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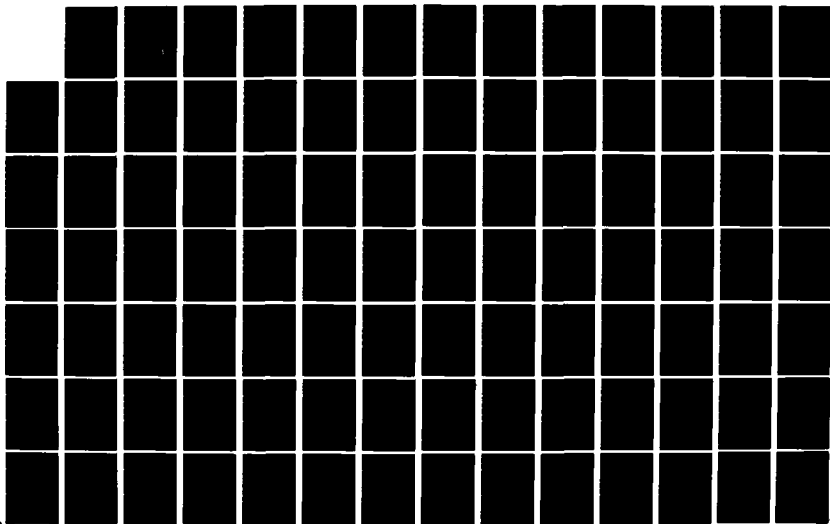
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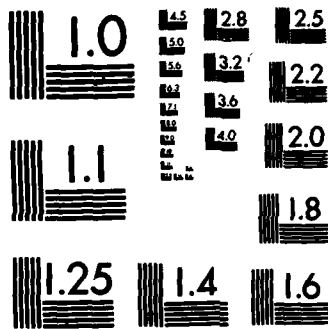
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AN ULTRASOUND CATALYZED OZONE OXIDATION PROCESS
FEASIBILITY STUDY FOR THE DESTRUCTION OF TNT
AND OTHER EXPLOSIVES IN AQUEOUS SOLUTION

CONTRACT NO. DAAK11-81-C-0030

BY

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OCTOBER 1982

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U. S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MD 21010

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Pinkwater containing TNT/RDX in the ratio 70%/30% was treated with ozone in the presence of ultrasound. Effects of the variables, initial solution pH, ultrasound power level and frequency, solution concentration and reaction temperature were studied. Reaction temperature and pH were the most important parameters with 99% TNT destruction achieved within one hour of ozonation at 59°C and an initial solution pH of 10.0.		

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ABSTRACT

This report summarizes the results of research on the treatment of primarily synthetically prepared aqueous solutions of TNT/RDX in the ratio 70%/30% but also on individual (i.e., TNT or RDX) munitions pollutants.

The first treatment process employed ozone/ultrasound. A parametric study investigated the relationship among the variables: (1) initial solution pH (5.43 $\rightarrow$ 10.0); (2) ultrasound power level (5 $\rightarrow$ 50 watts at 852.0 to 863.0 kHz); (3) ultrasound frequency level (60.6 $\rightarrow$ 1,007.0 kHz); (4) solution concentration (70/30 mg/L TNT/RDX solutions diluted with distilled water in the ratios 1/0, 1/1, 1/3); (5) reaction temperature (25 $\rightarrow$ 59°C). For example, at 59°C and an initial pH of 10.0, after 1.0 hour of ozonation, the solution pH decreased to 8.75, the TOC to 3.39 mg/L (12% remaining) and the TNT to less than 1.0 mg/L or a 99% reduction in concentration. Ultrasound was found to inhibit reaction kinetics at high temperatures and pH because it promoted radical-radical extinguishment reaction.

The second treatment process utilized Raney Nickel (Ra-Ni) either alone (Catalytic Destruction Process) or in combination with ozone (Catalytic Ozonation Process) to destroy the organics in synthetic munitions wastewaters. TNT and TOC destructions were found to be proportional to catalyst dose for both processes. At 3,475 mg/L of Ra-Ni all TNT was destroyed in less than 1.0 minute after contact with Ra-Ni. In the Catalytic Ozonation Process, TOC removals were enhanced with increased ozone dose, but TNT destruction rates were reduced.

The third study area involved the recycling of Ra-Ni. Activity levels of Ra-Ni were reduced with each successive recycle; however, with extended reaction periods, this problem was somewhat alleviated. The optimum reactivation procedure for Ra-Ni was not found.



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KEY WORDS

TNT, RDX, ultrasound-ozone, Raney-Nickel, wastewater treatment, munitions

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1.0 INTRODUCTION

Wastewaters generated in the production of trinitrotoluene (TNT), dinitrotoluene (2,4 DNT, 2,6 DNT), cyclotrimethylenetrinitramine (RDX), homocyclonite (HMX) and ammonium picrate (explosive D) represent difficult to treat effluents which present an array of environmental problems. One of the more visual problems occurs when after neutralization of these acidic wastewaters, they are exposed to sunlight resulting in a deep pink color.

Pink water is a aqueous solution of TNT which has turned pink from a virtually colorless condition after exposure to ultraviolet light (photolysis). The pink color persists even after dilution with uncontaminated clean water to a few ppm. In addition, it has been reported that 2.6 ppm of TNT is toxic to bluegill (*Lepomis macrochirus*) fish [1].

Pink water is produced from several process waste streams such as: (a) TNT contact with plant cleanup and scrubber water during manufacturing, and load, assemble and pack (LAP) operations; (b) condensate from red water evaporative concentration and incineration. Red water is a complex solution containing 17% (by weight) of organics which includes sulfonated nitro toluene isomers and complex, unidentified dye-bodies. Also a number of inorganic salts are present including sodium nitrate, sodium sulfate, sodium sulfite and sodium nitrite [2]. Pollutant concentration and wastewater volume of pink water vary from process to process and from plant to plant. Plants which manufacture TNT or unload TNT from obsolete warheads can be characterized as having a large wastewater volume containing high concentration of dissolved TNT. Table 1 presents TNT levels in pink water from several munitions plants [2].

TABLE 1. REPORTED TNT CONCENTRATION IN PINK WATER

<u>Source</u>	<u>Range (mg/L)</u>
Red Water Evaporator Condensate	1.4 - 16
LAP Cleanup	1 - 178
LAP Scrubbers	2 - 80
Laundry Wastes	2.7 - 25.4

Generally, wastewater from a typical manufacturing plant may contain from 40 to 120 ppm of TNT and lesser amounts of 2,4 dinitrotoluene (DNT) [3]. Pink water from

LAP facilities usually contains a higher concentration of TNT, which may exceed 100 mg/L and other nitrocompounds, chiefly RDX. RDX is extremely resistant to biological oxidation and is toxic to water fleas (*Daphnia magna*) [4].

Treatment approaches for munitions wastewater reported in the literature encompass biological, combinatorial biological-chemical and physical-chemical methods. In the latter category are included adsorption onto activated carbon or macro-reticular resins, chemical coagulation-flocculation with surfactants containing amino and quaternary ammonium groups followed by filtration to remove the precipitates [5] and catalyzed and noncatalyzed chemical oxidation with chlorine, ozone, and hydrogen peroxide [6].

The biological treatability of nitrocompounds (i.e., TNT and RDX) has been studied since 1938 [7]. However, treatment efficiency not only remains questionable but also has the disadvantage of requiring a long hydraulic detention time (e.g., 14 hours for 67% removal of 20 mg/L of TNT in the combination of munitions and domestic wastewater) to destroy the pollutants contained in the large daily output of wastewater (e.g., 240 gal/ton of TNT at Radford Army Ammunition Plant) [8].

Activated carbon adsorption following plain settling and diatomaceous earth filtration to remove suspended solids is one of the most effective physical-chemical treatment methods and is employed at a number of munitions installations [2]. However, spent adsorbents are difficult to regenerate chemically (i.e., with toluene or acetone) and hazardous to regenerate thermally, when the concentration of explosives exceeds 8% of the total adsorbent weight [9]. Adsorption by polymeric adsorbent resins manufactured by Rohm and Hass Company has been proved to be technically feasible [10], but the resin cost renders the process economically prohibitive.

An example of a combinatorial biological-chemical process is reported by Tucker et al. [11] in which a mixture of two industrial wastes from the Radford Army Munitions Plant were treated in a column reactor packed with either activated carbon or sand onto which an active biomass was attached.

Edwards and Ingram [12] have demonstrated that 90% of the color present in fresh TNT stellite waste could be removed by the oxidant, chlorine. Unfortunately, 9,000 ppm of chlorine were required.

In a report by Andrews and Osmon [13] it was noted that a 100-ppm synthetically prepared TNT solution could be eliminated in one hour by an optimum combination of ultraviolet light and hydrogen peroxide (H_2O_2) in a continuous flow system. In another report, Andrews [14] stated that 1:2 and 1:4 dilutions before UV/ H_2O_2 treatment of

munition plant pink water were necessary since the initial color of the effluent was sufficiently intense to absorb the UV light and thus negatively affected the photooxidation process. Also a wiper mechanism was required to keep the quartz tube, which encased the UV light, free from deposits which would likewise interfere with light transmission.

Fochtman and Huff [15] demonstrated the beneficial effect of UV light in the ozone oxidation of munitions wastewaters. Pink water containing 63 mg/L of total organic carbon (TOC) when treated with 2% ozone for one hour showed a TOC decrease from 63 to 56 mg/L but no further decreases were observed even after an additional 2.5 hours of ozonation. By comparison when the ozonations were carried out with UV-illumination, there was a decrease to 17 mg/L in two hours.

Farrell et al. also used ozone/UV light in combination to treat pink water on a volume basis for an influent TOC of 70 mg/L and an effluent of 1 mg/L, the ozone requirement was 910 mg/L and the UV requirement 770 watts/L. Actual pink waters showed greater resistance to oxidation than synthetically prepared munitions wastewater.

1.1 MUNITION INDUSTRY WASTEWATER TREATMENT SYSTEMS CHOICE

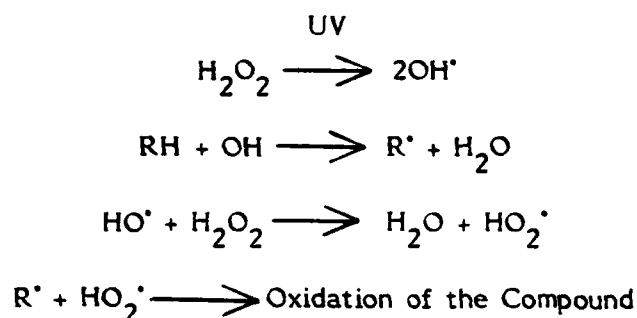
Each of the proposed munitions wastewater treatment approaches previously discussed has advantages and disadvantages. For example, aerobic biological systems have favorable stoichiometry in that only oxygen input is required. Likewise, the kinetics are generally acceptable if the system is operating at steady state. The major drawbacks of a biological system center on a lack of ability to handle shock loads, long start-up times, high manpower requirements, excess cell solids handling facilities and most importantly the generation of biological partial oxidation by-products which, in themselves, are more toxic than the original pollutants.

Adsorption systems overcome many of the above problems, such as toxicity and the fact that soluble materials are not converted to insoluble forms (i.e., biomass), yet they have other disadvantages. In the case of activated carbon, acceptable thermal regeneration procedures have not been developed and while chemical extractions such as the hot acetone methods proposed by Demek et al. [17] are technically feasible, they would in themselves create a difficult water pollution problem.

Total chemical oxidation to innocuous end products such as $\text{CO}_2 + \text{H}_2\text{O}$ would appear to be the most environmentally acceptable process. The major impediments to this technique are high stoichiometric demands and slow kinetics. The addition of a

catalyst would improve the latter and by judicious design also may improve the former.

Effective catalyst utilization requires consideration of the reaction mechanism. For example, Andrews and Osmon [13] proposed that the mechanism of the action of UV-light on H_2O_2 and the subsequent reaction of its photo-degradative species with organic material (R) proceeds by the following reactions:



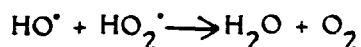
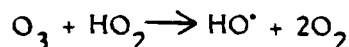
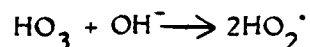
In these equations, $R^\bullet$ is representative of aromatic species (i.e., TNT) and it is apparently cleaved upon subsequent oxidations. These equations point out that UV-light initiates the breakdown of H_2O_2 to hydroxyl radicals which, in turn, oxidize other organic and inorganic materials.

1.2 AN ULTRASOUND CATALYZED OZONE OXIDATION SYSTEM

From the above discussion, it is evident that a catalyzed chemical oxidation system which would mineralize organic carbon and not produce toxic by-products would be an optimum munitions treatment system. A process consisting of an ozone-sparged reactor employing ultrasound as a catalyst is a potential treatment system choice and the subject of this research. Likewise, experiments were conducted with Raney-Nickel (Ra-Ni) as a catalyst for ozone oxidation. Additionally, experiments were conducted where Ra-Ni was contacted with aqueous solutions TNT/RDX.

1.2.1 Ozone Characteristics

Ozone (O_3) is an allotrope of oxygen which boils at minus 112°C and is 20 times more soluble than oxygen in water. The oxidant is harmful to humans at high concentrations, but is detectable by man at 0.01 and 0.05 ppm levels in the air's atmosphere. Ozone is relatively unstable in water and its decomposition has been described by the following model [18]:



Here the free radicals $\text{HO}_2^\cdot$ and $\text{HO}^\cdot$ are extremely chemically reactive and disappear by reaction with organics or inorganics and by self-quenching reactions. It should be noted that as pH increases the half-life of ozone decreases.

Due to the high oxidation potential of ozone and its by-products, it will react with a wide variety of materials. Ozone is best known for its ability to decolorize and to react with aliphatic carbon-carbon [19, 20] double bonds. Ozone reacts readily with phenol in aqueous solution to produce oxidized aromatic compounds (i.e., dihydroxylbenzenes, catechol) which upon further oxidation undergo ring cleavage to produce aliphatic unsaturated diacids and hydroxylated saturated diacids. Additionally, glyoxal, glyoxylic acid, glycolic acid, and oxalic acid are formed together with CO_2 . Nitro, amino and sulfuric acid groups on aromatic rings are split off by ozonation. Chlorobenzene reacts with ozone by ring rupture to yield the same aliphatic products as phenols [21].

1.2.2 Ultrasonics - Introduction, Background Theory and Applications

Piezoelectric effect is the name given to the redistribution of electrical charge resulting from pressure deformation of a crystal [22]. In the case of sonar, mechanical deformation of a transducer crystal generates electrical signals. Conversely, an ultrasonic generator involves the application of a high-frequency electrical voltage to a crystal which, in response, produces mechanical deformations. With the development of suitable transducer crystal materials, it is now possible to generate mechanical ultrasonic radiation with a relatively modest power expenditure. The amplitude of vibration can be increased by the use of a "horn" or mechanical transformer, which increases power intensity by stepping down the vibrating area.

The relatively low frequency (20 kHz) devices have found broad application in biological and biochemical research as cell disintegrators. Much of the literature available deals with biological applications of ultrasound.

As the cost of ultrasound equipment decreases and the potential of the technique becomes more apparent, the applications in science and in industry are multiplying rapidly. Shoh [23] has summarized the applications field. Although numerous investigators have studied the effects of ultrasonic irradiation on pure substances and on aqueous solutions, there are few examples of the use of ultrasound industrially to enhance a chemical processing operation. These process applications have been reported by Dutta [24].

An interesting and complex array of phenomena are observed when fluids, particularly dilute aqueous solutions, are exposed to ultrasonic irradiation.

An ultrasound wave subjects the fluid particles to rapid back-and-forth motion. The displacements, velocities, and accelerations associated with this motion are termed "first-order effects". A related group of phenomena resulting from the motion are termed "secondary effects". These phenomena are cavitation, acoustic streaming, sonoluminescence, and interfacial instability. There is sufficient literature available to strongly suggest that mass transfer, reaction rates, and reaction potentials would be enhanced by the application of ultrasonic irradiation to munitions wastewaters. The secondary effects of ultrasonic irradiation will follow, as it relates to the destruction of organic matter in aqueous solution [25, 26].

The term "cavitation" is used to describe the process of nucleation, growth, and collapse of bubbles containing either gas or vapor. The minimum acoustic intensity, or acoustic amplitude required to produce cavitation is called the cavitation threshold. The cavitation threshold of homogeneous liquids is often quite high, but the presence of bubble nucleation sites within the liquid can greatly reduce the effective strength of the liquid; and, with it, the cavitation threshold. In general, the onset of cavitation is influenced by the acoustical pressure, the nature and amount of dissolved gases present (i.e., ozone, oxygen, air) the temperature and the external pressure.

The expansion and collapse processes are nearly adiabatic, and in the bubbles extremely high local temperatures result. The collapse of the bubbles release energy in the form of ultraviolet radiation. Analysis of this radiation shows it to be comparable to 9,000° - 11,000°K blackbody radiation. The high energy of the bubbles has also been shown to result in the formation of various favored radical species including $H^\bullet$ and $OH^\bullet$ in water. A number of reactions have been shown to occur under ultrasonic radiation which were not favorable from thermodynamic considerations. It is the intense local heating associated with cavitation that is generally credited with the observed increased reaction rates.

Another phenomenon associated with high internal bubble temperature is sonoluminescence which is a weak emission of light from which a continuous spectrum can be observed. It is possible that sonoluminescence would likewise increase the rate of organic oxidation.

The occurrence of time independent or standing vortices within the liquid has been widely observed. The action of these vortices has been shown to increase both heat and mass transfer. Sierka [26] has proved that system overall oxygen mass transfer coefficients are increased by as much as 40% when soundwaves are added to an oxygen gas-sparged reactor over the no-sound condition.

When soundwaves, with frequencies exceeding 16 kHz are passed through liquids and gases, a range of beneficial responses occur. For instance, at liquid-liquid and gas-liquid interfaces, surface instabilities are produced. This, in turn, produces increased rates of mass and heat transfer as well as chemical reaction rates. Low frequency (20 kHz) radiation would be desirable from the standpoint of ease of cavitation and maximum particle displacement at a given power level.

Another important application of sonification is the accelerated decomposition of dissolved ozone to free radicals. This can be seen in Figure 1. The data for this figure were derived in an experiment [27] in which two liters of distilled water were brought to pH 7 and then buffered with a phosphate buffer solution. This water was then subjected to ozonation at a temperature of 25.5°C. In the first run, ozone at a concentration of 58.1 mg/L of oxygen was continuously admitted to the reactor and dissolved ozone measured as a function of time. From Figure 1 it can be seen that a saturation level of 8.0 (mg O_3 /L) was achieved within six minutes. After an additional four minutes of ozonation, the ultrasonic unit was turned on and a level of 250 watts of peak envelope power (PEP) maintained. Immediately the dissolved ozone concentration dropped; ultimately within six minutes to a level of 4.6 mg/L. Repeating this experiment at a concentration of 24 mg of ozone per liter of oxygen gave a saturation value of 4.4 mg/L of dissolved ozone. Here again, the effect of ultrasound at 250 PEP caused the dissolved ozone concentration to drop to a steady state value of 2.15 mg/L.

The reduction in saturation value for the same ozone partial pressure simply is due to the destruction of O_3 by the ultrasonic soundwaves, first to nascent oxygen ($O^{\bullet}$) which leads to other hydroperoxyl radicals being formed. The characteristic curves obtained look similar to those found by Hewes *et al.* [28] when they utilized ultraviolet light in the reactor and showed dropping levels of dissolved ozone with the admission

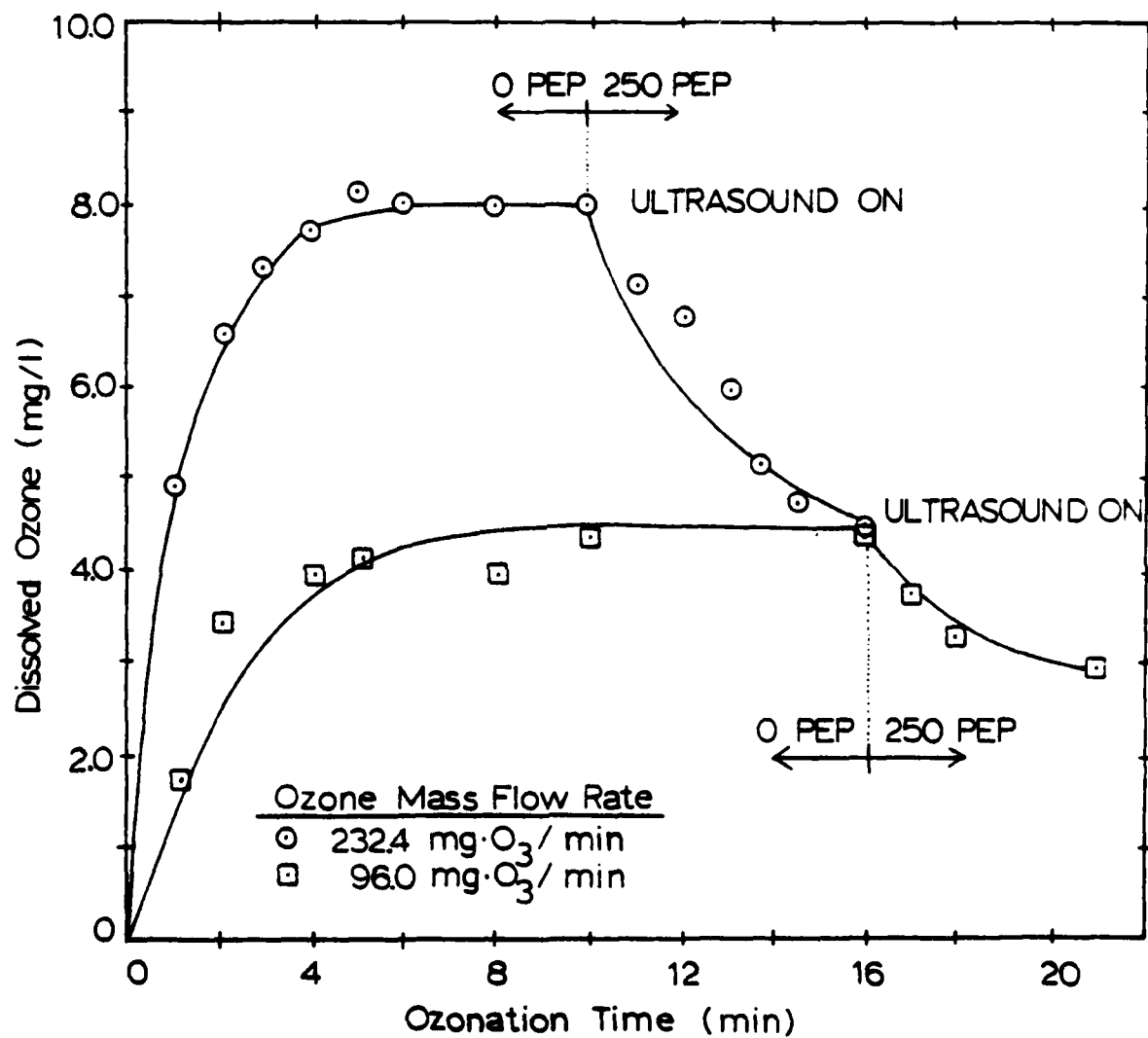


Figure 1 Ozone Uptake in the 2-liter Reactor at pH 7.0 Followed by the Application of Ultrasound

of light to the reactor. However, they stated that return to the plateau value was slow after the ultraviolet light was turned off. In the case of ultrasound the return is rapid.

In summary, the inclusion of acoustic soundwaves into the ozone reaction system may have the following benefits: (1) the apparatus has no moving parts and with current high solid-state technology would be a reliable and reproducible reactor element, (2) ultrasonic waves would not be attenuated as rapidly as would be the case with ultraviolet light, as seen in highly colored munitions wastewater, (3) the energy requirement to operate the sound generation equipment may be modest, (4) mass transfer of ozone to solution would be increased and therefore meet any high ozone demands by munitions wastewaters, and (5) net free radical production should occur due to the decomposition of dissolved ozone by sonification, essentially irrespective of pH levels in the reaction mass.

2.0 OZONE/ULTRASOUND EXPERIMENTS

2.1 INTRODUCTION

The optimum combination of operational parameters in ozone/ultrasound reactor requires an understanding of the interrelationship among the following: (1) solution pH, (2) ultrasound power level, (3) ultrasound frequency, (4) solution concentration and (5) reaction temperature.

A parametric study was conducted to access these relationships and the results reported and discussed in the following paragraphs.

2.2 EXPERIMENTAL

The experimental apparatus employed in this portion of the research is diagramed in Figure 2.

2.2.1 Ozonator

The ozonator used throughout the research was an Orec Model 03B1-0. Commercial grade oxygen with negligible hydrocarbon content was the feed gas for ozone production. Tygon and glass tubing were used to carry ozone and oxygen to the reactors. Tap water served as the cooling media for the generator. A powerstat permitted operation at the desired voltage. A wattmeter and voltmeter indicated primary values to the ozone generator. For the vast majority of experiments a gas pressure of 15 psig and 2.3 L/min of oxygen was used and together with 60 watts of electrical power, the ozonator produced 31.7 mg $O_3/L O_2$ or 72.91 mg O_3/min . When

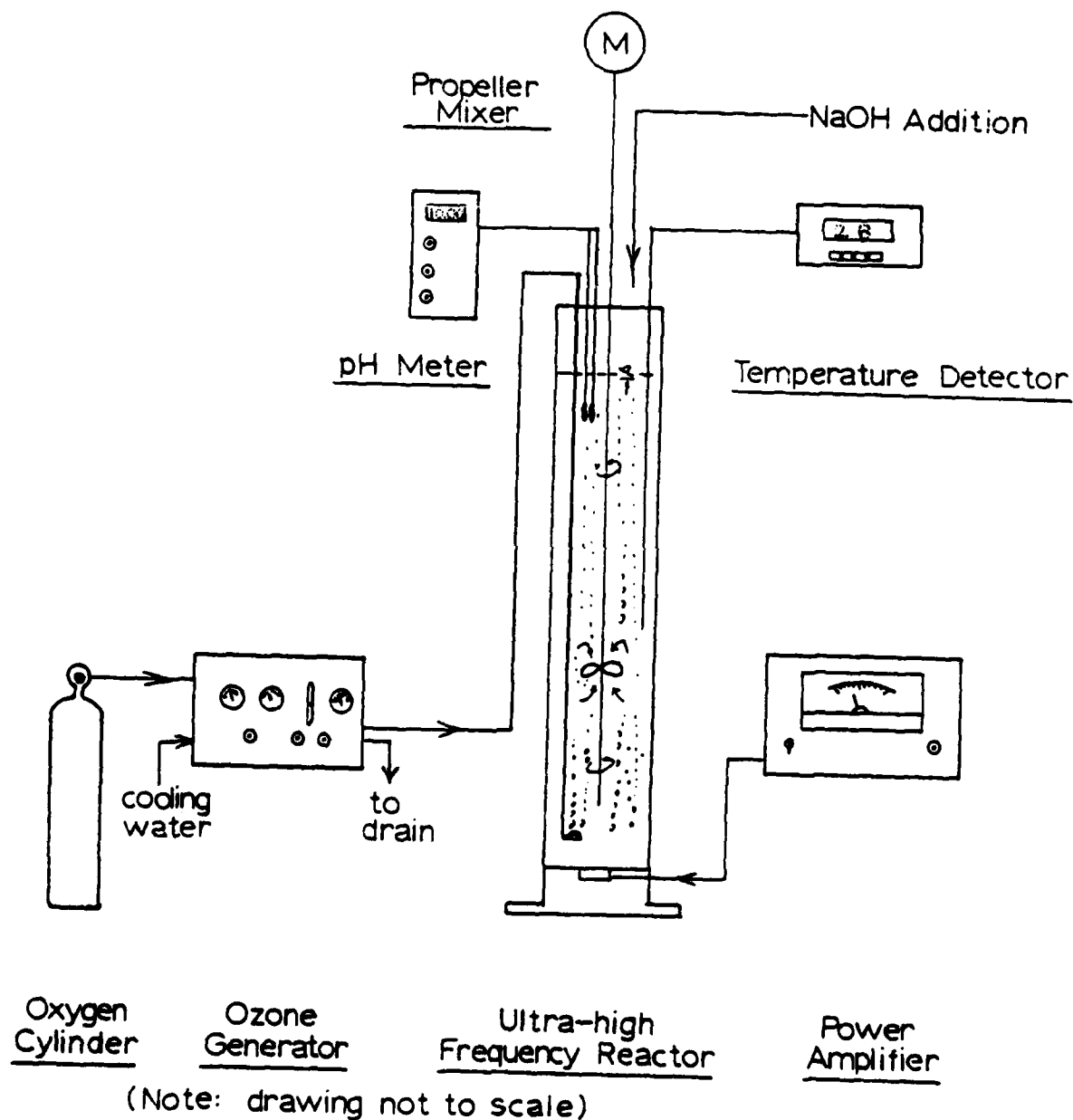


Figure 2 Experimental Apparatus for the Ozone/Ultrasound Treatment of TNT/RDX Solutions

175 watts of power was applied, at the same gas input flow rate, 60.7 mg $O_3/L O_2$ or 139.6 mg O_3/min was produced. Finally, some experiments employed ozone at a mass flow rate of 100 mg O_3/min which were generated from pure oxygen flowing at 4.0 L/min with a pressure of 10 psig in the ozonator operating at 60 watts.

2.2.2 Ozone Reactors

Two reactors were utilized during this portion of the research: (a) ultra-high frequency reactor (UHFR) and (b) a 1000 mL graduated cylinder.

The UHFR (see Figure 3) is constructed from a 2-3/4" I.D. x 18-1/4" long plexiglass cylinder bolted to a base containing a 3-3/8" x 0.003" thick stainless steel plate. A ceramic transducer was attached with silver epoxy resin to vibrate the stainless steel sheet. The reactor base contains a 1/4" air cooling line for the ceramic transducer with several holes drilled into the assembly to permit air to escape. Ozone/oxygen is sparged into the reactor through a 5/32" I.D. x 20" long glass pipe fitted with a sintered glass sparger. A temperature probe extended within one inch of the reactor bottom. For these experiments the reactor was uncovered.

The piezoelectric ceramic transducer is driven by a solid-state power amplifier covering a frequency range from 10 kHz to 12 MHz. Through the use of transducers of various thicknesses, (0.05", 0.08", 0.25" and 0.50") variable frequencies were obtained. Frequencies are measured by a Fluke Model 1900A frequency counter. A more complete description of the ultrasonic system can be found in Appendix B.

The 1000 mL graduated cylinder was only used for the variable reaction temperature experiments because the UHFR could not be externally heated due to the ultrasound equipment. For the variable temperature experiments all batches were preheated and a magnetic stirrer-heater plate was employed to maintain temperature. Mixing in this reactor was accomplished by gas sparging only. Heat loss was minimized by insulating the reactor.

2.2.3 Substrates

Two general types of substrates were employed in this research: (a) five actual munitions plant wastewaters (see Table 2 following for identification), and (b) synthetic solutions of TNT and RDX.

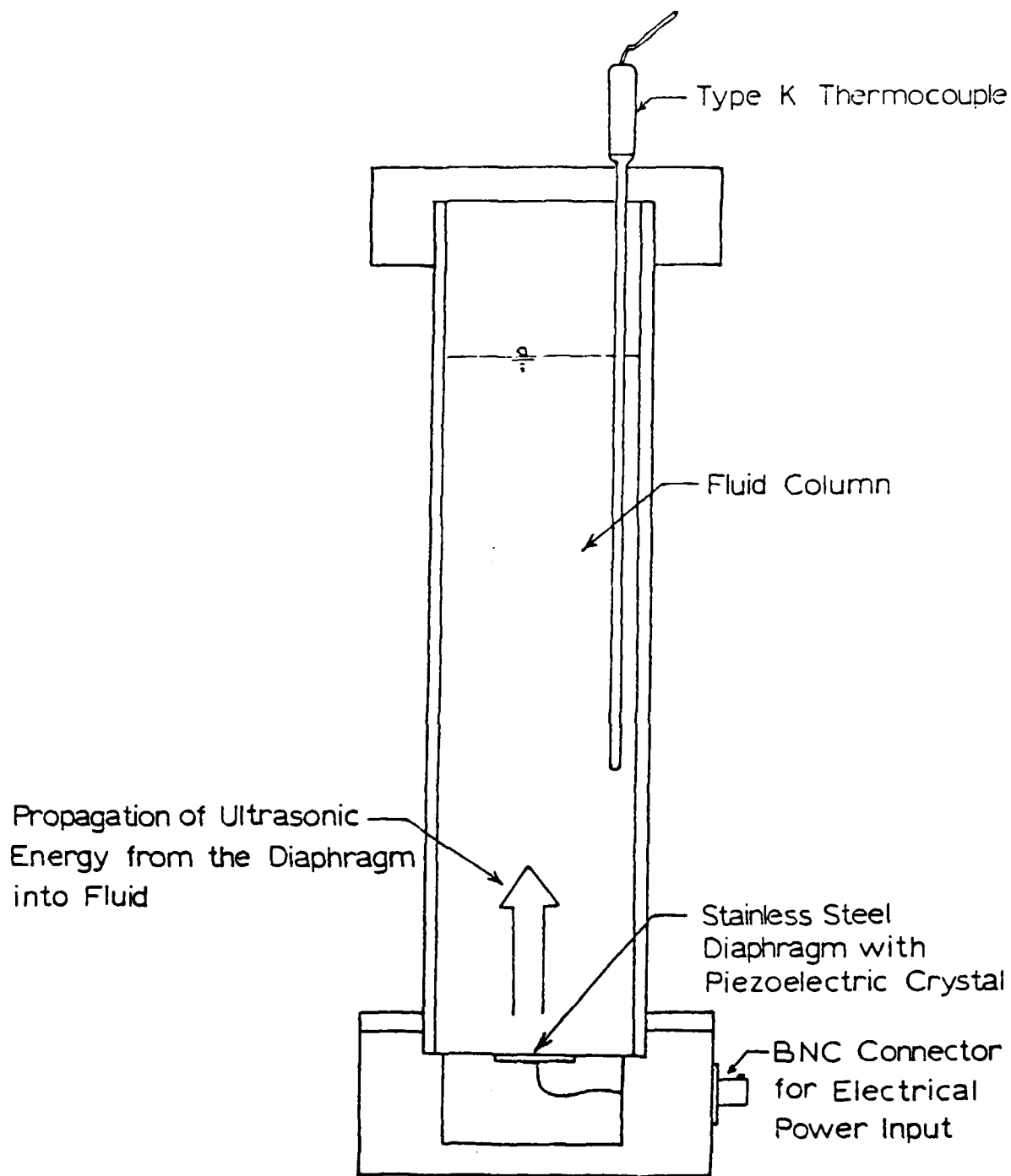


FIGURE 3 ULTRA-HIGH FREQUENCY REACTOR

TABLE 2 - MUNITIONS PLANT WASTEWATERS

<u>Sample No.</u>	<u>Identification</u>
1	Milan AAP - X41
2	Kansas AAP Pinkwater Building 008 After Treatment
3	Lone Star AAP - 0 - 48
4	Iowa - AAP Bldg 34 - 70 - 1 Pink Water
5	Iowa - AAP Bldg 34 - 70 - 1 Pink Water

A report on the results of the ozone/ultrasound treatment of munitions plant wastewaters can be found in Appendix C.

Synthetic aqueous solutions of (a) 70 mg/L TNT and (b) 70 mg/L TNT plus 30 mg/L RDX (70/30 mg/L TNT/RDX) were employed for this portion of the research. All solutions involving TNT were prepared from Practical Grade α -TNT produced by Eastman Kodak Company. RDX was supplied by the U. S. Army.

Because Eastman Kodak TNT contained 10% water by weight, 77.8 mg/L of its product was dissolved in laboratory distilled water to obtain 70 mg/L of TNT concentration. The U. S. Army supplied RDX contained acetone. To remove the acetone RDX was dissolved in distilled water then heated on a steam bath to evaporate the acetone and water. After the RDX was crystallized to a white powder, it was cooled, dried and stored in a desiccater.

Each batch of synthetic TNT/RDX solution was produced by dissolving 933.6 mg of Eastman Kodak TNT and 360 mg of recrystallized RDX in 12 liters of distilled water. Since the solubilities of TNT and RDX increase with temperature, the solutions were prepared with the aid of stirring and heat supplied by an electric heater (maximum temperature less than 90°C). In order to prevent photochemical degradation of TNT and RDX, solution preparation and storage was carried out in the absence of light.

The ambient pH of 70/30 TNT/RDX batches was approximately 5.54 (range 5.40 to 5.75). For those experiments where a higher solution pH was desired, 0.1N NaOH solutions were used.

2.2.4 Analytics

The primary parameters employed in monitoring changes brought about by reaction were pH, TOC and TNT.

All pH measurements were made with a Corning Model 125 pH meter. The TOC of each sample was performed on a Dohrman Total Organic Carbon Analyzer DC-80 (see Appendix A). TNT measurements were determined by the Silas-Mason Method (see Appendix A).

2.3 THE pH EFFECT

One of the most important parameters for ozone-organic reactions in aqueous solution is pH. The pH of the solution determines the autodecomposition rate of molecular ozone (O_3) to radicals. Hydroxide ions (OH^-) catalyze this reaction and the higher their concentration, the faster the rate of ozone decomposition to a variety of radicals including the hydroperoxyl radicals ($OH^\bullet$), the most powerful and effective oxidant occurring in aqueous solution [29].

The effect of pH on the half-life of ozone in water has been studied by Stumm [30] and Bader [31]. The results of these investigations are summarized in Table 3.

TABLE 3. HALF LIFE OF OZONE AS A FUNCTION OF pH

pH	Half-Life (min)	
	14.6°C	25°C
4.0		350
6.0		50
7.6	41	
8.0		33.3
8.5	11	
8.9	7	
9.2	4	
9.7	2	
10.0		0.33

Ozone reacts with solutes in two general ways: first, it can react directly as molecular ozone with the substrate, or secondly it can decompose to radicals before reacting in this form, or sometimes forming radical type intermediates. The formation of these radical intermediates can also lead to further ozone decomposition and thus a chain reaction ensues. Scavengers such as bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}) and aliphatic alcohols, can quench the chain reaction.

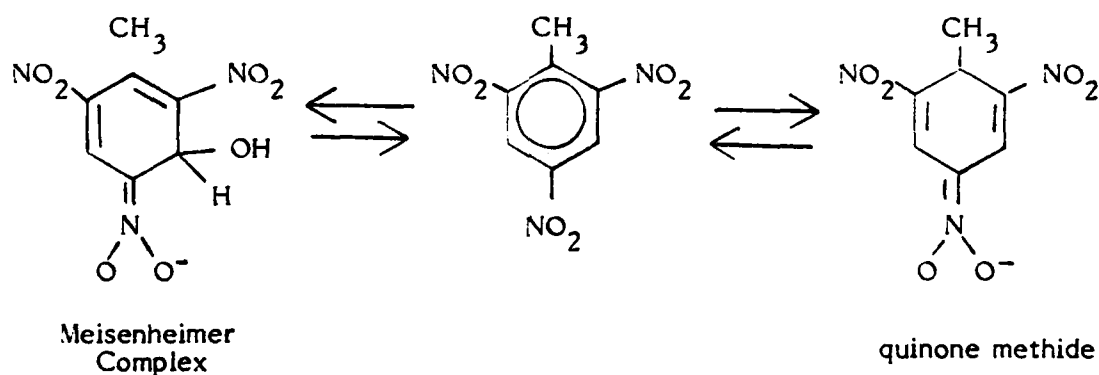
Direct ozone reactions in organics occur but they require a chemical bond specifically reactive to ozone. An example would be a double-bonded carbon atom. At very low pH levels, (i.e., below 2.0) oxidation by ozone is almost entirely ineffectual [32]. Radical reactions with substrate are not substrate specific and even though $OH^\bullet$ radicals exist only for microseconds they contribute much more to the overall oxidation of organics than molecular ozone (O_3) itself. A summary of these reactions is given in

Figure 4.

Consideration of which type of reaction (i.e., direct or radical induced) predominates is important since the partial oxidation products are quite different for the same substrate. This would also be reflected in the amount of total organic carbon removal.

The photolysis and subsequent photodecomposition products of 120 ppm aqueous solutions of TNT by a 450-watt medium pressure mercury lamp, with a Pyrex filter to eliminate radiation below 280 mN was studied by Burlenson *et al.* [33]. Experiments were performed with buffered solutions at pH's ranging from 1.1 to 11.1. They showed that the percent decomposition ranged from 17.5% to 95.9% after one hour of irradiation as the solution pH was increased through the above-mentioned range. Thus, once again this indicates the prime importance of pH as a reaction parameter for munitions wastewaters. Ultrasound has been shown [27] to likewise cause the decomposition of ozone in aqueous solution.

Brabets and Marks [34] speculate that in aqueous alkaline solution, TNT will equilibrate with two ionic forms the Meisenheimer complex and quinone methide. The former should be the predominant specie. It is derived by the addition of OH^- to the nucleus. The quinone methide results from the loss of a proton from the methyl group on TNT.



Both forms of this compound are susceptible to ozone attack.

To study the effect of solution pH, two experiments were conducted with 70 mg/L aqueous solution of TNT as the substrate. The volume in the reactor was 500 mL and the ozone gas admitted at a rate of 100 mg/min. For the first run the initial pH was 10.0 and for the second experiment it was 5.43. The data in Table 4 summarizes the responses with respect to TOC, TNT and pH.

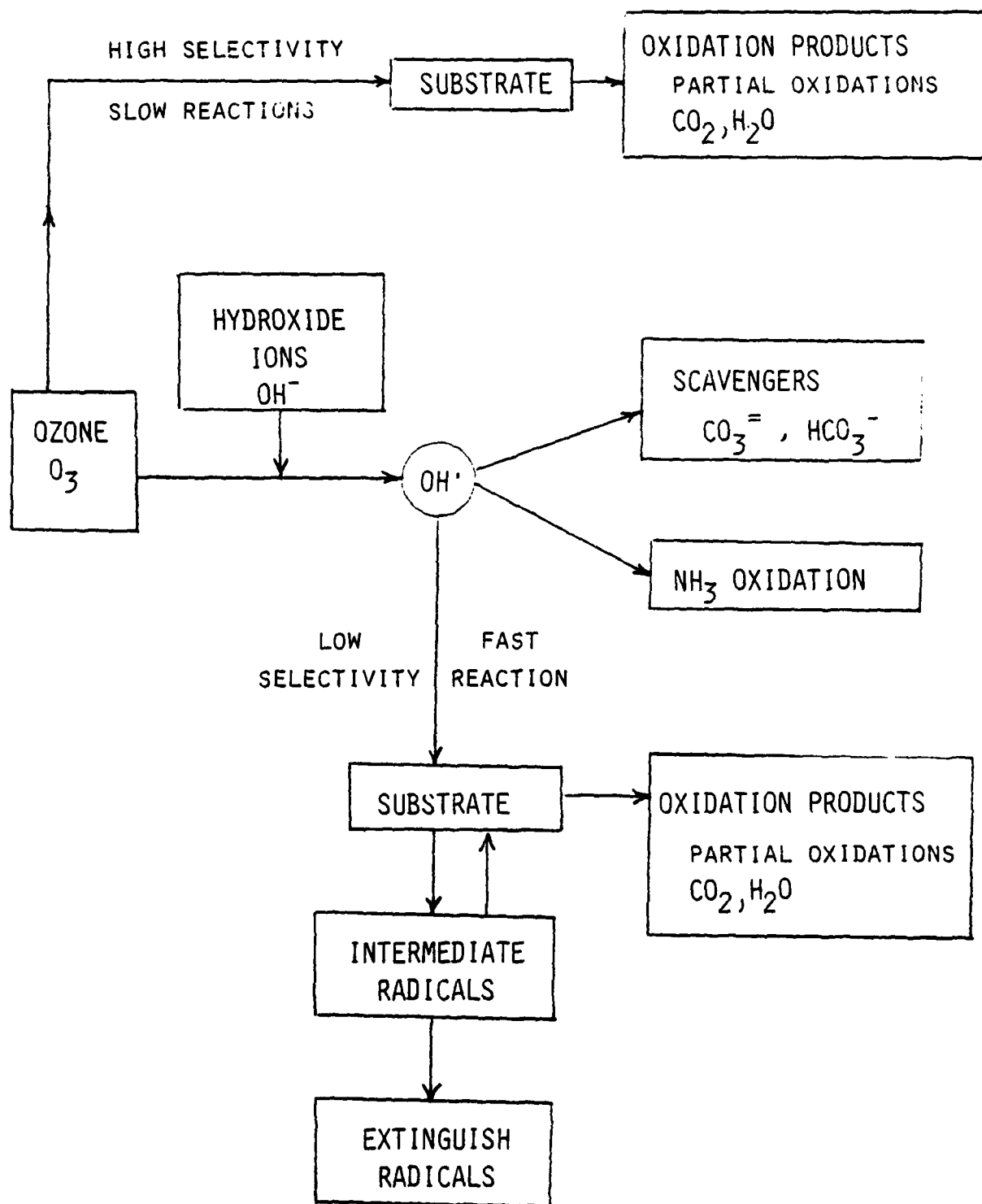


Figure 4. A Summary of Ozone-Organic Reactions in Aqueous Solution
(Modified from Hoigne and Bader, 1976)

TABLE 4. THE EFFECT OF pH ON THE OXIDATION OF 70 mg/L TNT SOLUTIONS WITH OZONE IN THE PRESENCE OR ABSENCE OF ULTRASOUND

Reaction Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Ultrasound Frequency (kHz) (min)
0	10.0	23.71	1.0	70.8	1.0	None
15	7.6	22.59	0.95	58.6	0.83	None
0	5.43	23.60	1.0	68.9	1.0	None
15	4.89	24.61	1.0	66.8	0.97	None
0	10.0	23.71	1.0	70.8	1.0	829.0
15	7.15	10.84	0.88	52.7	0.74	829.0
0	5.43	23.60	1.0	68.9	1.0	829.0
15	4.44	24.30	1.0	63.7	0.92	829.0

The largest change in TNT occurred when the solution pH was 10.0 when 12.2 mg/L was converted yet only 1.12 mg/L of TOC loss was seen. When the solution pH was 5.42, only 2.1 mg/L of TNT was removed over the 15 minutes of reaction.

Next, two more experiments with the same reaction conditions were performed with the exception that ultrasound was incorporated into the reactor.

Comparing the 15-minute data in Table 4, it is seen that when ultrasound is present (i.e., 829.0 kHz) lower pH levels are achieved. Likewise the experiments with ultrasound yield higher TNT and TOC changes. At both initial solution pH levels this may have been due to the higher temperatures achieved in the ultrasound run over the no-sound experiments. Insonation raised the temperature of the batch approximately 6°C from the starting temperature. For low pH runs, evaporation effects on TOC were greater than the destruction due to ozone oxidation.

Since the effect of solution pH was measurable a series of experiments were conducted to assess this effect for three reaction conditions: (1) ozone treatment, (2) oxygen plus ultrasound, and (3) ozone plus ultrasound.

For these runs 1.6 L of 70/30 (mg/L) TNT/RDX solution was employed as the substrate. The initial solution pH for each experiment was approximately 10.0 and in an attempt to retain this pH, 40 mL of pH 10.0 buffer solution was also added to the reactor. During each experiment NaOH was continuously added to maintain a high pH. Each reaction was carried out for one hour. For the runs with ozone a mass flow rate of 72.91 mg O₃/min was employed. The data for these runs is found in Table 5.

TABLE 5. THE EFFECT OF OZONE, OXYGEN/ULTRASOUND AND OZONE/ULTRASOUND TREATMENT OF 70/30 mg/L TNT/RDX

Reaction Condition	Reaction Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Temperature (°C)
Ozone	0	10.03	26.76	1.00	66.0	1.00	27
	30	10.00	19.13	0.71	14.4	0.22	27
	60	9.98	15.69	0.59	3.3	0.05	26
Oxygen + Ultrasound	0	10.14	26.69	1.00	65.2	1.00	29
	30	10.12	33.04	1.00	64.4	0.99	--
	60	10.57	27.39	1.00	65.2	1.00	41
Ozone + Ultrasound	0	10.14	10.11	1.00	66.0	1.00	26
	30	9.85	20.83	0.77	11.0	0.17	35
	60	9.77	13.34	0.49	0.6	0.09	42

In the ozone only run the TOC destroyed over the one hour of reaction was 41%, while the TNT destruction was 95%. By comparison in the run with ultrasound, at a frequency of 865.0 kHz and 50 watts, 51% TOC was destroyed and greater than 99% of the TNT had been converted. The increased removals with the O₃/ultrasound system can be partially explained by the increased temperature in the reactor. Energy imported from the vibrating crystal increased the reaction temperature from 26°C to 42°C.

The purpose of the oxygen/ultrasound experiment was to determine if the high pH environment together with ultrasound would cause the transformation of TNT to a specie not perceived by the Silas-Mason Test. From the data it is clearly evident that this did not occur. Thus, in the ozone/ultrasound experiment, the increased removal rate experienced is the result of ozone radicals-substrate reactions promoted by ultrasound and the increased temperatures. Both factors would tend to increase reaction rate by improved ozone mass transfer and ozone decomposition.

2.4 ULTRASOUND POWER LEVEL EFFECT

The effect of sonic vibrations on reaction kinetics has been the subject of many research projects. Chen and Kalback [35] studied the hydrolysis of methyl acetate by sonic ultrasound with a 23 kHz generator. While they found a direct relationship between increasing ultrasonic intensity and reaction rate, Fogler and Barnes studying the same system but at a frequency of 27.5 kHz [36], concluded that reaction rate does not increase indefinitely with increasing sonic intensity. They found

an optimum value then a decrease in performance at levels in excess of this power level.

Sierka [27] has shown that increasing sound power level increases the autodecomposition rate of ozone in the temperature range 24°C to 40°C. After 40°C the response was found no longer to be linear. At high temperature, ozone's decomposition rate due to thermal energy alone is sufficient to decompose the gases ozone transferred to the liquid and, therefore, ultrasound had little effect.

To derive the relationship between sound power level, at a fixed frequency and ozone oxidation, a series of eight experiments were conducted in the UHFR. For each run, 1L of 70/30 mg/L TNT/RDX solution was adjusted to pH 10.0 and ozonated for 1.0 hour each at a rate of 72.91 mg O₃/min. The ultrasound frequency employed ranged from 852.0 to 863.0 kHz and the power input to the crystal varied; from 5 to 50 watts (see Runs 1, 3, 5, and 7). In Runs 2, 4, 6 and 8, the companion experiments, without ozone but with ultrasound and oxygen sparging, were carried out. The results are listed in Table 6.

The first effect of increasing sound power from 5 to 50 watts to the reaction mass is the attainment of a final reactor temperature ranging from 30°C to 59°C after one hour of insonation. In terms of TNT destruction, increases were proportional to sound power level. For example, after 1.0 hours of ozonation, 50% of the TNT was removed at 50 watts, but only 18% at 5 watts. When ozone was excluded from the reactor, no TNT was destroyed by ultrasound alone. It should be noted that even at 60°C in Run 2 no TOC was destroyed. The pH drops seen in runs with ozone (i.e., 1, 3, 5, 7) were not seen in the runs without ozone (i.e., 2, 4, 6, 8). This is an indication of partial oxidation of TNT and RDX by ozone. Finally, TOC reductions, similarly to TNT changes, were proportional to sound power level.

In the experiments performed without ozone, even at a sound power level of 50 watts and an ultrasound frequency of approximately 852.0 kHz, no TNT or TOC removals took place. In the ozone plus ultrasound experiments, TOC and TNT removals appeared to be proportional to sound power level; however, the effect of reaction temperature as seen in Section 2.7 was largely responsible for these responses.

2.5 ULTRASOUND FREQUENCY LEVEL EFFECT

The use of ultrasound in ozone oxidation reactions is premised on the argument that both ozone mass transfer and oxidation reaction rate would be enhanced by its presence in the reactor. The proper frequency to employ is, however, unknown

TABLE 6. VARIABLE ULTRASOUND POWER LEVEL EXPERIMENTS WITH 70/30 TNT/RDX IN THE ULTRA-HIGH FREQUENCY REACTOR IN THE PRESENCE AND ABSENCE OF OZONE

Run No.	ULTRASOUND Frequency (Hz)	Power (Watts)	Reaction Time (min)	pH	TOC (mg/L)	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Ozone Mass Flow Rate (mg/min)	Temperature (°C)
1	852,000	50	0	10.0	27.73	71.7	1.0	72.91	31
			30	3.84	24.29	46.8	0.65	72.91	47
			60	3.40	22.10	35.6	0.50	72.91	59
2	852,000	50	0	10.0	28.24	70.0	1.0	0	28
			30	9.75	27.91	70.2	1.0	0	44
			60	9.73	28.56	70.5	1.0	0	60
3	854,000	30	0	10.0	27.04	70.3	1.0	72.91	28
			30	4.09	25.20	51.9	0.74	72.91	41
			60	3.68	24.78	46.5	0.66	72.91	42
4	854,000	30	0	10.0	27.40	70.3	1.0	0	29
			30	9.91	26.64	70.5	1.0	0	37
			60	9.75	27.00	70.0	1.0	0	43
5	856,000	15	0	10.0	27.63	72.2	1.0	72.91	27
			30	5.38	26.07	59.0	0.82	72.91	30
			60	4.28	25.87	53.0	0.73	72.91	32
6	856,000	15	0	10.0	29.30	70.5	1.00	0	28
			30	9.80	28.79	69.4	0.98	0	32
			60	9.79	29.57	69.4	0.98	0	35
7	863,000	5	0	10.0	27.15	71.9	1.0	72.91	28
			30	4.38	26.35	60.0	0.83	72.91	29
			60	4.06	26.70	59.0	0.82	72.91	29
8	863,000	5	0	10.0	27.75	70.6	1.0	0	28
			30	9.95	28.75	70.5	1.0	0	29
			60	9.84	28.87	70.3	1.0	0	30

and for that reason a series of experiments at three different frequencies (i.e., 60.6, 859, and 1007 kHz) with a fixed power input of 50 watts to the ceramic transducer were conducted.

In each run, 1.0L of 70/30 mg/L TNT/RDX was raised to a pH of 10.0 with NaOH and ozonated for 1.0 hour at a rate of 72.91 mg O₃/min. TNT, TOC, temperature and pH were measured at times 0, 30 and 60 minutes. The experimental results are reproduced in Table 7.

The data show that the maximum destruction effort for both TOC and TNT was obtained when the ultrasound frequency was 859 kHz at a power input of 50 watts.

From the temperature increases it can be surmized that the voltage and current for 859 kHz transducer were in phase producing a resonant frequency. Thus, the electrical energy imparted to the crystal was efficiently transferred to the reaction mass and the oxidation reaction kinetics were enhanced.

The effect of variable frequency was also investigated with 70 mg/L batches of TNT only. Two experiments were run at 60.6 kHz and 829.0 kHz frequencies. In both runs 1L volumes of solution were adjusted to pH 10.0 before ozonation. The ozonation rate for the lower frequency run was 72.91 mg/min while it was 100 mg/L for the higher frequency run. Even though the ozonation mass flow rates are different, the runs can be compared because the ozone admitted is far in excess of the theoretical amount required.

Listed in Table 8 are the analytical results which show that the higher frequency run produces the most positive effects. TNT was reduced by 35% and 51%, respectively, when the ultrasound employed had a frequency of 60.6 kHz and 829.0 kHz. TOC reduction differences were less dramatic with 8% and 35% removals achieved in the low and high frequency runs. This occurred in spite of the larger pH drop (10.0 to 5.0 vs. 10.0 to 6.32) in the run using 829.0 kHz ultrasound. However, in the high frequency run the batch temperature was increased to 38°C and therefore most probably the increased rates of TOC and TNT destruction are the result of the higher temperature and not the frequency level.

2.6 INITIAL SOLUTION CONCENTRATION EFFECT

The basic question with all ozonation reactions is, "What mechanism is controlling the reaction; is it reaction kinetics or mass transfer?" If it is reaction kinetics, the only plausible improvement route is the use of a catalyst which would increase the

TABLE 7. VARIABLE ULTRASONIC FREQUENCY LEVEL EXPERIMENTS WITH 70/30 (mg/L) TNT/RDX IN THE ULTRA-HIGH FREQUENCY REACTOR WITH OZONATION

Ultrasound Frequency (kHz)	Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Temperature (°C)
60.6	0	10.0	23.42	1.00	72.5	1.0	25
	30	6.68	21.51	0.92	51.1	0.71	25
	60	6.32	21.69	0.93	47.7	0.66	25
859.0	0	10.0	27.73	1.00	71.7	1.00	31
	30	3.84	24.29	0.88	41.8	0.65	47
	60	3.40	22.10	0.80	35.6	0.50	56
1,007.0	0	10.0	27.41	1.00	65.1	1.0	27
	30	4.67	25.43	0.93	48.7	0.75	33
	60	4.01	24.68	0.90	45.2	0.69	38

Ozone Mass Flow Rate - 72.91

TABLE 8. VARIABLE ULTRASONIC FREQUENCY LEVEL EXPERIMENTS WITH 70 (mg/L) TNT IN THE ULTRA-HIGH FREQUENCY REACTOR WITH OZONATION

Ultrasound Frequency (kHz)	Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Temperature (°C)
60.6*	0	10.0	23.42	1.00	72.5	1.00	25
	30	6.68	21.51	0.92	51.1	0.70	25
	60	6.32	21.69	0.92	47.3	0.65	25
829.0**	0	10.0	23.56	1.00	67.0	1.00	28
	30	6.75	18.06	0.77	43.2	0.64	34
	60	5.00	15.31	0.65	32.9	0.49	38

* Ozone Mass Flow Rate - 72.91 mg/min

** Ozone Mass Flow Rate - 100.0 mg/min

rate of approach to equilibrium. Mass transfer controlled reactions can be speeded-up by manipulation of the resistances to mass transfer.

In the case of ozonation reactions, the ozone must be transferred from the gas phase to the liquid phase across the two films (i.e., gas and liquid). Reduction of the liquid film thickness, for example by increased turbulence, will improve mass transfer. One method to accomplish this could be the inclusion of ultrasound into the reaction mass.

Ultrasound has an additional potential in that it can act as a catalyst by enhancing the auto-decomposition of ozone to free radicals, once the ozone has been dissolved in the aqueous phase.

To gain greater insight into these questions, a series of six runs were conducted; three in the presence and three in the absence of ultrasound with variable concentrations of TNT/RDX which were held constant in the ratio 70/30, respectively. This was accomplished by taking the standard 70/30 mg/L TNT/RDX batch and diluting it with an equal volume of distilled water (i.e., volume dilution ratio, 1/1) and also diluting to the ratio of 1/3.

These 1.7L batches were initially adjusted to pH 10.0 with NaOH and maintained at approximately this level throughout the ozonation period which utilized a mass flow rate of 72.91 mg O_3 /min.

Table 9 contains the data for the ozonation runs with and without ultrasound. The only major difference between these runs is seen in temperature. When ultrasound was employed the reaction mass was heated by approximately 8°C over the one hour of ozonation.

Examination of the TOC data reveals a very slight dependency on initial organic concentration. In the Runs 1, 2, and 3 where ultrasound was employed (i.e., 829.0 kHz) 52%, 50% and 47% of the TOC was removed while for the Runs 4, 5, and 6 without ultrasound, 53%, 50% and 47% was destroyed (see Figure 5). The data clearly indicate that the presence of ultrasound made no positive impact on the reaction.

The TNT destruction ratio data show slightly poorer results when ozone/ultrasound were used together than when this energy form was absent from the reactor. Virtually all of the nitrocompounds, as discerned by the Silas-Mason test, were destroyed within 60 minutes of reaction. Also, since the Silas-Mason test is not completely accurate at

TABLE 9. EFFECT OF INITIAL SOLUTION CONCENTRATION OF TNT/RDX ON VOLUME OZONE/ULTRASOUND (829 kHz) OR OZONE ONLY TREATMENT

Run No.	Dilution Ratio		Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$	Temperature (°C)
	70/30	TNT/RDX Distilled Water							
WITH ULTRASOUND									
1	1/0	0	9.90	27.20	1.0	67.6	1.0	26	
		15	9.54	21.93	0.81	25.9	0.38	28.5	
		30	9.83	18.38	0.68	9.4	0.14	31.0	
		60	9.68	13.02	0.48	1.4	0.02	34.0	
2	1/1	0	9.99	14.94	1.0	33.3	1.0	26	
		15	9.79	10.87	0.73	6.3	0.19	28.0	
		30	9.75	8.954	0.60	1.3	0.04	31.0	
		60	9.83	7.495	0.50	0.8	0.02	34.0	
3	1/3	0	9.47	8.267	1.0	16.2	1.0	25	
		15	9.20	5.664	0.69	3.0	0.19	29.5	
		30	9.35	4.906	0.59	1.7	0.10	31.0	
		60	9.57	4.380	0.53	1.4	0.09	33.0	
WITHOUT ULTRASOUND									
4	1/0	0	10.13	30.58	1.0	65.9	1.0	26	
		15	10.06	22.60	0.74	19.2	0.29	26	
		30	10.12	16.97	0.55	4.9	0.07	26	
		60	10.14	14.30	0.47	0.6	0.01	26	
5	1/1	0	10.00	15.55	1.0	31.3	1.00	25	
		15	9.97	11.06	0.71	6.0	0.19	25	
		30	10.01	8.995	0.58	1.3	0.04	25	
		60	9.93	7.757	0.50	0.3	0.01	25	
6	1/3	0	10.04	8.244	1.00	16.3	1.0	25	
		15	9.93	5.501	0.67	1.7	0.10	25	
		30	10.00	4.778	0.58	0.6	0.03	25	
		60	10.04	4.402	0.53	0.2	0.01	25	

Ozone Mass Flow Rate - 72.91 mg/min

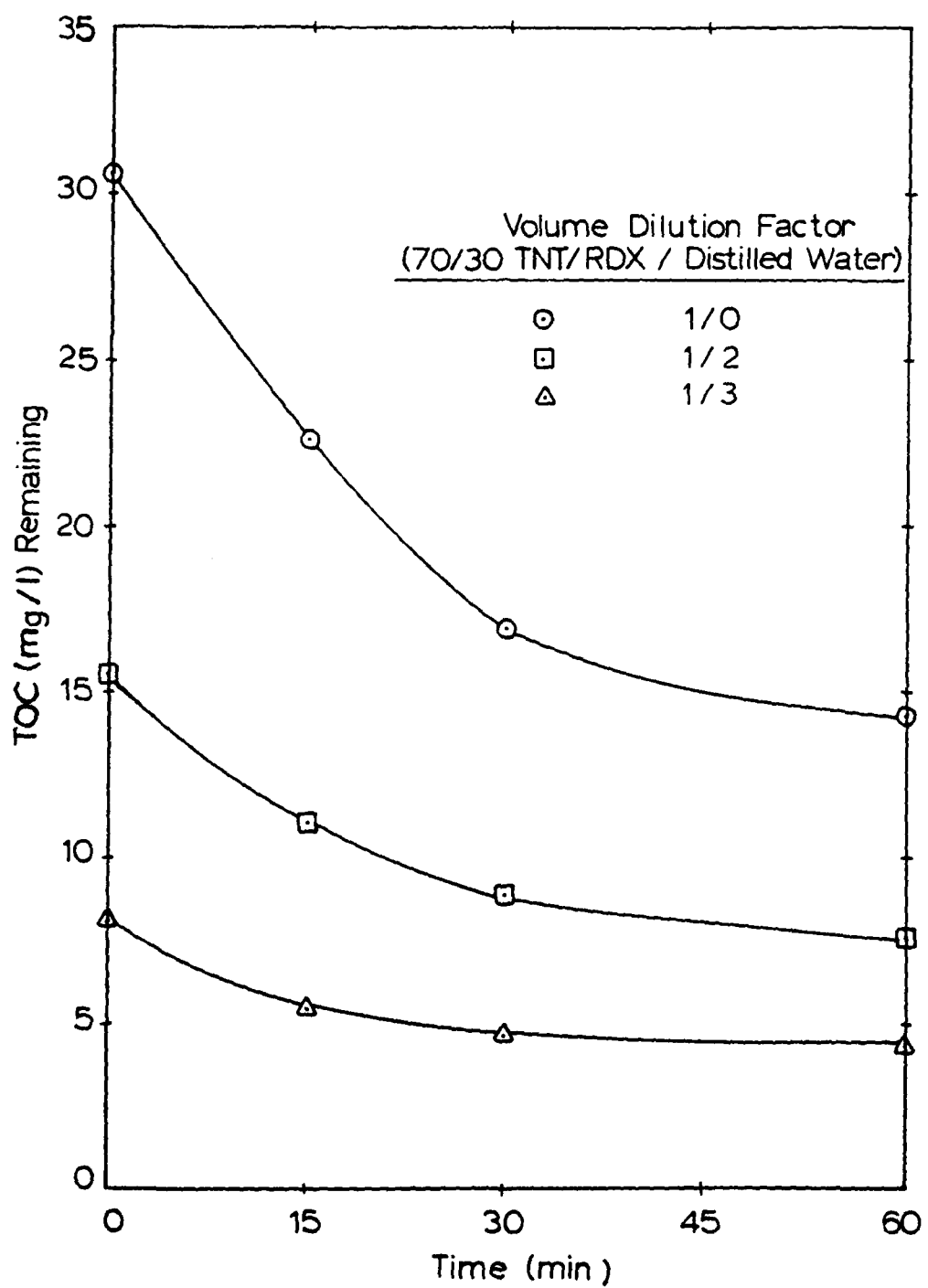


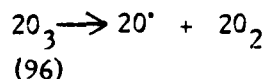
Figure 5 The Ozonation of Variable Initial Solution Concentrations of TNT/RDX

concentrations approaching zero, the results can be considered essentially identical. What these data do indicate is that the ring structure is being broken, since CO_2 is being evolved, as evidenced by the TOC loss.

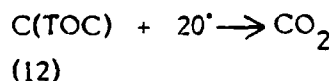
The fact that ultrasound appears to have no effect on the destruction rate of TOC or TNT, is probably due to the large excess of ozone applied to the reactor and the fact that high pH causes an increase in the autodecomposition of ozone. The half life of ozone in aqueous solution is 0.33 min at a pH of 10.0. Ultrasound can also cause ozone decomposition, but in this high pH and high ozone dose applied reaction environment, it is not required.

Since the percent TOC and TNT destroyed was essentially constant for all three concentrations of substrate, an analysis of the ozone applied and theoretical mass transfer ratio was undertaken.

The theoretical amount of ozone required to completely oxidize carbon (i.e., TOC) to CO_2 and H_2O on a mass basis is 8/1. This assumes that only nascent oxygen (O^*) only is capable of totally oxidizing the TOC to CO_2 as seen in the equations below:



and



Ozone is never transferred with 100% efficiency from the gas to the liquid. Based on previous experience a 10% transfer efficiency would be expected.

Shown in Table 10 are the times required to transfer at 100% and 10% efficiency the amount of ozone theoretically required to destroy all the TOC.

The ozone mass transfer lines (i.e., for 100% and 10% transfer efficiencies) together with actual TOC changes with reaction time are plotted in Figures 6, 7 and 8.

These figures together with the data in Table 9 show that a sufficiently large dose in excess of the theoretical demand and transfer efficiency were admitted to the reactor yet approximately only 50% TOC was removed in each case. Since the solution pH was approximately 10.0 and according to previous experimentation very beneficial to TNT and RDX oxidation, the reaction was not mass transfer limited.

TABLE 10. OZONE MASS TRANSFER REQUIREMENTS FOR VARIABLE
CONCENTRATION TNT/RDX EXPERIMENTS

Run No.	TOC in Reactor (mg) ¹	Theoretical O ₃ Requirement (mg) ²	Theoretical Time to Transfer Ozone (min) ³	Time to Transfer Ozone at 10 Percent Transfer Efficiency (min) ⁴
4	51.99	415.92	5.70	57.0
5	26.44	211.52	2.90	29.0
6	14.01	112.08	1.53	15.3

¹ Initial TOC (mg/L) x 1.7L

² 8 x TOC in Reactor

³ $\frac{8 \times \text{TOC in Reactor}}{72.91 \text{ (mg O}_3\text{/min)}}$

⁴ $\frac{\text{Column (3)}}{0.1}$

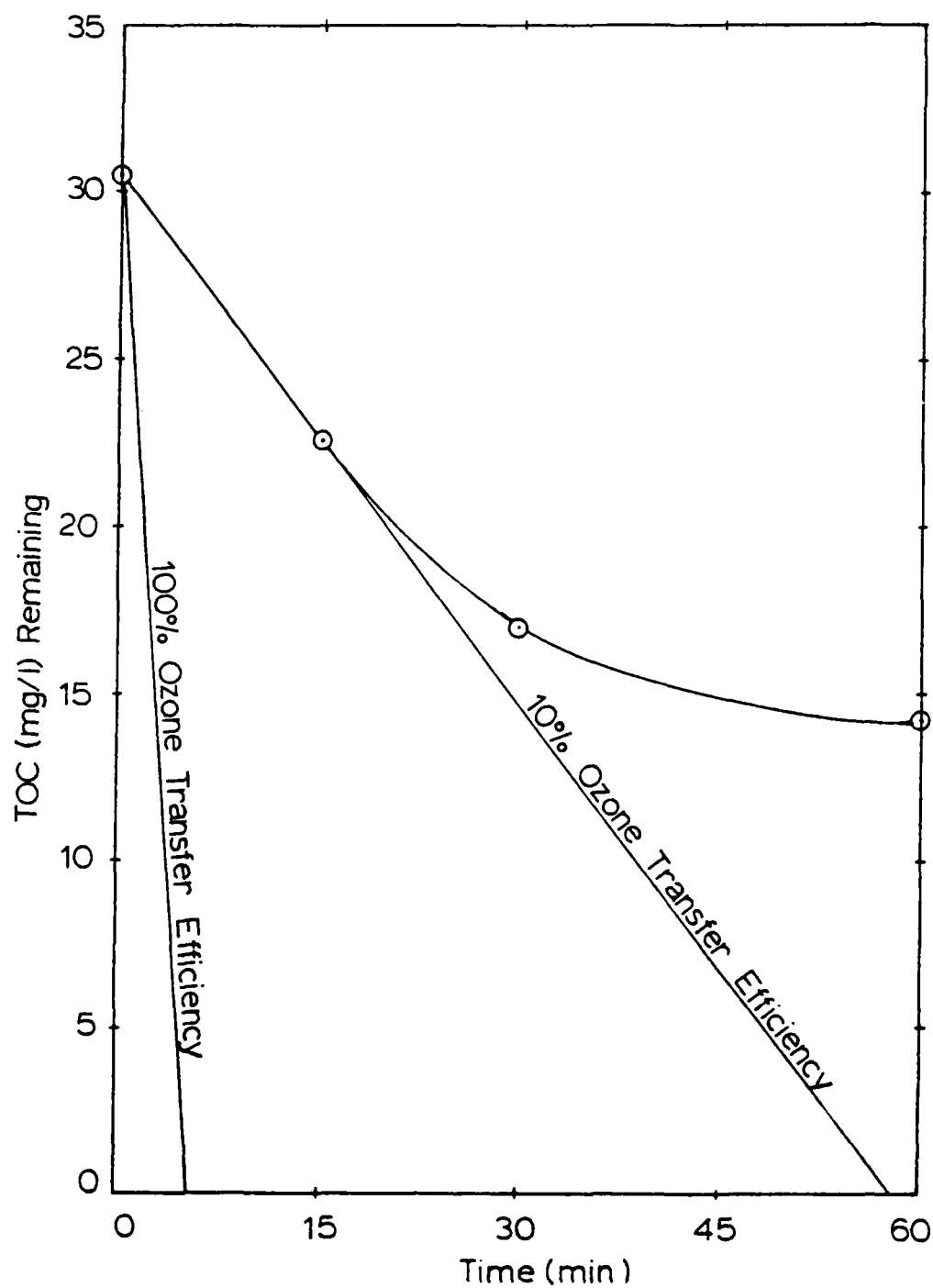


Figure 6 The Oxidation of 70/30(mg/l) TNT/RDX Solution with Ozone

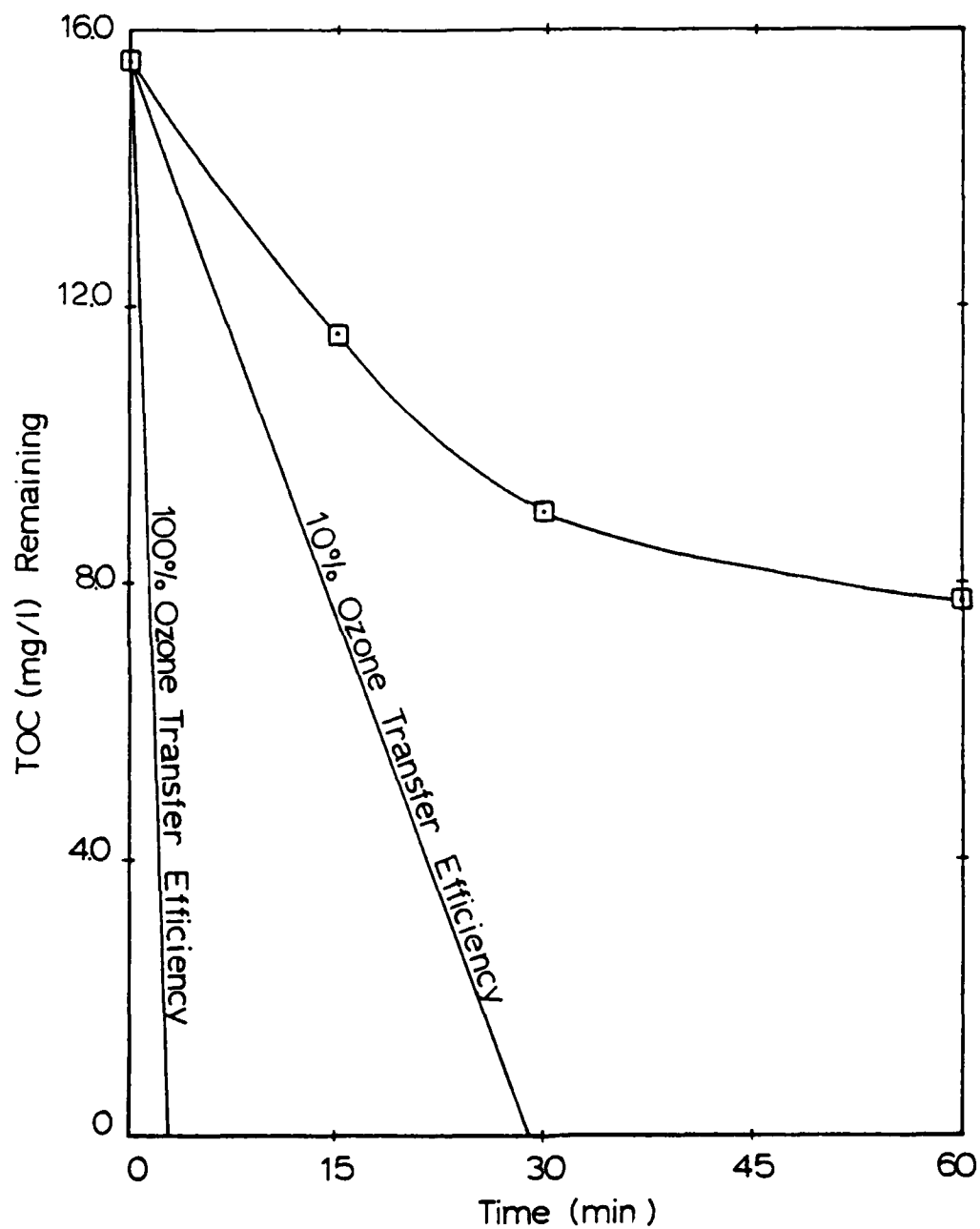


Figure 7 The Oxidation of 70/30 (mg/l) TNT/RDX Solution Diluted with an Equal Volume of Distilled Water by Ozone

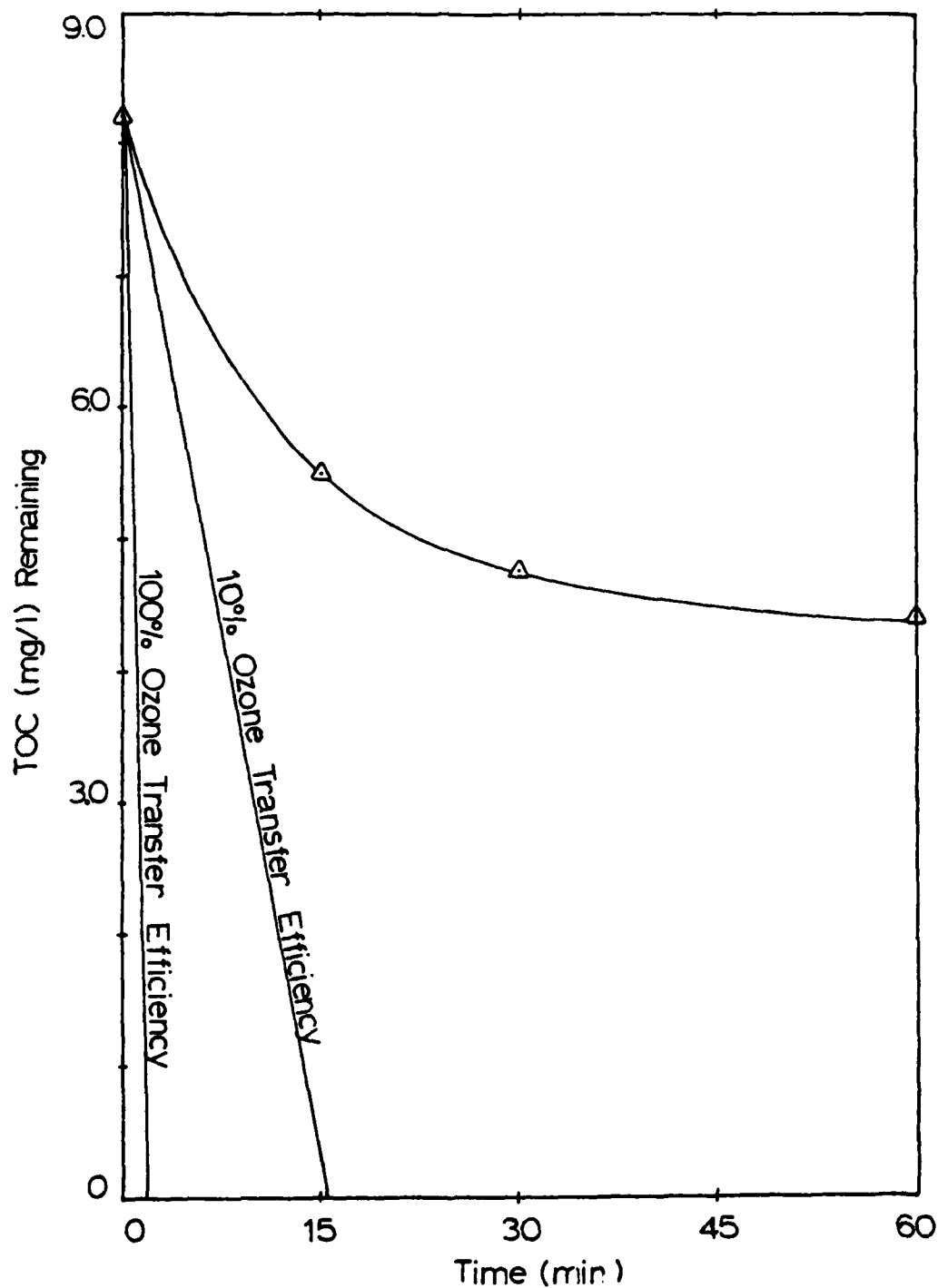


Figure 8 The Oxidation of 70/30 (mg/l) TNT/RDX Solution Diluted with 3 Volumes of Distilled Water by Ozone

Apparently as the TNT and RDX were being oxidized under these reaction conditions of temperature and pH, partial oxidation products formed which were refractory to ozone. Similar analysis for Runs 1, 2, and 3 lead to the same conclusion.

Ozone mass transfer to aqueous solution is also affected by the gas phase partial pressure. To make certain that the reaction was ozone limited, an experiment was performed (Run 7) in which Run 4 was duplicated except that the ozone mass flow rate was increased to 139.6 mg/min. Since the O_3/O_2 gas flow rate was constant in both experiments, this meant that the gas phase ozone partial pressure was increased from approximately 1% to 2%.

The results of this experiment and Run 4 in terms of TOC are plotted in Figure 9. The graph clearly demonstrates both that the reaction was not mass transfer limited and that ozone refractory species are being produced. Both runs had approximately 50% TOC removal after one hour.

2.7 REACTION TEMPERATURE EFFECT

The positive effect of temperature on reaction rate has been summarized in the generally accepted statement that for every 10°C rise in temperature, a doubling in reaction rate will occur.

In this research it has been shown that heating distilled water to temperatures as high as 90°C, to aid in the dissolution of TNT and RDX crystals, does not cause any degradation of either organic structure. Therefore, any changes in TOC or TNT destruction rates with temperature when a 70/30 mg/L TNT/RDX solution is ozonated can be ascribed strictly to the effect of thermal energy on the oxidation process.

Four experimental runs were carried out at $25 \pm 1^\circ\text{C}$, $37 \pm 1^\circ\text{C}$, $48 \pm 2^\circ\text{C}$ and $59 \pm 2^\circ\text{C}$ with 1L, 70/30 mg/L batches of TNT/RDX. The initial pH for all runs was 10.0 and an ozone mass flow rate of 72.91 mg/min was maintained for one hour. Samples were extracted after 30 and 60 minutes for analysis.

The reactor, a 1-L graduated cylinder containing the preheated batch employed a magnetic stirrer-heater system to maintain the desired temperature.

The analytical results of these runs are presented in Table 11 and in Figures 10 and 11.

The pH, during the course of each reaction, decreased. For the 25°C and 38°C run, the decrease was substantial; for example for the former reaction temperature after 60 minutes of ozonation, the solution pH was 4.30 while it was 3.84 in the latter

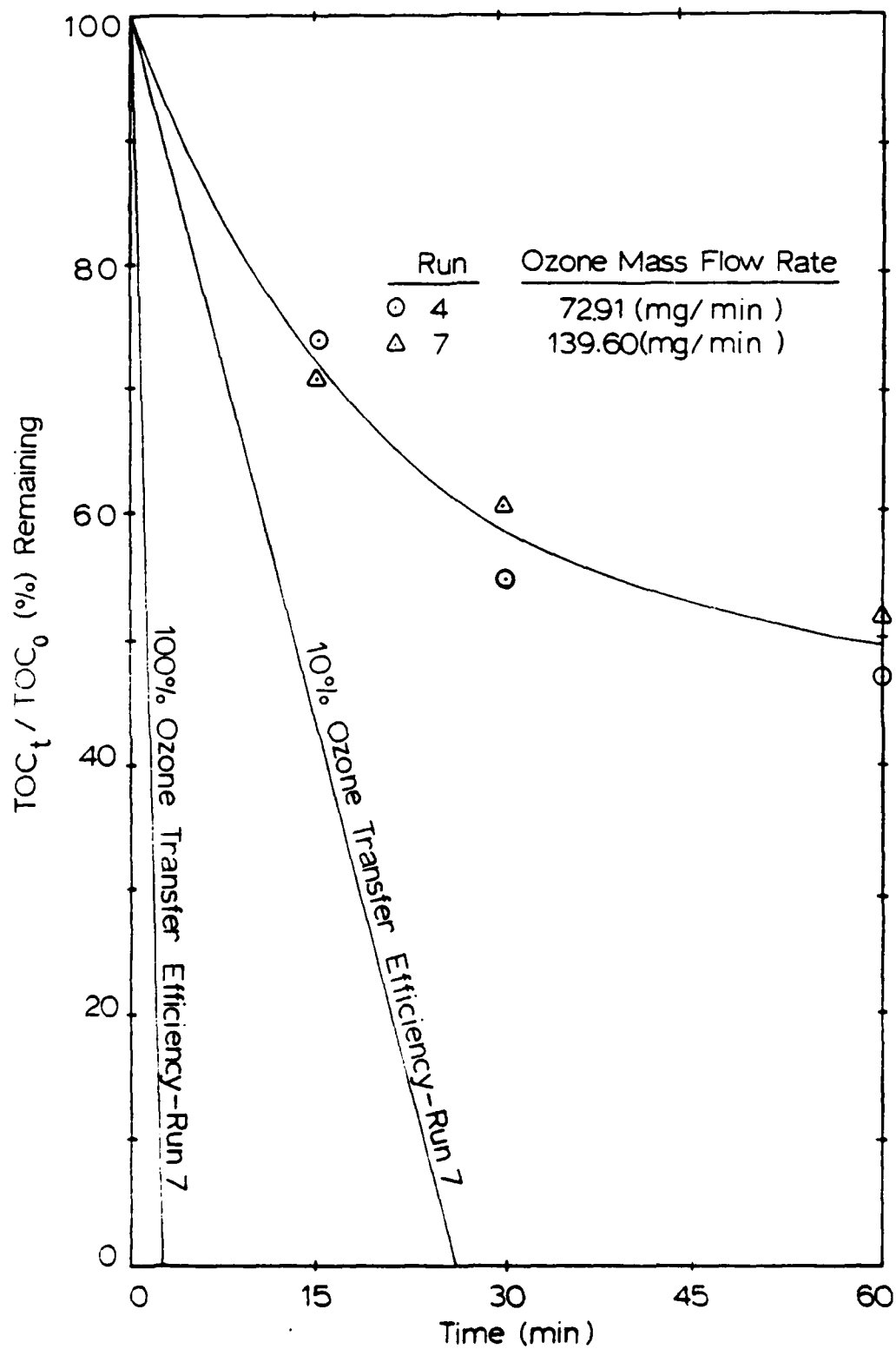


Figure 9 The Effect of Ozone Partial Pressure on Total Organic Carbon Removal of 70/30 (mg/l) TNT/RDX Solutions

TABLE 11. VARIABLE TEMPERATURE EXPERIMENTS - 70/30 (mg/L) TNT/RDX

Run No.	Temperature (°C)	Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$
1	25 ± 1	0	10.0	27.42	1.0	69.5	1.0
		30	4.72	25.35	0.93	54.0	0.78
		60	4.30	24.91	0.91	54.0	0.77
2	38 ± 1	0	10.0	27.61	1.0	69.5	1.0
		30	4.42	23.96	0.87	49.8	0.72
		60	3.84	23.78	0.86	44.4	0.65
3	48 ± 2	0	10.0	28.13	1.0	66.7	1.0
		30	7.45	15.98	0.57	13.5	0.20
		60	7.49	7.698	0.27	2.7	0.04
4	59 ± 2	0	10.0	28.72	1.0	76.8	1.00
		30	7.99	12.43	0.43	3.2	0.04
		60	8.75	3.39	0.12	0.8	0.01
5	59 ± 3	0	5.60	27.04	1.0	61.9	1.0
		30	3.56	24.81	0.92	49.7	0.8
		60	3.33	23.31	0.84	49.3	0.7
6	59 ± 6	0	6.34	27.04	1.00	62.3	1.0
		30	6.76	20.86	0.77	33.7	0.54
		60	6.69	14.46	0.53	13.5	0.22
		90	6.82	7.040	0.26	3.5	0.06
		120	7.46	1.094	0.04	0.0	0.00
7	59 ± 6	0	8.35	27.71	1.00	70.2	1.00
		30	7.65	18.74	0.68	17.0	0.24
		60	7.92	11.08	0.40	2.1	0.03
		90	8.20	2.221	0.08	0.0	0.00
8	56 ± 3	0	10.0	27.03	1.0	66.2	1.0
		30	9.78	20.60	0.76	9.2	0.14
		60	9.95	15.21	0.56	0.8	0.01
		90	10.01	13.13	0.49	0.0	0.00
		120	10.03	12.39	0.46	0.0	0.00

Ozone Mass Flow Rate - 72.91 mg/min

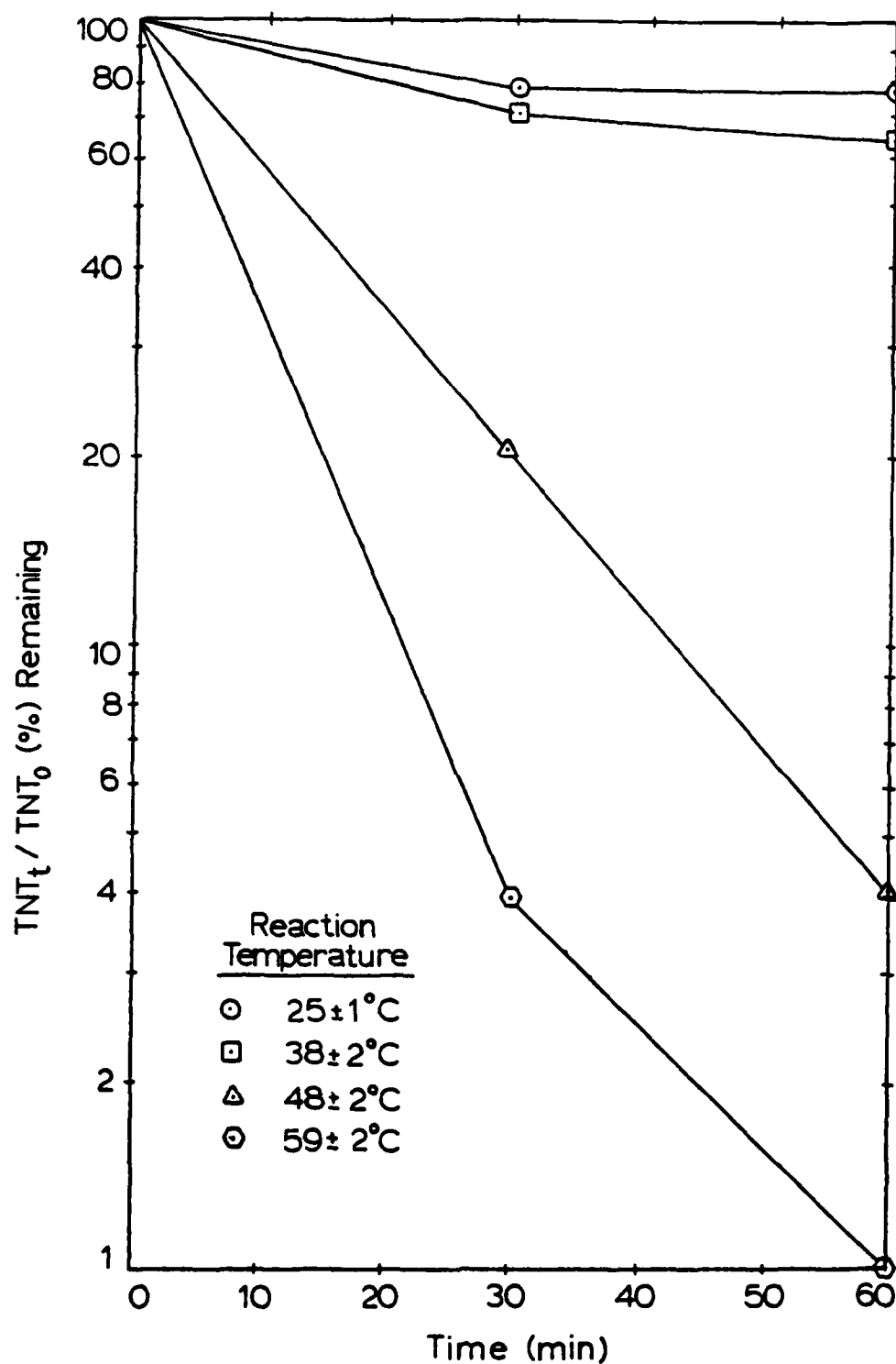


Figure 10 TNT Destruction with 72.91 mg/min of Ozone at Various Temperatures for 70/30 (mg/l) TNT/RDX Solutions

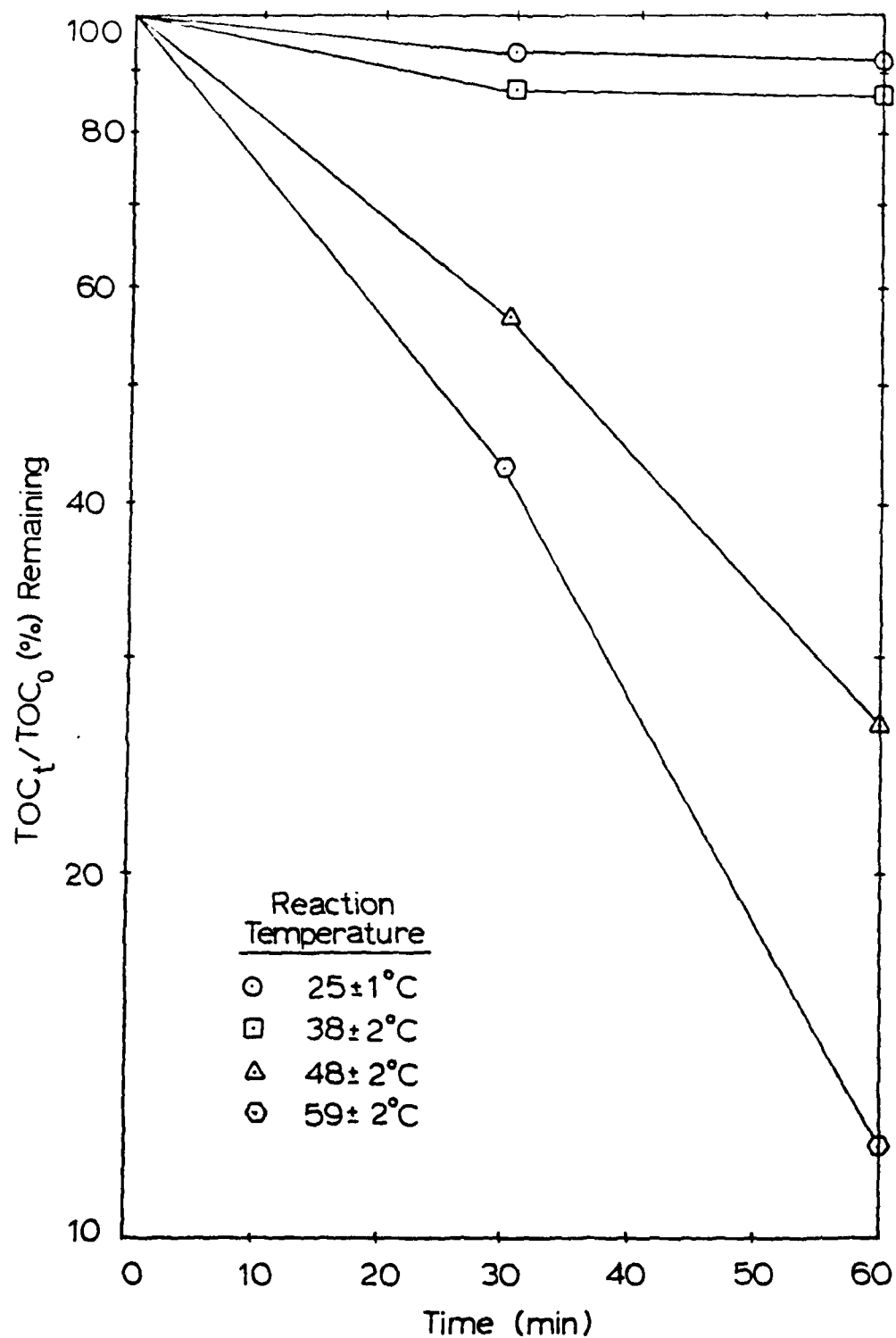


Figure 11 TOC Destruction with 72.91 mg/min of Ozone at Various Temperatures for 70/30 (mg/l) TNT/RDX Solutions

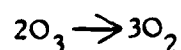
run. At the higher reaction temperatures 48°C and 59°C, the overall pH decreases during the 10 minutes of ozonation were slight, that is 10.0 to 7.49 and 10.0 to 8.75, respectively. In both of these runs the pH dropped over the first 30 minutes of reaction then increased. The different responses are possibly due to different reaction pathways which could yield variable amounts of HNO_3 or at higher temperatures the more complete oxidation of TNT and RDX would produce more CO_2 which would be readily stripped from the solution.

Elevating reaction temperature increased the destruction rate of both TNT and TOC. While at 25°C the TNT destroyed after 60 minutes of ozonation was 23%, 99% had been destroyed when the reaction temperature averaged 59°C (see Figure 10).

TNT removal simply indicates that the nitro-body structures identified by the Silas-Mason Test are no longer present. The loss of TOC, however, measures the carbon oxidized to CO_2 . At 25°C, 16% of the TOC was removed after 60 minutes of ozonation, but 88% was removed when the reaction was carried out at 59°C. The extent of TOC destruction compared to TNT removal is proportionately less at each of the four temperatures investigated (see Figure 11).

Basically, enhanced removal of TNT and TOC is due to the increased mass transfer of ozone into solution and the enhanced decomposition rate of ozone (O_3) to free radicals ($\text{OH}^\bullet$). These radicals have oxidation potentials far in excess of ozone and therefore should dramatically increase reaction rate.

Kuo, et al. [37] have studied the absorption and decomposition of ozone in aqueous solution as a function of temperature (15°C to 35°C) and pH (2.7 to 11.0). They proposed the model;



to fit the overall ozone decomposition reaction and state that the rate of decomposition of ozone can be given as;

$$-dC/dt = k_r C^n$$

where C is the ozone concentration, and k_r and n are the reaction rate constant and order of reaction, respectively. Their data yielded a value of $n = 3/2$.

These researchers have demonstrated that the Arrhenius Equation can be employed to model the data with the equation;

$$k_r = b \exp (-E/RT)$$

where E is the activation energy having the value 16.4 K cal/g mole and was independent of pH and temperature for the experimental conditions. The frequency factor b varies with pH from $2.91 \times 10^{11} \text{ M}^{-1/2}(\text{min}^{-1})$ at pH = 2.7, to $1.58 \times 10^{16} \text{ M}^{-1/2}(\text{min}^{-1})$ at pH = 11.0. Here M is equal to $k_r C_L^{1/2} D / k_L^2$ and C_L is the ozone concentration at the interface, D is the ozone molecular diffusivity and k_L is the mass transfer coefficient.

While k_r increased with all increases in pH, the rate of increase in this parameter was faster in alkaline solutions than in acidic solutions. Further, the most significant increases occurred when a neutral solution becomes slightly alkaline. For example, the rate constant increased from 0.33 to $6.67 \text{ M}^{-1/2} \text{ min}^{-1}$ when the pH value changed from 2.7 to 7.2 then rapidly increased to $1,030 \text{ M}^{-1/2} \text{ min}^{-1/2}$ at a pH of 8.4. In the 8.4 to 11.0 pH range the value of k_r varied from 1,030 to $12,200 \text{ M}^{-1/2} \text{ min}^{-1/2}$.

The effect of high temperature on ozonation reactions is to increase the systems' oxidation kinetics. This is accomplished not only by increasing the internal energy of the molecules, but as previously described by increasing the auto-decomposition rate of ozone. The effect of increased concentrations of OH^- ions is likewise to enhance ozone decomposition rates and therefore to determine if these two parameters would behave synergistically. Additional experiments at different pH levels were performed.

In Run 5, 1L of 70/30 TNT/RDX was reacted at $59^\circ \pm 3^\circ\text{C}$ for one-hour with the initial solution pH being 5.60. The ambient pH of a 70/30 mg/L batch of TNT/RDX for Run 6 the same reaction conditions except that an initial pH of 6.34 was employed and during the first hour of the experiment the pH was maintained at approximately that level. Run 6 was also continued for an additional hour, during which time the pH was not maintained. For Run 7 the initial pH was 8.35 and throughout the run NaOH was added to maintain the pH at approximately 8.0. The experimental results for these runs are depicted in Table 11 and Figures 12 and 13.

The data strongly suggest that pH played a major role in both the destruction of TOC and TNT. After 60 minutes of ozonation the percent TOC (Figure 12) removal was 16%, 47%, 60% and 88% when the initial solution pH was 5.6, 6.34, 8.35 and 10.0, respectively (i.e., Runs 5, 6, 7, 4). TNT destructions (Figure 13) followed the same pattern over one hour of reaction with 30%, 78%, 97% and 99% removals achieved when the initial reaction pH was 5.6, 6.34, 8.35 and 10.0, respectively.

The TOC results would have been expected based on the initial level and changes in pH with reaction time. At low pH values (Run 5) ozone doesn't decompose readily

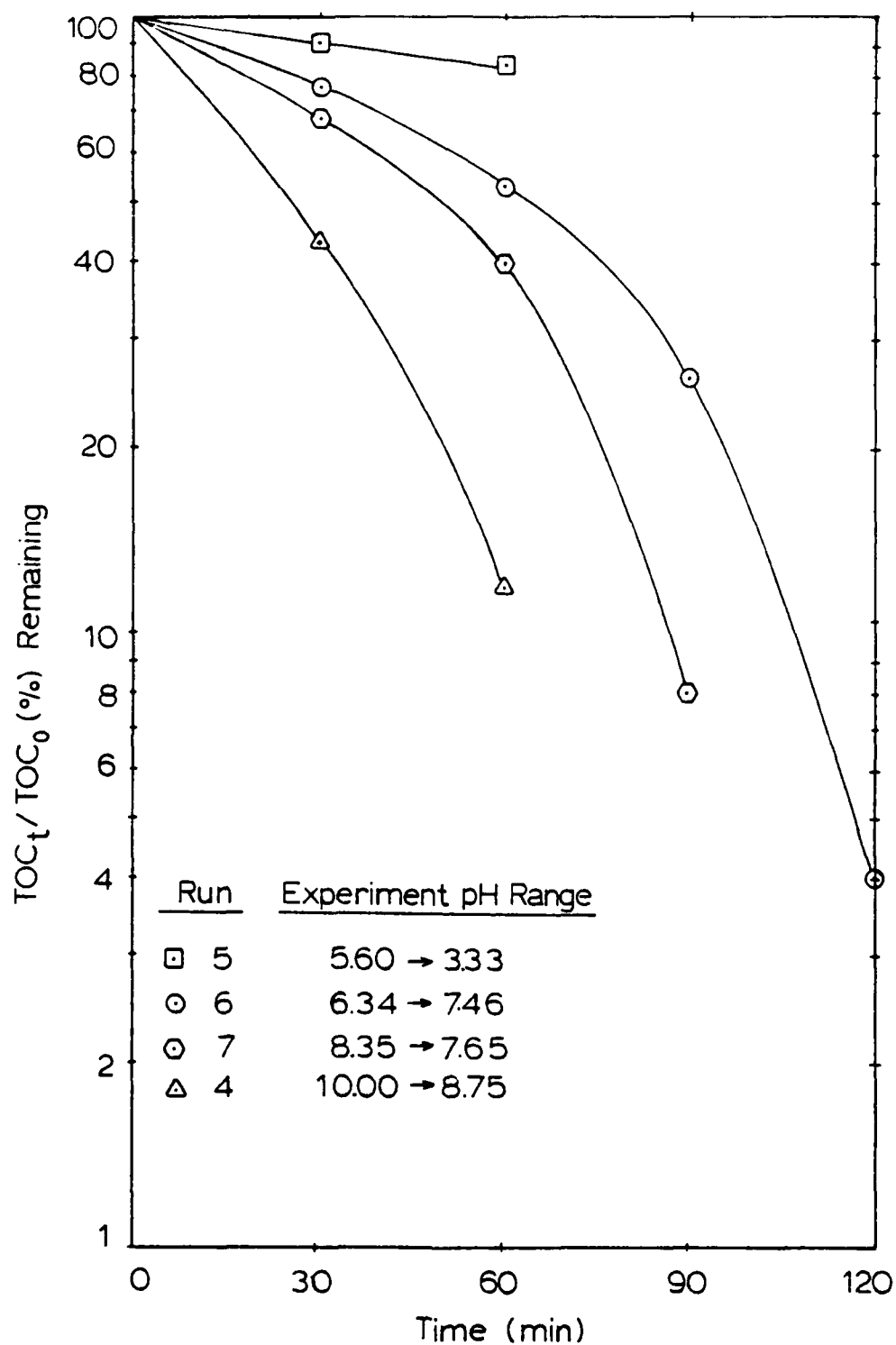


Figure 12 The Effect of Solution pH and High Temperature (59°C) Experiments with 70/30 (mg/l) TNT/RDX Solutions

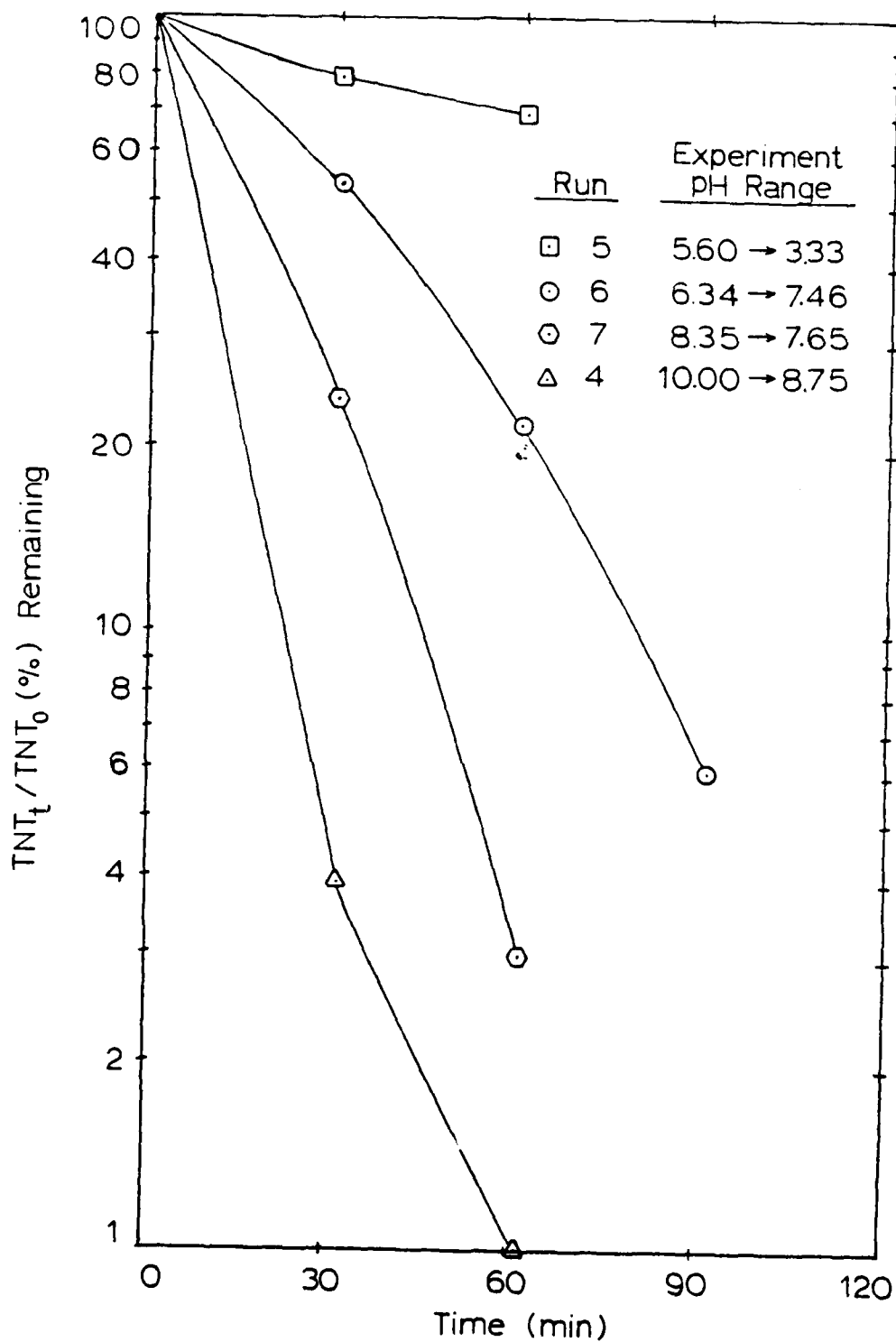


Figure 13 The Effect of Solution pH and High Temperature (59°C) Experiments with 70/30 (mg/l) TNT/RDX Solution

and oxidations are principally the result of molecular ozone and not free radicals. As the pH increases (Run 10), hydroxide ions catalyze the decomposition to $\text{OH}^\cdot$ which is a considerably more powerful oxidant.

It is interesting to note that in the controlled pH run (i.e., 7.0), after one hour of reaction, external additions of NaOH were not required to maintain an approximately neutral pH. In fact, the pH rose to 7.46 from 6.82 during the final 60 minutes of reaction.

One other run (Run 8) in this series of experiments was made to ascertain if a constant high pH (i.e., 10.0) and high temperature (i.e., 59°C) would produce high rates of reaction. The data in Table 11 demonstrate that this combination of high pH and temperature is not beneficial. For example, after 60 minutes of ozonation only 44% of the TOC had been oxidized. By comparison in Run 4 where the initial pH of 10.0 was not maintained, but permitted to decrease with reaction time, 88% of the TOC had been destroyed. However, in terms of TNT destructions, both Runs 4 and 8 exhibited a 99% reduction in one hour.

These data suggest that high temperature and pH both promote ozone decomposition and radical formation; however, radical-radical reactions are also promoted by these reaction conditions leading to extinguishment of these powerful oxidation species.

To test this hypothesis further, runs with high temperature (i.e., 59°C) together with high and low pH (i.e., 10.0 and 5.86) and ultrasound (859 kHz) were performed. Theoretically, radical-radical quenching reactions should be enhanced by ultrasound and organic destruction rates should be decreased in the presence of ultrasound.

According to the data listed in Table 12 and Figure 14 that is exactly what transpired. In essence for the low pH run (i.e., 5.6) it took 35 additional minutes of ozonation to reduce TOC by the same amount as in the no-ultrasound run (compare Run 5 with Run 9) and approximately 120 minutes more to duplicate the TOC reduction in the high pH (10.0) run (compare Run 4 with Run 10).

The additional ozonation time requirement for the high pH run was due to the fact that the rate of radical-radical extinguishment is probably a first-order reaction. Under those circumstances, more radicals would be quenched before they could react and thus the reduction in rate.

In essence the effects of reaction temperature and solution pH are both important to TNT and TOC destruction. Since this research has demonstrated the large positive

TABLE 12. THE EFFECT OF ULTRASOUND (829 kHz), HIGH TEMPERATURE (59°C) AND TWO INITIAL SOLUTION pH LEVELS ON TOC AND TNT DESTRUCTION OF 70/30 (mg/L) TNT/RDX

Run No.	Temperature (°C)	Time (min)	pH	TOC (mg/L)	$\frac{\text{TOC}}{\text{TOC}_0}$	TNT (mg/L)	$\frac{\text{TNT}}{\text{TNT}_0}$
9	56 ± 2	0	5.86	27.56	1.00	74.0	1.00
		30	3.52	25.56	0.93	57.3	0.77
		60	3.36	24.19	0.88	50.3	0.70
		90	3.24	23.31	0.85	42.5	0.57
		120	3.16	21.83	0.79	36.7	0.50
10	57 ± 3	0	10.00	27.19	1.00	71.4	1.00
		30	8.46	18.20	0.67	7.1	0.10
		60	7.48	11.61	0.43	1.4	0.02
		90	8.17	5.722	0.14	0.3	0.00
		120	8.50	3.397	0.12	0.3	0.00

Ozone Mass Flow Rate - 72.91 mg/min

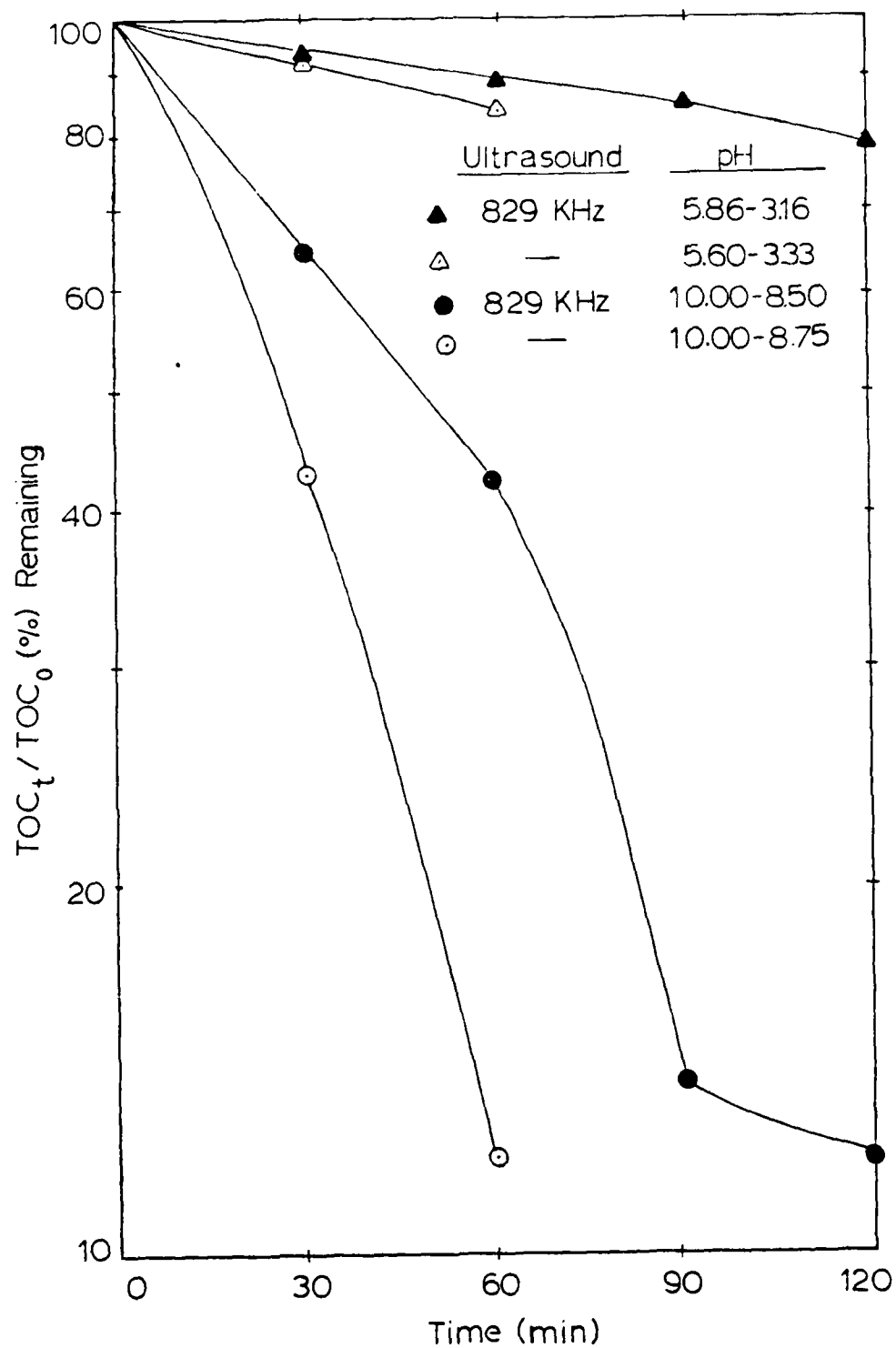


Figure 14 The Effect of Ultrasound at Two pH levels with Ozone Oxidation of 70/30 TNT/RDX Solutions at High Temperature ($\sim 59^{\circ}\text{C}$)

response to reaction temperature increases and since most of the high temperature experiments were conducted at approximately 59°C, the parameter solution pH was examined to isolate its effect on TOC destruction at this fixed (59°C) temperature.

Plotted in Figure 15 are the TOC removal rates, measured over 30-minute intervals, as a function of solution pH. The data suggest two conclusions. First, the optimum pH is decreased with reaction time. For example, during the first 30 minutes of reaction, the best TOC removal rates were obtained at a pH of approximately 9.6. For the second and third 30-minute intervals, the optimum solution pH's were approximately 8.7 and 8.1, respectively. The second conclusion is that maintaining a high pH (i.e. > 9.6) reduces the destruction rate of TOC.

2.8 COMPARISON OF ULTRAVIOLET-OZONE vs HIGH TEMPERATURE OZONE DESTRUCTION OF TNT PINK WATER

Tatyrek [6] described the state-of-the-art treatment methods for TNT wastewaters and classified the 14 methods under two general headings: (a) concentration methods and (b) destructive methods. Ozonation and ozone catalyzed reactions fell into the latter category.

Ciccone [40] economically evaluated seven feasible pink water treatment processes, one of which employed an ultraviolet catalyzed ozone system. The design evaluated by Ciccone was based on the process described by Farrell [16]. In this system the influent flowed to an equalization tank with a hydraulic detention time of one day, then was passed through a diatomaceous filter. The filtrate next entered an ozone precontactor before being pumped to the ozone reactor which contained 2,304 - 65-watt ultraviolet lamps, each of which was five-feet in length and slightly in excess of one-inch in diameter. Ozone was to be produced from chilled air by an ozonator. Treated wastewater would flow to a 25,000 gallon detention holding tank from where it could be discharged or returned to the diatomaceous earth filter for backwash.

The process received a relative low ranking of five out of seven feasible alternatives on the basis of the Present Value - Unit Cost (PVUC) methodology. This methodology permits treatment unit cost calculations based on a "systems" basis thereby accounting for all of the major system unit processes and components.

The capital costs for this process were influenced principally by the ozone reactor size, which is directly proportional to the hydraulic detention time. The time required to produce an effluent with 1.0 mg/L TNT, the effluent design requirement, was found

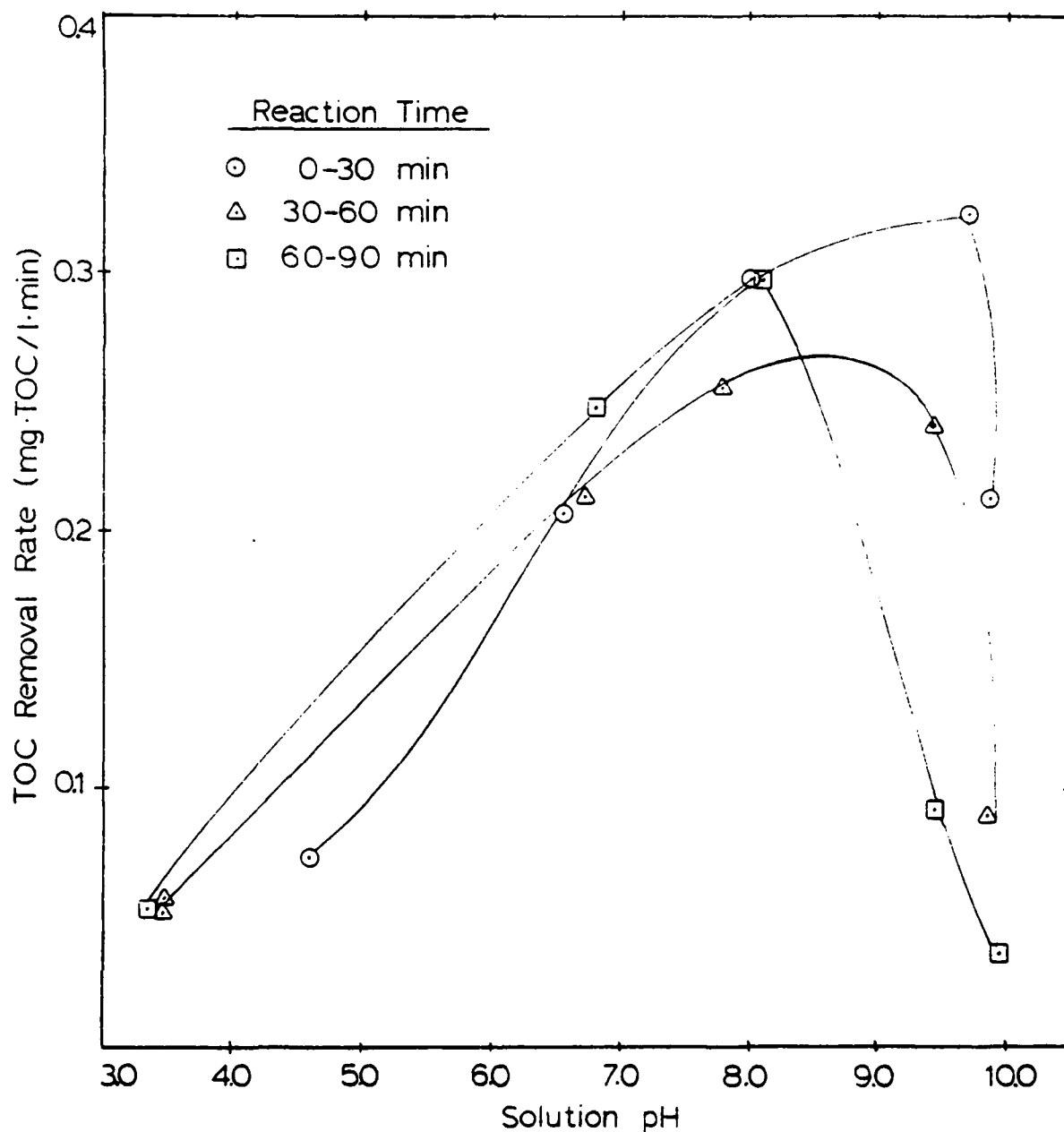


Figure 15 The Effect of Solution pH on the TOC Removal Rate for 70/30 (mg/l) TNT/RDX Solutions at High Temperature (~59°C)

to be 2.5 hours. Operational and maintenance costs were found to be high because of the large electrical energy requirement to operate the 2,304 UV lamps as well as the replacement costs for those lamps. A lamp lifetime of 7,500 hours was projected in the analysis. The total electrical energy requirement for the system was 5,794 kwh per 1×10^6 gpd treated and 1,498 kwh or 25.9% of that amount was due to the operation of the UV lamps.

It can be seen from this discussion that the use of ozone and ultraviolet light to treat pink water is a highly energy intensive system.

This research has shown that treatment of munitions wastewaters at elevated temperatures (i.e., 59°C) by plain ozonation, which shall be referred to as the thermal ozone process, is an effective technique possessing several major advantages over the UV-ozone system. For example, an effluent containing < 1.0 mg/L TNT was produced from a 70/30 (mg/L) TNT/RDX influent, after less than 1.0 hour of ozonation, when the batch had an initial pH of 10.0 and the temperature was approximately 59°C. Based on the 2.5 hour requirement by the UV-ozone process, this represents a 60% savings in reactor hydraulic detention time which would be reflected in a substantially lower system capital cost.

Similarly, no catalyst (i.e., UV radiation) is required in thermal-ozone processes and thus there is no energy requirement to operate the UV lamps (i.e., 1,498 kwh). Several additional operational parameters, such as no field replacement of 2,304 lamps each 7,500 hours and loss of catalytic activity due to deposition of materials on the quartz sleeve shielding the UV lamps, must also be considered. Finally, the reactor geometry is not constrained by the lamp size (i.e., 1-inch diameter by 5.0 feet in length) and therefore an optimum design, particularly with respect to ozone mass transfer, can be achieved.

Obviously, a source of energy must be provided to achieve a reaction temperature of 59°C. Since the temperature increase required is modest (i.e., 18°C $\rightarrow$ 59°C), and only sensible heat is required, the potential for obtaining free heat energy sources is improved. For example, waste heat is available within the munitions production facility and could be harvested. Also, solar energy has a potential for this purpose since it is within the present capability of passive solar heaters.

In conclusion, this research has demonstrated the benefits of the thermal-ozone process when compared to the UV-ozone process. Since reaction temperatures in excess of 59°C were not investigated, it is feasible even further improvements could be possible.

2.9 CONCLUSIONS

- (a) Increasing initial solution pH in the range 5.43 to 10.0 caused an increase in the rate of TOC and TNT destruction for 70 mg/L TNT solution. The addition of ultrasound into this reaction increased further the TOC and TNT destruction rates slightly, but this was attributed to the rise in reaction temperature due to the conversion of ultrasonic energy to thermal energy.
- (b) Oxygen sparging in the presence of ultrasound for one hour, even at high temperature (59°C) and a solution pH of 10.0 did not produce either TOC or TNT changes in 70/30 mg/L TNT/RDX solution.
- (c) Ultrasound power level in the range from 5 to 50 watts for a fixed frequency (i.e. 856.0 kHz), increased TOC and TNT removal rates but did so because of proportional increases in reaction temperature.
- (d) Of the three ultrasonic frequencies (i.e., 60.6, 859, 1007 kHz) studied, 859 kHz yielded the best results in destruction of TOC and TNT with both aqueous solutions of TNT or TNT/RDX.
- (e) Increasing initial solution pH in the range 5.60 to 9.6 when the reaction temperature was 59°C produced proportional increases in reaction rate; however, this was true only when solution pH was not controlled. At solution pH's maintained in excess of 9.6, the combination of high pH and temperature was not beneficial. This was due to the enhancement of radical-radical extinguishment reactions. The use of ultrasound likewise promotes the same behavior and thus destruction rates for TOC and TNT were both reduced.

- (f) Experiments at ambient temperature and a fixed pH of approximately 9.5 in an ozone nonmass transfer limited reaction mode showed virtually 100% TNT destruction but only 50% TOC loss in one hour, regardless of substrate (70/30 TNT/RDX) concentration, indicating the production of ozone resistant partial oxidation products for these reaction conditons.

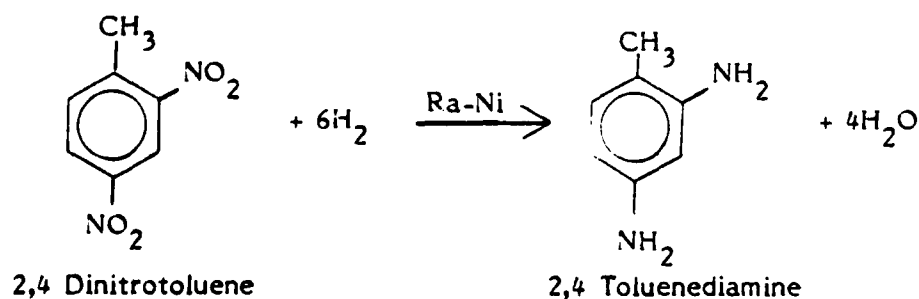
3.0 RANEY-NICKEL EXPERIMENTS

3.1 INTRODUCTION

The treatment of munitions wastewaters by ozonation without catalysis has undesirable kinetic responses. Catalysts such as ultraviolet light and hydroxide ions have been utilized in an attempt to increase reaction velocities. Another potential heterogeneous catalyst is Raney-Nickel (Ra-Ni).

Ra-Ni catalysts were developed originally by Mr. Murray Raney in 1925 (U.S. Patent # 1,563,587). They were prepared from powdered Ra-Ni aluminum alloys, usually containing 50% nickel and 50% aluminum (by weight). The activation process employing strong caustic- soda solution, removed most of the aluminum leaving a highly agglomerated spongy form of nickel, which had approximately 80-100 square meters of surface area per gram of catalyst. This material has a capacity for adsorbing hydrogen.

Known as Ra-Ni catalyst, it has been applied in a wide array of chemical processes, ranging from those producing petroleum, pharmaceuticals and plastics to those engaged in food processing. Ra-Ni has widely been used for hydrogenation, amination, reduction and oxidation. Typical reactions include the saturation of olefinic and acetylenic bonds, saturation of aromatic rings, and the reduction of aldehydes and ketones to their corresponding alcohols. Nitro groups are readily converted by Ra-Ni to amines as shown in the reaction below:



Smith, et al. [38] performed an extensive study of various catalysts for the oxidation of phenol in aqueous solution. They concluded that Ra-Ni was the best catalyst

for phenolic wastewater, especially when used in combination with ultrasonic irradiation. From the destruction of phenol and the decrease of chemical oxygen demand (COD), it was found that Ra-Ni could not only insert oxygen into the aromatic carbon-hydrogen bond, but also enhanced the rupturing rate of the aromatic rings. The intermediate products included di- and trihydroxybenzenes and certain organic acids (e.g., maleic acid and muconic acid).

3.2 EXPERIMENTAL

3.2.1 Experimental Process Flow Diagram

The experiments performed with Ra-Ni in this research are described in the experimental flow diagrams in Figure 16. The first procedure consisted simply of contacting Ra-Ni with TNT/RDX, separating the catalyst by vacuum filtration and analyzing the effluent. This procedure is referred to throughout this report as the Catalytic Destruction Process. Contacting TNT/RDX with Ra-Ni in the presence of ozone then using vacuum filtration to remove the catalyst is referred to as the Catalytic Ozonation Process.

3.2.2 Wastewater Preparation

The wastewaters employed in this research included: (1) a 70 mg/L aqueous solution of TNT, (2) a 30 mg/L aqueous solution of RDX and (3) an aqueous solution containing 70mg/L of TNT and 30 mg/L of RDX. The preparation of these synthetic solutions was described in Section 2.2.

3.2.3 pH Adjustments

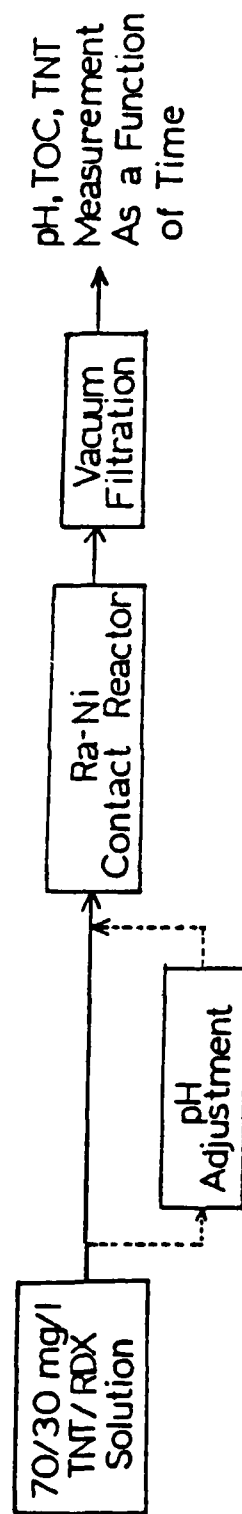
The ambient pH of batch TNT/RDX solutions was approximately 5.54 (i.e., pH ranged from 5.40 to 5.75). After adding the volumetrically measured Ra-Ni, which contained approximately 50% water (by weight) at pH 11-12, the solution pH increased immediately. The magnitude of the pH increase was proportional to the dosage of Ra-Ni. For example, the solution pH ranged from 8.85 to 10.61 by adding between 1/4 teaspoonful (tsp.) and 1 tablespoonful (tbsp.) of Ra-Ni to 3.0L of synthetic 70/30 mg/L TNT/RDX solutions.

For those runs in which pH's were adjusted to the desired pH (i.e., 10.74 and 11.00) before Ra-Ni addition, 0.1 N of NaOH aqueous solution was used.

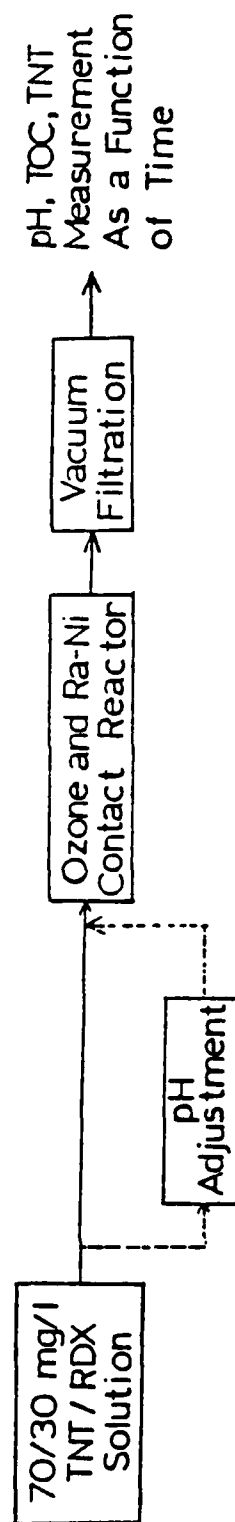
3.2.4 Catalyst Dose Determination

The catalyst used throughout this research was taken from a single batch of W. R. Grace No. 2,800 activated Ra-Ni. Since the Ra-Ni was pyrophoric, it was

1. Catalytic Destruction of TNT/RDX with Ra-Ni



2. Catalytic Ozonation of TNT/RDX with Ra-Ni



---[]---: Unit process only for certain pH effect experiment

Figure 16 Experimental Flow Diagram

supplied in slurry form (50% solids and 50% water, by weight) and therefore it was more convenient to add it in a volumetric fashion rather than weighing it prior to addition to the reactor. Common plastic measuring spoons (i.e., 1/4, 1/2, 1.0 tsp and 1.0 tbsp.) were employed as measuring tools throughout this study. To insure the consistent measurement, the appropriate sized teaspoon and tablespoon, which contained Ra-Ni, was leveled and its periphery cleaned to remove any extra Ra-Ni prior to admission to the reactor.

The amount of Ra-Ni in each size of spoon was determined from the difference of the weights of the empty spoon and the leveled spoon containing Ra-Ni slurry. The gross wet weights were 2,238, 4,836, 9,366 and 27,798 mg for 1/4, 1/2, 1.0 tsp. and 1.0 tbsp., respectively. Because the Ra-Ni slurry contained approximately 50% water (by weight), the approximate net weights of Ra-Ni were 1,119, 2,418, 4,638, and 13,899 for 1/4, 1/2, 1.0 tsp. and 1.0 tbsp., respectively.

3.2.5 Catalytic Destruction Process Apparatus

A 4L glass beaker with a dual-blade propeller mixer as shown in Figure 17, served as the reactor for all experiments. The reactor (Pyrex No. 1,000, 4,000 mL beaker) was 16 cm (6.3 inches) in diameter and 25.4 cm (10 inches) in height. The propeller mixer was driven by an 0.19 kw (1.7 hp) electric motor and its speed was controlled by a variable transformer (Talboys Instrument Corporation, Emerson, New Jersey). The 316 stainless steel axis of the propeller mixer was 0.64 cm (0.25 inches) in diameter and 28.2 cm (11.25 inches) in length and inclined from the liquid surface of the glass beaker with an angle of approximately 60°. The total immersion length of the shaft was approximately 15 cm (6 inches). The propeller had three 316 stainless steel blades which were 0.79 cm (0.3125 inches) in diameter. The two propellers were positioned at 1.25 cm (1.5 inches) and 10.80 cm (4.5 inches) from the tip of the mixer axis.

For each run, a volumetrically measured Ra-Ni dose was added directly into the reactor which contained 3.0L of synthetic TNT/RDX wastewater and was mixed with the mixer at a sufficient high speed (i.e., 40% of scale in this study) to cause all the catalyst to remain in suspension. Samples were extracted from the reactor with a 50 mL beaker (Pyrex No. 1,000, 50 mL) at various times. Normally, samples were taken after 1.0, 2.0, 5.0, 10, 20 and 30 minutes of treatment.

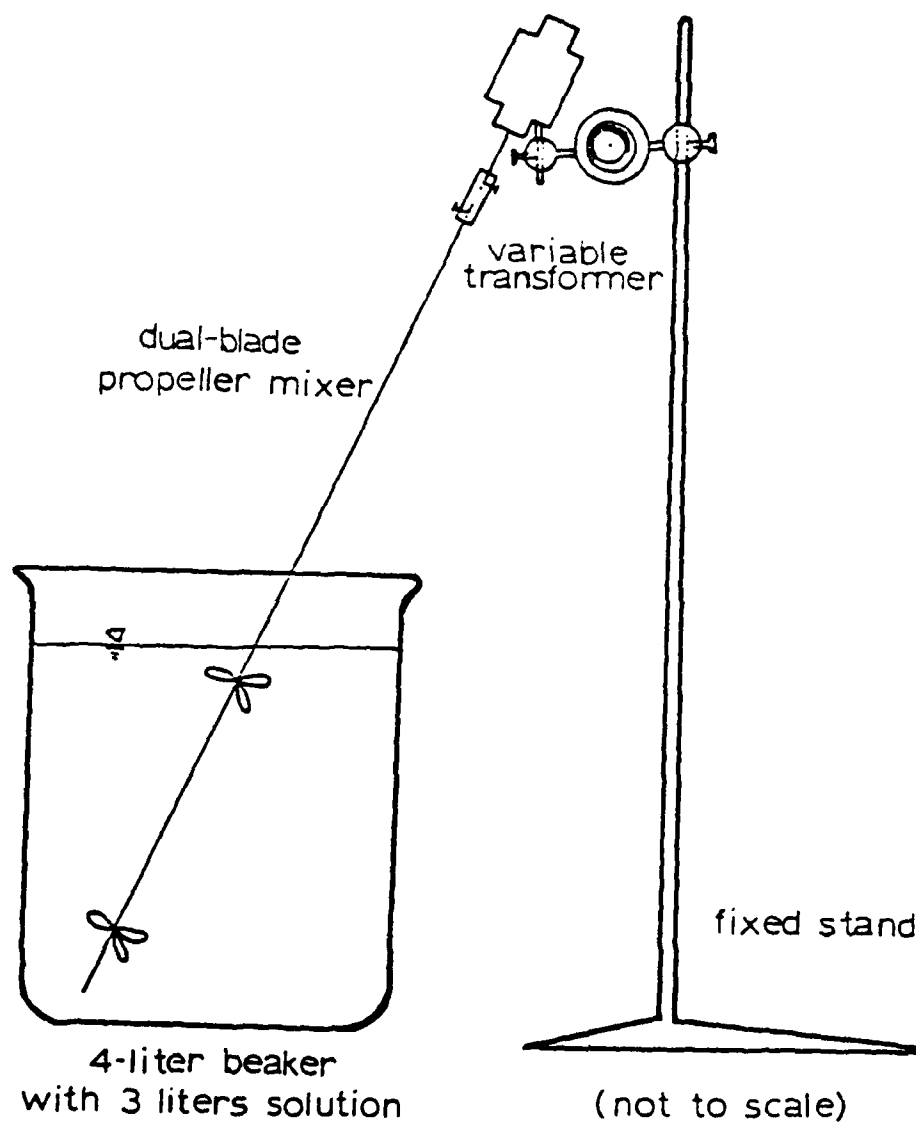


Figure 17 Reactor System for Catalytic Destruction with Ra-Ni

3.2.6 Catalytic Ozonation Process Apparatus

The catalytic ozonation reactor system shown in Figure 18 was identical to the one used for the catalytic destruction process. Ozone was added through a porous gas sparger (12.5 cm in diameter) at the bottom of the reactor. The gas sparger was produced from sintered 316 stainless steel and was capable of producing fine gas bubbles (i.e., 5 μ m average size).

The ozonation system employed is shown in Figure 19. Commercial-grade oxygen with negligible hydrocarbon content was fed to an Orec Model 03B1-0 Ozonator (Ozone Research & Equipment Corporation, Phoenix, Arizona) for ozone production. Tygon tubing was used for connections between the oxygen cylinder and the ozonator, and between the ozonator and the reactor. A powerstat in the ozonator was adjusted to permit operation at the desired voltage and wattage (i.e., 60 watts and 150 watts) in this study. A rotameter and pressure gauge indicated the flow rate of the ozone/oxygen gas into the reactor (i.e., 6L per minute at 10 psig). The ozone doses taken from the operating manual of the ozonator were 18.6 and 36.8 mg $O_3/L O_2$ at 60 watts and 150 watts, respectively, with a gas flow rate of 6L/min (i.e., 111.6 mg O_3/min and 220.8 mg O_3/min , respectively).

The experimental procedure for the catalytic ozonation with Ra-Ni was the same as that of the catalytic destruction with Ra-Ni with the exception that the gas sparger was moved manually in an up and down motion (about 100 times per minute with an amplitude of 2.5 cm), to prevent the settling of the catalyst. Ra-Ni settling occurred because of the presence of the gas sparger in the reactor even though turbine mixing intensity was the same as in the catalytic destruction with Ra-Ni and therefore, necessitated the above-described manual mixing.

3.2.7 Analytics

For each sample taken, a 40 mL volume was extracted from the reactor and then filtered, divided into two aliquots, one containing 15 mL for TOC analysis and the other 25 mL for pH measurement with a Corning Model 125 pH meter and TNT determination. The pH measurement was made prior to the TNT determination because the later involved a chemical reaction which would alter the solution pH. All analytical procedures are described in Appendix A.

3.3 CATALYTIC DESTRUCTION PROCESS

To evaluate the effect of Ra-Ni on the destruction of primarily TNT/RDX in aqueous solution but also aqueous solutions of TNT only, pH, TOC and TNT were

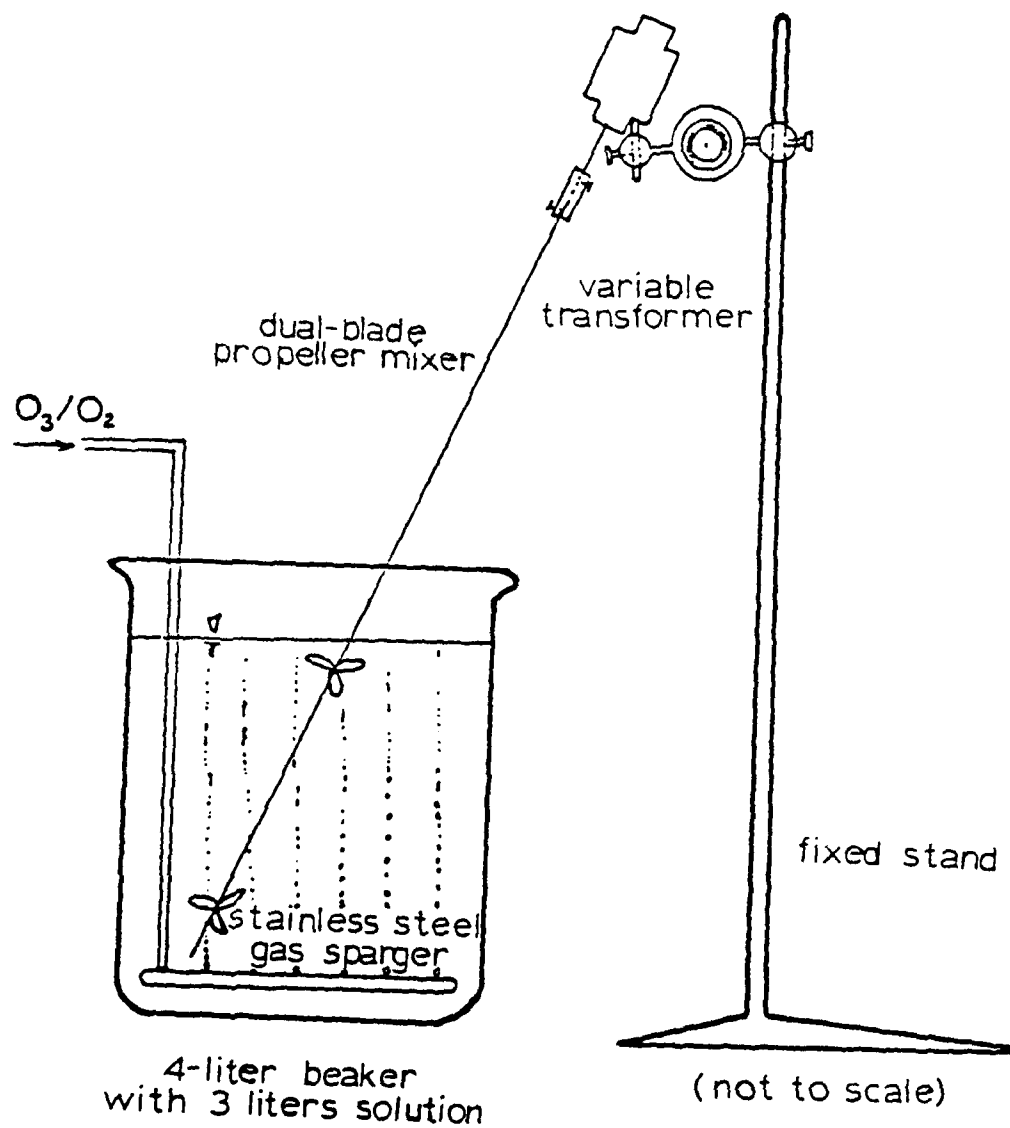


Figure 18 Reactor System for Catalytic Ozonation with Ra-Ni

monitored as a function of reaction time. The physical appearance of samples, such as color and turbidity, also was noted. From these data, the rate and extent of TOC and TNT destructions were determined.

The analytic data for the catalytic destruction of TNT and RDX with Ra-Ni are presented in Tables 13 and 14 and Figures 20, 21 and 22.

3.3.1 Physical Appearance Changes

The change in appearance of the TNT/RDX reaction solutions implied that the contact between TNT/RDX and Ra-Ni involved chemical reaction. For the 1/4 tsp run, the filtered ($0.45 \mu m$) samples exhibited a turbidity not seen in the other runs containing higher concentration of Ra-Ni for reaction times of 5, 7.5 and 15 minutes. Also, the reaction mass for this experiment was initially colorless but turned to a light yellow color and continued to increase in color intensity until 15 minutes into the run and then decreased with the contact time. For the 1 tbsp run, however, the yellow color only appeared during the first 2.0 minutes of reaction. For the 1/2 tsp and 1 tsp runs, the yellow color was more intense during the first two minutes and then became lighter with reaction time; however, it never completely disappeared.

In an attempt to explain the appearance of yellow color, individual batches of 70 mg/L TNT and 30 mg/L RDX were contacted with 1 tsp Ra-Ni. For the 30 mg/L RDX batch, it was found (see Table 14) that the reaction mass was colorless throughout the course of the contact period. Conversely, for the 70 mg/L TNT batch, it turned yellow-brown after one minute of contact with Ra-Ni and then became lighter with increased contact time. By comparison with the 70/30 mg/L TNT/RDX batch, with a catalyst concentration of 1 tsp Ra-Ni, the 70 mg/L TNT batch produced a darker yellow color. It can therefore be concluded that the yellow coloring resulted from the interaction between Ra-Ni and TNT.

3.3.2 pH Changes

With respect to the parameter pH, it was found that the initial pH of 70/30 mg/L TNT/RDX solution (i.e., 5.55-5.62) was always increased upon the addition of Ra-Ni. This was due to the high pH (i.e., 11-12) water used to package the Ra-Ni in slurry form, thereby avoiding problems due to the pyrophoric nature of the catalyst. However, the initial pH increase for 70 mg/L TNT batch was much smaller than that for 70/30 mg/L TNT/RDX batch (i.e., 5.94 to 7.90 vs. 5.5 to 10.13 for the 1 tsp run). These pH responses on the addition of Ra-Ni to the TNT/RDX batch were therefore probably due to the presence or absence of RDX.

TABLE 13. THE CATALYTIC DESTRUCTION OF 70/30 mg/L TNT/RDX IN 3L AQUEOUS SOLUTION

<u>1/4 tsp. Ra-Ni</u>									
Time (min)	0	1	2	5	7.5	15	30		
pH	5.62	8.85	8.91	9.06	9.16	9.36	9.11		
TOC (mg/L)	27.65	26.22	25.25	23.91	22.86	23.53	23.13		
TNT (mg/L)	67.3	48.8	40.1	31.0	34.1	30.5	30.0		
TNT/TOC	2.43	1.86	1.59	1.30	1.49	1.30	1.30		
Appearance	colorless	light yellow	yellow	yellow	dark yellow	yellow (turbid)	light yellow		
<u>1/2 tsp. Ra-Ni</u>									
Time (min)	0	1	2	5	7.5	15	30		
pH	5.55	9.22	9.17	9.21	9.28	9.21	8.92		
TOC (mg/L)	27.74	24.32	22.21	20.69	19.91	19.05	15.97		
TNT (mg/L)	67.8	44.3	35.6	26.5	24.1	19.84	13.0		
TNT/TOC	2.44	1.82	1.60	1.28	1.21	1.04	0.82		
Appearance	colorless	dark yellow	dark yellow	yellow	yellow	light yellow	light yellow		
<u>1 tsp. Ra-Ni</u>									
Time (min)	0	1	2	5	7.5	15	30		
pH	5.55	10.13	10.17	10.19	10.17	10.15	9.68		
TOC (mg/L)	27.38	21.49	19.45	16.93	16.05	13.91	13.70		
TNT (mg/L)	67.0	21.9	15.2	8.9	7.1	2.9	2.9		
TNT/TOC	2.45	1.02	0.78	0.53	0.44	0.21	0.21		
Appearance	colorless	dark yellow	dark yellow	yellow	yellow	light yellow	light yellow		
<u>1 tbsp. Ra-Ni</u>									
Time (min)	0	1	2	5	7.5	15	30		
pH	5.62	10.61	10.79	10.60	10.48	10.09	10.04		
TOC (mg/L)	27.65	12.55	10.36	8.298	6.403	4.288	2.682		
TNT (mg/L)	67.3	0.0	0.0	0.0	0.0	0.0	0.0		
TNT/TOC	2.43	0.00	0.00	0.00	0.00	0.00	0.00		
Appearance	colorless	light yellow	colorless	colorless	colorless	colorless	colorless		

TABLE 14. THE CATALYTIC DESTRUCTION WITH Ra-Ni FOR 3L OF
70 mg/L TNT BATCH AND 30 mg/L RDX BATCH

<u>1 tsp. Ra-Ni for 70 mg/L TNT Batch</u>							
Time (min)	0	1	2	5	7.5	15	30
pH	5.94	7.90	8.87	9.51	9.78	10.01	7.91
TOC (mg/L)	25.22	18.78	16.16	13.45	11.99	11.68	10.21
TNT (mg/L)	67.0	27.0	18.5	12.0	12.3	10.9	8.4
TNT/TOC	2.66	1.44	1.14	0.89	1.03	0.86	0.82
Appearance	colorless	yellow	yellow	yellow	yellow	light yellow	light yellow

<u>1 tsp. Ra-Ni for 30 mg/L RDX Batch</u>							
Time (min)	0	1	2	5	7.5	15	30
pH	5.95	9.95	10.01	10.05	10.02	9.99	9.98
TOC (mg/L)	4.669	3.936	3.582	2.910	3.371	3.386	3.518
Appearance	colorless	colorless	colorless	colorless	colorless	colorless	colorless

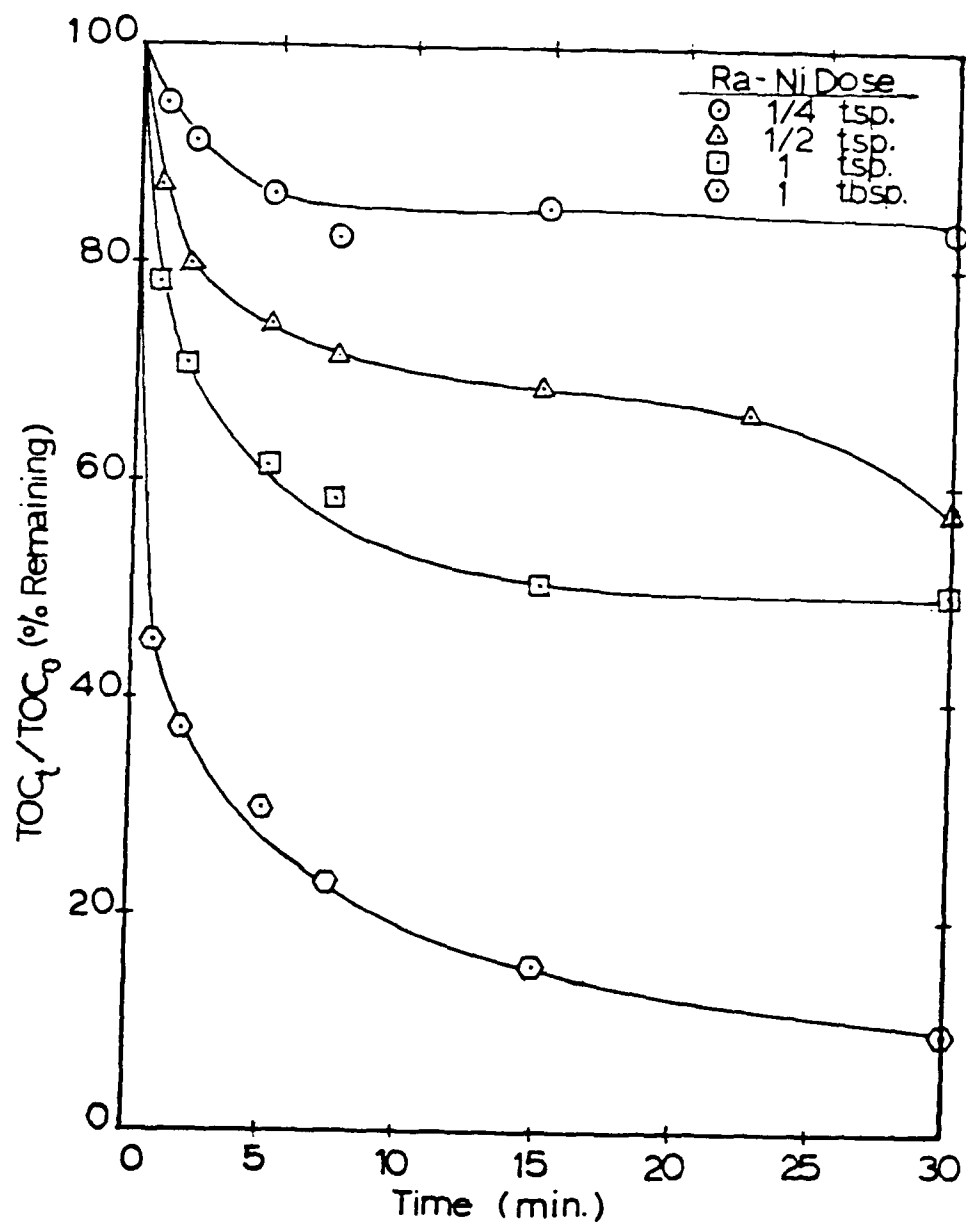


Figure 20 The Effect of Ra-Ni Dose on the Removal of TOC in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Destruction with Ra-Ni

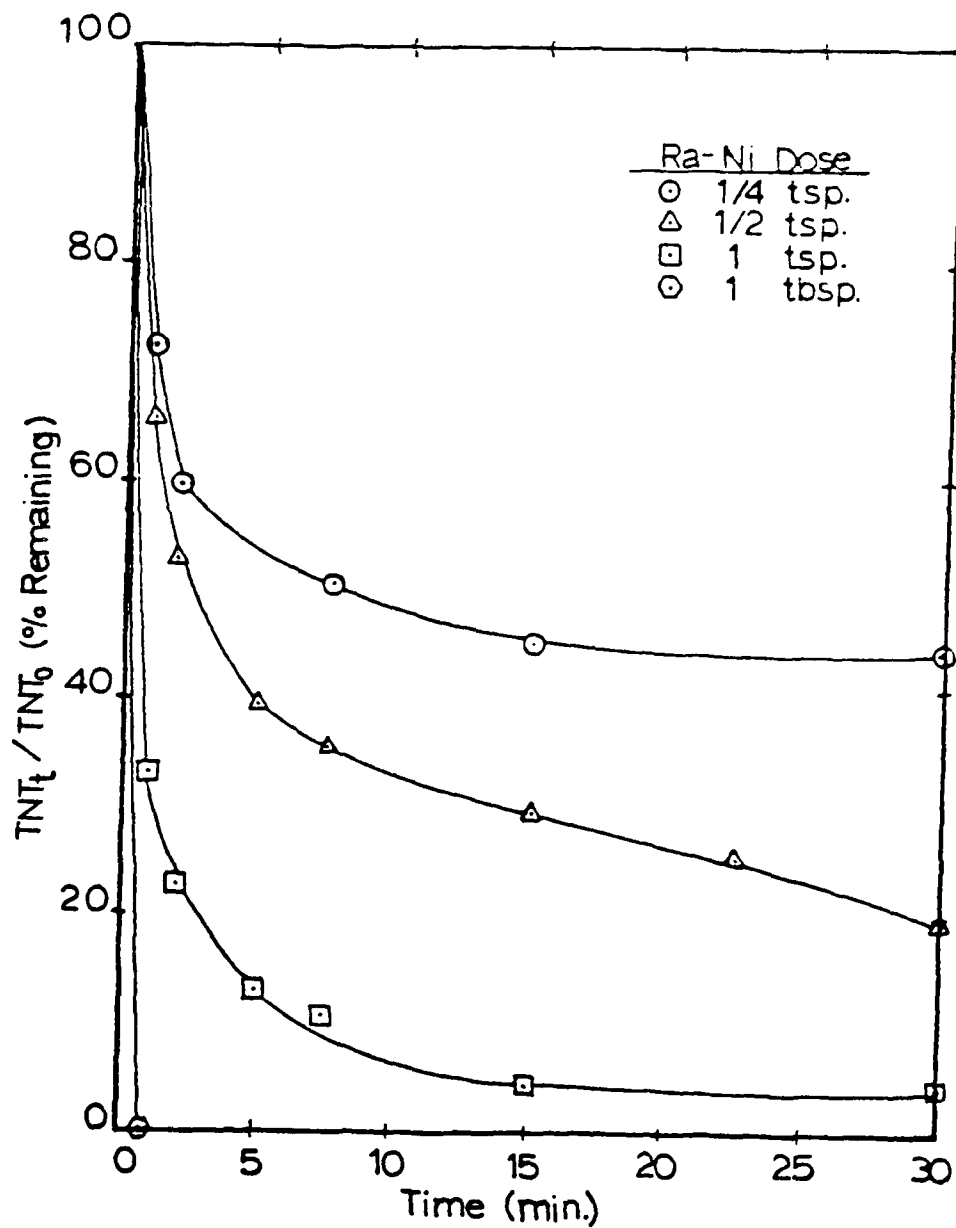


Figure 21 The Effect of Ra-Ni Dose on the Removal of TNT in a 3-liter Batch of 70/30 mg/l TNT/RDX Batch by Catalytic Destruction with Ra-Ni

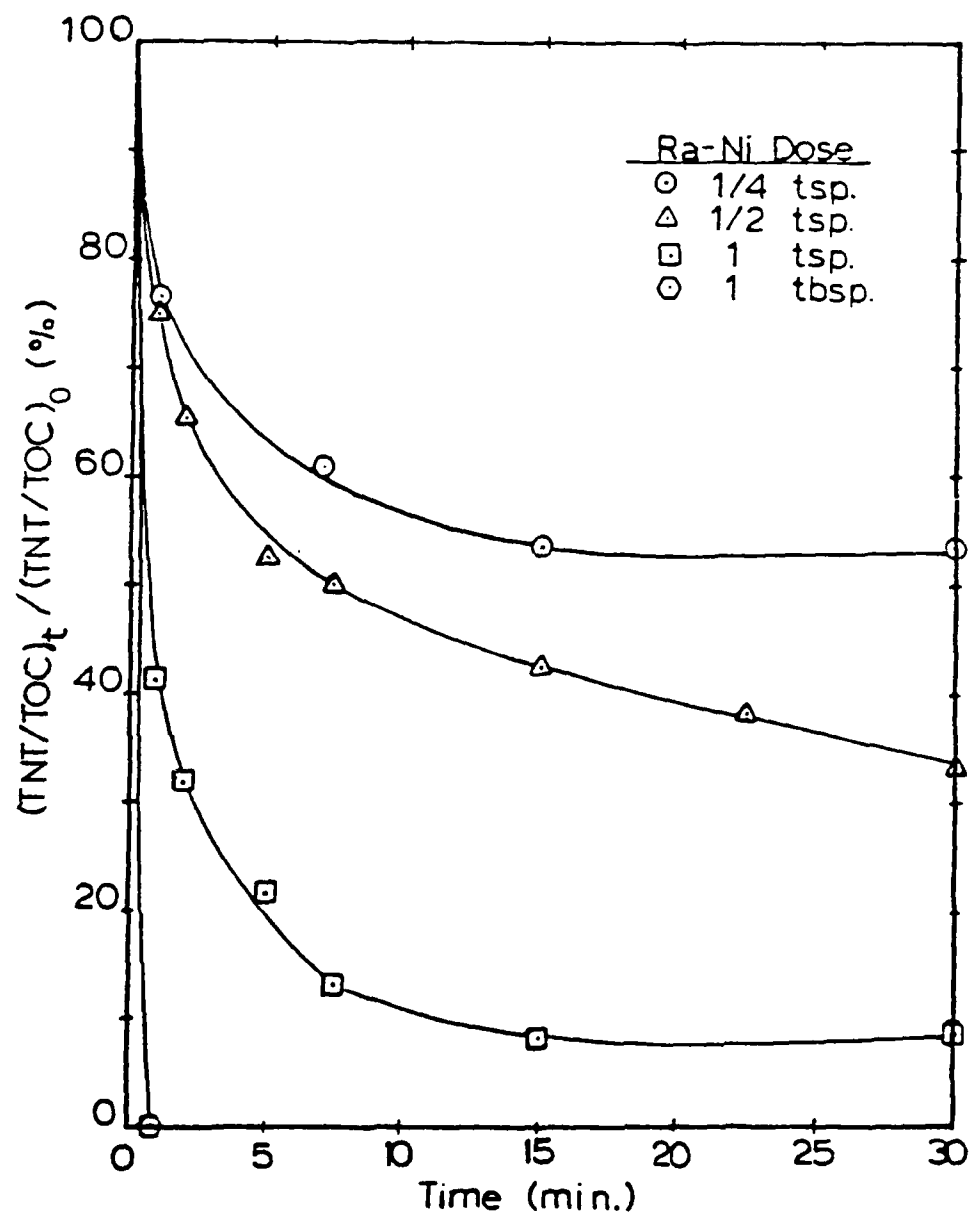


Figure 22 The Effect of Ra-Ni Dose on the Change of TNT/TOC Ratio in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Destruction with Ra-Ni

For the experiments with 70/30 mg/L TNT/RDX and Ra-Ni, the reaction solution pH continued to rise after adding the catalyst until it reached a peak and then decreased with increased contact time. It was found that increasing the concentration of Ra-Ni reduced the time required to reach the peak pH (e.g., 2 and 15 minutes for the 1 tbsp and 1/4 tsp runs, respectively, as seen in Table 13). The difference between maximum and minimum pH's achieved during reaction was smaller for the 70/30 mg/L TNT/RDX batch (e.g., 0.51 pH units for 1 tsp run) than that for the 70 mg/L TNT batch (e.g., 2.11 pH units for 1 tsp run). For the 1 tsp run of the 30 mg/L RDX batch, the pH difference was only +0.1 pH units (Table 14). These results indicated that the pH change was primarily due to the chemical reaction between TNT and Ra-Ni. Also, the decrease of RDX might result from the adsorption or other physical-chemical reactions on the Ra-Ni surface without the associated production of acidic or basic intermediates.

During this research it has been observed that pure α -TNT aqueous solutions turned pink when their pH was increased above 7.0. However, the TNT/RDX solutions in contact with Ra-Ni did not turn pink even though the pH level approached 10.0. This indicated that the contact between Ra-Ni and TNT involved chemical reactions associated with chemical structure change. Due to this, the structurally modified compound did not exhibit pink color in neutral or basic solution, but it was identified by the Silas-Mason test as TNT and therefore, it was regarded as the remaining TNT for evaluating the removal efficiency of Ra-Ni. It should be noted that the Silas-Mason test also identifies other aromatic nitrocompounds as TNT.

3.3.3 TOC and TNT Changes

The destruction rates for TNT (Figure 21) exceeded those for TOC (Figure 20) in all runs in this study. The TNT/TOC ratio also decreased with the contact time, but its rate change was faster than that of TOC and slower than that of TNT. It was also found that the destruction of TNT was accelerated in the presence of RDX. For example, after contact with 1 tsp Ra-Ni for 30 minutes under identical reactions, the TNT remaining in solution were 5% and 13% of the initial amount for a 70/30 mg/L TNT/ RDX batch and a 70 mg/L TNT batch, respectively. Also, the TNT/TOC ratios decreased to 9% and 30% of the initial ratios for the 70/30 mg/L TNT/RDX batch and the 70 mg/L TNT batch, respectively.

The effect of Ra-Ni dose on $(\text{TOC}/\text{TNT})_t / (\text{TNT}/\text{TOC})_0$ ratio of the 70/30 mg/L TNT/RDX batch is shown in Figure 22.

The experimental data for this portion of the research indicated that the destruction of TNT/RDX with Ra-Ni had the following characteristics: (1) the TNT and TOC decreased with the contact time, but the rate of TNT decrease was greater than that of TOC; (2) as the reactor concentration of Ra-Ni decreased, a smaller amount of time was required to reach a steady-state TOC value. For example, the rate of TOC decrease became insignificant after 5, 10 and 15 minutes of the contact time for the 1/4, 1/2 and 1 tsp runs, respectively. For 1 tsp runs, the rate of the TOC decrease still remained substantially high after contact with the Ra-Ni for 30 minutes (i.e., 5.8% decrease from 15 minutes to 30 minutes), but the approach to steady state had begun. These results suggested that the higher Ra-Ni dose not only increased the rate of TOC removal but also extended the effective reaction time before the rate of TOC change became inconsequential.

The data in Figure 21 indicated that all 70 mg/L of TNT was removed in less than 1.0 minutes for the 1 tbsp run. For the batches containing 1/4, 1/2 and 1 tsp Ra-Ni after 30 minutes of reaction, 44.6%, 19.2% and 4.3% TNT remained in solution, respectively.

Examination of TNT/TOC data as a function of reaction time and catalyst concentration revealed a constantly decreasing TNT/TOC ratio. For example, in Table 12, for the 1/4 tsp run the TNT/TOC ratio decreased from 2.43 to 1.30 in 30 minutes of reaction. This indicated that the TNT molecule was being altered and some organic carbon was converted to carbon dioxide and water resulting in a loss of TOC. The TNT/RDX ratio then reflected the presence of reaction products different from the original TNT and thus the theoretical TNT/TOC ratio of 2.28 mg/mg in the 70/30 mg/L TNT/RDX batch was changed.

3.3.4 Kinetics Study

Kinetic data for the catalytic destruction of TOC with Ra-Ni is shown in Figure 23, plotted in the initial-rate method form. The initial-rate of TOC destruction was the product of the initial TOC and the initial slope of the $\text{TOC}_t/\text{TOC}_0$ vs time curve (see Figure 20). The concentrations of Ra-Ni for 1/4, 1/2 and 1 tsp and 1 tbsp runs were approximately 373, 806, 1,561 and 4,633 mg/L, respectively.

Figure 23 indicated that for the constant substrate concentration in a 70/30 mg/L TNT/RDX batch, the initial-rate of TOC destruction was proportional to the concentration of Ra-Ni initially but did not follow the linear dependence for the batch with the highest concentration of Ra-Ni (i.e., 4,633 mg/L Ra-Ni for 1 tbsp run).

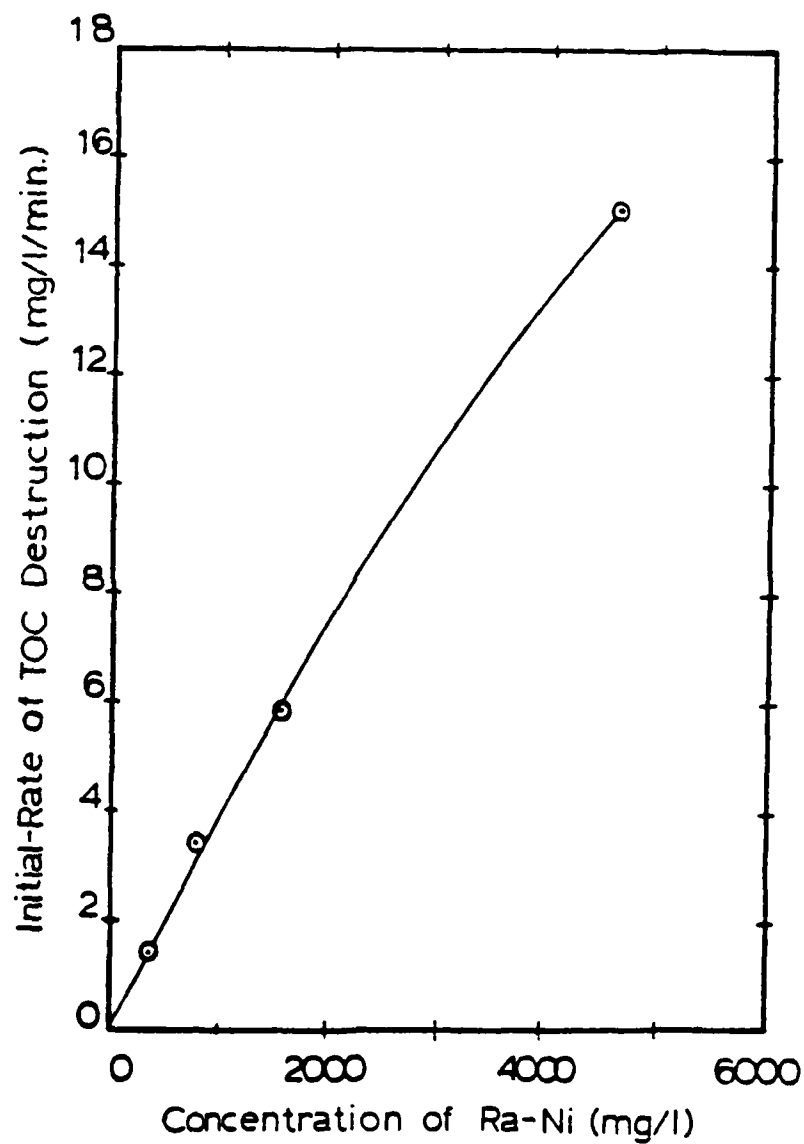


Figure 23 The Effect of Ra-Ni Dose on the Initial-Rate of TOC Destruction in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Destruction with Ra-Ni

In summary, from the changes in color, pH and TNT/TOC ratio with the reaction time, it was evident that TNT and RDX were reacting on the Ra-Ni surface and reaction products were diffusing into the solution. The decrease in the yellow color intensity of the batch with increased reaction time in 1/2 and 1 tsp runs indicated that the first-step reaction products (i.e., yellow colored species) were further reacted resulting in the presence of colorless species. These reactions resulted in both TNT and TOC removals. The fact that the rate of TOC destruction with time became inconsequential after 5, 10 and 15 minutes for the 1/4, 1/2 and 1 tsp doses of Ra-Ni was probably due to catalyst poisoning by the reaction products.

3.4 CATALYTIC OZONATION PROCESS

The catalytic ozonation process employed Ra-Ni and ozone. For a 70/30 mg/L TNT/RDX solution, ozonations were performed at two different ozone doses (i.e., 111.6 and 220.8 mg O_3 /min) at the O_3/O_2 flow rate of 6L/min. The analytic results are presented in Tables 15 and 16 and Figures 24, 25, and 26.

3.4.1 Physical Appearance Changes

With respect to their appearance, all the samples taken from the catalytic ozonation process were essentially free of turbidity and almost colorless. At an ozone dose of 111.6 mg O_3 /min, light-yellow coloring appeared in the batch initially but disappeared after 20 minutes for 1/4 and 1/2 tsp runs, and after 10 and 5 minutes for 1 tsp and 1 tbsp runs, respectively. At an ozone dose of 220.8 mg O_3 /min, color was never observed for the 1/4 tsp run. For the 1/2 and 1 tsp and 1 tbsp runs, the light-yellow coloring appeared initially but disappeared after 10, 5, and 2 minutes, respectively. The disappearance of the yellow coloring implied that the yellow-color species, produced by the interaction between TNT/RDX and Ra-Ni, was oxidized by ozone to colorless partial oxidation products. This was partially substantiated when the yellow coloring disappeared more quickly for the runs conducted at the higher ozone dose (i.e., 220.8 vs 111.6 mg O_3 /min) than those at the lower ozone dose. For the runs conducted at a constant ozone dose, the rate of yellow color disappearance increased with increased concentration of Ra-Ni. However, for the 1/4 tsp run at the higher ozone dose (i.e., 220.8 mg O_3 /min), the reaction mass appeared colorless throughout the course of the run. This response was probably due to the destruction rate of the yellow color species by ozone being higher than its production rate.

3.4.2 pH Changes

With respect to the parameter pH, it was found that the initial solution pH rose upon the addition of Ra-Ni, but once ozone was introduced into the reactor

TABLE 15. THE CATALYTIC OZONATION OF 70/30 mg/L TNT/RDX IN 3L AQUEOUS SOLUTION WITH 111.6 mg/min OF OZONE

111.6 mg O ₃ /min and 1/4 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.40	6.10	5.66	5.06	6.32	5.06	5.34		
TOC (mg/L)	28.29	27.72	27.27	25.00	--	22.23	21.00		
TNT (mg/L)	69.7	54.8	51.8	44.6	43.0	35.7	32.86		
TNT/TOC	2.46	1.58	1.90	1.78	--	1.61	1.56		
Appearance	colorless	light yellow	light yellow	light yellow	light yellow	colorless	colorless		
111.6 mg O ₃ /min and 1/2 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.43	7.55	6.85	5.92	6.04	6.06	6.65		
TOC (mg/L)	27.73	24.11	22.47	20.09	19.22	15.19	12.72		
TNT (mg/L)	69.0	41.0	34.8	28.1	21.1	15.4	12.1		
TNT/TOC	2.49	1.70	1.55	1.40	1.10	1.01	0.95		
Appearance	colorless	yellow	light yellow	light yellow	light yellow	colorless	colorless		
111.6 mg O ₃ /min and 1 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.55	9.08	8.75	7.16	6.71	7.05	7.46		
TOC (mg/L)	27.74	20.16	17.99	15.51	13.07	9.558	7.717		
TNT (mg/L)	67.8	30.5	22.9	17.3	10.8	5.2	2.4		
TNT/TOC	2.44	1.51	1.27	1.12	0.83	0.55	0.31		
Appearance	colorless	yellow	light yellow	light yellow	colorless	colorless	colorless		
111.6 mg O ₃ /min and 1 tbsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.43	10.30	10.38	10.38	10.43	10.23	10.23		
TOC (mg/L)	27.48	13.22	9.099	5.843	5.428	4.348	1.759		
TNT (mg/L)	68.3	5.2	3.1	0.0	0.0	0.0	0.0		
TNT/TOC	2.49	0.39	0.23	0.00	0.00	0.00	0.00		
Appearance	colorless	yellow	light yellow	colorless	colorless	colorless	colorless		

TABLE 16. THE CATALYTIC OZONATION OF 70/30 mg/L TNT/RDX IN 3L AQUEOUS SOLUTION WITH 220.8 mg/min OF OZONE

220.8 mg O ₃ /min and 1/4 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.40	5.35	5.59	5.42	5.66	5.84	6.37		
TOC (mg/L)	28.08	27.15	25.72	23.88	24.71	22.66	22.03		
TNT (mg/L)	68.1	50.0	49.2	44.3	41.0	38.7	36.4		
TNT/TOC	2.43	1.84	1.91	1.85	1.66	1.71	1.65		
Appearance	colorless	colorless	colorless	colorless	colorless	colorless	colorless		
220.8 mg O ₃ /min and 1/2 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.43	5.92	5.76	5.71	6.06	6.56	6.78		
TOC (mg/L)	27.62	24.07	22.03	19.96	17.79	14.04	11.19		
TNT (mg/L)	71.6	41.6	35.1	27.3	20.8	16.2	14.1		
TNT/TOC	2.59	1.73	1.59	1.37	1.17	1.15	1.26		
Appearance	colorless	light yellow	light yellow	light yellow	colorless	colorless	colorless		
220.8 mg O ₃ /min and 1 tsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.55	8.51	8.05	6.50	6.76	7.44	7.37		
TOC (mg/L)	27.74	20.53	18.12	14.09	10.90	6.975	4.558		
TNT (mg/L)	67.8	27.1	23.8	13.65	7.14	1.43	1.43		
TNT/TOC	2.44	1.32	1.31	0.97	0.66	0.21	0.31		
Appearance	colorless	light yellow	light yellow	colorless	colorless	colorless	colorless		
220.8 mg O ₃ /min and 1 tbsp. Ra-Ni									
Time (min)	0	1	2	5	10	20	30		
pH	5.43	10.28	10.31	10.37	10.34	10.34	10.34		
TOC (mg/L)	27.60	11.46	8.367	5.761	3.194	--	1.568		
TNT (mg/L)	70.5	4.6	2.7	0.0	0.0	0.0	0.0		
TNT/TOC	2.55	0.40	0.23	0.00	0.00	0.00	0.00		
Appearance	colorless	light yellow	colorless	colorless	colorless	colorless	colorless		

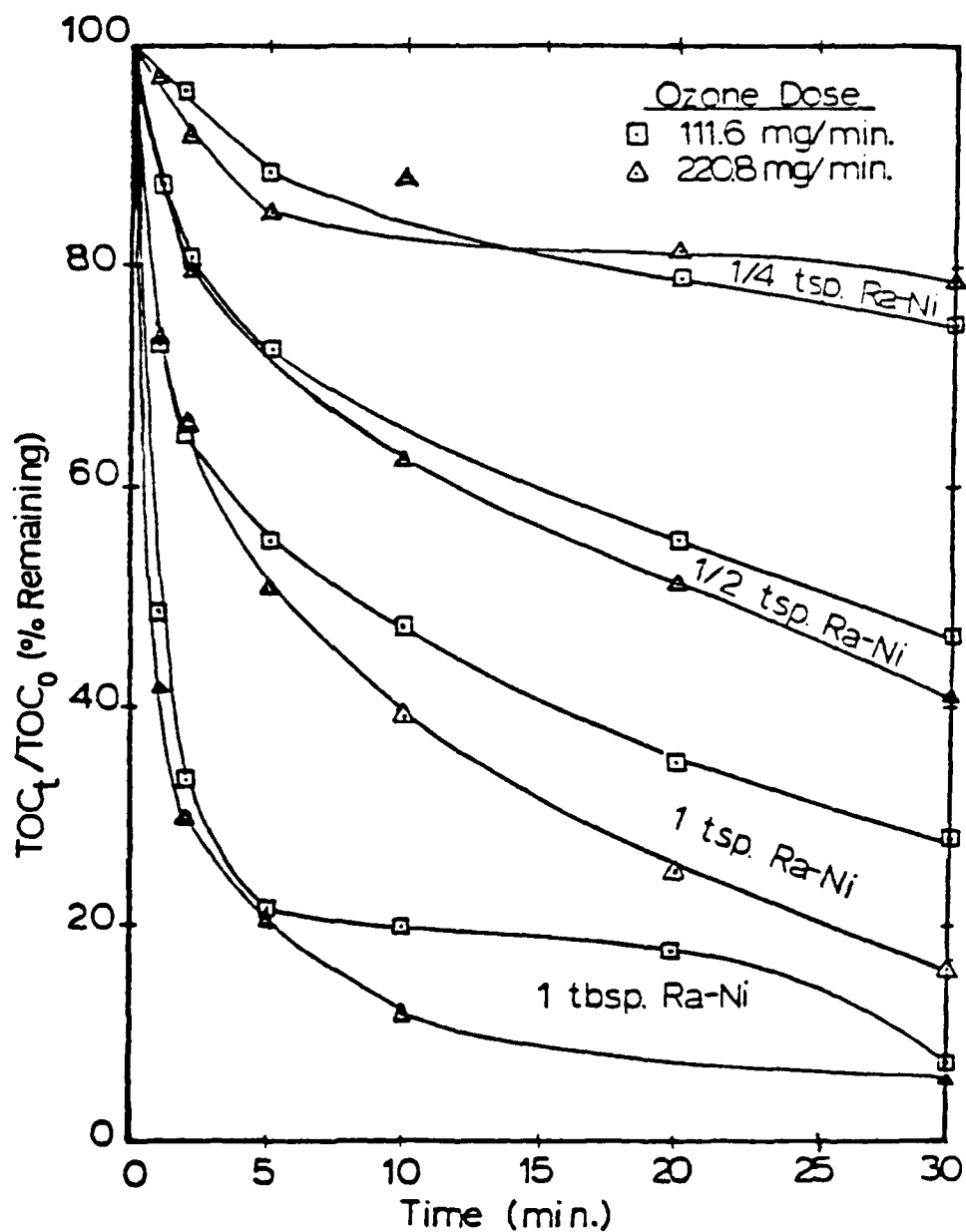


Figure 24 The Effect of Ozone Dose on the Removal of TOC in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Ozonation with Ra-Ni

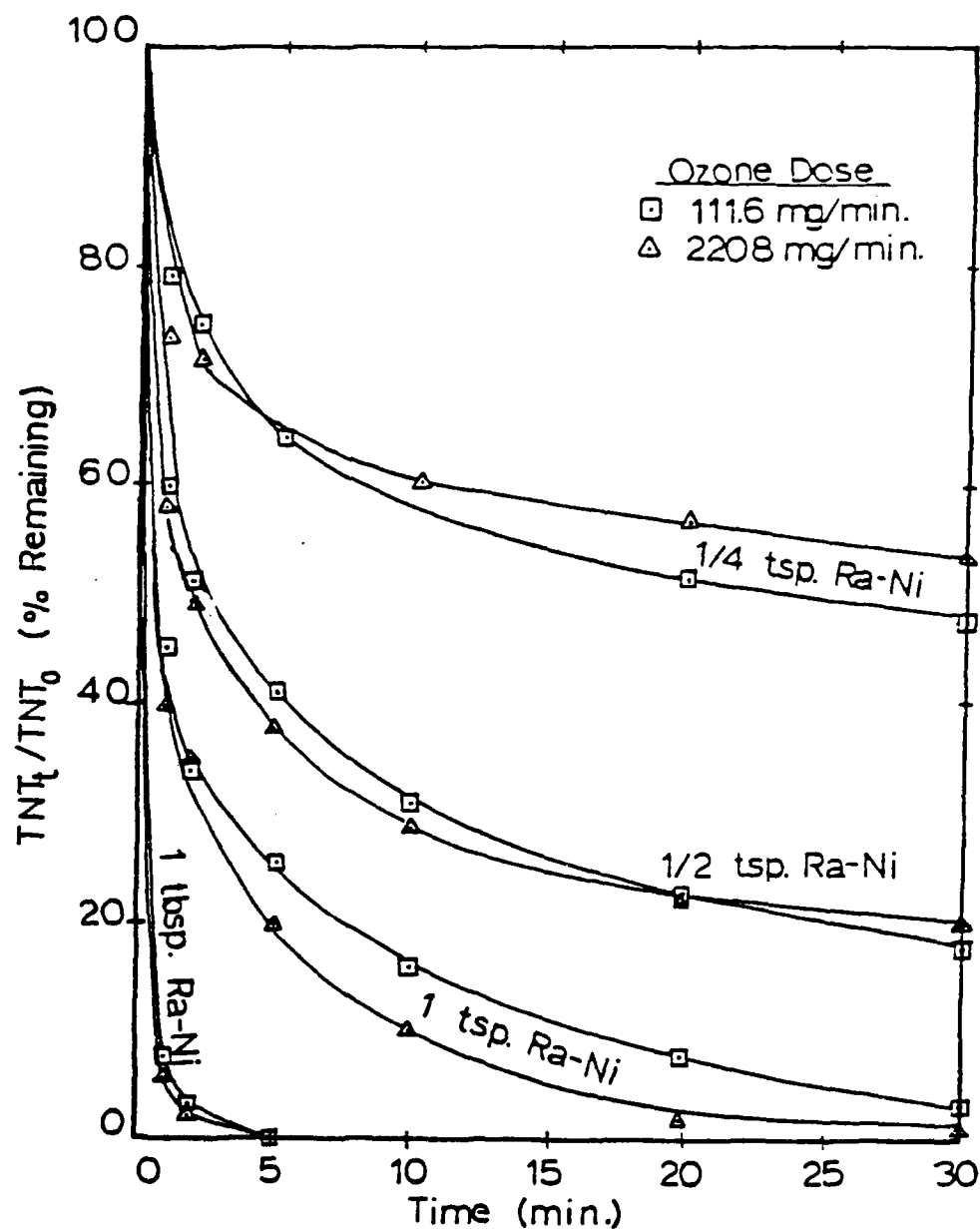


Figure 25 The Effect of Ozone Dose on the Removal of TNT in a 3-liter Batch of 70/30 mg/l TNT/ RDX by Catalytic Ozonation with Ra-Ni

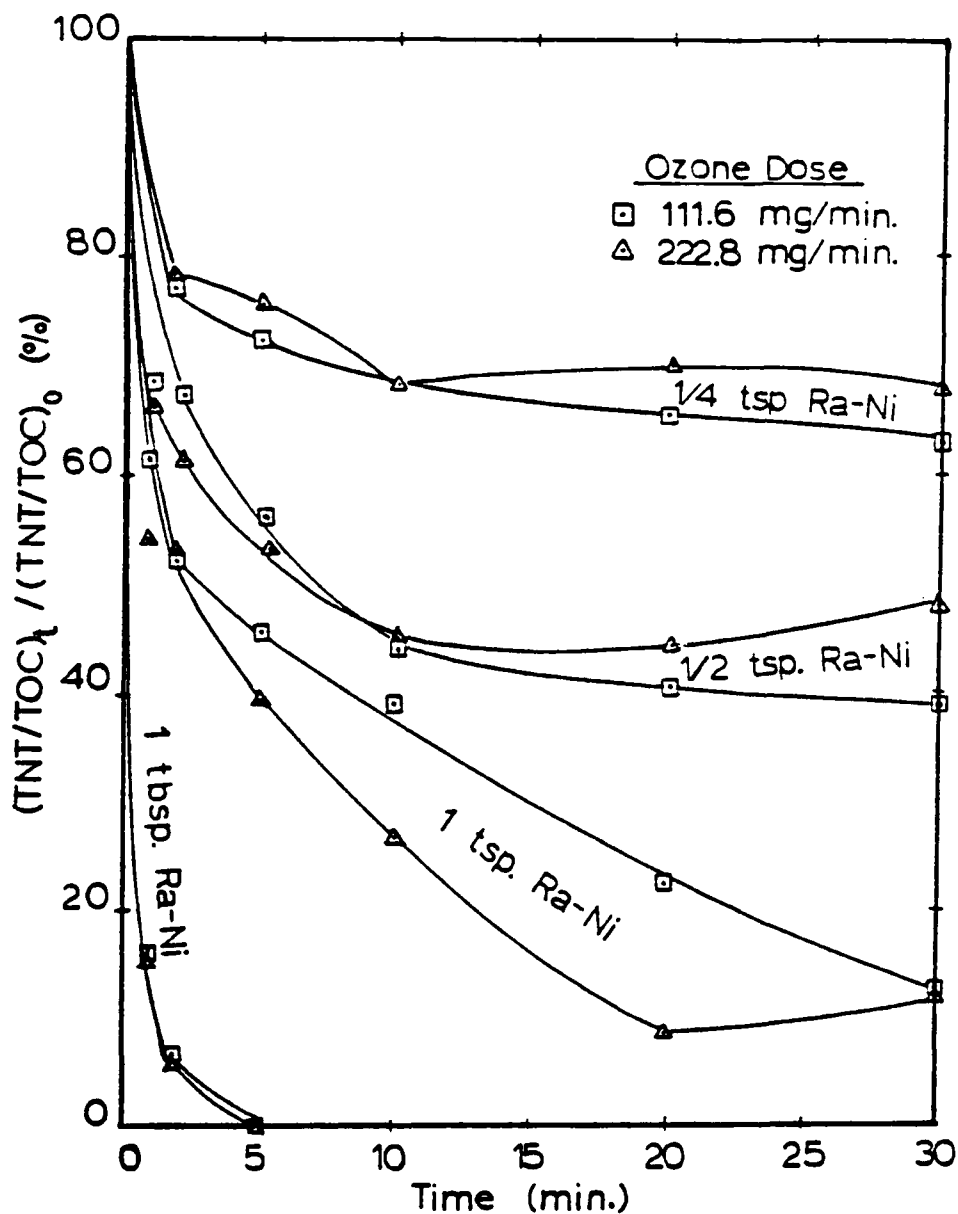


Figure 26 The Effect of Ozone Dose on the Change of TNT/TOC Ratio in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Ozonation with Ra-Ni

the solution pH decreased. The data in Tables 15 and 16 indicated that throughout the course of the run the solution pH was lower in the catalytic ozonation process with Ra-Ni than that in the catalytic destruction process with Ra-Ni (Table 13). This was especially apparent for the 1/4 tsp run at an ozone dose of 220.8 mg $\cdot$ O₃/min, where the solution pH was lowered to less than the initial solution pH (i.e., 5.35 vs. 5.40) after one minutes of reaction. However, for the runs with the highest concentration of Ra-Ni (i.e., 1 tbs), the difference of the solution pH between the catalytic ozonation process with Ra-Ni and the catalytic destruction process with Ra-Ni was negligible (i.e., 0.01 to 0.41 units) throughout the course of the run. This probably was due to the fact that most of the TNT (approximately 90%) and its yellow color derivatives were destroyed after two minutes of reaction. For the 1/2 and 1 tsp runs, after the initial pH increase which was due to the addition of Ra-Ni, the solution pH decreased with the contact time until reaching a low plateau value (i.e., 5.71 and 6.50 for the 1/2 and 1 tsp runs at an ozone dose of 220.8 mg $\cdot$ O₃/min) and then increased again with the contact time (i.e., 6.78 and 7.37 for the 1/2 and 1 tsp runs at an ozone dose of 220.8 mg O₃/min after 30 minutes of reaction). The phenomenon of pH rise after reaching a minimum value was accompanied by the disappearance of the yellow coloring. This result indicated that the ozonation of the yellow color species was associated with the production of acidic substances, which were colorless. Further, the ozonation of these colorless, acidic substances resulted in a slight increase in pH (i.e., 0.65 and 0.87 units for the 1 tsp runs at the ozone doses of 111.6 and 220.8 mg $\cdot$ O₃/min, respectively).

The data in Tables 15 and 16 also indicated that for the 1/2 and 1 tsp and 1 tbs runs, the difference in the solution pH between the different ozone doses (i.e., 111.6 vs 220.8 mg $\cdot$ O₃/min) was insignificant, especially after 30 minutes of reaction (i.e., 0.01-0.13 units). However, for the 1/4 tsp runs, the solution pH for the run at an ozone dose of 220.8 mg $\cdot$ O₃/min increased from 5.40 to 6.37 after 30 minutes of reaction, but for the run at an ozone dose of 111.6 mg O₃/min the solution pH increased from 5.40 to 6.10 upon the addition of Ra-Ni and then decreased to 5.34 after 30 minutes of reaction.

3.4.3 TOC and TNT Changes

The effect of the ozone dose on TOC, TNT and TNT/TOC ratio of the 70/30 mg/L TNT/RDX batch in the catalytic ozonation process with Ra-Ni can be seen in Figures 24, 25, and 26.

The data indicated that the catalytic ozonation of TNT/RDX with Ra-Ni has the following characteristics: (1) both the TNT and TOC decreased with the contact time:

however, the rate of TNT destruction was greater than that of TOC; (2) except for the 1/4 tsp runs, both the rates of TOC and TNT destruction were higher at the higher ozone dose (i.e., 220.8 vs 111.6 mg O_3 /min) than that at the lower ozone dose; (3) the differences of the destruction rates for both TOC and TNT were more significant between the runs with the different concentration of Ra-Ni than those between the runs with the different ozone dose (as seen in Figures 24 and 25).

The data in Tables 15 and 16 indicated that for the runs with the highest Ra-Ni concentration (i.e., 1 tbsp), the rate of change of TOC destruction became inconsequential after five minutes and ten minutes of reaction time at the ozone doses of 111.6 mg O_3 /min and 220.8 mg O_3 /min, respectively. When the rate of change of TOC destruction became inconsequential, all of the TNT, identifiable by the Silas-Mason test, had been removed but the remaining TOC's were 5.428 and 3.194 mg/L at the ozone dose of 111.6 mg O_3 /min and 220.8 mg O_3 /min, respectively. These results suggested that the TNT and its yellow color derivatives (identifiable by the Silas-Mason test) were more vulnerable to destruction by ozone than its colorless derivatives and other organics (i.e., RDX) in the catalytic ozonation process with Ra-Ni.

It was also found that for the 1/4 tsp. run, the lower destruction rate of TOC at the higher ozone dose was accompanied by the lower destruction rate of TNT at the higher ozone dose. Also, for the 1/2 and 1 tsp and 1 tbsp runs, the higher destruction rate of TOC at the higher ozone dose was associated with the higher destruction rate of TNT at the higher ozone dose. The results suggested that the TOC destruction reaction in the catalytic ozonation process was controlled by the transformation of TNT to yellow color species or substances that were not identifiable by the Silas-Mason test.

In comparison with the catalytic destruction process, with a catalyst concentration of 1/4 tsp. Ra-Ni, the rate of TOC destruction was higher for the catalytic ozonation process. For the 1/4 tsp run at an ozone dose of 220.8 mg O_3 /min, after 30 minutes of reaction the remaining TOC and TNT were 78.5 and 44.6% of the initial TOC and TNT, respectively, but for the catalytic destruction process with the same concentration of Ra-Ni, the remaining TOC and TNT were 83.7 and 53.4% of the initial TOC and TNT, respectively.

While the TOC removal was improved due to the introduction of ozone, the TNT removals either decreased or were not substantially improved in the catalytic ozonation process with Ra-Ni. It was found that for the 1/4 and 1/2 tsp runs, after 30 minutes of reaction the TNT removal was lower at the higher ozone dose than that at the

lower ozone dose. Further, the TNT removals at the higher ozone dose for the 1/4 and 1/2 tsp. and 1 tbsp runs were lower than that in the catalytic destruction process with the same concentration of Ra-Ni (as seen in Figures 19 and 23). These results suggested that ozone adversely affected the rate of the TNT destruction with Ra-Ni. This probably resulted from the lower solution pH after the introduction of ozone into the reactor and the blockage or alteration of the reaction sites on the Ra-Ni surface due to the interaction with ozone.

In an attempt to explain why the catalytic ozonation process yielded the lower TNT destruction rate than that for the catalytic destruction process with Ra-Ni, one run was conducted with 1 tbsp Ra-Ni which was pre-ozonated at an ozone dose of 220.8 mg O_3 /min in 3 liters of pH 10.8 distilled water for 30 minutes prior to contact with 3 liters of 70/30 mg/L TNT/RDX solution. The data in Table 17 showed that after 30 minutes of contact with the pre-ozonated catalyst, the remaining TNT was 53.5% of the initial TNT. Also, the remaining TOC was 88.3% of the initial TOC. In comparison with the 1 tbsp run with the fresh Ra-Ni (i.e., without pre-ozonation treatment), the data in Table 12 showed that TNT was totally destroyed in one minute and the remaining TOC was only 9.7% of the initial TOC after 30 minutes of reaction. These responses suggested that the presence of ozone would result in the poisoning of Ra-Ni reducing or destroying its catalytic activity.

In Figure 26, it was found that the TNT/TOC ratio decreased due to the introduction of ozone into the reactor in the catalytic ozonation process with Ra-Ni. The data showed that the TNT/TOC ratio was larger in the catalytic ozonation process than that in the catalytic destruction process (see Figure 22 and 26). For example, for the 1/4 tsp runs after 30 minutes of reaction, the TNT/TOC ratios were 1.65 and 1.30 for the catalytic ozonation and the catalytic destruction, respectively, at an ozone dose of 220.8 mg O_3 /min. These results indicated that the catalytic ozonation with Ra-Ni not only changed TNT to the substances which were not identifiable by the Silas-Mason test (i.e., partial oxidation) but also oxidized the reaction intermediates to carbon dioxide and water (i.e., complete oxidation). Also, the results suggested that the rate of complete oxidation was higher in the catalytic ozonation process with Ra-Ni than that in the catalytic destruction process with Ra-Ni only.

It was also found that the TNT/TOC ratio was larger at the higher ozone dose in the catalytic ozonation process with Ra-Ni than that at the lower ozone dose with the same concentration of Ra-Ni. These results suggested that the rate of complete oxidation of TNT and RDX in the catalytic ozonation process with Ra-Ni increased

with increased ozone dose. For the 1/4, 1/2 and 1 tsp runs at the higher ozone dose, the TNT/TOC ratio decreased initially with the reaction time until reaching a low plateau value (i.e., after ten minutes for the 1/4 and 1/2 tsp runs and 20 minutes for 1 tsp run) and then increased with the reaction time. Also, the increase of TNT/TOC ratio occurred at the same time that the rate of change of TNT destruction became inconsequential and, therefore, the increase of TNT/TOC ratio was primarily due to the TOC decrease. These results indicated that the rate of the complete oxidation of TNT/RDX increased with the reaction time in the catalytic ozonation even though the rate of change of TNT destruction became inconsequential.

3.4.4 Kinetics Study

The effect of Ra-Ni concentration on TOC destruction is shown in Figure 27 by the initial-rate method. The data in Figure 27 indicated that the initial-rate of TOC destruction was proportional to the concentration of Ra-Ni initially but did not follow the linear dependence for the batch with the highest concentration of Ra-Ni (i.e., 4,633 mg/L Ra-Ni for 1 tbsp. run). It was also found that the slope of the linear portion at the lower concentration of Ra-Ni was larger at the lower ozone dose (i.e., 0.0058 and 0.0053 min^{-1} for the runs at the ozone doses of 111.6 and 220.8 $\text{mg O}_3/\text{min}$, respectively). For the experiments conducted with the higher concentration of Ra-Ni, however, the slope of the linear portion was larger at the higher ozone dose (i.e., 0.0022 and 0.0029 min^{-1} for the runs at the ozonation rates of 111.6 and 220.8 $\text{mg O}_3/\text{min}$, respectively). These results suggested that the higher dose of ozone adversely affected the rate of TOC destruction with the lower concentration of Ra-Ni, but benefited the rate of TOC destruction with the higher concentration of Ra-Ni.

3.4.5 Initial Solution pH Effect

To investigate the effect of the initial solution pH on the catalytic ozonation of TNT/RDX with Ra-Ni, a 1/4 tsp run, whose initial solution pH was adjusted to 10.74, was performed at an ozone dose of 220.8 $\text{mg O}_3/\text{min}$. Also, two runs, at initial solution pH levels of 11.00 and 5.66, were performed without the addition of Ra-Ni at an ozone dose of 220.8 $\text{mg O}_3/\text{min}$. The analytic results are presented in Figures 28 and 29.

The data in Figures 28 and 29 indicated that after 30 minutes of ozonation at the ambient solution pH (i.e., pH 5.60), the remaining TOC and TNT were approximately 98.9 and 95% of the initial TOC and TNT, respectively. However, when the initial solution pH was adjusted to 11.00, after 30 minutes of ozonation the remaining TOC and

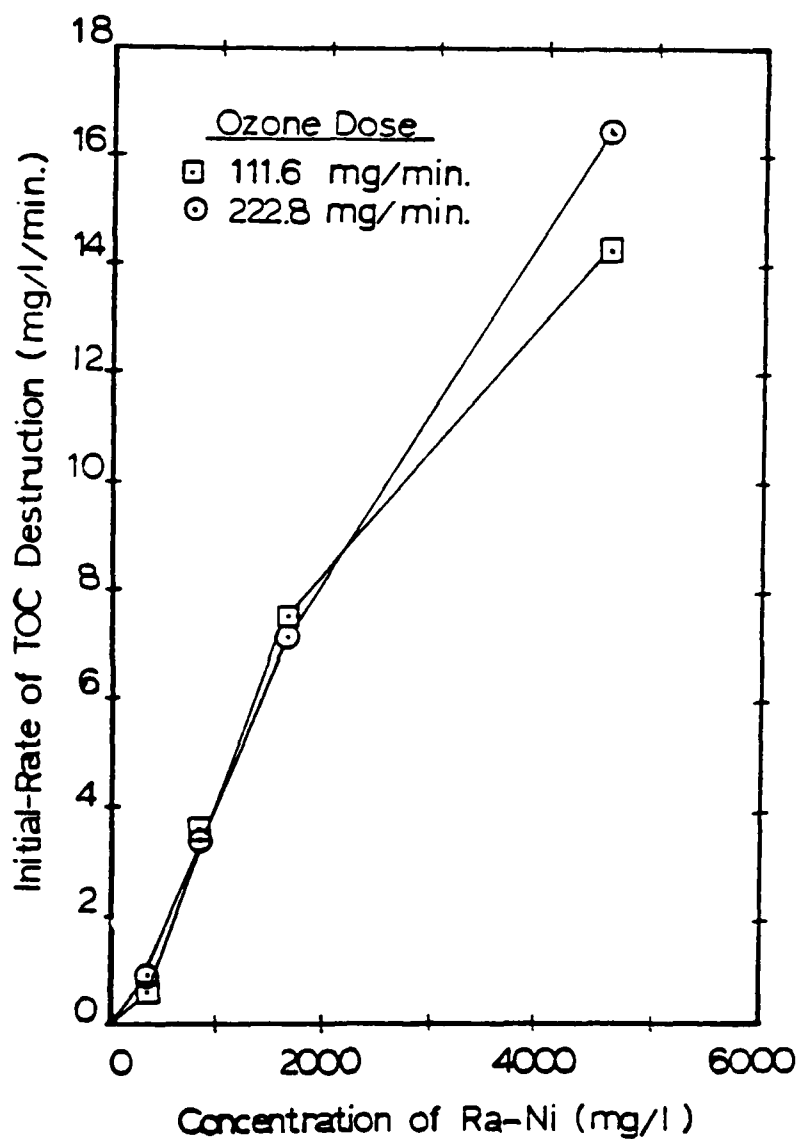


Figure 27 The Effect of Ra-Ni Dose on the Initial-Rate of TOC Destruction in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Ozonation with Ra-Ni

TABLE 17. THE CATALYTIC DESTRUCTION OF 70/30 mg/L TNT/RDX IN 3L
AQUEOUS SOLUTION WITH 1 TBSP. OF PREOZONATED Ra-Ni

	<u>1 tbsp. of Preozonated Ra-Ni</u>							
Time (min)	0	1	2	5	10	20	30	
pH	5.62	7.42	7.52	7.07	7.04	7.13	7.11	
TOC (mg/L)	26.90	27.74	26.67	26.76	26.76	26.65	23.83	
TNT (mg/L)	62.2	49.8	49.7	48.6	43.5	41.9	33.0	
TNT/TOC	2.31	1.80	1.86	1.82	1.64	1.57	1.38	
Appearance	colorless	colorless	colorless	colorless	colorless	colorless	colorless	colorless

TNT were 74 and 28.2% of the initial TOC and TNT, respectively. In comparison with the 1/4 tsp run of the catalytic destruction and catalytic ozonation with Ra-Ni at the ambient solution pH, the rates of TOC and TNT destruction were higher for the ozonation at initial solution pH of 11.00 (as seen in Figures 14 and 15). These results indicated that the rates of TOC and TNT destruction by ozonation were higher in the basic aqueous solution than those in the acidic one. This response was probably due to the fact that the rate of ozone decomposition increased with increased solution pH. Also, the higher pH environment produced oxidation with the $\text{OH}^\cdot$ radical as opposed to, the low pH run when the oxidant was O_3 . The results also suggested that for the 70/30 mg/L TNT/RDX batch the pink color species, due to the pH adjustment to 11.00, were more vulnerable to destruction than the yellow color species, due to the contact with Ra-Ni.

The data in Figures 28 and 29 also showed that the rate of TOC destruction for the 1/4 tsp run of the catalytic ozonation at the initial solution pH of 10.74 was higher than that for the ozonation without metal catalyst at initial solution pH of 11.00, but the difference of the remaining TNT's between these two runs was negligible (i.e., approximately 1.8% of the initial TNT). These results indicated that for a 70/30 mg/L TNT/RDX batch the rate of TOC destruction by ozonation was increased due to the presence of Ra-Ni, especially at the higher initial solution pH (i.e., pH 10.74).

3.4.6 Single Substrate Study - TNT, RDX

The catalytic ozonation with Ra-Ni for the 70 mg/L TNT batch and 30 mg/L RDX batch was performed with the reactor operating conditions of 111.6 mg O_3 /min and 1 tsp Ra-Ni. The analytic results are shown in Table 18.

For the 70 mg/L TNT batch, the data showed that the destruction rate of TNT by Ra-Ni alone was higher than that by the catalytic ozonation with Ra-Ni for the first five minutes of reaction (see Tables 14 and 18). However, after five minutes of reaction, the rate of TNT change by Ra-Ni alone became inconsequential and therefore, its TNT removal capability was lower than that accomplished in the catalytic ozonation with Ra-Ni. Further, after 30 minutes of reaction, the remaining TNT and TOC accomplished in the catalytic ozonation were 3.1 and 15.7% of the initial TNT and TOC, respectively, but the remaining TNT and TOC for the catalytic destruction by Ra-Ni only were 12.5 and 40.5% of the initial TNT and TOC, respectively.

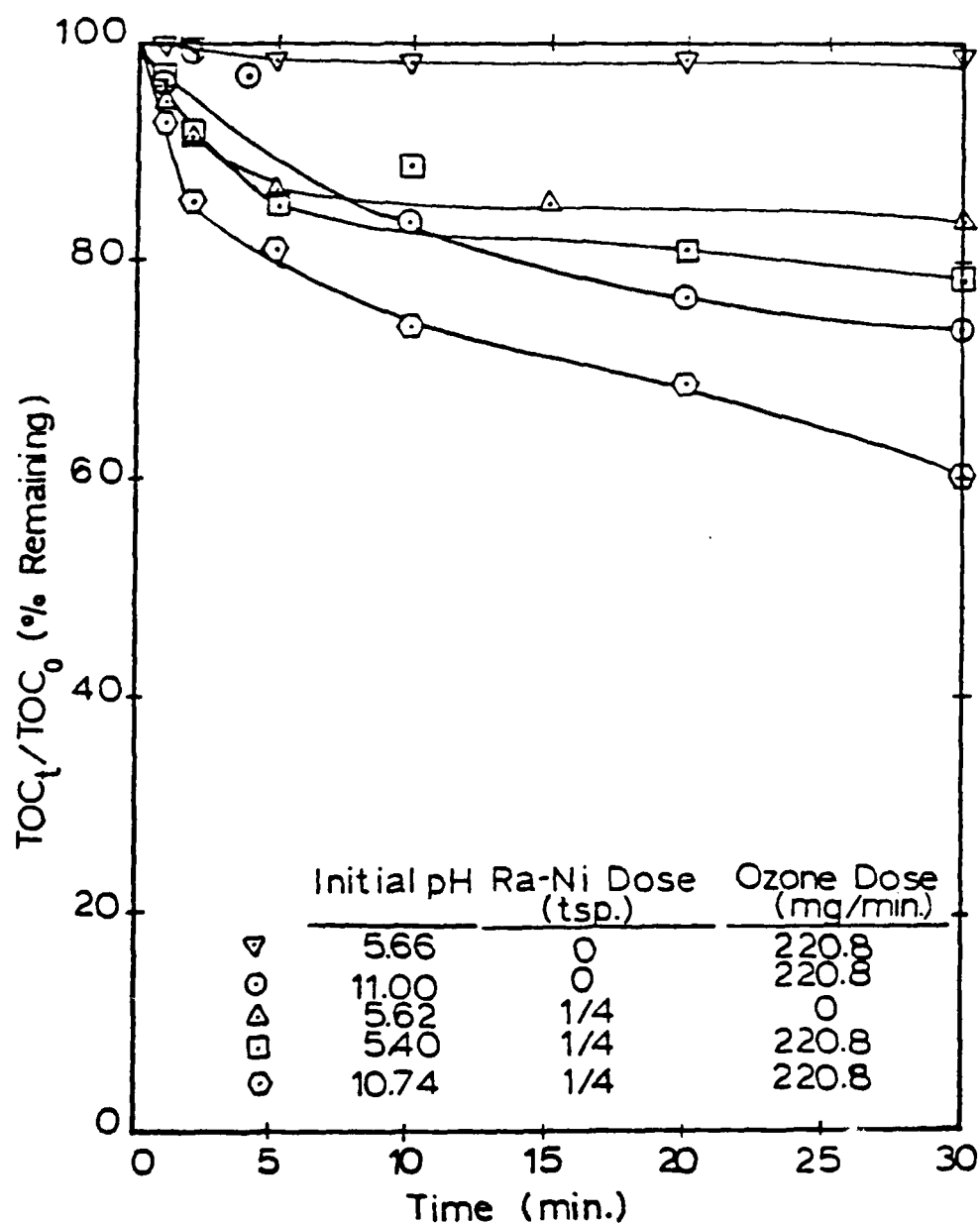


Figure 28 The Effect of the Initial Solution pH on the Removal of TOC in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Ozonation with Ra-Ni

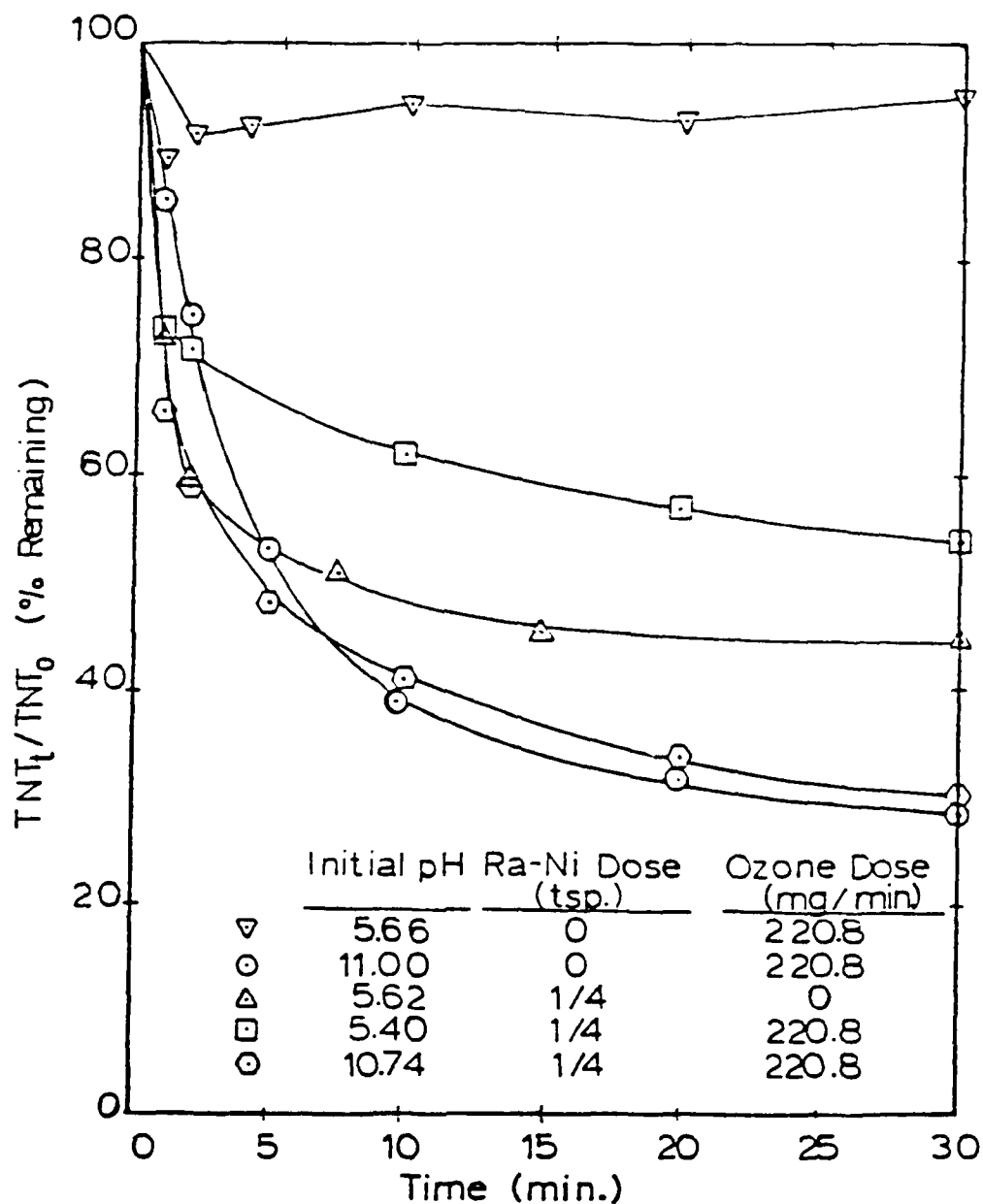


Figure 29 The Effect of the Initial Solution pH on the Removal of TNT in a 3-liter Batch of 70/30 mg/l TNT/RDX by Catalytic Ozonation with Ra-Ni

TABLE 18. THE CATALYTIC OZONATION WITH Ra-Ni FOR 3L OF
70 mg/L TNT BATCH AND 30 mg/L RDX BATCH

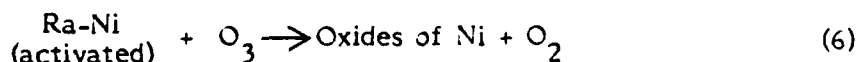
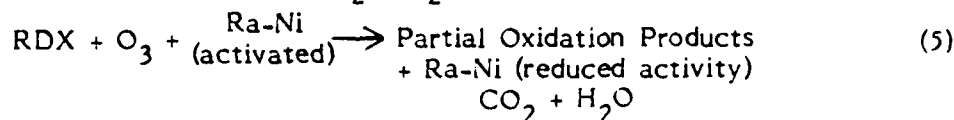
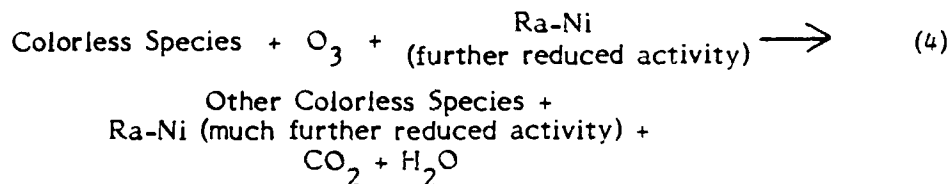
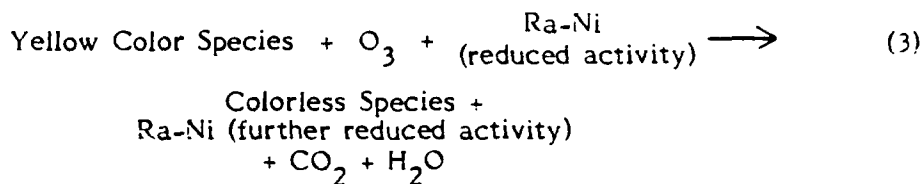
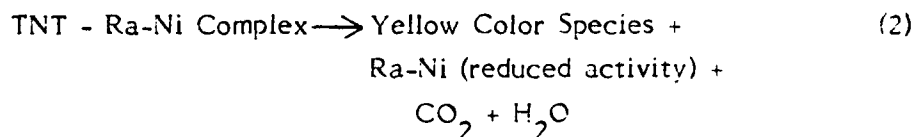
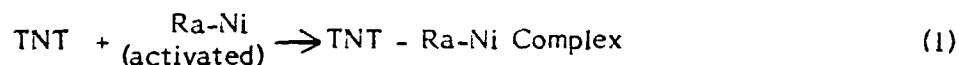
111.6 mg O ₃ /min and 1 tsp. Ra-Ni for 70 mg/L TNT Batch							
Time (min)	0	1	2	5	10	15	30
pH	5.94	7.06	7.11	6.88	6.62	6.90	7.28
TOC (mg/L)	25.22	18.99	16.39	13.00	9.690	8.431	3.947
TNT (mg/L)	67.0	35.6	26.2	16.0	9.3	5.7	2.1
TNT/TOC	2.66	1.87	1.60	1.23	0.96	0.68	0.53
Appearance	colorless	light yellow	light yellow	colorless	colorless	colorless	colorless

111.6 mg O ₃ /min and 1 tsp. Ra-Ni for 30 mg/L RDX Batch							
Time (min)	0	1	2	5	10	15	30
pH	5.59	10.12	10.11	9.92	9.38	7.44	7.73
TOC (mg/L)	4.699	4.238	3.860	2.522	1.657	1.288	1.136
Appearance	colorless	colorless	colorless	colorless	colorless	colorless	colorless

For the 30 mg/L RDX batch, the initial solution pH of 5.59 increased to 10.12 upon the addition of 1 tsp of Ra-Ni and then decreased to 7.73 after 30 minutes of reaction in the catalytic ozonation process, while for the catalytic destruction process with the same concentration of Ra-Ni the pH change was only +0.1 units (i.e., from pH 9.95 to 10.05) throughout the run. After 30 minutes of reaction, the remaining TOC for the catalytic ozonation with 1 tsp of Ra-Ni was 24.3% of the initial TOC, while for the catalytic destruction with 1 tsp of Ra-Ni the remaining TOC was 75.3% of the initial TOC.

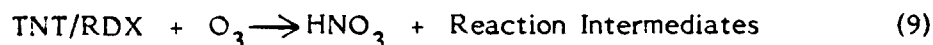
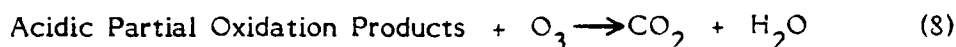
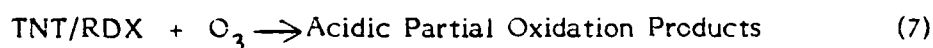
3.4.7 Reaction Mechanism Models

In summary, from the changes in color, pH and TNT/TOC ratio with the reaction time, the reaction mechanisms in the catalytic ozonation process with Ra-Ni were postulated as follows:



where TNT - Ra-Ni Complex was the intermediate complex of TNT and Ra-Ni. For steps (2), (3), (4) and (5), which were responsible for the TOC destruction, it was assumed that the rate of TOC destruction by ozone was enhanced by the catalytic effect of Ra-Ni. Step (6) was assumed to be the major reason for the catalyst poisoning which resulted in the lower destruction rate of TNT, especially for the runs with lower concentration of Ra-Ni (i.e., 1/4 and 1/2 tsp runs). This assumption was based on the following reasons: (1) Nickel has been shown to be oxidized by a powerful oxidizing agent such as hypochlorite, ClO^- [39]; (2) ozone had a higher oxidation potential than hypochlorite (i.e., -2.07 vs -1.60 volts) [40].

With respect to the pH decrease in the reaction mass when ozone was introduced into the reactor, this was probably due to the production of acidic substances which included partial oxidation products and/or nitric acids. Therefore, the pathways of oxidation and the production of nitric acids were postulated as follows:



In steps (7) and (8), the production of acidic partial oxidation products was accompanied by the decrease of TOC, but the production of HNO_3 in step (8) could be due to the substitution of nitro-groups in TNT and RDX by hydrogen and was not related to the cleavage of the ring structure.

3.4.8 Conclusions - Ozone/Ultrasound Experiments

The following conclusions are based on the results of the catalytic destruction of TNT/RDX with Ra-Ni:

1. For a 70/30 mg/L TNT/RDX batch, the rates of TOC and TNT destruction increased with increased concentrations of Ra-Ni.
2. For the 1 tsp Ra-Ni concentration, the rate of TNT destruction was higher for a 70/30 mg/L TNT/RDX batch than that for a 70 mg/L TNT batch, but the rate of TOC destruction was higher for the run in the absence of RDX.

For the catalytic ozonation of TNT/RDX with Ra-Ni, the following conclusions are drawn:

1. For a 70/30 mg/L TNT/RDX batch, the rates of TOC and TNT destruction increased with increased concentrations of Ra-Ni.

2. For the runs with the same concentration of Ra-Ni, the higher the ozone dose the higher the rate of TOC destruction. However, the rate of TNT destruction was not improved but it was adversely affected by the presence of ozone in the reactor. The adverse effect of ozone on TNT destruction was probably due to catalyst poisoning.

3. For the 1/4 tsp Ra-Ni concentration, the rates of TOC and TNT destruction increased with increased initial solution pH.

4. For the 1 tsp Ra-Ni concentration with an ozone dose of 111.6 mg O₃/min, both the rates of TOC and TNT destruction were higher for a 70 mg/L TNT batch than those for a 70/30 mg/L TNT/RDX batch.

3.5 RANEY-NICKEL RECYCLE EXPERIMENTS

3.5.1 Introduction

The technical proficiency of Ra-Ni catalyst either in the presence or absence of ozone to destroy TNT, RDX and their partial oxidation products, as measured by TOC loss, has been demonstrated. The number of contacts for the catalyst and substrates was limited to one time for each of the previously reported-on experiments. Obviously the economic viability of the process will demand recycling of this expensive catalyst.

3.5.2 Experimental

Two series of experiments were performed to ascertain the feasibility of recycling Ra-Ni. In the first series, either Ra-Ni was contacted with a 70/30 (mg/L) TNT/RDX solution (Catalytic Destruction Process) or Ra-Ni and 220.8 mg/min of ozone were added to the reaction suspension consisting of 70/30 (mg/L) TNT/RDX and 1 tbs of Ra-Ni (Catalytic Ozonation Process).

The experimental procedure in both series consisted of exposing the Ra-Ni to the substrate for 2.0 minutes, then separating the catalyst by filtration from the batch, washing it with distilled water which had been raised to pH = 11.0 with NaOH and repeating the procedure with fresh substrate, for a total of five exposures. In the sixth exposure a five-minute reaction time was permitted.

3.5.3 Results and Discussion

The analytical results for these experiments in terms of TOC, TNT, pH and appearance are listed in Tables 19 and 20.

From the data it is evident that after the first contact, the Ra-Ni partially loses its ability to remove both TNT and TOC whether employed in the Catalytic Destruction or Catalytic Ozonation Process. However, in both processes when the contact time

TABLE 19. CATALYTIC DESTRUCTION PROCESS - RAINEY NICKEL RECYCLE EXPERIMENTS
TNT/RDX - 70/30 (mg/L)

Recycle No.	1	1	2	3	4	5	6	6	Settling
Reaction Time (min)	0	2	2	2	2	2	2	5	24 Hours
TOC (mg/L)	26.99	10.49	20.70	22.07	24.93	24.73	24.59	18.03	13.82
TOC _i /TOC _o (%)	100	38.9	76.7	81.8	92.4	91.6	91.1	66.8	51.2
TNT (mg/L)	77.5	0	4.7	12.5	22.2	26.2	42.8	27.1	8.1
TNT _i /TNT _o (%)	100	0	6.1	16.1	28.6	33.8	55.2	35.0	10.5
pH	5.72	9.35	9.42	9.61	7.56	7.10	6.72	7.14	9.59
Appearance (After Reaction)	colorless	colorless	yellow	yellow	yellow	yellow		lt. yellow	yellow
			(clear)	(clear)	(turbid)			(more turbid)	(clear)

TABLE 20. CATALYTIC OZONATION PROCESS - RAINEY NICKEL RECYCLE EXPERIMENTS
TNT/RDX - 70/30 (mg/L)

Recycle No.	1	1	2	4	5	6	6	Settling
Reaction Time (min)	0	2	2	2	2	2	5	24 Hours
TOC (mg/L)	27.68	8.214	18.12	24.03	25.42	26.55	27.19	24.97 21.74
TOC _t /TOC _o (%)	99.1	29.4	64.9	86.1	91.0	95.1	97.4	89.4 77.9
TNT (mg/L)	72.0	1.4	21.1	46.3	54.3	57.8	61.0	55.9 46.8
TNT _t /TNT _o (%)	100	1.9	29.3	64.3	75.4	80.3	84.7	77.6 65.0
pH	5.75	10.41	6.82	5.48	5.85	5.77	6.00	6.21 8.58
Appearance (After Reaction)	colorless	yellow	yellow & pink	pink	pink	pink	pink	pink pink (light) (very light) (darker)

AD-A124 989

AN ULTRASOUND CATALYZED OZONE OXIDATION PROCESS
FEASIBILITY STUDY FOR THE (U) ARIZONA UNIV TUCSON DEPT
OF CIVIL ENGINEERING R A SIERKA OCT 82
UNCLASSIFIED DRXTH-TE-CR-82175 DAAK11-81-C-0030

2/2

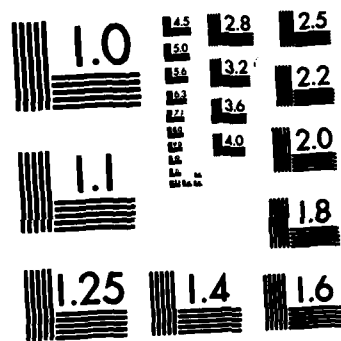
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

was increased to five minutes (i.e., in the sixth contact), the catalyst removed additional amounts of TNT and TOC. Further, when the Ra-Ni was permitted to stay in contact with the reaction mass after the sixth contact for an additional 24 hours without stirring, still further reductions in TOC and TNT were observed.

In terms of pH changes, it should be noted that in both series of experiments the solution pH after reaction, decreased. Since it has been shown previously that TNT and TOC destruction rates are both reduced as solution pH decreases, this would partially account for the reduced removal efficiencies.

While after each time the catalyst was filtered from the batch, it was washed with pH = 11.0 distilled water, evidently the hydroxyl ion concentration was insufficient to maintain high pH's in the batch. It should be recalled that Ra-Ni is suspended in a strong aqueous caustic solution due to its pyrophoric nature.

Examination of the physical appearance of each batch indicates that when ozone was employed the batch was pink in color while in the absence of ozone the batch color tended to be yellow in hue.

In summary, it appears that the recycle experiments may have been carried out at reaction times which were too short. Also, if the batch pH would have been maintained at a high level, their removal efficiencies would have been greater. Likewise, evidently the optimum treatment of the spent catalyst was not employed. For example, stronger caustic solutions could possibly have increased performance.

3.6 RANEY-NICKEL TNT/RDX DESTRUCTION MECHANISM EXPERIMENTS

3.6.1 Introduction

The mechanism(s) by which TNT and TOC are reduced in concentration when contacted with Raney-Nickel require study. The objectives of the following experiments were to investigate the mechanisms involved in TNT and TOC reduction and to gain knowledge which could lead to methodologies to recycle the catalyst since the use of Ra-Ni has been shown to be an efficient and quick method to destroy TNT/RDX.

3.6.2 Experimental

The basic experimental apparatus and substrates employed in these experiments have been previously described in sections 3.2.2. and 3.2.5. Figure 30 is a process flow diagram for the experiments and lists the analytical data obtained in each step of the experiment.

3.6.3 Results

In step 1, 3L of 70/30 (mg/L) TNT/RDX was added to a well-mixed reactor together with 1 tbsp of Ra-Ni. After 1, 2, 5, 10 and 15 min of contacting, samples were extracted.

The data indicates an immediate pH increase (i.e., 5.23 to 10.40) in the solution, and a decrease in TOC and TNT. Within 2.0 minutes all of the TNT had been removed but 11.57 of the 26.50 mg/L of TOC remained. After 15 minutes of contact, 9.305 mg/L of the original TOC still remained in solution. The yellow color appearing after 1.0 minutes of catalyst-substrate reaction disappeared coincidentally with complete TNT removal.

It can be concluded that since no TNT remained in solution after 2.0 minutes of reaction, the TOC remaining must have been reaction by-products of TNT/RDX contact with Ra-Ni.

Step 2 consisted simply of turning off the stirrer and permitting gravity sedimentation to take place. After 15 minutes of quiescent settling the supernatant was sampled and showed a slight decrease in TOC (9.305 - 7.768 mg/L) and no change in solution pH.

The next procedure (i.e., step 3) involved decantation of the treated munitions wastewater, permitting the once-used Ra-Ni to remain on the reactor bottom. Then, 3.0L of distilled water were admitted to the reactor and the mixer turned on. The distilled water, on mixing with the once-used Ra-Ni, rose in pH from 5.23 to 7.24 as did its TOC (from 0.327 mg/L to 4.52 mg/L). From the samples extracted from the reactor over a 30-minute period, it can be seen that TOC increased from 4.523 mg/L to 9.685 mg/L after 20 minutes. This decreased to 8.016 mg/L over the next ten minutes. No TNT appeared in the samples taken during this portion of the experiment.

These latter results indicate that contact of TNT with Ra-Ni brings about a reaction which changes the structure of this molecule so that it is not identified as a nitro-body in the Silas-Mason Test.

Step 4 consisted of removing 900 mL of the homogeneous suspension to another container (1L) and permitting the Ra-Ni to separate from the distilled water. Samples taken 24 and 48 hours later indicate a decrease in TOC to 4.473 mg/L and 3.805 mg/L, respectively. During the two days of contact with the catalyst, the pH decreased from 9.23 to 8.77. Once again no TNT was found in the solution. The solution remained colorless over the entire reaction period.

Immediately after taking the 48-hour sample, the contents of the tank were decanted and replaced by 900 mL of 70/30 (mg/L) TNT/RDX (step 5). Once again the batch was mixed with samples extracted at 0, 2, 5, 10, 15 and 30 minutes.

The fresh munitions wastewater upon contact with the catalyst, experienced a pH increase from 5.80 to 6.38. Likewise, the untreated batch TOC of 27.47 mg/L rose to 30.61 upon contact with the previously used catalyst; however, the TNT concentration was reduced to 54.3 mg/L. Reaction between substrate and catalyst continued with both TOC and TNT decreasing. In the case of the former, the reaction was 9.52 mg/L and 27.0 mg/L in the latter. The pH of the batch increased continuously from 6.38 to 7.24 over the run. Finally the batch color changed from colorless to yellow.

After sampling, approximately 450 mL of suspension remained and in step #6 the mixing was terminated and the catalyst permitted to separate by gravity from the liquid. A sample of the supernatant taken approximately 2.5 hours later revealed a slight increase in pH (i.e., 7.24 to 7.44) and decreases in TOC from 21.09 mg/L to 15.58 mg/L, and TNT from 27.3 to 15.5 mg/L.

In step 7, approximately 450 mL of treated wastewater was decanted and replaced with an equal amount of distilled water and mixing commenced. Sampling of the mixed batch took place after 10 and 30 minutes.

As was seen previously in step 3, when the distilled water came in contact with the catalyst its pH rose (i.e., 5.36 to 6.64) and continued to rise with contact time (i.e., 6.76 to 6.99). TOC values also were increased from 0.747 to 8.935 then decreased to 7.589 after ten minutes and finally increased to 8.98 mg/L after 30 minutes of catalyst-distilled water contact. Lastly, TNT was not found to be present in the distilled water which remained colorless.

Comparing the results of step 3 and step 7 in which the Ra-Ni after one then two contacts with fresh solutions of 70/30 (mg/l) TNT/RDX, it can be seen that more and more TOC is being leached from the metal. However, when the suspension in Run 7 was permitted to remain in contact without mixing for 18 hours, once again TOC was reduced. These data suggest a continued reaction between organic species diffusing from, then returning to the catalyst surface for reaction.

In step 8, the final portion of the experiment, a third contact between the original Ra-Ni and an untreated 70/30 (mg/L) TNT/RDX batch (350 mL) was brought about after the distilled water from step 7 had been decanted. A 500 mL flask employing a magnetic stirring bar served as the reactor.

The analytical data reveal that a small amount of TOC removal occurred over the first five minutes of contact (i.e., 32.36 to 29.39 mg/L) then the TOC increased (29.39 to 33.63 mg/L) over the next 25 minutes.

The Ra-Ni capacity to remove TNT still remained, although only slightly. The 70/30 (mg/L) batch contained 70.16 mg/L of TNT which was reduced to 57.9 mg/L in 20 minutes then the solution registered a 58.3 mg/L concentration at 30 minutes. pH values always increased throughout the run from 6.18 to 6.94.

The effects of contacting Ra-Ni with aqueous solutions of TNT/RDX then separating the suspension, and repeating the procedure three times are seen in Figure 31 and 32.

This data suggest that after one contact Ra-Ni loses a considerable portion of its ability to destruct TNT and TOC. In terms of TNT, the rate loss of this ability is more gradual than with TOC.

Evidently the mechanism of TNT removal is not simply adsorption but a combination of adsorption and reaction. This was evidenced by the fact that no TNT diffused back into the distilled water after the catalyst had been contacted with the wastewater even after three recycles.

3.7 CONCLUSIONS

1. The recycling of the Ra-Ni catalyst in both the Catalytic Destruction and Catalytic Ozonation Process shows considerable loss of activity in terms of TOC and TNT destruction with more than one recycle. Reactivity losses are greater when ozone is present than when it is not.

2. Organic destruction reactions with the catalyst surface apparently are diffusion-controlled and require increased contact time to maximize use of the Ra-Ni.

3. Regeneration of the partially spent catalyst surface by high pH (11.0) distilled water washes was ineffectual.

4. TNT once contacted with Ra-Ni, even after the catalyst has been recycled three times, was not merely adsorbed, but chemically reacted as evidenced by the fact that no TNT ever appeared in the distilled water washes between substrate-catalyst contact.

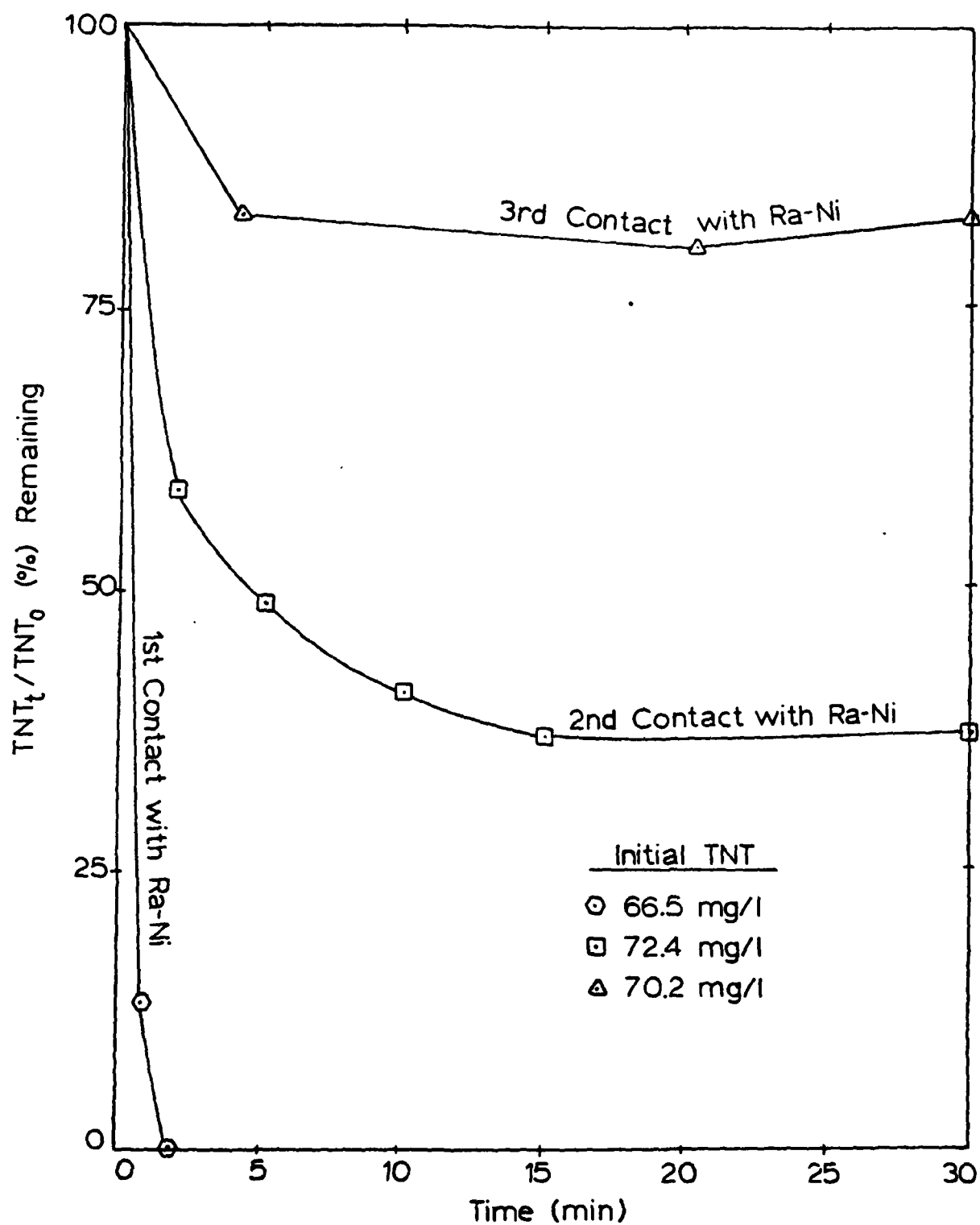


Figure 31 The Effect of Ra-Ni Recycle on the Removal of TNT from 70/30 (mg/l) TNT/RDX Solutions

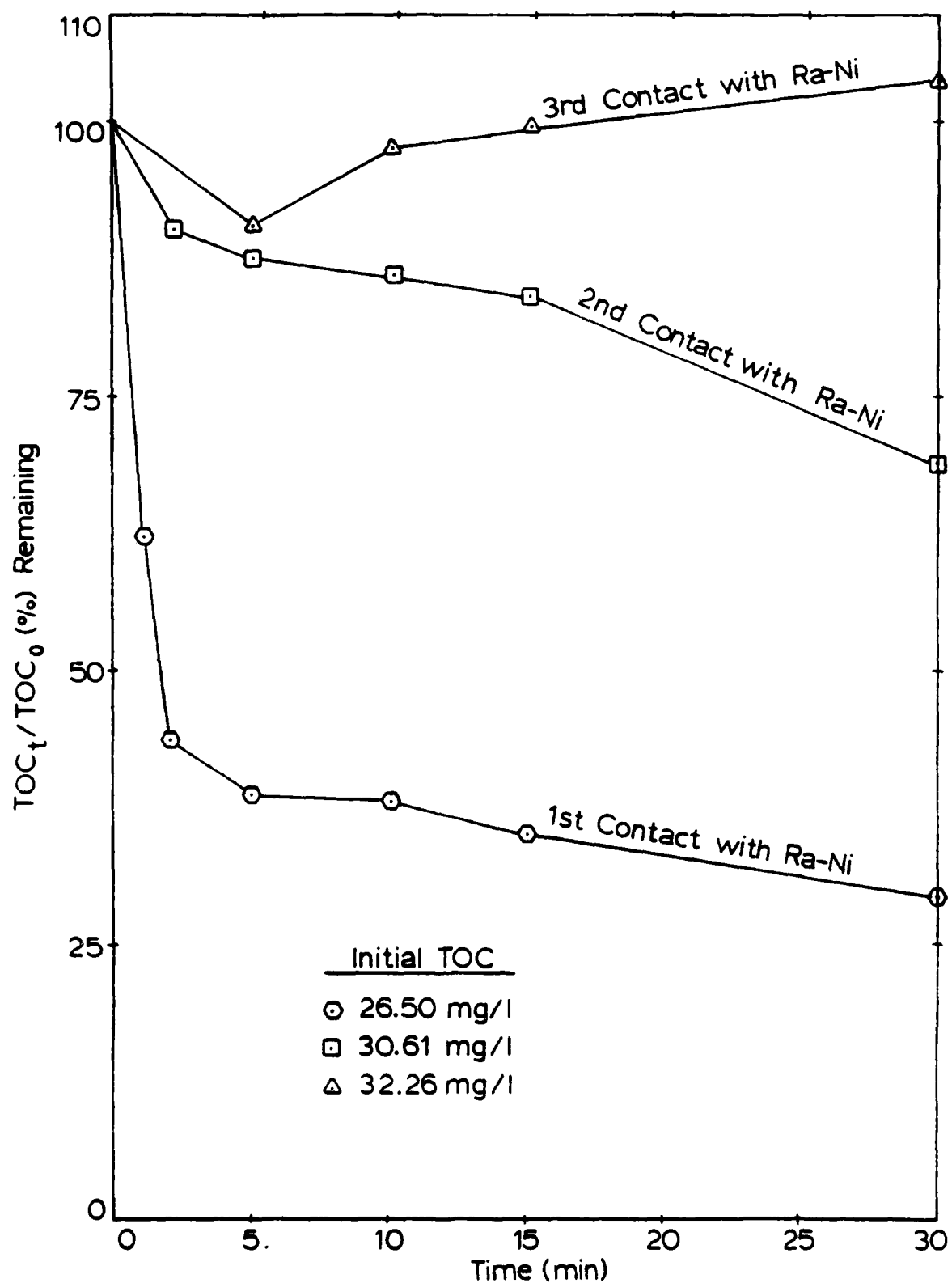


Figure 32 The Effect of Ra-Ni Recycle on the Removal of TOC from 70/ 30 (mg/l) TNT/RDX Solutions

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APPENDIX A

APPENDIX A - ANALYSIS METHODS

A. TOTAL ORGANIC CARBON ANALYSIS

The Dohrman DC-80 TOC Analyzer employs the ultraviolet promoted persulfate oxidation technique. A schematic is given in Figure A-1.

The operating principle begins when acidified persulfate reagent is continuously pumped from the external reservoir to the injection part and then into the bottom of the ultraviolet reactor.

A sample containing combined carbon is carried into the reactor by the reagent flow. In the reactor the oxidation of organics occurs rapidly. The reactor liquor is continuously sparged with zero-grade nitrogen and this sparge/carrier gas flows out of the top of the reactor to the nondispersive - infra-red detector (NDIR).

The NDIR produces an electrical output (peak) which is integrated and scaled by a number processor and then displayed and printed.

In this research, a 15 mL sample was taken at appropriate time intervals from the reactor for analysis. Prior to injection, the 15 mL sample was acidified by adding three drops of concentrated phosphoric acid (85-87% by weight) and then sparged with nitrogen for three minutes to removed inorganic carbon. Next, a 1 mL acidified and stripped sample was injected into the DC-80 for TOC analysis. All samples were analyzed twice and the average value reported.

A complete instruction manual for the DC-80 has been developed and is available from

Dohrman Division
Envirotech Corporation
3240 Scott Boulevard
Santa Clara, CALIFORNIA 95050

B. TNT MEASUREMENT BY THE SILAS-MASON METHOD

TNT concentration was determined by the Silas-Mason Test, a colorimetric method which complexed all TNT nitro bodies in 25 mL of sample with 5 mL of diethylamino-ethanol to a form with distinct color properties. After complexing, the absorbance of the test sample was compared with a blank sample in a Perkin-Elmer UV-VIS Spectrophotometer Model 200 at 252nm wavelength and using a cell that provided a light length of 1.0 cm. The measured absorbance was converted to the corresponding TNT concentration based on a standard curve which was prepared by a stock solution of pure alpha-TNT. The standard curve is shown in Figure A-2. A concentration range of 1 to 100 mg/L was used.

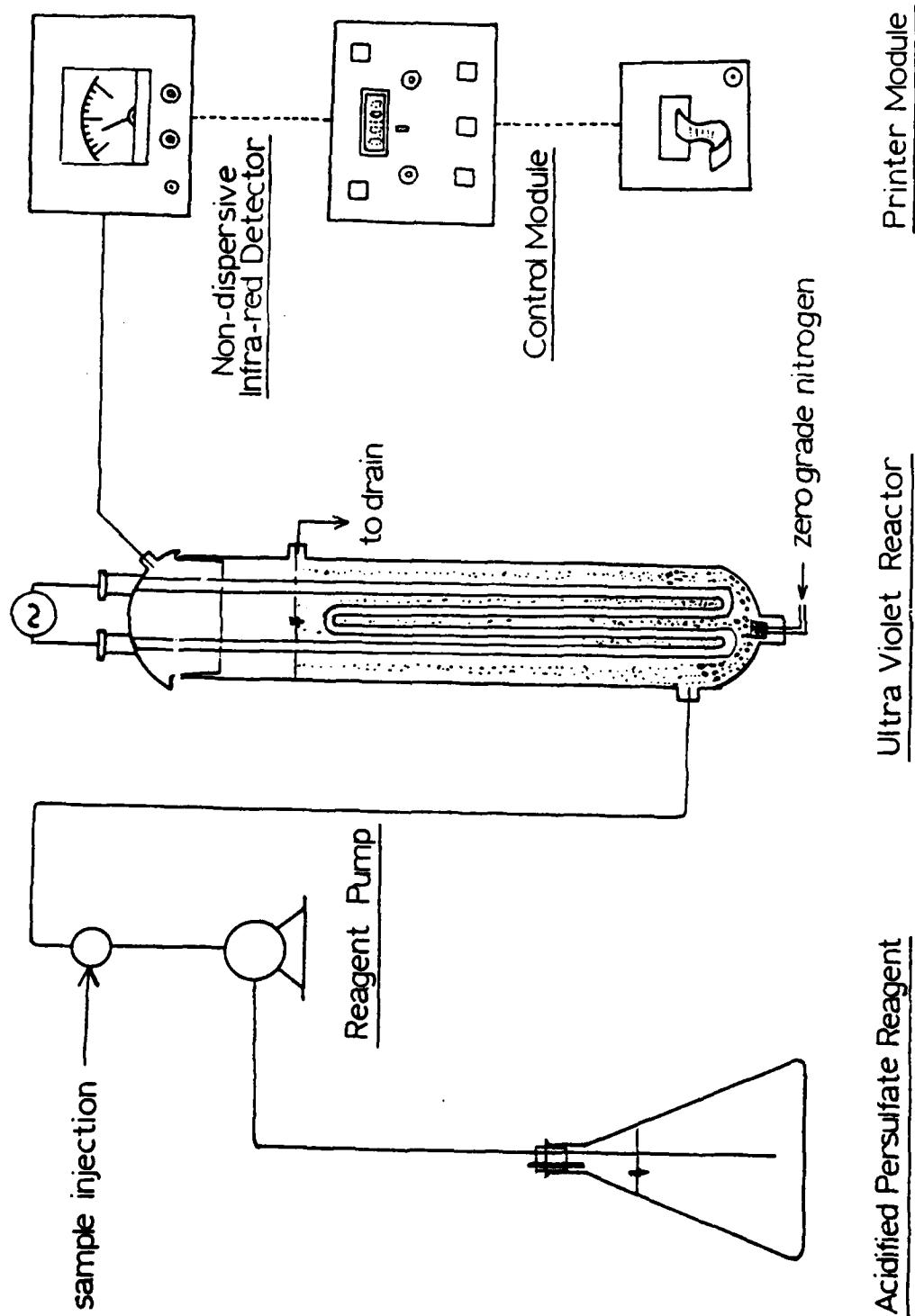


Figure A-1 The Dohrmann DC-80 Total Organic Carbon Analyzer Process Flow Diagram

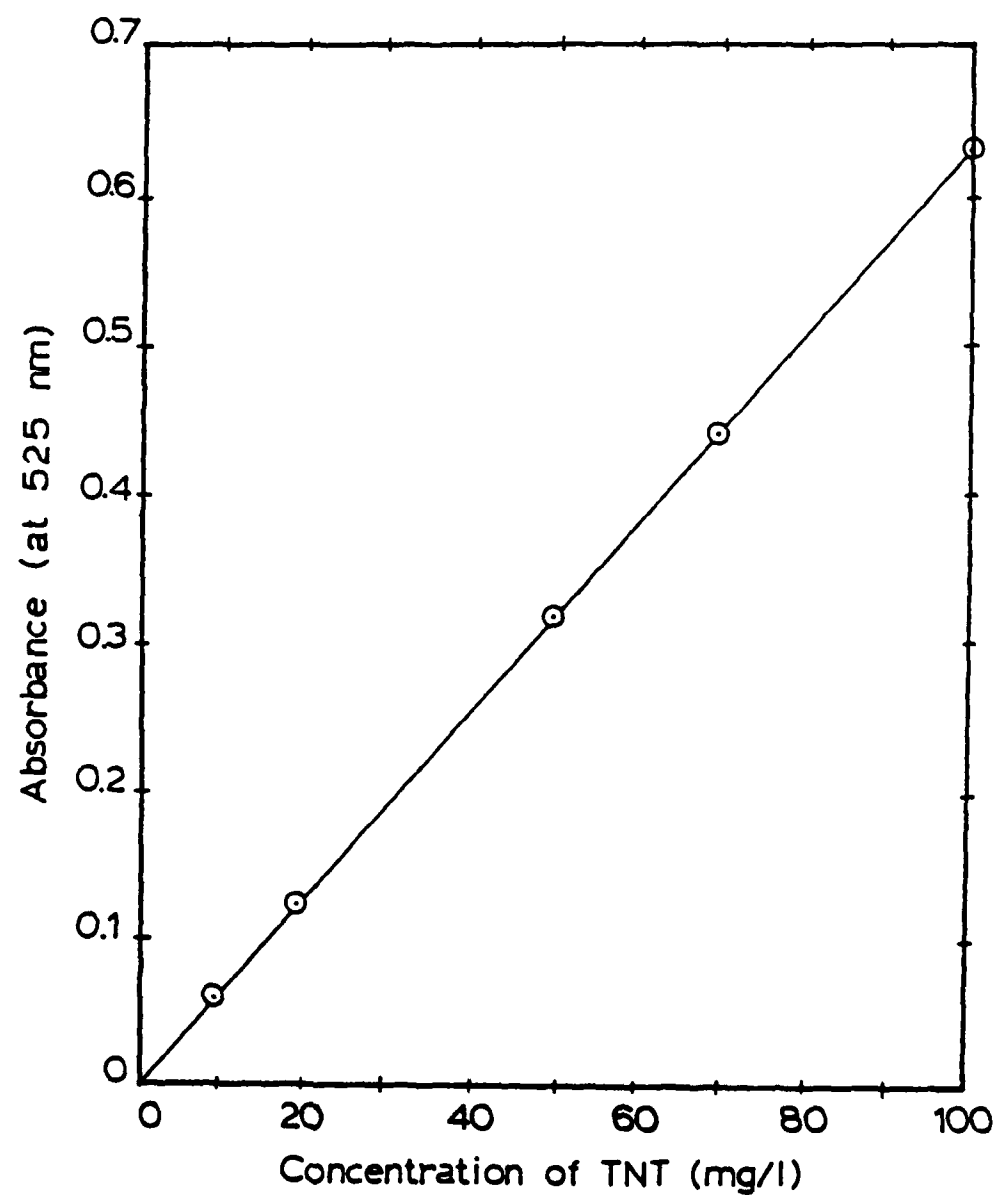


Figure A-2 The Standard Curve for the Silas-Mason Test

From the previous studies [40, 41], it was found that the reactable substances in the Silas-Mason Test included TNT, dinitrotoluene (DNT) and some other forms of nitroaromatic compounds (identified by gas chromatography) and therefore, was employed in this research to monitor changes in TNT with reaction time. RDX was not a reactable substance in the Silas-Mason Test.

APPENDIX B

APPENDIX B - ULTRASONIC SYSTEM DESIGN

The high frequency ultrasonic system can be divided into two parts: (1) ultrasonic transducer, and (2) high frequency power drive.

The experimental requirements called for frequencies greater than 40 kHz and power levels up to 100 watts. Most of the electronic equipment needed for the system was already available within the College of Engineering; however, it was necessary to purchase the power amplifier and to build the piezoelectric transducers.

The electrical equipment configuration is shown in Figure B-1. The oscillator, Model HP-3311A, was used to provide the variable frequency input as well as the power level control. The frequency was measured with a Fluke, Model 1900A frequency counter.

The oscillator output was fed into the power amplifier, ENI, Model 2100L. The power amplifier has a constant gain of 50 dB over a frequency range of 10 kHz to 12 MHz. It is capable of delivering 100 watts of continuous power over the entire frequency range. A vector impedance meter, Model HP-4815A, was used to check the transducer input impedance and for the resonant frequency of each transducer. Power output was monitored on the front panel meter of the power amplifier. The piezoelectric transducer shown in Figure B-1 was mounted in the base of the reactor.

The transducers were constructed from piezoelectric material, Type 5400, obtained from Channel Industries. The crystals were 1.00 inches in diameter; their thickness (0.05", 0.08", 0.25" and 0.50") was dependent on the required resonant frequency. A cross-section of the crystal is given in Figure B-2.

The crystals were supplied with fired-on metal electrodes through which the electrical power was applied. The piezoelectric crystals, Figure B-3, were then bonded onto one side of a 0.002" stainless-steel diaphragm using an electrically conductive silver epoxy, Epo-Tech, Type 31H. An additional wire was epoxied to the second surface of the crystal so that electrical power could be applied through the wire and also the diaphragm. For safety reasons, the diaphragm was grounded.

The diaphragm formed the bottom of the reactor as shown in Figure B-4. Electrical power was applied from the amplifier to the crystal through a BNC connector on the side of the reactor.

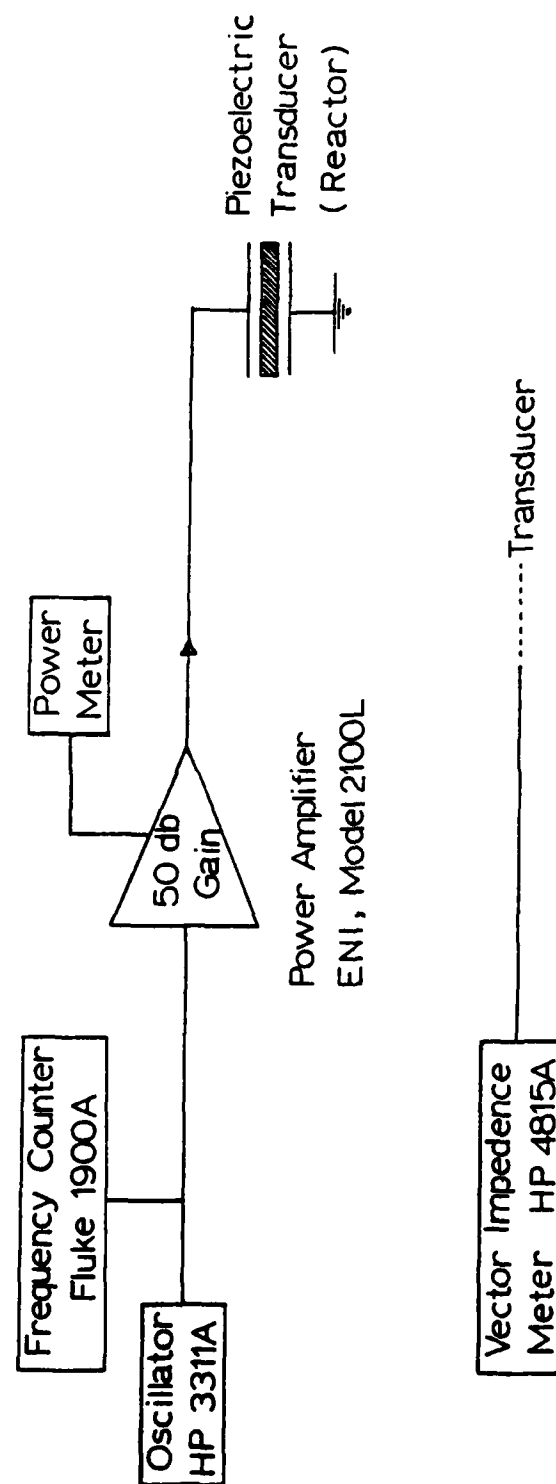
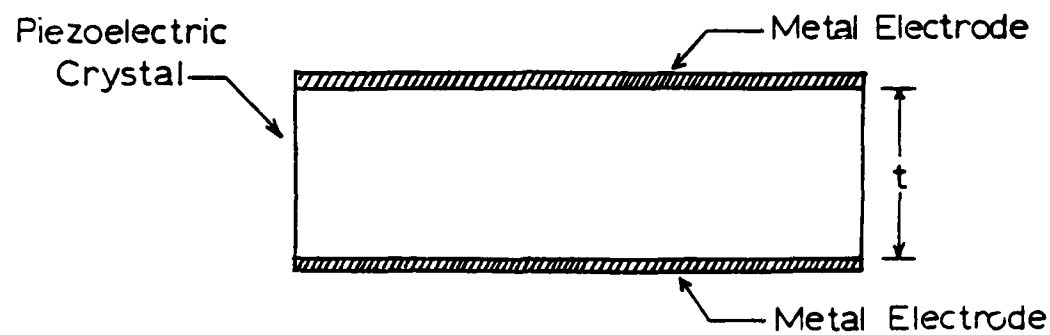


FIGURE B-1 ULTRASOUND ELECTRICAL EQUIPMENT DIAGRAM



Thickness (inch)	Operational Frequency
0.061	1,007 KHz
0.101	829 KHz
0.408	63 KHz

FIGURE B-2 TRANSDUCER SYSTEM

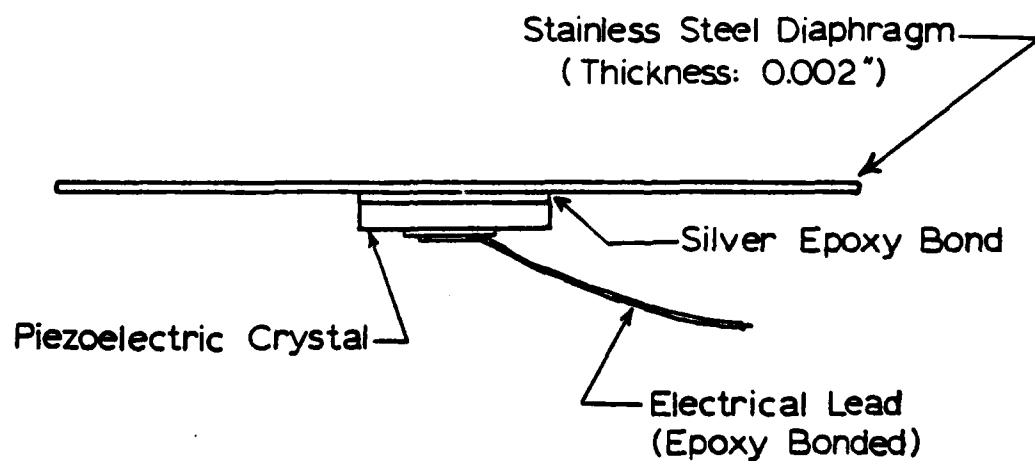


FIGURE B-3 TRANSDUCER SYSTEM WITH STAINLESS STEEL VIBRATING PLATE

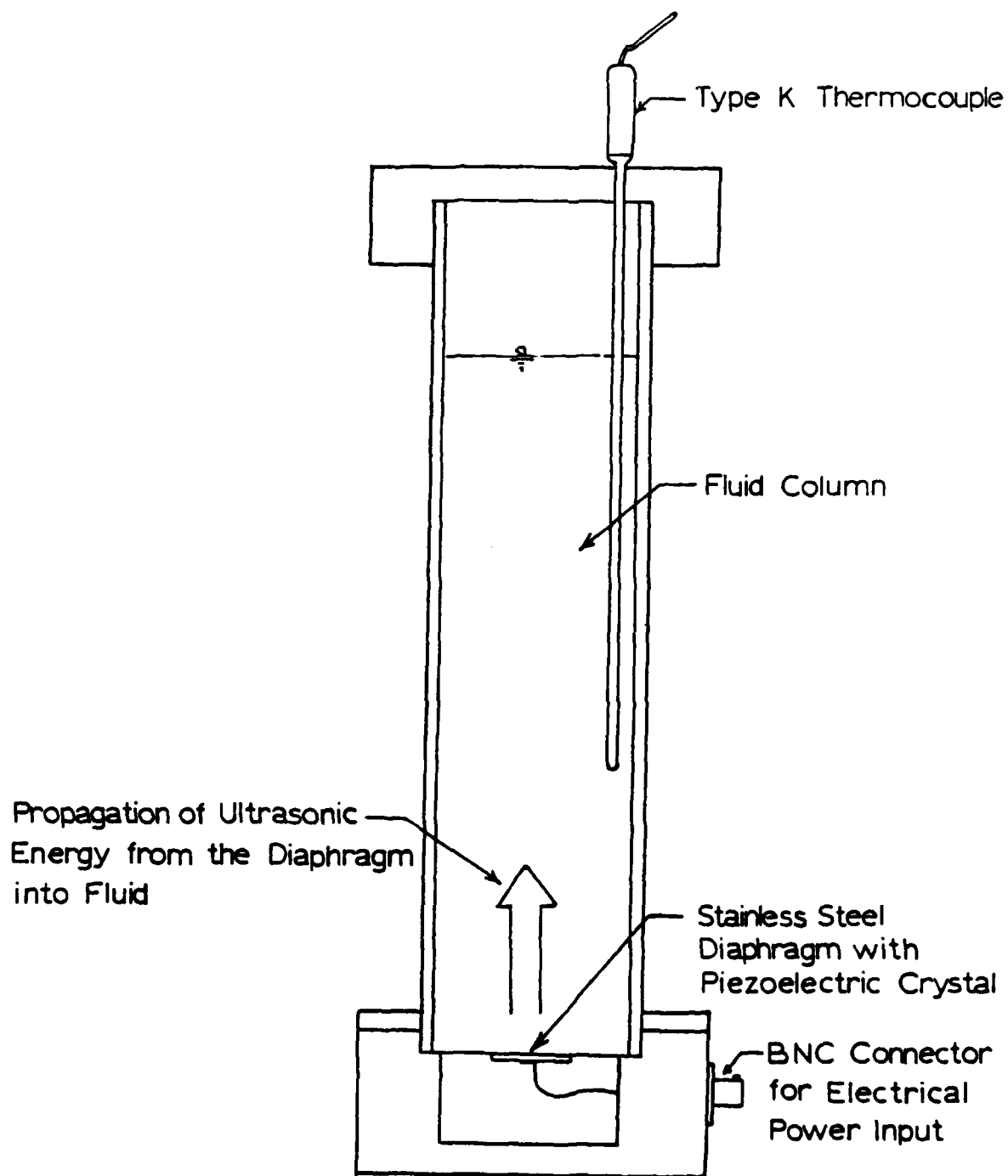


FIGURE B-4 ULTRA-HIGH FREQUENCY REACTOR

The high-frequency electrical signal was transformed into a sonic wave by the crystal. The sonic wave was then propagated through the diaphragm into the fluid column.

The maximum sonic amplitude was obtained when the system was operated at a resonant frequency. Resonant frequency was determined by using a vector impedance meter.

Power into the system was controlled by the output level control on the oscillator.

The fluid temperature was monitored with a type-K thermocouple attached to a Doric digital readout which was calibrated in degrees Celsius.

APPENDIX C

APPENDIX C - THE TREATMENT OF MUNITIONS WASTEWATERS BY SIMPLE AND ULTRASOUND CATALYZED OZONATION

Introduction

Five different munitions plant wastewaters were supplied for ozone treatment and analysis as part of this research project. Table C-1 identifies each of the samples as received in five-gallon containers.

TABLE C-1 - MUNITIONS PLANT WASTEWATERS

<u>Sample No.</u>	<u>Identification</u>
1	Milan AAP - X41
2	Kansas AAP Pinkwater Building 008 After Treatment
3	Lone Star AAP - 0 - 48
4	Iowa - AAP Bldg 34 - 70 - 1 Pink Water
5	Iowa - AAP Bldg 34 - 70 - 1 Pink Water

Examination of samples #4 and #5 showed these materials to be different, even though they were identically marked. Differences were noted in pH, TOC, and TNT concentration.

Throughout this report the substrates will be identified by sample number (i.e., #1, #5) and run number (i.e., Runs #1 and 2 come from Sample 1).

Objectives

The objectives of these experiments were to evaluate simple ozone oxidation of munitions plant pink wastewaters and to contrast those results with ozonation/ultrasound of the same wastewaters.

Experimental

The pretreatment and handling of the five samples were identical. First, approximately 8.1 l of sample was removed from the five-gallon sample container. Second, the entire 8.1 l was vacuum filtered through a one-inch depth of glass wool supported by a No. 42 Whatman filter (pore size = 98%, 2 μ). Third, a 50 ml time zero sample was extracted for temperature, pH, TOC and TNT analyses (Silas-Mason Method). Fourth, two 4l aliquots were each pH adjusted to 7.0 with 1.0 N HCl. Fifth, 4l of filtered, pH 7.0 wastewater was admitted to the reactor.

The reaction conditions for the ozonation were: (1) 10 psig feed gas (O_3/O_2) pressure, (2) 240 mg O_3 /min and (3) 7.5 l (O_3/O_2)/min. Ozonations for one hour were carried out in a glass pyrex reactor.

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For these studies a Biosonic IV ultrasonic system was utilized. The unit had a lead zirconium titanate transducer which delivered up to 95% current efficiency at optimum performance. This system had two ceramic discs in the transducer which provided a feedback from the probe to the generator and compensated for the required output assuring reproducibility in the reaction through constant power output. A power meter monitoring system was also used which indicated peak envelope power (PEP), measured in watts, delivered from the generator to the head in the tip. The unit was capable of delivering over 300 watts of accoustical power to the reaction liquid.

Ultrasound @ 160 watts of peak envelope power (PEP) was present in the reactor for one-half of the runs while the plain ozonators were carried out in the absence of ultrasound.

Samples were extracted from the reactor at 0, 15, 30, and 60 minutes and analyzed for pH, temperature, TOC and TNT by the Silas-Mason Method after 0.45µ Millipore filtration. In addition, unfiltered samples for time 0 and 60 minutes were analyzed for TOC and TNT.

Results and Discussion

Sample #1

The analytical data for Sample #1 is presented in Table C-2. Run #1 refers to plain ozonation (i.e., without ultrasound) while in Run #2, the catalyzed ozonation employed ultrasound.

TABLE C-2 - SAMPLE #1

Time	RUN #1					RUN #2				
	Temp	pH	TNT	TOC (mg/l)		Temp	pH	TNT	TOC (mg/l)	
	(°C)			Unfiltered	Filtered	(°C)			Unfiltered	Filtered
0	25.5	7.0	92.1	53.67	47.76	25.5	7.0	92.1	53.67	47.76
15	26.0	5.32	82.5	-	49.11	27.5	5.18	82.4	-	50.63
30	26.0	4.53	81.0	-	47.96	28.5	4.62	77.8	-	48.71
60	26.0	3.86	77.9	48.69	47.08	32.0	4.07	81.0	49.10	47.91

From the table it is evident that the use of ultrasound increases the temperature of the reacting mass. Run #2 for example, experienced a 6.5°C rise in temperature. Therefore, the sound power energy is being partially converted to thermal energy.

In terms of pH in both runs the pH decreased; however, the decrease was less (7.0 - 4.07) for Run #2 than Run #1 (7.0 - 3.86). Initially, the Sample #1 had a pH of 7.81. It would appear that these data are supported by the TNT destructions since in Run #1, 15.5% of the TNT was destroyed while in Run #6, only 12.1% of the TNT was destroyed. Since the destruction of TNT would properly produce acids, these observations would prove consistent.

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TOC destructions on a filtered basis yield erratic data with little or no removal. In both Runs #1 and #2, the TOC increases from time 0 to the 15-minute samples. Since both samples were filtered, these data merely reflect the efficiency of filtration. The raw, unozonated samples contain particulates that are readily filtered, however, after these particulates have been reacted with ozone, solubilization occurs and TOC rises. All 30- and 60-minute samples show a decline with ozonation time.

When the unfiltered 0 and 60-minute samples are examined, it can be seen that in Run #1, 9.3% of the TOC was removed while in Run #2, 8.5% was removed. Other researchers have shown that plain ozonation of TNT removed only 6 to 8% TOC after 60 minutes of reaction.

The color of the influent for both runs was a dark red. During the first minute of ozonation, both batches turned a light orange. Thereafter, both batches retained this color, but the intensity decreased slightly. Also, in both runs, the foaming was initially present but decreased with time. Contained in the foam were suspended solids which adhered to the walls of the reactor.

When Sample #1 was filtered through a 0.45 μ Millipore filter, the filtrate was a reddish-brown, and the residue on the filter dark brown. All other ozonated samples which were filtered in the same manner yielded a colorless filtrate.

Examination of the 0.45 μ filters showed that while in Run #1 the filtered material for the 15, 30 and 60-minute samples was orange, the intensity decreased slightly with ozonation time. In Run #2, this color on the filter cakes increased with ozonation time from a light brown to a dark brown.

Together with the other data, these filter residues support the conclusion that with ultrasound a different oxidation pathway was being followed.

Sample #2

The data for Sample #2 are given in Table C-3 where Runs #3 and #4 are the designation for the no-sound and ultrasound runs.

TABLE C-3 - SAMPLE #2

Time	RUN #3					RUN #4				
	Temp (°C)	pH	TNT mg/l	TOC (mg/l)		Temp (°C)	pH	TNT mg/l	TOC (mg/l)	
				Unfiltered	Filtered				Unfiltered	Filtered
0	27.0	7.0	10.0	68.58	56.88	25.0	7.0	10.0	68.58	56.88
15	27.0	7.81	4.37	61.24	53.95	27.0	7.84	12.4	63.36	51.23
30	27.5	7.81	7.54	59.75	50.47	29.0	7.86	6.5	59.20	49.04
60	27.0	7.74	4.76	54.53	48.36	31.5	7.80	4.4	51.55	43.37

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The temperature response in the series of two runs is identical to that seen in Runs #1 and #2; that is, with ultrasound the temperature increases by 6.5°C over the one hour of reaction.

The pH response for Runs #3 and #4 is dramatically different from Runs #1 and #2 in that the pH rises by 0.8 units from 7.0 to 7.8 and essentially remains there for the remainder of the run.

Figure C-1 is a plot of the TOC remaining as a function of ozonation time for Runs #3 and #4. In both curves, two first-order curves are seen; however, with Run #4 the extent and rate of TOC destruction is greater than with Run #3, the run without ultrasound.

The TNT concentration in Sample #2 is much less than in Sample #1 (i.e., 10 mg/l TNT vs 92 mg/l TNT). This accounts for the larger TOC removal percentages with this sample. Obviously, the organics present in the sample are less ozone refractory than those of Sample #1.

Variations in these types of wastewaters generated at different munitions plants make generalizations about wastewater treatment with ozone extremely difficult.

Sample #3

Runs #5 and #6 were conducted on Sample #3 and the resultant data listed in Table 4-C.

TABLE C-4 - SAMPLE #3

Time	RUN #5					RUN #6				
	Temp	pH	TNT	TOC (mg/l)		Temp	pH	TNT	TOC (mg/l)	
	(°C)		mg/l	Unfiltered	Filtered	(°C)		mg/l	Unfiltered	Filtered
0	26.0	7.0	66.5	35.23	32.22	26.0	7.0	66.5	35.23	32.22
15	26.5	5.50	55.5	-	31.85	27.5	5.22	58.0	-	33.04
30	26.5	4.94	55.0	-	32.20	28.0	4.78	55.5	-	32.98
60	26.0	4.63	56.0	32.55	32.78	29.0	4.47	54.0	32.63	31.95

For Runs #5 and #6, the solution pH decreased with ozonation time similarly to Runs #1 and #2. The run with ultrasound gave a consistently lower pH (see Figure C-2). The pH of the material as received was 7.71.

For this sample, the initial TNT and filtered TOC concentrations were relatively high with values of 66.5 mg/l and 32.22 mg/l respectively. Virtually no TOC removal occurred in either run while the removal of TNT was 10.5 and 12.5% in Runs #5 and #6, respectively. It should be noted that when TNT concentrations were analyzed in the unfiltered time 0 and 60-minute samples, the reductions were from 80.0 mg/l TNT to 58. and 60.5 mg/l in the plain ozonation (Run #5) and catalyzed (Run #6) experiments. The filtered 60-minute sample decreased from 66.5 mg/l TNT to 56 and 54 mg/l in Runs #5 and #6, respectively. The difference in the time zero filtered and unfiltered samples could be attributed to TNT removal by filtration or interferences in the Silas-Mason Test.

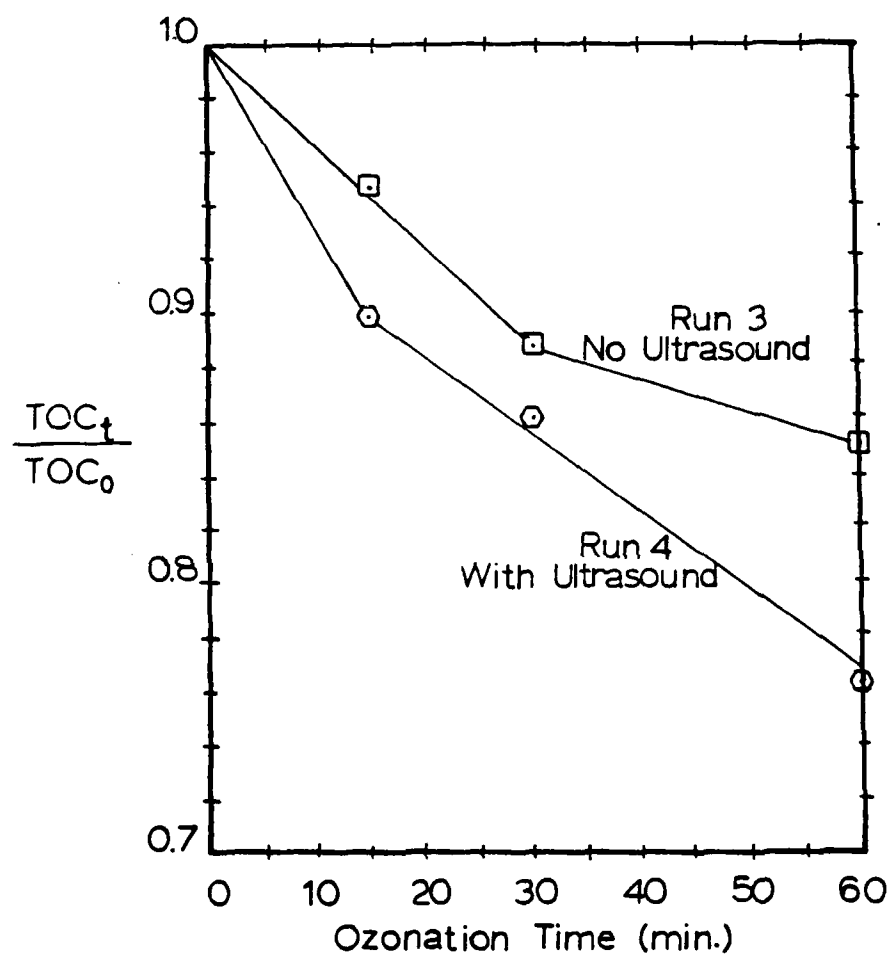


Figure C-1 Filtered TOC Remaining as a Function of Ozonation Times in the Presence and Absence of Ultrasound for Kansas AAP Pink Water from Building #008 after Treatment

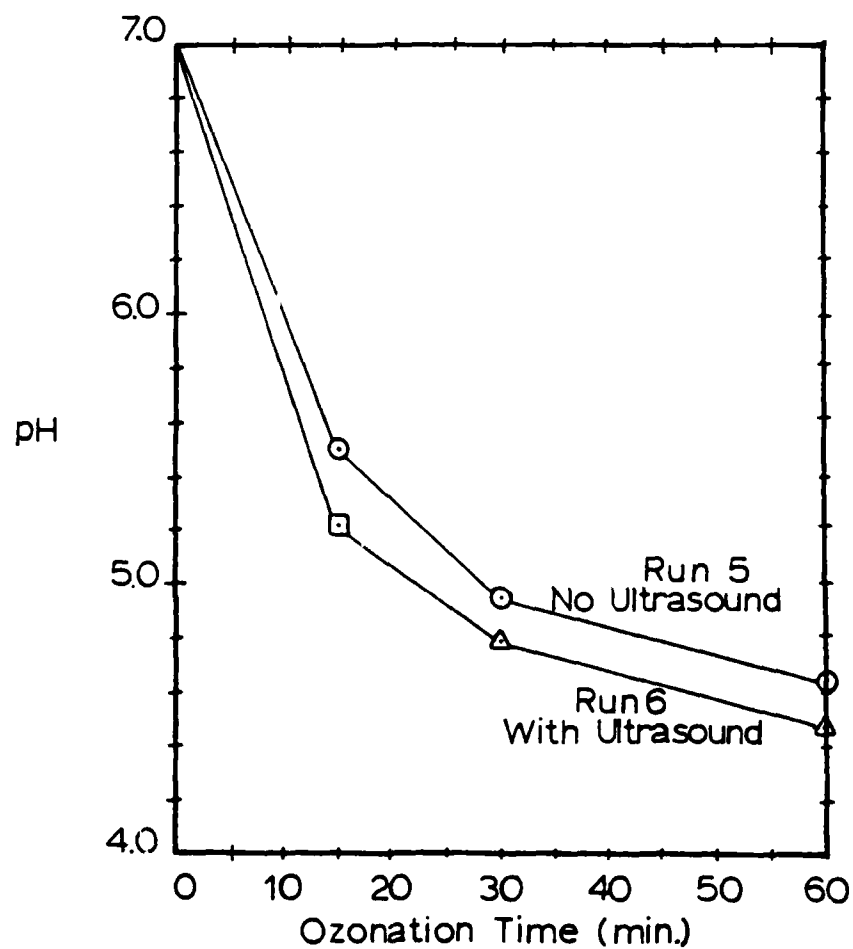


Figure C-2 pH as a Function of Ozonation Time
in the Presence and Absence of Ultra-
sound for Iowa AAP Pink Water from
Building 34-70-1

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The ratio of unfiltered to filtered untreated Sample #3 was 1.20 but after 60 minutes of ozonation, the ratios cover 1.04 and 1.12 in Runs #5 and #6. These data indicate that while the 0.45 μ filter initially plays a role in removing TNT after 60 minutes ozonation it does not appreciably affect the ratio.

The color of the batch changed from a dark red-orange to yellow within one minute of reaction; however, the batch was highly turbid. After five minutes, the turbidity was reduced substantially as was the batch color to a pale, straw yellow. The color and turbidity characteristics remained relatively constant over the remainder of the ozonation period.

During the run, the ultrasonic sound level was 100 watts PEP. This was reflected in the fact that the batch temperature increased by only 3.5°C over the one-hour reaction period.

Finally, the color of the 0.45 μ filters, after drying, decreased in intensity with reaction time for Run #5 but the converse was true in Run #6. The color of each filter in Run #5 was tan but was a darker tan for Run #6 at each corresponding sample. Again, the same pattern emerged as in previous experiments. The inclusion of sound waves affected the mechanism of oxidation by ozone.

Samples #4 and #5

Runs #7 and #8 produced treated effluent which was analyzed for pH, temperature, TOC and TNT. The results are listed in Table C-5. Table C-6 presents the data from Runs #9 and #10. Since both samples #4 and #5 came from the same source but were so obviously different, they will be discussed simultaneously.

TABLE C-5 - SAMPLE #4

Time	RUN #7					RUN #8				
	Temp (°C)	pH	TNT mg/l	TOC (mg/l)		Temp (°C)	pH	TNT mg/l	TOC (mg/l)	
				Unfiltered	Filtered				Unfiltered	Filtered
0	25.0	7.0	5.50	15.3	6.68	25.0	7.00	5.5	15.30	6.68
15	25.0	6.20	1.40		11.11	27.0	6.64	1.6		11.20
30	25.0	6.00	1.75		10.06	28.3	6.57	1.9		9.43
60	25.0	5.94	1.75	9.24	9.82	31.0	6.42	4.8	7.83	7.67

TABLE C-6 - SAMPLE #5

Time	RUN #9					RUN #10				
	Temp (°C)	pH	TNT mg/l	TOC (mg/l)		Temp (°C)	pH	TNT mg/l	TOC (mg/l)	
				Unfiltered	Filtered				Unfiltered	Filtered
0	24.6	7.00	47.6	31.03	25.75	25.0	7.00	47.6	31.03	25.75
15	25.8	5.09	36.3		27.38	27.0	4.75	37.1		25.82
30	25.8	4.75	37.9		29.05	28.0	4.41	40.5		26.65
60	26.0	4.43	37.9	29.76	29.15	31.8	4.19	40.8	26.46	26.02

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The first indication of differences between Samples #4 and #5 was the received pH values which were 8.6 and 7.95 respectively. The second major difference was in the test for TNT where Sample #4 was 5.50 mg/l while Sample #5 contained 47.6 mg/l of TNT. Finally, the initial unfiltered TOC values were 5.50 and 31.03 mg/l for Samples #4 and #5 respectively.

Examination of the 0.45 μ filters used to prepare raw and treated samples for analysis also displayed very different results. Filtration of raw Samples #4 and #5 both yielded a thick, dark cake which was chocolate brown in color and filtrates which were light yellowish (Sample #4) and yellowish brown (Sample #5). After ozonation, the filters were essentially all the same color for Run #9. The cake color was somewhat lighter than produced by the raw wastewater but in each case the filtrate was colorless. In Run #10, the 15, 30, and 60-minute sample yielded a progressively darker cake. This pattern of darker filter residue with ozonation carried out in the presence of ultrasound is once again shown. Here again all filtrates were colorless.

All five runs yielded decreases in pH with ozonation time. Final pH values for Runs #7 and #8 were 5.94 and 6.42, while in Runs #9 and #10, the decrease was higher with final attained values of 4.43 and 4.19 respectively. The differences in the pH reduction rates reflect the different component concentration.

CONCLUSIONS

1. The five wastewater samples utilized in this research are quite variable both in TNT (5.5 $\rightarrow$ 92 mg/l) and TOC (15.3 $\rightarrow$ 53.67 mg/l) content.
2. Reductions in both TOC and TNT by plain or sound catalyzed ozone did not follow a consistent pattern reflecting the wide range of ozone-degradable materials present.
3. Ozonation either in the presence or absence of ultrasound reduced pH in four of the five runs; however, in one run the pH rose with reaction time.

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