UNIVERSITY OF CALIFORNIA

Los Angeles

Treatment and Biodegradation of High Explosives

A Literature Review

A thesis submitted in partial satisfaction of the

requirements for the degree Master of Science

in Civil Engineering

by

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1994

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ABSTRACT OF THE THESIS

Treatment and Biodegradation of High Explosives:

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by

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Master of Science in Civil Engineering

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For more than 40 years of the period characterized as the Cold War, both the United States and Soviet Union built up nuclear stockpiles of tens of thousands of weapons. Now, as the Cold War has ended and tensions between the superpowers have subsided, the U.S. faces the task of significantly reducing its nuclear arsenal. Many thousands of nuclear weapons are being removed from the stockpile as a result of recent treaties and unilateral decisions.

Currently, the Department of Defense (DOD) has an inventory of 48 million kilograms of energetic materials (this includes explosives, propellants, and pyrotechnic materials), with 2.7 million kilograms added every year. Regulations that govern emissions from open burning are becoming more and more stringent, and it is expected that disposing of high explosives by open burning and open detonation will soon be prohibited.

This thesis reviews the literature on several different types of high explosives (HEs). The history and quantities of HE manufacturing, chemical properties and treatment

techniques that are currently used and considered possible in the future to replace open burning/open detonation are reviewed.

1 Introduction

The end of cold war and political changes that have occurred in Eastern Europe and the former Soviet Union have created a large surplus of munitions and chemical feed stocks that are used to produce munitions. Both conventional and nuclear weapons are surplus and need to be destroyed. The need to destroy these weapons is in addition to the need to destroy weapons for other reasons, such as obsolescence, deterioration of the chemical components and poor serviceability (Layton *et al.*, 1987). Disposing of thousands of tons of munitions from over-seas locations escalates this serious management problem. Finally, munitions destruction must be done in a secure fashion to avoid proliferation to terrorist groups and other organizations not authorized to possess weapons.

U.S. Department of Defense (DOD) enclosed ammunition storage facilities are saturated to the extent that energetic materials are now placed in open storage (Johnson and Bacon, 1993). The DOD demilitarization inventory contains 358,763,000 kg of ordnance items. The items are stored at 27 locations around the United States (Ansell, 1993). Traditionally, these materials have been disposed of by open burning/ open detonation (OB/OD). Table 1.1 shows the amount and composition of explosives expected to result from nuclear weapon dismantlement over the next ten years (Prundea *et al.*, 1993).

Soil and air contamination by OB/OD has occurred at open-burning and incinerator sites. This contamination is in addition to the contamination that has resulted for operational spills and seepage from landfills and wastewater holding facilities. Contaminant concentrations can be extremely high in wastewater lagoon sediments (Rosenblatt, 1991).

The U.S. Army operates munitions manufacturing facilities that load, assemble, and pack (LAP) explosives into military ordnance. Activities at these facilities can produce

wastewaters that contain both high explosive residue and other organic chemicals (Wujcik *et al.*, 1992).

A single trinitrotoluene (TNT) manufacturing plant can produce as much as 2,000,000 liters of wastewater per day. In shell loading plants, larger wastewater volumes can be produced from washing of residual explosives. Reducing water usage and controlling contaminants is difficult because of safety concerns. Many traditional water conservation and contaminant control techniques are not possible, due to concerns of accidental detonations. This type of wastewaters usually contain low concentration of high explosives (e.g.: 100 mg/L of TNT, 1-20 mg/L of RDX, and 1-20 mg/L of HMX).

Research is currently being conducted and sponsored by DOD and U.S. Department of Energy (DOE) at their national laboratories and through private companies and universities. Research has been underway in the UCLA Civil and Environmental Engineering Department for over 3 years to develop biological treatment processes for HE contaminated wastewaters: Ro and Stenstrom (1991), Hesselmann (1991), Wilkie *et al.* (1994). More recently, research on aqueous alkaline hydrolysis has begun (Heilmann *et al.*, 1994a, b).

This thesis reviews the literature on the several types of high explosives. The history and quantities of high explosives manufacturing, their chemical properties and treatment techniques are reviewed.

1.1 Classifications and General Characteristics of Explosives

An explosive is any substance or device which upon release of its potential energy will produce a sudden outburst of gas, thereby exerting high pressures on its surroundings

Table 1.1 Amount and composition of explosives expected to results from nuclear weapon dismantlement over the next ten years (Prundea *et al.*, 1993).

Explosive	Amount (kg)	Composition, wt%
Composition B-3	110	60% RDX[a] / 40% TNT[b]
Cyclotol 75/25	1,030	75% RDX[a] / 25% TNT[b]
LX-04-01	45,095	85% HMX[c] / 15% Viton A[d]
LX-07-02	753	90% HMX[c] / 10% Viton A[d]
LX-10-02	14,305	94.7% HMX[c] / 5.3% Viton A[d]
LX-11	23	80% HMX[c] / 20% Viton A[d]
LX-17	642	92.5% TATB[e] / 7.5% Kel-F 800[f]
PBX-9011	9,504	90% HMX[c] / 10% Estane[g]
PBX-9404	75,465	94% HMX[c] / 3% NC[h] / 3% CEF[i]
PBX-9501	4,917	95% HMX[c]/2.5% Estane[g]/ 2.5% BDNPA-F[j]
PBX-9502	18,365	95% TATB[e] / 5% Kel-F 800[f]
TOTAL	170,209	

a RDX (explosive): 1,3,5-trinitro-1,3,4-triazacyclohexane.
b TNT (explosive): 2,4,6-trinitrotoluene.
c HMX (explosive): 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane.
d Viton A (plastic binder): vinylidine fluoride / hexafluoropropylene copolymer (DuPont).
e TATB (explosive); 1,3,5-triamino-2,4,6-trinitrobenzene.
f Kel-F 800 (plastic binder): chlorotrifluoroethylene/vinylidine fluoride copolymer 3:1 (3M).
g Estane (plastic binder): polyurethane (B.F. Goodrich)
h NC (energetic binder): nitrocellulose.
i CEF (binder plasticizer); tris-ß-chloroethyl phosphate.
j BDNPA-F (energetic liquid plasticizer): bis (2,2-dinitropropyl)acetal/bis(2,2-dinitropropyl) formal (50/50 wt%).

(Cook, 1985). There are three fundamental types of the modern military and commercial explosives: mechanical, chemical, and atomic.

This thesis is restricted to chemical explosives of which there are two types: (1) detonating or "high" explosives, characterized by very high rates of reaction and high pressure, and (2) deflagrating or " low " explosives, which burn more slowly and develop much lower pressures. The main features of these two types of chemical explosives are compared in Table 1.2. Detonating explosives are usually sub-divided into (a) primary, and (b) secondary explosives. The primary high explosives nearly always detonate by simple ignition by such as a spark, flame, impact, or other primary heat sources of appropriate magnitude. The secondary explosives require, at least in practical application, the use of a detonator and frequently a booster. A detonator contains a primary explosive as an essential element but it may be more complex. This is true particularly of military detonators, or fuses and delay blasting caps in which timing, safety, and other concerns are incorporated into the design. A booster is a sensitive secondary high explosive which reinforces the detonation wave from the primary explosive, or detonator, thereby delivering a more powerful detonation wave to the secondary explosive charge (Cook, 1958).

Detonation is a process by which the explosive undergoes chemical reaction within a peculiar type of shock wave called the detonation wave. This detonation wave propagates through the explosive, supported and reinforced by the chemical reaction at velocities from about 1600 to 6400 m/sec, depending on the chemical and physical nature of the explosive. In general, except in the early stage of some types of detonation, the detonation wave travels through a column of explosive at a constant speed, a fact which greatly simplifies the mathematical solution of the "hydrodynamic theory", which applies to this complicated process.

Table 1.2 Characteristics of high and low explosives (Cook, 1958).

	High	Low
Method of initiation	Primary by ignition and secondary by detonator	By ignition
Time to complete conversion of explosive to gaseous products	Microseconds	Milliseconds
Velocity of combustion of explosive grains	1,600 to 6,400 m/sec	A few centimeters to 30 cm per sec
Velocity of flame front	1,600 to 6,400 m/sec	540 to 1,600 m/sec
Pressure of explosion	3,400 to 270,000 atm	Up to about 3,400 atm
Rock breakage in borehole blasting	2,000 to 60,000 kgs/kg	2,000 to 60,000 kgs/kg
Exploded in gun	Shatters gun	Good propellant
Demolition	Excellent to poor	Not applicable
Uses	Demolition, blasting	Propellant, blasting

The initiation of detonation in a primary explosive is always preceded, for at least a small fraction of a second, by an explosive combustion or deflagration. Fig.1.1. illustrates the development of a detonation in a primary explosive initiated by a spark, flame, or hot wire. The reaction starts as a slow combustion but quickly builds up through the stage of explosive deflagration, and finally undergoes a sudden transition to the detonation. The detonation is proceeded, particularly in gaseous explosives, by pulsating reactions and shock interactions. Irrespective of the transition period, however, the chain of events is apparently always the same in all detonation processes. Usually, but not invariably, when a secondary explosive is detonated without a detonator, the rate of built up of the explosive

reaction and the transfer to detonation is much slower. For example, ship loads of ammonium nitrate at Texas City (Texas), Brest (France), and the Black Sea burned for several hours before exploding. This indicates that probably all secondary explosives in sufficiently large quantities can eventually detonate following ignition (Cook, 1958).

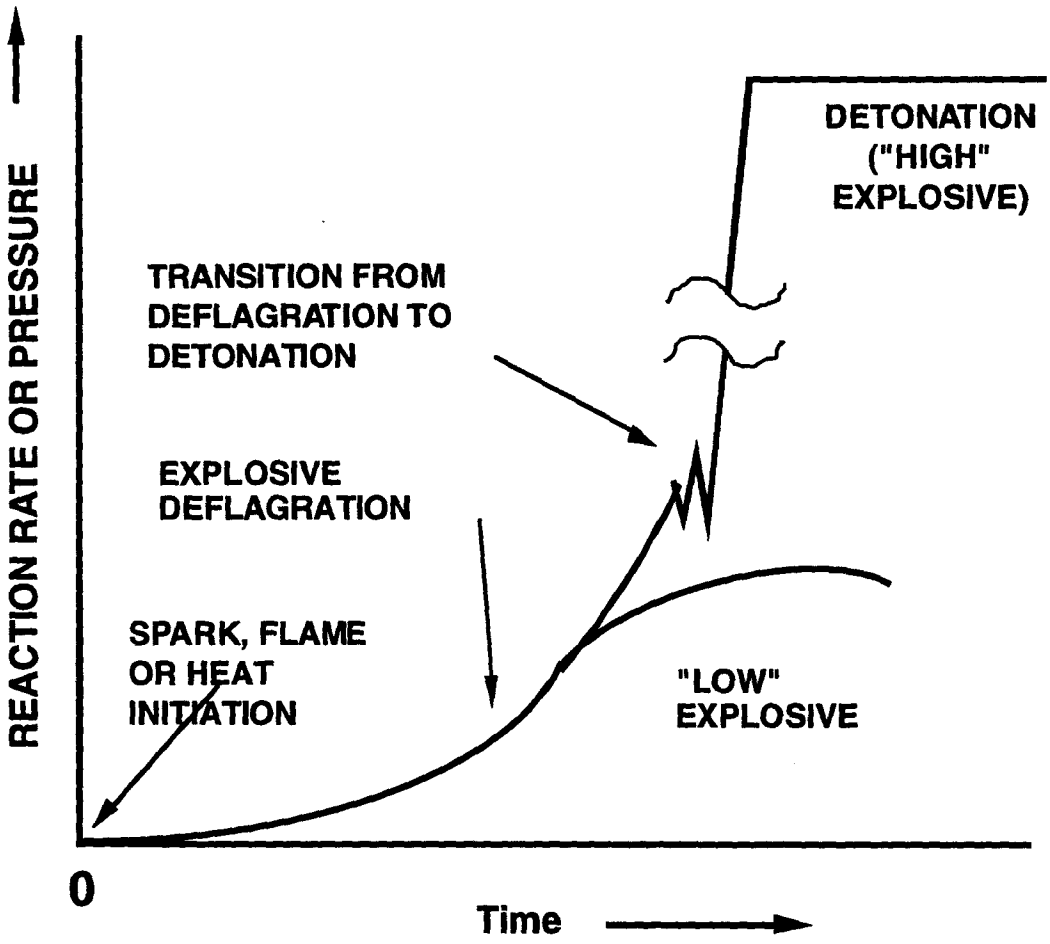


Figure 1.1 Explosive deflagation versus detonation and transition from deflagation to detonation (Cook, 1958).

The chief difference between low explosives and primary detonating explosives, is that they usually do not under go the transition from deflagration to detonation under normal application. Normally, low explosives react chemically at a rate which increases as

the pressure increases; conversely, the pressure increases as the chemical reaction increases. A feedback loop is created which quickly leads to explosion, usually within a fraction of a second. The rate of reaction in low explosives is seldom greater than a few tenths of 1 per cent of that in detonating explosives. Furthermore, the peak pressures attained are seldom higher than a few per cent of that existing in a detonation. Even the low explosives react or burn rapidly enough, however, so that their energy may be fully utilized when they are adequately confined or when exploded in large quantities. Hence the blasting potential of low explosives may be comparable to that of high explosives of the same chemical-reaction potential. This also applies to the destructive potential of low explosives in the accidental explosion of large quantities; in fact, as far as the destructive potential of accidental explosions is concerned, it often makes little difference whether the explosive involved is low or a high explosive (Cook, 1958).

In many specific applications the pressure generated by the explosive is a matter of great technical importance. For instance, in launching shells and projectiles from guns, one requires a carefully controlled rate-of-pressure development which is high enough to impart the required velocity to the projectile but low enough that to avoid shattering the gun. Only low explosives have these requirements, and propellants are therefore restricted to the low or deflagrating explosives.

1.2 Common Explosives and Ingredients Used in U.S. Explosives Industry

Between the needs for very low-pressure explosives such as propellants and the high-pressure military explosives, there exists an almost continuous distribution of conditions requiring explosives of all sorts of pressure and rate characteristics. Hence a great variety have been designed and used in various fields. Fortunately it has been

possible to attain the necessary blasting characteristics for the many varied needs for explosives by means of different combinations of ingredients and physical conditions (density, granulation) using relatively few explosive and chemical ingredients, Table 1.3. lists most of the more important chemicals used in the American commercial and military explosives (Cook, 1958).

Since 1958 many improvements have been achieved in common explosives used by U.S. explosive industries. For example fertilizer grade ammonium nitrate has been mixed with fuel oil to formulate a safe non- nitroglycerin alternative to dynamite. This ammonium nitrate-fuel oil mixture (ANFO) is easy to manufacture at low cost. It is very hydroscopic and is used only in large diameter boreholes because it will not sustain a detonation in small diameter holes.

These limitations of ANFO led to the development of explosives with better water resistance and excellent performance. These aqueous based ammonium nitrate explosives include slurries and water-in-oil emulsions. Greater water resistance and sensitivity of slurries and emulsions is provided by the intimacy between fuel and oxidizer (Henderson and Sarri-Norhaus, 1992).

A significant amount of work on new high energy materials is conducted at defense companies in U.S.. Ammonium dinitramide (ADN) is high on the list of promising new energetic materials for a variety of space and military applications. It can act as an explosive or can serve a dual role as an oxidizer and fuel. A second promising dinitramide salt formulation is KDN-AN, a cocrystalized form of potassium dinitramide (KDN) and ammonium nitrate (AN).

Another new energetic material has the imposing chemical name hexanitro-hexaazaisowurtzitane, but is better known as CL-20. CL-20 is a very high-energy crystalline compound whose method of synthesis and detailed performance data are still classified.

Table 1.3. Common explosives and ingredients used in U.S. explosives industry (Cook, 1958).

Military		Commercial
	Primary High Explosives	
Mercury fulminate		Mercury fulminate
Lead azide		Lead azide
Diazodinitrophenol		Diazodinitrophenol
Lead styphnate		Lead styphnate
Nitromannite		Nitromannite
	Secondary High Explosive	
TNT (trinitrotoluene)		NG (nitroglycerin)
Tetryl (trinitrophenyl-methynitramine)		AN (ammonium nitrate)
RDX (cyclotrimethyl-enetrinitramine)		TNT
PETN (pentaerythritol tetranitrate)		DNT
Ammonium picrate		Nitrostarch
Picric acid		PETN
Ammonium nitrate		Tetryl
DNT (dinitrotoluene)		
EDNA (ethylendi-aminedinitrate)		
	Low Explosives	
Smokeless powder, ni-trocotton		Smokeless powder
NG (nitroglycerin)		Nitrocotton
Black powder (potassium nitrate, sulfur, charcoal)		NG (nitroglycerin)
DNT(dinitrotoluene ingredient)		Black powder (potassium nitrate, sulfur, charcoal)
	Nonexplosive Ingredients	
Aluminum		Metal nitrates
Waxes		Metals (aluminum, ferrosilicon)
Diphenylamine		Wood pulps, meals, other combustibles
Metal nitrates		Paraffin, other hydro-carbons
Mononitroluene		Chalk, diphenylamine, wax, sulfur, carbon

Another high energy material of interest to the military is the explosive 1,3,3-trinitroazetidine (TNAZ). TNAZ is more powerful than the two widely used explosives of British origin, HMX and RDX. An advantage of TNAZ over HMX and RDX, in addition to its higher energy content, is that it is melt-castable, which is a real valuable property. The major problem with TNAZ is that it is very expensive (Borman, 1994).

Although much explosives are being developed, materials like HMX and RDX should continue to be mainstay explosives in Army munitions for some time (Borman, 1994).

1.3 Magnitude of Commercial and Military Explosives Industries

Commercial Use: The oldest commercially successful of explosive is black powder, an intimate blend of potassium nitrate, charcoal, and sulfur. All three ingredients were reasonably available, even in the ancient world. Black powder was first used in mining in the early years of the 17th century. It took a century or so to develop effective techniques for explosive-assisted mining. This development was also delayed by limitations in the supply of potassium nitrate.

During the development of the black powder explosive industry, synthetic chemistry came of age. In 1846, an Italian chemist reacted strong nitric acid with glycerol, a byproduct of soap manufacturing. The oily product was glyceryl trinitro, a new explosive which had greater energy and high sensitivity, but, limited practical application due to the extreme hazards associated with its synthesis and use. Practical use of nitroglycerin (NG) is documented after 1859, and it quickly acquired an appalling safety record.

In 1876 scientists observed that diatomaceous earth (kieselghur) was able to absorb up to three times its own weight of NG to form a relatively dry, leak resistance paste. This paste proved to be a powerful explosive, and it was called "Dynamite".

Dynamites became, and for some 70 years remained, the world's workhorse explosives. Ammonium nitrate (AN) was widely used as a supplemental oxidant in dynamites since the 1870's. It was also demonstrated that blends of AN and carbonaceous materials were powerful explosives in their own right. Further studies led to the institution of safe practices in handling AN and, unexpectedly, to the development of whole new families of industrial explosives. Ironically, these economical and powerful explosives, which have now replaced dynamites in most applications, are distinguished by their exceptional safety. Ammonium nitrate, one of the simplest, least costly, and most readily available of all synthetic chemicals has become the active ingredient in the bulk of the world's industrial explosives. Table 1.4 illustrates the history of use in the US of the three workhorse industrial explosives: black powder, dynamite, and ammonium nitrate. World trends are similar (Meyers and Shanley, 1990).

Table 1.4. US explosives consumption in kilotons (Meyers and Shanley, 1990).

Year	Black powder	Nitroglycerin dynamites	Ammonium-nitrate based explosives
1800	0.2	-	-
1850	9.1	-	-
1900	100.0	100.0	-
1925	115.0	200.0	-
1950	10.0	310.0	10.0
1975	0.1	120.0	1300.0
1985	0.1	80.0	1700.0

In the U.S. coal mining typically accounts for about 65% to 68% of commercial explosives demand, quarrying and nonmetal mining, 13% to 15%, metal mining, 10%; construction, 7%, and miscellaneous use, 2% to 4% (U.S. Department of Interior, 1993). In their 1993 industrial survey, the U.S. Department of Interior, Bureau of Mines, reported that U.S. apparent consumption of domestic and imported industrial explosives materials increased by a moderate 2.3% based on producer sales totaling 2.1 billion kilograms. Explosives sales were recorded in 49 states in 1992. Fifteen states accounted for more than 80% of U.S. industrial explosives demand in 1992; 13 of these 15 states produced 85% of U.S. Nation's coal. Hopler (1993) noted that the explosives research and development has historically been motivated by coal mining. Whether to solve safety problems or to improve productivity and cost, the result has been the same: better explosive products and initiation systems.

Ammonium nitrate-based explosives sales increased 3.1 % to 2.05 billion kilograms and accounted for about 98% of U.S. apparent domestic consumption of industrial explosives. Domestic production of industrial grade ammonium nitrate increased by 5% to 2.0 billion kilograms in 1992, according to U.S. Bureau of the Census.

Military Use: Between January 1940, and V-J (victory over Japan in World War II) Day, the United States manufactured roughly 30 million tons of military explosives and ammunition, reaching an outstanding peak monthly production of 700,000 tons in July, 1945. This was approximately 35 times greater than the normal commercial production of explosives in the United States. While facilities for the manufacture of military explosives in the United States were only sufficient in 1939 to supply an army of less than 100,000 soldiers, by March, 1944, 73 new plants has been built, covering a total acreage larger than the combined areas of New York City, Chicago, Philadelphia, and Detroit. The investment cost of this tremendous capacity for explosives production was about 3 billion dollars.

Moreover, the cost of the ammunition program for the last year of the war reached a total of 5 billion dollars.

A comparison of the military and commercial explosives production in the United States since 1912 to 1948 is given in Fig.1.2. it is of interest that commercial production fluctuated between 1912 and 1950 between the relatively narrow limits of 125 and 375 million kilograms annually (Adams *et al.* 1943; U.S. Bureau of Mines and Mineral Market Reports, 1950). This peculiar stability, which parallels the population of the US, as opposed to its industrial trends since 1912, may seem very surprising in view of the extremely important position of explosives during this period of tremendously scientific and industrial expansion. The explanation may be that advances in explosives technology made their use more effective and efficient, which allowed slower growth in explosives manufacturing (Cook, 1958).

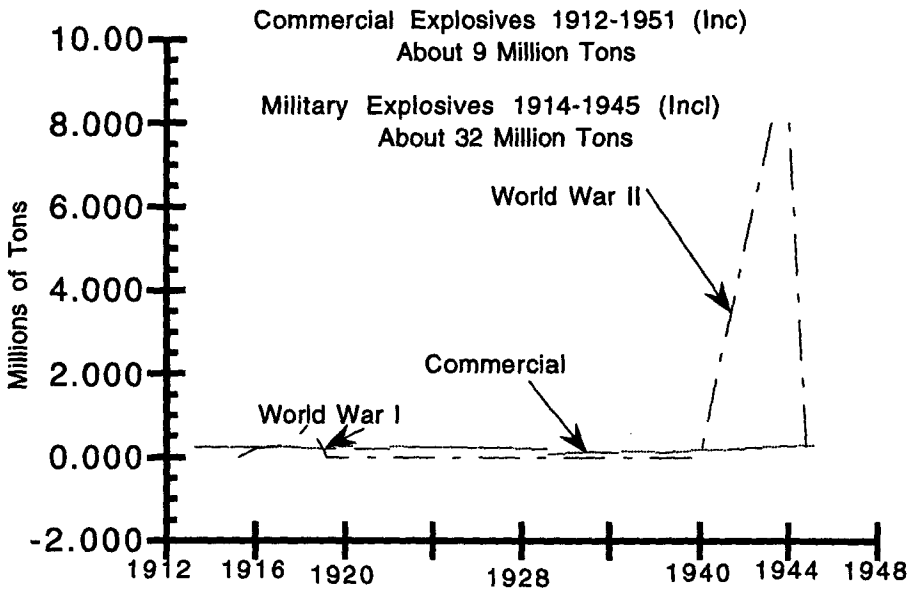


Fig.1.2. Explosives production in America, 1912 to 1950 (Cook, 1958).

The U.S. military munitions industry is government owned. The U.S. Army owns seventeen "Army Ammunition Plants (AAPs)" engaged in explosives and/or propellants activities. Seven AAPs are involved in manufacture. One AAP is on stand-by status. Eight AAPs are involved only in "Load, Assemble and Pack (LAP)" activities, which include the mixing, blending, and loading of explosives or propellants into munitions. Two AAPs, are engage both in manufacturing and LAP. For reason of safety most AAPs are located far from population centers (Patterson *et al.* 1976).

2 TNT Properties, Importance, Toxicity and Environmental Fate

Trinitrotoluene, most commonly refereed to as TNT, historically the most important and most widely used military high (or "secondary") explosive, has not been produced in the U.S. for several years (Rosenblatt, 1991). In the 1902 TNT began to find important applications in German military, and it was soon adapted by other countries (Yinon, 1990). TNT was manufactured during World War II, the Korean War, and the Vietnam War, millions of tons of TNT were produced and used mainly as an ingredient in binary explosives (Spalding and Fulton, 1988). Averaged over 1969 - 1971, approximately. $20x10^7$ Kg per month were produced in the United States (Patterson *et al.* 1976).

TNT wastewater consists of nitrobodies which are toxic, explosive, and frequently highly colored. There are several kinds of wastewaters generated during the manufacturing of TNT. "Red water" is the wastewater formed during the sellite purification of TNT, and "pink water" is the waste formed when partially purified TNT is finally water washed following the sellite purification step (Walsh *et al.* 1973). Until a solution for effective red water treatment is found, all U.S. TNT plants are closed in a standby mode, and no TNT can be produced (Tsai, 1991). TNT is currently manufactured in Canada and exported to the U.S. It is an important constituent, along with RDX, of formulations of the high explosive known as composition B. It is also the high explosive that is present in the largest quantity in the demilitarization inventory (Layton *et al.* 1986).

The structure, and physical properties of TNT are shown in Fig.2.1. In addition, to the problem associated with disposal of pink and red water, this explosive has the greatest number of co- contaminants of potential concern. Pruneda *et al.* (1993) reported that TNT and RDX, are less expensive than HMX (between $4/kg and $6/kg).

Empirical formula: $C_7H_5N_3O_6$
Molecular weight: 227.15
Melting point (°C): 80.75
CAS Reg. No.: 118-96-7
(more data in Rosenblatt, 1991)

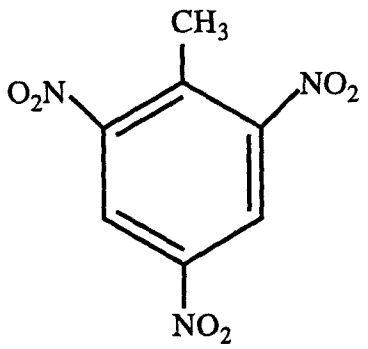


Fig. 2.1 Structure and properties of TNT.

Toxicity: TNT toxicity to humans, including liver damage and anemia, has been reported (Bridge *et al.* 1942; Hamilton, 1921). It can cause headache, weakness, and may be absorbed through skin (The Merck Index, 11th Edition). Concentrations above 2 μg/mL are toxic to some fish (Navy and Water Poll, 1974; Osmon and Klausmeier, 1972) and toxicity to rats, mice, unicellular green algae, cope pods, and oysters have been reported (Kamley *et al.*, 1989). TNT inhibits the growth of many fungi, yeasts, actinomycetes, and gram-positive bacteria and exhibits mutagenicity in the Ames screening test (Kaplan and Kaplan, 1982; Ames *et al.*, 1975). Aquatic organism and mammalian toxicities of TNT in water are 60 and 44 mg/L. Effluent guidelines of 10 mg/L for TNT have been proposed by the U.S. Army Medical Bioengineering R&D Laboratory to the Surgeon General (Freeman and Colitti, 1982). Furthermore, it is known that TNT may be aerobically degraded to 1,3,5-TNB, 2-4-DNT and 2,6-DNT (Spalding and Fulton, 1988). The last two are potential carcinogens and have RMCLS of 1 mg/L or less (U.S. EPA, 1980), and may be the most dangerous of the munitions residues from a health standpoint.

Environmental Fate: 2,4,6-trinitrotoluene (TNT) is the primary explosive compound employed by the military. The manufacturing, loading and packing processes of TNT involve significant quantities of water. This TNT Containing wastewater has contaminated groundwater, soil and sediment at numerous federal facilities (Fernando et al. 1990). It is beyond doubt that discharge of untreated TNT wastewaters into streams and rivers constitutes a serious pollution hazard (Yinon, 1990). In general, TNT wastewater discharge affects receiving water quality in the following ways: increased the chemical oxygen demand (COD), increased dissolved and suspended solids (TDS, TSS); increased nitrogen (nitrates, nitrites, and total Kjeldahl nitrogen), and increased sulfate (Ryon *et al.*, 1987).

To gain insight into the potential behavior of TNT in the environment media, Layton *et al.* (1987) estimated fractional distributions of TNT among eight compartments, consisting of the atmosphere, air particles, biota, upper soil, lower soil, groundwater, surface water, and sediments. They based their analysis on a steady state input of TNT to the upper (surface) soil layer. They predicted that most of the TNT should reside in the subsurface environments (i.e., soil and groundwater). They also concluded that preferential movement of TNT toward the subsurface compartments indicates that the most important transformation process should be those that can be sustained in subsurface environment (e.g., biotransformation rather than photolysis).

Hale *et al.* (1979) studied downward movement of TNT and its transformation through intact soil columns, for 6 months. Very little detectable movement of TNT or its known transformation products were observed in this time frame. They also calculated the water solubility of TNT (85.8 $\pm$ 0.9 mg/L at 21°C). Spanngord *et al.* (1983) measured solubility values for TNT at 10°, 20°, and 30°C at 67, 104, 165 mg/L. TNT has low vapor pressure as indicated by a vapor pressure of only 3.7×10^{-6} to 8.02×10^{-6} atm. (25°C) and a Henry's law constant of 1.1×10^{-8} atm m^3/mole (25°C) (Rosenblatt, 1991).

The persistence of TNT in environment is very limited. Both physical and biological degradation processes affect the residence time of TNT in environment (Ryon *et al.*, 1987). TNT has a high sorptivity on sand $Kd_{(Sand)}$: 53 ± 20 (Spanggord *et al.*, 1980). K_d is the actual partition coefficient, K_d, of a chemical between soil and water is based on the assumption that the soil's organic content is the only determinant of the sorption of a compound from water to soil . K_{oc} is the soil organic carbon/ water partition coefficient, and is defined as: µg adsorbed chemical per g organic carbon/µg chemical per mL of solution, thus, $K_d = f_{oc} \times K_{oc}$, where f_{oc} is the fraction of organic carbon in the soil. A number of equations have been developed to derive log K_{oc} from other environmentally relevant partition coefficients. TNT also has a high sorptivity to soil organic carbon (log K_{oc}: 2.72, Rosenblatt, 1991). TNT is about 25 times more retarded by sorption on sand than RDX (Splading and Fulton, 1988). Trucker *et al.* calculated the K_{oc} (soil organic carbon (S_{oc})/ water partition coefficient) for TNT to be 534 and experimental measured K_{oc} values ranging from 910 to 2500, with a mean of 1600 (Spanggord *et al.*, 1980b). The discrepancy between their values could be due to differences in soil characteristics, such as cation-ion-exchange capacity (CEC) and the pH of soils tested (Layton *et al.*, 1987). Data on movement and uptake of TNT in environmental media, and its potential exposure pathways to humans via plants, crops, fish, etc. are unfortunately very limited (Layton *et al.*, 1987).

2.1 Physico-chemical Treatment of TNT Wastes

Adsorption: Activated carbon treatment is effective, although large quantities of carbon are required, and there are no proven methods to regenerate the carbon (Patterson, 1976; Andern, 1975). Burrows (1984) determined the Freundlich isotherm constants K and n as

0.3370 L/mg and 5.429, respectively for Filtrasorb 300 (Calgon Carbon Co.) The treatment of mixed high explosives wastewater is problematic; removal of each additional munition species is substantially less efficient, since adsorption is competitive. TNT readily displaces the nitramines and itself desorbed to at lesser extent than RDX and HMX (Burrows, 1984; Hesselmann, 1992). Although Subette *et al.* (1992) reported 99.5% removal for TNT using carbon adsorption following particulate removal by multilayer filtration, the method suffers from serious deficiency of the inability to regenerate the carbon. Current practice is to dispose of spent carbon by incineration after a single use (Sublette *et al.*, 1992). This lack of regenerative capacity results in three disadvantages for carbon system: (a) the economics of carbon use are much higher than for other industrial wastewater carbon systems: (b) there is no potential to recover and reuse the TNT captured by the carbon: and (c) the incineration of the carbon is a potential source of air pollution (Patterson *et al.*, 1976), and may be not be permissible in the future.

Conventional thermal carbon regeneration is not applied due to the safety problems when the explosive in the carbon exceeds 8% weight fraction (Walsh, 1973; Andern, 1975). A recent study (Ping, 1991) suggested a new way of regenerating TNT-laden activated carbon he reported that 80% TNT can be desorbed from saturated carbon in 30 min. at a temperature of 900°F when adsorptive capacity reaches 0.217g/g. His process consists of two parts: a thermal regeneration process and the suggesting facility. The thermal process, this technology is characterized by 4-step treatment, i.e., the activated carbon saturated with explosive substance undergoes drying, thermal decomposing, activating and cooling. Corresponding measures were taken to insure the safety operation. Ping claims that thermal regeneration is feasible, but the safety problems of thermal decomposition need further study and verification . Ping (1991) does not present his data.

A direct alternative to activated carbon adsorption is synthetic polymeric adsorbents. Polymeric resins, although processing a lower adsorption capacity than activated carbon,

have the potential advantages of easy regeneration and a long life cycle. One disadvantage is the leakage of color compounds through the polymeric resin adsorption column (Patterson *et al.*, 1976). For complete color removal activated carbon is required (Andern *et al.*, 1975). Also, Andern *et al.* (1975) noted that polymeric adsorbents have a greater affinity for aromatic nitrobodies, such as TNT, than for non-aromatic nitrobodies, and solvent regeneration with acetone was demonstrated.

Several researcher have tried to find physicochemical treatment alternatives for TNT. Although none of these alternatives are widely used today, they are briefly reviewed in the following sections, with an emphasis on wastewater with low to medium concentrations.

UV-Radiation: Exposure to sunlight or any source of UV light produces fairly rapid breakdown of the TNT and its associated compounds, including many impurities and degradation products (Ryon *et al.*, 1987). U.S. Pat.No. 4,038,116 to Andrews et al. discloses a method for treating an aqueous solution of aromatic explosives whereby explosive molecules, such as TNT, are destroyed, and the resulting effluent is safe for disposal. Hydrogen peroxide is added to an aqueous solution of an aromatic explosive, and this mixture is exposed to ultraviolet light. The light exposure of the hydrogen peroxide provides a free radical such which strips hydrogen molecules from the aromatic explosive to produce unstable intermediate compound. Continued exposure of the unstable intermediate to ultraviolet light converts it to carbon dioxide and ammonia. While satisfactory for its intended purpose, that of disposing of aromatic explosives such as TNT, the invention of U.S.Pat.No. 4,038,116 is not very efficient for large scale treatment of contaminated waste disposal sites, can require a considerable expenditure of funds to obtain the required materials and equipment, and has obvious limitations, such as treating soil contaminated with TNT (U.S. Pat. No.5,085,998, 1990, and Burrows *et al.*, 1984).

Rapid decomposition of TNT with UV radiation was also reported by Ruth and Boyce (1978) .

Burrows and Koylinski (1984) found decomposition of TNT with ozone alone to be very slow, but in combination with ultraviolet radiation at 254 nm and ozone, TNT was destroyed with complete ring destruction (first half-life time: 8.9 min.). The treatment procedure incorporating ozone was more efficient than H_2O_2 in reducing the total organic carbon levels (Ruth and Murphy, 1978). The UV-H_2O_2 process is more efficient in treating water solutions of 2,4-dinitrotoluene, 2,6-dinitrotoluene and explosive D than TNT wastes (Anderns, 1980).

Oxidative Treatment: Ozone and hydrogen peroxide slightly degraded TNT (Burrows *et al.*, 1984; Semmens, 1984). Iron catalyzed hydrogen peroxide (Fenton Reagent) was not successful (Semmens *et al.*, 1984). Semmens' research (1984) on chlorination of TNT was encouraging. Two sources of chlorine were tested : 1) Liquid sodium hypochlorite (NaOCl); and 2) Chlorinated Lime $Ca(OCl)_2$. His results indicated that initial oxidation of TNT was very rapid, and calcium hypochlorite was more effective than sodium hypochlorite. Unfortunately he made no effort to identify the end products.

Reverse Osmosis: Sullivan *et al.* (1979) reports that Jackson *et al.* (1976) evaluated reverse osmosis for TNT treatment. He reports "break through" after 24 hours, which implies that reverse osmosis is not effective in treating TNT wastewaters. The information about reverse osmosis are mixed. Bhattacharyya *et al.* (1976) considered reverse osmosis feasible for removing nitrobodies from TNT manufacturing wastes (pink water). They used both actual and synthetic pink water. Among the four membranes that were investigated, Millipore PSAL was the optimum membrane both in terms of superior organics rejection and high water flux. TNT was the main constituent of the waste and the

rejection was a strong function of pH, at the optimum pH of 11.0, an average rejection of 88% was obtained with the PSAL membrane. A gel polarization limited condition was observed at a channel velocity less than 100 cm/sec.

Chemical Hydrolysis: TNT reacts with water at high pH, and especially at elevated temperatures (Aye, 1980). Hydrolysis of TNT was observed at a pH of approximately 8, after 108 days in sea water (Hoffsommer and Rosen, 1973). Based upon these results, we do not expect hydrolysis to be significant degradation mechanism in natural waters (Layton *et al.*, 1987). Spontarelli *et al.* (1993) reported TNT hydrolysis at high pH and elevated temperature gives a very dark, water soluble product that have not yet identified.

Two types of surfactants have demonstrated effectiveness in precipitating TNT from solution at elevated pH. The first has a primary amine while the second has a quaternary amine (Freeman, 1985). The precipitation of TNT from solution is the result of reaction between TNT and the surfactant in an alkaline medium to form an intermediate substance (identified as the Jonovsky Complex; Okamoto, 1977 and Okamoto, 1978). This intermediate, reacts with the protonated surfactant and precipitates as a salt. Increasing the reaction temperature (50°C) produced very high overall removal, and allowed the use of lower pHs 11.5 to 11, as compared to pH 12 at 25°C (Freeman, 1985). The surfactant is expensive, which suggests that optimization with the molar ratio of surfactant/TNT, temperature and pH is required to insure commercial success.

2.2 Biological Degradation of TNT

Biological approaches, if appropriate, usually offer the most advantageous cost benefits and effectiveness in reducing contaminated wastewater (Kaplan, 1989). However,

the effectiveness of this treatment depends heavily on the adaptability and survival of the microorganisms capable of degrading the target compound (Tsai, 1991). The biodegradation pathways often require co-metabolites and follow reductive, oxidative or hydrolytic sequences. In the case of TNT, as shown in Fig. 2.2, the reductive pathway leads to the accumulation of amino derivatives and polymerized or conjugated products, and has not provided significant evidence of mineralization (Kaplan, 1992).

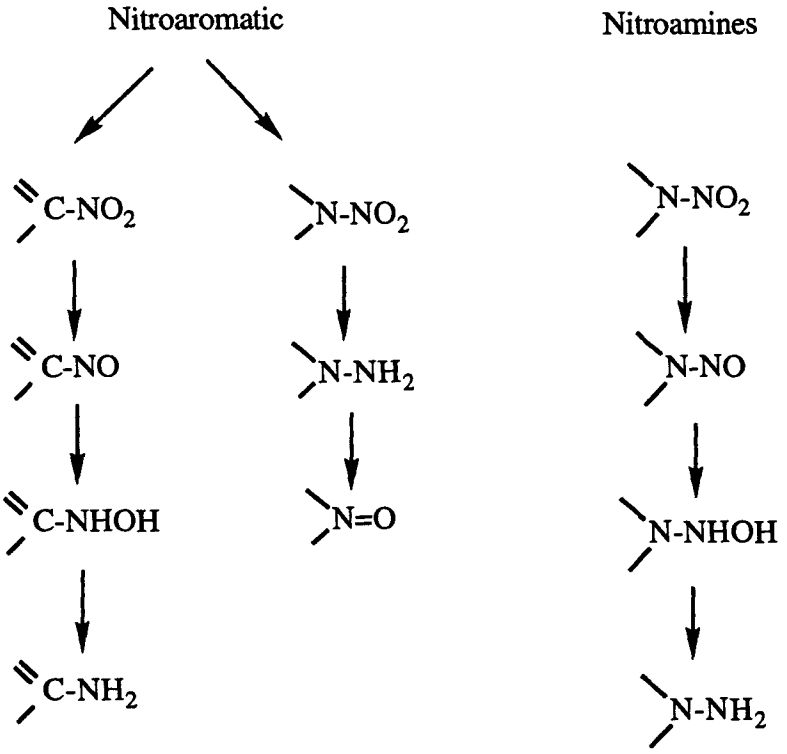


Fig. 2.2 Biodegradation of nitroaromatics, and nitramines by reduction, oxidation (Kaplan, 1992).

Many bacteria, yeasts, and fungi reduce the nitro groups in TNT to amines or azoxy dimers. The degree of reduction varies with the types of organisms and environmental

conditions. With appropriate conditions, all nitro groups, can be converted, but reduction stops without mineralization of aromatic ring (Fig. 2.3, Layton *et. al.*, 1987).

Microorganisms and Fungi: Microbes that have or can develop the ability to biotransform TNT are common (Leyton *et al.*, 1987). Osmon and Klausmeier (1972) found that many soils and water samples had microorganisms with TNT biotransforming ability. The percentage of the microflora capable of growth on TNT- containing medium was significantly greater for soil near a loading facility than soil in a remote area (36 vs. 14%), which suggest that microorganisms can acclimate to TNT. Klausmeier *et al.* (1973) also studied the effect of TNT on 24 fungi, representing 9 genera, in medium containing glucose. Parrish (1977) studied 190 fungi to determine their ability to transform TNT in culture with 0.5% glucose at 29°C. Of the 190 organisms, 183 were able to transform TNT under the test conditions.

Nutrients: Many researchers have studied microbial degradation of TNT in the presence of added nutrients and/or concentrated microbial populations. Nutrients increase the rates of the reactions and in some cases, enable recalcitrant reactions (i.e., mineralization) to proceed (Layton *et al.*, 1987). Osmon and Klausmeier (1972) reported that degradation was more rapid, with greater mass conversion when other organic nutrients were added to medium. Yeast extract added to basal mineral-salts medium enabled a variety of microorganisms to transform TNT in an aerobic environment. Osmon and Klausmeier (1972) tested microorganisms collected from sewage effluent, a TNT loading facility, soil suspension, pond water, and aquarium water for their ability to biodegrade 100 mg/L TNT in a mineral-salts medium, supplemented with 1% yeast extract. In all cases biotransformation was complete within 6 days. When the TNT reducing organisms were

Figure 2.3

isolated, the majority were " Pseudomonas-like". Likewise, Kayser *et al.* (1977) found that organisms in local sewage and "a psudomonas strain isolated from TNT contaminated stream at NAD, McAlester" were equivalent in their ability to reduce TNT in aqueous solution when supplemented with corn-steep nutrients. Won *et al.* (1974) studied the influence of the yeast extract and glucose on the biotransformation of TNT, and on adapted pseudomonas organism . TNT disappeared most rapidly in cultures supplemented with 0.5% yeast extract. After 24 hours the TNT concentration was reduced from 100 mg/L to less than 1μg/mL, as compared to the cultures without yeast extract where a substantial amount of TNT persisted up to 96 hours. In a 3-year pilot plant feasibility study, Hoffsommer *et al.* (1978) studied microbiological degradation of TNT in order to destroy and remove TNT in wastewater. When the concentration of TNT in water was 10 to 50 m/L, 97% of the TNT was biotransformed by activated sludge microorganisms supplemented with corn-steep water nutrient.

Aerobic and Anaerobic: Biotransformation products and rates are also affected by the presence of oxygen in the medium (Layton *et al.*, 1987) . Kayser *et al.* (1977) measured the loss of TNT in aerobic and anaerobic media supplemented with corn-steep liquor. After 24 hours, the aerobic sample lost 99.5% of the TNT. In the anaerobic medium, only 69% of the TNT disappeared. The anaerobic products contained three times as many amines as the aerobic products. McCormick *et al.* (1976) investigated the biochemistry of bacterial transformation of nitroaromatic compounds under aerobic and anaerobic conditions. They used an enzymes preparation from *Veillonella alkaescens* to biotransform TNT in the presence of hydrogen. The pattern of reduction of TNT depended on the type of preparation (cell-free extract, resting cells, or growing culture), on the species, and on the atmosphere (air or H_2). Transformation products identified included 4-A, 2,4-DA, 4-OHA, 4,4'-Az and 2,4,6-triaminotoluene (TAT). The presence of azoxy compounds

(4,4'-Az and traces of 2,2'-Az) was believed to be due to nonenzymatic oxidation of the very reactive intermediate 4-OHA. During storage, the 4-OHA content was found to decrease with an increase of 4,4'-Az. It was shown that nitro groups of TNT molecules were biotransformed by both aerobic and anaerobic systems. Depending upon the transforming potential of the system, one, two or three of the nitro groups could be transformed to amino groups. The reduction of nitro groups to amino groups proceeds through the nitroso and hydroxylamino compounds according to the following equations:

$$R\text{-}NO_2 \xrightarrow{H2} R\text{-}NO + H_2O$$

$$R\text{-}NO \xrightarrow{H2} R\text{-}NHOH$$

$$R\text{-}NHOH \xrightarrow{H2} R\text{-}NH_2 + H_2O$$

Thus, 3 moles of hydrogen are required to biotransform each nitro group to an amino group. Cell free extracts of the anaerobic organisms, utilizing molecular H_2, biotransformed the nitro groups to corresponding amino groups. Addition of the hydrogen donor was required to achieve reduction of the third nitro group; without this addition only two of the three nitrogroups were reduced to the corresponding amino groups.

Boopthany *et al.* (1993) studied a sulfate reducing bacterium, *Desulfovibrio* sp. (B strain) isolated from an anaerobic reactor treating furfural containing wastewater for its ability to metabolize TNT. The result showed that this isolate could transform 100 mg/L TNT within 7 to 10 days of incubation at 37°C, when grown with 30 mM pyruvate as the primary carbon source and 20 mM sulfate as electron acceptor. Under these conditions, the main intermediate produced was 2,4-diamino-6-nitrotoluene. Under culture conditions where TNT served as the sole source of nitrogen for growth with pyruvate as electron donor and sulfate as electron acceptor, TNT was first converted to 2,6-diamino-6-nitrotoluene within 10 days of incubation. This intermediate was further converted to

toluene by a reductive deamination process via triaminotoluene. Apart from pyruvate, various other carbon sources such as ethanol, lactate, formate, and H_2 and CO_2 were also studied as potential electron donors for TNT metabolism. They also compared the rate of TNT biotransformation of *Dsufovibrio* sp. (B strain) with other sulfate- reducing bacteria. *Desulfovibrio* sp. (B strain) transformed 100% of TNT in a relatively short period of time (7 days). Other *Desulfovibrio* spp. converted 59 - 72% of the TNT within 21 to 23 days. Where as *Desulfobacterium indolicum* transformed 82% of the TNT in 36 days of incubation. However in their study, the aromatic ring structure was not cleaved and they did not identify metabolites other than toluene even after 6 months of incubation.

Biotransformation rate: Other researchers have reported different ratios of the bioreduction products. Parrish (1977) studied 190 fungal organisms for their ability to transform TNT, and the transformation products of TNT were identified as 4-amino-2,6-dinitrotoluene, 4-hydroxylamino-2,5-dinitrotoluene, and 4,4'-azoxy-2,2',6,6'-tetranitrotoluene. Parish did not observe reduction of nitro groups at positions other than C_4 . Kayser *et al.* (1977) found unequal amounts of the amino-DNT isomers in their oxidation ditch facility using sludge, microorganisms and corn-steep liquor (the 4-amino-2, 6-DNT to 2-amino-4,6-DNT ratio was 8.3). Won *et al.* (1974) did not detect 4-amino-2,6-DNT in cultures of three pseudomonas-like organisms. Each organism showed different oxidation capability. The organisms were designated as isolate "Y" (nitrate reducer), "I" (indole former) and "II". Isolate "Y" oxidized or degraded TNT most effectively, where as isolate "II" was the least effective. The oxygen consumption by isolate "Y" with TNT during a 4 hours period was 23% greater than endogenous uptake. Degradation of TNT occurred most rapidly in "Y" cultures supplemented with 0.5% yeast extract. TNT was metabolized to yield 2,2',6,6'-tetranitro-4-azoxytoluene (4-Az), its isomer 2,2',4,4'-tetranitro-6-azoxytoluene (6-Az),4,6-dinitro-2-aminotolouene (2-Am),

2,6-dinitro-4-hydroxyl-aminotoluene (OH-Am), and nitrodiaminotoluene (Di-Am). After depletion of TNT (24 hours) the azoxy compounds degraded gradually. Approaching complete disappearance at 96 hours. However, these organisms seemed incapable of oxidizing the intermediates 2-Am and Di-Am, the levels of these appearing to remain constant throughout the 96 hours observation.

In a 3-year pilot plant feasibility study, Hoffsommer *et al.* (1978) found by-products, including 4 - A, 2 - A, 2, 4 - DA, and 2,6 - DA at a ratio of 1 to 0.12 to 0.1 to 0.013. The total amount of nitramines was 12% of the TNT feed concentration.

Kaplan and Kaplan (1982) investigated the bioreduction of TNT in compost containing thermophilic bacteria, actinomycetes, and fungi. The compost , incubated with ^{14}C-labeled TNT, was cured for 91 days. TNT, 2-A, and 4-A were identified in the extract from the 24-day compost. 4-A accounted for the majority of the two amines. After 91, days, the ether fractions contained the more nonpolar metabolite 4,4' - Az and 2,4' - Az, while the ethanol and acetone extracts contained the polar metabolites 2,4-DA and 2,6-DA and TNT. 2-A and 4-A were present in all three extracts. A biotransformation scheme for TNT proposed by Kaplan and Kaplan is shown in Fig.2.4.

The biological reduction of nitroaromatic compounds may modify toxicity (Kaplan, 1989). TNT and the biotransformation intermediate have been determined by a variety of analytical techniques, including high performance liquid chromatography (Kaplan and Kaplan 1982).

pH: The microbial degradation of TNT is directly affected by the pH of the medium (Layton *et al.*, 1987). Kayser *et al.* (1977) found 99% of TNT in batch-type experiments (using sewage sludge supplemented with nutrients) disappeared at pH 7.4 to 7.8, but only 45% at pH 6.0 to 6.2. Neuma *et al.* (1983) found a larger percentage of 2-amino-4,6 DNT

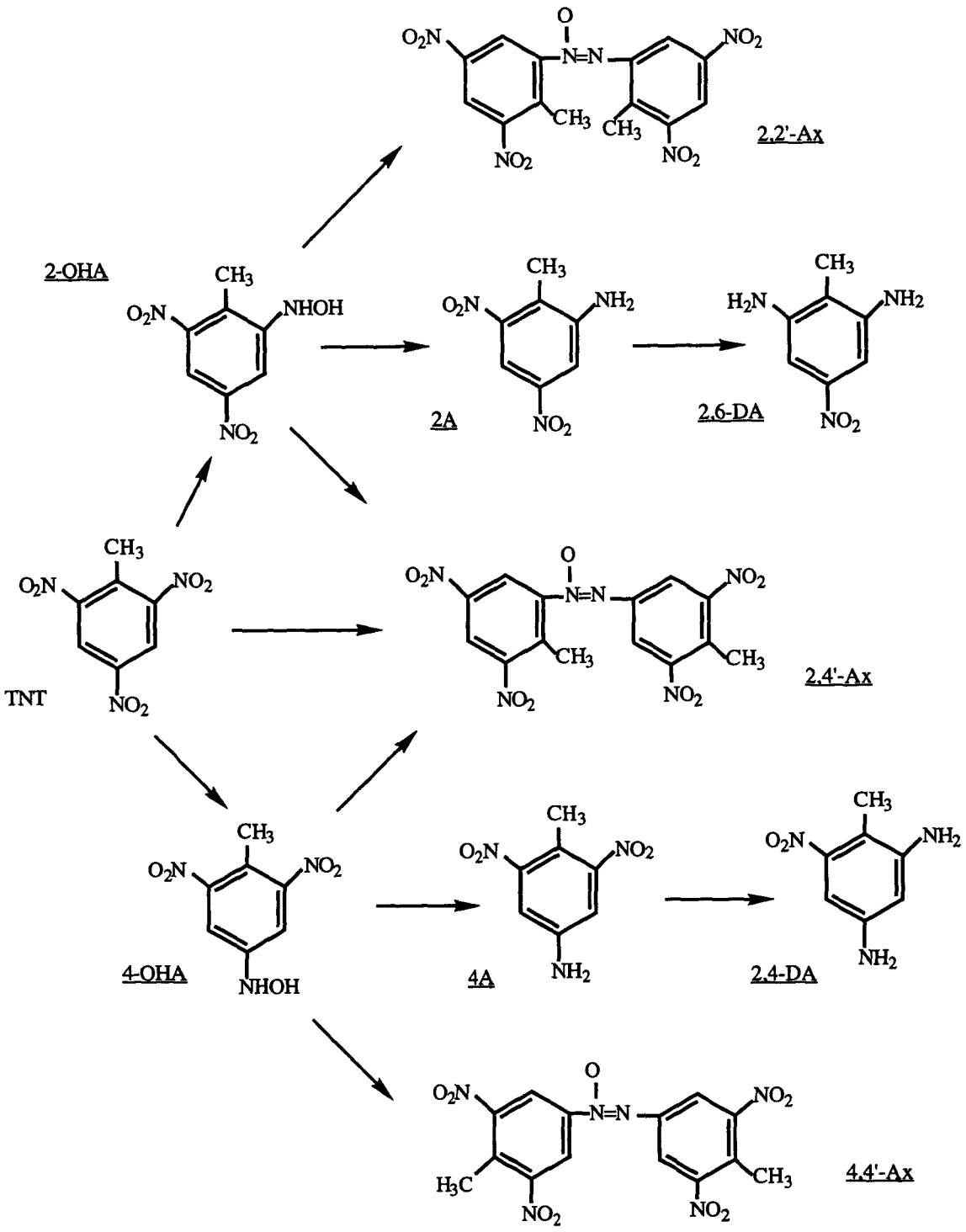


Fig. 2.4 Biotransformation scheme of TNT in compost. 2,6 DA=2,6-diamino-4-nitrotoluene; 2OHA=2,6-2,4Az=4,2',6,6'-tetranitro-2,4'-azoxytoluene (Kaplan and Kaplan, 1989)

in cell cultures that had been treated with TNT at pH of 5.5 than at a pH of 7.8 (In the culture fluid of *Psudomonas denitrificans*). However, the affect of a pH increase from 5.5 to 7.8 was slight; the ratio of 2-amino-4,6-DNT to 4-amino-2,6-DNT changed from 3.9:1 to 3.2:1; where as with *E. Coli,* the ratio changed from 4.1:1 to 1.9:1. Won *et al.* (1974) reported that cultivations at pH 6.5 to 7.2 appeared to affect TNT oxidation more effective than those of lower or higher pH values.

Only very slight mineralization of TNT (0.4%) occurred when Kayser *et al.* (1977) measured $[^{14}C]CO_2$ produced in a composting experiment with corn-steep nutrients and sludge microorganisms. Likewise, Carpenter *et al.* (1978) found less than 0.5% $[^{14}C]CO_2$ in activated sludge system after 3 to 5 days in an aerated reactor.

Layton *et al.* (1987) noted that, many yeast, fungi, and bacteria reduce the nitro groups of TNT. Products include dimers of reduction intermediates and mono-,di-and triamines. It appears that the 4-nitro group is attacked most rapidly, but it dimerizes in preference to reduction to the amine. Aerobic conditions produce mono-and diamines, whereas anaerobic conditions may produce triamines as well. No cleavage of the aromatic ring is expected from microbial action. Maximum influence on reaction rates was observed by adding nutrients so that co-metabolism could result.

Mineralization: Nitroaromatic compounds are usually considered to be resistant to oxidation by oxygenate enzymes, because electron-withdrawing nitro groups are present on the benzene ring. This reduction in electron density inhibits any electrophilic reaction with oxygen (Kaplan, 1992). Until recently, there was little evidence for nitrate, nitrite or ammonia accumulation during the metabolism of nitro-aromatic compounds.

Recent studies have demonstrated that there are oxidative, or perhaps a combination of reductive and oxidative steps in the pathway, and have provided new insight to biotransformation of TNT, although the detailed mechanisms need to be clarified (Kaplan,

1992). In a number of these studies a white-rot fungus was used as the active ingredient in the TNT degrading process. Recent studies have shown that the wood-rotting fungus, *Phanerochaete Chrysosporium*, posses remarkable biodegradative properties (Arjmand *et al.*, 1985; Leathman *et al.*, 1983), *P.Chrysosporium* has the ability to degrade a wide variety of environmentally persistent organopollutants to carbon dioxide (Bumpus *et al.*, 1985). This fungus is one of the relatively few microorganisms known to be able to degrade lignin, a naturally occurring and recalcitrant biopolymer, to carbon dioxide (Bumpus, 1989). Fungi and bacteria are the principal degrades of organic matter. Because organic nutrients are often presented to fungi as large, insoluble macro molecular complexes, these complexes must first be degraded to smaller molecules, which may then internalized and used as a source of nutrients. This initial degradation is accomplished as a result of secretion by the fungi of a group of stable extracellular enzymes, which may include proteases, pectinases, lipases, cellulases, and in the case of *P.Chrysporium*, ligniniases (Bumpus *et al.*, 1985). The free radical mechanism of the lignin-degrading system of *P.Chrosporium* is highly nonspecific and nonstereo-selective. Also, the very low relative concentrations of some organopollutants in the environment may profoundly affect their susceptibility to biodegradation. It has been postulated that the evolution of microorganisms capable of degrading recalcitrant man made compounds may occur only in ecological niches where the concentration of these organopollutants are high enough to exert selective pressure. In some cases, microorganisms may have the enzymatic capability to degrade the organopollutant, but the organopollutant may not be present in sufficient concentrations to induce the enzymes required for degradation. In either case, pollutants which are present in low concentrations may not be degraded. In *P.Chysosporium*, the degradation of organohalides and lignin is initiated by (nitrogen, carbon or sulfur) starvation rather than the presence of substrate. Thus large concentrations

of organohalides or other recalcitrant pollutants need not be present to induce the enzymes required to initiate biodegradation (Bumpus *et al.*, 1985).

Fernando and Aust (1991) in a separate experiment, tested *P.Chrysosporium* for its ability to mineralize the [^{14}C]TNT in both liquid and soil cultures at levels commonly formed at TNT contaminated sites, i.e., 100 mg/L of water and 10,000 mg/Kg in soil. *Phanerochaete Chrysosporium* mineralized 51% of the [^{14}C]TNT over a period of 30 days incubation; 50.8 ± 3.2 % of the total radioactivity evolved as $^{14}CO_2$, 21.9% was present as water soluble metabolites, 10.7% was found in the methylene chloride fraction, and 9.3% was associated with mycelial fraction. A total recovery of 92.7% was achieved. HPLC analysis of the methylene chloride extract identified only about 2.8% of the [^{14}C]TNT initially present as undegraded TNT. The remaining 9% represented unidentified metabolites formed during the 30 day incubation period. Almost all the unidentified metabolites formed in the incubation period were more polar than TNT.

Biodegradation was also examined over a 30 day period in a system in which [^{14}C]TNT adsorbed to soil that was amended with corn cobs previously incubated with *P. Chrysosporium* . Analysis showed that 6.3 ± 0.6% of the recovered radioactivity was liberated as ^{14}CO, and 63% was found in the acetonitrite fraction. 25.2% was not extractable by the organic solvents, and was found in the soil-corn cob mixture. The material could not be identified, as it could not be extracted from matrix. A total mass recovery of 95.1% was observed. HPLC analysis of the radio labeled material in the actonitrate extract revealed that only about 2.2% of the [^{14}C] TNT initially added to the cultures was undegraded TNT.

The same test repeated after 60 and 90 days formed a total mass recovery of 95.2% and 92.5% . However, it is worth noting that in contrary to other reports (McCormick et al. 1976; Won et al. 1976) *P.Chrysosporium* was able to cleave the ^{14}C-ring as evidenced by the liberation of $^{14}CO_2$ from the ^{14}C- ring labeled TNT (Fernando and Aust, 1991).

Also, in contrast to other microbial degradation systems, in which degradation occurs by a stepwise reduction of NO_2 groups, *P.Chrysosporium* appears to degrade TNT by an oxidative mechanisms. Another study by Tsai (1991) suggested that the white rot fungal system is effective in causing some bioconversion changes in a red water stream after 1-week laboratory incubation. Certain components of red water were biotransformed, and the acute cytotoxicity was reduced after biotreatment.

Sublette *et al.* (1992) demonstrated that TNT, simulated and actual pink water can be effectively treated by *Phanerochaete Chrysosporium* immobilized on the disks of a rotating biological contractor (RBC), in both batch and continuos modes. Greater than 90% removal of TNT from a simulated pink water was observed in a continuous RBC residence time of about 24 hours. They conducted 35 batch experiments: 24 used only TNT in the feed at initial concentration of 40-60% mg/L. The balance consisted of three batches with actual pink water, two with RDX only, and seven with simulated pink water containing TNT and RDX. In all these tests, TNT was removed to less than 3 mg/L in about 24 hours. In an experiment using actual pink water, however, the RDX concentration appeared to increase with time, while the TNT was degraded. Sublette et al. (1992) attributed this observation to the production of an intermediate from the degradation of TNT, which had a retention time on HPLC similar to that of RDX. The results of 78 hours continuous experiments showed the same, the "RDX like" component in the effluent. Test with simulated pink water over the 163 hours of operation, showed an averaged removal of 91 - 94% . After 216 hours, TNT was consistently removed to very low levels in the final effluent of the treatment system, even with increased feed concentrations.

The ability of soil bacteria to utilize TNT as a sole carbon source, under aerobic conditions after initial growth with succinate, has been reported (Unkefer *et al.*, 1990), although details relating to mineralization have not been published (Kaplan, 1992). Kupla *et al.* (1991a, b) have reported an aerobic aqueous and soil microbial consortium,

consisting of four *Psedomonas* sp. enriched from TNT contaminated soil, that slowly mineralize, TNT via co-metabolic processes with succinate as the energy source . Their studies demonstrated the ability of the microbial consortium to convert [^{14}C]TNT into $^{14}CO_2$. The consortium converted 3.1% [^{14}C]TNT to $^{14}CO_2$. The rate of conversion was very slow however, possibly reflecting difficulty in metabolizing the TNT intermediates to CO_2. The control, a killed consortium, showed less than 0.7% $^{14}CO_2$ evolution. Related studies with soil bacteria and a soil-slurry reaction have been described (Montemango and Irvine, 1990). Some mineralization data with [^{14}C]TNT are provided which indicate recovery of 2.5% as $^{14}CO_2$ in 48 days in liquid supplemented with succinate, and less than 1% recovery in soil slurries in 33 days.

Composting: Garg *et al.* (1991) used composting process by which organic materials are biodegraded by microorganisms, resulting in the production of inorganic/organic byproducts and energy in the form of heat, carbon dioxide and water. The heat generated is trapped within the compost matrix, leading to self-heating which is characteristic of composting. They recommended this process to remediation of soils contaminated with any biodegradable compounds. Material required for the process include a biodegradable organic substrate, nutrients (C, N, P), bulking agents and means to provide oxygen to the composting materials.

Griest *et al.* (1990) studied determination of 2,4,6-trinitrotoluene metabolites in composts. They used both static pile and mechanically stirred composts in a field composting optimization, to provide data for the evaluation of composting efficiency to decontaminate explosives contaminated soil. Two mechanically stirred composts with 25 and 40% contaminated soil also were examined. The concentrations of explosives in the composts and their leachates, bacterial mutagenicity in the compost and aquatic toxicity of the leacates decreased rapidly after approximately 20 days of composting. The percentage

decreased observed in the final composts versus the 100% soil ranged as follows: TNT: 77.5-99.9% and RDX: 0-97.2% and HMX: 0-85.0%. Generally, greater soil percentage in the compost was associated with reducing efficiency. Extraction and digestion of a compost inoculated with radio-labeled TNT suggested that a major portion of the biotransformed TNT was chemically bound to compost and not mineralized. The small levels of explosives and metabolites, bacterial mutagenicity, and leachable aquatic toxicity remain after composting. The ultimate fate of the biotransformed explosives, and the source (s) of residual toxicity and mutagenicity remain unknown.

Garg *et al.* (1991), examined both mesophilic and thermophilic composting. Compounds considered in their study were three common explosives: namely TNT, RDX, and HMX. In an aerated static pile, bulking agents and additional carbon sources such as alfalfa and horse feed were added to increase the organic carbon content and porosity. The temperature variations for mesophilic pile were generally between 35 and 40° C, and those for thermophilic pile ranged from 55 to 60°C. Total explosive concentrations in the mesophilic and thermophilic piles at the end of the study were reduced by 98% , and 99.6%, respectively. Total volume and mass of the compost remaining in the pile decreased by 17% and 25% for the mesophilic and thermophilic piles, respectively. Half lives for TNT were mesophilic 21.7 hours and 13.1 hours for thermophilic conditions, respectively. TNT transformation/degradation products were reported: amino-dinitrotoluene, diamino-nitrotoluene, hydroxylamino-DNT, and tetranitro-azoxytoluene. Complete mineralization to inorganic products was not observed.

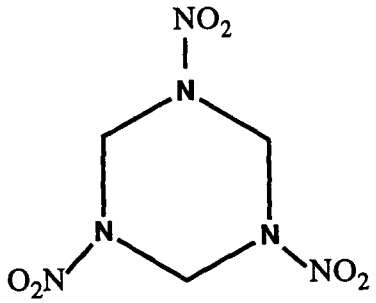
3 RDX Properties, Importance, Toxicity and Environmental Fate

Hexahydro-1,3,5-trinitro-1,3,5-triazine or, Hexogen (German) or, Cyclonite (British) or RDX, is one of the most important military high explosives today in use. It has a high chemical stability (not much less than that of TNT) and an explosive power much greater than that of TNT (Urbanski, 1977). RDX has approximately 130% the explosive power of TNT (Sullivan *et al.*, 1979). It is considered a stable, relatively inexpensive explosive, and can be stored up to 10 months at 85°C without perceptible deterioration (Meyer, 1977; Pal and Ryon, 1986).

RDX (British code name for Research Department or Royal Demolition Explosive) (Rosenblatt, 1991) or (Rapid Detonation Explosive) (Hesselmann, 1992).is the most important military high explosive in the U.S. A homolog, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), is a by product of synthesis of RDX and is also used in RDX formulations. Most commercial grade RDX contains 9% HMX (McCormick *et al.*, 1981).

During World War II, RDX became an important high-power explosive and was used in detonators, primers and boosters. Today it is used as a component in mixtures with other explosives such as TNT (Yinon, 1990). RDX and HMX are major components in nuclear and conventional weapons. They are widely used as part of high-performance explosive in the U.S.A.. Recently HMX has replaced its homologue RDX in importance in the U.S., and it is more prevalent in recently manufactured explosive devices. This is due in part to HMX's greater yield and resistance to unwanted detonation (Heilmann *et al.*, 1994). RDX structure, physical properties and other names are shown in Fig.3.1. RDX dose not have the stable aromatic ring of TNT; therefore, it degrades to low-molecular-weigh compounds, and ultimately to carbon dioxide and water (Layton *et al.*, 1987).

Empirical formula: $C_3H_6N_6O_6$
Molecular weight: 222.15
Melting point (°C): 205-207
CAS Reg. No.: 121-82-4
(more data in Rosenblatt, 1991)



Also known as: Cyclonite (British), Hexogen (German), Hexogene (French), T4 (Italian), cyclo-trimethyenetrinitramine, 1,3,5 - triaza - 1,3.5-trinitroclohexan, Chemical 506.

Fig. 3.1 Structure, properties and names of RDX.

Toxicity: RDX exerts its primary toxic effect in humans on the central nervous system, but also involves gastrointestinal and renal effects (Etnier *et al.*, 1990). Evidence for carcinogenicity of RDX from mammalian studies is limited (Rosenblat, 1991); consequently RDX has been classified by the U.S. Environmental Protection Agency (EPA) as class C "Possible Human Carcinogen". The U.S. EPA. (1988) reported a lifetime drinking water health advisory of 2 µg/L. Sullivan *et al.* (1979) recommended a 24 hours average maximum allowable concentration of 0.3 µg/mL in wastewater to protect aquatic life . The products of the biological degradation of RDX may pose more serious toxicological problems than of RDX itself (McCormick *et al.*, 1981). RDX has also used as rat poison (ACGIH, 1980; Merck Index, 1989)

Environmental Fate: Potential environmental exposure to RDX exists not only in manufacturing plants where dust is generated, but also in nearby waterways where RDX may have been discharged, and near RDX demilitarization sites where RDX could reach potable groundwater (Yinon, 1990). Doseburg (1984) estimated that one specific

munitions plant wasted 7,300 Kg of RDX during the Korean War, and another plant discharged up to 450 Kg per 24-hr period into a nearby river (Patterson, 1976b).

Hale *et al.* (1979) determined the solubility of RDX in water as 23.6± 2.0 mg/L at 21°C. Spanngord *et al.* (1983) measured solubility values for RDX at 10°, 20°, 30°C, 21.9, 38.4, 67 mg/L respectively. In contrast to Hale *et al.* (1979) and Spanngord *et al.* (1983), and Pal and Ryon (1986) reported the solubility of RDX in water as 7.6 mg/L at 25°C and 1.3 mg/L at 83°C. Because of the degree of solubility of a substance depends on concentration and temperature of solvent, the reader should consult the original references to determine the experimental conditions (Dobartz, 1981).

Volatilization is not significant in the environmental fate of RDX, as indicated by vapor pressure of 4.06 $x10^{-6}$ atm (25°C) and a Henry's law constant of $1.96x10^{-11}$ atm m^3/mole (25°C) (Rosenblatt, 1991).

Transformation of RDX in the environment occurs fastest by photolysis (Layton *et al.*, 1987). Spanngord *et al.* (1980b) measured the degradation of RDX in distilled and filter-sterilized natural water in sunlight during a cloudy January period with air temperatures from -2 to 18°C. They calculated a half-life of 13 and 14 days from their measurements of RDX disappearance from distilled and filtered water. In a subsequent experiment during a sunny period in March with water temperature ranging from 5° to 20°C, they measured the half life of RDX as 1.8 days in distilled water.

Hale *et al.* (1979) studied downward movement of RDX and its transformation through soil columns over a 6 months period. They observed very little movement of RDX. Spalding (1988) found RDX to spread out with almost no detention in a groundwater aquifer. Spalding *et al.* (1987) reported munition residues from waste disposal on an ordnance plant property resulted in a defined plume of RDX-contaminated groundwater stretching 6.5 km in length, covering an area of 6.5 km^2. From his field monitoring data, Spalding concluded that RDX is much more persistent than TNT.

Spanggord *et al.* (1980b) measured K_d values of 4.2 and 1.4 hr^{-1} for two sediments, and associated K_{OC} values were 127 and 42, respectively. Recently, it was reported that RDX accumulates in hydroponic plants, raising concern that this could be an entry into food-chain (Harvey *et al.*, 1991). The role of biodegradation in the environmental fate of RDX is reviewed in a later section.

3.1 Physico-chemical Treatment of RDX Wastes

Adsorption: Burrows *et al.* (1984) reported fair removal efficiency of RDX from wastewater at concentration levels below 25 mg/L, using granular activated carbon, under batch conditions. The current industrial method for treating pink water (pink water may contain RDX and HMX) is adsorption using activated carbon, and removal of 99.5% for both TNT and RDX have been reported (Sublette *et al.*, 1992). Hinshaw *et al.* (1987) also presented a multiphase study providing quantitative data on the ability of activated carbon to remove RDX from pink water. Burrows *et al.* (1984) determined the Freundlich isotherm constant K and n as 0.1118 L/mg and 2.938, respectively for Filtrasorb 300 (Calgon Carbon Co.). Wujcik *et al.* (1992) conducted laboratory GAC isotherm studies to evaluate the ability of activated carbon to remove RDX from the explosives contaminated groundwater at the Millan Army Ammunition Plant (MAAP). The Freundlich adsorption equation was used to define the carbon isotherm test results. They calculated empirical constants for the Freundlich adsorption equation for the five test carbon isotherms for MAAP, which are presented in Table 3.1. Also, they conducted three continuos-flow column tests at MAAP using two different carbons: Filtrasorb 300 and Hydrodarco 4000. Test one was run for a total of 7.6 days; RDX was detected at a concentration that

approximately 1% of its influent concentration. Test two was run for a total of 16.5 days, and no RDX was detected in the effluent. Test three was run for a total of 54.5 days, at which time because of cold weather, they decided the unit should be shut down, so that no damage would occur.

Table 3.1 Empirical constants for Freundlich adsorption equation for five test carbons using groundwater from monitoring well at the Milan Army Ammunition Plant (Wujcik, 1992).

	RDX Isotherm	
Activated Carbon Type	K $(mg/L)^{-1/n}$	1/n
Filtrasorb 200	0.052	0.535
Filtrasorb 300	0.031	0.413
Filtrasorb 400	0.049	0.555
Filtrasorb 4000	0.0012	0.100
Atochem, Inc.	0.045	0.630

RDX adsorption suffers from the serious deficiency of the inability to regenerate the carbon. The current practice is to dispose of spent carbon by incineration after a single use (Sublette *et al.*, 1992). Thermal regeneration is not suitable due to the safety problems when the explosive in the carbon exceeds 8% (w/w) (Andern, 1975). Treatment with activated carbon is therefore expensive and the RDX disposal problem is not solved. Incinerating RDX or RDX-laden carbon is not expected to meet the future environmental regulations.

There were some efforts in the past to find physicochemical treatment alternatives. Although none of these alternative are widely used, they are briefly reviewed in the following, specifically, under the perspective to treat low contaminated water.

The direct alternative to activated carbon is synthetic polymeric adsorbents. They were found to be less efficient in removing RDX than activated carbon (Patterson, 1976). Solvent regeneration with acetone was demonstrated (Andern, 1975); however, the mixture of solvent and RDX is still a hazardous waste. This waste problem is probably the main reason that polymeric adsorbents are not widely used (Semens, 1984).

Szachta (1978) found that TNT inhibited RDX adsorption. In the presence of TNT activated carbon had capacity of 76 mg RDX/g carbon as opposed to 125 mg RDX/g carbon for RDX alone.

UV-Radiation: Burrows and Kobylinski (1984) used ultraviolet (UV) light to destroy RDX, which followed first order kinetic model, with first half-life of 3.7 min. Kubose and Hoffsommer (1977) have shown that concentrations of 20 to 40 mg/L RDX in aqueous solution could be reduced by 98% using photolysis, using the full spectral output from medium mercury lamp (220 nm to 1367 nm) with irradiation period of 15 seconds in a laboratory column flow system. Exposure of aqueous solutions of RDX to UV light resulted in the formation of nitrate, nitrite, ammonia, formaldehyde, nitrous oxide, formamide, and N-nitroso-methylenediamine (Glover and Hoffsommer, 1979). Jain (1977) used UV irradiation in adsorption-oxidation studies of TNT and RDX degradation and successfully oxidized of adsorbed RDX by ozone to UV pretreatment were observed.

Ozone has no significant effect on photolysis rates, and addition of hydrogen peroxide above 0.1% actually reduces decomposition rates. RDX production wastewaters often carry high concentrations of acetic acid, cyclo-hexanone, and nitrate (McCormick,

1984b) which are strong UV-absorbents. Therefore, using UV-radiation may not be suitable in these cases.

Fischer *et al.* (1982) found UV and ozone to be effective in treatment of wastewaters containing 1 to 20 mg/L of RDX and cost competitive with activated carbon adsorption for small systems. Nevertheless, using UV-radiation for groundwater remediation is problematic because of hazardous decomposition intermediates (e.g. N-nitroso-methylenediamine, formaldehyde, formamide) (Rosenblatt, 1991; Yinon, 1990).

Oxidative treatment: Ozone, hydrogen peroxide, iron catalyzed hydrogen peroxide (Fenton's Reagent) and chlorine did not react RDX to any measurable extent (Semmens, 1984).

Reverse Osmosis: Sullivan *et al.* (1979) reported that Jackson *et al.* (1976) evaluated reverse osmosis for RDX treatment. He reports "break through" after 24 hours, which implies that reverse osmosis is not effective in treating RDX wastewaters.

Chemical Hydrolysis: RDX does not hydrolyze to an appreciable extent in either fresh water or sea water at neutral or acidic pH values. Hoffsommer and Rosen (1973) found approximately 12% of 956 mg/L RDX mixture in sea water degraded in 112 days. Rosenblatt (1974) reported that boiling RDX with 5% NaOH will destroy it. Dilute sulfuric acid also decompose RDX to N_2 and CH_2O or NH_3, and CH_2O; depending on the acid strength. However, acid or alkaline hydrolysis of dilute solutions of RDX is impractical, since the amount of acid or base required for treatment and subsequent neutralization will be large (Sullivan *et al.*, 1979).

In a more recent study by Spontarelli *et al.* (1993) RDX and other energetic materials were quickly decomposed to non-energetic products at 93°C, during base

hydrolysis above pH 13. Heilmann *et al.* (1994), found pseudo-first-order and second-order rate dependencies for the alkaline hydrolysis of RDX. For elevated temperatures ranging from 50 to 80°C the reaction was second-order. The temperature dependency of the rate constants was predicted using the Arrhenius-model.

Freeman (1985) applied surfactants to accelerate RDX hydrolysis in wastewater. He also increased the reaction rates using high pH values (10 - 12) and elevated temperature (> 50°C). It should be noted that the enhancing effect of surfactants was reduced with increasing temperatures and pH.

3.2 Biological Degradation of RDX

Aerobic: The majority of available research indicates that RDX cannot be aerobically degraded when it is the sole carbon source (Osmon and Klausmeier 1972; Hoffsommer *et al.*, 1978; Spanggord *et al.*, 1980; McCormick *et al.*, 1981).

RDX biotransformation was evaluated in Holston River water; RDX (10 mg/L) in river water collected in July was not significantly degraded during 78 days incubation. The same result was obtained in August after 73 days of incubation. The addition of 30 mg/L of yeast extract in river water did not significantly affect the disappearance of RDX (Spanggord *at al.*, 1980). In the August experiment 1% Holston River sediment was added, and the initial RDX concentration (10 mg/L) remained unchanged for 20 days, but was reduced to 4 mg/L after another 16 days. Water from a local eutrophic pond was collected, and RDX biotransformation was also tested with 10 mg/L of RDX only, RDX plus 1% local pond sediments, and RDX plus 1% Holston River sediment. The RDX concentration in pond water alone or pond water plus pond sediments did not change significantly during 90 days of incubation. The RDX concentration in pond water plus

Holston river water sediment, however, had decreased to nearly 1 mg/L at 76 days, after 20 days of lag period. This corresponds to a half-life of 18 days. Microorganisms from the pond water plus Holston river water were introduced into shaker flasks containing basal-salts medium and 10 mg/L RDX, 10 mg/L RDX plus 50 mg/L of yeast extract, and RDX plus 1% Holston River sediment. No biotransformation was observed in any of the shaker flasks after 30 days of incubation. From these data Spanggord *et al.* (1980) suggested that RDX will be resistant to biotransformation under aerobic conditions.

Degradation of TNT in the presence of RDX was monitored by Hoffsommer *et al.* (1978), in a 3 year pilot plant study. The initial concentrations were 15.1 mg/L of TNT and 7.3 mg/L of RDX. With aerobic activated sludge microorganisms in a batch experiment, 99.6% of the TNT was transformed. No bioconversion of RDX was observed.

One of the most recent examinations of aerobic RDX degradation was conducted by Ro and Stenstrom (1991). They studied enrichment with and without additional carbon sources, using several inocula from sites contaminated with RDX. No significant and reproducible reduction of RDX occurred the tests conditions. Toxicity of RDX was not a limiting factor, because cultures with organic cosubstrates did grow well (Hesselmann *et al.*, 1992).

Anaerobic: In contrast to the obvious recalcitrance in aerobic environments, RDX is readily degraded anaerobically in the presence of suitable organic cosubstrates (Hesselmann, 1992).

Spanggord *et al.* (1980), studied RDX transformation anaerobically with small amounts of extra organic nutrient, and RDX was readily transformed. RDX in Holston River water with 30 mg/L yeast extract, was transformed to less than 0.1 mg/L within 10 days. In local pond water containing 10 mg/L RDX and 50 mg/L yeast extract, RDX

decreased to less than 0.1 mg/L in 10 days. No significant RDX transformation was observed in aerobic flasks without added yeast extract. In the transferring flasks containing RDX and yeast extract, RDX disappeared in 2 to 3 days. The dissolved oxygen concentration was less than 1% of saturation in these flasks. Spanggord *et al.* (1980) suggested that aerobic bacteria in a mixed culture may utilize the yeast extract to grow and consume oxygen to maintain anaerobic conditions. Spanggord *et al.* (1980) also performed experiments to determine if yeast extract was needed as nutrients for RDX transformation, or to maintain anaerobic environment. They concluded that RDX degradation depends on extra organic nutrients, and that a co-metabolic process is probably involved in the degradation.

McCormick *et al.* (1981) studied RDX at concentrations of 50 or 100 μg/mL, and showed that RDX disappeared rapidly from anaerobically incubated nutrient broth cultures. RDX disappearance was essentially complete after 4 days. HPLC analysis of the anaerobic reaction mixtures revealed the presence of intermediates (TNX, MNX, and DNX) formed during the disappearance of RDX . McCormick *et al.* (1981) concluded that, concurrent with the disappearance of RDX, is the sequential buildup and disappearance of the mono-, di-, and tri-nitroso analogs of RDX. From the accumulated data McCormick *et al.* (1981) proposed a pathway for the biodegradation of RDX as illustrated in Fig.3.2. He postulated that the molecule becomes unstable when any one of the nitro groups is reduced beyond the nitroso level. At this point hydrolytic cleavage, followed by rearrangements, gives rise to the end-products observed. It should be noted that non-aromatic nitroso compounds are also subject to spontaneous hydrolytic reactions themselves, without preceding further reduction (Hesselmann *et al.*, 1992).

McCormick *et al.* (1984b) also studied continuous culture systems under denitrifying conditions. Degradation of RDX (30 mg/l) was evaluated using a digester

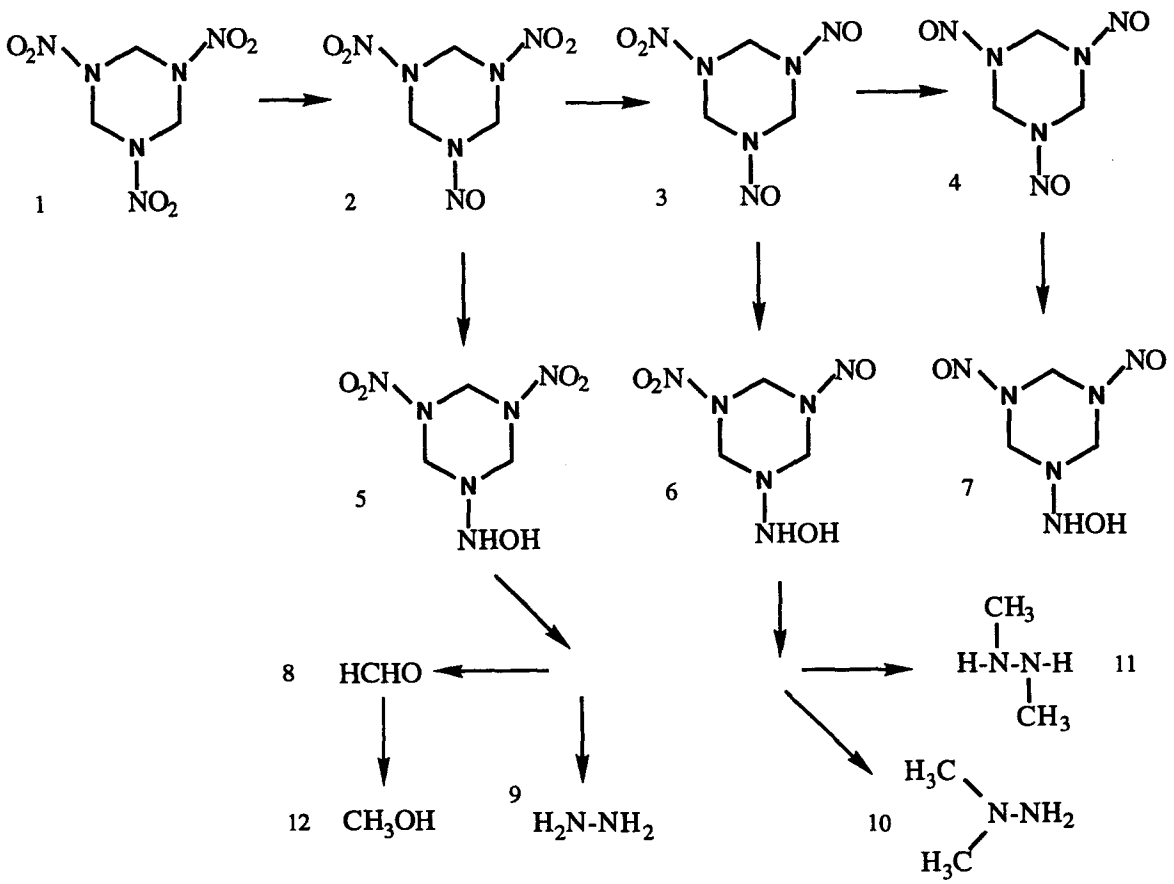


Fig. 3.2 Proposed pathway for the anaerobic biodegradation of RDX. Compounds: 1, RDX; 2, MNX; 3, DNX; 4, TNX; 5, 1-hydroxlamino-3,5-dinitro-1,3,5-triazine; 6, 1-hydroxylamino-3-nitroso-5-nitro-1,3,5-triazine; 7, 1-hydroxylamino-3,5-dinitroso-1,3,5-triazine; 8, formaldehyde; 9, hydrazine; 10, 1,1-dimethyhyrazine; 11, 1,2-dimethylhydrazine; 12, methanol (McCormick, 1981).

sludge inoculum and various organic cosubstrates with nitrate as the terminal electron acceptor. RDX disappeared completely from a molasses or nutrient broth based system. The retention times for the nutrient broth system varied between 10 and 14 days. Complete denitrification was observed at all times. The activities of the various systems appeared to be proportional to the concentration of available carbon in the medium. The highest activity

was observed in 0.8% nutrient broth media with the next highest activity in 30% acid hydrolyzed sludge. River waters normally are aerobic, but lakes, ponds and other shallow, standing waters have anaerobic sediments rich in organic materials. Supplementation of the basal salts methanol system with sediments contributed to a higher rate of disappearance of the RDX. Hydrazine was not detected. Analytical results for MNX, DNX, or TNX were not reported. Gas Phase analysis with GC revealed CO_2 and N_2 as the major components; CH_4 and N_2O were never found. The stimulation in the rate of disappearance of RDX by added phosphate, basal salts, and rich organic sediments suggested that the process may proceed naturally at low rate wherever local anaerobic habitats exist in the environment such as may be present in sediments.

Ryon *et al.* (1984) experienced RDX to anaerobic sediment-populations of bacteria and extra nutrient; and observed transformations within 4 to 38 days. Bacteria that degrade RDX were identified as *Pseudomonas* Spp., *Alcaligenes* spp., *Thiorhodaceael* (Photosynthetic) and *Athiorhodacea* (Photosynthetic). Transformation products were identified, including formaldehyde, methanol, hydrazine, trinitrosotriazine, and series of RDX nitroso reduction products.

Hesselmann *et al.* (1992) proposed a treatment concept for low concentrations of RDX in groundwater or wastewater which uses adsorption on activated carbon and indirect bioregeneration of exhausted activated carbon. In the two step regeneration process, RDX is first desorbed and then biodegraded in an external anaerobic bioreactor. After a cell separation process to prevent biofouling of the adsorbent, the water is reused for desorption. The advantage of this process is that the anaerobic biotreatment affects only a small volume of recirculated process water. They examined the effect of elevated temperature and the use of organic solvents to increase the RDX desorption in batch experiments. The desorbed RDX concentration increased exponentially with increasing water temperature. Raising the water temperature from 29° to 90°C enhanced the

desorption 15 times. Using various organic solvents increased the desorption of RDX between 480 times (propanol) and 830 times (ethyl acetate) as compared to water.

Microbiological experiments were conducted to find the best organic substrates and bacteria populations, and to examine the influence of oxygen, nitrate and sulfate as terminal electron acceptors. Biodegradation of RDX occurred under fermentative, sulfate-and nitrate-reducing conditions. The presence of oxygen decreased the RDX degradation somewhat, but was not strongly toxic to the responsible bacteria. Under sulfate-reducing conditions, peptones and amino acids were successful cosubstrates for RDX degradation. Ethanol and propanol did support RDX degradation in a mixture with amino acids or peptones. Under nitrate-reducing conditions, the same co-substrates were successful, as in the case of sulfate-reducing conditions. Experiments using methanol, Na-formate, and acetone were less encouraging. A temporary accumulation of RDX metabolites was observed mainly under fermentative and sulfate-reducing conditions. Metabolites were not identified. They found significant differences in degradation rates using various organic substrates. Sugar were utilized as growth substrates but did not support RDX degradation. Even between different peptone types significant differences in RDX degradation could be observed.

Sublette *et al.* (1992) studied RDX treatment by *Phanerochaete Chrysosporium* immobilized on the disks of a rotating biological contactor (RBC) in batch mode. Experiments were conducted at 39 - 40°C. In two batch tests, RDX was observed to be degraded, although more slowly than TNT. However an auxiliary carbon source, such as glucose, was required to sustain viability.

Wilkie *et al.* (1994) further investigated a the treatment process suggested by Hesselmann *et al.* (1992) that employs continuous flow anaerobic biodegradation. In this process, RDX degradation is accomplished in two steps: adsorption of RDX onto activated carbon with subsequent desorption and indirect biological degradation. RDX removal

efficiencies up to 80% were found for the continuous flow anaerobic reactor operating at 35°C. The growth of mixed denitrifying cultures is supported using nitrate as the terminal electron acceptor and ethanol as the cosubstrate. The affects of co-substrate type and concentration, retention time and temperature on culture growth and RDX removal were examined. Adsorption isotherms were generated for several carbons. Filtrasorb-400 had the highest adsorption capacity for RDX at 417 mg/g GAC. The overall degradation process can be fit to a pseudo first-order rate equation. The rate constants calculated for glass, silicone and Tygon packed reactors are 1.7, 4.2 and 4.2 hr^{-1} respectively.

Mineralization: McCormick *et al.* (1981) studied the fate of the RDX-carbon with [^{14}C] RDX. Almost no radioactivity was ever adsorbed at or incorporated in to the biomass. This confirmed that the disappearance of RDX was not due to adsorption and it could mean that an exoenzymatic degradation was taking place. The final radioactive products were volatile, neutral, organic substances, just as MeOH and HCOH, but they were not specifically identified. Mineralization to CO_2 or CH_4 did not occur.

Fernando and Aust (1991) determined the ability of *Phanerochaete Chrysosporium*, to degrade [^{14}C] RDX in liquid culture and also, soil. In [^{14}C] RDX contaminated cultures, *p. Chrysosporium* mineralized 67% of the initial [^{14}C] RDX over a period of 30 days incubation. Mass balance was done at the end of the 30 day incubation period and a total of 66.6 ± 4.1 % of the initial radioactivity added to cultures was liberated as $^{14}CO_2$, which 20.2% was recovered as water soluble metabolites, 4.8% was present in the methylene chloride fraction and 2.1% was associated with the mycelical fragments. A total of 93.7% radioactivity added to the culture was recovered. HPLC analysis of the methylene chloride fraction demonstrated that only about 4% of the [^{14}C] RDX added to the cultures was undegraded. No metabolites were found in the methylene chloride fraction. In control cultures, where the *p. chrysosporium* was not added but identical

culture parameters were included, 97-98% of the radioactivity initially added was recovered in the methylene chloride fraction and was identified as undegraded [^{14}C] RDX.

Biodegradation was also examined in a system in which[^{14}C] RDX was separately adsorbed onto soil that was amended with corn cobs previously inoculated with *p. chrysosporium*. After 30 days in a soil corn cob mixture, 76.0 ± 3.9% of the recovered radioactivity was evolved as $^{14}CO_2$, which 4.5% was present in the acetonitrite extract, and 9.7% was unextractable and present in the soil/corn cob matrix. A total mass recovery of 90.2% was achieved. Analysis of the radiolabeled material in the acetonitrile extract revealed that only 4% of the [^{14}C] RDX initially present was identified as undegraded RDX. In uninoculated control cultures, incubated under the same conditions, greater than 99% of the radioactivity added was found in the acetonitrile fraction as unmetabolized [^{14}C] RDX. From these studies Fernando and Aust (1991) concluded that *p. chrysosporium* was able to cleave the ring as evidenced by liberation of the $^{14}CO_2$ from the ^{14}C -ring labeled RDX. In contrast to other microbial degradation systems, which degradation occurs by stepwise reduction of NO_2 groups, *p. chrysosporium* appears to degrade RDX by an oxidative mechanism.

Composting: In a review by Garg *et al.* (1991), composting data for mesophilic and thermophilic temperature ranges have been reported. Compounds considered in this study were three common explosives; namely TNT, RDX, and HMX. In an aerated static pile, bulking agents and additional carbon sources such as alfalfa and horse feed were added to increase the composts organic carbon content and porosity. The temperature variations for mesophilic pile were generally between 35 and 40°C, while the thermophilic pile ranged from 55 to 60°C. Total explosive concentrations in mesophilic and thermophilic piles at the end of the study were reduced to 98%, and 99.6%, respectively. Total volume and mass of the compost remaining in the pile decreased by 17% and 25% for the mesophilic and

thermophilic piles, respectively. Half lives calculated for each case are presented in Table 3.2. As can be seen from Table 3.2, the life of HMX is the longest among the three contaminants studied. While composting would be an effective and rapid remedial alternative for sediments with high concentrations of TNT and RDX, it may not be as advantageous for sediments with high concentration of HMX. Thermophilic piles, in general, demonstrated a higher extent of explosive degradation and a faster rate than mesophilic piles. It may be concluded that composting would be most effective for sediments contaminated with high concentrations of TNT and RDX (which is often the case), and operated with pile temperatures in the range of 55 - 60°C.

A brief summery of the biodegradation products of three common explosive materials and optimum conditions required for the reaction are provided in Table 3.3.

Table 3.2 Composting half-lives of primary contaminants (Garg, 1991).

Explosive Contaminant	Half Life (hours)	
	Mesophilic (35° - 40°C)	Thermophilic (55° - 60°C)
TNT	21.7	13.1
RDX	31.1	17.3
HMX	43.3	24.8
Total	27.7	16.5

Table 3.3 Biodegradation by-products and optimum conditions for transformation and degradation of TNT, RDX and HMX (Garg, 1991).

Explosive Compound	Transformation/ Degradation Products	Optimum Conditions
TNT	Amino-dinitrotoluene Diamino-nitrotoluene Hydroxylamino-DNT Tetranitro-azoxytoluene Complete mineralization to inorganic products not normally realized	High organic concentration Aerobic conditions Biodegradable co-substrates
RDX	Ring cleavage and complete mineralization; products include mono and dinitroso RDX derivatives, methanol, formaldehyde	Anaerobic conditions Low redox potential High TOC
HMX	Complete mineralization not demonstrated; maximum 53% achieved; products include mono and nitroso HMX derivatives, methanol and formaldehyde	Anaerobic conditions Low redox potential High TOC; conditions similar to RDX but at slow rate

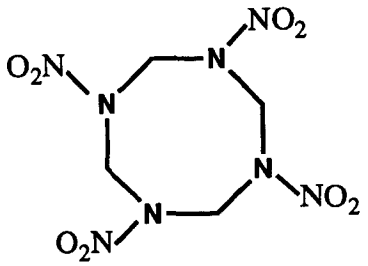
4. HMX Properties, Importance, Toxicity and Environmental Fate

Cyclotetramethylenetetranitramine,1,3,5,7-tetranitro-1,3,5,7-tetrazacy-clooctane, Octogen, or best known as HMX, has been used in military applications as "buster" charges for artillery shells (Yinon, 1990). It has a higher density and much higher melting point than RDX. It was named HMX for High Melting Explosive (Gibbs and Popolato, 1980). Because of its higher density, HMX has replaced RDX in explosive applications for which energy and volume are important. HMX, is the most energetic production explosive available in the world (E & TR, 1993).

HMX is used to implode fissionable material in nuclear devices to achieve critical mass and as a component in plastic-bonded explosives (Sullivan *et al.*, 1979; and Kitchen *et al.*, 1979). HMX widely used as part of high performance explosives in the U.S., Table 1.1 shows the combination of HMX plastic bonded high explosives. HMX has approximately 130% of the explosive power of trinitrotoluene (TNT) (Sullivan *et al.*, 1979). Recently HMX has replaced its homologue RDX in importance in the U.S., and it is more prevalent in recently manufactured explosive devices. This is due in part to HMX's greater yield and resistance to unwanted detonation (Heilmann *et al.*, 1994).

HMX is a by-product of RDX synthesis and is present in military-grade RDX at levels between 8 and 12 wt%. Because HMX has a chemical structure that is similar to that of RDX, its environmental properties parallel those of RDX (Sullivan *et al.*, 1979; Layton *et al.*, 1987). Its structure, physical properties and other names are shown in Fig. 4.1. Patterson *et al.* (1976) averaged over 1969 - 1971, approximately $1x10^5$ kg per month, HMX were produced in the United States.

Empirical formula: $C_4H_8N_8O_8$
Molecular weight: 296.20
Melting point (°C): 286
CAS Reg. No.: 269-41-0
(more data in Rosenblatt, 1991)



Also known as: Cyclotetramethylenetetranitramine, HMX, Octogen, PRI, Octahydro-1,3,5,7-tetranitroazocine, Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, 1,3,5,7-tetranitro-1,3,5,7-tetraazocy clooctane.

Fig. 4.1 Structure, properties and names of HMX.

Toxicity: Available data indicate that HMX is less toxic than TNT and RDX (Ryon *et al.*, 1984). Its primary toxic effect cardiovascular depression, is characteristic of nitrite toxicity indicating cleavage of the NO_2 groups (Ryon *et al.*, 1980). HMX was not mutagenic in the Ames spot test (Whong *et al.*, 1980). The U.S. EPA (1988) classified HMX in group D: "Not classified as to Human Carcinogenicity". The suggested maximum concentration of HMX in air is 1.5 mg/m^3 (Gibbs and Popolato, 1980).

Environmental Fate: Routes of entry to environment are similar to those of TNT and RDX. Patterson *et al.* (1976a) reported that HMX wastewaters are generally discharged without treatment. Beader *et al.* (1977, as cited in Pal and Ryon, 1986) found contamination of RDX and HMX at manufacturing areas and disposal sites at Holston AAP, occasional disposal of sewage treatment sludge and explosive generated incineration ashes in landfills. This disposal was particularly hazardous because the landfill area was affected by sinkholes and subsidence, indicating that ground water contamination was a distinct possibility. Patterson *et al.* (1976a) state that major wastewater sources from RDX

and HMX manufacturing result from dewatering of explosives and floor and equipment clean up.

Kitchens *et al.* (1978) reported data from Holston AAP for the amount of HMX discharged per day at various operating conditions. They estimated that at full mobilization, minimum values for discharge would be 61 Kg HMX per day. They also reported HMX concentrations for effluents at several internal sampling points and in the river. The average concentrations ranged from 0.01 to 2.6 mg/L. In receiving the information on environmental effect of HMX , and associated pollutants, it appears that although the short term impact has been minimal, the potential for a greater long term impact exists (Ryon *et al.*, 1984).

The vapor pressure for HMX is estimated to be between 7.6×10^{-8} to 7.6×10^{-13} atm, and consequently it is subject to uncertainty. Similarly, the Henry's law contrast is only an approximation because of uncertainty in the vapor pressure estimate (Layton *et al.*, 1987). Rosenblatt *et al.* (1991) reported the vapor pressure for HMX (25°C) 2.52×10^{-11} atm and Henry's law constant of 2.60×10^{-15} atm.m^3/mole (25°C).

Layton *et al.* (1987) studied the fractional distributions of HMX among the eight compartments (air, air particles, biota, upper soil, lower soil, surface water, sediments) of the environmental landscape representing areas in the U.S. where demilitarization operations have occurred. Distributions are based on the assumption of steady state addition of HMX to the upper soil layer, and it is clear that this compound preferentially resides in subsurface soils and groundwater. Spanngord *et al.* (1982) tested HMX and found that physical transport of volatilization, sediment sorption, and biosorption were not major factors in its environmental transport. Garg *et al.* (1991) predicted mobility of contaminants in subsurface, based on partitioning coefficients. A contaminant with high partitioning coefficient typically poses lesser migration problems. Partitioning coefficients are typically a function of the organic carbon content of the soil. Garg *et al.* (1991) showed

that TNT and HMX have higher partitioning coefficients than RDX. They concluded that the higher partitioning coefficient of HMX may cause it to be significantly less mobile. HMX has low solubility in water (5 mg/L, 25°C, Rosenblatt *et al.*, 1991).

Spanngord *et al.* (1983b) studied the impact of photolysis and biotransformation on the persistence of HMX in Holston River water and LAAP lagoons. In these environments, photolysis was found to be the dominant transformation process with half-lives ranging from 17 days in Holston River water to 7600 days in lagoon water. In the latter case, poor light transmission through the lagoon water inhibited photolytic oxidation. Major photolytic transformation products were nitrate, nitrite, and formaldehyde. Spanngord *et al.* (1983b) also, calculated the light absorption rate at selected wave lengths for HMX and RDX and found that RDX photolyzed nearly three times as fast as HMX. RDX photolysis also appears to be slightly sensitized by HMX or its photolysis products, where as HMX photolysis was not affected by presence of RDX. In HAAP water, diluted or not, HMX photolyzed at half the rate of RDX.

4.1 Physico-chemical Treatment of HMX Wastes

Adsorption: Jackson *et al.* (1976) studied HMX removal using activated carbon and resins. Both completely removed the munition compounds from HAAP wastewater. Activated carbon, however, was superior to resin. Breakthrough occurred with carbon after 176 hr and for resin after only 16 hr. Burrows (1984) determined the Freundlich isotherm constant K and n as 0.1682 L/mg and 2.169, respectively (for Filtrasorb 300, Calgon Carbon Co.). Szachta (1978) evaluated laboratory, pilot plant, and full scale plant test of carbon and resin adsorption to treat pink water from load, pack, and assemble facilities. Certain resins had a higher capacity for TNT than carbon; carbon however had a

higher capacity for RDX and HMX. Despite of the fact that polymeric absorbent resin, potentially are easier to regenerate, this has not been developed. This is, primarily because it has a lower capacity than activated carbon and non-aromatic nitrobodies such as RDX and HMX tend to rapidly breakthrough the column (Semmens, 1984).

UV-Radiation: Andrews and Osmon (1977) found that UV light completely degraded 5 mg/L of HMX within 2 hours. Noss and Chyrek (1984) studied the degradation of HMX using UV radiation, hydrogen peroxide addition, and ultrasound cavitation. Hydrogen peroxide or ultrasound cavitation had no effect on munitions degradation. During treatment with UV radiation in combination with 0.01% hydrogen peroxide, HMX was degraded rapidly (half life = 11.6 min.). Burrows *et al.* (1984) studied the decomposition of HMX by UV radiation. HMX was readily destroyed by UV radiation at rates which obey mixed zero and first-order kinetics (first half life = 1.3 min.). Ozone addition has no significant effect on photolysis rates, and hydrogen peroxide addition above 0.1% actually reduced decomposition rates. Higher treatment costs would be expected to generate UV light.

Oxidative Treatment: Chemical oxidation using potassium dichromate, potassium permanganate, or calcium hypochlorite will destroy RDX and HMX (Sullivan *et al.*, 1977). Ozonation apparently is not effective for HMX oxidation (Jain, 1976).

Reverse Osmosis: Sullivan *et al.* (1979) reports that Jackson *et al.* (1976) evaluated reverse osmosis for TNT treatment. He reports "break through" after 24 hours, which implies that reverse osmosis is not effective in treating TNT wastewaters.

Chemical Hydrolysis: Small and Rosenblatt (1974) reported that boiling with 5% NaOH will destroy HMX. NH_3, CH_2O, NO_2^-, NO_3^- are known by-products. HMX is apparently more resistant to base hydrolysis than RDX (Sullivan *et al.*, 1977). The rate of RDX and HMX base hydrolysis can be enhanced by adding a cationic surfactant catalyst (Croce and Okamoto, 1979). Epstein and Winkler (1951), found RDX hydrolysis at a greater rate and with a greater catalytic enhancement than HMX. The difference in RDX and HMX reactivity with alkalis has been used to develop an analytical procedure for the determination of HMX content of RDX.

In a more recent study by Spontarelli *et al.* (1993) they performed a large number of hydrolysis experiments with plastic-bonded explosive (PBX) 9404, which is 94.0% HMX, 3% Nitrocellulose (NC) and 3% of tris-(2-chloroethyl) phosphate (percent by weight). Base hydrolysis experiments have been performed on PBX molding powder, 2.5 cm by 2.5 cm pressed pellets (23 g), 13 cm diameter hemispheres (1.1 kg), and 4.12 cm pieces (63 g) encased in 0.3 cm steel. The amount of sodium hydroxide used in the reactions was 6 moles per mole of HMX contained in the PBX. Four moles are required for complete reaction with HMX and a two mole excess were added for reaction with the binder and plasticizer.

Upon mixing PBX 9404 and sodium hydroxide at ambient temperature, there was no visible reaction. When the mixture was heated to temperatures above 60°C, the NC binder decomposed quickly, leaving behind HMX powder. In the 70 to 80°C, range, vigorous gas evolution was observed and the mixture began to foam. When the solution boiling point was reached, 93°C, the foaming was sever enough that an antifoaming agent had to be added. During the reaction, the odor of ammonia was detected. Upon completion of the reaction, the resulting homogeneous solution was clear brown and had a pH of approximately 13. Titration of the solution to determine the amount of hydroxide consumed showed that 4.4 moles was used per mole of HMX in the PBX 9404.

They have observed that the time required for complete destruction of the PBX depends on temperature, stirring efficiency, particle size, and volume of the hydrolysis solution. Reactions in which the solution volume was 4 milliliters per gram of PBX did not react completely after many hours of heating. When the volume was increased to 15 mg/L PBX 9404, reaction was complete after several hours of boiling. Subsequent experiments were carried out with volumes of 7 and 10 mg/L of PBX. In most cases, a solution volume of 10 mg/L was used to effect complete decomposition of PBX 9404 in reasonable amount of time. Typically, the reaction is finished after 2 hours of boiling with constant stirring. The rate of HMX hydrolysis appears to become progressively slower as the reaction proceeds. Spontarelli *et al.* (1993) suggested that this may be due to "salting out" of the HMX from hydrolyzing the solution as the concentration of the product salts increases. The solubility of HMX in water is very low, 5 mg/L at 20°C, and is likely to be lower in concentrated salt solution.

Spontarelli *et al.* (1993) postulated that the rate-limiting step of the alkaline hydrolysis of HMX to be a bimolecular elimination reaction producing nitrous acid, as shown in Fig 4.2. The intermediate produced in the slow step of the reaction is very unstable at high pH, and quickly decomposes to the products shown. Of the gases products listed in Fig.4.2., they found that nitrous oxide is produced in much larger quantity than ammonia or nitrogen.

Heilmann *et al.* (1994) found pseudo-first-order and second-order rate dependencies for alkaline hydrolysis of HMX and RDX. He found out, for elevated temperatures ranging from 50 to 80°C the reaction was second-order. The temperature dependency of the rate constants was predicted using the Arrhenius-model.

Heilmann *et al.* (1994) showed that the alkaline hydrolysis of HMX in the presence of hydroxide ions is roughly 10 times slower than the alkaline hydrolysis of RDX. Since HMX is a frequent contaminant in RDX, the compounds always occur together in

explosives contaminated wastewater and at contaminated sites. Therefore, the rate of the alkaline hydrolysis of HMX may be rate limiting in the design of a treatment system using alkaline hydrolysis; however, his results showed that an increase in temperature has a higher influence on the rate of the alkaline hydrolysis of HMX than RDX. Higher temperatures (80°C) may be preferable to further increased hydroxide concentrations (more than 25 nmol/L) for treatment of HMX using alkaline hydrolysis.

Heilmann *et al.* (1994) considered with respect to their results, the alkaline hydrolysis of HMX and RDX in presence of intermediate alkaline concentrations (2 to 25 nmol OH^-/L) and elevated temperatures (above 50°C) a feasible chemical process as part of an off-line-regeneration treatment scheme.

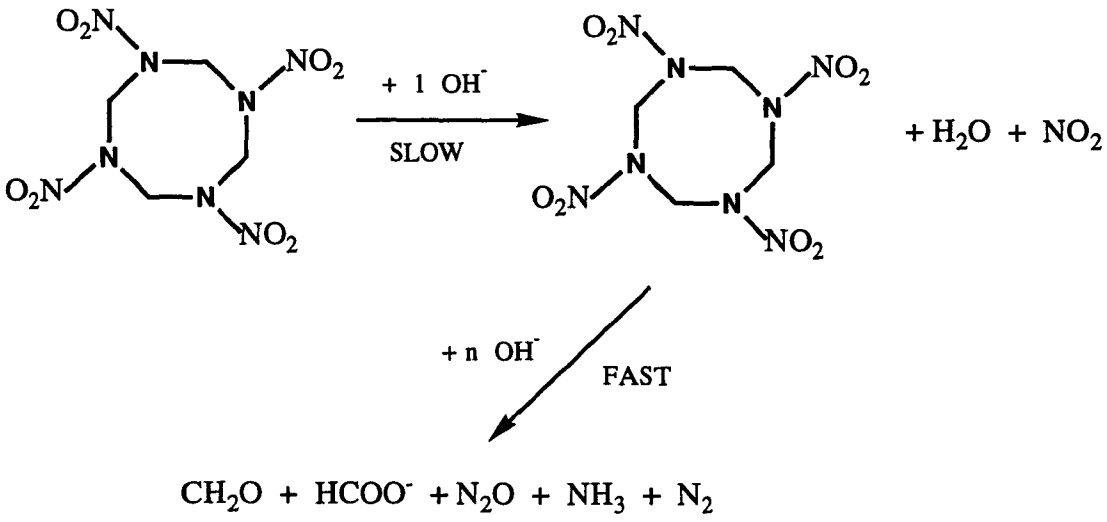


Fig 4.2 The alkaline hydrolysis reaction of HMX (Spontarelli *et al.*, 1993).

4.2 Biodegradation of HMX

Biodegradation of HMX occurs aerobically under very specialized conditions and under anaerobic conditions, the addition of nutrients is necessary (Layton *et al.*, 1987). The majority of available data indicate that HMX cannot be degraded when it is the sole source of carbon (Ryon *et al.*, 1984). Spanggord *et al.* (1982) studied microbial degradation of HMX in aerobic studies where 4 mg/L HMX and yeast extract were added to river water or river water with HMX sediments collected near the wastewater effluent. The 4 mg/L concentration was reduced to 0.1 mg/L in three days of incubation of yeast extracted-added water. A similar rate of degradation was observed with water taken below a waste out fall in the Holston River. Apparently, microorganisms are present in these materials that can aerobically degrade HMX. Under anaerobic conditions, similar results were obtained. No degradation occurred with river water, slow degradation occurred with water and HMX waste line sediment (reduced from 4 mg/L to < 0.2 mg/L in 91 days), and fast degradation occurred with yeast extract added to water and HMX waste line sediment (reduced from 4 mg/L to < 0.1 mg/L in 3 days).

Jackson *et al.* (1976) achieved 100% removal of HMX by anaerobic fermentation from waters containing 15 mg/L HMX in conjunction with supplemental carbon sources: sucrose, methanol, and hydroxyethyl/cellulose. The time required for complete removal of HMX were 5 days with methanol and 7 days with others.

Spanggord *et al.* (1983b) found that HMX was not degraded aerobically by naturally occurring microbes in samples of water from uncontaminated ponds and streams near Menlo Park, California, even with added yeast extract. However, the adapted microbes in the effluent water from the Holston Army Ammunition Plant reduced HMX concentrations by 50% (6.1 to 3 mg/L) in 2 days when 50 mg/L yeast extract was added to that water.

They were unable to culture the organism or find a chemical that was affecting the transformation. They also performed anaerobic biotransformation studies with HMX in basal salts medium containing yeast extract. They found that the amount of HMX transformed increased as the amount of yeast was increased. In another set of experiments they studied the effect of different nutrients on biotransformation rates. Glucose, peptone, sodium, acetate, and yeast extract did not significantly alter the transformation rates. When ground and washed bacterial cell were used, yeast extract was more effective in promoting HMX biodegradation.

RDX and HMX exposed to anaerobic sediment-population of bacteria and extra nutrient, both were reduced or transformed within 4 to 38 days (Ryon *et al.*, 1984).

Microbial degradation of HMX begins with non-selective, but sequential reduction of the nitro groups of HMX to their nitroso analogous (Layton *et al.*, 1987). Spanggord *et al.* (1983b) identified mono, di-, tri-, and tetranitroso-HMX from mass spectral analysis of the metabolites of HMX biodegradation. McCormick *et al.* (1984) found the same intermediates in anaerobic biodegradation experiments using sewage sludges and nutrient broth (Fig 4.3). They found no hydrazine among the HMX metabolites, although hydrazine intermediates were detected in a similar biodegradation experiment with RDX.

McCormick *et al.* (1984) also found that HMX degrades more slowly than RDX under the same conditions. They speculated that the absence of hydrazines from HMX degradation was due to a slower initial rate of attack on HMX, which prevented accumulation of hydrazine.

Composting: Garg *et al.* (1991) reported complete mineralization of RDX and not complete mineralization of HMX (53%) by a microbial consortium under anaerobic conditions, low redox, and high TOC. The products they found from composting of HMX include, mono and nitroso HMX derivatives, methanol and formaldehyde. Garg *et al.*

(1991) showed decay of HMX with time. Temperature variations for mesophilic pile were generally between 35 and 40°C and those for thermophilic pile ranged from 55 to 60°C. Total explosive concentrations in mesophilic and thermophilic piles at the end of study were reduced by 98% and 96% respectively. Composting half life for mesophilic and thermophilic of HMX were 27.7 hours and 16.5 hours respectively.

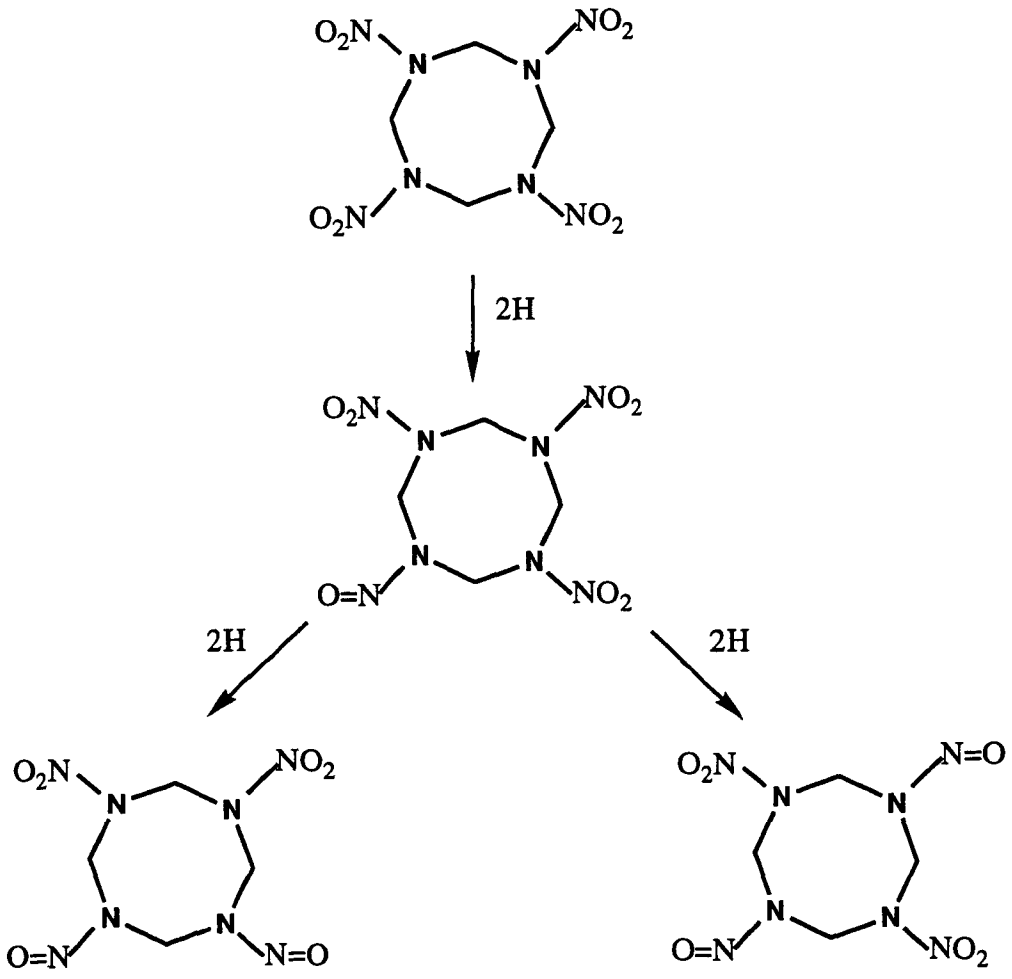


Fig. 4.3 Stepwise reduction of nitro groups on octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (McCormick *et al.*, 1984).

5 Reusing the High Explosives from Dismantled Nuclear Weapons

Until recently, there had never been a reason to treat the surplus high explosives as anything other than waste. For environmental reasons, the impetus has now turned from treating surplus materials as wastes to treating them as assets. There are new DOD and DOE directives that encourage minimizing the amount of waste generated within the Nuclear Weapons Complex wherever practical. Second, regulations that govern emissions from open burning are becoming more and more stringent, and it is expected that disposing of high explosives by open burning will soon be prohibited (Pruneda, 1993). The U.S. Army, the single manager for DOD energetic material demilitarization activities, has a self-imposed mandate to ban open burning at demilitarization facilities by 1997 (Pruneda, 1993).

The high explosives in nuclear weapons use plastic binders, which for many plastic-bonded explosives (PBXs) contain halogens such as chlorine and fluorine. Table 1.1 shows the amount and composition of high explosives expected to result from nuclear weapon dismantlement (retirement) over next ten years. Burning halogen-containing explosives generates highly toxic hydrogen chloride and hydrogen fluoride gases as well as other combustion by products. The burning of these explosives is tightly controlled: the limits for emitted halogenated species are so low, especially for hydrogen fluoride, that only small quantities-between 4.5 and 13.6 kg of these explosives can be burned at one time.

Beyond environmental concerns, burning surplus high explosives dose not sense potentially valuable materials. PBXs, which are used by the DOE in nuclear weapons, are primarily composed of HMX. Synthesizing HMX is expensive: between $20 and $28 per kilogram plus the cost of processing the HMX into a PBX and fabricating it into end-use

shapes. Fig.5.1 shows possible ways of reusing the surplus explosives in many different forms (Preunde *et al.*, 1993).

Brown *et al.* (1994), in more detailed report to support viable alternatives to destruction, studied the following DOE energetics: LX-40, PBX-9404, and Composition B-3. They concluded that demilled LX-40 can be reworked, and the resulting products meet the military specification for LX-40. Demilled PBX-9404 can be reworked, but extensive degradation of the nitrocellulose (NC) component of the formulation precludes compliance with the military specification for PBX-9404. Reworking of the demilled PBX-9404 may enhance the commercial marketability of this material since the form of demilled PBX-9404 can be significantly improved by reworking. Demilled Composition B-3 can be reworked, and the resulting products meets the military specification for Composition B-3.

HMX can also be recovered from demilled LX-04 and PBX-9404, the producing very pure HMX. Additional development is needed before HMX recovery is commercially viable, and treatment or recycle of HMX-containing wastewater needs to be developed.

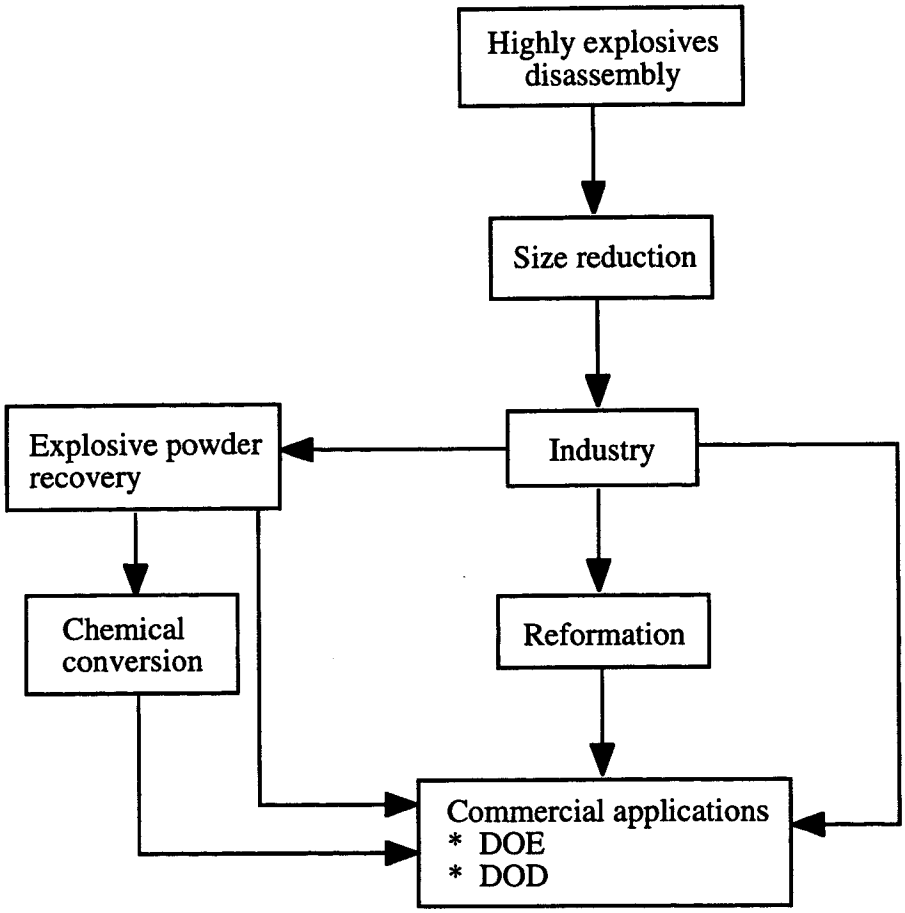


Fig. 5.1 Various processes to make possible the reuse of expensive high explosives.

6 Summary

TNT: Activated carbon is a proven method for removing TNT from wastewater, But there is no proven, full scale technique for regenerating or disposing of the spent carbon. UV-Radiation in combination with hydrogen peroxide is effective treating aqueous solutions of TNT, and the resulting effluent is safe for disposal. This method is not very efficient for large scale treatment of TNT. Oxidative treatment is not very promising, and there is not enough information about the end products. Information on reverse osmosis is mixed and it does not seem that this is an effective method for TNT treatment. We do not expect hydrolysis to be significant degradation mechanism in natural water. There is not enough information at high pH and elevated temperature on the chemical hydrolysis of TNT.

TNT biotransforms aerobically and anaerobically, and there is no information on combined aerobic and anaerobic treatment technique, which may be able to mineralize TNT. Except for white rot fungi, nutrients increase the rates of the biological reaction and in some cases, enables mineralization.

New oxidative pathways that avoid the accumulation of toxic intermediates and lead to mineralization are being characterized for explosives such as the highly substituted nitroaromatic compound TNT. Once mechanisms have been well characterized, progress may be made towards the construction of new metabolic pathways to enhance mineralization.

Composting was not a promising method to mineralize TNT.

RDX: Activated carbon is a proven method for removing RDX from wastewater, but there is no proven, full scale technique for regenerating or disposing of the spent carbon. Using UV-radiation for groundwater remediation is problematic because of hazardous

decomposition intermediates. Using UV radiation and ozone may be effective in treatment of wastewater containing 1 to 20 mg/L of RDX and cost competitive with activated carbon adsorption for small systems. UV-radiation may not be suitable when RDX production wastewater contains other UV-absorbents. Information on oxidative treatment and reverse osmosis does not seems promising. Chemical hydrolysis in high pH and elevated temperature will destroy RDX. It is expected that this method will be a cost effective only for bulk quantities, since alkaline hydrolysis of dilute solutions of RDX will require large amounts of base and great waste lines containing nitrite and nitrate.

There is no conclusive evidence to show that RDX can be degraded or transformed aerobically. RDX is readily degraded anaerobically in the presence of suitable organic cosubstrates to some known and unknown by-products, and some mineralization occurs.

There is some evidence to show that RDX transformation and mineralization occur in composting.

HMX: Activated carbon is a proven to method for removing HMX from wastewater, but there is no proven, full scale technique for regenerating or disposing of the spent carbon. UV-radiation degrades HMX, but is expensive. Certain chemical oxidants will destroy HMX. Reverse osmosis is not effective for HMX treatment. Base hydrolysis of bulk quantities of HMX at elevated temperature and pH is an effective method to destroy HMX, and appear to be cost effective.

Biodegradation of HMX occurs aerobically under very specialized conditions. Under anaerobic conditions, with nutrient addition biotransformation and degradation may be possible.

Complete HMX mineralization has not demonstrated in composting.

Reusing of HMX from dismantled nuclear weapons seems cost effective.

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