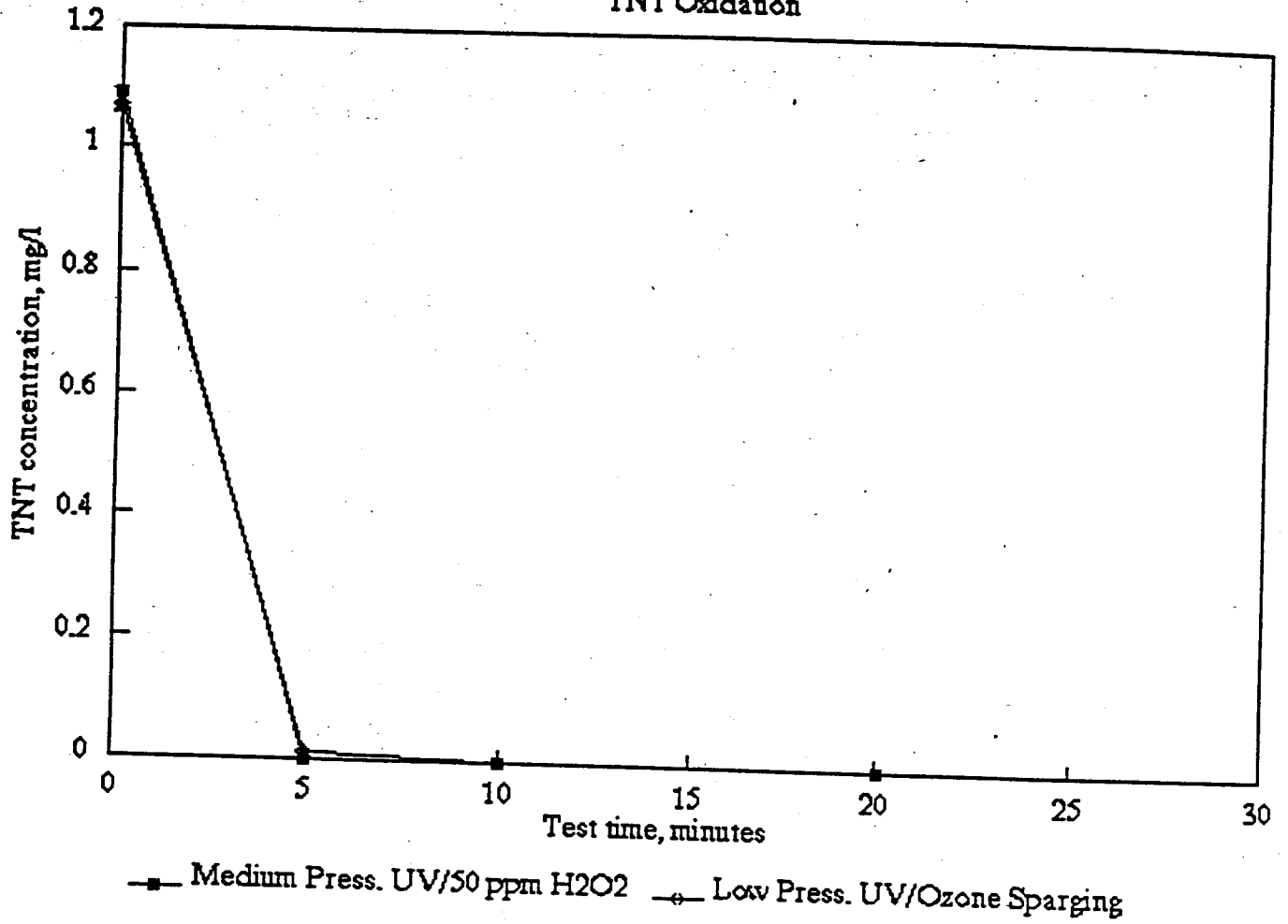


Figure 3. Comparison of Non-Traditional AOPs
Impact of Sonolysis on Reaction Kinetics

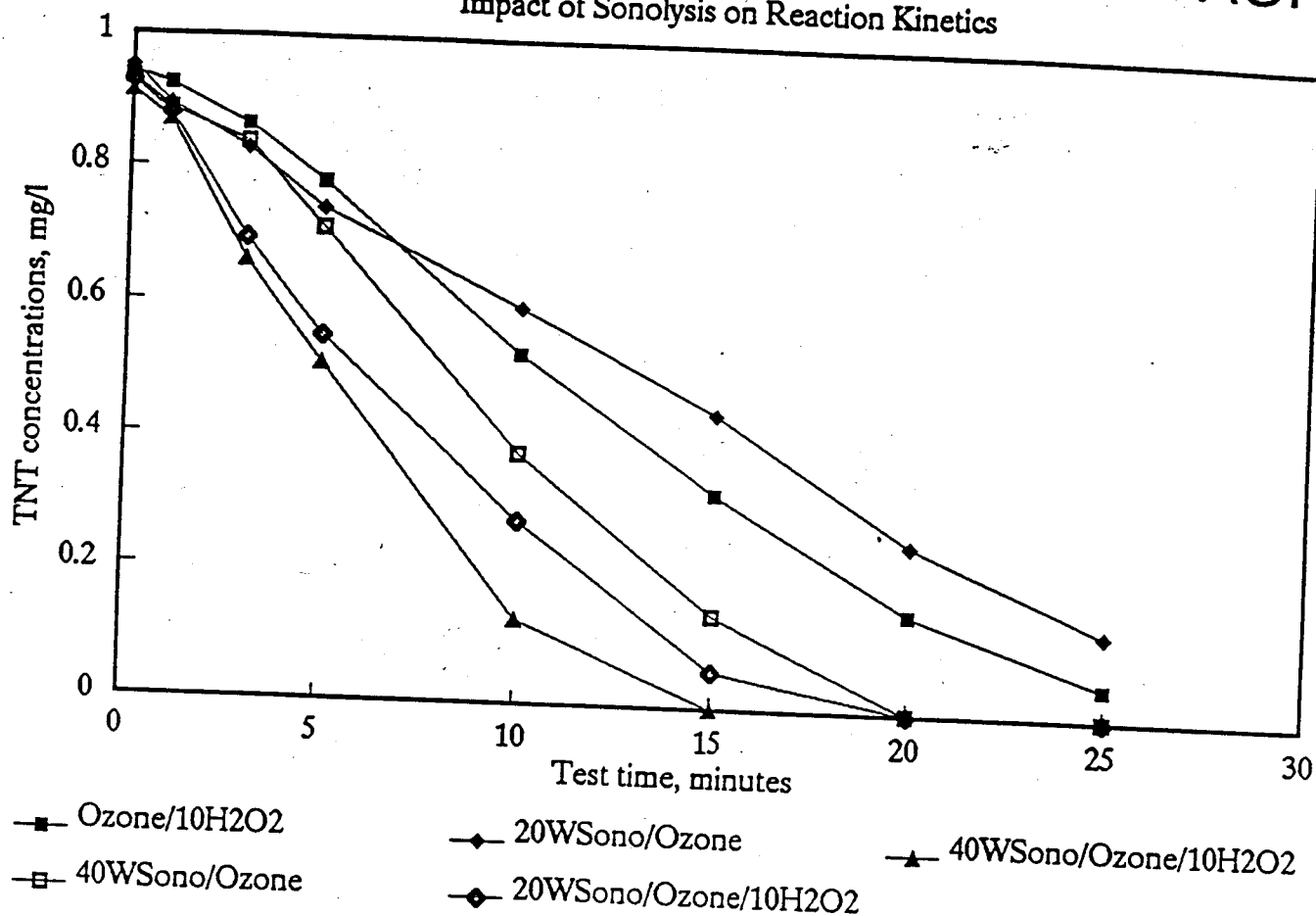


Figure 4. Comparison of Non-Traditional AOPs
 TNB Formation during Oxidation

