



# PERFORMANCE EVALUATION DEMONSTRATION

Performance and Cost Evaluation  
March 1998



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**13. ABSTRACT (Maximum 200 words)**  
An independent evaluation of a field-scale plant designed for the treatment of explosives-contaminated groundwater was performed. The evaluated facility was constructed at the Cornhusker Army Ammunition Plant. The target compounds were trinitrotoluene (TNT), trinitrobenzene (TNB), (N)-trinitro-1,3,5-triazacyclohexane (RDX) and other nitrocompounds. The process chosen was oxidation with a combination of ozone and hydrogen peroxide (Peroxone). The plant was capable of treating 25 gal-min<sup>-1</sup> with a dose of ozone as high as 55 mg-L<sup>-1</sup> in each of six bubble column reactors with hydraulic retention times of 24 minutes per reactor. Hydrogen peroxide was fed in the influent water prior to ozonation. The purpose of the study was to determine the feasibility and projected costs for reducing explosive compounds level to 2 ug-L<sup>-1</sup> for the specific nitro-compounds and 30 ug-L<sup>-1</sup> for total nitrocompounds. The demonstration was carried out over a period of three months.

In summary, the pilot plant, as designed and constructed, performed well. It continuously produced treated effluent approaching drinking water standards before the granular activated carbon (GAC) unit processes, which primarily served as a safety net to ensure compliance with State of Nebraska discharge standards during this demonstration. One contaminant of concern, TNB, only satisfied the demonstration goal of less than 2 ug/L<sup>-1</sup> 25% of the time during the second phase of the demonstration. During Phase II, the plant flow rate was increased from 13 gpm to 25 gpm. The projected cost per 1,000 gallons (\$13.83) was sufficiently high, thus making the pilot plant system economically noncompetitive when compared with the current treatment standard of GAC with an estimated treatment cost of \$2.86/1,000 gallons.

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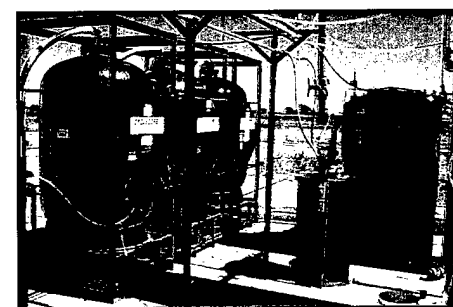
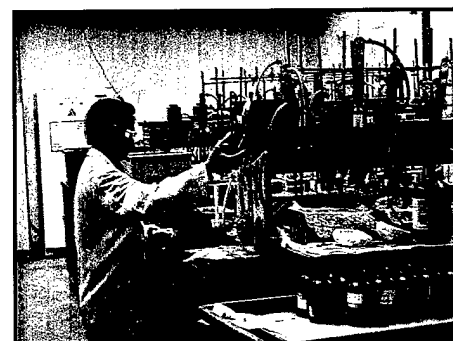
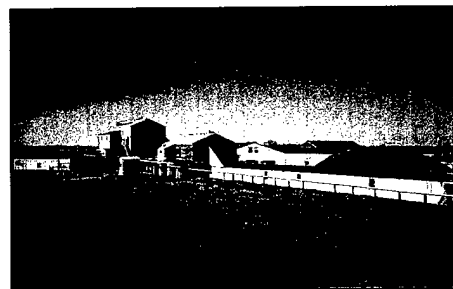
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**Independent Evaluation of the  
Perozone Demonstration at  
Cornhusker Army Ammunition Plant,  
Nebraska**

**March 1998**

# Peroxone Demonstration Overview

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# *Acronyms and Abbreviations*

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µg/L	microgram per liter
A&E	Architectural and Engineering
ACOE	Army Corps of Engineers
AFOTEC	Air Force Test and Evaluation Center
AOP	Advanced Oxidation Processes
AR	Army Regulation
BQL	below quantitation limit
CAA	Clean Air Act
CAAP	Cornhusker Army Ammunition Plant
COC	contaminants of concern
CONUS	Continental United States
cu ft	cubic feet
DESA	Defense Evaluation Support Activity
DoD	Department of Defense
DOE	U.S. Department of Energy
EFF	decontaminated groundwater
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FTE	full-time equivalent
GAC	granular activated carbon
gpm	gallons per minute
HMX	High Melting Explosive (cyclotetramethylenetetranitramine)
HPLC	High Performance Liquid Chromatography
IDLH	immediately dangerous to life and health
INF	influent groundwater
kWh	kilowatt hours
LOE	level of effort
LOX	liquid oxygen
mg/L	milligram per liter
mg/mg	milligram per milligram
mgd	million gallons per day
MIB	methylisoborneol
NAAQS	National Ambient Air Quality Standards
NEPA	National Environmental Policy Act
NIOSH	National Institute for Occupation Safety and Health
NPDES	National Pollutant Discharge and Elimination System
NPL	National Priority List
O&M	operations and maintenance
ORP	oxidation reduction potential
oz	ounce

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POPS	Peroxone Oxidation Pilot System
ppb	parts per billion
RDX	Royal Demolition Explosive (1,3,5-trinitro-1,3,5-triazine, or cyclotrimethylenetrinitramine, also known as cyclonite)
scfm	standard cubic feet per minute
SERDP	Strategic Environmental Research and Development Program
SOW	statement of work
SW	Solid Waste
TCLP	Toxicity Characteristic Leaching Procedure
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TOC	total organic carbon
USAEC	U.S. Army Environmental Center
UV/OX	ultraviolet radiation and oxidation
WES	Waterways Experimentation Station (U.S. Army Corps of Engineers)

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# 1 Executive Summary

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## 1.1 Introduction

The U.S. Army Environmental Center (USAEC) implemented the Peroxone groundwater treatment plant demonstration to study the performance and analyze the cost of the new Peroxone technology. The effort is part of the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP).

TRW and their subcontractor, Montgomery Watson, demonstrated the Peroxone system shown in Figure 1 at the Cornhusker Army Ammunition Plant (CAAP) in Grand Island, Nebraska. The CAAP groundwater was contaminated from the manufacture and loading of explosives for World War II, the Korean Conflict, and the Vietnam Conflict, and was placed on the National Priority List (NPL) (i.e., Superfund site). Therefore, CAAP was a candidate for the Peroxone technology, which is suitable for remediation of groundwater contaminated with residuals and wastes from the manufacturing and loading of conventional explosives products.

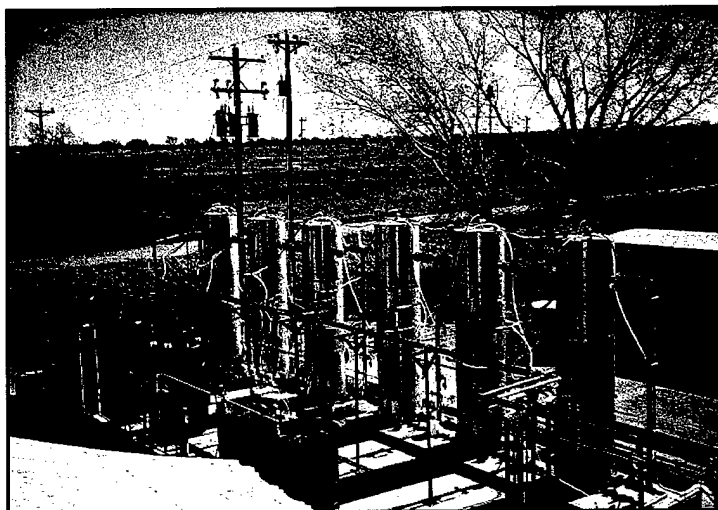


Figure 1. The Peroxone treatment plant was assembled on site. The independent evaluators and demonstration operators worked together from the trailer (on the right).

## 1.2 Performance Results

The principal measure of performance of the system was the ability to remove the explosive contaminants cyclonite (Royal Demolition Explosive or RDX); 1,3,5-trinitrobenzene (TNB); and 2,4,6-trinitrotoluene (TNT) to 2.0 micrograms per liter ( $\mu\text{g/L}$ ) or less, and discharge no more than a total of 30  $\mu\text{g/L}$  of explosives manufacturing residual-contaminated groundwater. Concentrations of TNT and TNB began as high as 500  $\mu\text{g/L}$  before treatment. RDX concentrations were as high as 40  $\mu\text{g/L}$ .

The Peroxone system operated at two volumetric flow rates of groundwater: 13 gallons per minute (gpm) and 25 gpm. At 13 gpm, the system effectively removed the target contaminants to below 2.0  $\mu\text{g/L}$  100% of the time. At 25 gpm, the system removed all the contaminants to the desired level except for TNB, which was removed to 3.5  $\mu\text{g/L}$  90% of the time.

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At 25 gpm, the system removed all the contaminants to the desired level except for TNB, which was removed to 3.5  $\mu\text{g/L}$  90% of the time.

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### 1.3 Cost Results

The evaluation of the Peroxone system included comparing the cost of the system with another innovative advanced oxidation process (AOP) groundwater treatment technology, ultraviolet oxidation (UV/OX), and the traditional granular activated carbon (GAC) system. The oxygen source that supports the ultraviolet oxidation process is ozone.

Theoretical Peroxone costs were used in the comparison. The theoretical costs were within 20% of the operational costs observed at the CAAP demonstration. Theoretical costs were used instead of observed operational costs due to perceived process inefficiencies that should be overcome with more pilot-scale development and

proper scaleup to a field-scale prototype. General *estimated* cost comparisons are presented in Table 1.

The cost per 1,000 gallons of treated water is calculated in detail for all three systems in Section 5. The costs of the two AOP systems, Peroxone and UV/OX, are considered to be within the margin of estimation. With design improvements of the Peroxone system, the cost could be reduced. The amount of savings is unknown without further demonstrating selected modifications of the Peroxone pilot plant system.

Table 1. GAC, UV/OX, and Peroxone Estimated Cost Comparison

Process	Cost
GAC	\$2.86/1,000 gallons
UV/OX	\$9.66/1,000 gallons
Peroxone	\$13.83/1,000 gallons

### 1.4 Conclusions

The pilot plant, as designed and constructed, performed well. It continuously produced treated effluent approaching drinking water standards before the GAC unit processes, which primarily served as a safety net to ensure compliance with State of Nebraska discharge standards during this demonstration. One contaminant of concern, TNB, only satisfied the demonstration goal of less than 2 µg/L 25% of the time during the second phase of the demonstration. During Phase II, the plant flow rate was increased from 13 gpm to 25 gpm. The projected cost per 1,000 gallons (\$13.83) was sufficiently high, thus making the pilot plant system economically noncompetitive. The redundancy within the pilot plant influenced this projected high cost. Cost drivers include the number of contactors, the support plumbing, and the ozone generation.

### 1.5 Recommendations

A field-scale prototype 1,000-gpm system should not be attempted at this time. More pilot-scale developmental work needs to be accomplished to better define and understand the technical

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issues associated with maximizing Peroxone generation, optimizing reactant dosages, maximizing ozone mass transfer, and improving ozone generation on site. Moreover, consideration should be given to integrating a Peroxone unit operation process with a GAC polishing unit in an integrated unit process train.

The redundancy within the pilot plant influenced this projected high cost.

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## 2 Introduction

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### 2.1 Background

Some DoD installations have groundwater contaminated with energetic material resulting from the manufacture, loading, assembly, and packing of conventional munitions. Within the U.S. Army, there are an estimated 20 such installations (References 1 and 2).

The primary method for the removal of the energetic material from groundwater involves the use of GAC adsorption. However, GAC operations merely transfer the contaminant form, not eliminate it, and can be costly depending on the extent of contamination. Processes that are more cost effective than GAC and result in the immediate destruction of contaminants are being sought for the restoration of DoD sites. Rapidly developing AOPs involve the use of various chemical processes to produce *hydroxyl radicals* for the oxidation of contaminants contained in the groundwater. **Hydroxyl radicals are powerful oxidizers capable of recombining with other chemicals to effect water purification.** The specific chemical products of a hydroxyl oxidation depend on the contaminants treated. These technologies have been developed commercially and by government laboratories as an alternative process to remove groundwater contaminated with materials used to manufacture conventional explosives. **The Peroxone groundwater treatment system is an AOP that involves the use of ozone in conjunction with hydrogen peroxide for the treatment of contaminated groundwater** (see Figure 2). Figure 3 illustrates the resources required for the production of Peroxone. This report will not evaluate UV/OX or GAC performance, but will include a cost comparison of the UV/OX, Peroxone, and GAC processes.

The USAEC is investigating the technical and economical applicability of the Peroxone AOP for the removal of explosives contamination from groundwater as part of the DoD ESTCP. An initial ESTCP effort was conducted by the U.S. Army Corps of Engineers Waterways Experimentation Station (ACOE WES). This effort consisted of a small-scale pilot demonstration at the Cornhusker Army Ammunition Plant (CAAP) in Grand Island, Nebraska, during 1995. The WES study was a 4-week on-site operation of a Peroxone groundwater treatment system operating at 0.9 gpm, which initiated this demonstration effort. The final results of the WES study were published in April 1997 (Reference 3) after this field demonstration was completed. Some preliminary results of the WES study were used to guide the planning efforts of this demonstration.

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GAC operations merely transfer the contaminant form, not eliminate it, and can be costly depending on the extent of contamination.

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Figure 2. The Peroxone treatment plant was comprised of six water towers, oxygen tank, ozone generator (not seen), three GAC filters (behind water towers), and holding tanks.

USAEC tasked the Defense Evaluation Support Activity [DESA (now transitioned to the Air Force Operational Test and Evaluation Center or AFOTEC)] to independently evaluate the Peroxone groundwater treatment system during a small-scale demonstration. The DESA evaluation team was independent from the demonstration effort to ensure an objective evaluation. TRW Space and Technology Division was the prime contractor for system development and demonstration. Montgomery Watson was the lead TRW subcontractor for system development, including design, construction, installation, operation, and demobilization of the Peroxone ground-

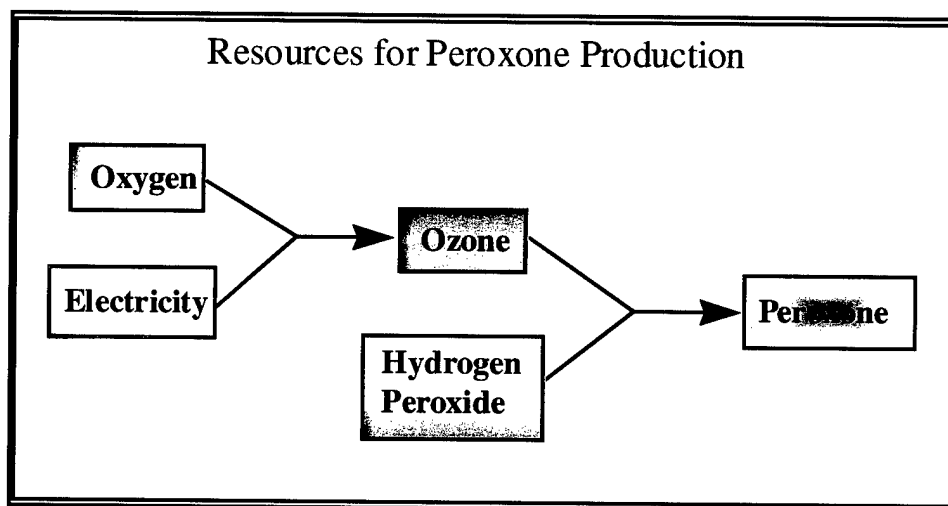


Figure 3. In the production of Peroxone, the excess ozone in the aqueous phase is "scavenged" by sodium thiosulfate.

water treatment system plant. The demonstration plan was prepared in July 1996 (Reference 4). The demonstration was conducted from September to November 1996. The demonstration took place at the CAAP in Grand Island, Nebraska, where the groundwater is contaminated with various energetic compounds including TNT, RDX, TNB, and other nitrocompounds. The CAAP was also the demonstration host for the pilot-scale test previously conducted by WES.

The only regulatory issues for the demonstration of the Peroxone technology are the State of Nebraska requirements for the effluent (see Section 3).

## 2.2 Site Selection

USAEC selected the CAAP near Grand Island, Nebraska, as the site of the Peroxone treatment system. Grand Island has a population of about 40,000 and is approximately 5 miles from the CAAP. The CAAP is located on 11,936 acres and was constructed in 1942 by the U.S. Army for the production of artillery rounds, bombs, boosters, and supplementary charges. The plant operated intermittently for 30 years, with recent operations ending in 1973. Figure 4 is a current photograph of one of the ammunition factories known as "load lines."

The groundwater at the CAAP was contaminated with nitrocompounds as a result of disposal practices that are now considered poor by today's standards. This was common in the 1950s and 1960s in both the military and civilian sectors (i.e., collecting process wastewaters in often unlined evaporation ponds, pits, and

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On July 22, 1987, the CAAP was listed as a site on the NPL, also referred to as a Superfund site.

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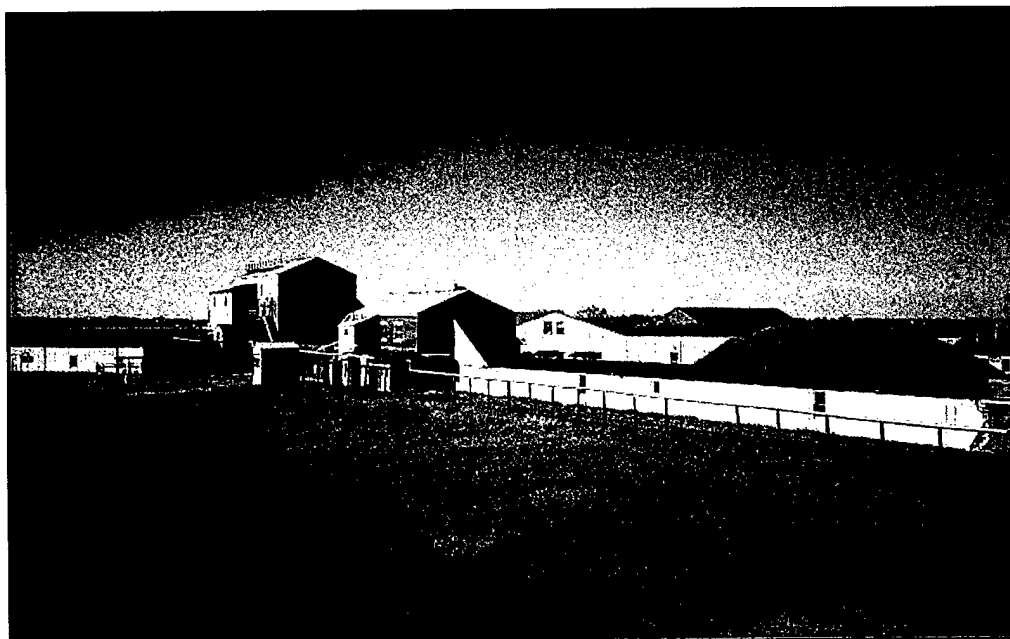


Figure 4. The Peroxone system was set up beside one of four inoperable load lines (seen above) for the manufacture of ammunition at the CAAP.

lagoons). Subsequently, on July 22, 1987, the CAAP was listed as a site on the National Priority List (NPL), also referred to as a Superfund site. In addition, the nitrobody-contaminated groundwater migrated approximately 4 miles beyond the CAAP boundary and approximately 2 miles into the Grand Island city limits. Figure 5 shows the contaminant plume extending into Grand Island.

A contaminant of major concern was cyclonite, or RDX, because it was spreading outside the CAAP boundary. Pollutants resulting from the manufacture of RDX (Royal Demolition Explosive) can also include HMX (High Melting Explosive), and nitrate-nitrite nitrogen. Information on the human health effects resulting from

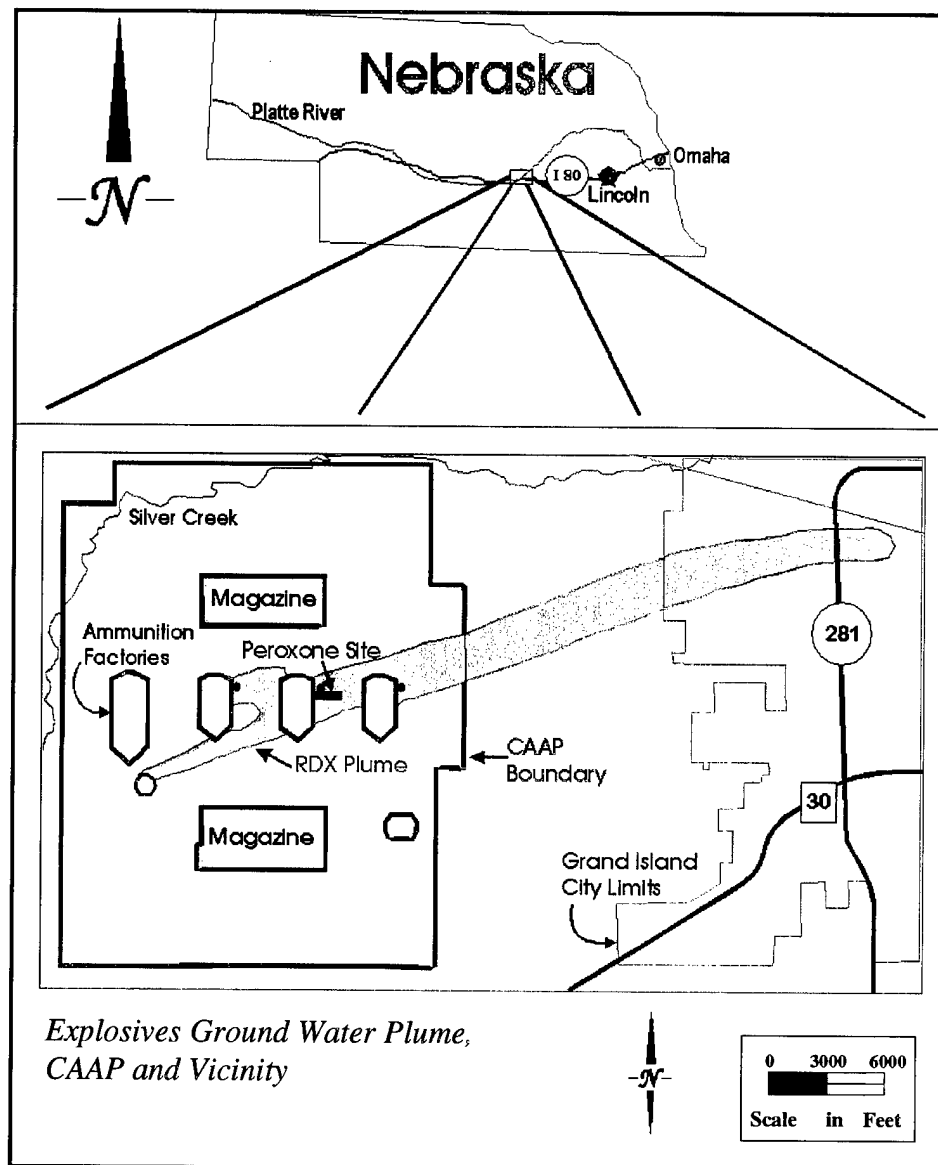


Figure 5. Location of the Cornhusker Army Ammunition Plant and the RDX contaminant plume extending into the City of Grand Island, Nebraska. The Peroxone treatment plant demonstration is shown adjacent to the third factory from the left (Reference 8).

overexposure to RDX primarily comes from workers exposed during munitions production. At high concentrations, RDX affects the central nervous system and may cause headaches, seizures, and unconsciousness. In addition, RDX may cause irritation of the skin, eyes, and upper airways (References 5 and 6).

There are no federal enforceable standards for RDX in drinking water. The U.S. Environmental Protection Agency (EPA) has developed *recommendations* for safe levels in water. This recommendation, called a Lifetime Health Advisory, is **2 parts per billion (ppb) or 2 µg/L of water**. This means the EPA believes humans can safely consume water containing RDX at or below 2 ppb (2 µg/L) for a lifetime without causing adverse health effects (Reference 7).

The contaminated aquifer in and around the CAAP is approximately 6-miles long and 0.5-mile wide, and the total volume is approximately 7.2 billion gallons. Sources of the contaminants in the groundwater were the explosives-manufacturing wastewater ponds and leachpits located at the center of the plant.

USAEC conducted a site characterization study to identify the types, concentrations, and extent of the substances associated with the CAAP groundwater. RDX levels were found to be over 50 ppb in some areas. The results of the site characterization are found in Reference 8. With initial characterization complete, USAEC conducted technology screening activities as part of a feasibility effort and determined a Peroxone system could be effective as a remediation method for this contaminated groundwater.

The site was selected based on the characteristics of the CAAP groundwater and the opportunity to demonstrate a candidate innovative technology for explosives-contaminated groundwater cleanup. Prior to the inception of this innovative remedial technology demonstration, U.S. Army officials preferred two groundwater cleanup alternatives to protect human health and the environment. One alternative addressed the groundwater within the boundaries of the installation, and the other addressed the affected groundwater in the off-post area, or distal end (Reference 8). Both the preferred alternatives utilized GAC as the solution for the removal of the nitroaromatics and other organic contaminants. However, this was only a contaminated medium transfer process, and not a final technical solution for contaminants destruction. One remedy in the feasibility study considered as a remedial action alternative was "enhanced oxidation," i.e., the utilization of ozone and hydrogen peroxide, or Peroxone. This demonstration project provided the forum for this concept to be considered.

USAEC requested the contaminants TNB, TNT, and RDX be specifically analyzed. While these contaminants are target contaminants of concern (COCs) and the focus of the performance evalua-

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A contaminant of major concern was cyclonite, or RDX, because it was spreading outside the CAAP boundary.

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At high concentrations, RDX affects the central nervous system and may cause headaches, seizures, and unconsciousness.

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### ***Peroxone Reactions***

The kinetics associated with the reactions that occur with Peroxone oxidation to establish these hydroxyl radicals are:

1. Complex,
2. Occur in a series of reactions,
3. Not instantaneous,
4. Probably temperature dependent, and
5. Neither fixed nor stable.

These reactions are described in References 3 and 10, and especially in Chapter 2 of Reference 3. The steady state hydroxyl concentration model reported as equation #26 on page 13 of Reference 3 and the supporting detailed chemistry narrative should be reviewed by all interested technical parties. By WES's own admission (Reference 3/page 18), more work with this model is needed, but for the present, it serves as a credible baseline. This WES report documents the *pilot*-scale demonstration accomplished by WES with their small-scale Peroxone Oxidation Pilot System (POPS) performed at CAAP in 1995. This latest demonstration is an extension of the POPS, but at a larger scale. The POPS unit operated at 0.9 gpm, and the new system independently evaluated in this report was to operate at 50 gpm (but later only operated at 25 gpm because of limitations with the existing wells' production capacity).

tion of the Peroxone system, all the nitro bodies tested were examined for levels considered to be a health hazard (see Table 5 in Section 3). Changes in the concentration of HMX were also monitored as an associated COC. HMX, similar in structure to RDX, is separately manufactured. However, a small amount of HMX can be formed in the manufacture of RDX, and for this reason, this additional parameter was monitored during the evaluation of this demonstration (References 6 and 9).

### **2.3 Peroxone Chemistry**

Peroxone chemistry is an AOP that utilizes the synergistic results of combining two already effective oxidizers (hydrogen peroxide and ozone) into even more effective hydroxyl radical oxidizers. The purpose of this project was to demonstrate a field-scale system operating at a volumetric flowrate of 25 gpm, with actual contaminated groundwater under realistic field conditions, and gather resulting analytical performance data as well as cost data.

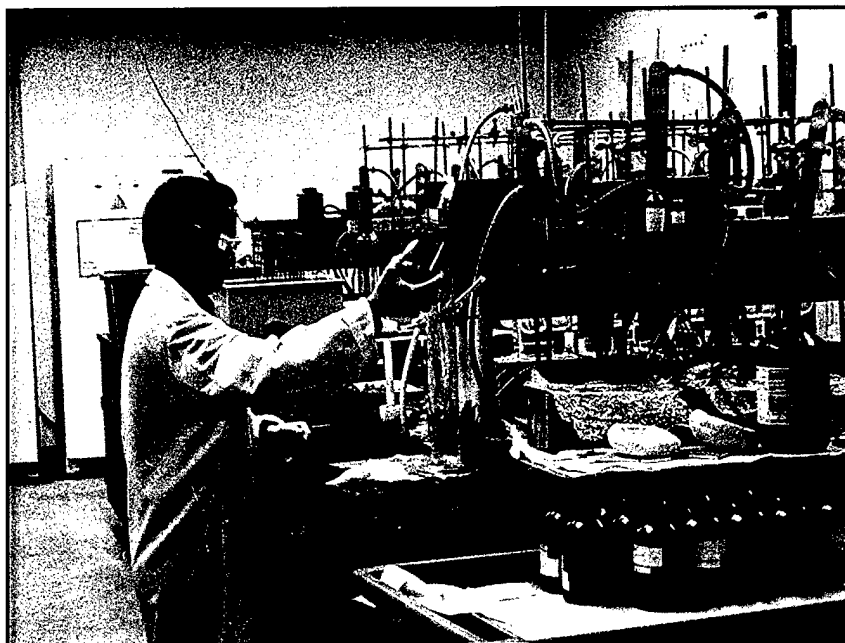
Unfortunately, the WES report (see sidebar) was not published until April 1997, **after** this larger scale demonstration was completed. The impact of the reporting untimeliness is that some of the knowledge gained by the WES POPS demonstration was not available to be applied to this larger scale demonstration. It is not clear how much of the knowledge gained by the 1995 WES effort was available to readily assist the USAEC/DESA/ACOE effort addressed in this report. Based on interviews and observations, some technology transfer did occur, but not as much as could have occurred if the WES report been completed and available to the demonstration subcontractor. As an example, if the demonstration subcontractor had access to the completed final report, perhaps more attention would have been placed on pH and molar ratios of the two reactive constituents; thus start up, optimization, and the subsequent performance might have been better.

The reactions that occur in an AOP system are nonselective. This means the two reacting constituents will react with themselves to produce Peroxone\*, **and** they will independently react with the contaminant constituents in the flowstream on a random basis. In a given flowstream where there are constituents that can be oxidized, and as hydrogen peroxide and ozone are introduced, there will be two types of competing chemical reactions occurring. These are:

1. Hydrogen peroxide and ozone oxidizing flowstream contaminants independently of one another.
2. Hydrogen peroxide and ozone synergistically reacting with one another first, to produce the Peroxone hydroxyl radicals (more effective oxidizers), and then oxidizing flowstream contaminants.

\* Peroxone is a process descriptor used to describe the fact that ozone and hydrogen peroxide were utilized simultaneously to effect a concentration of hydroxyl radicals.

Key to designing, constructing, and operating an effective Peroxone system is to minimize the first series of reactions, and maximize the second series of reactions. The high cost of ozone generation and the follow-on mass transfer of the ozone gas to the bulk of solution in the liquid phase flowstream requires more attention on process activity in the interest of economics. The cost of ozone generation is the process driver. *A critical requirement for Peroxone systems is to determine how to accomplish cost-effective feeding of the ozone and hydrogen peroxide in real time, to ensure maximum oxidative destruction of the targeted contaminants is achieved, but not at the expense of overdosing and wasting resources.*



*A chemist at the laboratory conducts the explosive loading waste residual analysis from a sample taken during the demonstration.*

The constituents in the contaminated water need to be identified and quantified to predict the **oxygen demand** that will be placed upon the system. With the concentrations of these constituents known, approximate calculations of the amount of hydrogen peroxide and ozone required for the system to properly operate can be determined for process operations. These constituents can be described in the following three categories:

1. Inorganic salts, the cations of which are not in their highest valence state
2. Aliphatic hydrocarbons (straight chain molecules)
3. Aromatic hydrocarbons (benzene ring chain molecules)

The target COCs, nitroaromatics, are in the third grouping, and will be the most recalcitrant to be destroyed. The benzene ring requires a greater amount of energy to break and oxidize than the other potential constituents in the contaminated water. The complicating factor is that all three constituents will be reacted upon by not only Peroxone, but also by hydrogen peroxide and ozone. Peroxone is most effective, thus the desire is to generate Peroxone and allow it to do the destructive oxidation rather than its constituents. Hydrogen peroxide is only limited in its effectiveness against aromatic molecules (Reference 11). These competitive simultaneous reactions are illustrated in Table 2.

These competitive simultaneous reactions, sometimes described as dual ozone/hydroxide mechanism reactions, are described in

Table 2. Peroxone Competitive Simultaneous Reactions.

Contaminated Water Constituents	Reactants		
	Hydrogen Peroxide (H <sub>2</sub> O <sub>2</sub> )	Ozone (O <sub>3</sub> )	Peroxone (OH)
Inorganic Salts	++	++	+++
Aliphatic Hydrocarbons	++	++	+++
Aromatic Hydrocarbons	+	++	+++

Note: The more +s, the more effective the oxidizer will be at reacting with the constituent in the contaminated groundwater.

Reference 12. In addition, some aromatic hydrocarbons are more readily destroyed than others by oxidative means. There is some indication that symmetrical molecules are more difficult to destroy (Reference 1). Of the target COCs in this demonstration, HMX, RDX, and TNB are symmetrical. TNB is illustrated in Figure 6. During this demonstration, TNB was the most difficult nitrobody to destroy.

The following tools might support optimizing the Peroxone reaction over the other competitive simultaneous reactions :

- Operating the system at **elevated pH** ranges which favor the amount of hydroxyls available.
- Mixing hydrogen peroxide and ozone together independent of the contaminated water flowstream

to avoid the competitive nonselective reactions with the flowstream constituents in a **prereactor** vessel.

The WES report (Reference 3/page 17) recommends increasing the pH, and further advises that a pH value of 9 is considered the upper limit. However, this recommendation is not explained. One reason for the recommendation may be that hydrogen peroxide stability is affected by pH. At a higher pH, the stability of hydrogen peroxide deteriorates very rapidly (Reference 13/ page 5). Also, at pH values above 9 there are prohibitions for release of such waters to receiving streams in discharge permits, and would thus require neutralization and greater process costs. At higher pH values, there is the risk of precipitating out metal salts and fouling the unit process equipment.

The concept of a prereactor would avoid the competing reactions problem, however, the hydroxyl radical produced would probably have a half-life measured in milliseconds, and would have to be sustained via a steady-state continuous reaction, by being fed the two components (hydrogen peroxide and ozone) on a continuous basis.

*Without knowing how to maximize the desired reaction of Peroxone generation and minimize the other competing and less effective reactions, cost effectiveness of treatment will be very difficult to control.* A parallel to this Peroxone process is chlorine chemistry in domestic wastewater treatment. In this application, other constituents create a chlorine demand on the chlorine added to the wastewater before a free chlorine residual can be established to destroy the pathogenic bacteria in the flowstream. The Peroxone system may be effectively managed by determining the parameter that would best serve as the residual indicator of effective oxidation

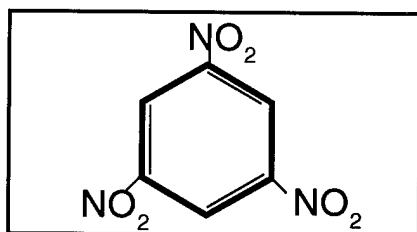


Figure 6. TNB chemical structure

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in order to determine the optimum cost effective treatment. Such residual indicators would have to be immediately measured by field techniques, and may be a combination of pH, dissolved oxygen, ozone concentration, total organic carbon (TOC), and/or oxidation reduction potential (ORP). Demonstration efforts such as this one should move the professional community closer to determining this system management factor.

## 2.4 System Design Review

The pilot plant demonstration system employed was not designed in the conventional manner common to most Architectural and Engineering (A&E) services deliverables. The approach may have undermined the effectiveness of the end-product from a cost/scaleup perspective. Instead of giving the design team the required final effluent standards, and allowing them to design a functional system around the technology chosen, the team was given specific unit process planning parameters to be employed (Reference 14). The planning factors for which the design of this pilot plant was to be based upon were very thorough and based on the preliminary results of the WES POPS demonstration effort concluded at the CAAP. Although the WES report was not released until April 1997, this demonstration pilot plant was very similar in unit process treatment train layout to the WES POPS system. Moreover, the WES POPS system was similar to the pilot plant used by the Metropolitan Water District of Southern California, based in Los Angeles (References 15, 16, and 17). The only exception was that in lieu of using GAC filters as the final unit process, the Southern California plant used dual media filters. The Peroxone pilot plant system performed functionally well and achieved very high levels of contaminant destruction. However, as will be reported in this independent evaluation, the system was not cost effective. This demonstration is similar to both the WES POPS plant (Reference 3) operated in 1995 and to the pilot plant operated by the Metropolitan Water District of Los Angeles in 1989–1990 (References 15 and 16). Whereas the POPS plant targeted nitrobody contaminants, the Los Angeles pilot plant targeted taste and odor contributing contaminants in drinking water. In addition, the Los Angeles plant dealt with contaminant concentration ranges in the parts per trillion range (not ppm). The parts per million range is the order of magnitude that nitrobody are commonly found in groundwater at U.S. Army sites where this technology could be used. Much less ozone is required to destroy contaminants in the parts per trillion range. Clearly, these are different applications of this technology, and scaling up such efforts has the potential to magnify any redundancies and impact cost.

The following planning guidance was the basis of this design:

1. Transportable by common freight carrier
2. Volumetric flow rate: 50 gpm
3. Mass ratio of hydrogen peroxide to ozone: 0.3 milligram per milligram(mg/mg)
4. Ozone dose: 180 milligrams per liter (mg/L)
5. Ozone dosage maximum: 10% by weight
6. Diffusers: bubble
7. Contactors: multiple 20-foot high and unpacked columns (additive alternate - packed)
8. Flow type: co-current (additive alternate: countercurrent)
9. Hydraulic retention time: 120 minutes (overall)
10. Scale up level: 1,000 gpm (without further comment or justification)
11. Backup: GAC with a 30 minute retention time

As a result of these unit process parameter guidelines and a tight timeline (the Notice to Proceed was given to the demonstration subcontractor in May 1996 for a demonstration start-up in August 1996), **a redundant and expensive system was fielded and tested.** Six stainless steel contactors were chosen. Stainless steel has the ability to be easily relocated for further utilization and provides good resistance to ozone. However, six contactors were employed, and as the results demonstrate, the majority of the contaminant destruction, with the exception of TNB, occurred in the first three reactors (see Figure 22 in the Results section).

Neither of the two existing wells were pump tested in advance to determine if they could satisfy the 50 gpm design flow rate. When they were tested, they could not satisfy the flow rate. Another well was tested and could only produce 25 gpm. In response to the limited volumetric flow rate available, the height of the six series contactors was substantially reduced from 20 feet (as originally planned) to 12 feet. [The precursor WES pilot plant used four contactor vessels, 6 inches in diameter and 14-foot high (Reference 3).]

The groundwater quality was not fully understood prior to system design. Influent characteristics were not totally known, and as a result, oxygen demand was not known. In response, a number of mass ratios and ozone dosage rates were experimented with during the demonstration. This impacted optimization efforts, as it detracted from attaining steady state conditions during the scheduled time for system start up.

An equalization tank was omitted from this pilot plant, although a tank was used in the WES POPS (holding tank). Unfortunately, the chemical characteristics of the contaminated groundwater were not

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constant, and steady state conditions during the demonstration were not achieved.

A baffled equalization basin may have negated or overcome some of these matters that may have detracted from system performance; a baffled system would have disrupted any plug flow, and would have encouraged mixing and stabilization of the influent characteristics. In addition, because a maximum ozone dosage of 10% was stipulated by the Ad Hoc Planning Group (Reference 14), this required a liquid oxygen (LOX) system to be used to support the ozone generator. However, there may be an alternative: using an electrochemical generation system. There are commercial sources now available that report of manufactured systems that can produce ozone gas phase concentrations between 10 to 18 percent from water (Reference 18). Moreover, this ozone generation could possibly be done in situ, in the influent flow stream.

Finally, the GAC backup unit was oversized. The GAC system utilized in the Peroxone demonstration consisted of three 1,000 lb GAC filter vessels for a total of 3,000 lbs of GAC. The system was designed to provide ten minutes of retention time each at a flow rate of 25 gpm, for a total GAC system retention time of 30 minutes. A unit as small as one 500-pound filter might have sufficed (Reference 19). However, the activated carbon system was not intended to be an integrated unit process for the system design of the pilot plant. The real intent was that of a safety net to ensure there were no releases to the environment, in case a Peroxone contactor or other subcomponent failed. In summary, redundancy was intended in the system design.

To the credit of the demonstration subcontractor, they were able to design by integrating the unit process parameter planning guidelines, fabricate and assemble the connecting electrical and mechanical system components, and carry out the site planning and site preparation all with congruent hydraulic and energy gradelines in a record short period of time. Moreover, the system worked and performed well, and generated much useful data (see Section 4.7). In addition, USAEC officials had the foresight to not totally dismantle the pilot-scale system at the CAAP. Most of the system remains in place, and is available to support further test demonstrations of the system. A large part of the project test and evaluation dollars spent on this project are capital equipment funds (53%, see Table 17) that can be reutilized to support follow-on work with the continued goodwill and support of the host CAAP and Nebraska regulatory officials.

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...they were able to design, fabricate, and assemble the system components and carry out the site planning and preparation in a record short period of time.

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## 2.5 System Description

The Peroxone groundwater treatment system consisted of six conventional bubble diffuser type water towers (referred to as contactors) for the chemical oxidation of the contaminants. The water towers were connected via aboveground, temporary piping to two well heads that supplied contaminated groundwater to the treatment system (see Figure 7). The contaminated groundwater supply is referred to as the “influent” (INF), and the decontaminated water exiting the treatment process is referred to as the “effluent” (EFF). Given the direction of water flow for this demonstration, there is no difference between the effluent and the C6 (contactor #6) sample ports. Figure 8 is a drawing of the Peroxone treatment system that depicts the contactors and the sample collection points used for groundwater sampling.

The contactors were unpacked stainless steel towers in which the groundwater for treatment flowed downward through the tower countercurrent to the upward gas flow. Ozone was injected through ceramic diffusers into the treatment water through the base of each tower. Hydrogen peroxide was introduced into the pipeline prior to each tower. The ozone and hydrogen peroxide were used to produce hydroxyl radicals that reacted with the treatment water inside each tower (contactor) to perform the AOP treatment. Any excess gaseous ozone flowed upward through each contactor, collected at

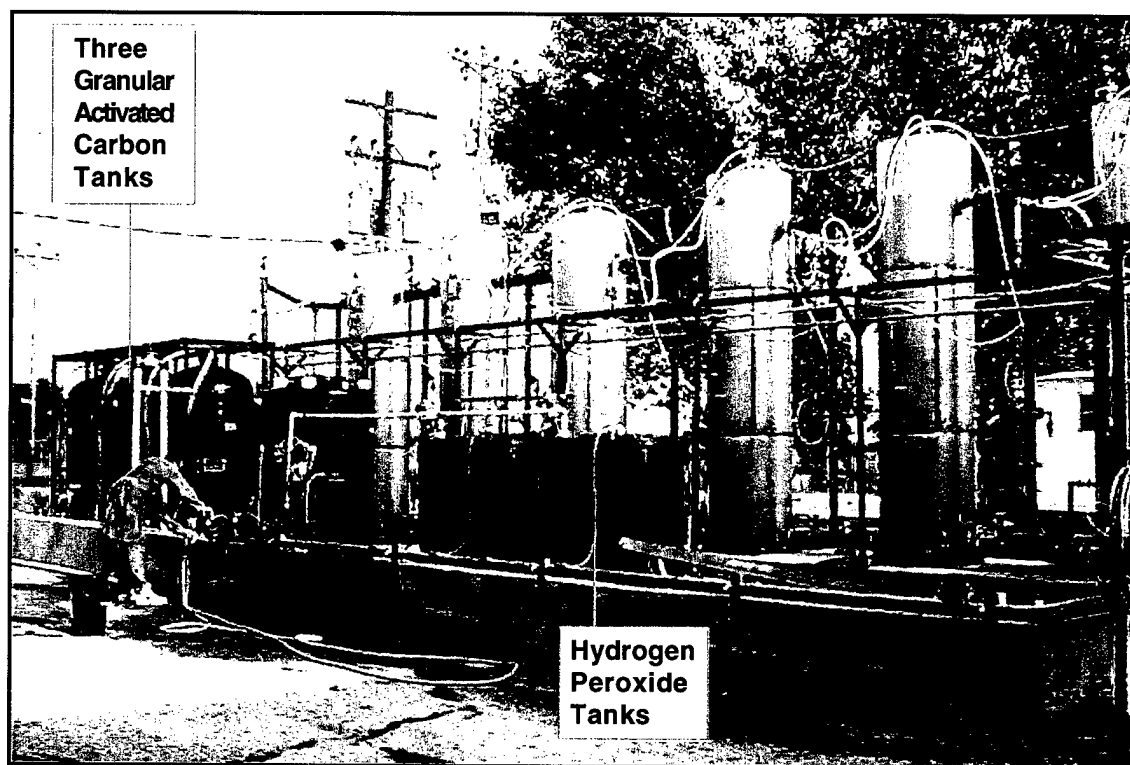


Figure 7. An operator mixing hydrogen peroxide to add to the Peroxone system. The six contactors are the tall stainless steel towers.

the top, and then fed to a residual ozone destruction unit where it was destroyed by passing the gas through a catalyst bed. This prevented any discharge of ozone to the atmosphere during the demonstration. Excess ozone in the aqueous phase was consumed by combining it with sodium thiosulfate in the effluent holding tank.

Readers need to be sensitive that ozone is considered an air pollutant and is addressed in the Clean Air Act (CAA). National Ambient Air Quality Standards (NAAQS) currently exist for ozone. Moreover, the EPA has proposed these standards be tightened (Reference 20). For this reason, the ozone scavenger systems needed to be part of this demonstration system.

The hydrogen peroxide was consumed as it passed through the contactor and reacted with the treatment water. All treatment water processed through the contactors was discharged into an effluent holding tank where it was pumped through a GAC filtration system for final treatment as an added measure. This prevented the possible inadvertent discharge of contaminants into the surface water system as a result of this demonstration. The "twice treated" water was then discharged to adjacent natural surface drainage (see Figures 9 and 10).

Because the demonstration required ozone concentrations up to 10%, **liquid oxygen** was required to serve as the oxygen source for the ozone generator. The heat generated from this system was cooled by water from a local public water supply source at the job site. The spent cooling water was discharged to local surface drainage. The ambient temperature upon discharge was in the 80 degree Fahrenheit range, which is not considered to be a thermal pollutant. However, in a large-scale application, such as supporting the 1,000-gpm targeted field-scale prototype, the discharge, as well as rainwater, would be a matter that would have to receive a much closer engineering evaluation. The plan during the demonstration was to capture all precipitation in the secondary containment, and run the collected stormwater through the system for treatment. During the demonstration, there was negligible pre-

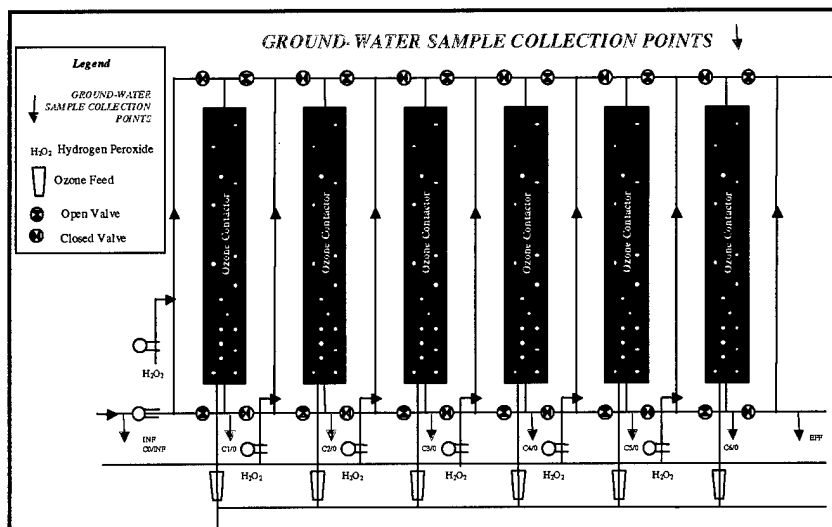


Figure 8. Equipment schematic for water sampling



Figure 9. The treated water was released to natural surface drainage.

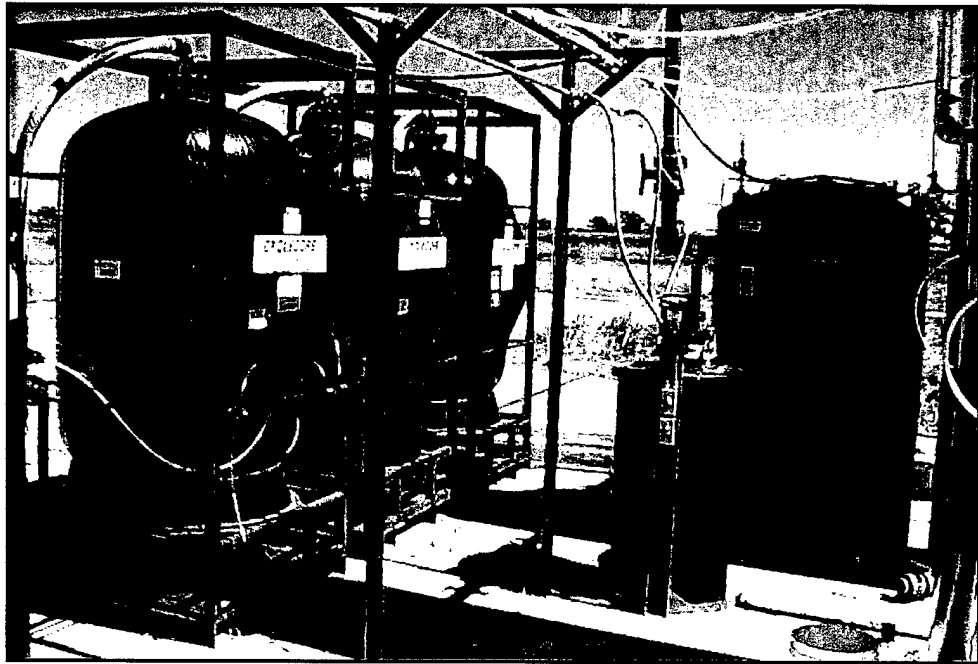


Figure 10. From left to right three GAC tanks, sodium thiosulfate tank, and the effluent holding tank.

ciptation, and thus this was not an issue. However, at other geographic locations, or at other times of the year other than the fall, this could become a serious matter. For a more detailed description of the system, see the TRW-Montgomery Watson report (Reference 21).

## 2.6 Demonstration Schedule

The Peroxone demonstration began with optimization procedures on August 26, 1996, and ended on November 8, 1996. The 12-week demonstration consisted of only 8 days of optimization, 21 days of Phase I operations, and 20 days of Phase II operations. The Peroxone system operated for 10 days at a time followed by 4 days of down time. Due to operators pressing with a very tight schedule (the task was given in May to design, build, and run the system in August for 12 weeks of operation before freezing weather ruined the plumbing), there were no weather-related difficulties and only a few maintenance problems. Freezing pipes were not a consideration because winter weather arrived after the conclusion of the demonstration.

## 2.7 On-Site Demonstration Participants

Two groups at the demonstration site are mentioned frequently in this report, the **demonstrator** and the **independent evaluator**. The demonstrator's objectives were to design, build, and operate the Peroxone system as optimally as possible. The demonstrator conducted on-site chemical analyses to monitor the efficiency of the system and made adjustments accordingly. Daily records were kept of the analyses and of the chemical usage required to operate the

system. The independent evaluator's job was to gather all information needed to perform an objective independent evaluation. Their on-site responsibilities included obtaining all necessary water samples, getting laboratory results of the samples, and keeping records of activities, costs, and analyses. This report is the result of the independent evaluator's efforts.

## 2.8 Demonstration Changes

The plan for the demonstration was to operate the system at 25 gpm pumping water from well #1 for the first half of the demonstration (Phase I), and switching to a second well for the last half of the demonstration (Phase II). The demonstration was changed to:

1. Use one well, rather than two.
2. Operate at 13 gpm for Phase I.
3. Operate at 25 gpm for Phase II.

USAEC and the evaluation team decided to operate the system using well #1 for the entire demonstration (see Figure 11). This decision was based on well #2 not being able to deliver 25 gpm (demonstrators determined the second well was able to pump water consistently at only 18 gpm). During the accelerated optimization effort in which the system was made testbed operational, water samples were taken and the results of the analysis showed the system was unable to remove the contaminant TNB to the target level of 2.0 µg/L when operating at 25 gpm. The flow rate affects the ability of the system to remediate the contaminants because a slower flow rate allows more time for the necessary chemical processes to occur. Since TNB was requiring more treatment time, the flow rates were 13 gpm and 25 gpm for Phases I and II, respectively.

TNB was not expected to be removed to the target level of 2.0 µg/L during Phase II due to the increased flow rate of 25 gpm.

Nonetheless, testing proceeded to explore the projected upper operational limit of the system and gather the data. However, the demonstration participants decided to allow small amounts of TNB to be adsorbed by the GAC system end of the treatment system for insurance against a polluted discharge. The high flow rate data was desired because, theoretically, the cost per 1,000 gallons of treated water would decrease at higher flow rates.



Figure 11. Well #1 (red casing) was located approximately 250 feet from the Peroxone system. The pipe to the system is seen here going through the load line building.

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## 3 Execution

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The evaluation methodology provides the framework for describing the detailed demonstration data collection and data analysis approach.

The performance of the system was measured using the results of the laboratory analysis. The laboratory analyzed the water samples collected by the evaluation team using High Performance Liquid Chromatography (HPLC) for the contaminants TNT, RDX, TNB, and several other explosive compounds. Additional constituents (mineral organics) were measured four times from the influent to characterize the groundwater. The results of the laboratory analysis are provided in Section 4.

The system cost was measured by documenting all resources required to build, operate, maintain, and mobilize the system. Costs of three other treatment systems were obtained through research of currently operating systems.

### 3.1 Evaluation Objectives

The objective of this independent evaluation was to gather and analyze performance and cost data from a 25 gpm Peroxone pilot plant testbed, profiled under realistic field conditions. The demonstration was limited in available demonstration time and was threatened by the onset of harsh winter weather. The objective was accomplished by collecting sufficient data (9,900 data points) across a broad test profile to support the analysis and evaluation of two critical issues: effectiveness and supportability. Evaluation objectives and subobjectives associated with each of these operational issues are defined and presented in Table 3.

The operational effectiveness issue is: ***Does the system meet standards for removal of contaminated groundwater?*** The objective and subobjectives of this issue were addressed by the evaluation team collecting groundwater samples, a certified laboratory analyzing the samples, and the evaluation team comparing the results with a target level of decontamination. Table 4 shows the *target design levels* for the primary COCs.

These system target design levels set by the USAEC in the Spring of 1996 were demonstration goals only and are similar in magnitude to drinking water standards (Reference 7). In the Fall of 1996, a USAEC official, responding to an interview, advised that a goal of 50 µg/L (0.05 ppm) was now trying to be attained for nitroaromatic contaminants (Reference 1). This is more flexible than the target goals used during this demonstration and is easier to attain. However, it should be understood that cleanup requirements

Table 3. List of Evaluation Objectives and Measures

<b>Operational Effectiveness Issue:</b>		Does the system meet standards for removal of contaminated ground water?
Objective 1.	Assess the level of decontamination achieved by the PEROXONE treatment system during the CAAP demonstration.	
Subobjective 1.1	Measure contamination levels before and after treatment at 25 g.p.m.	
Subobjective 1.2	Measure contamination levels after each stage of treatment.	
<b>Operational Supportability Issue:</b>		Is the PEROXONE system more cost effective than existing systems for ground water treatment of explosives?
Objective 2.	Determine the total resources used in treating explosives-contaminated ground water during the CAAP PEROXONE system demonstration.	
Subobjective 2.1	Document staff hours and skill levels to support operation of the CAAP PEROXONE system.	
Subobjective 2.2	Document chemicals and other supplies to support operation of the CAAP PEROXONE system.	
Subobjective 2.3	Document electrical power need to support operation of the CAAP PEROXONE system.	
Subobjective 2.4	Document maintenance requirements and equipment costs.	
Subobjective 2.5	Document setup and demobilization costs.	
Subobjective 2.6	Determine total costs to support operation of the CAAP PEROXONE system.	
Objective 3.	Compare the cost of the current systems with the PEROXONE system.	
Subobjective 3.1	Identify costs of the UV/OX system.	
Subobjective 3.2	Identify costs of the GAC system.	

Table 4. Anticipated Contaminant and Target Design Levels

Contaminant	TNT	RDX	TNB	Total
Anticipated Concentration (µg/L)	500	200	100	1,000
Target Concentration (µg/L)	2.0	2.0	2.0	30

will vary among locations and will be established by the cognizant regulatory authorities. As a case in point, the cleanup standards for a similar innovative technology demonstration applying the AOP catalytic ozonation process, at Volunteer AAP, Tennessee, were:

- TNB <3 µg/L
- TNT <3 µg/L
- 2,4-DNT <3 µg/L
- 2,6-DNT <3 µg/L
- Total nitrobodyes <1,000 µg/L

There was no presence of RDX or HMX at this location (References 22 and 23).

The State of Nebraska standards for the primary contaminants listed in Table 5 are less stringent than the target standards listed in Table 4. The State of Nebraska standards will be referred to as the *required standards* (verses the *target levels* set by USAEC). All the contaminants listed in Table 5 were analyzed throughout the demonstration. The total nitrobodyes is simply the sum of all the individual nitrobody results.

Readers need to be sensitive to the subject of “nitrobody gap-other” (see Table 4: the Total vs. the three target contaminants) when considering cleanup standards. For example, a gap of 24 µg/L or 80% exists [ $30\mu\text{g/L} - 3(2\mu\text{g/L}) = 24\mu\text{g/L}$ ] when compared to the mandated USAEC goals of 2 µg/L for each of the three specifically named nitroaromatics and the 30 µg/L goal for total nitrobodyes. There will be potentially a wide variety of other nitroaromatic compounds encountered as contaminants. Many are associated

manufacturing by-products. In addition, in the oxidative destruction process present in the Peroxone system, TNB can be generated as an intermediate by-product of TNT destruction. Table 5 provides a listing of such nitrobenzenes. Moreover, if color development should become an issue, other transient isomers can develop. Depending on the nature of the influent characteristics, other serious by-products can be generated that can be of regulatory concern (References 10, 12, and 24). For this reason, it is important to fully characterize the influent to be treated by a Peroxone system, and have a full understanding of the next beneficial use the effluent is to serve.

In this demonstration, all effluent discharges from the Peroxone system remained well below levels required by the State of Nebraska (see Section 4, Results). In addition, the three USAEC directed target nitroaromatics (TNT, RDX, and TNB) accounted for the majority (88%) of the detected residual nitrobenzenes in the treated effluent. This observation substantiated the planning direction for this demonstration. However, the residual gap of 12% other nitrobenzenes demonstrates that other residual nitrobenzenes can be present in the treated effluent and justify the need to analyze for all potential nitrobenzenes.

Table 6 provides a list of **additional parameters**, tested twice from the influent and twice from the effluent, used for the characterization of the groundwater at the CAAP. These additional parameters can impact the effectiveness of a Peroxone system as they can impact reagent consumption via competitive simultaneous reactions previously described in Section 2.3. These additional parameters can also provide, on a case-by-case basis, an indication of the potential for undesirable intermediate by-products. Under some conditions, final effluent characteristics can be predicted. As an example, high ammonia and/or Kjeldahl nitrogen in the water would alert one to anticipate high nitrate concentrations in the final treated effluent. Considering the potential stringent regulatory

Table 5. Nitrobenzene Analyses Series Requirements

Nitrobenzenes	State of Nebraska Requirements (µg/L)
High Melting Explosive (HMX)	40
Royal Demolition Explosives (RDX)	100
1,3,5-Trinitrobenzene (TNB)	4
1,3-Dinitrobenzene	5
2,4,6-Trinitrotoluene (TNT)	20
4-Amino-2,6-dinitrotoluene	40
2,6-Dinitrotoluene	40
2-Amino-4,6-dinitrotoluene	40
2,4-Dinitrotoluene	100
Methyl-2,4,6-trinitrophenylnitramine	100
2-Nitrotoluene	100
3-Nitrotoluene	100
4-Nitrotoluene	20
Nitrobenzene	5
Nitrate as Nitrogen	100 mg/L

Table 6. Groundwater Mineral Constituent Test Methods

Constituent	Suggested Method
Total dissolved solids	Standard Methods 2540
Total suspended solids	Standard Methods 2540
Alkalinity	Standard Methods 2320
Total organic carbon	Standard Methods 5310
Bicarbonate	Standard Methods 4500-CO2
Carbonate	Standard Methods 4500-CO2
Total Kjeldahl Nitrogen	Standard Methods 4500-N
Nitrate	SW 846-9056
Nitrite	SW 846-9056
Ammonia-Nitrogen	Standard Methods 4500-N
Total phosphorus	Standard Methods 4500-P or SW 846-6010
Sulfate	SW 846-9056
Calcium	SW 846-6010
Iron	SW 846-6010
Magnesium	SW 846-6010
Manganese	SW 846-6010
Potassium	SW 846-6010
Sodium	SW 846-6010
Volatile and semi-volatile organics	SW 846-8260/8270



Figure 12. An evaluator takes a nitrate sample from the influent port on the Peroxone system.

standards that can exist for nitrate-nitrogen (depending on the next beneficial use for the treated water) this can cause a concern. Another example is that if a large concentration of calcium, iron, magnesium and/or manganese were present, as the water was further oxidized and the pH increased, scaling could occur in the unit process chambers and associated piping. This condition could cause a system maintainability problem and add to long-term operating costs.

The daily analytical laboratory work supported two main series of analysis: nitrobenzenes (the explosives contaminants) and nitrates as nitrogen. Approximately 590 samples of nitrobenzenes were analyzed. The nitrobenzenes were analyzed using Solid Waste (SW) 846 Method 8330 for nitroaromatics and nitramines using HPLC, and EPA Method 353.2 for nitrate as nitrogen.

Water samples for the nitrobenzenes were collected in 1-liter amber glass bottles, and the nitrate as nitrogen samples were collected in 250-milliliter plastic bottles. All samples during the optimization effort to make this system testbed operational were analyzed, and results provided to the evaluation team within 24 hours from time of arrival at the laboratory.

The turnaround time of the laboratory analysis was within 72 hours for the rest of the demonstration. The collection of samples is shown in Figure 13.

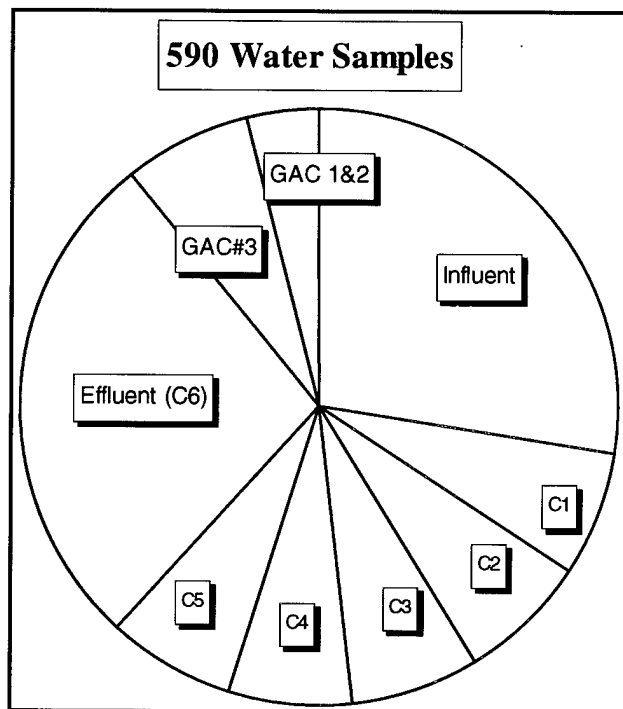


Figure 13. The distribution of sampling activity emphasizes the influent and effluent results.

### 3.1.1 Assessment Methodology for Objective 1

Objective 1 for the operational effectiveness issue is: *Assess the level of decontamination achieved by the Peroxone treatment system during the CAAP demonstration.* This was achieved through charting the results obtained from the laboratory. Contamination results were obtained from water samples at several locations in the treatment system. The majority of the samples were taken pre- and post-treatment (influent and effluent) to compare contamination levels before and after the process. Some samples were taken in “mid-stream” of treatment. There were a total of seven locations in the system where samples were taken to observe how the contaminants

were affected at each stage. The influent sample was taken for the “before treatment” analysis, and the six subsequent samples (one after each contactor) were taken for comparison analysis. Finally, the last sampling location was placed after the GAC treatment to ensure no contamination of the area was occurring from the discharge of the treatment plant. Each of the three GAC tanks had a sampling port. Figure 13 is a summary of the sampling activity; “C1” is the first contactor, and so on.

The influent and effluent samples were taken four times per day. Samples from C1 through C5 were taken once per day. The third GAC tank (GAC #3) had samples taken once per day, and the first and second GAC tanks were sampled weekly.

The resulting analytical data were graphically displayed by contaminant in an effort to search for trends, overall system and individual component performance, and data anomalies. Concentrations of each primary contaminant were plotted using Minitab™ and Excel™ software to examine the influent, effluent, and middle stages of the system. The results of the laboratory analysis are discussed in Section 4 and summarized in Appendix B.

The operational supportability issue is: *Is the Peroxone system more cost effective than existing systems for groundwater treatment of explosives?* The objectives and subobjectives of this issue were evaluated **collecting cost data (quantitative and qualitative) during the demonstration and evaluating the operation costs for two other systems.** There are no target or comparison measures of performance for the cost data collection effort at this time. Rather, cost data were collected for each of the subobjectives listed in Table 3, then evaluated for its applicability to operational supportability of current AOP groundwater treatment systems.

### **3.1.2 Assessment Methodology for Objective 2**

Objective 2 addresses the operational supportability issue: *Determine the total resources used in treating explosives-contaminated groundwater during the CAAP Peroxone system demonstration.* This was achieved through documenting all operational supportability issues. The flowchart in Figure 14 illustrates what data was collected and how it relates to the objective.

The assessment of this objective involved the conversion of some of the parameters into a common unit, namely dollars per 1,000 gallons of water treated. This conversion is used to compare effectively the small scale CAAP site system to the GAC and UV/OX systems. The power usage and chemical usage were calculated in dollars per 1,000 gpm of treated water. Results of the cost analysis of the CAAP site Peroxone system is in the Results section.

### 3.1.3 Assessment Methodology for Objective 3

Objective 3 addresses the operational supportability issue: *Compare the costs of current systems to the Peroxone system.* This objective was addressed by **combining the information obtained from Objective 2 and the cost information from the GAC and UV/OX system.** Information on the costs associated with GAC operations was obtained from Calgon Carbon (Reference 25); telephone interviews with operators at the Milan, Tennessee, GAC facility (Reference 26); and data supplied by USAEC (Reference 27). The Strategic Environmental Research and Development Program (SERDP), which is operating a UV/OX system in Milan, Tennessee, provided the UV/OX system cost information to the evaluation team (Reference 28). System costs were calculated for the capital costs and annual operating costs, presented in Section 5.0.

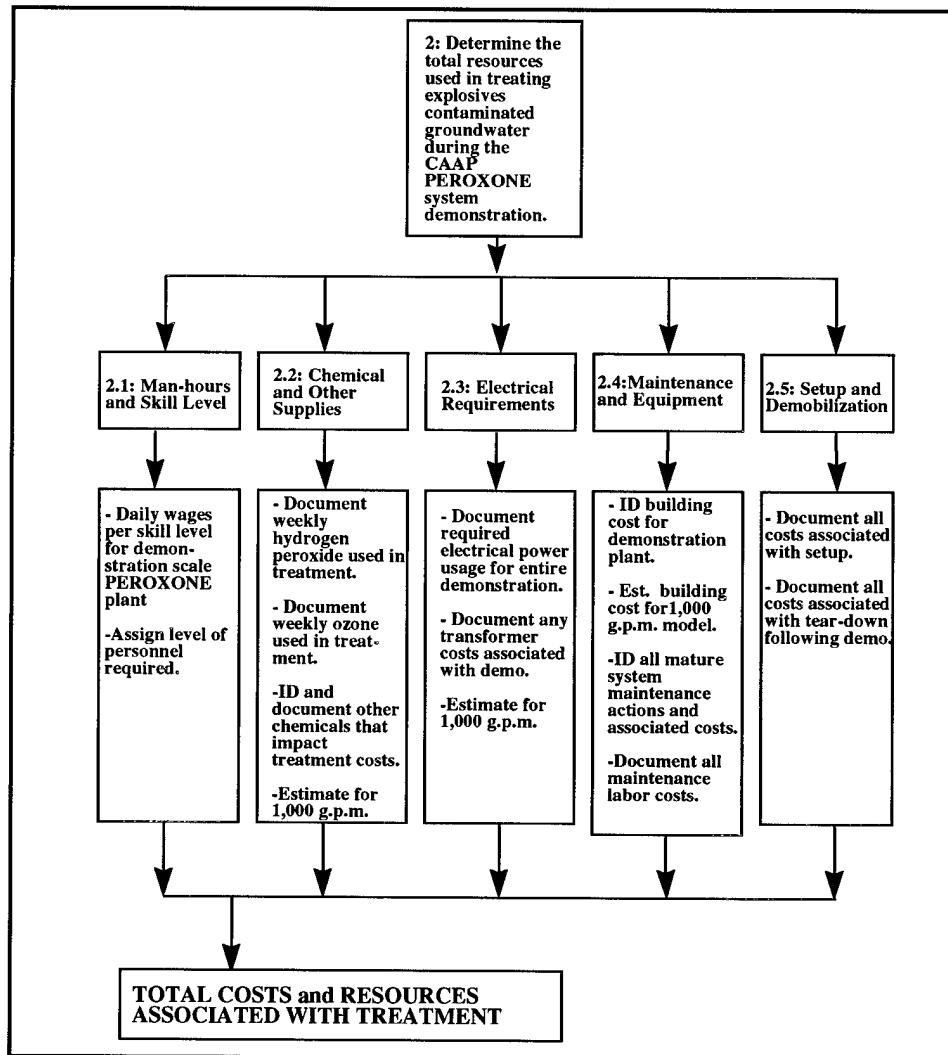


Figure 14. This resource data collection flowchart shows the methodology for estimating the cost of the Peroxone system at the Cornhusker Army Ammunition Plant.

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## 4 Performance Results

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The performance of the system was determined from the laboratory analysis. The three areas of consideration regarding system performance are the influent contaminant levels, the levels observed after each stage of treatment within the system, and the final contaminant levels observed in the effluent.

### 4.1 Operations

The first objective of the demonstration required examining the contamination levels before and after treatment. The required dosages of hydrogen peroxide and ozone were of interest to the demonstration operators to determine what levels were needed to decontaminate the water. Ideally, the system would be optimized for the required dosages and would remain constant throughout the demonstration. However, because this was the first time to demonstrate this particular Peroxone pilot plant system, adjustments to the dosages were made more frequently (Figure 15).

Before analyzing the results of the water samples, the operator records were examined to identify exactly when system parameters were changed or adjusted. The evaluators discovered that the dose of hydrogen peroxide was adjusted three times during Phase I. (Note: During Phase I, the system was operated at 13 gpm, and during Phase II, the system was operated at 25 gpm.) According to one operator, this unplanned change was made because the ratio of hydrogen peroxide to ozone established by the previous WES study (Reference 3) did not provide the most effective chemical reaction. The change in contactor height from 20 to 14 feet (see page 14) might have affected the ratio requirement, however, this is unconfirmed. The operators measured the effectiveness of the chemical reaction by the amount of ozone residuals found in the gaseous and aqueous phases. High ozone residuals implies there could be more hydroxyl radicals created with the addition of hydrogen peroxide. Although the system was optimized or made testbed operational for the required **ozone** dose to remove the contaminants, it was not optimized for the **hydrogen peroxide** dose until the 18th day of the demonstration because of a logistical problem with flow control valves. The addi-

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The operators measured the effectiveness of the chemical reaction by the amount of ozone residuals found in the gaseous and aqueous phases.

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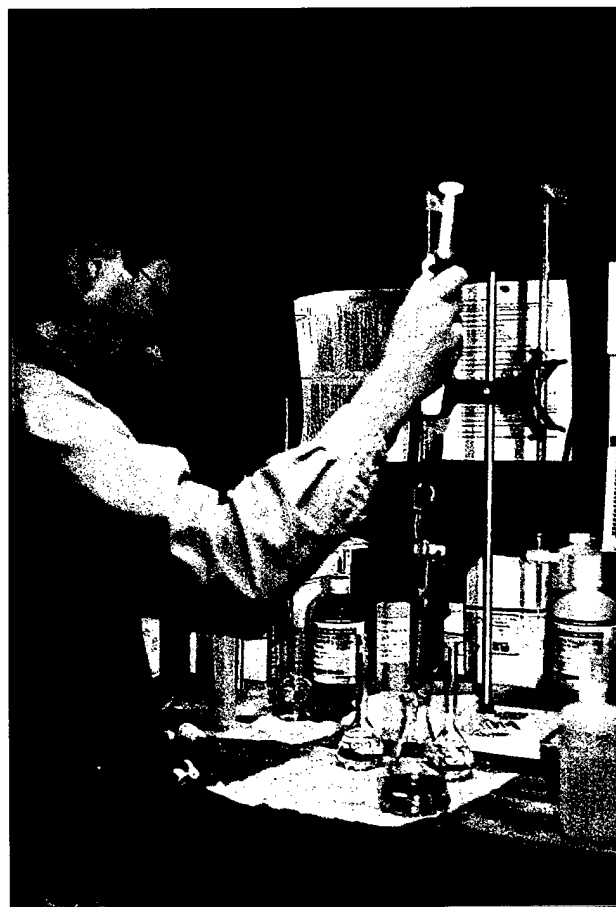


Figure 15. An operator on location tests for the hydrogen peroxide concentration.

tional hydrogen peroxide dose (hence, additional hydroxyl radicals) did not affect the laboratory results of the water samples and served only to “use up” as much of the ozone molecules as possible. In other words, the concentrations of the target contaminants were not reduced due to the additional hydrogen peroxide. The additional hydroxyl radicals in the system could be required to obtain the same level of decontamination *if the influent concentrations were higher*. The increased hydrogen peroxide dose did, however, increase the cost of the system. Figure 16 shows the dose mass ratios throughout the demonstration.

The “Target” mass ratio series is the Peroxone mass ratio that the demonstration operators fed to the system to get the most efficient “Actual” mass ratio. This was done by setting the ozone generator to the dose setting and the hydrogen peroxide pumps to a feed rate setting appropriate to the water flow rate. The “Actual” mass ratio was determined from the ozone monitor off-gas readings. Adjustments to the H<sub>2</sub>O<sub>2</sub> dosage is observed in the “Target” ratio series of Figure 17. No adjustments were made in Phase II.

Data sets 1 and 2 were selected as individual data sets based on the “Actual” mass ratios of approximately 0.3-0.4 and 0.5-0.6, respectively. The peaks observed in the two data sets are probably due to the difficulty the operators experienced in trying to control the hydrogen peroxide feed rate. The hydrogen peroxide pumps were not equipped with valves for flow control. Valves were added to the system on the 18th day of the demonstration.

The erratic ratios observed in data set 3 (Phase II) were explained by the demonstration operators as “ozone monitor” error.

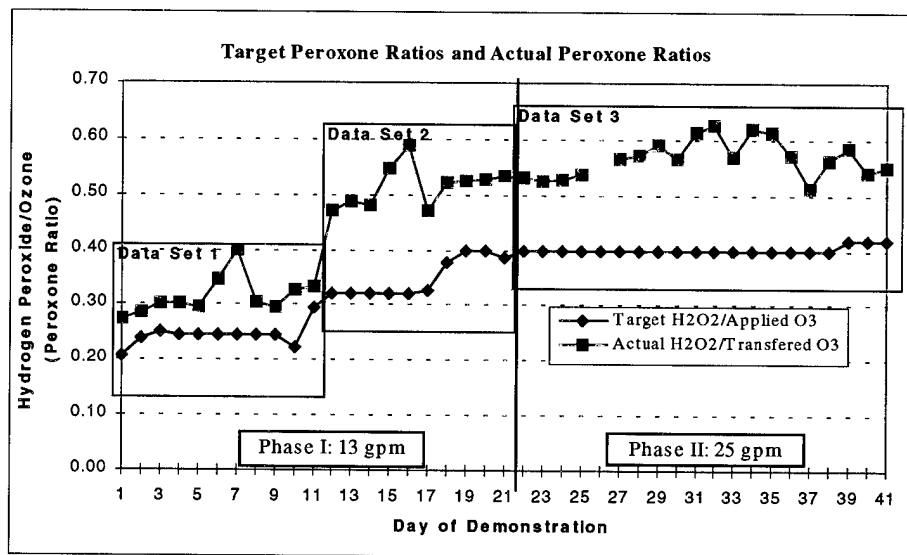


Figure 16. Based on operator adjustments during the demonstration, three separate data sets were considered. There was no performance difference from data set 1 and 2. Data set 3 was a 25-gpm operation that affected both cost and performance.

The ozone monitor required the most maintenance of any equipment at the site.

The monitor was replaced twice, and each monitor functioned improperly. The operator theorized that the monitor was not resistive to corrosion from the high ozone concentrations and, for one repair, he replaced a piece of corroded wire with a common paper staple.

The hydrogen peroxide feed pumps also needed significant attention. Nearly halfway through the demonstration, the operators were able to obtain valves for the pumps delivering a constant feed to the system.

During Phase II, demonstration operators observed the hydrogen peroxide feed pumps were operating at a constant feed rate, and the ozone residuals in the water (measured by laboratory technique, rather than a monitor) were also constant, therefore the ozone monitor was the source for the erratic readings.

The oxidation mechanism employed in the demonstration may not have been Peroxone by itself, but instead a combination of Peroxone and the two constituents hydrogen peroxide and ozone. In the demonstration, hydrogen peroxide was introduced into the contaminated groundwater flowstream, and then brought into the contactors where ozone was introduced. There may not have been sufficient time for Peroxone to form and the hydroxyl radicals to effectively oxidize the contaminants, based on the following observations.

The demonstration subcontractor operators initially attempted to operate the system at a mass ratio of 0.3 (hydrogen peroxide to ozone). However, early into the demonstration they observed the ozone residual being measured in the contactor effluents was higher than calculated and anticipated; the point being was that the hydrogen peroxide appeared to be reacting with constituents other than ozone, such as a variety of groundwater contaminants (see Section 2.3 Peroxone Chemistry). A major industrial supplier of hydrogen peroxide advised that hydrogen peroxide is effective as an oxidant of inorganics and aliphatic hydrocarbons, but not of aromatic hydrocarbons (Reference 11). There will be some oxidation, however such molecules will not be destroyed, only altered. Thus, one interpretation is that hydrogen peroxide reacted first with salts and aliphatic hydrocarbons, then with ozone to produce limited amounts of Peroxone. The ozone and Peroxone then reacted with the re-

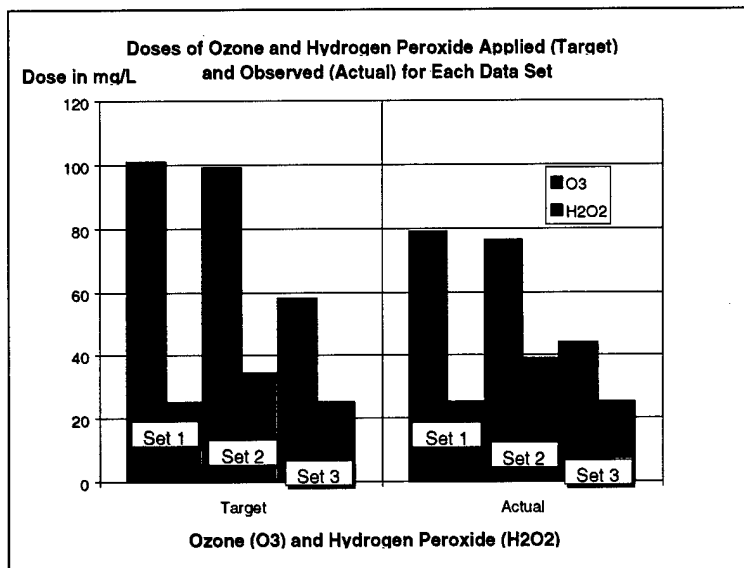


Figure 17. The average "Actual" or "Transferred" doses for data set 1 were about 80 mg/L of hydrogen peroxide ( $H_2O_2$ ) to about 24  $\mu$ g/L of ozone ( $O_3$ ).

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The ozone monitor required the most maintenance of any equipment at the site.

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There was only a very slight increase in system pH overall, and the system was never operated at the pH value of up to 9, as the WES report recommends.

mainder of the target contaminants, as the aromatics were largely unaffected by the hydrogen peroxide.

The gap that appears between the two series in Figure 16, is interpreted by the evaluation team to be the individual hydrogen peroxide reactions occurring with some of the more readily oxidized compounds in the groundwater influent. Most of the target contaminants were destroyed by the end of the third contactor (see Figure 22), the exception being TNB. Because of its molecular symmetry, this molecule may be more difficult to oxidize (Reference 1), thus implying that other competitive simultaneous reactions were occurring (Reference 12), and that some hydrogen peroxide was reacting with other constituents. This is substantiated as the demonstration subcontractor operators responded to the higher than anticipated ozone residuals in the contactor effluents by increasing the mass ratio up to as high as 0.65 (Reference 21, Figure 4-3); the ozone residual in the effluent responded and was reduced to a target value of less than 1 mg/L.

Further evidence of these interferences occurring is demonstrated by observing the pH values associated with the demonstration. The goal was to generate a suitable concentration of Peroxone, the hydroxyl radical associated with this reaction and the most effective oxidant. If an ample amount of hydroxyl radicals were present in the bulk of solution, the pH would increase. The ambient pH values of the groundwater influent were in the neutral region. There was only a very slight increase in system pH overall, and the system was never operated at the pH value of up to 9, as the WES report recommends (Reference 3, page 17). The TRW report (Reference 21, Section

4.7.2.7.) reports the following: "As the water went through each of the six contactors, the pH increased to 7.1, 7.3, 7.5, 7.6, 7.8, and 7.9 respectively. No specific testing was conducted to determine the cause of the pH drift." When the data is plotted (see Figure 18), it is really not a drift, but a slow and steady increase. Thus, there was an increase in pH, interpreted as some indication of the generation of Peroxone, but sufficient data does not exist to determine if this represents optimal generation.

The influent groundwater was alkaline with alkalinity values reported in the 300 mg/L range. As a consequence, it must be recognized that some natural buffering capacity existed. This may also have impacted on the observed increase in pH.

The average doses for "Actual" and "Transferred" Peroxone in each data set are displayed in Figure 17. The

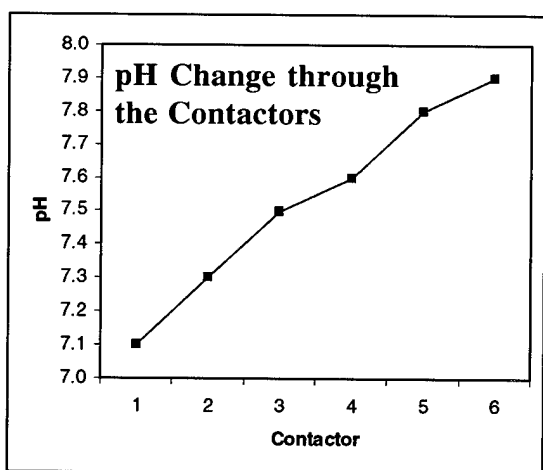


Figure 18. A pH increase was noted through the contactors, indicating Peroxone generation.

flow rate was increased from 13 gpm to 25 gpm in data set 3; therefore, a lower dose of ozone is transferred into the water flow even though the ozone generator was operating at capacity.

## 4.2 Influent Results

The evaluators took the “before treatment” water samples four times a day. All samples were shipped overnight to the laboratory for analysis every day. Figure 19 shows the influent concentrations (before treatment) for the primary contaminants during the demonstration (13 Sept to 8 Nov 1996).

The downward trend of contaminant seen in the influent concentration samples indicates that the concentration was decreasing as the groundwater was pumped out. This is a unique observation. It may indicate that the source of the groundwater contamination was site specific (such as infiltration from historically old surface evaporation ponds and pits), and because the treated groundwater was not reinjected back into the aquifer, the water table was depressed and moved away from these contamination sources. There was no measurable rainfall during this demonstration period. This analysis shows that the influent concentrations did not reach a steady state

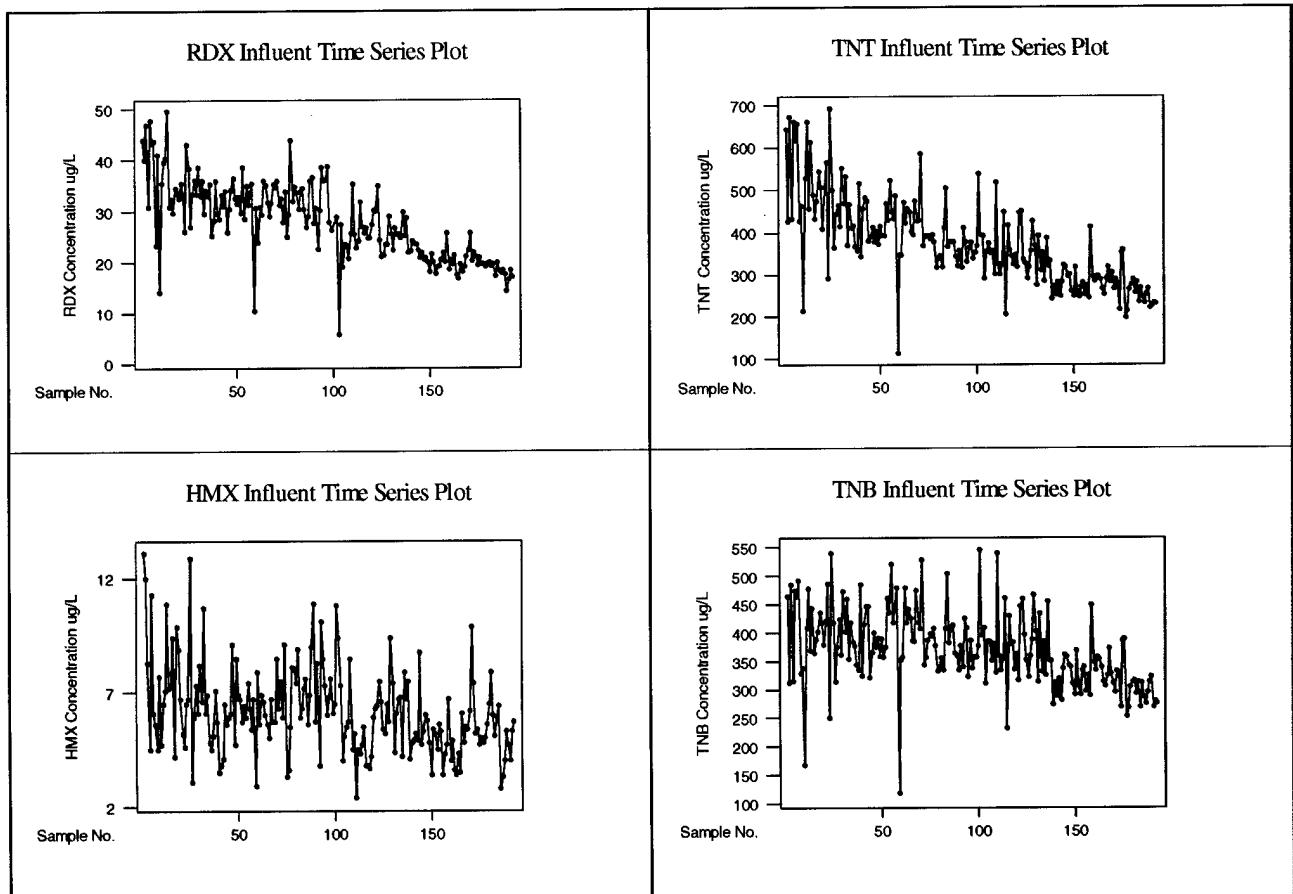


Figure 19. The time series plots of the contaminants before treatment (influent samples) show the common trend of a decrease in concentration over the demonstration (41 days).

during the demonstration. Occasionally, when pump-and-treat remediation systems, such as the Peroxone pilot plant demonstration system, are prematurely stopped and the groundwater has not been completely cleaned, the contaminant concentration can rise back towards the original level of contamination. Some pump-and-treat systems can operate for 10 years or more (Reference 29).

The distribution of the contaminant levels of the influent is shown in Figure 20. The line across the middle of the boxplots shows the median value. The level of TNB was four times greater than anticipated, and the RDX level was only 1/6 of what was expected (see Table 4). TNB and TNT levels were much higher than the State of Nebraska's required levels. HMX and RDX levels were well below the State of Nebraska's requirements.

### 4.3 Treatment Process

Samples were collected by the evaluators once per day after each contactor stage in the treatment process. The results of the contaminants after each contactor stage are plotted in Figure 21. The stages of treatment are divided by demonstration phase since there were two different operation settings in flow rate (Phase I: 13 gpm and Phase II: 25 gpm). Individual contactor performances are reflected in Tables 7 and 8. Phase I values were consistently higher in destruction effectiveness than Phase II values. It is deduced this occurred because the hydraulic retention times were greater in the Phase I events due to the lower volumetric flow rate applied. Individual contactor removal efficiencies from contactor to contactor by contaminant in each phase were fairly consistent.

Analysis for the two phases of the demonstration showed all the contaminants except TNB met the treatment goals before the last stage of treatment (contactor 6). Figure 22 shows the stage within

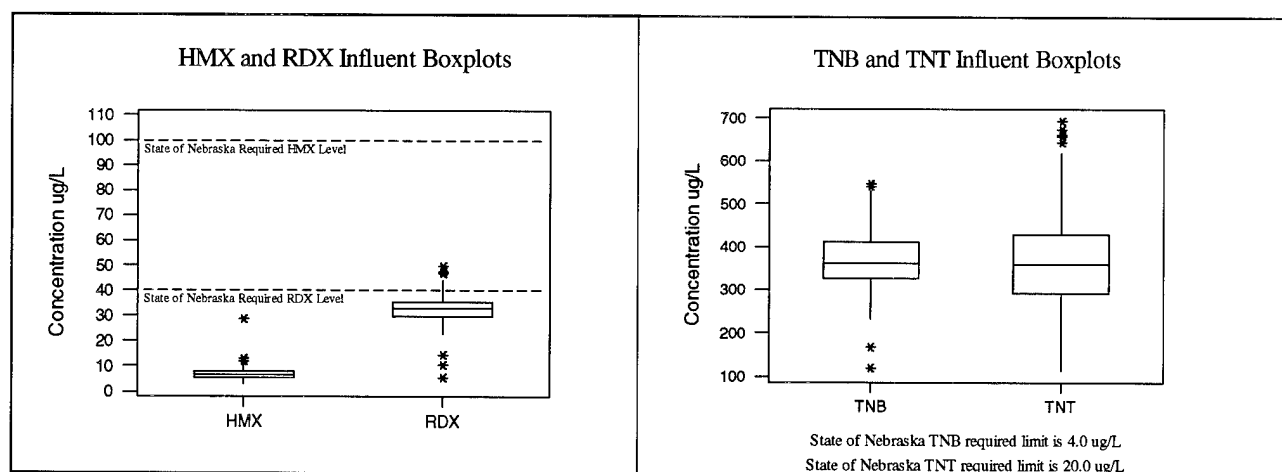


Figure 20. The influent samples show HMX and RDX were below Nebraska cleanup requirements, but TNB and TNT were both above. All were above demonstration target goals (see Figure 23 for boxplot interpretation).

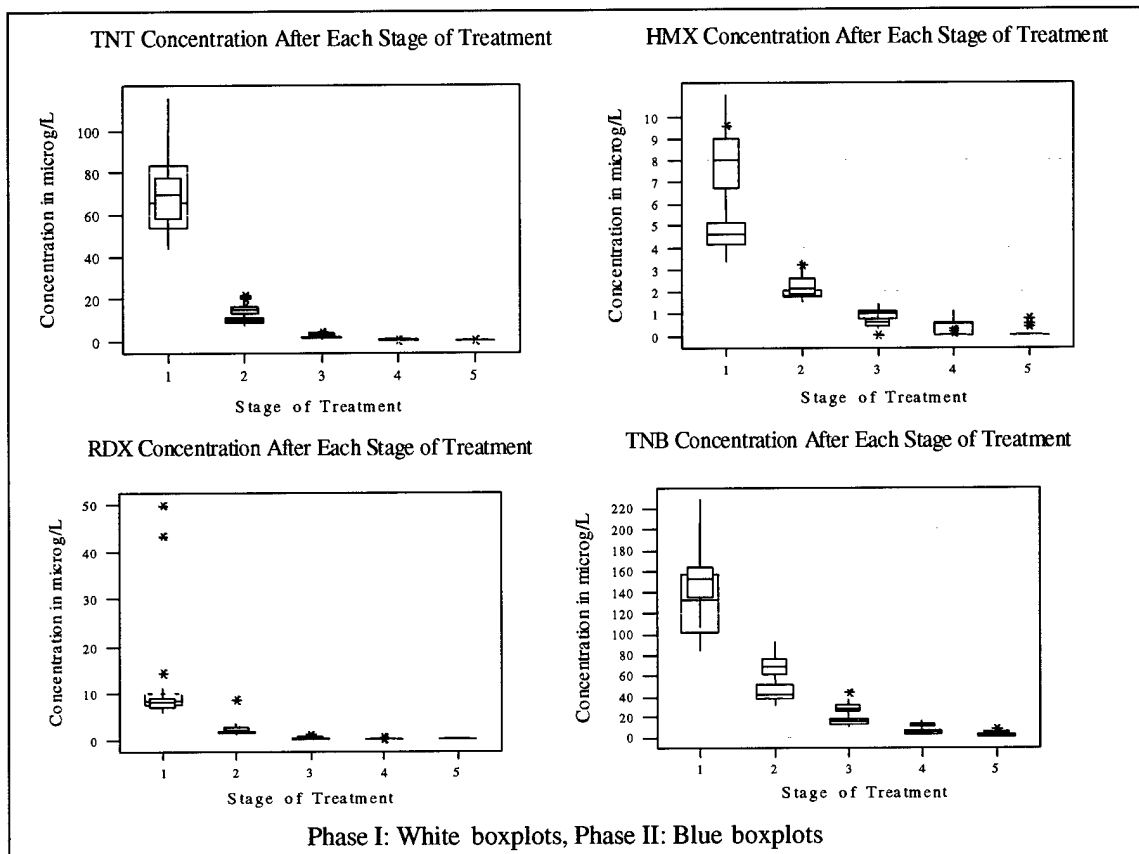


Figure 21. Contaminant remediation from stage to stage. See effluent results for contactor 6 (see Figure 23 for boxplot interpretation).

Table 7. Contactor Destruction Effectiveness

Contaminant	INF	C1	C2	C3	C4	C5	C6 (EFF)
<b>Phase I</b>							
TNB	396.00	133.00	45.10	15.10	5.26	1.92	0.61
TNT	437.00	69.60	10.70	1.64	0.24	0.01	0.00
HMX	7.00	4.91	1.95	0.96	0.54	0.10	0.00
RDX	33.00	10.30	1.88	0.28	0.00	0.00	0.00
<b>Phase II</b>							
TNB	346.00	152.00	69.90	28.30	12.10	5.43	2.58
TNT	312.00	69.00	14.90	3.16	0.64	0.11	0.00
HMX	5.60	4.50	2.44	1.38	0.86	0.58	0.00
RDX	23.00	10.20	2.29	0.60	0.03	0.00	0.00

Average concentration of contaminants is in µg/L.

Table 8. Removal Efficiency by Contactor (%)

Contaminant	C1	C2	C3	C4	C5	C6
TNB (Phase I)	66.41	66.09	66.52	65.17	63.50	68.02
TNB (Phase II)	56.07	54.01	59.51	57.24	55.12	52.49
TNT (Phase I)	84.07	84.63	84.67	85.18	94.24	100.00
TNT (Phase II)	77.88	78.41	78.79	79.91	83.46	100.00
HMX (Phase I)	29.86	60.29	50.92	43.36	81.55	100.00
HMX (Phase II)	19.64	45.78	43.44	37.68	32.79	100.00
RDX (Phase I)	55.65	77.55	73.80	95.00	100.00	N/A
RDX (Phase II)	68.79	81.75	85.32	100.00	N/A	N/A

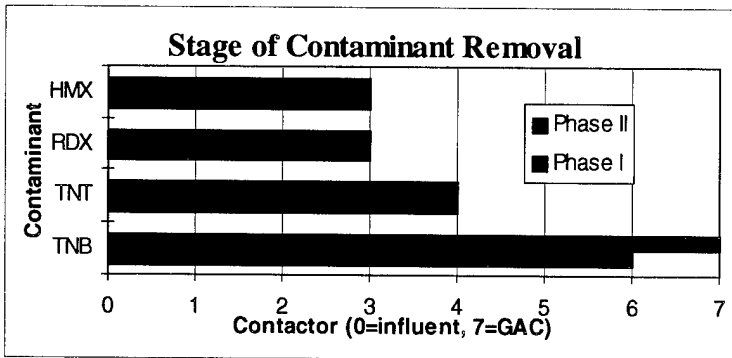


Figure 22. TNB was the only contaminant that required all stages of treatment.

the system when the *primary* contaminants were below the target goal 90% of the time. TNB was the only contaminant requiring all stages of treatment to be remediated. TNB may have been the most recalcitrant COC and was difficult to destructively oxidize because of its molecular symmetry. Also, because it is an intermediate by-product of the destructive oxidation of TNT, this also could have been a contributing source. The GAC system removed any small amount of TNB during Phase II before the water was

discharged. Phase II required the use of the GAC system to remove the TNB down to the target level of 2.0 µg/L because of the higher flow rate of 25 gpm.

#### 4.4 Effluent Results

Evaluators took samples four times a day from the Peroxone system effluent (contactor 6). The results of the analysis are

The change in the Peroxone ratio did not improve the performance according to the analysis results.

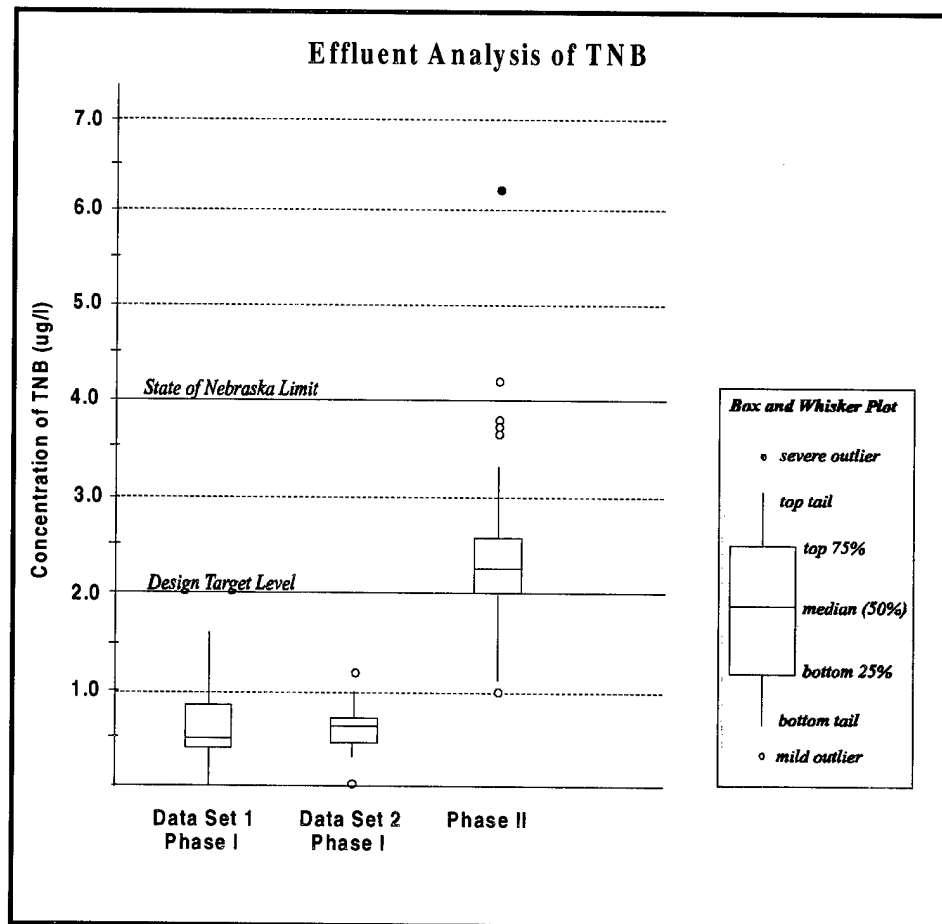


Figure 23. TNB results after treatment were very close to the design target levels when operating at 25 gpm.

shown in Figure 23 for both phases of the demonstration. All of the contaminants were removed to below detection levels except for TNB. **The TNB results were well below the design target level of 2.0 µg/L in Phase I, but not in Phase II.** The Peroxone system met all the performance goals in Phase I due to the lower flow rate used. In Phase II, the TNB concentration was below the state-required level of 4.0 µg/L more than 90% of the time, but below the design target level of 2.0 µg/L only 25% of the time. Therefore, all of the performance goals for the system were met in 25% of the samples taken in Phase II. The higher flow rate in Phase II decreased the amount of time the chemical reaction could occur and resulted in more contaminant left in the water. The effluent analysis of TNB for each data set does not reveal a performance difference between data sets 1 and 2; therefore, the change in the Peroxone ratio did not improve the performance according to the analysis results.

The total nitrobody count was the only other parameter reported and it is simply the sum of all the nitrobodyes detected (TNT + TNB + RDX + HMX + ...). Therefore, the total nitrobody results were identical to the TNB results in the effluent analysis. For example, in Phase I, the total nitrobody median value was 0.5 µg/L, as was TNB. The target level for total nitrobodyes was 30 µg/L, and the result concentration after treatment was below 2 µg/L in Phase I.

**This system operated at the µg/L order of magnitude, i.e. the parts per billion range.** One must wonder if it is reasonable to invest in such a treatment system as is discussed in this report to address the remediation of nitrobody contaminants, or if other remedies such as natural attenuation or GAC treatment would be sufficient. If the existing levels of contamination were in the parts per million range, and the regulatory standards were in the parts per billion range, then there would be much less doubt as to the economic soundness of such an approach. More normal contamination levels at other ammunition plants are in the mg/L or parts per million range (Reference 1). Thus the investment made in this demonstration has a sound purpose if applied to a ppm range of contamination. As an example, see the influent characteristics and remediation goals for the contaminated groundwater pumped to the ULTROX pilot demonstration plant (another version of AOP technology, Reference 23) at Volunteer AAP, outside of Chattanooga, Tennessee (side bar).

For this Cornhusker demonstration, there is a gap between the three listed target contaminants (2+2+2) and total nitrobodyes (30). This leaves a "nitrobody gap - other" of 24 ppb or 80%. Many other nitrobodyes can fill this space and include:

### Cleanup Criteria

For a point of comparison, the influent characteristics and achieved effluent levels at Volunteer AAP for the Ultrox demonstration was as shown below:

Parameter	Influent	Effluent
• 2,4,6 TNT	2,000 ppb	ND
• 2,4 DNT	8,000 ppb	80 ppb
• 2,6 DNT	3,500 ppb	120 ppb
• 1,3,5 TNB	100 ppb	18 ppb
• Total Nitrobodyes	38,000 ppb	>1000 ppb

When comparing this data to Tables 4 and 5, one wonders about the reasonableness of the imposed cleanup criteria. Each situation will be evaluated on a site-unique basis, and for the Cornhusker effort, there were drinking water issues that impacted the local area. The Nebraska Department of Environmental Quality chose not to issue a National Pollutant Discharge and Elimination System (NPDES) permit per se, but they provided daily maximum limits guidance for 17 criteria (Reference 30). Later this criteria was further tightened by USAEC to four more stringent target treatment goals, which were:

• TNT	2 ppb
• RDX	2 ppb
• TNB	2 ppb
• Total Nitrobodyes	30 ppb

These goals were essentially drinking water standards. In a normalized application, based on protocols being followed today, a risk-based assessment would be conducted, and such performance standards would be developed from this effort with the appropriate regulatory agency maintaining advocacy over these efforts. Moreover, a less rigid goal of 50 µg/L per nitrobody constituent is now considered as a more reasonable goal (Reference 1). By way of comparison, for the demonstration work just completed at Volunteer AAP, the cleanup goals were:

• TNT	<3 ppb
• TNB	<3 ppb
• 2,4 DNT	<3 ppb
• 2,6 DNT	<3 ppb
• Total Nitrobodyes	<1,000 ppb

There was no presence of RDX or HMX at this location. Since this demonstration was planned and executed, these cleanup criteria target goals applied appear to be somewhat stringent, compared to the most current information available. As an example, if the criteria goals were 50 µg/L, this demonstration would have easily satisfied the criteria.

- 1,3 dinitrobenzene
- 2,4 dinitrotoluene
- 2,6 dinitrotoluene
- 2-amino 4,6 dinitrotoluene
- 2-nitrotoluene
- 3-nitrotoluene
- 4-amino 2,6 dinitrotoluene
- 4-nitrotoluene
- HMX
- nitrobenzene

The concern over this “nitrobody gap - other” is that some potentially toxic intermediate oxidation by-products or transient multibenzene ringed isomers associated with color development could occur.

More normal contamination levels at other ammunition plants are in the mg/L or parts per million range.

Other compounds that could contribute to this were also analyzed during the demonstration. Their values were very small, and were often below detection limits. Moreover, the three target contaminants accounted for the majority of the nitrobody in the demonstration, with the “nitrobody gap - other” value approximating only 12%. **Thus the majority of the nitrobody was represented by the three target contaminants of concern.**

Because the cleanup goal was essentially based on drinking water quality standards, the most current document available from the EPA was reviewed (Reference 7, October 1996) to determine if other measured nitrobody were listed. Four of 10 were, however no standards were published for them, only health advisories. Health advisories are based on exposure risk to cancer, have historically been conservatively developed, and are currently undergoing revision. There are two population groups considered, children and adults, with various exposure scenarios. By way of comparison, both RDX and TNT are similarly listed, and the health advisory category applied for this demonstration was “lifetime exposure,” the most stringent. For these two nitrobody, the value is 2 ppb, the same target treatment goals in this demonstration. The other four nitrobody found in this publication and their corresponding values were:

- 1,3-dinitrobenzene 1 ppb
- 2,4-dinitrotoluene none reported, but the reference dose is 2 ppb
- 2,6-dinitrotoluene none reported, but the reference dose is 1 ppb
- HMX 400 ppb

A review of the data in Appendix A shows that occasionally the nitrobody 2,4 dinitrotoluene would

Table 9. NIOSH Pocket Guide to Chemical Hazards Summary

Nitrobody	10 hr TWA (ppm)	IDLH (ppm)
Nitrobenzene	1	200
2-Nitrotoluene	2	200
3-Nitrotoluene	2	200
4-Nitrotoluene	2	200

TWA = time weighted average

IDLH = immediately dangerous to life and health

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exceed the above level in influent samples, but was always reduced to below quantitation limit (BQL) values after being treated in the contactors. A further review in the Public Health Service National Institute for Occupational Health (NIOSH) Pocket Guide to Chemical Hazards reports on four additional nitrobenzenes. This information is summarized in Table 9.

#### 4.5 GAC Results

The treated water was pumped through three tanks of GAC filters for insurance against contaminating the surface area with the discharge. Evaluators took water samples from the GAC filters a minimum of once per day. Daily analysis of the GAC samples indicated that almost all of the contaminants tested for were below detection limits. The only parameter always detected was the nitrate as nitrogen with a maximum value of 5.37 mg/L. Nitrate as nitrogen was not treated by either the Peroxone system or the GAC filters. The State of Nebraska's requirement for nitrate as nitrogen is 100 mg/L in the released effluent (Reference 30). Therefore, the levels remained well below required standards.

Nitrites were not routinely analyzed during this demonstration, whereas nitrates were. In the dissolved oxygen rich aqueous environment that characterized this demonstration, it was suspected that any nitrite ions in solution would be quickly oxidized to nitrate ions, in which nitrogen would be at its highest valence state. On six separate occasions, nitrite was analytically measured. Of these six events, nitrite appeared as a measurable ion once. That event occurred on October 1, 1996 in an influent water sample drawn from well #2. The concentration measured was 0.52 mg/L. Incidentally, the nitrate concentration measured on that same groundwater sample was 9.72 mg/L, almost 19 times greater. This observation substantiated the assumption that nitrites were not of a consequence in the initial sampling plan. With regard to the magnitudes observed, the Nebraska Department of Environmental Quality stipulated a limit of 100 mg/L nitrate as nitrogen as the daily maximum limit to be released for the short duration of this demonstration. They did not address nitrites. The average value observed for this demonstration was 2.67 mg/L, so this would not pose a problem for regulatory authorities should this have been a system operating at 1000 gpm. For comparison, the drinking water standard for nitrate is 10 mg/L.

TNB was detected about one third of the time during Phase II at a value (for every detection) of 0.3 µg/L. This level is still well below the required standard of 4.0 µg/L. No other parameter was detected using EPA Method 8330 during the demonstration following the GAC treatment.

At the end of the demonstration, the GAC supplier tested a sample of the used GAC to determine if it was suitable for thermal regeneration. It was not. Testing resulted in the inability to “pop” into a new high specific surface reconfiguration. Upon close examination, trace concentrations of metals were found to be present. None exceeded any Toxicity Characteristic Leaching Procedure (TCLP) action levels to warrant this material being considered a hazardous waste.

Evaluators believe that the process oxidized these metal salt cations, the solubility was reduced, and subsequently precipitated into the GAC interfacial fissures, interfering with thermal regeneration (Reference 31). Insufficient information is available to determine if this is unique to the Peroxone system for all applications, dependent upon influent water quality characteristics and/or the type of GAC used.

Another supplier of GAC was consulted, and they advised not to attempt to regenerate GAC used in this application (Reference 19). More work needs to be accomplished in this technical support

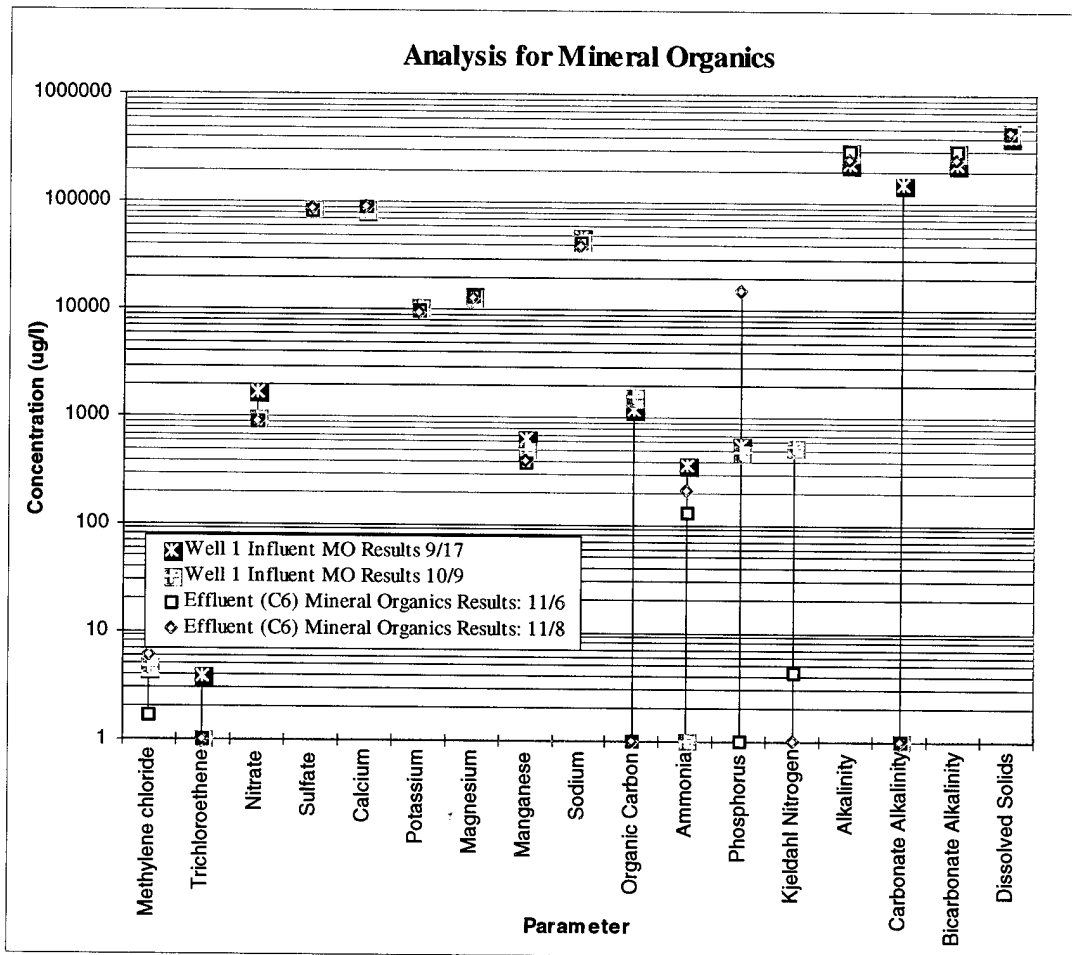


Figure 24. The mineral organics results show no consistent change in the water characterization from before to after treatment.

area. If this GAC cannot be thermally regenerated for recycling, but instead landfilled, the cost of this innovative technology will increase.

#### 4.6 Water Characterization: Mineral Organics

##### Results

The evaluators took four water samples for a mineral organics analysis (verses the explosives analysis) to characterize the groundwater from well #1. Two samples were drawn from the influent and two samples from the effluent end of the Peroxone system. Figure 24 shows the results of the influent and effluent characteristics. Well #2 (the well not used for the demonstration) influent concentrations were examined during the optimization period of the demonstration, and the results are provided in Appendix C. This laboratory analysis was not a requirement for the evaluation, but was included to characterize the water.

#### 4.7 Laboratory BQL Levels and Quality Assurance

All the nitrobodyes listed in the analysis for Method 8330, but not mentioned in this evaluation, were at the laboratory's "BQL" before the last treatment stage. BQL stands for "below quantitation limit" and is a term used when performing laboratory analysis. BQL means that for the laboratory to detect and measure an amount of some substance, it must be above the BQL used by that laboratory for a specific unit of analytical equipment that is properly calibrated within the range of the subject analyte. For example, the laboratory set their instrumentation to detect TNT down to levels of 0.1 µg/L. Therefore, any value below 0.1 µg/L will show up as BQL, or below quantitation limit. When the results show BQL as the contaminant concentration, it is determined that none is detected. To clarify exactly how much of a contaminant there may be when "none is detected," Table 10 lists the BQL levels used at the laboratory for the effluent results. These values are the highest concentrations that could remain in the treated water.

As part of the independent evaluation, a quality assurance review of the laboratory analytical data results was accomplished by the evaluators. The 13-week test and evaluation period of this innovative remedial technology consisted of the following, after the system was constructed:

- System startup period (2 weeks)

Table 10. Nitrobody Analyses BQL Levels

Nitrobodyes	BQL (µg/L)
Nitroaromatics and Nitramines by High Performance Liquid Chromatography	
High Melting Explosives (HMX)	0.6
Royal Demolition Explosives (RDX)	0.6
1,3,5-Trinitrobenzene (TNB)	0.3
1,3-Dinitrobenzene	0.3
2,4,6-Trinitrotoluene (TNT)	0.3
4-Amino-2,6-dinitrotoluene	0.3
2,6-Dinitrotoluene	0.3
2-Amino-4,6-dinitrotoluene	0.3
2,4-Dinitrotoluene	0.3
Methyl-2,4,6-trinitrophenylnitramine	0.6
2-Nitrotoluene	0.6
3-Nitrotoluene	0.6
4-Nitrotoluene	0.6
Nitrobenzene	0.3
Nitrate as Nitrogen	0.25 mg/L

- Optimization/testbed operational period (2 weeks)
- Demonstration period (8 weeks)

During system startup (i.e., debugging), the data generated was used by the demonstration operators only to bring the system to satisfactory operating conditions. For the remainder of the test and evaluation period, approximately 12,000 data points were generated, 9,900 of which were generated during the demonstration period and are the subject of analysis of this independent evaluation and included in Appendix A.

The laboratory analytical data was generated in four discrete steps:

1. Field sampling
2. Laboratory processing
3. Development of the individual daily demonstration binders
4. Transposition of data from binders to the process evaluation analysis database

Field sampling methods were carried out in accordance with established demonstration procedures (References 32, 33, and 34). This guidance covered all aspects of field sampling including the amount and type of preservatives per sample, documentation on chain-of-custody forms, and laboratory sample receipt checklists. Field sampling of the treatment train included the influent groundwater, post contactor sample ports, the final contactor (C6, considered to be the process effluent), and treated water discharging from the GAC units. Duplicate sampling procedures were randomly applied. All field samples were placed in amber glass bottles, bubble wrapped, packed in ice, and shipped for overnight delivery to the analytical laboratory.

Some analytical testing was done on site, and included :

- Ozone residual analyses by Standard Method 4500-O3-B Indigo Colorimetric with a Hach Model DR-700 colorimeter
- ORP by Standard Method 2580 with an Orion Model 9678BN probe and an Orion Model 920 meter
- pH with a Hach Model EC-10 portable pH meter and probe

A review of the laboratory results included reviewing the field sampling documentation, sample preparation, handling and shipping, sample receipt actions by the laboratory (their internal checklist), chain-of-custody protocol, laboratory wet chemistry narratives reviews, laboratory instrument calibrations, surrogates recoveries, matrix spikes and matrix spike duplicate recoveries, and their relative percent differences. No incidences of out of calibration instruments were observed. Of a 20% in-depth analysis of laboratory analytical narratives reviewed, it was observed that the surro-

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gate recovering values appeared low. This is interpreted as matrix interference during the HPLC analysis for the various nitro bodies. Considering the number of nitro body isomers that can exist, this was not considered significant.

In some other cases, due to high concentrations of some samples, dilution techniques had to be applied. Of the 53 days of sampling, two incidences occurred in which containers were received with melted ice. This was not considered serious. One container involved samples before the demonstration evaluations occurred, and the other occurred on the last day of the demonstration, November 8. A review of the facts and circumstances found that the container sat over a weekend before it was opened and logged in by the laboratory. The results of the nitrate nitrogen test could have been impacted by this occurrence by driving some of the nitrates back towards nitrites. However, there were not duplicates in other containers, so such can not be determined. However, the samples were preserved and the sample results were very similar to one another and similar in magnitude to values of other data recorded on previous days for this analyte.

During the demonstration period, 590 discrete samples were sent to the analytical laboratory. Seven of these samples arrived broken, for a less than 1% breakage rate. There was also one incident of a chain of custody form not being completely filled out, as it was missing a signature on one page. In all cases, the collected samples arrived at the laboratory in less than 24 hours, as desired.

The individual demonstration daily binders were used for multiple purposes and included daily tracking of system performance on specially-prepared data log sheets, noting special occurrences, maintaining quick-look preliminary faxed copies of laboratory analytical data, and the final laboratory reports. These documents were the data source for the transfer of all analytical parameter results to the process evaluation database.

A 100% review of the data transfer to the process evaluation database was accomplished as part of the quality assurance process for this project. Some minor errors were noted and were corrected. The majority of errors were rounding errors associated with the nitrate nitrogen parameter.

**In summary, the independent quality assurance reviewers conclude that the field sampling, shipping and handling, and laboratory analyses were performed satisfactorily, and the resulting analytical laboratory data produced were valid to support this innovative remedial technology demonstration.**

## 4.8 System Performance Findings

The design of the Peroxone pilot plant system could be adjusted to improve the efficiency. For example, the ozone bubbles emanating from the diffusers inside each contactor should be as fine as possible to disseminate the ozone throughout the water for more efficient treatment. The diffusers at the CAAP site did not create fine bubbles (as in carbonation). Fine bubbles provide an efficient transfer of the ozone into the aqueous phase. This, in turn, remediates the contaminants more efficiently. This was visually confirmed through a site portal and could also be heard by the demonstration operators and evaluators when standing within 2 to 3 feet of the contactor. System demonstration operators estimated the size of some of the bubbles to be as large as 0.5 inch.

Another observation of the system was the ability to adjust the settings of the chemical doses. The advantage in this is the flexibility to set the doses in a variety of combinations. The system need not be "hardwired" for one operational process, but can be easily altered for several different treatment needs. For example, once the influent concentration stabilizes, a lower dose of chemicals may remediate the contaminants effectively, and the system could be adjusted accordingly and operate more inexpensively.

There may also be opportunities to improve ozone gas mass transfer to the bulk of solution. The demonstration subcontractor performed dye tests to demonstrate that complete mixing occurred in the contactors (Reference 21). This is not necessarily an indicator of complete mass transfer of the ozone gas to the bulk of solution, which is more a surface chemistry phenomena, as described by Henry's Law and applied today by industry following the two-film theory and applied in aeration systems, air stripping towers, and more. Many variations of surface interfaces are applied such as trays, bubble diffusers, and tower packing systems (References 35 and 36). The intent is to have a large specific surface area value, a large gradient between the partial pressure of the gas being transferred and the molar fraction of the gas in solution, and as little headloss through the system as possible.

In the demonstration, reliance was left to the diffuser bubble stream alone. The height and quantity of contactors affected this mass transfer more than the mixing. The Ad Hoc Planning Group recommended conventional bubble diffusion type reactors be used, and they were. However, observations of the bubbles generated were described as large (0.5 inch in diameter), as opposed to the fine mist diffusers (millimeter range of diameter size), that some observers expected to witness. From these observations, it is concluded that better specific surface values could have been achieved. Initially the demonstration

subcontractor had some maintenance difficulties with the gaskets sealing the diffuser stones, but reported that this was repaired.

The Ad Hoc Planning Group also recommended some consideration be given to using packed columns as well as unpacked columns. The latter was utilized, however there is no indication that packed columns were even considered, and if so, why they were not used. Column packing should have been more seriously considered in an effort to improve mass transfer of the ozone to the bulk of solution and thus possibly reduce the number of contactors utilized as well as their height, and also reduce the amount of ozone required to be generated. If this could be successful, there would be an opportunity to both reduce system capital and operations and maintenance costs. This point will be revisited in the Recommendations section.

The demonstration system did not reach steady state conditions. Groundwater influent characteristics varied (and demonstrated considerable standard deviations) as did the dependent variables of flow rate, detention time, and oxidant dosing applied in response to these loadings. The impact of this condition, placed more burden on the operating parameters and dosing requirements of the reagents, and detracted from the demonstration effort to obtain data from a stable system. However, this loading may come much closer to representing realistic field operating conditions that could be encountered at other Army depots.

To the system's credit, it was able to perform well under these conditions, which further strengthens its endorsement for further utilization. An interesting observation was that for the four target COCs (RDX, HMX, TNT, and TNB) the influent concentrations of all four decreased during the demonstration as the various runs proceeded. This is illustrated in Figure 19, and is especially apparent for RDX and TNT. It seemed that even the pilot plant was effective at cleaning up the aquifer during this short demonstration. However, this demonstration did not return the treated groundwater through reinjection to the aquifer, but instead discharged it to a natural surface drainage. Moreover, data is not available of the ambient levels returned to in the groundwater when the demonstration testing was complete. Nevertheless, reviewers should take note of this observation. Perhaps Peroxone oxidation could be employed as a rapid short-term solution to lower contamination to safer levels and then allow natural attenuation with no further action. However, this scenario has not been demonstrated and was not part of this effort.

Based on personal discussions with two of the subcontractor's personnel involved with this project (References 37 and 38), there were observations of color development, i.e., "pink water" being

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The system was not optimized in the classic sense, in which all the variables are first identified and then one is deliberately varied, and the impact observed and recorded.

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observed in the influent groundwater. The same observation was made during the WES work (Reference 3, page 24). This is a cause for some concern because the possibility exists that some transient multibenzene ringed isomers could form that could have toxicity impacts. This demonstrated system was shielded from the sunlight with the exception of a few observation ports in the contactors. Thus there was limited exposure of the contaminated groundwater to sunlight. Perhaps the color development observed was generated at the time the wastewater from plant operations was first discharged to the surface lagoons, pits and ponds, and then percolated through the vadose zone to the aquifer. This requires more consideration. In future testing, color should be a monitored parameter, and analytical work with gas chromatography should be sensitive to unusual spiking on the resulting analytical printouts.

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One way to maximize the Peroxone reactions and minimize the competing hydrogen peroxide and ozone oxidation reactions with flow stream constituents may be to operate the system at very high pH.

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The system was not optimized in the classic sense, in which all the variables are first identified, and then in a very disciplined manner, all are held constant, save one which is deliberately varied, and the impact on output observed and recorded. The demonstration subcontractor was severely time constrained and immediately after a short 4-week system startup/debugging cycle, entered a two week "optimization" cycle, in which eight planned experimental runs were carried out. Nonetheless, the subcontractor demonstration operators did effectively bring the system to a *testbed operational* configuration. The system variables that the subcontractor worked with during these experimental runs were:

- Volumetric flow rate
- Hydraulic detention time
- Ozone dose
- Mass ratio of hydrogen peroxide to ozone
- Well source from the aquifer

No effort was made to control pH (which varied in the neutral range from the high 6s to the high 7s) or temperature, and the influent water quality characteristics varied also (see Figures 20 and 25). By the demonstration subcontractor's own admission (Reference 21, page 4-12), changing more than one variable at a time did not conform to the "ideal" approach to such a task. Nonetheless, to their credit, they succeeded in tuning up the system well enough to successfully operate it for the 8-week demonstration period that followed until winter weather forced the effort to be retired.

Their efforts produced some results that were difficult to understand, the most challenging being the mass ratio observed not supporting their stoichiometric assumptions. It is believed there were competing nonselective oxidation reactions occurring between the hydrogen peroxide and ozone reacting with the contaminants in the

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flowstream independently of the Peroxone hydroxyl radicals (previously presented in this section and Section 2.3). The recently released WES report (Reference 3) may offer insight into this situation and provide a means of better understanding the complex series of reactions that are occurring, specifically (Reference 3, page 18) the importance of pH in controlling these reactions. One way to maximize the Peroxone reactions and minimize the competing hydrogen peroxide and ozone oxidation reactions with flow stream constituents may be to operate the system at very high pH values to greatly increase the molar concentration of hydroxide radicals present in the bulk of solution. No effort was made to do so in the demonstration. Experimental efforts need to be conducted to investigate the efficiency of this effort. One needs to consider the impacts of operating at a high pH range (10 to 12), because there are some potential negative impacts. These are:

- Precipitating out metal salts that might be in the contaminated groundwater flowstream and creating caking and sliming in the contactors and a responding expensive operations and maintenance (O&M) requirement.
- Raising the pH of the system will represent an expense. After the treatment is complete and before the effluent is discharged to the environment, the water will have to be neutralized and its pH returned to the neutral range.
- The need to have two other reagents, such as sodium hydroxide and hydrochloric acid, on site in large volumes will add additional risk to the operators and the ambient environment, and needs to be addressed in a site-specific health and safety plan and a spill prevention, control, and countermeasures plan, and will require additional site preparation work.

Nonetheless, this element needs more investigation to better understand this technology. The variables that warrant close scrutiny are:

- Oxygen demand (inorganics, aliphatics, and aromatics) of the contaminants in the flowstream
- Hydraulic detention time
- Volumetric flow rate
- Mass application rate of hydrogen peroxide
- Mass application rate of ozone
- Mass transfer rate of ozone to the flowstream
- pH
- Temperature
- Color development
- Oxidation molecular reaction sites
- Concentration gradients of target contaminants

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**In summary, this demonstration system performed well in the field under realistic loadings, and generated much information to allow a better understanding of the process kinetics involved. However, many questions remain, and the unit processes can be more efficiently reconfigured to provide for more cost-effective operations.**

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# 5 System Costs

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## 5.1 Peroxone System Cost

The evaluation methodology section described two objectives required to adequately address the Operational Supportability Issue for the Peroxone demonstration.

They were:

- *Objective 2* - Determine the total resources used in treating explosives-contaminated groundwater during the CAAP Peroxone system demonstration.
- *Objective 3* - Compare the costs of the current systems with the Peroxone system.

Reviewers will note that *Objective 1* (Section 3.1) was to assess the level of contaminant destruction achieved, i.e., operational effectiveness. The levels of performance achieved were previously addressed in Section 4.0.

The resources required to meet Objectives 2 and 3 were broken into subobjectives as follows.

- Subobjective 2.1* Document labor hours and skill level to support CAAP operation.
- Subobjective 2.2* Document consumable supplies that support the CAAP operation.
- Subobjective 2.3* Document the electrical power consumption of the CAAP operation.
- Subobjective 2.4* Document the maintenance requirements and equipment costs.
- Subobjective 2.5* Document the setup and demobilization costs.
- Subobjective 3.1* Compare cost data with UV/OX.
- Subobjective 3.2* Compare cost data with GAC.

The following sections describe the data collection and analysis for each subobjective.

The efforts described here develop the costs associated with the as-fielded and demonstrated pilot plant and project total system costs in 1,000-gallon increments. Both capital and operations and maintenance costs are addressed. This analysis is based on a 10-year operational system life cycle.

### 5.1.1 Labor-Hours and Skill Level

The purpose of this subobjective was to determine the skill level required to operate a Peroxone system and the required staffing levels. This was accomplished by interviewing the site operators and soliciting their estimates of the skill mix and level of efforts required to operate the system in a production versus demonstration environ-

ment. The consensus estimate of the skill mix and the corresponding level of effort (LOE) is shown in Table 11.

Table 11. Peroxone Skill Mix and Level of Effort

Skill Set	Evaluator Skill Estimate	Evaluator LOE Estimate
Operator	Assoc. Tech. Degree or BS Arts & Science	1/2 Full Time Equivalent
Supervisor	BS Engr. or Mgt.	1/8 Full Time Equivalent
Administrator	Non-Degree	1/2 Full Time Equivalent
<b>Nominal Individual Skill Mix and LOE</b>	BS Arts & Science	<b>3/4 Full Time Equivalents</b>

From 1996 human resources hiring data, the mid-range salary for a B.S. in Arts and Sciences graduate is approximately \$25,000/yr, or dividing by 2,000 hours in a working calendar year equals an approximate \$12/hour individual. From Table 11, the nominal LOE for the site

operation was approximately 3/4 Full Time Equivalent (FTE). In addition, the evaluators' consensus for site operation is based on the process operating 24 hours a day, staffed during the day shift and left in unattended operation during the night. This means that for every hour of day shift cost, there are two hours of processing performed during the night; i.e., \$12/hour x 1/3, or \$4/process hour. In addition, only 3/4 FTE is required; therefore, 3/4 x \$4 equals \$3/process hour. This value was multiplied by the total hours in each phase, then divided by the gallons processed in each phase to determine a usage unit. The critical data collected and analyzed for this subobjective is presented in Table 11 (and summarized later with the other resource data in Table 17).

This data assumes the demonstration site is in a location where other activities are taking place to justify estimating operation, supervision, and administration personnel on a fractional basis. The sites where this type of contamination exists are at large Army ammunition plants, arsenals, and depots under the administrative direction of the Industrial Operations Command (References 1 and 2). Overhead costs are not included in any of the cost comparisons.

### 5.1.2 Electrical and Chemical Consumption

This section combines the two subobjectives dealing with consumable chemicals and electrical resources required to operate the system. The purpose of these subobjectives was to identify the consumable resources required to operate the process, then record the consumption during the demonstration. The optimization phase of the demonstration identified the following consumables.

- Electrical power
- Hydrogen peroxide
- Liquid oxygen
- Sodiumthiosulfate

Electrical power was used to operate the site unit process treatment equipment, such as hydrogen peroxide pumps, the well pump, and the ozone generator. Hydrogen peroxide is part of the process chemistry. Liquid oxygen was used as the source of oxygen for the ozone generator. Sodium thiosulfate was used as a scavenger agent consuming excess ozone in the effluent fluid stream prior to discharge. Detailed descriptions of the consumable materials, the data collection methodology, and data analysis are described in the following subsections.

### 5.1.2.1 Electricity Consumption

Electrical power was used for all equipment operation. The electrical feed for the site was configured through a split bus to provide two separate power source feeds, one for the site test support facility (office space for the demonstration operators and evaluators) and the second for the Peroxone demonstration equipment. The equipment feed provided power to all site equipment such as the influent and effluent pumps, hydrogen peroxide metering pumps, catalytic combustion unit, and the ozone generator. The largest single consumer of electricity at the site was the ozone generator, which required electricity to convert oxygen to ozone. This equipment is shown in Figure 25. It was not possible to monitor or record the power consumption directly from the ozone generator due to the lack of metering equipment at the test site. Instead, data was recorded daily from meter readings on a cumulative power meter located on the power feed to the equipment. The electricity used for the office space was not part of these readings.

From these readings, the total kilowatt hours (kWh) of electricity consumed per the total gallons of water treated and the total hours of operation were calculated for each phase of the demonstration. The summaries of the calculations by phase are shown in Table 12.

Table 12 is presented so that consumables can be calculated on a cost per 1,000-gallons of treated water basis or a cost per processing-hour basis. This is useful when comparing different sets of process costs. The Nebraska Public Power district provided a range of electricity usage rates

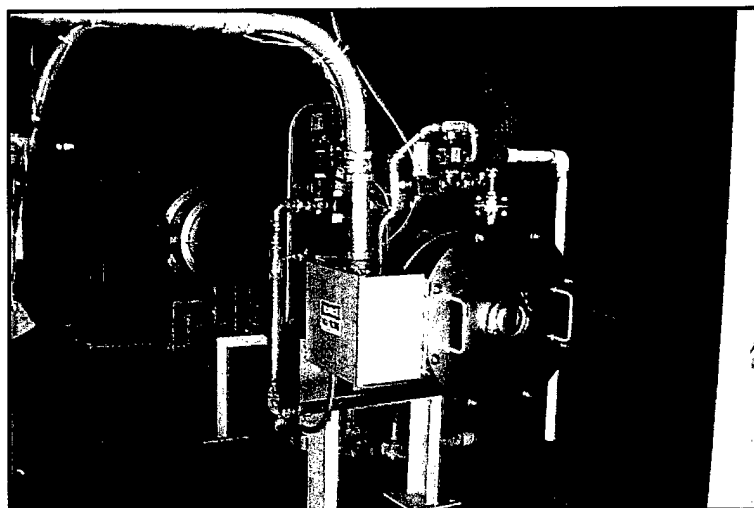


Figure 25. The ozone generator was the source of most of the electricity consumption.

Table 12. Peroxone Electrical Usage Summary

Electrical Usage Resource Data	Demonstration Phase I	Demonstration Phase II
Electricity Consumption (kWh)	8,480	10,360
Gallons of Water Processed (Gallons)	375,180	580,125
Hours of Equipment Operation (Hours)	481	387

from which a cost of \$0.06/kWh was used to estimate the cost of operation on a 1,000-gallon treated water basis. The amount of electricity consumed was divided by the amount of water processed. To obtain a usage amount, this value was then multiplied by the cost to obtain a cost per 1,000 gallons. The critical data collected and analyzed for this subobjective is summarized later with the other resource data in Table 17. More details of the calculations are in Appendix D.

The cost of producing and transferring the ozone into the process stream is primarily dependent upon the electrical usage/cost, the oxygen usage/cost, and the efficiency of the ozone mass transfer in the aqueous phase. During the demonstration, the ozone diffusers were found to operate at a lower than expected mass transfer efficiency. The designed mass transfer efficiency was approximately 90%, and the actual or measured efficiency was only 60% to 75%. If the diffusers had operated at the designed efficiency, the system would have required less ozone, and therefore less electricity and oxygen, to produce the same amount of treated water. This would have lowered the cost per 1,000 gallons of treated water. However, the degree of cost improvement is difficult to estimate and is not included in this report.

#### 5.1.2.2 Liquid Oxygen

The ozone was created by feeding oxygen to the electrical ozone generator. The oxygen was produced by passing liquid oxygen (LOX) through a tube and fin heat exchanger where it is converted to gaseous oxygen and fed to the ozone generator. The equipment for this process is shown in Figure 26.

The oxygen consumption was calculated based on a constant flow rate of oxygen during the entire demonstration. A constant flow rate of 9 standard cubic feet per minute (scfm) was set by the demonstration operators during start up. This value was

then multiplied by the runtime (process hours) to produce the estimated total for each phase of the demonstration. The summaries of the consumption by phase are shown in Table 13. The number of cubic feet (cu ft) of oxygen used per phase was divided by the gallons of water processed to obtain a usage value. The cost per cubic foot for LOX was estimated at \$0.0069/cu ft by the supplier of the LOX.

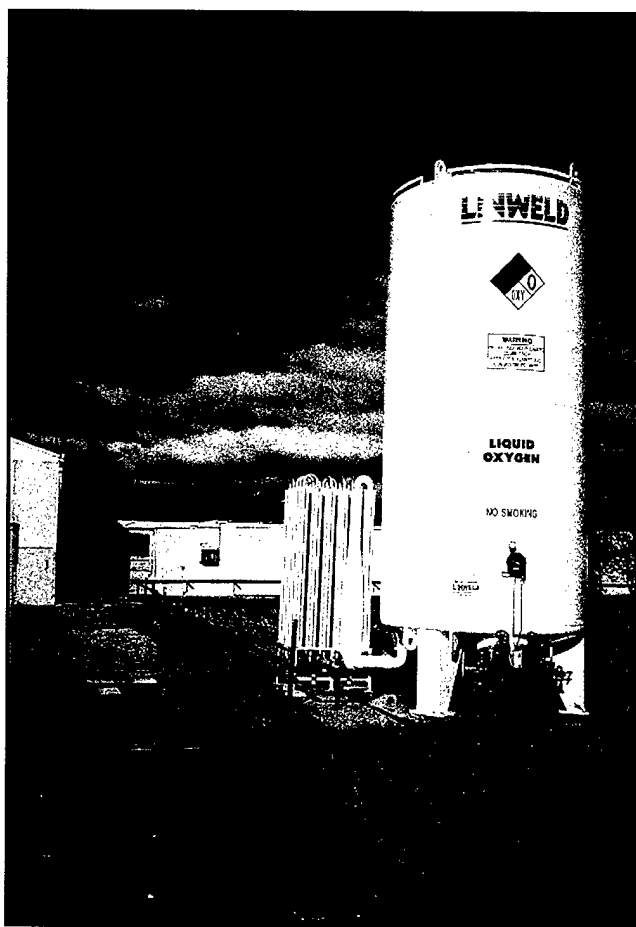


Figure 26. The liquid oxygen tank fed into the ozone generator housed in a shed, which can be seen in the background.

The data for this subobjective is summarized with the other resource data in Table 17. More details of the calculations are in Appendix D.

It should be noted that this method omits any LOX escaping from the tank due to environmental temperature changes and tank fillings. The oxygen supplier estimated that 6% to 10% of the LOX can be expected to be lost due to these effects. The usage amounts presented later in Table 17 should be increased by 6% to 10% if these losses are to be included. There are other sources of oxygen, such as air-oxygen generators, that may be more cost effective than LOX. This matter was previously addressed in Section 2.4. A driver in any decision will be the ozone gas transfer percentage required to be transferred. The greater the nitroaromatic influent mass concentrations and amounts to be destroyed, the more ozone will be required.

### 5.1.2.3 Hydrogen Peroxide

Hydrogen peroxide was used as a source of oxygen and hydrogen in the formation of the process hydroxyl radicals. It was batch prepared by the operators in a holding tank at the site from a concentrated hydrogen peroxide solution. The dilute solution was pumped from the dilution holding tank to the individual contactors where it was injected into the incoming fluid stream of each contactor. The preparation of a diluted batch of hydrogen peroxide is shown in Figure 27.

The hydrogen peroxide consumption approach involved the theoretical calculation of peroxide usage based on the peroxide feed rate, the feed solution concentration, batch preparation mixture concentration, and the runtime for each day of the demonstration. These calculations were performed each day of the demonstration, and the usage quantities were summed to derive the total gallons used in each phase. The summaries of hydrogen peroxide consumption by phase are shown in Table 14. This value was multiplied by the cost per gallon, for hydrogen peroxide was estimated by the supplier at \$4.00/gal.

More details of this approach are in Appendix D, and the summaries of the peroxide consumption by phase are shown later in Table 17.

The operators adjusted the dose of hydrogen peroxide during the first half of Phase I operation. As previously presented in Section 4.2, Phase I was divided into two

Table 13. Peroxone Oxygen Usage Summary

Oxygen Usage Resource Data	Demonstration Phase I	Demonstration Phase II
Theoretical Oxygen Consumption (cu ft)	247,049	208,846
Gallons of Water Processed (Gallons)	375,180	580,125
Hours of Equipment Operation (Hours)	481	387

#### Theoretical vs. Operational Data

In reviewing the data presented in Tables 13, 14, and 15, and elsewhere in the text of this report, the term "theoretical" is occasionally used to differentiate from the term "observed." Theoretical, as used in this report, is based on stoichiometric relationships between the reacting compounds involved in the Peroxone process, i.e., electron balanced chemical reactions and the resulting proportional based quantitative calculations used to determine masses and concentrations of reactants and products. In the demonstration, there were marked differences between these theoretical values and the observed values, such as with the mass ratio of hydrogen peroxide and ozone, and ozone mass transfer efficiencies. The former is attributed to parallel random competing oxidative reactions of the hydrogen peroxide and ozone with Peroxone. This was previously addressed in Sections 2.3 and 4.0. The latter is attributed to the lack of fine bubble aeration achieved by the ceramic diffusers. In addition, some random line leakage and ozone monitor maintenance challenges contributed to these observations.

Table 14. Peroxone Hydrogen Peroxide Usage Summary

H <sub>2</sub> O <sub>2</sub> Usage Resource Data	Demonstration Phase I	Demonstration Phase II
Theoretical H <sub>2</sub> O <sub>2</sub> Consumption (Gallons)	159.56	211.37
Gallons of Water Processed (Gallons)	375,180	580,125
Hours of Equipment Operation (Hours)	481	387

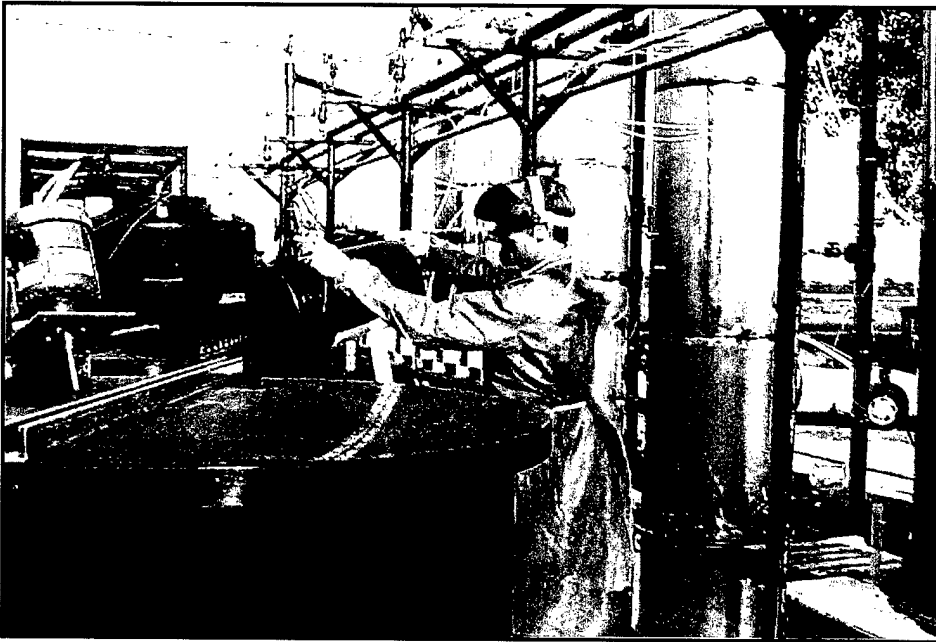


Figure 27. The operator mixed the hydrogen peroxide in batches and added it to the holding tank that fed into the system.

data sets to examine the cost difference between the first and second settings of hydrogen peroxide usage. Using the theoretical method of calculating the cost, data set 1 had a hydrogen peroxide cost of \$1.23/1,000 gallons of treated water, and data set 2 had a hydrogen peroxide cost of \$1.24/1,000 gallons of treated water. A mature system design (rather than the *pilot design* of this system) may operate efficiently at the initial hydrogen peroxide dose as WES had determined and, therefore, may be less expensive to operate.

#### 5.1.2.4 Sodium Thiosulfate

Sodium thiosulfate was used as a scavenger to destroy any remaining ozone in the effluent prior to discharge. It was batch prepared in a holding tank and fed into the effluent tank at a constant rate to achieve complete neutralization of all excess ozone.

The operational flow rate of thiosulfate used during the demonstration reflected an amount that would ensure complete neutralization of all excess ozone. The theoretical usage was calculated as the minimum amount needed to neutralize all excess ozone and was multiplied by a safety factor of three to ensure enough thiosulfate was present. The summaries of the sodium thiosulfate consumption by phase are shown in Table 15. More details of the calculations are in Appendix D.

The rate of sodium thiosulfate used per phase was then converted to ounces/minute and multiplied by the total hours of operation, then divided by the total gallons processed. This value was multiplied by the cost per ounce (oz), or \$0.96/oz, obtained from the supplier of the sodium thiosulfate.

The critical data collected and analyzed for this subobjective, including the calculations for all phases of the demonstration, is summarized with other resource data in Table 17.

Regardless of the amount of ozone residuals in the water, the same dose of sodium thiosulfate was always used, enough to ensure no ozone was left in the discharge effluent, with an ample margin of

safety. In future systems, the sodium thiosulfate feed would be optimized to use only the necessary amount and thus reduce the cost.

### 5.1.3 Equipment and Maintenance Cost (Recurring Capital Costs)

The equipment capital costs were obtained from the ACOE, Omaha District (Reference 39), and represent the line item capital costs proposed for the demonstration program in 1996 dollars.

These capital costs are shown in Table 16.

The costs are itemized by their respective implementation phase and are in the approximate sequence required for full-scale program development. In addition, there are costs included, such as site planning, that are not solely for the procurement of capital items.

However, procurement of another system or a full-scale system will require some siting or environmental assessment work prior to full-scale design and build, and are considered recurring costs. The total cost to execute the Peroxone system program has been itemized along with the cost of each item in the column "Total Cost." The cost to fabricate and install a second or future system is estimated in the column "Recurring Cost." In this column, the one-time costs, such as demonstration testing and data collection and analysis, are removed and the remaining costs are costs applicable to a second, third, or tenth unit if they were purchased. The third column itemizes the cost of the "Non-recurring" one-time or site-specific costs associated with the total costs.

To compare different system costs, annual capital and maintenance costs are required. The capital cost is simply the total recurring cost of \$427,724 (Table 16) divided by 10 years of operation, or \$42,772/year. Using an estimate for capital equipment maintenance costs of 10% of capital cost, the maintenance cost is also \$42,772/year.

To equate the capital and maintenance costs to a cost per 1,000-gallon basis, the annual cost was dividing it by the gallons per year processed. For Peroxone, the system was designed for 25

Table 15. Sodium Thiosulfate Usage Summary

Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> Usage Resource Data	Demonstration Phase I	Demonstration Phase II
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> Theoretical Consumption (ounces/minute)	0.01275	0.01275
Gallons of Water Processed (Gallons)	375,180	580,125
Hours of Equipment Operation (Hours)	481	387

Table 16. Peroxone Equipment Cost Summary for the CAAP Demonstration

CAAP PEROXONE Demonstration Activities	TOTAL COSTS(\$)	TOTAL RECURRING COSTS(\$)	TOTAL NON-RECURRING COSTS(\$)
Design and Procure System	\$38,644	\$38,644	\$0
Predemonstration Activity (Site Planning)	\$12,200	\$12,200	\$0
Construct System	\$339,948	\$339,948	\$0
System Startup and Debug	\$36,932	\$36,932	\$0
Demonstration	\$262,639	\$0	\$262,639
Demobilize	\$24,237	\$0	\$24,237
<b>TOTAL CAPITAL COST</b>	<b>\$714,600</b>	<b>\$427,724</b>	<b>\$286,876</b>

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gpm continuous operation; i.e., 25 gpm x 1,140 minutes per day x 365 days per year, or 13,140,000 gallons per year.

The data for this subobjective is summarized for all phases of the demonstration in Table 17. The costs in this table are costs resulting from scaling up the 25 gpm pilot plant to 1,000 gallons, and not the costs of developing a 1,000-gpm field-scale prototype plant.

#### **5.1.4 Equipment Setup and Demobilization Cost (Non-recurring Capital Costs)**

The purpose of this subobjective was to collect data on the existing equipment setup and demobilization costs. This was necessary to ensure these non-recurring costs were not included in any analysis of future system costs since they are one-time costs associated with the demonstration.

In Table 16 under the column "Non-recurring," the one-time costs, such as demonstration testing and data collection and analysis, are itemized. The remaining costs applicable to a second, third, or tenth unit (if they were purchased) are zeroed out. This column represents the cost of the "Non-recurring" one-time or site-specific costs associated with the demonstration. There is no cost analysis performed with this data other than to ensure it is accounted for and not included in future system cost analyses.

#### **5.1.5 Peroxone System Cost Summary**

The previous subsections addressed the purpose, approach, and results of each subobjective data element. A summary of these cost data elements and the analysis results, or costs, for each are shown in Table 17. Figure 28 is a graphical representation of the consumable Peroxone system costs. The values are presented on a cost per 1,000-gallon basis for Phase I and Phase II of the demonstration. Phase II was approximately 30% less expensive due to the doubling from 13 gpm to 25 gpm of the flow rate. Using the Phase II cost elements and the capital plus maintenance costs, the **total cost of the Peroxone system is \$13.83/1,000 gallons.**

For the system cost analysis, theoretical consumable costs of operation were used. The operation costs were also calculated and, in most cases, the consumable costs were within 20% of the theoretical value. The costs for sodium thiosulfate had a 40% difference between operational and theoretical values. This could be attributed to losses or inefficiencies of the Peroxone system because it is still an innovative prototype. However, this condition is interpreted to signify that there was a greater amount of ozone in the effluent than anticipated, probably caused by parallel random competing oxida-

tive reactions. The hydrogen peroxide first reacted with other contaminants in the influent groundwater, and the ozone was overdosed as indicated by the high mass ratios. Ozone generation is costly as is the subsequent destruction of its residuals. More work

Table 17. Peroxone System Cost Summary

PEROXONE EVALUATION OBJECTIVE	UNITS	\$/UNIT	USAGE UNIT /1,000gd.	COST \$/1,000 gd.
<b>OPERATIONAL COST RESOURCES</b>				
MANHOURS AND SKILL LEVEL(PHASE I)	\$/Process-hr	3.00	1.282	\$3.85
MANHOURS AND SKILL LEVEL(PHASE II)	\$/Process-hr	3.00	0.667	\$2.00
<b>ELECTRICAL AND CHEMICAL</b>				
ELECTRICAL(PHASE I)	kW/hr	0.06	22.6	\$1.36
ELECTRICAL(PHASE II)	kW/hr	0.06	17.86	\$1.07
LIQUID OXYGEN(PHASE I)	cu ft	0.0069	658.5	\$4.54
LIQUID OXYGEN(PHASE II)	cu ft	0.0069	360	\$2.48
HYDROGEN PEROXIDE(PHASE I)	gal.	4.00	0.4253	\$1.70
HYDROGEN PEROXIDE(PHASE II)	gal.	4.00	0.3644	\$1.46
SODIUM THIOSULFATE(PHASE I)	oz/min	0.96	0.38	\$0.36
SODIUM THIOSULFATE(PHASE II)	oz/min	0.96	0.31	\$0.30
ANNUAL MAINTENANCE COST	\$/yr		\$42,772.00	\$3.26
ANNUAL CAPITAL COST	\$/yr		\$42,772.00	\$3.26
Total Phase I COST				\$18.33
Total Phase II COST				\$13.83

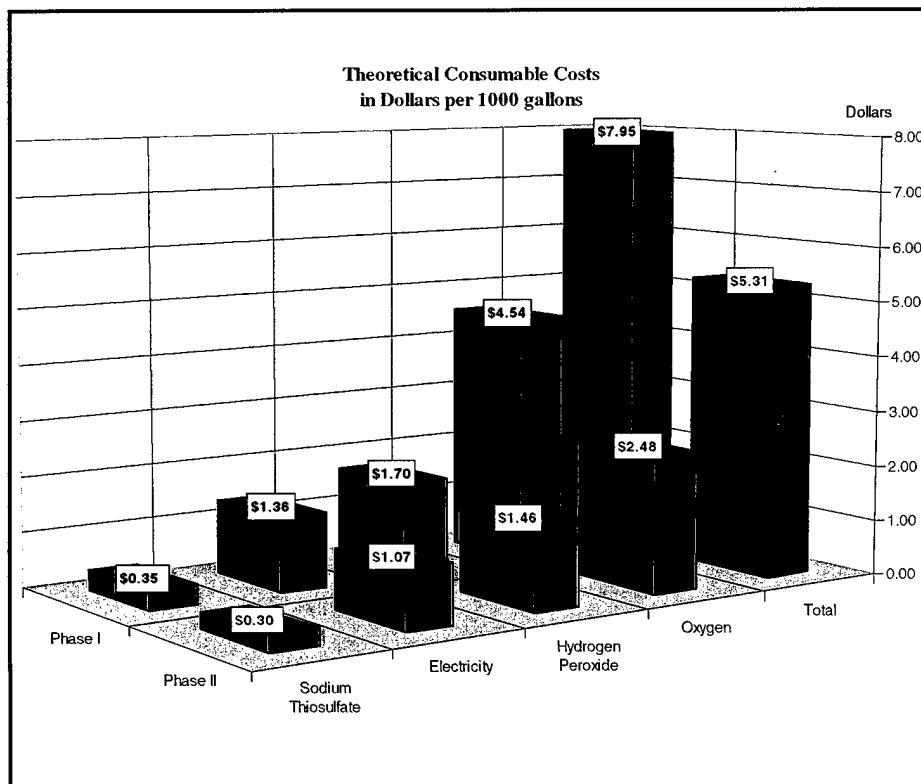


Figure 28. Phase II was more cost effective than Phase I due to increased process flow in Phase II.

on optimal dosing is required to reduce this occurrence that drives up operating costs.

## 5.2 Alternative Process Cost

This analysis compares the cost of two alternative processes for the treatment of explosives-contaminated groundwater with the Peroxone process costs. The alternative processes evaluated are the Ultraviolet/Ozone and the Granular Activated Carbon. The data previously presented for Peroxone covered all cost data resources, including both phases of the demonstration. For these alternative cost comparisons, the data for the Phase II subset of the Peroxone demonstration system is used.

To compare the costs of the three systems, a baseline set of parameters was identified to be the basis for comparison. The following parameters were used:

Flow Rate:	25 gpm
Basic Cost Units:	\$/1,000 gallons
Contaminants:	Explosive nitrocompounds (TNT, RDX, TNB, and HMX)
Contaminant Levels:	1,135 µg/L
Capital Costs:	Cost/10 years
Maintenance Costs:	10% of capital costs

To standardize the costs for the Peroxone, GAC, and UV/OX systems, the amount of contaminant removed from the CAAP groundwater by each system was calculated. The costs were converted to a cost per 1,000 gallons of treated water.

### 5.2.1 UV/OX, GAC, and Peroxone Cost Comparison

The UV/OX process, like Peroxone, is included in the class of Advanced Oxidation Process technologies. A demonstration of UV/OX process methods was conducted for USAEC and is summarized in a final report (Reference 26). The ULTROX system, currently operating in Milan, Tennessee, was selected by the evaluators as their first choice in terms of cost and operational success. From Reference 28, the UV/OX consumable data is shown in Table 18, in which the consumable cost elements are listed on the left side of the table, and the right side of the table converts the unit costs to the standard cost per 1,000-gallon basis.

To compare different system costs, annual capital and maintenance costs are required. From Reference 6, the UV/OX capital cost is \$393,000 divided by 10 years of operation, or \$39,300/year. Using an estimated capital equipment maintenance cost of 10% of capital cost, the maintenance cost is also \$39,300/year. To equate the capital and maintenance costs to the standard dollar per 1,000-gallon basis, each cost per year is converted by dividing by the gallons per year processed with the equipment. Based on 25

Table 18. PEROXONE, UV/OX, and GAC Annual Cost Summary for Consumables

LABOR and CONSUMABLE COST	UNITS	\$/UNIT	USAGE UNIT /1,000 gal.	COST \$/1,000 gal.
<b>UV/OX Costs</b>				
ELECTRICAL	KW/hr	0.06	40.8	\$2.45
NaOH	lbs	0.10	0.1681	\$0.02
H <sub>2</sub> SO <sub>4</sub>	lbs	0.07	2.95	\$0.21
UV Lamps	lamps	50.00	0.019	\$0.95
Air Filters	filters	30.00	0.00034	\$0.010
Compressor Filter	filters	100.00	0.000038	\$0.0038
Compressor Oil	volumes	50.00	0.000038	\$0.0019
UV/OX Labor	minutes	0.2840	0.0059	\$0.0017
* MANHOURS AND SKILL LEVEL	\$/Process-hr	UNK	UNK	\$0.00
Pre/Post Treat Labor	minutes	0.2840	0.14	\$0.0398
Lamp Replacement Labor	minutes	0.2840	0.0000381	\$0.000011
ANNUAL MAINTENANCE COST	\$/yr		\$39,300.00	\$2.99
ANNUAL CAPITAL COST	\$/yr		\$39,300.00	\$2.99
TOTAL COST				\$9.66
<b>GAC Costs</b>				
** MANHOURS AND SKILL LEVEL	\$/Process-hr	1.00	0.67	\$0.67
GAC Material	lb	0.95	0.0970	\$0.092
GAC Material Disposal	lb	1.25	0.0970	\$0.121
ANNUAL MAINTENANCE COST	\$/yr		\$13,000.00	\$0.99
ANNUAL CAPITAL COST	\$/yr		\$13,000.00	\$0.99
TOTAL COST				\$2.86
<b>Peroxone Costs (PHASE II)</b>				
MANHOURS AND SKILL LEVEL	\$/Process-Hr	3.00	0.667	\$2.00
ELECTRICAL	KW/hr	0.06	17.86	\$1.07
LIQUID OXYGEN	cuft	0.0069	360	\$2.48
HYDROGEN PEROXIDE	gal	4.00	0.3644	\$1.46
SODIUM THIOSULFATE	oz/min	0.96	0.31	\$0.30
ANNUAL MAINTENANCE COST	\$/yr		\$42,772.00	\$3.26
ANNUAL CAPITAL COST	\$/yr		\$42,772.00	\$3.26
TOTAL COST				\$13.83

\* Skill level and cost unknown; immature technology data not available (Reference 9)

\*\* Skill and cost best estimate based on CAAP experience

gpm continuous operation for 365 days per year, this is 13,140,000 gallons of processed water. Dividing \$39,300/year by 13,140,000 gallons, the maintenance costs are \$2.99/1,000 gallons of water treated. This was also performed for the annual capital costs. Details of the UV/OX calculation are in Appendix D.

The GAC process is a simple decontamination filtering process with some benefits, primarily operational and maintenance simplicity, when compared to a member of the class of AOP technologies, such as Peroxone. However, the process is relatively fixed in terms of process variability and requires additional processing for either thermal regeneration of the spent carbon, or disposal via landfilling

as a solid waste (either nonhazardous or hazardous). The disposal costs are third party costs that cannot be assumed to be constant in outlying years, nor should the liability for the contamination be assumed to be transferred to the third party. Data for the cost of GAC material and disposal was obtained from Calgon Carbon Corp. (Reference 25), Pittsburgh, Pennsylvania, a leading manufacturer and reclaimer of GAC systems and from telephone interviews with operators of GAC systems in Milan, Tennessee (Reference 26). The disposal cost is included in Table 18. The cost of the GAC material is based on a 15% design usage rate. This design rate accounts only for the explosive load and not other possible contaminants.

According to Reference 28, the capital cost of the GAC system operating in Milan, Tennessee, is \$130,000. As was done previously for UV/OX and Peroxone, the maintenance cost is 10% of the capital cost, or \$13,000/year, and the yearly capital cost (assuming 10 years of operation) is \$13,000/year. On a cost per 1,000-gallon basis, this is \$0.99/gallon. The transportation and disposal costs of the GAC material were obtained from Calgon Carbon and verified by the Milan operator to be \$1.25/pound. This converts to a cost of \$0.48/1,000 gallons of processed water. These consumable and capital costs are shown in Table 18 for the Peroxone, UV/OX, and GAC systems. Details of the calculations are in Appendix D.

In summary, the cost scaleup from the 25-gpm pilot plant, when projected to costs per 1,000 gallons, is **not** cost effective (see Table 19). Moving forward in this manner will require a number of contactors and a very large capacity ozonation system. To avoid a cost prohibitive system, more work must be done to reduce both capital and operating costs. Efforts need to be focused on more efficient reagent dosing, ozone mass transfer, and ozone generation. Recommendations will be presented in Section 7.

In addition, reviewers need to take care in cost comparing GAC

systems with other treatment options when using cost per 1,000 gallons as the common denominator. The critical independent variable for GAC is the mass of the contaminants of concern that a specific, commercially-available GAC can adsorb on its interstitial specific surface area. The dependent variables that must be specifically stated are the influent loading rate in mg/L or equivalent, the volumetric flow rate, and the effluent target rate the system is attempting to achieve. This latter parameter will determine the detention

Table 19. Peroxone Estimated Cost Comparison

Process	Cost
GAC	\$2.86/1,000 gallons
UV/OX	\$9.66/1,000 gallons
Peroxone	\$13.83/1,000 gallons

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time and thus the mass of GAC required, and the size of the filter vessel. Unless all these parameters are addressed, cost comparison in dollars per 1,000 gallons will lead to potential economics-based engineering decisions of questionable value.

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## 6 Conclusions

### 6.1 Overview

The Peroxone system employed for this demonstration worked well but operated at a high cost. In a relatively short period of time (May through August 1996), the demonstration subcontractor (based on response to detailed system planning factors) designed, fabricated, assembled, site prepared and constructed a very functional "demonstration industrial" water treatment plant. The many unit processes and supporting components worked in harmony with one another. There were no major component failures, environmental releases, and no injuries to personnel. The system performed at a contaminant destruction rate in the 98% range, and at near drinking water standards. The contaminant TNB was more recalcitrant than others, and during Phase II of the demonstration in which a shorter detention time was applied, effluent TNB values were above the target level of 2 µg/L (ppb), and were often in the 2 to 4 µg/L range. There is some indication that symmetrical organic molecules are more difficult to oxidize, and this may be a factor. Also, TNB may be an intermediate by-product of the destruction of TNT, and this also may have contributed to this observation. As a result of this demonstration effort the following conclusions are made, with supporting narratives to follow:

1. *The design employed was functionally effective.*
2. *The design employed was not economically effective.*
3. *This technology has limited adverse environmental impact.*
4. *The functional results parallel those of the previous WES effort.*
5. *Peroxone by itself was not the only oxidation process occurring.*
6. *Mass transfer of the ozone to the bulk of the process flow was not complete.*
7. *Steady state conditions were not achieved.*
8. *Color development occurred in this system and was not addressed.*
9. *The system was not optimized.*
10. *GAC, as employed here was not able to be thermally regenerated.*
11. *The effluent limit goals may not be prudent.*
12. *The potential exists for by-products to be formed and not detected in the establishment of effluent standards.*
13. *Nitrates will increase in concentration as a result of applying this technology.*

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14. *It is premature to scale up this technology to a 1,000-gpm field-scale prototype plant.*

## **6.2 Environmental Impact**

This innovative remedial technology has **limited adverse environmental impact**, which favors Peroxone systems for full-scale field application. Like any other remedial technology, there are impacts associated with its application. Those impacts associated with Peroxone can be readily addressed through proper site planning and applying proper engineering controls during the construction and follow-on O&M phase. Generic environmental considerations for applying Peroxone technology are presented in Appendix F to assist future applications. Reviewers are reminded that an environmental assessment for each and every site-specific application of a remedial technology is required per U.S. Army Regulations (AR 200-1 and 200-2), which implement the provisions of the National Environmental Policy Act (NEPA).

## **6.3 Comparison with WES POPS**

These **results** of this demonstration **parallel** those from the **WES precursor** pilot plant demonstration done in 1995 at Cornhusker AAP. In many cases the percent removal efficiency achieved by this demonstration was better. However, there were some differences noted between the two pilot plants employed with regard to volumetric flow rates, ozone dosages, and hydraulic detention times. The unit process flow diagrams between the two plants closely complement one another. The greatest difference is that the WES ozone generator sourced its oxygen from the ambient atmosphere, while the unit supporting this demonstration relied on LOX. The latter was able to apply much larger doses of ozone to the flowstream as a result, and more realistically represents the order of magnitude of dosages that will be required under full field-scale applications. The fact that the results of the two demonstrations complemented each other is encouraging, and further reinforces the effectiveness of this technology. The challenge is to apply it in a more cost-effective manner.

## **6.4 Functionalism Versus Efficiency**

The design employed in this demonstration was strongly influenced by the planning factors that were established in the demonstration subcontractor's statement of work (SOW). The results, though **functional** and **successful**, are **not cost effective** to move forward towards a larger field-scale application such as the 1,000-gpm scale up that is desired as the next level of demonstration. The unit costs per 1,000 gallons is \$13.83 per 1,000 gallons, based on a scaleup projection from the pilot plant. This is not cost competi-

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tive. The perceived redundancy of some processes are magnified by this cost scaleup, and contribute to this high cost projection. There is an opportunity to reduce these costs by further experimenting with some modifications to the pilot plant that will be addressed in the Recommendations section. Currently, major cost drivers are:

- Number and size of the contactors
- Associated support plumbing
- Ozone generation

Prior to moving forward with a system that can handle volumetric flow rates of up to 1,000 gpm, and much higher nitroaromatic loading rates, more effort must be put forth to attempt to lower the costs of these system components.

## 6.5 Optimizing Peroxone Chemistry

The principal oxidation mechanism employed in the demonstration appears **not** to have been Peroxone by itself, but instead a combination of Peroxone and two constituents, hydrogen peroxide and ozone operating as independent oxidizers. In this demonstration, hydrogen peroxide was introduced into the contaminated groundwater flowstream, and then brought into the contactors where ozone was introduced. There may not have been sufficient time for Peroxone to form and the hydroxyl radicals to effectively oxidize the contaminants. The demonstration subcontractor initially attempted to operate the system at a mass ratio of 0.3 (hydrogen peroxide to ozone). However, early into the demonstration the ozone residual being measured in the contactor effluents was higher than calculated and anticipated. Hydrogen peroxide appeared to be reacting with constituents other than ozone, such as a variety of groundwater contaminants. It appears that hydrogen peroxide reacted first with salts and aliphatic hydrocarbons, then with ozone to produce limited amounts of Peroxone. Then the ozone and Peroxone reacted with the remainder of the target contaminants. Most of the target contaminants were destroyed by the end of the third contactor, the exception being TNB.

Hydrogen peroxide was reacting with other constituents. This is substantiated as the demonstration subcontractor responded to the higher than anticipated ozone residuals in the contactor effluents by increasing the mass ratio up to as high as 0.65. The ozone residual in the effluent responded and was reduced to a target value of less than 1 mg/L. Further evidence of this occurring is demonstrated by observing the pH values associated with this demonstration. The goal is to generate a suitable concentration of Peroxone, as the hydroxyl radical associated with this reaction is the most effective oxidant. If an ample amount of hydroxyl radicals were present in the bulk of solution, the pH would increase above the neutral range. The ambient pH values of the groundwater influent were in the

neutral region. There was an increase in overall *system* pH, indicating the creation of Peroxone, although not to the desired concentration.

Dye tests were performed to demonstrate that complete mixing occurred in the contactors. This is **not** necessarily an indicator of **complete mass transfer** of the ozone gas to the bulk of solution, which is more a surface chemistry phenomena, as described by Henry's Law and applied today by industry following the two-film theory and applied in aeration systems, air stripping towers, etc. Many variations of surface interfaces are applied such as trays, bubble diffusers, and tower packing systems. The intent is to attempt to have a large specific surface area value, a large gradient between the partial pressure of the gas being transferred and the molar fraction of the gas in solution, and as little headloss through the system as possible. In this demonstration, reliance was left to the diffuser bubble stream alone. The height and quantity of the contactors utilized, as well as their number (six) more affected this mass transfer than it did mixing. The Ad Hoc Planning Group recommended that conventional bubble diffusion type reactors be used, and they were. However, observations of the bubbles generated were described as large (0.5 inch in diameter), as opposed to the fine mist diffusers (millimeter range of diameter size) that some observers expected to witness. From these observations, this evaluation concludes that better specific surface values could have been achieved. Initially the demonstration subcontractor had some maintenance difficulties with the gaskets sealing the diffuser stones, but reported that these were repaired. The Ad Hoc Planning Group also recommended some consideration be given to using packed columns as well as unpacked columns. The latter was utilized, however there is no indication that packed columns were even considered, and if so, why they were not used. Column packing should have been more seriously considered in an effort to improve mass transfer of the ozone to the bulk of solution and thus possibly reduce the number of contactors utilized as well as their height, and to reduce the amount of ozone that was required to be generated. If this could be successful, there would be an opportunity to both reduce system capital costs and O&M costs.

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Column packing should have been more seriously considered in an effort to improve mass transfer of the ozone to the bulk of solution and thus possibly reduce the number of contactors utilized as well as their height and reduce system capital costs and O&M costs.

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## 6.6 Steady State

The demonstration system **did not reach steady state conditions**. Groundwater influent characteristics varied as did the dependent variables of flow rate, detention time, and oxidant dosing applied in response to these loadings. The impact of this condition placed more burden on the operating parameters and dosing requirements of the reagents, and detracted from the demonstration

effort to obtain data from a stable system. This loading may come much closer to representing very realistic field operating conditions that could be encountered at other Army depots.

## 6.7 Future Concept of Operations

To the system's credit, it was able to perform well under these realistic field loading conditions, which further strengthens its endorsement for further utilization. For the four target COCs (RDX, HMX, TNT, and TNB) the influent concentrations of all decreased during the demonstration as the various runs proceeded. This was illustrated in Figure 19, and is especially apparent for RDX and TNT. It seemed that the pilot plant was effective at cleaning up the aquifer during this short demonstration. However, this demonstration did not return the treated groundwater through reinjection to the aquifer, but instead discharged it to a natural surface drainage. Nevertheless, reviewers need to take note of this observation. Perhaps Peroxone oxidation could be employed as a rapid short-term solution to lower contamination to safer levels and then allow natural attenuation with no further action. However, this scenario has not been demonstrated and was not part of this effort.

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It seemed that the pilot plant was effective at cleaning up the aquifer during this short demonstration.

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## 6.8 Color Development

There were observations of **color development**, i.e. "pink water" in the influent groundwater. The same observation was made during the WES work (Reference 3, page 24). This is a cause for some concern because the possibility exists that some transient multi-benzene ringed isomers could form and have toxicity impacts. This demonstrated system was shielded from the sunlight with the exception of a few observation ports in the contactors. Thus, there was limited exposure of the contaminated groundwater to sunlight. Hence, sunlight was not the apparent cause of the color development observed during this demonstration. Perhaps the color development observed was generated at the time the wastewater from plant operations was first discharged to the surface lagoons, pits, and ponds, and then percolated through the vadose zone to the aquifer. This requires more consideration. In future testing, color should be a monitored parameter, and analytical work with gas chromatography should be sensitive to unusual spiking on the resulting analytical printouts.

## 6.9 Optimization

The system was **not optimized** in the classic sense, in which all the variables are first identified, and in a very disciplined manner are held constant, save one which is deliberately varied, and the impact on output observed and recorded. Because of influent characteris-

tics, steady-state conditions were not achieved as well. The demonstration subcontractor was severely time constrained and immediately after a short 4-week system start up/debugging cycle, entered a 2-week "optimization" cycle, in which eight planned experimental runs were carried out. Nonetheless, the demonstration subcontractor did effectively bring the system to a *testbed operational* configuration. The system variables the subcontractor worked with during these experimental runs were:

- Volumetric flow rate
- Hydraulic detention time
- Ozone dose
- Mass ratio of hydrogen peroxide to ozone
- Well source from the aquifer

No effort was made to control pH or temperature, and the influent water quality characteristics varied.

## 6.10 Granular Activated Carbon

The spent activated carbon was not thermally regenerated as is the normal practice during site demobilization, but instead taken to a waste landfill in Utah. There were difficulties in the sample testing for thermal regeneration caused by some metals contamination in the spent carbon. This may be a factor associated with this innovative technology, or a function of the chemical characteristics of the groundwater to be treated. More work is warranted here. Possibly the U.S. Army would wish to avoid landfilling such material, in an effort to avoid future third party liabilities.

Incineration may be an acceptable alternative, as it offers the ultimate disposal solution in real time. However, the trend in the Continental United States (CONUS) is to move away from this technical approach because of more stringent air quality standards. The recent international treaty developed in December 1997 in Kyoto, Japan over greenhouse gasses control to abate global warming (but not yet ratified by the U.S. Congress) may further contribute to this trend. Nonetheless, on a regional basis, incineration is a viable candidate solution, should GAC from Peroxone applications not be able to be thermally regenerated.

## 6.11 Performance Standards

The effluent limit goals established for this demonstration were essentially drinking water standards. These may not be prudent for a remediation system to work towards. The next beneficial use of such treated water will be to return it to the aquifer, where it will be diluted. Regulatory agencies will play a major role in determining what these effluent limits will be, based on careful risk analysis. Each application will be a unique consideration. The

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effluent limits may not be as stringent in future applications, and thus will not impose such high costs.

## 6.12 By-Products

Associated with effluent limits is the potential for some **by-products** to form and not be detected in performance standards. The concern over this "nitrobody gap - other" is that some potentially toxic intermediate oxidation by-products, or transient multibenzene ringed isomers associated with color development could occur. During this demonstration, the majority of the nitrobodyes were represented by the three target COCs. However, for each application of this innovative remedial technology, this matter should be carefully considered during the early planning stages.

## 6.13 Nitrates

One of the consequences of applying this innovative remediation technology is that the level of **nitrates will increase**. There are multiple sources of nitrogen contributing to these nitrates. The most obvious source is the target contaminants themselves--the nitroaromatics.\* Another source of nitrates can be from the amino acids in proteins, if there are such organic contaminants present in the contaminated groundwater. If this type of contamination is present, Peroxone interaction will readily oxidize this material as well. A water quality parameter indicative of the presence of proteins is total organic carbon (Reference 29, page 193). Kjeldahl nitrogen is another water quality parameter that can be used as an indicator of the presence of protein material in water. During this demonstration both these parameters were monitored. (See Figure 24).

It should be noted there could be nitrate sources percolating into the groundwater from activities related to adjacent properties. As an example, if an airport was nearby and urea or other nitrogen-based compounds were used for snow and ice control, perhaps such surface runoff could be entering the groundwater. The same argument could be made if this practice was conducted on nearby highways, or if nitrogen-laden fertilizer was applied to nearby farm lands. The point is, one needs to be alert for other sources, based on nearby land uses.

Depending on the level of nitrates in the final effluent, there can be impacts and consequences ranging from health issues for which there are regulated standards associated with drinking water crite-

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\* This benzene ring family of chemicals all have various nitrite radical groupings electrochemically bonded to the various six carbon stations of their molecules. When these nitroaromatics are chemically oxidized by Peroxone interactions, the benzene ring is broken, and the nitrites are released and oxidized to nitrates.

ria, to other issues such as eutrophication. How the effluent is discharged, what the follow on beneficial use of the water will be, and other factors must be evaluated. Perhaps the most readily available engineering control tool that can be employed in the treatment train to remove such nitrates or reduce them to a safe level is an ion exchange resin specific to nitrates. Thus, this should not hinder the field development of this technology. A final point on the nitrate increase and this particular demonstration is that although increases were consistently noted, the State of Nebraska standards were never exceeded or even closely approached. The standard established for the demonstration was 100 mg/L (Reference 30). The average value observed for the final effluent discharge in the effluent from GAC Unit 3 was 2.67 mg/L. The EPA Drinking Water Standard for nitrate nitrogen is 10 mg/L.

### **6.14 Future Applications**

It is **premature** to scaleup this technology to a **1,000-gpm field-scale prototype** plant at this time. Although functionally effective, the projected unit costs are not competitive. More pilot-scale work should be accomplished to determine if more cost effective methods can be applied to Peroxone formation, ozone generation, and reagent mixing and control.

### **6.15 Summary**

In summary, this innovative technology has potential to serve the U.S. Army and other DoD agencies for remediating nitroaromatics in groundwater. First, effort needs to be conducted at the pilot scale to better understand the complex chemistry associated with the technology to lower the application costs. There are other AOP systems being demonstrated and studied in addition to Peroxone by the U.S. Army at this time. This Peroxone system appears to be potentially cost competitive with the UV/OX system.

Care should be applied when reviewing cost data for GAC based on cost per 1,000 gallons because it is purchased on a per mass basis. A given unit of GAC will have a chemically defined contaminant mass absorption capacity. The other two system parameter variables that complement the volumetric flow rate for full cost comparison are:

- Detention time
- Target contaminant concentration

The former determines the size of the filter vessel, and the latter determines the mass absorption capacity required and when "break-through" will occur, i.e. when the GAC capacity will have been utilized ("spent"). Without full knowledge of these parameters, cost comparisons may not contribute to effective engineering design and operational decisions.

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## 7 Recommendations

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**B**ased on the functional success of this demonstration, it is apparent this technology can be applied to satisfy DoD needs at selected installations. However, it is premature to scale up this technology to a field-scale pilot plant (1,000-gpm rate) because of the technical issues that adversely impact cost. Nine specific recommendations are offered as well as some observations on the technology demonstration community as a whole, not only within the U.S. Army, but nationally as well.

### 7.1 Recommendations

1. Better understand the **competitive reactions** that occur with hydrogen peroxide independently oxidizing contaminants in the flowstream; ozone independently oxidizing contaminants in the flowstream; and the generation of Peroxone and its subsequent oxidation reactions. All three of these reactions were probably randomly occurring during this demonstration. Understanding this process may help explain the variation in the mass ratio observed. Efforts to better maximize Peroxone generation to achieve the most cost effective destruction of target contaminants requires more concerted effort. Two approaches to achieve such maximization may be to:

(a) Operate the system at a **higher pH** (above the neutral zone, and incrementally towards the 9 range and higher).

(b) Employ a **prereactor** unit process vessel in which hydrogen peroxide and ozone are mixed with one another, but without the presence of target contaminants, in an effort to generate Peroxone hydroxyl radicals, and then introduce the Peroxone into the contactor chambers. Continue to add hydrogen peroxide and ozone in the contactor chambers to sustain the Peroxone reaction.

2. Develop a **more cost-effective design**, to reduce both capital and operating costs. This pilot plant demonstrated was greatly influenced by the planning factors directed in the SOW. This plant was functionally very effective, but was redundant and expensive. The number of contactors used and the ozone consumed need to be reduced, by the application of alternate process engineering tools. In addition, the mass of GAC used in the final polishing system was excessive, and also needs to be revisited. Two approaches that may have merit to achieve more cost effectiveness may be to:

(a) Employ an **equalization basin, such as the WES POPS**, to stabilize the influent groundwater analytical characteristics. The

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Understanding this process may help explain the variation in the mass ratio observed.

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A **packed** contactor might provide an alternate for maximum mass transfer of ozone to the bulk of solution, in lieu of the height of contactors currently employed.

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demonstration described here intended to utilize one, but was not used in the demonstration pilot plant. Influent water quality parameters are going to vary, therefore, the parameters should be stabilized to better apply reagents for stable oxidation in downstream unit processes.

(b) Reduce the size and number of contactors required. The contactors represent a significant capital cost. A **packed** contactor might provide an alternate for maximum mass transfer of ozone to the bulk of solution, in lieu of the height of contactors currently employed. If the associated chemistry demonstrates effectiveness in ozone mass transfer, and the size and number of contactors can be reduced, then the effort becomes one of economic trade-off with the cost of packing. Other factors to consider with packing would be the additional headloss generated, the cost required for additional pumping, and O&M costs associated with the packing employed if scaling or clogging were to become an issue. Certainly, packing would also need to be considered if a prereactor was used to generate Peroxone, as earlier recommended. Associated with this is the need to use ceramic diffusers that produce bubbles with a greater specific surface.

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There may be other categories of groundwater contamination, such as solvents, where this innovative technology set may have potential application.

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3. Better understand the issue of **color development** and whether it will be a problem in AOP plants, especially if an equalization basin is used that is exposed to sunlight. This parameter could be profiled through a pilot plant operated in the field during a follow-on demonstration.

4. Better understand the level of **nitrates** that can be generated by this process, and whether an ion exchange column can effectively reduce or eliminate the nitrates. Potential environmental impact that could generate regulatory or local public concern exists. Raising the level of nitrate in groundwater, especially if the water is a potential source of drinking water, is certain to draw attention.

5. Reconvene the U.S. Army Ad Hoc Peroxone Oversight Planning Group to collectively report what their individual actions have been since they met at WES in September 1995. Details on activities, successes, lessons learned, problems encountered, and current requirements should be identified. During this session, the results of this demonstration, the WES effort at CAAP, the WES effort at Rocky Mountain Arsenal, and others germane to this innovative technology should be critically reviewed.

6. Determine from the user community, such as the Industrial Operations Command, the scope of the problem with groundwater contaminated with residuals from munitions manufacturing and

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A more normalized test and evaluation period of 6 months would have been more desirable considering the number of variables that can impact this process.

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loading at their installations. There may be other categories of groundwater contamination, such as solvents, where this innovative technology set may have potential application. The WES community may be able to provide current input on this subject.

As a result of this rebaselining effort, a clearer understanding of requirements should be achieved concerning: technology capabilities currently available; technology voids that need further understanding; level of regulatory acceptance that could be expected; potential range of scaled up performance costs that could be reached; a roadmap for future developmental work; and resources required to advance this innovative technology to a full-scale prototype, i.e., a system capable of performing at the 1,000-gpm level of performance, with 95 percent effectiveness.

7. Recognize the CAAP system as a **testbed asset** for an additional short period of time. The majority of funds expended for this demonstration project were capital costs expended to field the pilot plant, the majority of which is still in place. The test and evaluation phase was run for only a short 8 weeks and was terminated before the onset of winter weather. A more normalized test and evaluation period of 6 months would have been more desirable considering the number of variables that can impact this process. Take advantage of this asset, and replumb some of the contactors in such a manner to investigate the effectiveness of some of the recommendations made here before the system is retired. Use the as tested configuration from this demonstration as a point-of-departure for comparison. As an example, establish one process line that features the following unit processes:

- Equalization tank (baffled)
- Prereactor
- Three packed contactors in series

For comparison, configure the other remaining three contactors as operated before, that is without an equalization tank, without a prereactor, and without packing in the contactors. Carefully design a test plan where all variables are held constant, save one and with good data quality objectives, determine what the performance is of each system. One variable strongly encouraged to be incrementally varied would be system pH, at the high end. The use of a GAC unit process at the end of the treatment train as a safety net during these other tests is also strongly endorsed.

8. Consider whether a **mobile/relocatable treatment system** is appropriate to satisfy Army needs as a result of program rebaselining. A concept of operations for employment has not been addressed. The demonstration subcontractor based their system

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Perhaps a concept of operations is a mobile system that can be periodically relocated from site to site.

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Instead of having a competitive approach between the two technologies, perhaps a synergistic integration between the two should be considered.

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One of the largest and most successful applications of a Peroxone system has been developed by the Metropolitan Water District of Los Angeles.

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cost scaleup amortized over 30 years, such as with typical industrial water treatment plants. The CAAP system cost projection presented in this report is based on a 10-year operating life, considered to be the upper limit for remedial pump-and-treat systems. However, as observed in this demonstration, the destruction capability of this system was such that even during the short demonstration period, the contaminant levels in the influent were falling. Perhaps a concept of operations is a mobile system that can be periodically relocated from site to site. In September 1995, when the U.S. Army Ad Hoc Planning Group convened to establish their recommendations for the unit process parameter planning guidelines, they stipulated the "system should be transportable by common freight carrier." Could this have been their intent albeit perhaps somewhat subconsciously? The precedent for this is present with other types of remediation systems (rotary kilns, thermal oxidation systems, soil washing systems, soil-vapor extraction systems, etc.). Considering the target flow rate for a field-scale application, this statement may be slightly modified to read "components of the system should be transportable by common freight carrier," but the intent would still be the same, that is reduce the amortized capital cost of the treatment system by fabricating components sufficiently ruggedized, thus the various unit processes can be relocated, remobilized, and used for other project applications. The contactors are the best example of such a component. Pumps and valves will periodically need replacing.

9. Consider an **integrated Peroxone system with a GAC unit**. Up to now, this innovative technology has been approached as an alternative to GAC, which the EPA has determined to be the best available technology for this category of contaminated water. Instead of having a competitive approach between the two technologies, perhaps a synergistic integration between the two should be considered. A compromise and **low-cost approach** would be to employ a single large Peroxone contactor to remove the bulk of the nitroaromatic contaminants followed by GAC unit process for polishing, to satisfy the regulatory imposed cleanup standards. This has not been fully demonstrated, however, this Peroxone demonstration utilized this concept as the GAC did remove the small (2.5 µg/L) of TNB in Phase II operations. On a larger scale, the concept would have to be tested to ensure the carbon would not be consumed by the Peroxone system's by-products at an inefficient rate, nullifying any cost savings. This approach may serve as the most cost effective approach to processing contaminated groundwater, and warrants some consideration. This approach may also offer the U.S. Army a low-cost technical solution to the requirements. The demonstration subcontractor also proposed such in their technical

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report. They referred to this as a "hybrid system." Whatever the name applied, the evaluators agree with their recommendation, although this concept was approached from a different perspective.

## 7.2 Observations

While the demonstration was occurring, parallel activities occurred in the general technical arena of AOP. In fact, some activities were conducted by members of the U.S. Army Ad Hoc Peroxone Oversight Planning Group. As an example the WES POPS unit has been deployed and operated at Rocky Mountain Arsenal, outside of Denver, Colorado. Specific details are not clear, other than it is a demonstration to explore the potential of contaminated groundwater at the Arsenal's north boundary. In addition, ECO Purification Systems has recently completed a demonstration of their AOP system at Volunteer AAP which employed a catalytic oxidation process. They are currently completing a draft report. Other efforts at nearby Milan AAP have also recently been completed employing a UV/OX system. In addition to DoD interest in this family of technologies, the Department of Energy (DOE) has also shown interest, and has established an Advanced Oxidation Laboratory featuring an advanced waste treatment test bed at their Los Alamos facility. However, the major thrust at this laboratory is plasma-technology based. In addition, the Army Corps of Engineers has expressed much interest in this technology area as well, and there has been mention of their commitment to prepare an applications and design manual.

Another activity of interest is the Peroxone work being done for taste and odor control in drinking water treatment. Some Ad Hoc Group members made references to this work, briefly described here. One of the largest and most successful applications of a Peroxone system has been developed by the Metropolitan Water District of Los Angeles. This utility successfully operates a 5.5 million gallons per day (mgd) Peroxone water treatment plant. The success has been such that plans are now in motion to construct two additional plants, thus moving away from the widespread use of chlorine.\* The Los Angeles utility has been involved with this innovative technology since the late 1980s. Their pilot plant and initial work was originally described in References 15 and 16. Remarkably, the WES POPS and the pilot plant discussed in this report are very similar. The ozone dosages the Los Angeles utility

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\* Reviewers need to keep in mind the principal purpose of this application is to control taste and odor in the drinking water supply, and the secondary purpose is to inactivate microorganisms including viruses. **Therefore, there are two separate technical purposes: drinking water polishing applications and nitroaromatics contaminated-groundwater remediation applications.** The COCs concentration levels, which are methylisoborneol (MIB) and geosmin (taste and odor compound) and not nitroaromatics, are in the low parts per billion range to nanograms per liter, or parts per trillion. This application is an order of magnitude less than the concentrations at CAAP.

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apply are lower than used in this demonstration, and vary between 1 to 4 mg/L. The mass ratios used are lower as well, in the range of 0.05 to 0.3. In addition, their total contact times are lower, approximately 12 minutes. A 90% or better removal rate is achieved. They estimate Peroxone is 12 to 25% more effective than ozone alone. In summary, the Los Angeles utility has gained much success in a parallel application of this innovative technology, and might contribute to this effort in an advisory capacity to the USAEC.

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## 8 References

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1. Changing the Army's 'Color Guard,' Ms. Carol Mouché, Contributing Editor, Pollution Engineering, December 1996, pp. 30-33.
2. U.S. Army Industrial Operations Command (IOC), External Affairs Office, HQ, Rock Island, IL, April 1996. Pamphlets:  
IOC Army Ammunition Plants  
IOC Depots and Depot Activities  
IOC Arsenals
3. "Evaluation of Peroxone Oxidation Techniques for Removal of Explosives from Cornhusker Ammunition Plant Waters," by Ms. Elizabeth Fleming, et al., U.S. Army Corps of Engineers, Waterways Experiment Station (WES), Technical Report SERDP-97-2, April 1997.
4. Work Plans for Peroxone Demonstration Program, Cornhusker Army Ammunition Plant, Grand Island, Nebraska, TRW, July 1996.
5. U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, MD, June 1991 pamphlet.
6. "Draft Toxicological Profile for RDX," U.S. Department of Health and Human Services, Public Health Services, Agency for Toxic Substances and Disease Registry, May 1993.
7. "Drinking Water Regulations and Health Advisories," U.S. Environmental Protection Agency (USEPA), Office of Water - 4304, EPA 822-B-96-002, October 1996.
8. Proposed Plan. Cornhusker Army Ammunition Plant (CAAP) Operable Unit One, Explosives Groundwater Plume, Grand Island, Nebraska, April 26, 1994. (A concise summary of the Site Characterization document and the Feasibility Study.)
9. "Draft Toxicological Profile for HMX," U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, June 1994.

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10. "Peroxone Treatment of Contaminated Groundwaters," Strategic Environmental Research and Development Program (SERDP) Document "EnviroSense," July 7, 1995.
  11. Mr. Martin Jeff, Solvay Interlox, Houston, TX, (713) 525-6500.
  12. "Ozone and Advanced Oxidation Processes for Water Treatment," Professor William H. Glaze, ESE Notes, Fall 1995.
  13. "Hydrogen Peroxide - Safety and Handling," Solvay Interlox Publication HH-050B, November 1996.
  14. Conference Report - U.S. Army Ad Hoc Peroxone Oversight Planning Group (Subtask 03-87), Waterways Experiment Station, September 26, 1995, as reported by TRW, October 2, 1995.
  15. "Comparing Peroxone and Ozone for Controlling Taste and Odor Compounds, Disinfection By-products, and Microorganism" David W., et al., Journal of the American Waterworks Association (AWWA), April 1990, pp 181-191.
  16. "Applying Ozone for Organics Control and Disinfection: A Utility Perspective" by David W. Ferguson et al., Journal of the American Waterworks Association (AWWA), May 1991, pp 32-38.
  17. Mr. Brad Coffee, Metropolitan Water District of Los Angeles, California, (909) 392-5045.
  18. "Electrochemical Ozone Generator," Manufacturer's Brochure, Model 524, Lynntech, Inc., College Station, TX, 1-800-269-0531.
  19. Mr. Ryan Gonsalves, U.S. Filter/Westates Carbon, Oakland, CA, (510) 639-7274.
  20. "Bracing for the New Ozone and Particulate NAAQS," by Ms. Susan Bassett, Pollution Engineering, May 1997, pp 60-64.
  21. "Peroxone Groundwater Treatment Demonstration Program Final Reports," TRW & Montgomery Watson, December 1997.

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22. "Treatment Process Removes TNT from Groundwater, Optimizes Ozone Use," by Ms. Kellye Kratch, Water Environment and Technology, November 1996, pp 34-36.
  23. Mr. John Johns, Eco Purification Systems USA, Inc., Baltimore, MD, (410) 455-5777.
  24. "The Disinfection Decision," A Panel Discussion Report, Water Environment and Technology, October 1997, pp 41-45.
  25. Calgon Carbon Corporation, P.O. Box 717, Pittsburgh, PA 15230-0710, (800) 422-7266, ext. 6756, Point of Contact is Mike Prevad.
  26. Mr. Mike Robinson, Milan AAP, Tennessee; Pinkwater GAC Operations; (901) 686-6727.
  27. U.S. Army Environmental Center (USAEC), USAEC PEROXONE Groundwater Treatment System Demonstration, January 16, 1997.
  28. U.S. Army Environmental Center (USAEC), "Evaluation of Ultraviolet Oxidation (UX/OX) Methods for the Remediation of Explosives-contaminated Ground Water: Final Report," Weston, West Chester, PA, June 1995.
  29. Hazardous Waste Management, Michael D. LaGrega, et al, The Environmental Resources Management Group, McGraw-Hill, Inc., 1994, pg. 993.
  30. Letter from the State of Nebraska, Department of Environmental Quality to the Commander's Representative, Cornhusker AAP, Subject: "Wastewater Discharge Criteria from the Peroxone Pilot Plant System at Cornhusker AAP," dated August 11, 1995.
  31. Mr. Keith Johnson, Montgomery Watson, Salt Lake City, Utah, (801) 273-2408.
  32. Program Plan, Peroxone Groundwater Treatment System Demonstration Independent Evaluation at Cornhusker Army Ammunition Plant, July 25, 1996.

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33. Execution Plan (Draft) Peroxone Groundwater Treatment System Demonstration Independent Evaluation at Cornhusker Army Ammunition Plant, July 19, 1996.
  34. GP Environmental Services Quality Assurance Program Plan, General Physics Environmental Services, Inc., Gaithersburg, MD, October 1996.
  35. Jaeger Products, Inc. (High Performance Tower Packings and Column Intervals), Catalog, Houston, TX.
  36. Lantec Products, Inc. (Packing Technology Services), Agoura Hills, CA.
  37. Mr. Tom Metzger, Montgomery Watson; Boulder, CO, (303) 546-6671.
  38. Mr. Vivek Agrawal, Montgomery Watson; Salt Lake City, UT, (801) 273-2466.
  39. Mr. Lindsey Lien, U.S. Army Corps of Engineers, 215 North 17th Street, Omaha, NE 68102, (402) 697-2580.
  40. Mr. Neil Anderson, Milan AAP, Tennessee, UV/OX Operations, (901) 686-6195.

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***Appendix A***

***Nitrobody Laboratory  
Analysis Results***













































## Well 1 - 11/08 DEMONSTRATION

Parameter (ug/L)	0302INF08 001108	0302INF10 401108	0302INF10 451108	0302INF14 151108	0302INF16 001108	0302C1/01 4201108	0302C2/01 4201108	0302C3/01 4201108	0302C4/01 4301108	0302C5/01 4301108	0302C6/01 4301108	0302C6/00 8001108	0302C6/01 0401108	0302C6/01 6151108	0302GAC3 16301108	0302GAC2 16301108	0302GAC1 16301108
1,3,5-trinitrobenzene (TNB)	314	323	270	280	278	130	76.4	21.3	8.3	3.7	1.5	1.5	1.6	1.6	BQL	BQL	BQL
1,3-dinitrobenzene	0.9	0.6	1	1.1	1	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
2,4,6-trinitrotoluene (TNT)	269	222	228	235	232	54.4	14	2.2	0.4	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
2,4-dinitrotoluene	11.3	9.5	10.5	11.2	10.6	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
2,6-dinitrotoluene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
2-amino-4,6-dinitrotoluene	42.2	31.3	37.5	39.8	38	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
2-nitrotoluene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
3-nitrotoluene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
4-amino-2,6-dinitrotoluene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
4-nitrotoluene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
High Melting Explosives (HMX)	5.3	4.7	4	5.3	5.7	3.6	2.1	1.3	0.8	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
Nitrobenzene	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
Royal Demolition Explosives (RDX)	17.6	14.4	16.7	18.5	17.2	5.7	2.1	0.4	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
methyl-2,4,6-trinitrophenyltriamine	2.8	2.8	2.4	2.9	3.6	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL	BQL
Total Nitroblodies	663	608	570	594	586	194	94.6	25.2	9.5	3.7	1.5	1.5	1.6	1.6	BQL	BQL	BQL
Nitrate as nitrogen	0.873	0.858	0.84	0.875	0.827	1.05	1.17	1.2	1.19	1.27	1.25	1.28	1.31	1.25	1.47	1.25	1.36

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***Appendix B***  
***Summary Statistics***  
***of Results***

## Appendix B

### Phase I Influent Concentration Statistics (9/13 - 10/11)

MTB > Describe 'TNB' 'TNT' 'HMX' 'RDX' 'Total Ni' 'Nitrate'.						
	N	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
TNB	92	394.96	393.50	398.00	65.77	6.86
TNT	92	434.24	419.50	431.73	94.11	9.81
HMX	92	7.035	6.500	6.743	3.087	0.322
RDX	92	32.625	32.900	32.845	6.645	0.693
Total Ni	92	1008.5	970.5	1002.7	176.2	18.4
Nitrate	91	1.6414	1.5600	1.6325	0.4571	0.0479
	MIN	MAX	Q1	Q3		
TNB	119.00	529.00	358.00	437.00		
TNT	114.00	672.00	380.00	475.00		
HMX	2.900	28.600	5.600	7.975		
RDX	5.600	49.500	29.700	35.475		
Total Ni	469.0	1470.0	902.3	1100.0		
Nitrate	0.8020	2.6900	1.3400	1.9800		

### Phase II Influent Concentration Statistics (10/12 - 11/08)

MTB > Describe 'TNB' 'TNT' 'HMX' 'RDX' 'Total Ni' 'Nitrate'.						
	N	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
TNB	100	346.34	336.50	342.94	56.71	5.67
TNT	100	312.08	297.50	308.30	64.26	6.43
HMX	100	5.597	5.350	5.512	1.566	0.157
RDX	100	22.538	21.800	22.574	6.095	0.609
Total Ni	100	758.1	729.0	749.6	134.7	13.5
Nitrate	100	0.9000	0.8730	0.8733	0.3564	0.0356
	MIN	MAX	Q1	Q3		
TNB	233.00	546.00	312.00	380.25		
TNT	198.00	538.00	268.00	354.00		
HMX	2.400	10.800	4.550	6.475		
RDX	0.230	38.800	19.525	25.575		
Total Ni	535.0	1200.0	661.5	835.0		
Nitrate	0.3700	3.8500	0.7105	1.0075		

**TNT, TNB, HMX, RDX Concentration Levels for Each Treatment Stage in Phase I**  
 (See *Effluent Concentrations* for Last Stage)

```
MTB > Describe 'tnblcl-5' 'tntlcl-5' 'hmxlcl-5' 'rdxlcl-5';
SUBC> By 'stage'.
```

	Stage	N	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
tnblcl-5	1	21	133.06	133.00	130.52	34.59	7.55
	2	21	45.13	42.10	44.69	9.79	2.14
	3	21	15.133	15.200	15.068	3.402	0.742
	4	21	5.262	4.900	5.195	1.684	0.368
	5	21	1.924	1.800	1.858	0.787	0.172
tntlcl-5	1	21	69.63	65.60	68.53	20.15	4.40
	2	21	10.743	9.700	10.347	3.325	0.725
	3	21	1.643	1.500	1.542	0.703	0.153
	4	21	0.2429	0.2000	0.2474	0.0978	0.0213
	5	21	0.0143	0.0000	0.0053	0.0478	0.0104
hmxlcl-5	1	21	4.910	4.600	4.742	1.300	0.284
	2	21	1.9524	1.8000	1.9105	0.3696	0.0807
	3	21	0.9571	1.0000	0.9842	0.2942	0.0642
	4	21	0.4524	0.5000	0.4421	0.3341	0.0729
	5	21	0.1000	0.0000	0.0684	0.2236	0.0488
rdxlcl-5	1	21	10.29	8.40	8.78	7.80	1.70
	2	21	1.876	1.500	1.558	1.585	0.346
	3	21	0.2762	0.3000	0.2474	0.3404	0.0743
	4	21	0.00000	0.00000	0.00000	0.00000	0.00000
	5	21	0.00000	0.00000	0.00000	0.00000	0.00000

	stage	MIN	MAX	Q1	Q3
tnblcl-5	1	85.40	229.00	102.00	157.00
	2	31.10	67.50	38.00	51.20
	3	10.200	21.300	12.300	18.050
	4	3.200	8.600	3.650	6.600
	5	0.900	4.200	1.350	2.350
tntlcl-5	1	44.20	116.00	53.65	83.65
	2	7.400	21.600	8.850	11.400
	3	1.000	4.200	1.200	1.850
	4	0.0000	0.4000	0.2000	0.3000
	5	0.0000	0.2000	0.0000	0.0000
hmxlcl-5	1	3.400	9.600	4.150	5.150
	2	1.5000	3.2000	1.7500	2.0500
	3	0.0000	1.4000	0.8000	1.1500
	4	0.0000	1.1000	0.0000	0.6000
	5	0.0000	0.8000	0.0000	0.0000
rdxlcl-5	1	5.80	43.40	7.60	9.80
	2	1.100	8.700	1.400	1.700
	3	0.0000	1.1000	0.0000	0.4000
	4	0.00000	0.00000	0.00000	0.00000
	5	0.00000	0.00000	0.00000	0.00000

**TNT, TNB, HMX, RDX Concentration Levels for Each Treatment Stage in Phase II**  
 (See *Effluent Concentrations* for Last Stage)  
 (Data sets 1 and 2 are combined)

```
MTB > Describe 'tnb2c1-5' 'tnt2c1-5' 'hmx2c1-5' 'rdx2c1-5';
SUBC> By 'stage'.
```

	stage	N	N*	MEAN	MEDIAN	TRMEAN
tnb2c1-5	1	20	0	151.55	153.00	151.11
	2	20	0	69.91	69.10	69.48
	3	20	0	28.29	28.00	27.97
	4	20	0	12.140	12.850	12.194
	5	20	0	5.425	5.350	5.406
tnt2c1-5	1	20	0	68.95	70.00	68.56
	2	20	0	14.900	14.500	14.778
	3	20	0	3.155	3.050	3.128
	4	20	0	0.6350	0.7000	0.6333
	5	20	0	0.1050	0.1000	0.1000
hmx2c1-5	1	19	1	8.063	8.000	8.029
	2	20	0	2.285	2.150	2.261
	3	20	0	0.6000	0.6000	0.6000
	4	20	0	0.0300	0.0000	0.0167
	5	20	0	0.00000	0.00000	0.00000
rdx2c1-5	1	20	0	10.16	8.15	8.19
	2	20	0	2.285	2.150	2.261
	3	20	0	0.6000	0.6000	0.6000
	4	20	0	0.0300	0.0000	0.0167
	5	20	0	0.00000	0.00000	0.00000

	stage	STDEV	SEMEAN	MIN	MAX	Q1	Q3
tnb2c1-5	1	22.51	5.03	106.00	205.00	134.75	163.75
	2	10.39	2.32	56.00	91.50	60.50	76.02
	3	5.43	1.21	18.90	43.50	25.17	30.95
	4	2.141	0.479	8.200	15.100	10.300	13.650
	5	1.232	0.275	3.100	8.100	4.525	5.950
tnt2c1-5	1	13.07	2.92	45.00	100.00	57.75	77.75
	2	2.732	0.611	11.000	21.000	13.000	15.750
	3	0.729	0.163	2.100	4.700	2.525	3.600
	4	0.1565	0.0350	0.4000	0.9000	0.5000	0.7000
	5	0.0887	0.0198	0.0000	0.3000	0.0000	0.2000
hmx2c1-5	1	1.432	0.329	5.700	11.000	6.700	9.000
	2	0.504	0.113	1.600	3.400	1.900	2.550
	3	0.1864	0.0417	0.3000	0.9000	0.4000	0.7000
	4	0.0801	0.0179	0.0000	0.3000	0.0000	0.0000
	5	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
rdx2c1-5	1	9.48	2.12	5.70	50.00	6.85	9.00
	2	0.504	0.113	1.600	3.400	1.900	2.550
	3	0.1864	0.0417	0.3000	0.9000	0.4000	0.7000
	4	0.0801	0.0179	0.0000	0.3000	0.0000	0.0000
	5	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Note: N\* is the frequency; there was no value, i.e., a BQL (Below Quantitation Limits). The Sum of N and N\* is the total number of data points.

### Effluent (Stage 6) Concentrations for Phase I

```
MTB > Describe 'TNBln2' 'TNTln2' 'HMXln2' 'RDXln2' 'TtlNi12' 'NiasNi12'.
```

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
TNBln2	71	0	0.6141	0.5000	0.6032	0.3213	0.0381
TNTln2	5	66	0.540	0.400	0.540	0.456	0.204
HMXln2	0	71	*	*	*	*	*
RDXln2	1	70	0.70000	0.70000	0.70000	*	*
TtlNi12	60	11	0.7133	0.5000	0.6722	0.4359	0.0563
NiasNi12	70	1	2.8787	2.8000	2.7853	0.7217	0.0863

	MIN	MAX	Q1	Q3
TNBln2	0.0000	1.6000	0.4000	0.9000
TNTln2	0.200	1.300	0.200	0.950
HMXln2	*	*	*	*
RDXln2	0.70000	0.70000	*	*
TtlNi12	0.2000	2.3000	0.4000	0.9000
NiasNi12	1.8400	5.5600	2.4700	3.0750

### Effluent (Stage 6) Concentrations for Phase II

```
MTB > Describe 'TNB' 'TNT' 'HMX' 'RDX' 'Total Ni' 'Ni as Ni'.
```

	N	N*	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
TNB	80	0	2.582	2.200	2.300	2.307	0.258
TNT	2	78	0.400	0.400	0.400	0.283	0.200
HMX	7	73	0.571	0.400	0.571	0.547	0.207
RDX	1	79	1.1000	1.1000	1.1000	*	*
Total Ni	80	0	2.656	2.300	2.331	2.680	0.300
Ni as Ni	79	1	1.4950	1.4300	1.4762	0.3308	0.0372

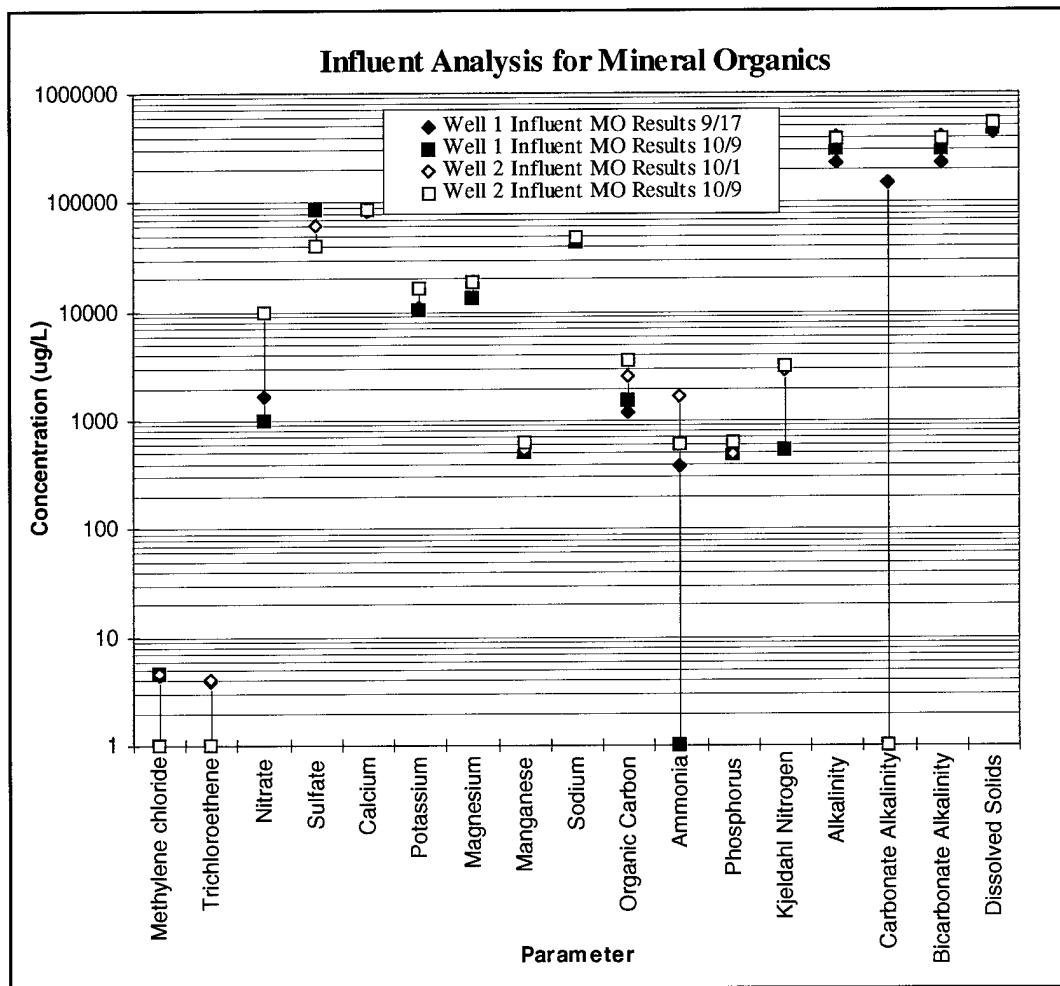
	MIN	MAX	Q1	Q3
TNB	1.000	21.900	2.000	2.575
TNT	0.200	0.600	*	*
HMX	0.300	1.800	0.300	0.500
RDX	1.1000	1.1000	*	*
Total Ni	1.000	25.400	2.000	2.600
Ni as Ni	0.9060	2.5200	1.2800	1.5700

---

*Appendix C*

*Mineral Organics Table  
for Wells #1 and #2*

The characteristics of wells #1 and #2



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***Appendix D***

***Peroxone Cost Calculations***

## ***Cost Calculation Methodology***

### ***PEROXONE Cost Calculations Oxygen (O<sub>2</sub>) Consumption***

Two sources of data were collected to provide two cost estimates for the O<sub>2</sub> use. The two sources were:

1. Daily log of the O<sub>2</sub> tank level.
2. Daily operator log of theoretical use.

#### **Method 1 (Operational)**

The daily tank level readings were subtracted from each previous day's level reading to find the inches of liquid oxygen (LOX) consumed for that day. These values were then multiplied by the tank conversion factor (1 gal. LOX = 115.1 cu ft of O<sub>2</sub>) to obtain the cubic feet (cu ft) of O<sub>2</sub> used that day. The cost of the O<sub>2</sub> was \$0.0069/cubic foot. The total gallons of water treated for Phase II (as an example) were 580,125 gallons.

So, for phase two the calculations are:

$$(2,244.34 \text{ gal. of LOX}) \times 115.1 = 258,323.534 \text{ cu ft of O}_2$$

$$258,323.534 \text{ cu ft of O}_2 \times (0.0069/580,125 \text{ total gal. treated in Phase II}) \\ = \$0.00307249/\text{total gal. treated in Phase II}$$

$$(\$0.00307249/\text{total gal. treated}) \times 1000 \text{ gal.} = \$3.07/1,000 \text{ gal. of treated water.}$$

#### **Method 2 (Theoretical)**

This method is based upon the constant daily flow rate of 9 standard cubic feet per minute (scfm) and a known amount of runtime. The O<sub>2</sub> flow rate was adjusted by the operators to provide a constant 9 scfm of O<sub>2</sub> to the ozone generator. These calculations omit the loss of oxygen from the LOX tank to the ozone generator. The 9 scfm was multiplied by the runtimes for each day of operation and converted from scfm to gallons of LOX as follows:

$$V_o = 9 \text{ scfm} \times 60 \text{ min/hr} \times (\text{runtime-hrs}) \times \text{gal./115.1 cu ft.}$$

$$V_o = 208,980 \text{ cu ft.}$$

For each phase of the demonstration, the daily consumption amounts, based on the runtime x flowrate calculation above, were summed, then converted to cu ft billing units, and multiplied by 0.0069 \$/cu ft (the cost provided by LINWELD, the LOX vendor). This figure was then divided by the total amount of water processed to find the cost per gallon of water.

So, for Phase II the calculations are:

$$\text{O}_2 \text{ cost} = (1,814.47 \text{ gal.}) \times (115.1 \text{ cu ft/gal.}) \times (0.0069 \text{ \$/cu ft}) \times (1/580,125 \text{ gal. of} \\ \text{treated water in Phase II})$$

$$= \$0.002484/\text{gal.}$$

$$= \$2.48/1,000 \text{ gal.}$$

## *Electricity Consumption*

### **Method**

The electricity consumption was obtained by recording the power usage indicated on the cumulative electrical utility meters that fed power to the demonstration equipment. The equipment operating on electricity included the ozone generator, the ozone destruct unit, the hydrogen peroxide pumps, the influent and effluent pumps, the well pump, the deionized water pump, the sodium thiosulfate pump, and the hydrogen peroxide mixers.

The cumulative power consumption was calculated for each phase of testing by subtracting the last day of the meter reading for the demonstration phase from the first day. The average electrical cost per gallon of treated water was calculated for each phase by multiplying the total kilowatt hours (kWh) of electricity (the meter reading must be multiplied by 40 to get kWh) by the cost of a kWh of electricity and divided by the gallons of water processed for that phase. The cost of a kWh was \$0.06.

Using Phase II as an example:

- a) Calculate power consumption.

$$\text{Power} = (\text{Day 11/8 reading} - \text{day 10/12 reading}) \times 40$$

$$\text{Power} = (544.7 - 285.7) \times 40$$

$$\text{Power} = 10,360 \text{ kWh for Phase II}$$

- b) Calculate the cost per gallon processed.

$$\text{Cost} = \text{Power(Phase II)} \times \text{cost of kWh/total gal. processed in phase II}$$

$$\text{Cost} = 10,360 \text{ kWh} \times \$0.06/\text{kWh} / 580,125 \text{ gal.}$$

$$\text{Cost} = \$0.00107/\text{gal.}$$

$$\text{Cost} = 1.07/1,000 \text{ gal.}$$

## *Hydrogen Peroxide Consumption*

### **Method 1 (Operational)**

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) usage as calculated using method 1 was based upon the operator's consumables record. The total gallons of  $\text{H}_2\text{O}_2$  consumed for each phase was divided by the gallons of water processed during each phase and then multiplied by the cost per gallon of  $\text{H}_2\text{O}_2$ .

So, for Phase II the calculations are:

$$\text{Cost} = (246.7 \text{ gal. of H}_2\text{O}_2 \text{ used in Phase II}) \times (\$4.00/\text{gal.}) / (580,125 \text{ gal. of treated water})$$

$$\text{Cost} = \$0.00170/\text{gal.}$$

$$\text{Cost} = \$1.70/1,000 \text{ gal.}$$

## Method 2 (Theoretical)

This method was based on the feed rate of H<sub>2</sub>O<sub>2</sub> supplied to the PEROXONE system and the feed tank concentration. The measured feed rates and the batch concentration were converted to gallons per minute of stock H<sub>2</sub>O<sub>2</sub> using the following equation. The feed rate in this example is 66.6 ml/min, the H<sub>2</sub>O<sub>2</sub> feed tank concentration is 34.9 mg/ml, and the nominal concentration of stock H<sub>2</sub>O<sub>2</sub> used to prepare all the batches of H<sub>2</sub>O<sub>2</sub> is 39%.

$$\text{g.p.m.} = \text{feed rate ml/min} \times (\text{feed tank concentration})\text{mg/ml} \times 1\text{g}/1,000\text{ mg} \times (\text{stock concentration \%})100/39 \times \text{liter}/1,000\text{ g} \times 0.264\text{ gal./liter} \times 6\text{ contactors}$$

So, for day 10/14, the g.p.m. of H<sub>2</sub>O<sub>2</sub> used was:

$$\text{g.p.m.} = 64.9 \times 35.7 \times 1/1,000 \times 1/390 \times 0.264 \times 6$$

$$\text{g.p.m.} = 0.009410\text{ gal./min.}$$

Next, the g.p.m. flow rate was multiplied by the runtime for that day's operation to produce the final gallons of H<sub>2</sub>O<sub>2</sub> consumed on that day. For the 10/14 example, the rest of the calculations are:

$$\begin{aligned}\text{Gal. of H}_2\text{O}_2 &= \text{g.p.m.} \times \text{runtime} \\ &= 0.009410\text{ gal./min} \times 60\text{ min/hr} \times 24\text{ hrs} \\ &= 13.55\text{ gal. of H}_2\text{O}_2\text{ on 10/14.}\end{aligned}$$

Total gallons for each phase were summed and multiplied by the cost of \$4.00/gallon and divided by the total gallons of water treated for that phase as in method 1.

For example, using the Phase II data:

$$\begin{aligned}\text{Cost of H}_2\text{O}_2 &= 211.37\text{ gal. of H}_2\text{O}_2 \times \$4.00/\text{gal.} / 580,125\text{ gal. of water treated} \\ &= \$0.0014574/\text{gal.} \\ &= \$1.46/1,000\text{ gal.}\end{aligned}$$

### *Sodium Thiosulfate Consumption*

Sodium thiosulfate usage was also calculated theoretically and operationally. The first method of calculating sodium thiosulfate consumption is operational—by measuring what was used during each phase of the demonstration.

## Method 1

The sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solutions were batch mixed and then fed to the effluent holding tank to completely neutralize all excess ozone. The amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used in each batch varied depending on the tank level and concentration. The average usage rate in ounces per minute for each phase was calculated from the operator's log of the amount used in each batch preparation.

For example, in Phase II:

$$\text{Total hours of operation in Phase II} = 406.25\text{ hr}$$

Total  $\text{Na}_2\text{S}_2\text{O}_3$  used during Phase II = 547 oz.

So, Phase II usage rate of  $\text{Na}_2\text{S}_2\text{O}_3$  =  $(547 \text{ oz}) / (406.25 \text{ hr}) \times (1 \text{ hr} / 60 \text{ min.})$   
= 0.0224 oz/min.

The usage rate was multiplied by the total gallons of water processed for each phase and divided by 1,000 to represent a 1,000 gallon treated water basis, then multiplied by the flow rate and cost per ounce. (Per operator's records, the usage rates for Phases I and II were approximately the same.)

Now, the cost of  $\text{Na}_2\text{S}_2\text{O}_3$  (lab grade) =  $(\$84.30 / 2.5 \text{ kg}) \times (1 \text{ kg} / 2.2 \text{ lb.}) \times$   
 $(1 \text{ lb.} / 16 \text{ oz}) = \$0.96/\text{oz}$

Using a flow rate of 25 g.p.m for Phase II (Phase I would be 13 g.p.m) and a total water treated of 580,125 gallons (Phase I would be 375,180), the cost for Phase II is calculated to be:

$(0.0224 \text{ oz/min.}) \times (1 \text{ min.} / 25 \text{ gal.}) \times (580,125 \text{ gal.} / 1,000 \text{ gal.}) \times (\$0.96/\text{oz})$   
= \$0.50/1,000 gal.

## Method 2

Theoretical  $\text{Na}_2\text{S}_2\text{O}_3$  usage is calculated based on the average contactor 6 (C6) effluent ozone residual and dose of 7 mg/liter of  $\text{Na}_2\text{S}_2\text{O}_3$  per 1 mg/liter ozone residual.

With an average C6 ozone residual in Phase II of 0.6 mg/l,

and a process flow rate of 25 g.p.m.,

and 0.58 gm/25 gal. of Thio• $5\text{H}_2\text{O}$  required per 1000 gal. of treated water,

then, the theoretical optimized dose of  $\text{Na}_2\text{S}_2\text{O}_3 \bullet 5\text{H}_2\text{O}$  is 0.17 oz/1,000 gal.

So,  $\text{Na}_2\text{S}_2\text{O}_3$  use in oz/min.

=  $0.17 \text{ oz} / 1,000 \text{ gal.} \times 25 \text{ gal/min.} \times 1 / 1,000 \text{ gal.}$

= 0.00425 oz/min.

Using the same method as in method 1 for calculating the cost per 1,000 gallons, the  $\text{Na}_2\text{S}_2\text{O}_3$  would theoretically cost \$0.10/1,000 gallons of treated water. However, because a safety margin must be built in to ensure that all ozone is neutralized, the figure used is the standard "three times the calculated amount."

Therefore, the theoretical cost of  $\text{Na}_2\text{S}_2\text{O}_3$  use is \$0.30/1,000 gallons for Phase II operations.

### ***PEROXONE Labor Cost Calculation***

Labor Skill Cost =

3/4 FTE individuals x \$12/individual-hr x 8 individual-hr/24 process-hr

Labor Skill Cost = \$3/process-hr

(1,008 hr/1,093,125gal.) x 1,000 = .92 hr/1,000gal.

\$3/process-hr x .92 = \$2.77/ 1,000 gal.

### ***Capital Equipment & Maintenance Costs***

Annual capital equipment costs were determined by dividing the total capital costs over a 10 year period.

For the PEROXONE system, the capital cost was \$427,720.

$$\$427,720/10 = \$42,772$$

Maintenance costs were determined using 10% of the capital costs.

$$\$427,720 \times .10 = \$42,772$$

Using the equipment capital and maintenance costs per year value of \$42,772/yr, the cost per 1,000 gallons is as follows:

Capital and Maintenance Cost per 1,000gal. =

$$(((\$42,772/\text{yr})/(25 \text{ gal./min} \times 60 \text{ min/hr} \times 24 \text{ hr/day} \times 365 \text{ day/yr}))) \times 1,000$$

$$\underline{\text{Capital and Maintenance Cost per 1,000 gal.} = \$3.26/1,000 \text{ gal.}}$$

Similar calculations were done using input from referenced documents to determine the capital and maintenance costs for the UV/OX and GAC systems.

### ***UV/OX Cost Calculations***

An example of the electricity cost per 1,000 gallons for UV/OX is:

$$\$/1,000 \text{ gal.} = (\$0.06/\text{kWhr}) \times (40.8 \text{ kWhr}/1,000 \text{ gal.})$$

$$\text{Electrical consumption cost} = \$2.45/1,000 \text{ gal.}$$

Similar calculations were done using input from referenced documents for the other consumable items for the UV/OX system.

### ***GAC Cost Calculations***

From the supplier Calgon Carbon, the critical cost parameters are as follows.

GAC purchase cost/lb.-dry = \$.96/lb.-dry

GAC loading = 2.5 lb.-wet per 1 lb.-dry

GAC disposal cost/lb.-wet = \$.5/lb.-wet

Therefore, the disposal cost per pound of wet GAC is:

$(2.5 \text{ lb.-wet}) \times (\$.5/\text{lb.-wet}) = \$1.25/\text{lb wet.}$

The operational purchase and disposal cost per lb. of original dry GAC is:

GAC cost/lb. = (\$.96/lb.-dry) + \$1.25/lb wet

GAC cost/lb. = \$2.21/lb.

The second critical parameters are the design loading, which are:

GAC density = 29 lb.-dry/cu ft.

GAC design rating is the point the carbon becomes clogged and begins to impede flow. Typical design ratings are 15% to 20% load by weigh; this is based on information obtained from the manufacturer. For this calculation, a 15% design rating was used.

GAC design rating = 1,977 g-Exp./cu ft (15% design load rating)

The following calculations were done to arrive at the load listed above.

$(.15) \times (1,000\text{g/kg}) \times (\text{kg}/2.2 \text{ lb.}) \times (29\text{lb-dry}/\text{cu ft}) = 1,977 \text{ g-Exp./cu ft}$

Load (CAAP water) rating = 0.001135 g-Exp./l-H<sub>2</sub>O

The CAAP water load used for calculations is the total quantity of explosive contaminants found in one liter of ground water based on laboratory results. To arrive at the level listed above, the first five days of influent contaminant totals were averaged together. Therefore, the amount of GAC consumed per gallon of treated water is:

$1/\{(1,977 \text{ g-Exp./cu ft}) \times (1\text{-H}_2\text{O}/.001135 \text{ g-Exp.}) \times$   
 $(\text{gal.}/3.785 \text{ l-H}_2\text{O}) \times (1 \text{ cu ft}/29 \text{ lb.-dry}) \times 1,000\}$

GAC consumption = .09653 lbs-dry/1,000 gal.

or in calculating the cost per 1,000 gallons of treated water,

GAC cost = (0.09653 lb.-dry/1,000 gal.) x (2.21 \$/lb.-dry)

GAC cost = 0.213 \$/1,000 gal.

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***Appendix E***  
***Points of Contact***

Points of Contact for the Peroxone Demonstration				
NAME	POSITION	ORGANIZATION	ADDRESS	PHONE
Heffinger, James	Program Manager	US Army Environmental Center	US Army Environmental Center SFIM-AEC-ETD - Bldg E4430 Aberdeen Proving Ground, MD 21010	410-612-6849
Jaimeson, Tom	CAAP Commander	Commander, Comhusker Army Ammunition Plant (CAAP)	CAAP 102 N. 60th Road, Grand Island, NE 68803	308-381-0313
Lamb, John J.	Contracted Program Manager	TRW	TRW 01240 One Space Park Redondo Beach, CA 90278	310-813-9354
Lien, Lindsey K.	Advisor	US Army Corps of Engineers	US Army Corps of Engineers CEMRO-HX-E (Lien) 12565 West Center Road Omaha, NE 68144-3869	402-697-2580
Liptak, Lynda	Project Leader/ Evaluator	DESA/AFOTEC/TA	AFOTEC/TA 2700 Clark Carr Loop, SE - Bldg A Albuquerque, NM 87106	505-262-4583
Maloney, Steve	Advisor	US Army Corps of Engineers	US Army Corps of Engineers 2902 Newmark Drive Champaign, IL 61826	212-373-3482
Najm, Issam	Subcontracted Project Manager	Montgomery Watson	Montgomery Watson 555 E. Walnut Street Pasadena, CA 91101	818-568-6744
Nay, Marshall	Contracted Evaluator	BDM Federal, Inc.	BDM Federal, Inc. 1801 Randolph Road, SE Albuquerque, NM 87106	505-848-5281
Stewart, Bryan	Contracted Evaluator	BDM Federal, Inc.	BDM Federal, Inc. 1801 Randolph Road, SE Albuquerque, NM 87106	505-848-4019

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***Appendix F***

***Generic Peroxone Environmental Assessment  
Considerations***

## GENERIC PEROXONE ENVIRONMENTAL ASSESSMENT CONSIDERATIONS

What follows is a generic environmental assessment of an application of Peroxone to a typical groundwater cleanup scenario. These responses are based on lessons learned at the CAAP demonstration.

### *Does the proposed activity conform with the installation master plan?*

**No.** For this reason, a site license or permit per specific service real estate directives will be required. Such a document will provide specific descriptions of what activities may be carried out and for how long.

In the long run, the activity will allow for the installation master plan to be executed and provide the installation more options to use the property in question.

### *Would the proposed project alter land use on the installation?*

**Yes,** but only during the time period the system is in active operation. A worst-case scenario would be operating the system close to an occupied building or an open flame source. The matter of storing liquid oxygen (LOX) on site and generating ozone, must be seriously considered during the site planning and sitting phase. The installation fire marshal and other life-safety authorities must be included in any decision-making.

### *Describe project activities that could affect the archeological and/or cultural resources and the qualities of air, land, and water (such as clearing, digging, or leveling).*

All such actions will need to be coordinated with the installation environmental management office that has cognizant responsibility. Careful sitting and associated site planning and site preparation will be necessary to minimize disturbances. This will include sound engineering controls such as in a storm water pollution prevention (SWPP) plan; spill prevention, control, and countermeasures SPCC plan, and similar requirements.

### *Is prior use of the property and condition of the equipment a potential issue?*

There may be a chance that under some circumstances the contaminated groundwater at the site could be considered a Resource Conservation and Recovery Act (RCRA) hazardous waste. The basis of this is the "derived - from rule" [40 Code of Federal Regulations (CFR) 261.3(c)]. If the source of the contamination was the manufacture, assembly, and packing of explosives, such could be categorized as a "listed" hazardous waste (K044 - 047, and K111 - 115). Each site is evaluated under its own merits by the regulatory community, but the potential for such exists. The DoD Range Rule may have some applicability as well.

***What is the proposed use of the property, equipment, and/or the completed project?***

Remediation is not an end to itself, but instead makes a property safer to use for its intended purpose, or makes it usable for a new beneficial use. If the latter is the case, such a change in use should have been addressed in an environmental assessment, to include the remediation anticipated. If the intent is to restore the property and make it safer for its intended purpose, such environmental consequences will have to be specifically addressed.

Areas of potential impact during implementation and operations are as follows:

***Is there a potential to cause air pollution?***

**Yes.** There could be ozone leaks to the atmosphere. Because ozone is considered an air pollutant as it contributes to the formation of smog, it is addressed in the National Ambient Air Quality Standards (NAAQS). The current national primary standard is 0.12 ppm measured over a 1-hour period. Certainly sound engineering controls can counter this potential, however the issue of attainment versus non-attainment zone and other regional considerations will potentially impact this approval of such a system.

***Is there the potential to cause water pollution?***

**Yes.** There are a number of issues that must be evaluated. By and large, the most sensitive issue is that this system will generate nitrogen salts in their highest oxidized state, i.e., nitrates. If the receiving water that hosts the effluent is a source of public drinking water, then the United States Public Health Service (USPHS) drinking water standards must be seriously considered. If the receiving water is a surface body of water, then the potential for algae blooms and eutrophication must also be considered. If the treated water is reinjected back into the aquifer, and there are random wells being serviced from the aquifer, the same concern for drinking water issues such as methemoglobinemia must be considered. A bench-scale treatability study should be performed to address this potential early in the feasibility study. Engineering controls can be applied to mitigate such potential. As an example, the process water could also be treated to remove the nitrates if they were considered high, but at added cost to the system. Certainly, sound SPCC and SWPP plans will be needed for additional protection.

***Is there a potential to impact quality or quantity of groundwater?***

**No.** The purpose of this remedial application is to clean up groundwater. Care needs to be taken in some areas. As an example:

The pumping rate and reinjection rate need to be analyzed and modeled to ensure the equilibrium of the plume containing the contaminants of concern within the aquifer is not disturbed so that it migrates, especially across property lines (off site). This would be most serious. The notional prototype goal of scaling up to a 1000-gpm system for the next application is a very **high** flow rate. The pumping

rate and reinjection rate needs to be modeled by a competent hydrogeologist who has a good understanding of the local geology.

The quality of the reinjected water needs to be well understood before such action is carried out. Care must be taken that nitrates are not reinjected to such a level as to negatively impact further beneficial use by the next user. Another concern is if only partial chemical oxidation is achieved, what are the byproducts and consequences. Utilization of GAC as a safety net unit process for effluent polishing would help abate such a consequence. Prior to the high capital investment in mobilizing such a technology, a detailed and well planned bench-scale treatability test must be carried out.

Should the treated water not be reinjected into the aquifer, but instead pumped and discharged to a surface body of water, a NPDES permit will be required. In addition, the impact of the drawdown of the water table in the local area must be evaluated. If adjoining properties have active wells in place, their beneficial use could be adversely impacted.

***Is there a potential to affect wetlands, floodplains, wild and scenic rivers, and other related areas of critical environmental concern?***

If the answer is "yes" to any of these scenarios, **replan** the effort to avoid such potential. The clearinghouse responses and results of such discussions before a Remedial Advisory Board (RAB) will be adverse in all probability.

***Is there a potential for discharging or releasing a hazardous substance?***

**Yes**, but only in the most **limited** way. This remedial technology compared to so many others, requires only a limited amount of hazardous substances on site. A limited number of material safety data sheets (MSDSs) need to be available on site, and this is a credit to this technology. There will be some potential for hydrogen peroxide (and Lox, should such be used to support ozone generation) leaks or spills, however a basic SPCC plan can readily address this. Also there is the potential for some offgassing of ozone, but a detection system will be required from a health and safety perspective, with equipment automatic shutdown procedures provided with the technical equipment.

***Is there a potential to generate hazardous waste?***

**Yes**, but again, only in the most **limited** way. If the "derived-from" rule is interpreted as such, then the discarded Personal Protective Equipment (PPE) would probably be so categorized. In addition, if GAC is used as a final polishing unit process, and/or safety net to guard against chemical oxidation system failure, the carbon will become contaminated with nitrobenzenes as it reaches break-through. This spent carbon would probably become classified as a hazardous waste, and is routinely thermally regenerated, or landfilled. Manifesting and related administrative matters would have to be accomplished.

***Is there a potential to cause soil contamination?***

**Yes.** If the contaminated groundwater spilled onto the ground surface adjacent to the site operations area where the unit processes were set up, such would be the case. However, this would probably be very limited in impact because the native soil bacteria would soon metabolically assimilate the nitroaromatics of concern. Routine engineering controls consisting of a sound SPCC plan and a companion SWPP plan would adequately control such risk. In all applications, the technical equipment for the associated unit processes should be mobilized inside a bermed impervious area, with a sufficient foundation to guarantee structural stability.

***Is there potential to violate safety, health, or noise standards?***

**Yes,** but only if the approved site-specific health and safety plan is not adhered to. Noise excursions above 85 A-weighted decibels (dBA) were not observed. The greatest risks are working in a potential oxygen-rich environment, and hydrogen peroxide spills in the face, especially the eyes. Special attention should be focused on grounding of the ozone generator(s), especially if LOX rather than ambient air is the oxygen source.

***Is there a potential to impact protected or endangered species or their habitat?***

If there is, the effort should be replanned if possible. ESA issues such as habitat loss and "taking" are very complex, and the potential to have associated projects impacting protected or endangered species or habitats should be avoided.

In summary, there are some potential environmental impacts that can result from applying this innovative remediation technology, however, they are minimal and the potential resulting consequences can be controlled by applying sound engineering controls. This must be documented, and the purpose of this brief narrative was to support such efforts by providing this roadmap so users can comply with the provisions of U.S. Army regulations 200-1 and 200-2. Some will wonder if a categorical exclusion (CX/CATEX) applies. Each application must be considered on its own specific merits. However, Chapter 4, of AR 200-2, does provide some opportunities possibly under CX A-7 and A-18. In both instances, a Record of Environmental Consideration (REC) must be completed.