Journal of Hazardous Materials, 7 (1983) 303—316
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

TREATMENT OF WASTEWATERS CONTAINING PROPELLANTS AND EXPLOSIVES

L.L. SMITH
Hercules Incorporated, Radford Army Ammunition Plant, Radford, Virginia
J. CARRAZZA and K. WONG
U.S. Army Research and Development Command, Dover, New Jersey

ABSTRACT

Studies were conducted at Radford Army Ammunition Plant (RAAP) to compare selected wastewater treatment methods, to define the treatment parameters and to prepare the design criteria for facilities to treat wastewater containing dissolved nitroguanidine (NGu), nitroglycerin (NG) and other nitrate esters and colloidal nitrocellulose (NC).

The design criteria for two pretreatment facilities were prepared based on the results of the pilot plant evaluation and transmitted to the Army Corps of Engineers who constructed the facilities at RAAP.

INTRODUCTION

Most of the U.S. Army propellant and explosives plants were built in the early 1940's to supply munitions for World War II. Since pollution abatement requirements were considerably less strict than at present, these plants could not meet current standards. The wastewater from the munitions manufacturing plants required treatment to meet both effluent discharge and safety regulations. In addition, Army safety regulations limit the amount of dissolved or suspended explosives in wastewaters transported in underground pipelines. To comply with this regulation, pretreatment facilities were required at RAAP to reduce the concentration of explosives in the wastewaters discharged into the underground collection system for transport to a central biological treatment plant.

Studies were conducted at RAAP to determine the feasibility of selected wastewater treatment methods, to define the treatment parameters, and to prepare the design criteria for the required facilities to treat wastewater containing NGu, NG and other nitrate esters, and colloidal NC.

LABORATORY-SCALE STUDIES

Extensive laboratory-scale studies were conducted on the various waste streams containing propellants and explosives to determine the most effective treatment methods (ref. 1).

Wastewater from NG manufacturing

Wastewater from the manufacture of NG contains dissolved NG; 1,2-dinitroglycerin (1,2-DNG); and 1,3-dinitroglycerin (1,3-DNG). The following are the results of the various methods studied:

Chemical oxidation. Chemical oxidation studies were conducted to determine the removal of NG and DNG from wastewaters. The initial tests used potassium permanganate and indicated that the NG and DNG were decomposed (Fig. 1); however, large quantities of permanganate were required for complete oxidation, making the method uneconomical.

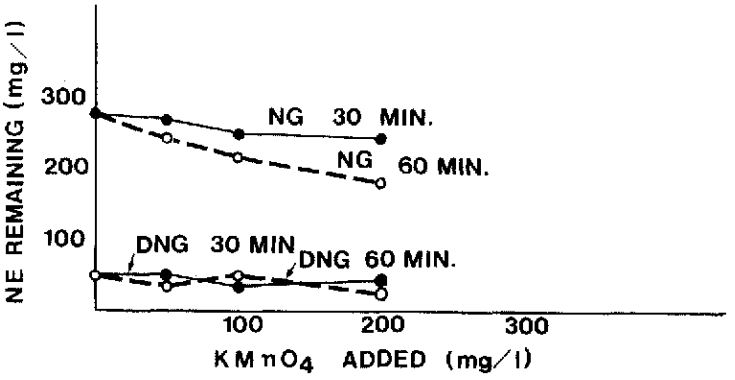

Fig. 1. Oxidation with potassium permanganate, wastewater from NG nitration

Additional studies were conducted to determine the oxidation rates using ozone at various wastewater pH levels. Results showed that ozone can completely oxidize NG in wastewater using a six-hour retention time and DNG using a 4-1/2-hour retention time (Fig. 2). Based upon the average concentration of NG and DNG in the wastewater, the ozone requirement was calculated to be 437 lb/1000 gal of wastewater, also making this method uneconomical.

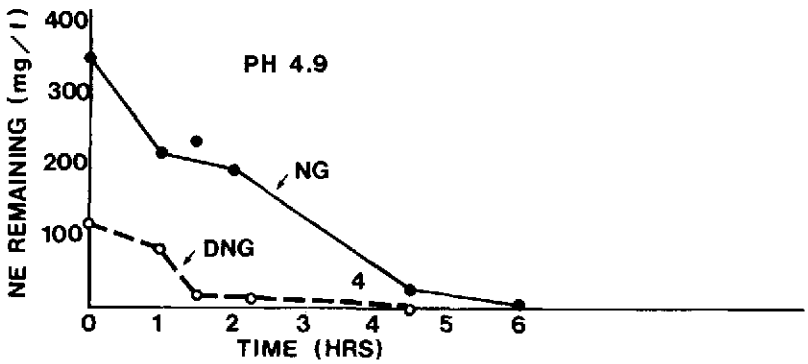

Fig. 2. Oxidation with ozone, wastewater from NG nitration

Chemical decomposition using sodium sulfide. Sodium sulfide solution has long been used for nitrate ester denitration. The chemical reaction has been given as: $4C_3H_5(NO_3)_3 + 6Na_2S + 6H_2O \rightarrow 12NaNO_2 + 6S + 4C_3H_5(OH)_3 + 3O_2$

Studies conducted using wastewater containing NG and DNG showed that sodium sulfide was effective in the decomposition of NG and DNG using a 30-minute retention time and a wastewater pH of 10.0 (Fig. 3). The quantity of sodium sulfide required to decompose these compounds was as follows:

1 lb NG required 0.706 lb Na_2S

1 lb DNG required 0.590 lb Na_2S

Based upon the average concentration of NG and DNG in the wastewater, the sodium sulfide requirement was calculated to be 2.7 lb/1000 gal wastewater.

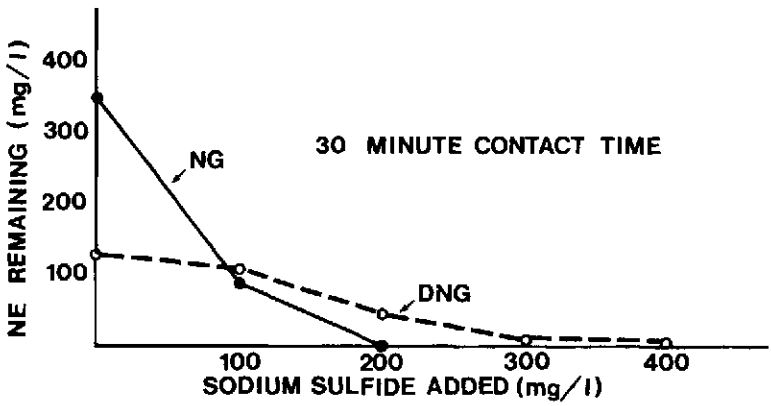

Fig. 3. Sodium sulfide treatment, wastewater from NG nitration

Chemical hydrolysis. Studies were conducted to investigate the chemical hydrolysis of NG and DNG with lime. The results of this study showed that by adding sufficient lime to increase the wastewater pH to 11.5, most of the NG was hydrolyzed within one hour and the DNG was hydrolyzed within 30 minutes (Fig. 4).

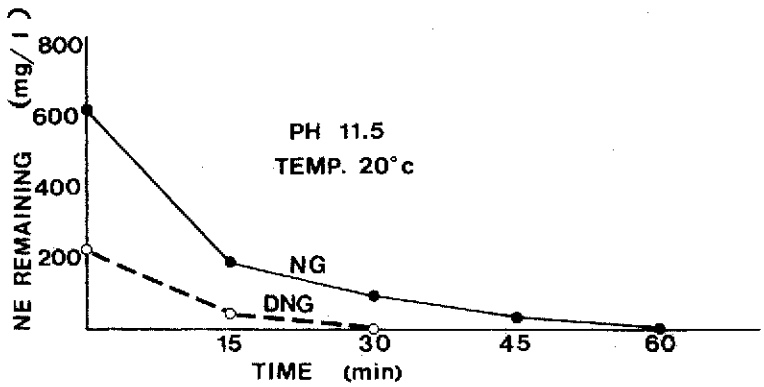

Fig. 4. Chemical hydrolysis, wastewater from NG nitration

Biodegradability. Studies conducted by Wendt (ref. 2) showed that NG is biodegradable; however, it does exert a toxic or inhibiting effect on the biological metabolism.

Studies were conducted to further define the biodegradability of NG using a laboratory-scale rotating biological contactor (RBC). This study was conducted using a simulated wastewater consisting of ethyl alcohol, NG manufacturing area wastewater, nitrates and phosphates. During the first phase of the study, the RBC was operated at a constant chemical oxygen demand (COD) loading while slowly increasing the NG concentration from 10 to 130 mg/l. This caused the COD removal efficiency to decrease from 94 to 70 percent (Fig. 5). These data showed a direct correlation between the NG concentration and the COD removal efficiency.

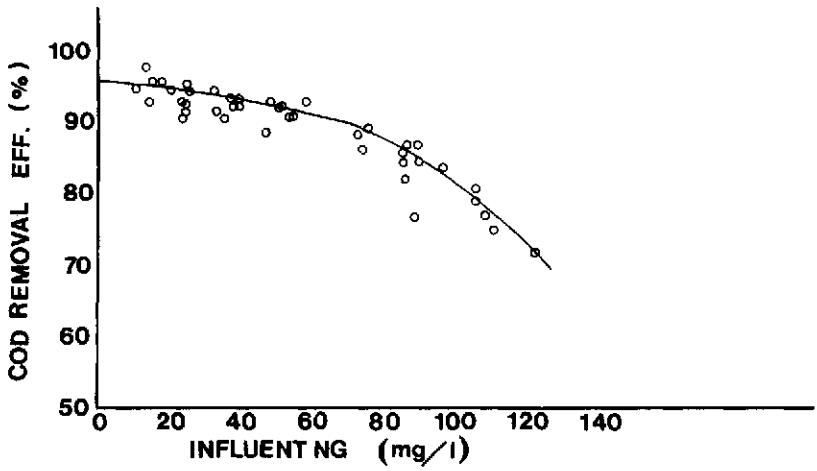

Fig. 5. Effect of influent NG concentration on COD removal efficiency

Additional studies were conducted maintaining a constant influent NG concentration and varying the COD and flow rate. It was found that decreasing the flow rate did not affect the COD removal efficiency. The data from this study were plotted along with the previous data from Figure 5 (see Fig. 6). These new data do not correlate with the previous data. It was also noted that an increase in the influent COD concentration caused an increase in the COD removal efficiency.

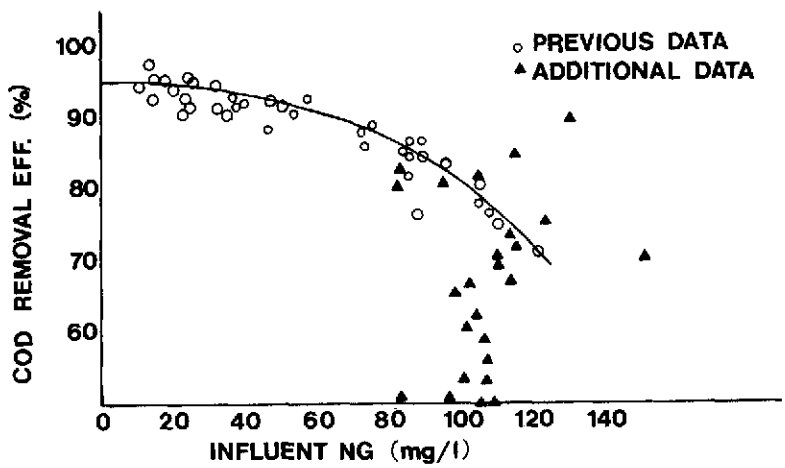

Fig. 6. Effect of influent NG concentration on COD removal efficiency

In order to explain this development, all of the data were replotted to determine the effect of the influent COD/NG ratio on the COD removal efficiency (Fig. 7). This graph shows that the COD removal efficiency is controlled by the influent COD/NG ratio rather than the NG concentration alone. The COD removal efficiency is not affected greatly by the NG until the COD/NG ratio decreased to less than 7, at which time the curve drops off sharply. During this entire study, the NG removal efficiency of the RBC system remained at 100 percent.

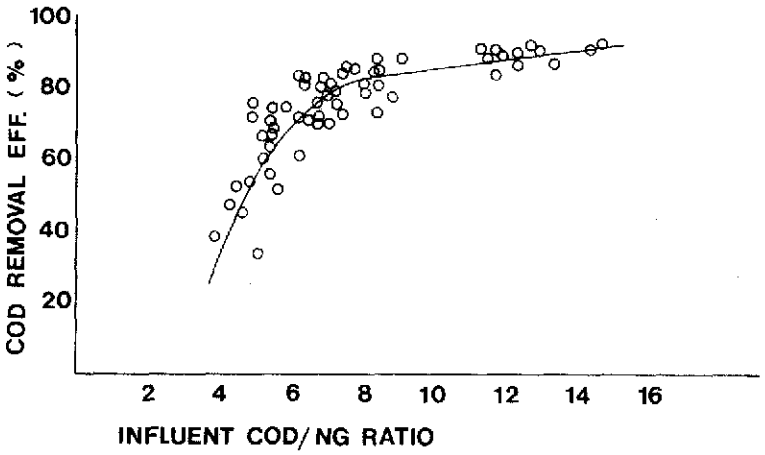

Fig. 7. Effect of influent COD/NG ratio on COD removal efficiency

It can be concluded that the quantity of NG which can be treated in a RBC system without affecting the COD removal efficiency is limited by the availability of other readily biodegradable organics, not on the NG concentration alone.

Wastewater from other nitrate ester manufacturing. Wastewater from the manufacturing of other nitrate esters, propylene glycol dinitrate (PGDN), diethylene glycol dinitrate (DEGDN), and trimethylol ethane trinitrate (TMETN) were used to determine the effectiveness of chemical hydrolysis and sodium sulfide decomposition. These studies showed that hydrolysis using lime or sodium hydroxide was not effective for the decomposition of these nitrate esters in wastewater. However, the nitrate esters were readily decomposed by the sodium sulfide (Fig. 8).

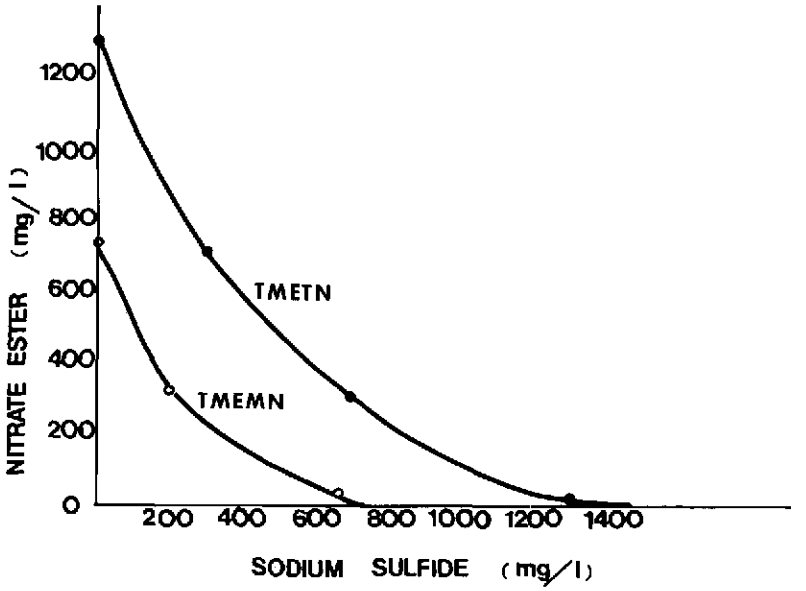

Fig. 8. Denitration of nitrate esters using sodium sulfide

Wastewater containing colloidal nitrocellulose fines. Wastewater from slurry mixing and alcohol rectification contains NC fines which will not settle under normal conditions. Initial NC settling studies were conducted using polymer flocculants alone. It was found that the addition of the polymers improved the solids settling rate; however, the dosage required made the method uneconomical.

Additional tests were conducted to determine the effect of lime precipitation on the removal of colloidal NC. This test showed that when sufficient lime was added to increase the wastewater pH to 11.6 the solids settled out within 30 minutes without a flocculant. When a small dosage of a cationic polymer flocculant was added with the lime, a large floc was formed which settled out within 5 minutes (see Fig. 9).

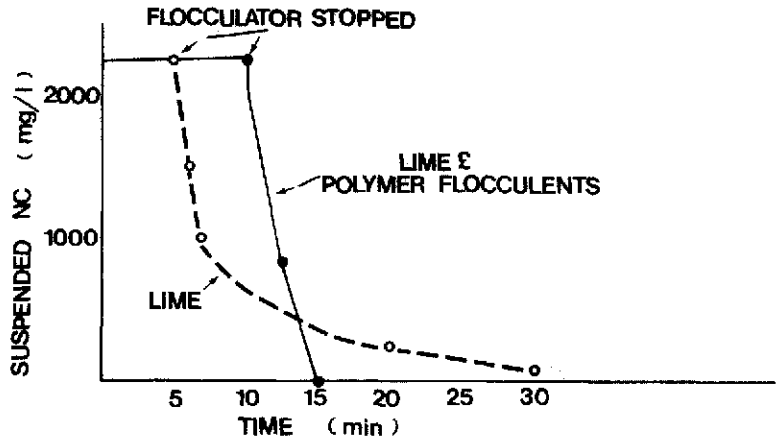

Fig. 9. Removal of colloidal NC using lime and polymer flocculants

Wastewater containing nitroguanidine. Studies were conducted to determine the decomposition rate of NGu by the use of sodium sulfide and sodium hydroxide. These studies showed that NGu cannot be effectively decomposed with sodium hydroxide alone; however, a combination of sodium hydroxide and sodium sulfide was an effective method. The sodium hydroxide was added to increase the pH to above 11.0 and increase the sulfide reaction rate. These studies showed that

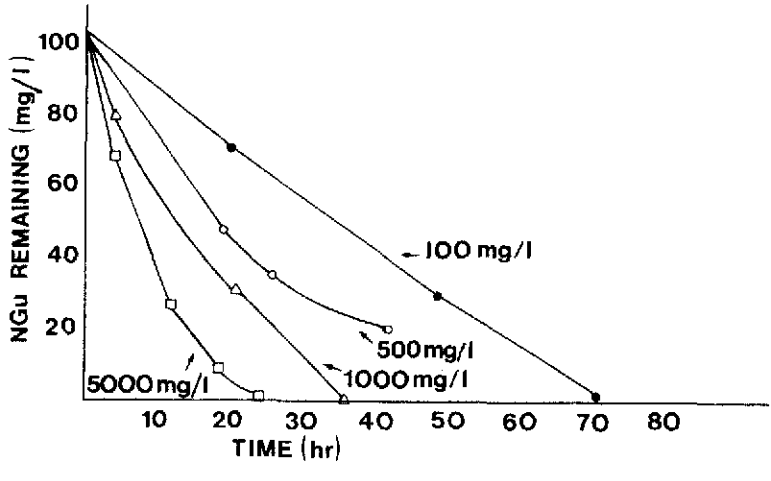

Fig. 10, Rate of denitration of NGu using various concentrations of sodium sulfide

the NGu decomposition rate was a function of the sulfide concentration added (Fig. 10).

Although successful, the use of such relatively large amounts of sulfide is undesirable; therefore, studies were conducted to determine the biodegradability of NGu using the Hach biochemical oxygen demand (BOD) test kit. The tests were set up to determine the oxygen uptake rate of a readily biodegradable wastewater alone and with various concentrations of NGu added (Fig. 11). In all of these tests, the oxygen uptake rate increased substantially when NGu was added to the wastewater. However, the increase in the oxygen uptake rate was not proportional to the NGu added. These tests indicated that NGu, like NG, is not biodegradable by itself but requires the presence of a readily biodegradable carbon source and that the rate of biological metabolism of NGu is a function of, and is limited by, the ratio of NGu to the readily biodegradable carbon compound.

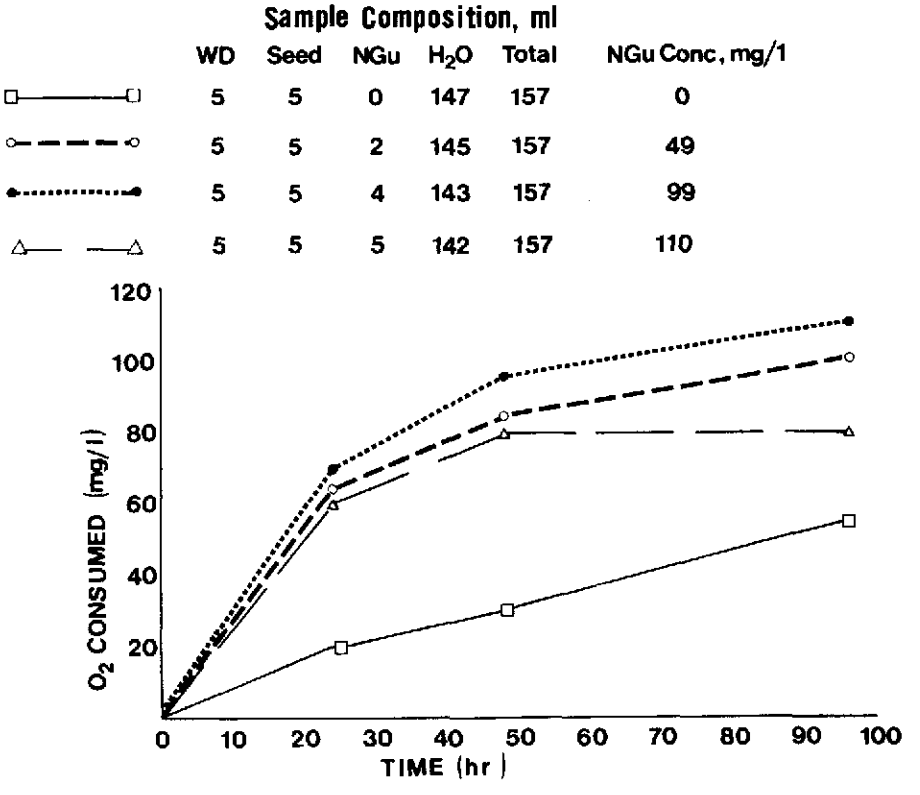

Fig. 11. Biodegradability of NGu, Hach BOD test kit

PILOT PLANT STUDIES

The results of the laboratory-scale studies were evaluated and it was determined that a central biological wastewater treatment facility would have the capability for biodegrading the NGu and nitrate esters in the combined manufacturing areas wastewater. However, the NG and nitrate esters in the wastewater discharged from the manufacturing areas would require pretreatment to decrease the concentration of NG and nitrate esters to meet the Army's safety regulations in regard to the quantities of explosives contained in wastewater flowing in underground pipe lines. Pretreatment facilities would also be required for the removal of NC fines in wastewaters from the alcohol rectification and slurry mix processes since NC is not biodegradable.

Pilot plant evaluations were conducted at RAAP in conjunction with the U.S. Army Mobility Equipment Research and Development Command (MERDCOM), Fort Belvoir, Virginia, for the development of the design criteria for these pretreatment facilities. A flow diagram of the pilot plant is shown in Figure 12.

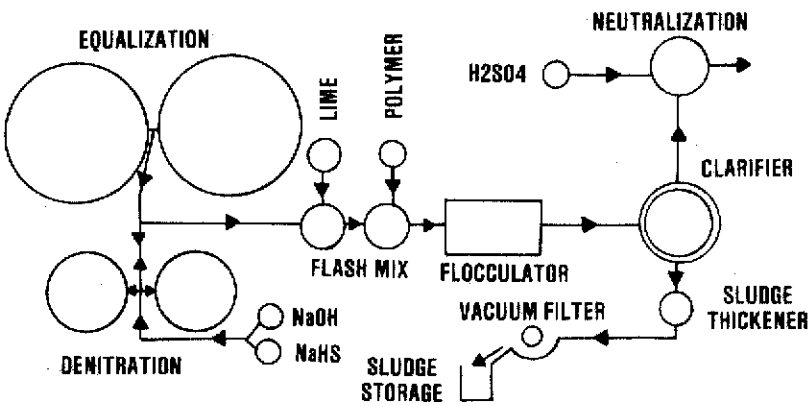

Fig. 12. Pilot plant flow diagram

Wastewaters containing colloidal NC

A study was conducted in this pilot plant using the wastewater from the alcohol rectification process for the removal of the NC fines by lime and polymer flocculants (ref. 3). The design criteria for the processes of coagulation, flocculation, clarification, neutralization and sludge dewatering were developed. A flow diagram for this process is shown in Figure 13. The pilot plant proved to be capable of consistently reducing the NC content of the wastewater from above 2000 mg/l to less than 50 mg/l.

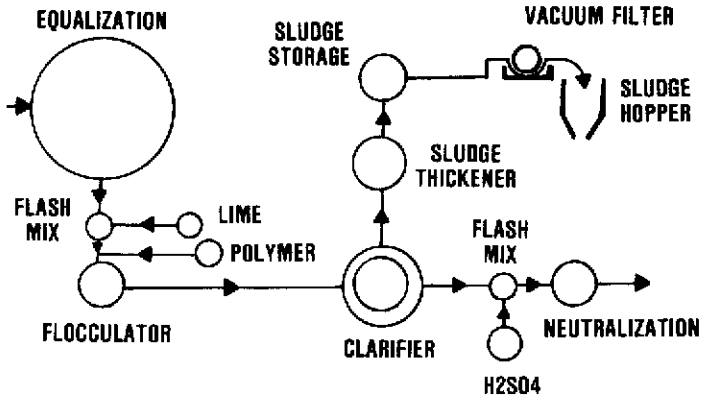

Fig. 13. Alcohol rectification wastewater treatment flow diagram

Nitroglycerin manufacturing area (NG-2)

A pilot plant study was continued using the wastewater generated from the manufacture of NG to define the design parameters for the chemical hydrolysis of NG using lime (ref. 4). The design criteria for the processes of denitration (hydrolysis), flocculation, clarification, neutralization and sludge dewatering were prepared. The flow diagram for this process is shown in Figure 14. The pilot plant study demonstrated that the NG in the wastewater could consistently be decreased from over 1000 mg/l to less than 50 mg/l.

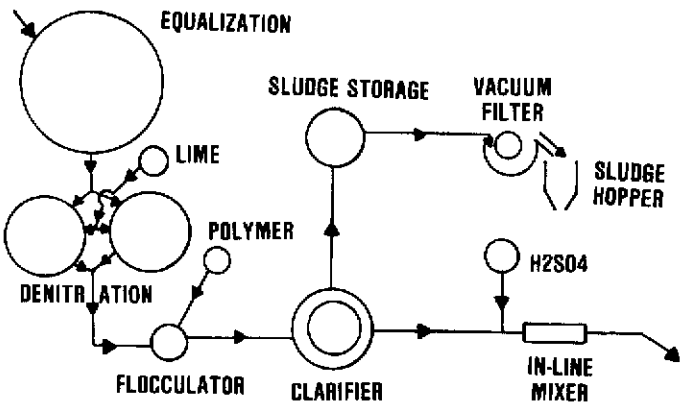

Fig. 14. NG-2 area wastewater treatment flow diagram

Nitrate ester manufacturing area (NG-1)

The final pilot plant evaluation was conducted using wastewater generated during the manufacture of nitrate esters to define the design parameters for the denitration of the nitrate esters using lime or sodium hydroxide with sodium sulfide (ref. 5). The design criteria for the processes of denitration, flocculation, clarification, neutralization and sludge dewatering were prepared. The flow diagram for this process is shown in Figure 15. The pilot plant study demonstrated the consistent reduction of the nitrate ester from an influent concentration of over 1400 mg/l to produce an effluent containing less than 50 mg/l.

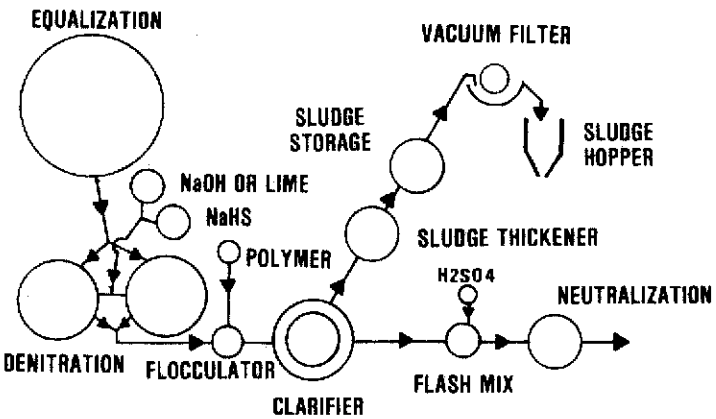

Fig. 15. NG-1 area wastewater treatment flow diagram

Pretreatment plant design and construction

The design criteria developed from the pilot plant evaluations were used for the design of two pretreatment facilities. The NG-2 pretreatment facility (Fig. 16) was designed to treat the wastewater from the NG-2 area and the slurry mix process.

A second pretreatment facility (Fig. 17) was designed to treat the wastewaters from the NG-1 area and the alcohol rectification house.

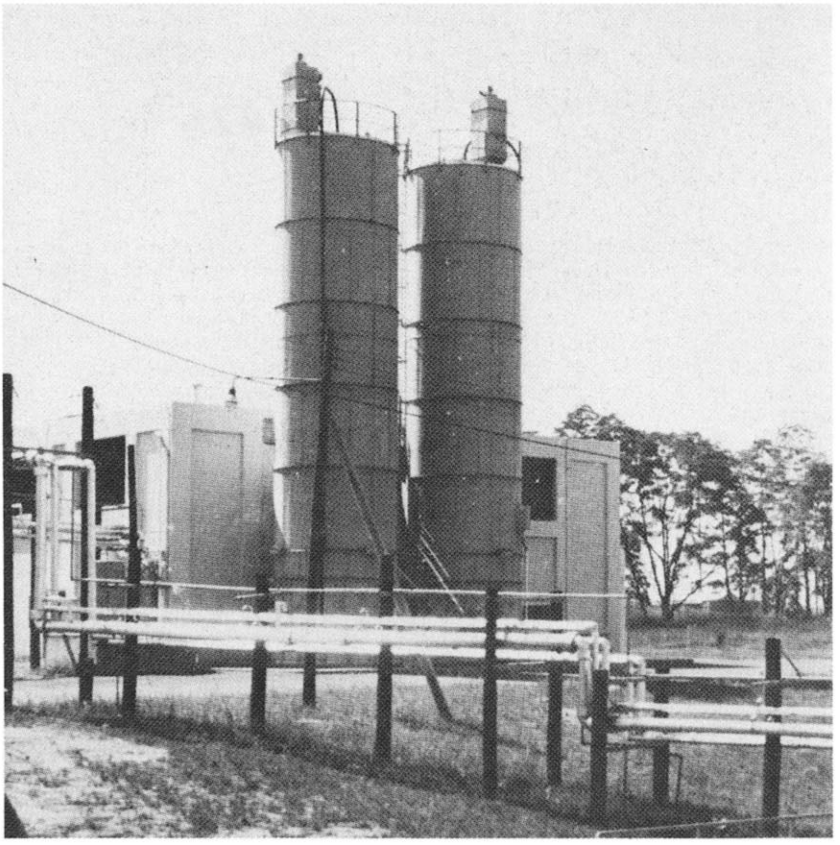

Fig. 16. NG-2 area wastewater pretreatment plant

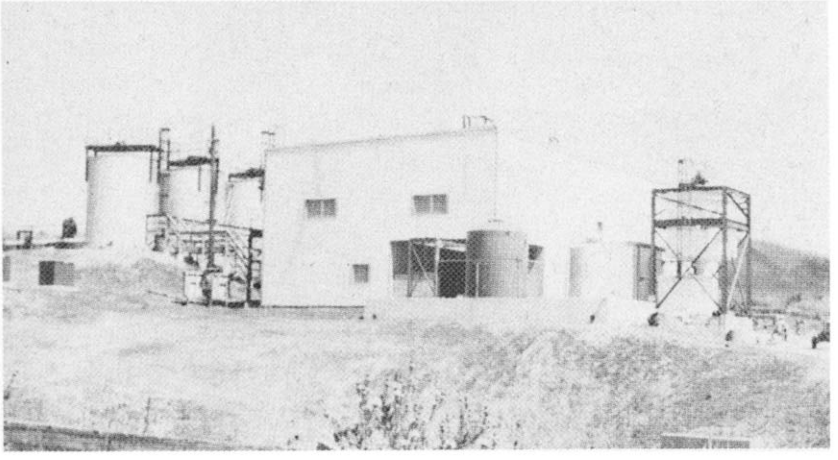

Fig. 17. NG-1 and alcohol rectification house wastewater pretreatment plant

The Army Corps of Engineers has completed construction of the two facilities at RAAP. The NG-2 facility has been placed in operation and is consistently meeting the design requirements. The NG-1 wastewater pretreatment plant will be placed in operation when this area resumes manufacturing operation.

REFERENCES

1 L.L. Smith and R.L. Dickenson, Engineering Investigation to Develop Optimum Control Measures to Prevent Water Pollution, Final Engineering Report PE-249 (Phase II), Radford Army Ammunition Plant, Radford, Virginia, 1974.

2 T.M. Wendt, J.H. Cornell, and A.M. Kaplan, Microbial Degradation of Glycerol Nitrate, Applied and Environmental Microbiology, 1978, pp. 639-699.

3 V.J. Ciccone, R.P. Carnahan, L.L. Smith, J.A. Carrazza and A.L. Hunter, Physical/Chemical pilot Plant Study for Treatment of Propellant Manufacturing Wastewaters (Phase I - Alcohol Rectification House, Radford Army Ammunition Plant), Technical Report ARLCD-TR-79032, U.S. Army Armament Research and Development Command, Dover, New Jersey, 1980.

4 R.P. Carnahan, L.L. Smith, and J.A. Carrazza, Physical/Chemical Pilot Plant Study for Treatment of Propellant Manufacturing Wastewaters (Phase III - NG-2 Area, Radford Army Ammunition Plant), Technical Report ARLCD-TR-79001, U.S. Army Armament Research and Development Command, Dover, New Jersey, August 1979.

5 R.P. Carnahan, L.L. Smith, and J.A. Carrazza, Physical/Chemical Pilot Plant Study for Treatment of Propellant Manufacturing Wastewaters (Phase II - NG-1 Area, Radford Army Ammunition Plant), Technical Report ARLCD-TR-78063, U.S. Army Armament Research and Development Command, Dover, New Jersey, June 1979.