

WISCONSIN DEPARTMENT OF NATURAL RESOURCES
REPORT OF AN INVESTIGATION OF THE
E.I. DUPONT DENEMOURS COMPANY'S EXPLOSIVES PLANT
AT BARKSDALE, BAYFIELD COUNTY, WISCONSIN

SPOONER, WISCONSIN
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Introduction

This report summarizes an investigation of duPont's Barksdale works by the Wisconsin Department of Natural Resources (WDNR). The investigation was initiated by the report of a Mr. James Thannum of Ashland concerning environmental degradation on the site and his expressed concern over the possibility of toxic and hazardous wastes remaining on the site. The investigation was conducted by Barry O'Flanagan, Gary LeRoy and Tom Jerow of WDNR with the cooperation of duPont, specifically with the assistance of Mr. Bruce Lawrence, Environmental Coordinator at duPont's Seneca, Illinois facility.

Objectives

The principal objective of the investigation was to respond to a citizen complaint and ascertain whether any significant environmental degradation had or was occurring in specific locations at the Barksdale site.

Background

The Barksdale works is owned and was operated by the E.I. duPont deNemours Company headquartered in Wilmington, Delaware. The property consists of approximately 1700 acres and is located along Chequamegon Bay in north-eastern Bayfield County, Wisconsin (see maps and photos in Appendix A).

The site is bordered on the east by the bay and on the remaining sides by privately owned land. The private land is either wooded or in

agricultural use. State Trunk Highway 13 parallels the bay and passes through the east side of the site. Most of the facility is fenced and posted and maintained by a caretaker employed by duPont.

The site is predominantly wooded although there exist many roads and openings. Surface drainage is toward the bay. Boyd Creek, a warm water stream, cuts a meandering ravine from west to east through the center of the site. The remainder of the facility is relatively level. The soils consist of fine textured materials of which red or reddish brown clay is the dominant material. The site is underlain by 50 to 100 feet of glaciolacustrine deposits consisting primarily of red clay. The direction of groundwater flow is not known for certain, but may be assumed to be toward the creek, the bay or both.

The facility operated for 72 years from 1904 through 1976. During this time many changes took place; production processes were upgraded or changed, production lines for new products were added, old lines were torn down or burned. When the facility was finally closed most of the structures were burned and/or buried. The result is that today there are a few key buildings left standing while most of the facility is leveled and growing over with vegetation. From aerial photos and visual examination, it appears that a significant portion of the 1700 acres was at one time or another utilized in some capacity.

Presently there is no official use of the site. However, there is some indication that the site is used by local residents for hunting and other activities.

The Barksdale facility was primarily involved in the production of dynamite and trinitrotoluene (TNT). There were, however, minor products. Among others, Nitramex, Nitramon and trinitroxylene (TNX) were produced for limited periods.

Attached are two appendices which provide further information on major products and wastes at Barksdale. Appendix B is a description of the Barksdale operation put together by duPont for the Department. Waste products associated with the principal production processes are included in this narrative. Appendix C is extracted from an EPA Report (SW-118c) on industrial hazardous waste practices. Included are process descriptions and waste streams associated with TNT, dynamite and nitroglycerine (NG) production. These process descriptions indicate very little hazardous waste associated with the manufacturing processes.

Additional information on processes and particularly on waste streams has been gleaned from the files of state wastewater and sanitary engineers who visited the site.

The earliest observations are from 1943 when the facility was operating 24 hours a day. Boyd Creek was sampled at that time and analysis showed considerable pollution:

NO ₃ -N	38 mg/l
SO ₄	784 mg/l
Total Solids	2614 mg/l
pH	2.3

At this time the "red water" waste from TNT production was channeled into the creek.

In October of 1950 the creek was observed to be "running red" and discoloring the bay out 300 feet and for 1000 feet along the shore. During that same year the state's district sanitary engineer performed an industrial process investigation. The following processes and wastes were identified:

<u>Process</u>	<u>Waste</u>
Sulfuric Acid Production (burning sulfer)	Cooling water and acid from leaks.
Nitric Acid Production (oxidize anhydrous ammonia)	Cooling water and acid from leaks.
Ammonium Nitrate Production (react HNO_3 and NH_4)	Minor spillage of solid product.
Acid Concentration (HNO_3 and H_2SO_4)	None identified.
Recovery of Waste Acids From TNT and N.G.	Small amounts of acids lost in washing.
Production of Trinitrate of Glycerol (Nitration of Glycerine by addition of HNO_3 and H_2SO_4)	Some overflow of soda ash and washings as well as nitroglycerin into Boyd Creek.

TNT Production -

(3 stage nitration of Toluene)

Soda ash, H_2SO_4 , HNO_3 , TNT isomers.

Na_2SO_3 was added to dissolve isomers.

This produced a dye red in color. All waste was channeled into Boyd Creek.

Explosives production at Barksdale fluctuated widely. High production coincided closely with war-time periods. Between conflicts, production was geared more toward commercial explosives, for example, some explosives were produced for mining activities on the Iron Range.

During the final years the facility operated, some metal cladding was done and synthetic diamonds were produced. No production or process waste information has been obtained for these activities.

In December 1980, the Department received a report from James Thannum of Ashland. Mr. Thannum expressed concern over several observations he had made at the Barksdale facility:

1. Alleged sulfur and lead deposits with no plant growth evident;
2. A drainage pipe with a yellowish-orange liquid running toward Boyd Creek;
3. Downed power insulators and transformers, and;
4. An old dump with metal drums and assorted containers.

After meeting with Mr. Thannum it was decided that duPont should be contacted and an on-site investigation made. This was done and in January 1981, representatives of dupont, the DNR and Mr. Thannum toured

the site. Results of that investigation are summarized in Appendix D. No immediate danger or environmental contamination was evident. It was decided to wait until spring 1981, to conduct a more thorough site investigation.

More detailed inspections were conducted on July 1, and September 3, 1981. During these inspections we again looked at the areas of concern expressed by Mr. Thannum and at other parts of the site which appeared to have been used in the past. No immediate environmental threats were observed during either site visit. The plan view in Appendix A shows the general facility layout and the areas addressed in our investigation. Soil, surface water and groundwater samples were taken. Analytical results and implications are discussed below.

Results and Discussion

On July 1, 1981, nine (9) samples were taken. This included four (4) surface water samples and five (5) soil samples.

On September 3, 1981, four (4) samples were obtained, including two groundwater samples and two soil samples.

Information about the samples and analytical results are summarized in Table 1.

Because of the size of the area, the diverse nature of the operation, and the number of sampling points, we concluded that specific analyses would be done only on a limited sample set. This set included samples 7 and 9 which were analyzed by Ral-Tech Laboratories in Madison. The analyses were limited by the standards Ral-Tech had available. Testing was done only for trinitrotoluene (TNT) and some associated breakdown products.

The remaining samples were analyzed for general indicators of soil or water quality degradation.

Water sample analysis and the heavy metals analysis of the soil was done by the Wisconsin State Laboratory of Hygiene. The remaining soils analyses were done by the University of Wisconsin Soils Laboratory.

TABLE 1
ENVIRONMENTAL SAMPLE RESULTS FROM DUPONT'S BARONSDALE FACILITY

K

Sample Identification	Date	Cond. (umhos) cm	pH (su)	Temp. (°C)	CL- (mg/l) (ppm)*	COD (mg/l)	NO ₂ + NO ₃ (mg/l)	NO ₃ (ppm)	SO ₄ (mg/l)	NB**2-NT	26-DNT	24-DNT	246-TNT	135-TNB	Comments
1) Soil sample in non-vegetated area southeast of water tower	7/1/81		3.5		8.5		5.0								This was the nitric acid production area sample taken from top 4-6" of soil.
2) Pipe effluent in drainage ditch	7/1/81	1850	3.5	15.4			36		1100						Orange precipitate.
3) Drainage water in ditch near sulfur storage area	7/1/81		4.3	22			.02		120						H ₂ SO ₄ production and sulfur storage areas are drained by this ditch.
4) Boyd Creek above Barrel Dump	7/1/81	110	6.7	18	2	39	.05		12						
5) Boyd Creek below Barrel Dump	7/1/81	120	7.0	18	2	41	.05		11						
6) Soil sample from base of Barrel Dump	7/1/81		7.2		1.5										Heavy metals analyses run- Pb - 10 ppm Cd - 1 ppm Cr - 5 ppm
7) Soil sample near 2nd berm on north side of the site (TNX)	7/1/81		5.6		4.0			75.5	4.64	4.72	4.80	6.60	5110	6.12***	This sample from a small bare patch in berm area. Possibly old trinitroxylyene production area.
8) Soil sample from wetland south of the bermed area	7/1/81		4.1		10.0			2.5							This area appeared to be an old dump.
9) Soil sample from ridge and furrow area	7/1/81		7.0		7.0			.5	4.68	4.62	4.90	4.88	4.70	2.48	This is the ridge and furrow system used for treating the red water.
10) Well sample at front gate	9/3/81	365	6.5	9.5			.02		6						Well located at front gate-well was not bailed prior to sampling.
11) Power plant well sample	9/3/81	460	7.5				.02		2						Well is broken off improperly abandoned. Well was not bailed. Water level - 34'.
12) Soil sample from sandy soil in old nitramex area	9/3/81		5.6		.5			7.0							Sandy-gravelly area with little vegetation.
13) Soil sample from old burning area	9/3/81		6.5		.5			26.0							Burn area used for refuse and waste explosives disposal.

*ppm - parts per million from soils analysis

** Results in micrograms per gram

Definitions: NB - Nitrobenzene
NT - Nitrotoluene
DNT - Dinitrotoluene
TNT - Trinitrotoluene
TNB - Trinitrobenzene

*** TNT peak interferes with TNB peak

Samples numbered 1 through 6 were taken in areas where Mr. Thannum had expressed concern. Number 1 is a soil sample from a former nitric acid production area. There was very little vegetation growing in this area and no vegetation in the immediate area of the soil sample. The pH of this soil is 3.5. Sample 2 is from an underground pipe system. It appears this liquid is a combination of surface and groundwaters draining the nitric and sulfuric acid production areas. This liquid has a high conductivity, low pH and showed a very high sulfate (SO_4) concentration. Sample 3 was a water sample from a ditch draining the sulfur storage and sulfuric acid production areas. Relatively low pH--4.3, and a high sulfate concentration--120 mg/l were found. Samples 4, 5 and 6 are from Boyd Creek and the creek bed at the base of the Barrel Dump. Samples 4 and 5 are from Boyd Creek. Values of all parameters measured for these samples are within expected ranges. Sample 6 is a soil sample from the base of the dump. Heavy metals analysis was performed on this sample. For the analyses run, no unusual values were found.

Samples 7 through 13 were taken in areas where it appeared considerable activity had taken place or where historical records suggested a problem might exist. Sample 7 was a soil sample from outside the second berm in what was judged to be a former trinitroethylene (TNX) production area. The entire area was heavily vegetated except for the sampling location. This 2 to 4 square foot area was sampled because no vegetation existed; it is likely not typical of the general area. The results show a relatively high nitrate concentration and very high levels of 2, 4, 6 trinitrotoluene (TNT). Several breakdown products of TNT were present also. Sample 8

was a soil sample from a small wetland just south of the TNX area. This was sampled as it appeared the area had at one time been used as a dump. The pH of the sample is a bit low, but apparently not low enough to have any affect on vegetative growth. Sample 9 was from the ridge and furrow area used for "treating" the TNT red water waste. TNT and breakdown products were found. However, there were no extremely high concentrations noted. Samples 10 and 11 were groundwater samples. Sample 10 was from a well near the front gate and 11 was from an old well near the power house. The wells were not bailed prior to sampling so it is not known how representative the results are of the surrounding groundwater. The conductivities were somewhat higher than those of the creek, but not excessively high. Sample 12 was from a lightly vegetated sand and gravel fill in the Nitramex area. Nothing unusual was found in this sample. Sample 13 was from the burning area. This is where plant refuse and waste explosives were burned. The area was covered with cinders. Again, nothing unusual is noted in these results.

Discussion and Recommendations

This section will focus on the samples where results indicated possible environmental problems.

The area around sample 1 (HNO_3 production) has a soil pH which very probably inhibits revegetation. It is recommended this area be treated with a neutralizing agent to raise the near-surface (3-5 inches) soil pH to approximately 7.0. This should be done such that the neutralizing

agent is mixed with and incorporated into the soil. Following neutralization, the area should be seeded with suitable grasses.

Sample 2 shows low pH, and high conductivity, sulfates and nitrates. The low pH enhances dissolution and probably contributes to the other parameters being high. It is recommended the pipe be removed, the ditch filled in and the area graded to prevent future erosion. This will allow for infiltration and cleansing of this drainage water.

There were no problems identified with samples 4, 5 or 6. However, the barrel dump and surrounding areas should be cleaned up. The drums and other debris lying along the stream bed must be collected and buried. All dump sites adjacent to flowing water, particularly along Boyd Creek, must be cleaned up and the material landfilled. At the dump site where samples 4, 5 and 6 were taken, the rubbish must be pulled up and away from the creek and buried. The bank should be graded, then covered and seeded to minimize soil erosion. This area should be checked periodically and maintained until it is stabilized.

Sample 7 showed some potential problems. In particular, the TNT concentration was quite high. The uniqueness of the small area where sample 7 was taken was mentioned previously. It is possible the high values are peculiar to the small unvegetated patch. However, the possibility also exists that some other factor inhibits vegetation growth and a substantial area around the north berms is contaminated with TNT. It is recommended further sampling be done by duPont to delineate the contaminated area.

These recommendations address the concerns of Mr. Thannum and the Department only for the areas mentioned and to the extent they were investigated. It is important to point out that the Barksdale site is very large and operated for many years producing a variety of explosives products. This investigation looked at only a portion of the site and the results should not be taken as representative of the remainder of the site nor as an endorsement by the Department that the site does not pose any environmental problems.

Conclusions

This investigation was performed to address the concerns of an Ashland, Wisconsin resident, James Thannum, over environmental pollution at duPont's Barksdale facility. Generally, the results show no immediate environmental danger in those areas of the site sampled. The sampling did not reveal any significant human health hazards in these areas either. There remain significant areas on this property which have not been evaluated.

The fact that the site is fenced and posted mitigates possible environmental and human health concerns. There are, however, several areas where cleanup work will eliminate gradual environmental degradation and aesthetically improve the site. At one location follow-up sampling is recommended. Should duPont transfer ownership of this property or propose any substantial change in its use, it is strongly recommended that a thorough evaluation be completed on the entire facility.

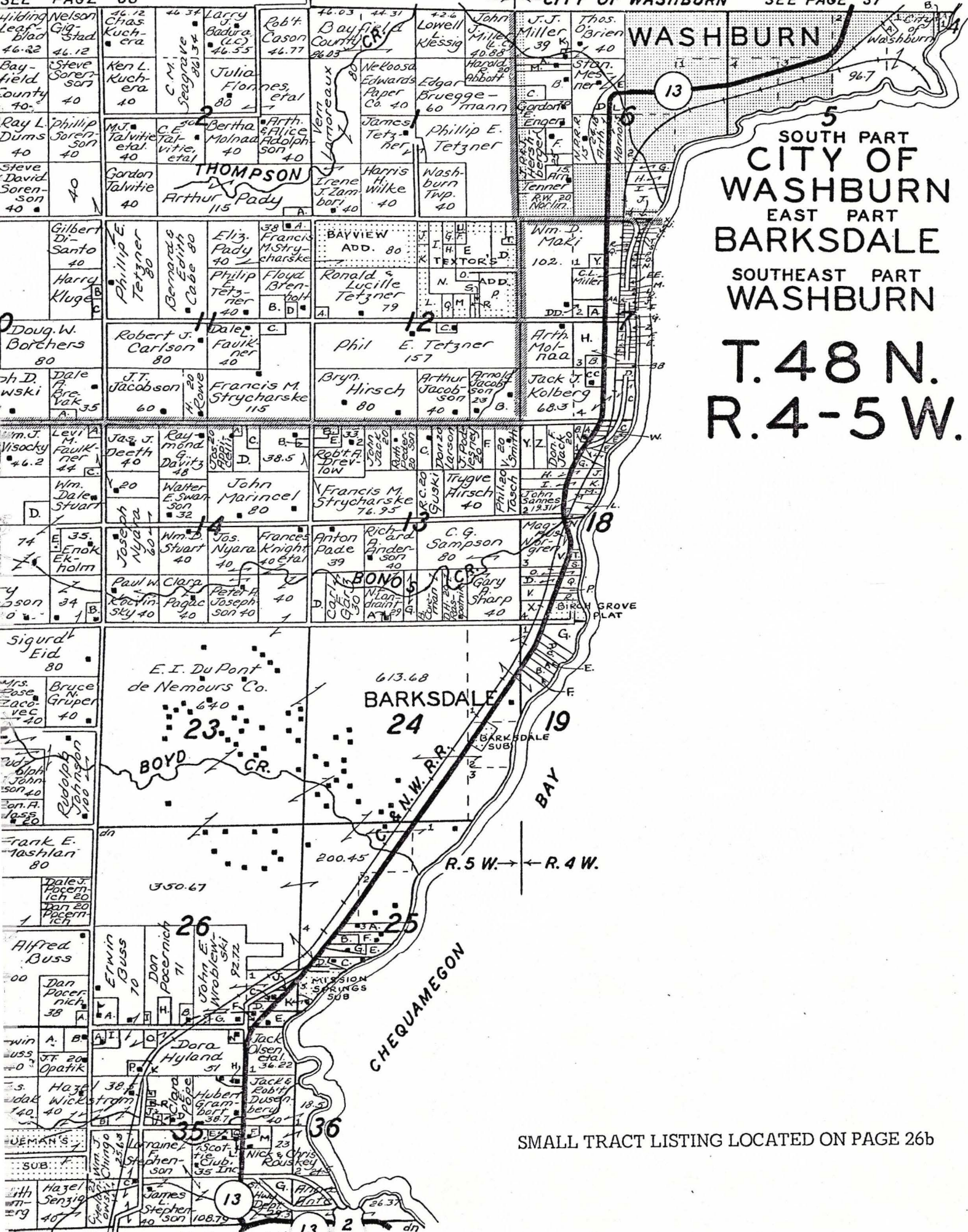
Follow-up work by the Department should document the extent the recommendations made herein are implemented by duPont. Further sampling and analysis by the Department does not appear to be warranted at this time.

APPENDIX A

BARKSDALE MAPS AND PHOTOS

SEE PAGE 36

SEE PAGE 37



WASHBURN

SOUTH PART
CITY OF
WASHBURN

EAST PART
BARKSDALE

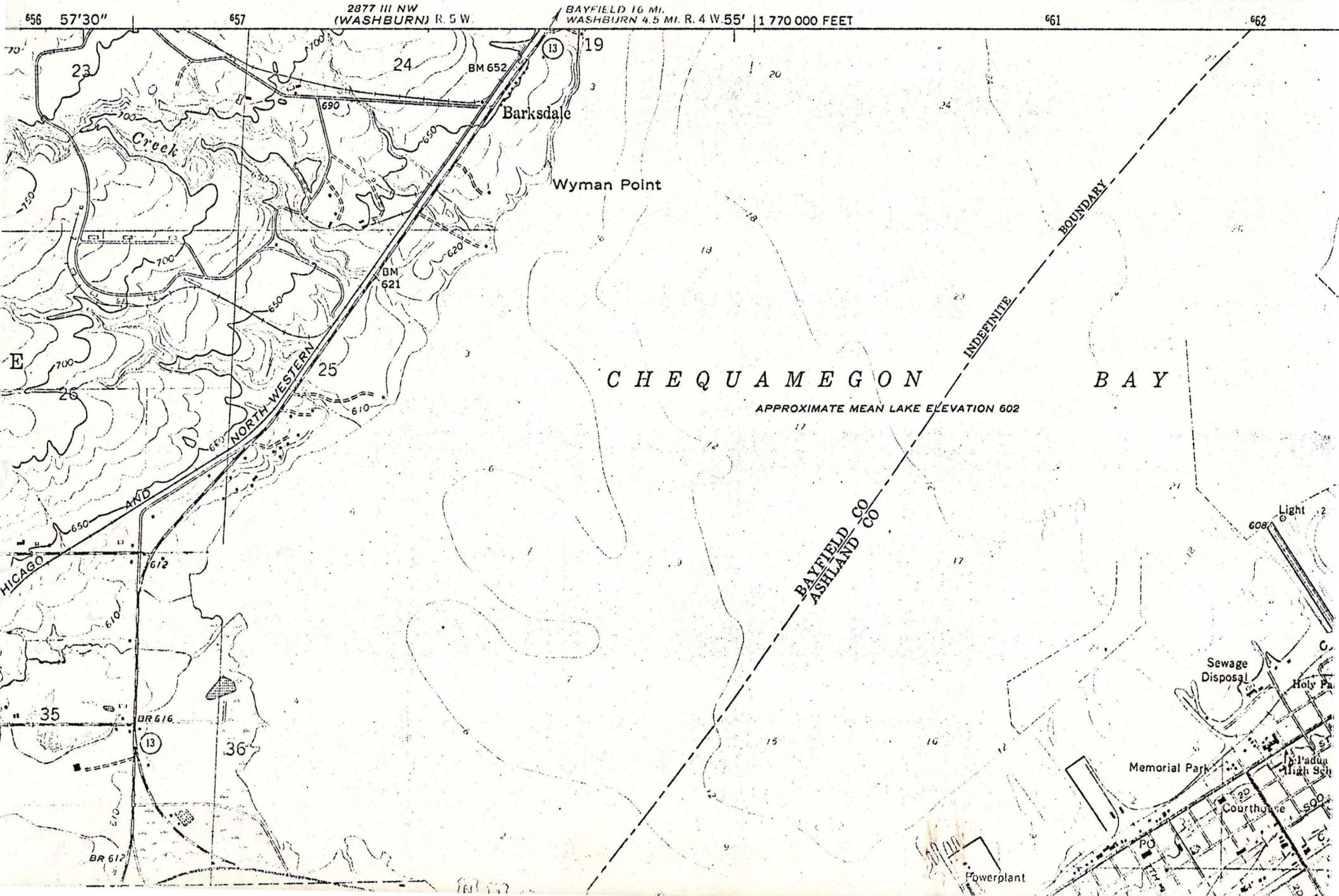
SOUTHEAST PART
WASHBURN

T. 48 N.
R. 4-5 W.

SMALL TRACT LISTING LOCATED ON PAGE 26b

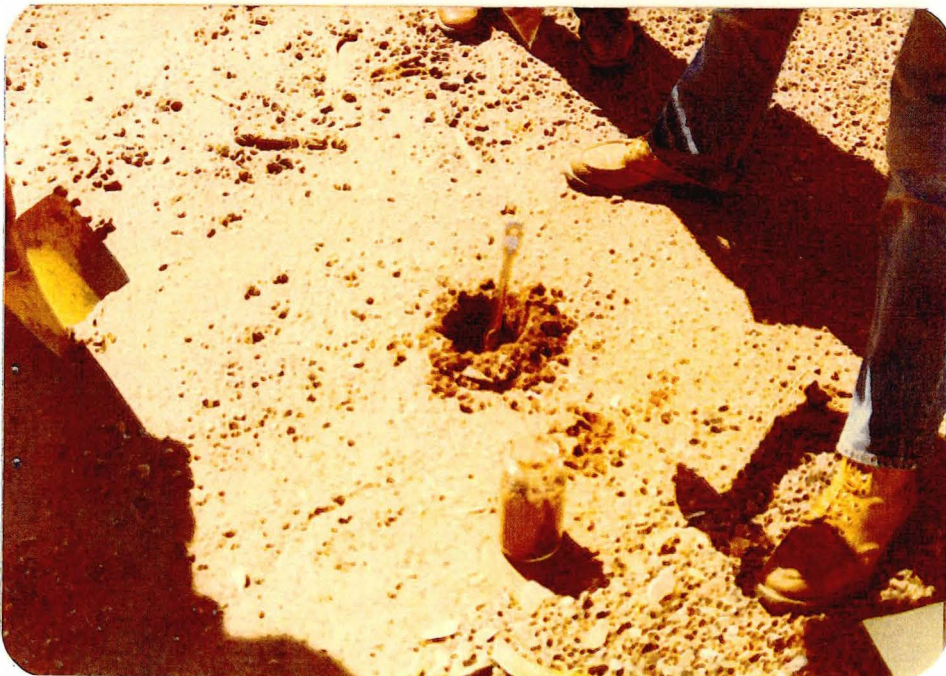
Figure 42
Topographic Map Showing Barksdale Works

15
ASHLAND WEST QUADRAN
WISCONSIN
7.5 MINUTE SERIES (TOPOGRA
SW/4 ASHLAND 15' QUADRANGLE





Nitric Acid Production
Area - Sample
Location 1 (7/1/81)





Drainage pipe with yellow precipitate
sample location 2 (7/1/81)





Sulfur Storage Bunker



Stream draining sulfuric acid production area
Sample Location 3 (7/1/81)



Metal (barrel) dump adjacent to Boyd Creek
Sample sites 4, 5 and 6 located here (7/1/81)





Barren soil patch in former TNX production area
Sample location 7 (7/1/81)



Marsh dump site south of TNX production area
Sample location 8 7/1/81)



Ridge and furrows area for red water treatment
Sample location 9 (7/1/81)



Power plant well site
Sample location 11 (9/3/81)



Views of a portion of the Nitramex area
Sample location 12 (9/3/81)





Views of burning area
Sample location 13 (9/3/81)



APPENDIX B
BARKSDALE PROCESS DESCRIPTIONS
FURNISHED BY DUPONT

Barksdale Works
General Process Descriptions

The Barksdale plant was in operation from 1905 to 1976, and the major products manufactured were dynamite (thru 1961) and TNT (thru 1971). Nitric and sulfuric acid of various strengths and ammonium nitrate were manufactured for use in the production of dynamite and TNT.

Dynamite manufacturing used nitroglycerine, ammonium nitrate and sodium nitrate which were mixed with carbonaceous combustibles such as wood pulp. All solid waste from dynamite manufacturing was burned. Nitroglycerine (NG) required a soda ash washing for neutralization. An elaborate NG-wash water separation system was used to remove NG prior to discharging the wash water to the ditch. Spent acid was concentrated for reuse, and residual sulfuric acid was sold as a by-product. After production was discontinued, ditches in the NG manufacturing area were purposely "shot" with explosives.

TNT manufacturing required toluene and nitric acid for raw materials, and 109% sulfuric acid (40% oleum) was used to aid the reaction. Crude TNT was neutralized with soda ash and treated with sellite (sodium sulfite) to remove undesirable isomers. This aqueous solution was red because of the presence of these isomers. As was standard practice, this "red water" was discharged to the ditch, although plans had been developed to incinerate the red water stream. This incinerator was never completed because TNT operations were shutdown. All solid TNT waste was burned, and spent acid was concentrated for reuse. Residual sulfuric acid was sold as a by-product.

Early processes for manufacturing nitric acid used sodium nitrate and sulfuric acid. A by-product of this reaction was sodium sulfate, which was initially kept on site and later was sold. Sodium sulfate is soluble in water, and none remains on site, to the best of our knowledge.

Beginning in 1928, nitric acid was produced by reacting ammonia and air over a platinum catalyst (AOP process). Spent catalyst was shipped off-site to be recovered for precious metals. The only discharge from the AOP process was cooling water which was used to remove the heat of reaction.

The first sulfuric acid produced at Barksdale used iron pyrite ore as a raw material to obtain sulfur. Cinders from this process were used to construct plant roadbeds. A later manufacturing process for sulfuric acid production (O.V. plant, or oil of vitriol) burned sulfur directly, and the SO_2 was passed through a precious metal catalyst to produce SO_3 before being absorbed in water to make various acid strengths. Spent catalyst was refined off-site, and the only discharge from the OV plant was cooling water used to remove the heat of reaction.

As a part of the acid area shut-down, all equipment was washed and neutralized with soda ash prior to discharge. Ditches were monitored for pH to determine that neutralization was complete. Over 70 tons of soda ash were consumed in this clean-up.

Other products produced on-site were mixes of the ingredients already discussed (i.e., nitramex® was a blend of TNT, ammonium nitrate, and sodium nitrate). Any waste from these operations was burned. Typical waste would be spoiled containers, floor sweeping, and other combustible material.

APPENDIX C

EXPLOSIVES PLANT PROCESSES AND WASTE STREAM DESCRIPTIONS

FOR TNT, NG AND DYNAMITE

5.4.1 Typical Plant Process and Waste Stream Descriptions

5.4.1.1 Manufacture of Basic Explosives

TNT Production

TNT manufacture involves the nitration of toluene with a mixture of nitric acid and fuming sulfuric acid (oleum). The sulfuric acid acts as a catalyst and a dehydrating agent, absorbing and reacting with the water which is formed by the nitration reactions. The operation may be batch type ("old" technology) or continuous ("new" technology). Although in 1973 both methods were being used for TNT production, plant modernization programs planned for the Army ammunition plants (AAPs) call for replacement of all the remaining existing batch TNT lines with the new Canadian Industries Limited (CIL) continuous TNT lines.

Figure 5-29 is the schematic flow diagram for the batch TNT process and the associated satellite operations.* (The flow diagram is for the Joliet AAP which was the largest TNT producer in 1973). The nitration reactions are carried out in three consecutive batch units referred to as "mono-", "bi-", and "tri-" houses. The feed chemicals to the mono-house are toluene and the waste acid from the bi-house which is fortified with 60% HNO_3 . The charge is allowed to settle, the waste acid is transferred to a storage tank (for subsequent recovery), and the partially nitrated toluene (mono oil) is pumped to the bi-house where further nitration is effected in the presence of waste acid from the tri-house fortified with 60% HNO_3 . The nitrated product (bi oil) from the bi-house is pumped to the tri-house where the feed acid is a mixture of 98% nitric acid and oleum. The nitrated product from this third-stage operation is crude TNT containing α -TNT (2,4,6-trinitrotoluene) which is the desired product, and TNT isomers which are the impurities. The crude TNT is gravity fed to the wash house for purification.

The purification of crude TNT involves crystallization in water, neutralization of free acid with soda ash and solubilization and removal of undesirable nitrated products by treatment with a solution of sodium sulfite

*The satellite operations, with the exception of Red Water Disposal, will not be considered in this study. (Red Water Disposal is discussed in Section 6.4.1.)

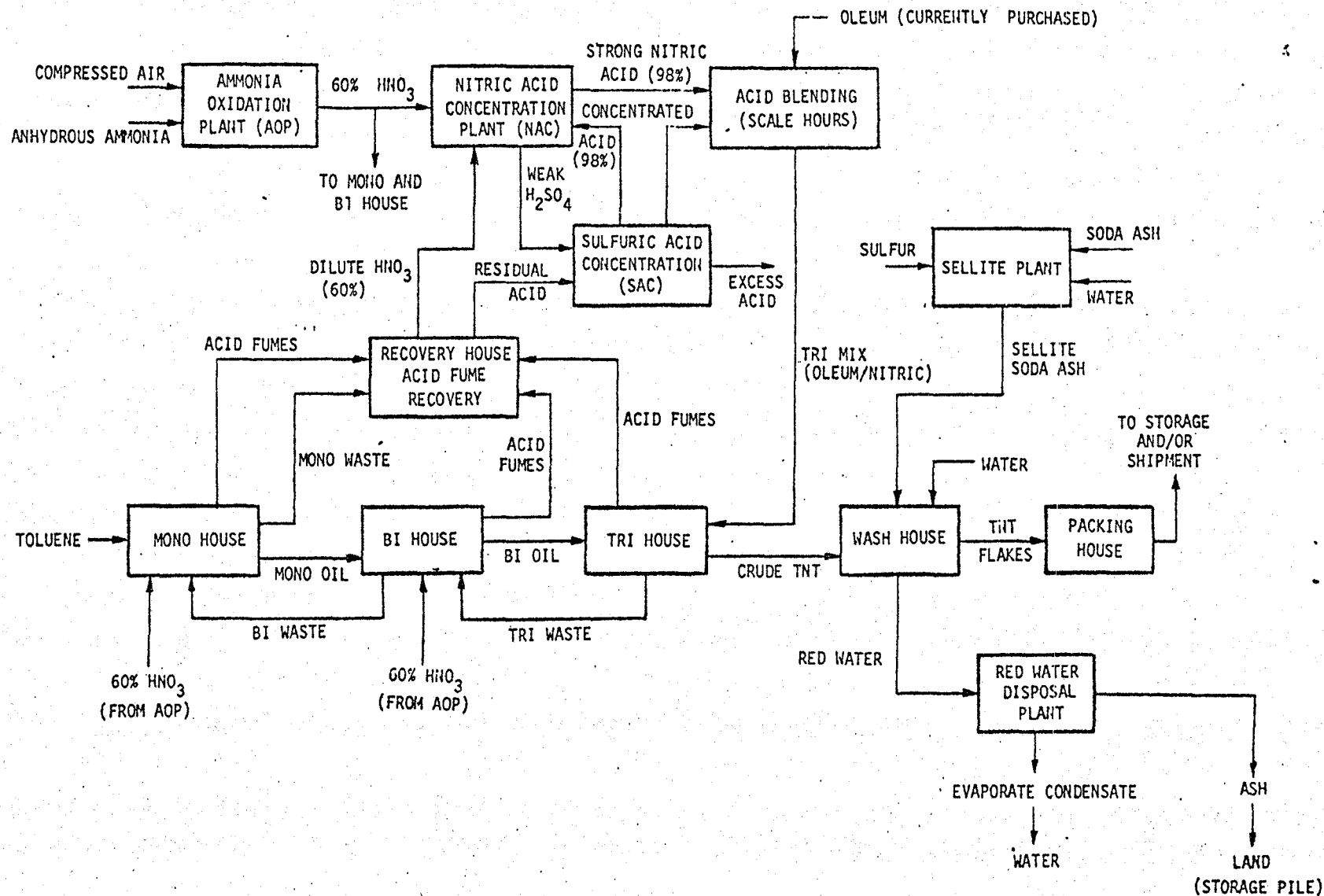


Figure 5-29. Batch Process TNT Manufacturing and Satellite Operations

(sellite). The wastewater from the sellite purification stage is the "red water" which is sent to the red water treatment plant for disposal by evaporation/concentration and concentrate incineration. The TNT slurry is transferred to a filter tank where it is washed and filtered on a screen leaving layers of TNT crystals. The crystals are reslurried with water and pumped to a melt tank where TNT is melted and most of the water is removed by evaporation. The molten product is run into hot air driers for the removal of residual water. The water-free product is solidified on a water-cooled flaker drum and the resultant film is removed in the form of small flakes by scraping with a beryllium blade scraper. The flake TNT is boxed and sent to a packing house for transfer to the magazine storage area.

Continuous TNT lines were in operation at Radford AAP (Va.) in 1973. As of September 1974, when Joliet AAP was visited, three continuous TNT lines were expected to become operational soon and three additional lines were under construction.* In the production of TNT by the continuous process, the nitration of toluene is carried out in six nitrator-separator stages with the organic phase (toluene-nitrobody mixture) flowing counter-current to the acid phase. Nitric acid fortification is provided at intermediate points in the process. The first and third nitration stages have two nitration vessels per separator, whereas the remaining four stages have only one nitration vessel per separator. Extensive instrumentation provides for safe operation and automatic process control. If the process temperature in a nitrator vessel exceeds a pre-set level, the feed to the nitrator is automatically shut off and the contents of the nitrator and separator are automatically discharged into drowning tubs. For TNT purification, the crude TNT first passes through a mixer-settler washer where five separate countercurrent water washes remove the free acids. The acid wash is returned to the second nitrator as acid make-up. The TNT flows through two sellite washers in series where it is neutralized with soda ash and treated with sodium sulfite. Each of the sellite washers is followed by a separator which separates the aqueous phase (red water) from the purified

*Flow diagrams for TNT production by the continuous process have not been given due to time and effort constraints.

TNT phase. The dilute red water from the second separator is returned to the first separator, and the more concentrated red water from the first separator is sent to the red water treatment plant. The sellite-treated TNT receives final countercurrent water washes and is slurried and pumped to the finishing building for drying, flaking and packaging.

The major sources of aqueous wastes in TNT manufacturing are red water, spent acids, acid spills, TNT spills, cooling water, and overflows from catch basins and drowning tubs. As indicated in Figure 5-29, the red water is disposed of in the red water treatment plant and the spent acids are treated in the acid recovery facilities. The remaining wastewaters from TNT manufacturing are treated (usually in combination with other plant wastewaters) prior to final disposal. The major objectionable constituents of these wastes are TNT particles, nitro bodies, sulfate, nitrate, acidity (low pH), and color (due to the presence of nitro bodies). The gaseous wastes in the TNT manufacturing are acid fumes which evolve from the nitration and separation vessels. These fumes are withdrawn by the application of a constant suction above the tanks and sent to the fume recovery facility (see Figure 5-29) for treatment/disposal. The solid wastes associated with TNT manufacturing are scrap TNT, and settled TNT sludges collected in sumps in the TNT wash and recovery houses. As discussed in Section 6.4.1, the current disposal method for waste explosives is open-burning.

Table 5-21 presents the material balance for batch TNT production and associated satellite operations. The data are for Joliet AAP and are based on 1969 production and operating conditions. From the standpoint of pollutant discharges to the environment, somewhat lower values would be expected for the present-day operation due to improvements in process control and housekeeping and increased environmental awareness on the part of operating personnel and plant management. Material balance data for the continuous TNT lines are presented in Table 5-22. These data were obtained from Radford AAP (Radford, Va.) which in 1973 operated three CIL continuous TNT lines.

Nitrocellulose (NC) Production

Nitrocellulose is produced by nitration of cellulose (wood pulp or cotton linters). A mixture of nitric and sulfuric acids is used for nitration, with the sulfuric acid acting as a catalyst and dehydrating agent. A block

the future this loss of NC fines will be significantly reduced when the neutral boil wastewater is isolated and treated separately by centrifugation. Based on data for Radford AAP, for a production rate of 66,000 kg/day and with a considerable amount of water recirculation, the total volume of the final wastewater effluent from NC production is estimated at 9500 m³ per day (2.5 million gallons per day). The major solid waste from the process is contaminated NC which is estimated at 1-2 percent of the NC production. Acid fumes are the major air pollutants from NC production.

Plant modernization program for Radford AAP calls for the replacement of the batch operation with a continuous NC production process. Table 5-23 presents mass balance data for the proposed continuous lines. The data are based on the production of 50 percent linters NC and the use of Delaval centrifuges for the removal of NC fines from wastewaters.

Nitroglycerin (NG) Production

Nitroglycerin is manufactured by a closely controlled reaction between glycerin and a mixture of nitric and sulfuric acids. The reactor is equipped with cooling coils through which a cold brine solution is circulated. Both batch and continuous (Biazzi) processes are in current use. One commercial nitroglycerin manufacturing plant uses a mixture of glycerin and ethylene glycol as the starting material; the product obtained in this plant is a mixture of nitroglycerin and ethylene glycol dinitrate.

Following nitration, the NG is separated from the spent acid by gravity separation and purified by washing with water and with a solution of sodium carbonate. Most facilities are equipped with settling pits and catch basins for the capture and return to process of most of the nitroglycerin particles entrained in the wastewaters. At Radford AAP, the spent acids are recovered and reused. Steam is used for denitrifying the spent acid at one commercial facility. At this facility, the effluent steam containing nitric acid is discharged directly to the atmosphere, and the sulfuric acid is stored in a lagoon for sale as a by-product. A block flow diagram for NG production is presented in Figure 5-31. Table 5-24 presents the material balance for NG production (based on operating conditions at Radford AAP).

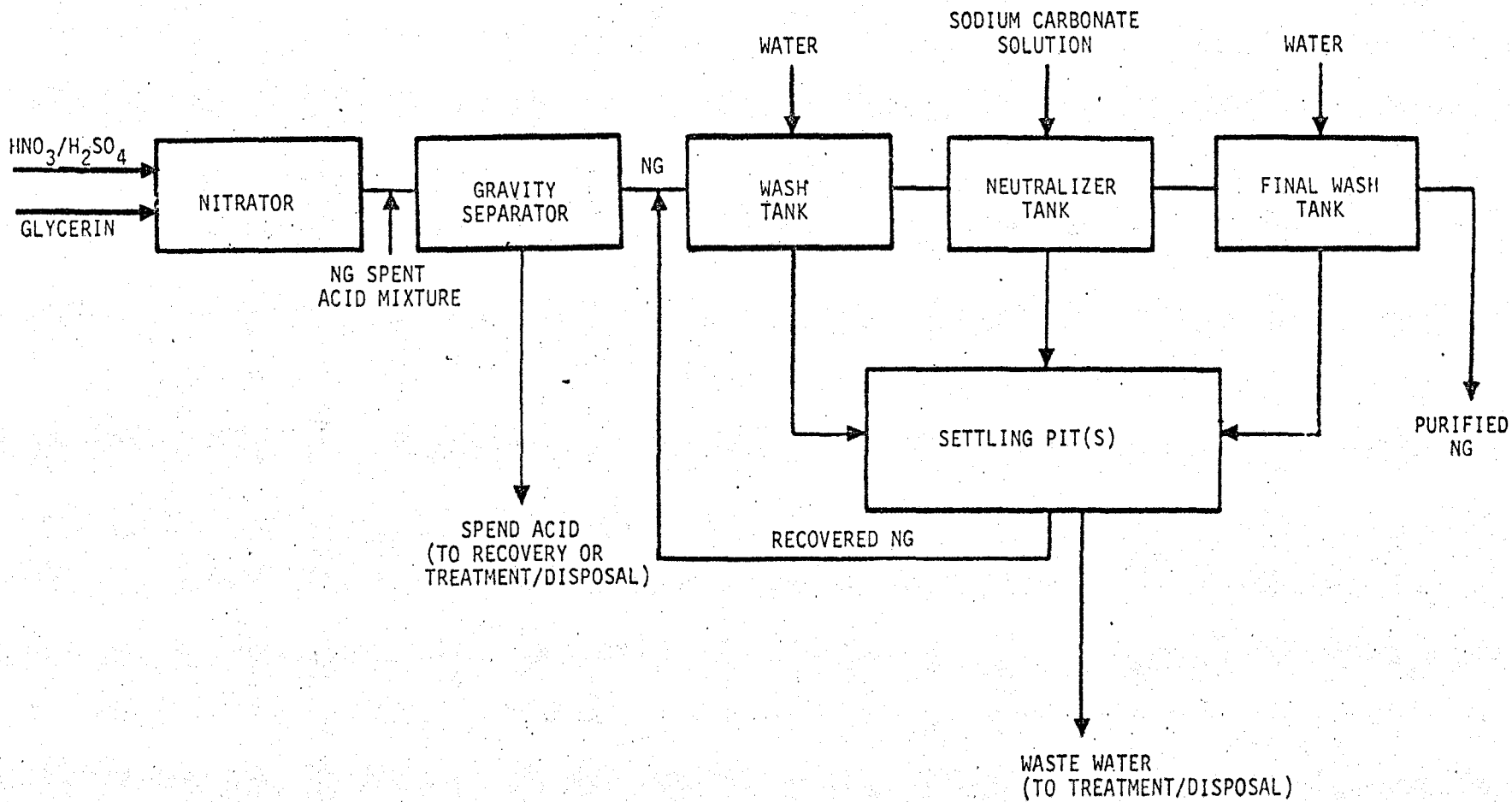


Figure 5-31. Schematic Flow Diagram for NG Production

Table 5-24. Mass Balance Data for Nitroglycerin (NG)
Production (kg per kg NG Produced)

Mixed Spent Acid Input	2.13
Glycerin	0.42
Soda Ash	0.12
Spent Acid	0.15
Waste water	6.25
NG Lost to Waste water	0.006

properties and contain RDX or HMX as their prime ingredient. The production operation involves addition of RDX (or HMX) to various explosives (e.g., TNT), and nonexplosive (e.g., wax) compounds to produce a plastic bonded material or a solidified end product. The make-up of a number of major military explosive compositions are presented in Table 5-26.

Based on the weekly Burning Ground record for May 20 to July 22, 1974,⁽⁵⁶⁾ and the 1973 production data,⁽¹⁸⁾ the solid waste generated in the formulation of Composition B is estimated at 0.0005 kg of waste per kg of final product.

Dynamites

Although there are many different dynamite formulations, most commercial dynamites contain nitroglycerin and sodium and/or ammonium nitrate as their major ingredients. Many dynamites are formulated to the customer's specifications and some also contain a number of proprietary ingredients. The most common ingredients of dynamites are listed in Table 5-27. Typical composition for "straight" dynamite with "active" base (sodium nitrate) is presented in Table 5-28.

Dynamite formulation involves, first, mixing ammonium and/or sodium nitrate with various nonexplosive ingredients. Nitroglycerin is then added and the product is transported to a cartridge house for packaging into waxed cardboard boxes or plastic tubes, for final shipment or storage in magazines.

Wastes from dynamite formulation originate from spills, off-spec products, and equipment clean-up. A waste generation factor of 0.3 percent of the production rate is estimated for the formulation of dynamite.⁽⁵⁷⁾

Ammonium Nitrate-Fuel Oil Mixture (ANFO)

In 1973 ANFO compositions accounted for close to 70 percent of all commercial explosives used. ANFO is a mixture of ammonium nitrate (about 94 percent) and fuel oil (about 6 percent) to which may be added a variety of minor ingredients such as aluminum powder, ferrophosphate, coal, calcium silicate, Atticote, and mineral oils. Some ANFO compositions may contain up to 5 percent aluminum powder. ANFO formulation may be a batch or a continuous

Table 5-26. Makeup of Major Explosive Compositions

Explosive Composition	Principal Ingredients
Composition A-3	RDX (91%), Wax (9%)
Composition B	RDX (60%), TNT (39%), Wax (1%)
Composition C-4	RDX (91%), Polyisobutylene (2.1%), Motor oil (1.6%), di(2-ethylhexyl) sebacate (5.3%)
Cyclotol 70/30	RDX (70%), TNT (30%)
Octol 70/30	HMX (70%), TNT (30%)
Octol 75/25	HMX (75%), TNT (25%)

Table 5-27. Common Ingredients of Dynamites

Nitroglycerin
Ammonium Nitrate
Sodium Nitrate
Sodium Chloride
Calcium Carbonate
Sulfur
Nitrocellulose
Phenolic Resin Beads
Bagasse
Sawdust and Wood Pulp
Coal
Corn Meal and Corn Starch
Trace Inorganic Salts
Grain and Seed Hulls and Flours

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Grain and Seed Hulls and Flours

APPENDIX D

SUMMARY OF JANUARY 1981 BARKSDALE SITE INSPECTION

Northwest District Headquarters
Box 309
Spooner, Wisconsin 54801

January 26, 1981

4400

Mr. Riley Williams
E. I. DuPont Company
PO Box 68
Seneca, Illinois 61360

Dear Mr. Williams:

This letter will document the tour of the E. I. DuPont facility at Barksdale, Bayfield County, Wisconsin. On January 16, 1981, Bruce Lawrence, Environmental Coordinator, and Stanley Bye, Occupational Health Coordinator, from DuPont's Seneca, Illinois facility accompanied Gary LeRoy and Barry O'Flanagan, Wisconsin Department of Natural Resources (WDNR), and James Thannum, student of Northland College, on the facility tour. The objective of the visit was to investigate concerns of environmental pollution expressed to WDNR by Mr. Thannum.

Initially, we discussed the operation of the plant as recalled by Mr. Bye. The plant was in operation from 1905 through 1976. The major products were dynamite, produced until 1961 and TNT, produced until 1971.

The processes and associated wastes we discussed are as follows:

- 1) Ammonium nitrate--no waste;
- 2) Nitric and sulfuric acids--cooling water and spilled sulfur;
- 3) Dynamite--neutralization wash from production of nitroglycerine and;
- 4) TNT--red water from washing the crude TNT.

These waste streams were, apparently, liquid and were all channeled into Boyd Creek. Mr. Bye said he did not recall any sludge-like wastes being produced.

Mr. LeRoy asked about the solid wastes that were produced on the site. Specifically, the garbage, sweepings and other refuse which presumably would be generated at a facility this size. Mr. Bye indicated there was a "burn area" on the site where material of this sort was openly burned. We did not get a chance to inspect the "burn area".

I inquired about wells on the site. Stanley Bye said there had been a number of wells, but that he did not know their location nor their present disposition. He said the drinking water was pumped from a well near the main entrance on the east side of the site. Apparently, this well is still in place as there is a wooden shelter sitting on its location.

The investigation of the site was directed toward the items Mr. Thannum had reported. Specifically we looked for:

- 1) Sulfur and lead deposits with no plant growth evident;
- 2) A "sewer" pipe with a yellowish-orange liquid running toward Boyd Creek;
- 3) Downed power insulators and transformers and;
- 4) An old dump with metal drums and assorted containers.

The sulfur deposits were located near a concrete foundation. There were a number of small sulfur "nuggets" laying on the ground in the immediate area. This was, according to Mr. Bye, a sulfur storage area. There was no vegetation growing in the immediate vicinity. Apparently, this was also a heavily travelled area with some cinder roadbeds present. We found no lead deposits.

The "sewer" pipe emptied into a ditch which drained toward Boyd Creek. There was frozen liquid in the pipe and trench, but it wasn't a yellowish-orange color.

A downed power pole with several insulators was located, but no transformers were found.

Dump sites for metal containers were located along a portion of the creek bed and flood plain during the investigation. The one immediately adjacent to the creek was looked at more closely. There were many types and sizes of containers. All visible containers were rusted and appeared empty with either the containers being punctured on the top or the bung removed. Some of the containers, including barrels, had washed downstream a distance. Gary LaRoy indicated to Bruce Lawrence that it would be necessary to clean the dump site up as it was, at the least, an aesthetic nuisance. The extent of the dump sites was impossible to determine because of the snow cover and frozen ground.

Only part of the site was toured and the portion observed wasn't investigated in enough detail to substantiate or refute all the concerns of Mr. Thannum and the Department. I told Messrs. Bye and Lawrence that there appeared to be no imminent hazards on the site, consequently, there is no need for any immediate action. However, I indicated that I believe a follow-up inspection of the entire site this spring after the vegetation is up is necessary to resolve this issue. Please do not attempt to clean up the dump sites mentioned above before we have an opportunity to more fully evaluate them this spring. The spring inspection will potentially include soils, surface water and groundwater sampling. I will contact DuPont this spring concerning this second inspection.

Mr. Riley Williams - January 26, 1981

3.

This is a brief summary of our discussions and facility tour. I would like to thank you for the cooperation shown in this initial contact. If you have any questions concerning this letter, please contact me at 715-635-2101.

Sincerely,

Barry D. O'Flanagan
Hazardous Waste Specialist

BDO:sw

cc: T. Jerow—Brule