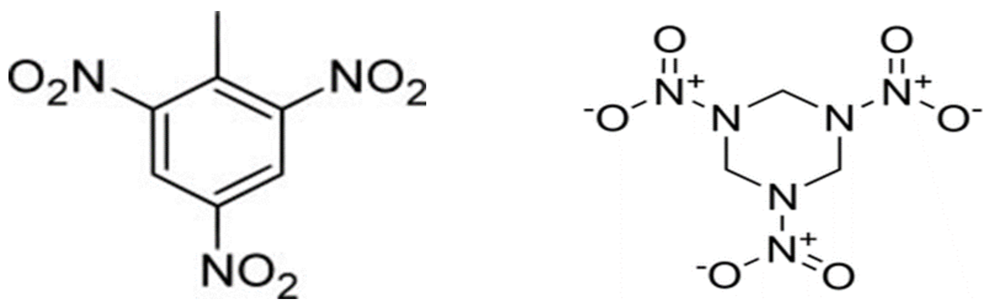
Technical Brief:
TNT and RDX Interactions with Ozone

Widely used in military and industrial applications, 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are popular explosives. TNT is identified as a yellow, odorless solid, while RDX is known to be crystalline white in its pure form.[1,2] Major manufacturing of TNT began in 1916 at the start of World War I and since then it has been heavily produced in enormous quantities at government ammunition plants for use in military munitions.[1] The Department of Defense (DOD) used a steam out and melt out processes to identify off spec, unserviceable, and obsolete munitions and reclaim unused TNT and TNT/RDX containing explosive filters. As a result, these processes generated large quantities of toxic, explosive contaminated waste and groundwater. Due to their explosive nature and high toxicity, TNT is classified as a Group C (possible human) carcinogen. TNT and RDX are compounds which must be removed when present in high concentrations in the environment.[1,2]



TNT molecule **RDX molecule**

Figure 1: TNT and RNX Molecular Structures

Methods such as ozonation alone, bioremediation, Fenton's reagent, and Advanced Oxidation Processes (AOP), such as UV/O_3, UV/H_2O_2, and O_3/H_2O_2, have proven effective in TNT degradation. However, studies involving direct molecular ozone reactions report a wide range of results on the effectiveness of ozone in TNT remediation. A study reported that TNT is destroyed through ozonation while in the presence of base, generating the 2,4,6-trinitrobenzyl anion.[4] While these laboratory results are not disputed, Piper Environmental Group Inc. (Piper) successfully utilized ozone alone to remediate TNT.

Ozone alone has demonstrated effectiveness with TNT degradation in actual remedial activities. However, most published research of laboratory studies indicate AOP reaction results have been more consistent. These studies have also supported AOP's increased effectiveness in TNT degradation in controlled settings. Lang, et al. noted that treatment of TNT with AOPs such as UV/ozone and UV/hydrogen peroxide lead to mineralization of TNT when allowed to react for 1-2 hours, producing nitric acid, carbon dioxide and water as final products.[3] Additional studies also support UV/O_3 advanced oxidation in order to achieve complete mineralization of TNT. Fleming, et al. used a 1:1 mixture of O_3 and H_2O_2 in conjunction with a pH greater than 7 to generate hydroxyl radicals and reported that RDX, HMX, and other nitroaromatics in groundwater were degraded by at least 64%.[5] Lastly, in another study, more than 99% of a TNT/RDX mixture was rapidly destroyed through UV photolysis.[6] AOP reactions are also effective for TNT by product removal of Total Organic Carbon (TOC).[6]

The Department of Energy's storage facility located near Amarillo, Texas was once used to produce munitions from high explosives during World War II. The plant became an EPA Superfund site due to elevated levels of numerous contaminants of concern (COC's), including TNT and RDX, were found in the surround-

-ing soil and groundwater. The RDX concentrations at the site are of particular concern because they are the most widespread contaminant.

A study by Adam, et al., evaluated ozone efficacy to break down and mineralize RDX in unsaturated soils and found the method was quite effective when the soil was used as a buffer to the solution pH.[7] Laboratory experiments showed that ozone (27 mg L^{-1}; 150 mL min^{-1}) was effective in mineralizing 80% of the RDX (30 mg RDX L^{-1}) provided that some soil was present to buffer the solution pH.[7] Soils treated with ozone produced 50% RDX mineralization within 1 day and greater than 80% within 7 days. These experiments also revealed that the pH of the soil is directly related to ozonation effectiveness of RDX. Elevated pH increased ozone effectiveness, while acidic conditions had the opposite effect. It was postulated that while the molecular ozone was not expected to directly attack the RDX, the hydroxyl radicals produced via indirect ozonation should be able to break down RDX in a similar form to that of an AOP.[7]

As one of the most persistent and dangerous explosive compounds found in the environment today, it is vital that TNT and RDX are broken down into safer, less hazardous compounds. Additional factors including pH and temperature also play a factor in the amount of time needed for ozone to react with 2,4,6-trinitrotoluene. It is important to note that external variables can also influence the effectiveness of this technique on TNT. Similar studies with RDX have proven the efficacy of ozone oxidation in degrading this contaminant of concern. Piper worked closely with consultants to design a pilot system here utilizing ozone alone. It was deemed successful and larger scale system was designed based on pilot study results. Piper has had extensive experience with both molecular ozone and AOP's and design custom ozone systems that will best fit the needs and specific to the Contaminants of Concern.

[1] US Environmental Protection Agency Office of Solid Waste and Emergency Response. (2012, May). *Technical Fact Sheet-2,4,6 Trinitrotoluene (TNT)*.

[2] US Environmental Protection Agency Office of Solid Waste and Emergency Response. (2012, May). *Technical Fact Sheet: Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)* (US EPA, Comp.).

[3] Lang, P. S., Ching, W.-K., Willberg, D. M., & Hoffmann, M. R. (1998). Oxidative Degradation of 2,4,6-Trinitrotoluene by Ozone in an Electrohydraulic Discharge Reactor. *Environ. Sci. Technol.*, (32), 3142-3148.

[4] *Military Explosives* (United States Department of the Army, Comp.). (1989). Headquarters, Department of the Army.

[5] Kalderis, D., Juhasz, A. L., Boopathy, R., & Comfort, S. (2011). Soils contaminated with explosives: Environmental fate and evaluation of state-ofthe- art remediation processes. *Pure Appl. Chem.*, *83*(7), 1407-1484.

[6] Lankford, P. W. (1997). *Chemical Oxidation: Technologies for the Nineties* (Vol. 4). CRC Press.

[7] Adam, M., Comfort, S., Shaw, D., Cassada, D., Morley, M., & Clayton, W. (2006). Evaluating Ozone as a Remedial Treatment for Removing RDX from Unsaturated Soils. *J. Environ. Eng.*,

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting. Our area of expertise is large remediation

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