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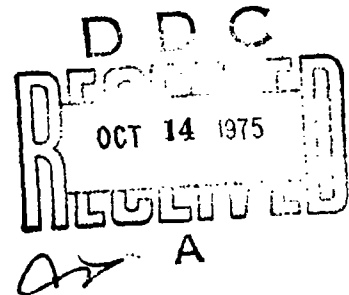
EXPLOSIVES REMOVAL FROM MUNITIONS WASTEWATERS

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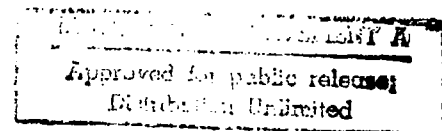
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U.S. ARMY NATICK DEVELOPMENT CENTER, NATICK, MASSACHUSETTS



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Removal of Explosives  
From Wastewater  
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by

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Pilot plant studies conducted at the Iowa Ammunition Plant, Burlington, Iowa, have demonstrated a safe, practical and economical polymeric adsorption process for removing trinitrotoluene (TNT) and other hazardous explosive materials, such as DNT and nitroresols, from waste streams. The loaded adsorbent can be regenerated with solvent. To minimize operating costs, the solvent can be easily recovered for reuse, leaving only a concentrated aqueous sludge of explosive contaminants for ultimate disposal.

As a result of the success of this pilot-scale study, full-scale demonstration installations of the process are being planned for several ordnance plants in this country. The same process is equally applicable to industrial waste streams containing aromatic nitrocompounds.

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### Background

Generally, pollution in munitions plant waste water stems from washing and steam cleaning operations. Waste water from a typical TNT manufacturing plant may contain from 40 to 120 ppm of TNT and lesser amounts of 2,4, DNT. Waste water from load, assemble and pack (LAP) facilities usually contain higher concentrations of TNT and other nitrocompounds chiefly RDX (cyclotrimethylenetrinitramine) and HMX (cyclotetramethylenetetranitramine), which are constituents of Composition B explosive. These nitrocompounds are toxic, explosive and frequently highly colored.

This pollution problem has been recognized for some time and has been dealt with to some extent (Ref. 2). However, today stringent federal and state effluent standards require more effective control than has been accomplished in the past.

Previous treatment of munitions waste has included neutralization, settling and dilution. Neutralization and exposure to sunlight in open settling basins causes effluents to have a deep pink color. Biological treatment is partially effective, but complete breakdown of the TNT molecule to harmless products has not proved successful. Also, there is some evidence that the presence of TNT may actually inhibit the performance of a conventional activated sludge system. Chlorination, ozonolysis and liquid-liquid extraction have also been proposed as possible solutions.

In general the technique which has been found to be most effective is fixed-bed adsorption following clarification and filtration to remove suspended solids. Activated carbon adsorbent is used at a number of munitions installations. This material adsorbs a wide variety of organic materials including TNT. However, the use of activated carbon to remove nitroaromatic materials

poses difficult problems. Conventional thermal regeneration is not practiced because of the hazard involved. Limited success has been attained with solvent regeneration using toluene, but large volumes of solvent are required, and regeneration effectiveness diminishes rapidly. After only about three cycles of operation, the capacity of the carbon cannot be restored. As a result, those installations presently employing activated carbon make no attempt to regenerate. Rather they discard the loaded adsorbent and replace it with fresh material. Of course, handling the TNT-loaded carbon is itself a delicate task involving an occupational hazard. Frequently wax, used as a desensitizer in Composition B, slips through the prefilters and causes the activated carbon to cake. When this happens the TNT-loaded carbon bed must be loosened by chipping and prying.

#### Polymeric Adsorbent Resins

In 1974 the Natick Laboratories (NLABS) conducted bench-scale studies of the ability of a polymeric adsorbent to remove the nitrocompounds from munitions plant waste streams (Ref. 3). These studies indicated that this adsorbent not only has excellent capacity for aromatic nitrocompounds such as TNT, but also that the adsorbent can be effectively regenerated to restore its original capacity throughout many cycles of operation. Further, it appeared feasible that the solvent regenerant used to remove the nitrocompounds from the surface of the adsorbent can be reclaimed for reuse, thus minimizing operating costs.

The polymeric adsorbents in question are manufactured by Rohm and Haas Company under the trademark Amberlite<sup>®</sup>. They consist of hard, insoluble, porous resin beads formed from co-polymers of styrene and divinylbenzene or acrylic esters. They are similar in physical structure to macroreticular ion exchange resins, but exhibit no ionic functionality. Having a high surface

area to weight ratio (Figures 1 and 2), the resin beads employ Van der Waals forces to effectively adsorb many water soluble organics. The process is reversible, and the adsorbed organics can be desorbed from the surface of the resin by a number of polar organic solvents.

#### Pilot Study

As a result of the encouraging results of the Natick bench-scale tests, the U.S. Army contracted with the Fluid Process Chemicals Department of the Rohm and Haas Company to perform an on-site pilot plant study of these new adsorbents. The Rohm and Haas Company's Fluid Process Services Group conducts studies of specific pollution problems in order to devise, design and install pollution control facilities. Under the terms of the contract the group conducted an on-site study to demonstrate the practicality of using polymeric adsorbent resins to remove explosive residues from munitions waters and to recommend a full-scale system if the results of the study proved favorable. The pilot plant operation was conducted at the Iowa Army Ammunition Plant (IAAP), Burlington, Iowa during January and February of 1975.

The IAAP is a government-owned load, assembly and pack facility operated by Mason & Hanger, Silas Mason Co., Inc. of Lexington, Ky. In addition to TNT, an aromatic nitrobody, wastewaters at this plant also contain the non-aromatic nitrobodyes RDX and HMX and other undefined contaminants.

The objectives of the pilot study were to evaluate the performance of Amberlite XAD-4, the polymeric adsorbent which the NLABS experiments had indicated as the most effective for removing TNT. Specifically these objectives were:

1. To determine resin capacity for three service and regeneration cycles taken to a 1-ppm instantaneous TNT breakthrough.

2. To determine resin capacity at saturation.
3. To evaluate several ion exchange resins, the polymeric adsorbent resin and activated carbon as polishing agents for removing residual color and residual non-aromatic nitrobodyes from the effluent of the primary adsorbent column.
4. To develop optimum adsorbent regeneration techniques.
5. To develop a method for recovering the solvent regenerant.

#### Equipment and Procedures

The pilot plant (Figure 3) was established at one of the waste treatment facilities at the depot. The existing treatment system consisted of two settling tanks, two diatomaceous earth filters and four activated carbon columns.

Waste water for the study was drawn as needed from the effluent of the diatomaceous earth filters and stored in an 800-gallon polyethylene reservoir. Two 4-inch stainless steel columns containing Amberlite XAD-4 were installed. Column #1 was used for the 3-cycle service and regeneration study. Its effluent was also used for the polishing study. The saturation study was conducted with Column #2.

Positive displacement pumps metered the feed from the reservoir to the 4-inch columns at a rate of 1 gpm per cubic foot of adsorbent. The effluent of Column #1 was split between four 1-inch glass columns containing the polishing agents and their effluent returned to the settling tank.

During the study, influent and effluent samples were collected every 8 hours. Samples were analyzed by liquid chromatography to identify specific nitrobody content. This relatively new measurement technique enables one to identify the specific nitrobodyes in the stream down to a fraction of one part per million. Flow rates were also checked every 8 hours and verified by comparison with the volume of water withdrawn from the influent reservoir.

Column #2 operated continuously throughout the test period to determine the saturation point of the resin. Column #1 was run until TNT leakage reached 1 ppm. At that point it was regenerated with acetone. This procedure was repeated for three complete cycles of exhaustion and regeneration. Regeneration procedures and results will be discussed later.

#### Adsorption Test Results

Preliminary investigations had shown that the polymeric adsorbent has a greater affinity for aromatic nitrocompounds, such as TNT than for non-aromatic nitrocompounds, such as RDX. As the LAAP waste water contains both aromatic and non-aromatic nitrocompounds cycling tests were run to a TNT breakthrough rather than a total nitrocompound end point. The purpose of the polishing columns was to remove any residual non-aromatic nitrocompounds.

Table I summarizes the data of the three-cycle, service-regeneration test as well as the saturation investigations. For comparison purposes the table also includes performance data of one of the plant's activated carbon columns developed during an earlier study (Ref. 4). The volume of water treated is expressed in bed volumes of resin to eliminate this parameter as a variable.

Figures 4 through 6 present daily data on influent and effluent concentrations from Column #1. Similar data on the continuous saturation run of Column #2 are given in Figure 7. As shown in Table I, data for the first service run of adsorbent Column #1 and the first portion of the simultaneous run on Column #2 are remarkably similar to that for the activated carbon.

A slight loss of total capacity of the polymeric adsorbent is noted during cycles 2 and 3. The possibility that this was caused by incomplete regeneration of the adsorbent cannot be ruled out. However, previous studies of a similar resin, Amberlite XAD-2, indicated that it was capable of undergoing continuous

regeneration cycles without any significant decrease in adsorption efficiency (Ref. 2). Figure 8 shows the multiple regeneration efficiency of this polymeric adsorbent (Ref. 5). Breakthrough of 1 ppm TNT occurred at approximately 230 bed volumes during the first cycle. Breakthrough occurred at approximately 175 bed volumes for each of the next 9 succeeding cycles indicating that an equilibrium had been attained in which the organic pollutants were adsorbed and desorbed with equal efficiency. This study was conducted for 15 cycles with no loss of adsorption efficiency before being discontinued.

Analysis of the data from the pilot study suggests an explanation for the capacity variations. Whereas previous laboratory studies were conducted on influents containing constant concentrations of only TNT, the pilot study was conducted on actual plant waste waters which contained other nitrocompounds as well, and varying concentrations of each. It appears likely that the polymeric adsorbent's capacity for TNT depends upon the influent concentration of the various nitrocompounds.

During cycle #2, lower concentrations of nitrocompounds were introduced at the same flow rate as cycles #1 and #3, thus providing longer contact times with the adsorption sites. The possibility that this resulted in preferential adsorption of TNT could be inferred from the fact that during this cycle capacity was greater for TNT and lower for RDX than in the other two cycles.

In cycle #3 the total influent concentration of nitrocompounds was similar to that in cycle #1. Although the total capacity of cycle #3 is lower than that of cycle #1 or #2, it correlates well with the equilibrium data in Figure 8.

As expected, the data in Figure 9 show that the polymeric adsorbent is less effective in removing RDX. Data for only one cycle are shown but they are characteristic of all three cycles. During each cycle, 1 ppm RDX leakage

occurred about one-quarter into the TNT cycle in terms of volume of water treated before breakthrough. There is also some indication that TNT may displace RDX previously adsorbed on both the polymeric adsorbent and activated carbon. However, two of the four 1-inch polishing columns proved completely effective in removing RDX leakage from the Column #1 effluent. Because TNT leakage from Column #1 never exceeded 1 ppm, only RDX was present in the influent to the polishing columns. Although neither of the two ion exchange resins was effective in removing this RDX leakage, both the polymeric adsorbent and the activated carbon were. Either could be used as a polishing agent for controlling total nitrobody concentration in munitions plant effluents.

#### Regeneration Procedure and Results

A major objective of the pilot study was to verify the ability to regenerate the loaded adsorbent for reuse, rather than having to discard it, as is presently the case with activated carbon.

Column #1 was regenerated three times. The resin bed was drained and flushed with compressed gas to remove interstitial water. The column was then filled with acetone introduced upflow and the resin bed mixed with compressed gas. At this point, water still remained in the pores of the resin beads.

Next acetone was introduced at the top of the column at a rate of 0.125 gpm per cubic foot of resin with the effluent collected in 0.5 bed volume increments and analyzed. Figure 10 plots the percentage concentration of displaced water and total solids in the regenerant effluent after cycle #3 as a function of effluent regenerant volume. It will be noted that 1.5 bed volumes of regenerant displaced most of the water and provided the peak in solids removal. Figure 11 contains a plot of nitrobodyes removed from the resin as a function of regenerant flow and shows that regeneration was virtually complete

when 2.0 bed volumes had flowed through the resin. The remaining bed volume was then drained from the column and the column was flushed, backwashed and returned to service. Total regeneration time required about 4 hours.

#### Solvent Recovery

One of the keys to the economics of this process is the ability to recover the solvent regenerant after it has been used. Laboratory tests suggest that as much as 99% of the solvent can be recovered by distillation (Ref. 6). More recent pilot studies conducted with Artisan Industries confirm this conclusion.

After distillation of the solvent, the still bottoms consist of an aqueous sludge of highly concentrated nitrobenzenes. Impact tests on dried samples of this sludge indicate that it is much less sensitive to shock than either TNT or RDX (Ref. 6). Using a 2 kg weight, a drop height of 22.3 inches was required to obtain a 50% probability of detonation. Comparative values for TNT, RDX and Composition B are 15, 3 and 14 inches respectively. However, the still bottoms need not be dried. They can be pumped back to the wastewater influent sump or settling basin where cooling will cause most of the nitrobenzenes to precipitate. Those which do not precipitate will be returned to the adsorption process. This closed loop approach keeps the nitrobenzenes wet at all times and completely eliminates manual handling. As a result the process is much safer than techniques presently used.

#### Proposed Process

On the basis of these studies a continuous adsorption process has been proposed for the complete removal of nitrobenzenes from the IAAP waste stream (Figure 12). This regenerable process would utilize two parallel polymeric adsorption columns in the one-on, one-off mode and two smaller polishing columns operated in a similar manner.

The polishing columns could use either additional polymeric adsorbent or activated carbon. As a polisher the polymeric adsorbent will efficiently remove residual RDX and some color. Being capable of regeneration it will not have to be discarded manually after becoming loaded with nitro bodies. However, for complete color removal activated carbon would be required. Although the carbon cannot be regenerated, much smaller quantities would be used for much longer periods than is now the case. Nevertheless, the carbon would ultimately have to be discarded making this polishing technique the more hazardous of the two.

Perhaps the ultimate system would be to use polymeric adsorbent and activated carbon as polishers in series. The regenerable resin would remove residual RDX and the carbon the residual color bodies. The relative safety of this system is a matter of conjecture as the explosive nature of the color bodies is unknown.

After regeneration of the exhausted polymeric adsorbent, the solvent would be reclaimed by distillation and condensation, and the still bottoms would be recycled to the clarifier.

Estimates projected by Mason and Hanger, Silas Mason Co., Inc. and the Naval Ammunition Production Engineering Command (NAPEC) indicate that this process is significantly more economical than the present practice of continuously replacing activated carbon. With recovery of the solvent regenerant, operating chemical costs would be low. Concentration of removed nitro bodies in an aqueous sludge would substantially reduce solid waste disposal problems and hazards. Finally, the process would completely eliminate the discharge of toxic nitro bodies to local streams.

TABLE I

## LOADING AND EXHAUSTION DATA

## BURLINGTON IAAP

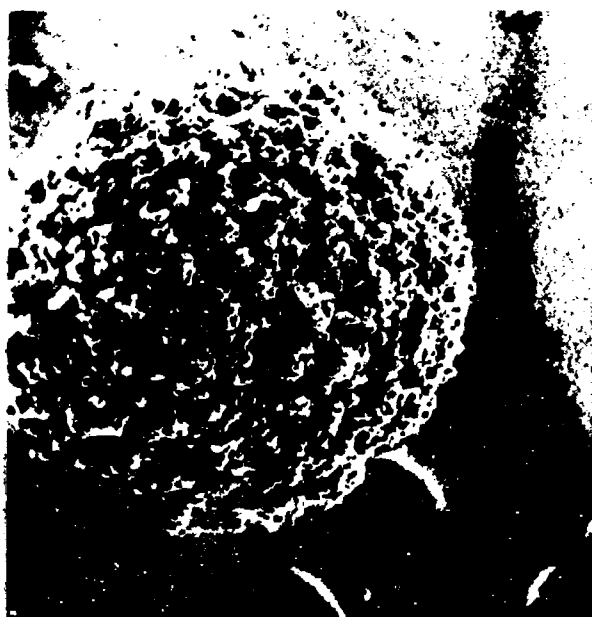
| Adsorbent          | Bed Volume | TNT Leakage, ppm | Flow Rate gpm/ft. <sup>3</sup> | Average Inlet Concentration (ppm) |     | Adsorbent Capacity (gm NB/gm Adsorbent) |       | Capacity Loss, % |
|--------------------|------------|------------------|--------------------------------|-----------------------------------|-----|-----------------------------------------|-------|------------------|
|                    |            |                  |                                | TNT                               | RDX | TNT                                     | RDX   |                  |
| AMBERLITE XAD-4    | --         | --               | --                             | --                                | --  | --                                      | --    | --               |
| Cycle 1            | 804        | 1                | 1.0                            | 107                               | 90  | 0.139                                   | 0.057 | --               |
| Cycle 2            | 1196       | 1                | 1.0                            | 81                                | 46  | 0.154                                   | 0.031 | 5.6              |
| Cycle 3            | 633        | 1                | 1.0                            | 116                               | 69  | 0.116                                   | 0.042 | 14.6             |
| AMBERLITE XAD-4    | 3886       | Sat'd (2)        | 1.0                            | 114                               | 74  | 0.435                                   | 0.057 | 0.49             |
| Filtersorb 300 (1) | 600        | 1                | 0.9-1.0                        | 108                               | 89  | 0.125                                   | 0.074 | 0.199            |

(1) Carbon Column System Removal Efficiency Study No. 24-033-73/74 at the Burlington IAAP 5/2/73 to 6/22/73

(2) Breakthrough Capacity = 40% of Saturation Capacity

FIGURE 1

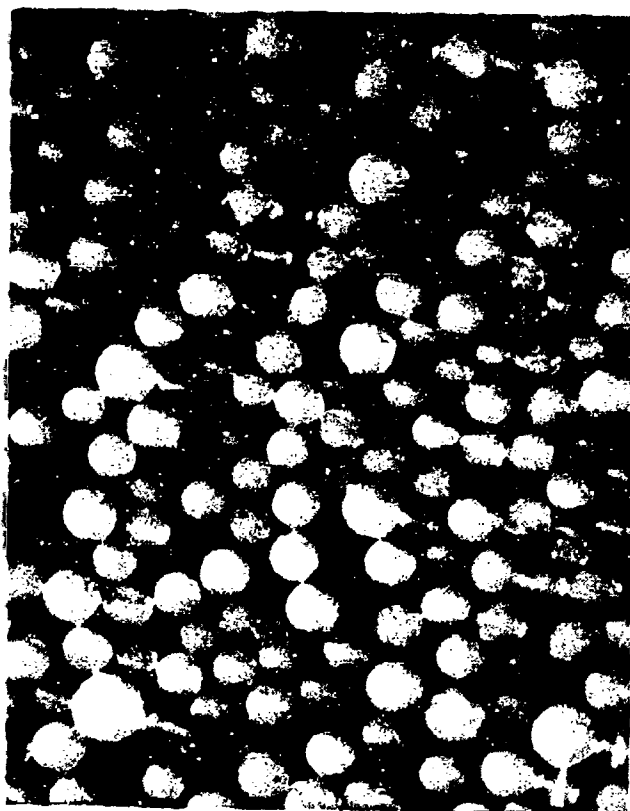
This photograph of a macroreticular bead of non-ionic synthetic resin polymer, obtained with the scanning electron microscope, clearly confirms the microsphere-agglomerate structure of the macroreticular type resin.



0.1 mm

Amberlite IRA-938

FIGURE 2



AMBERLITE-XAD-4

Spherical beads of Amberlite XAD-4 polymeric adsorbent magnified approximately 10 times.

SCHEMATIC OF PILOT PLANT AND EXISTING  
IAAP WASTE WATER TREATMENT SYSTEM

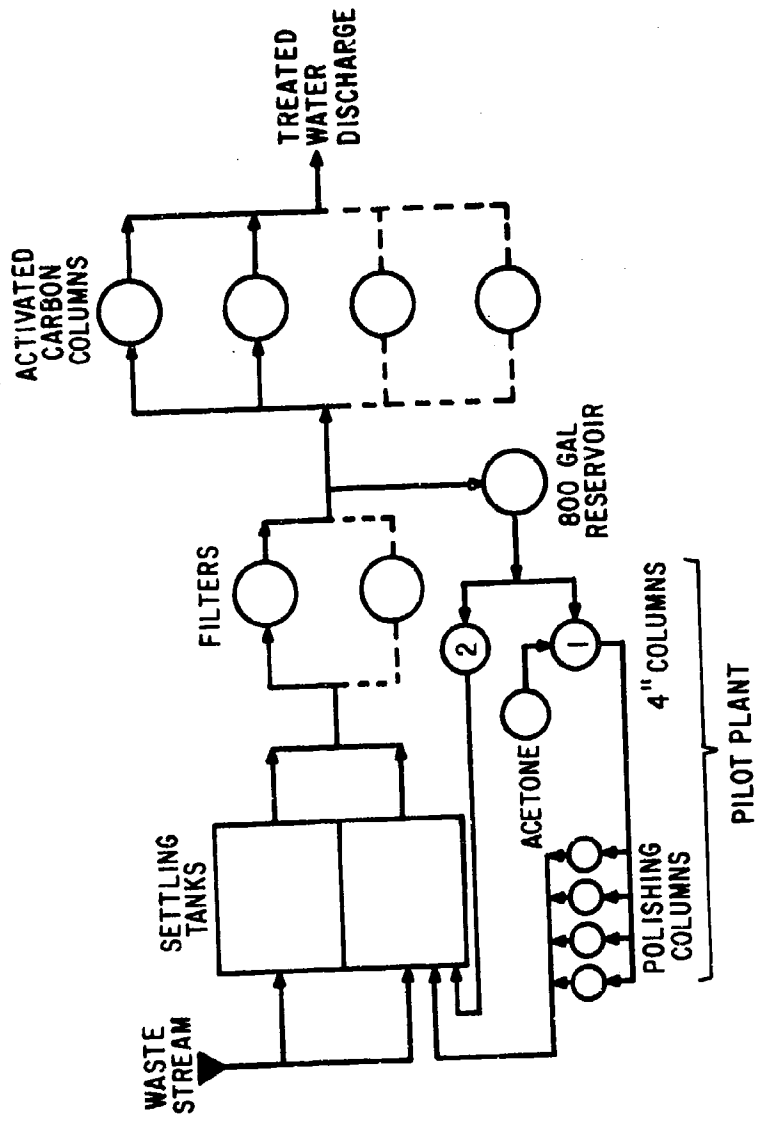


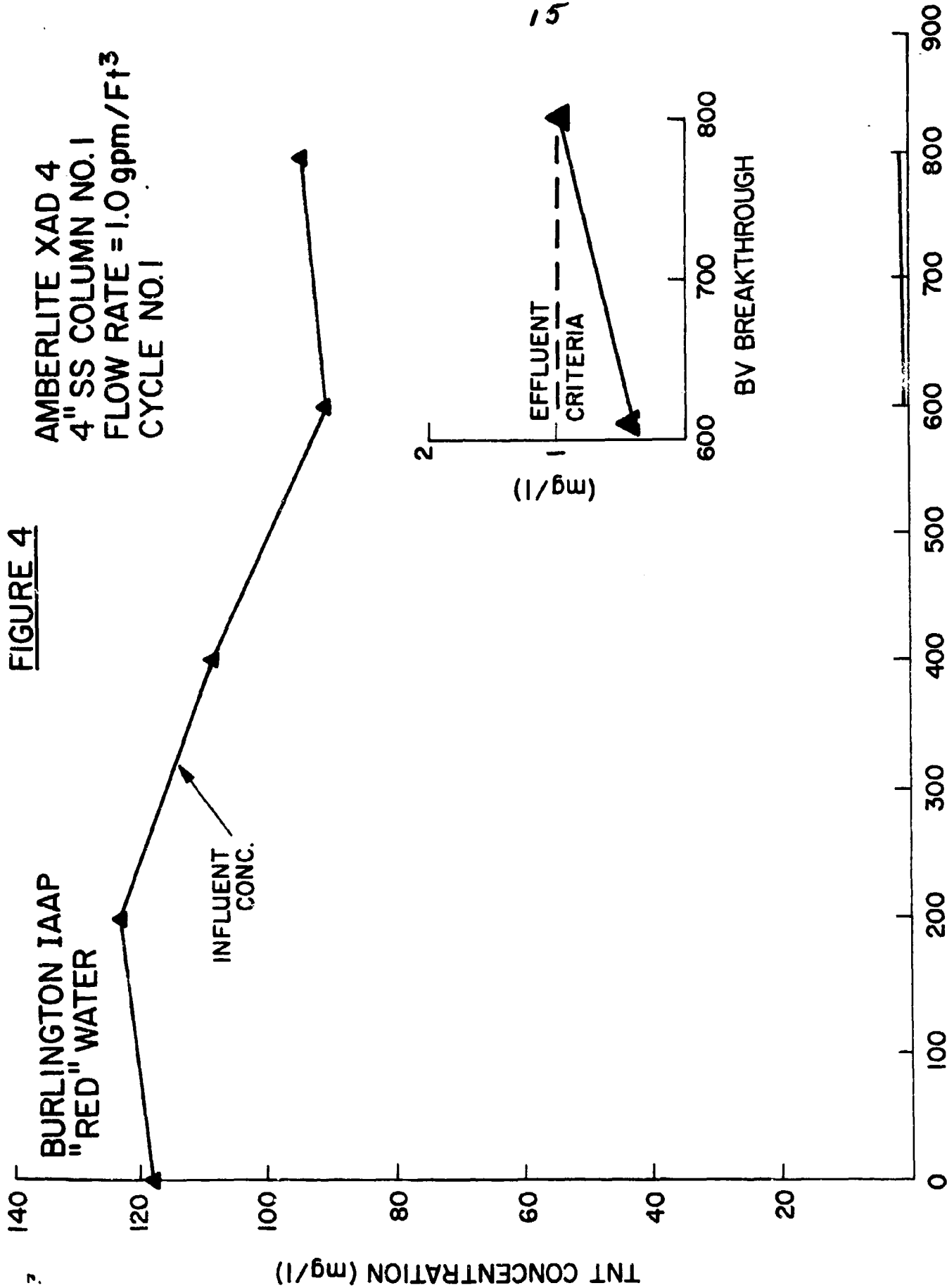
FIGURE 3

**FIGURE 4**

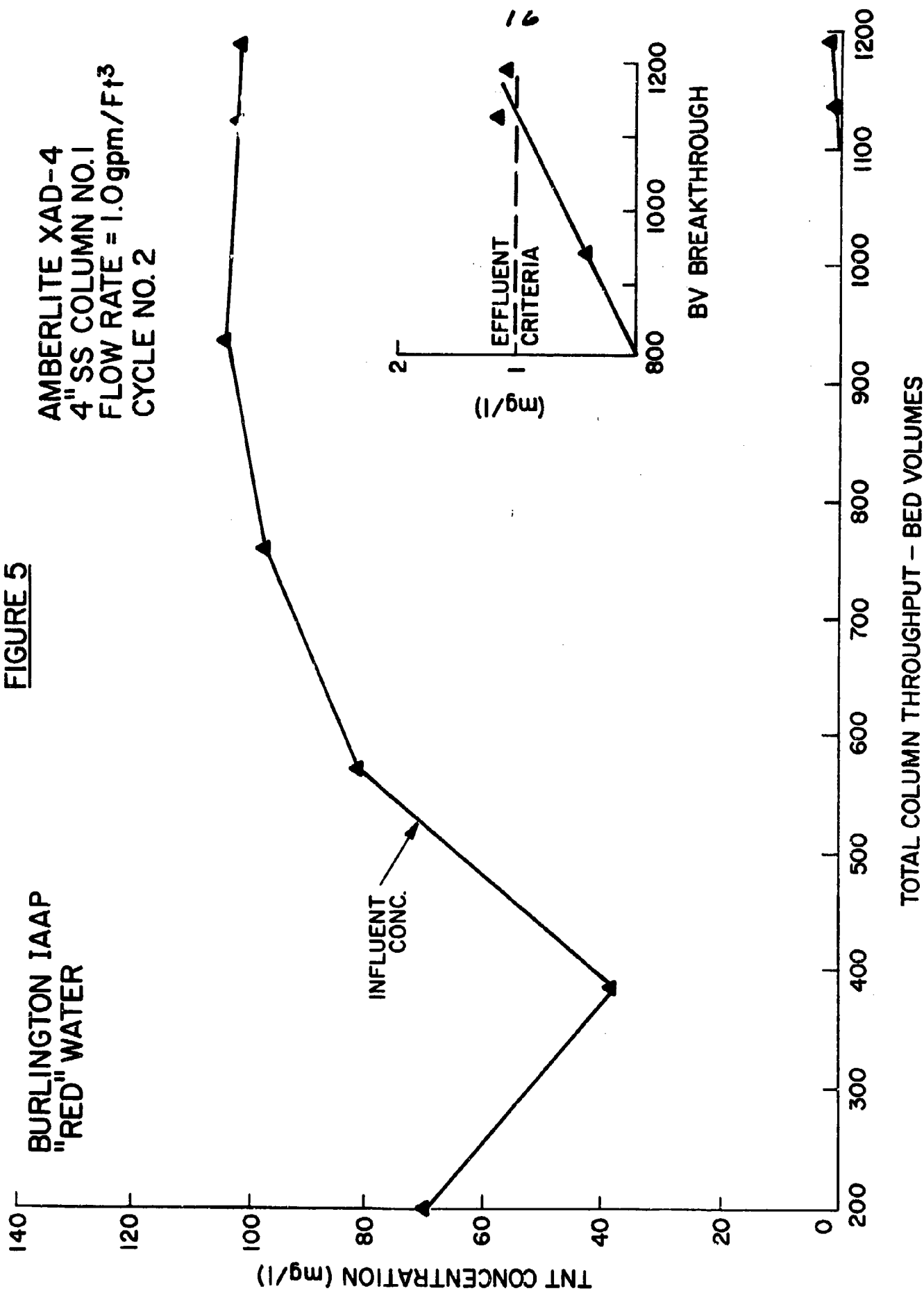
BURLINGTON IAAP  
"RED" WATER

AMBERLITE XAD 4  
4" SS COLUMN NO.1  
FLOW RATE = 1.0 gpm/Ft<sup>3</sup>  
CYCLE NO.1

INFLUENT  
CONC.



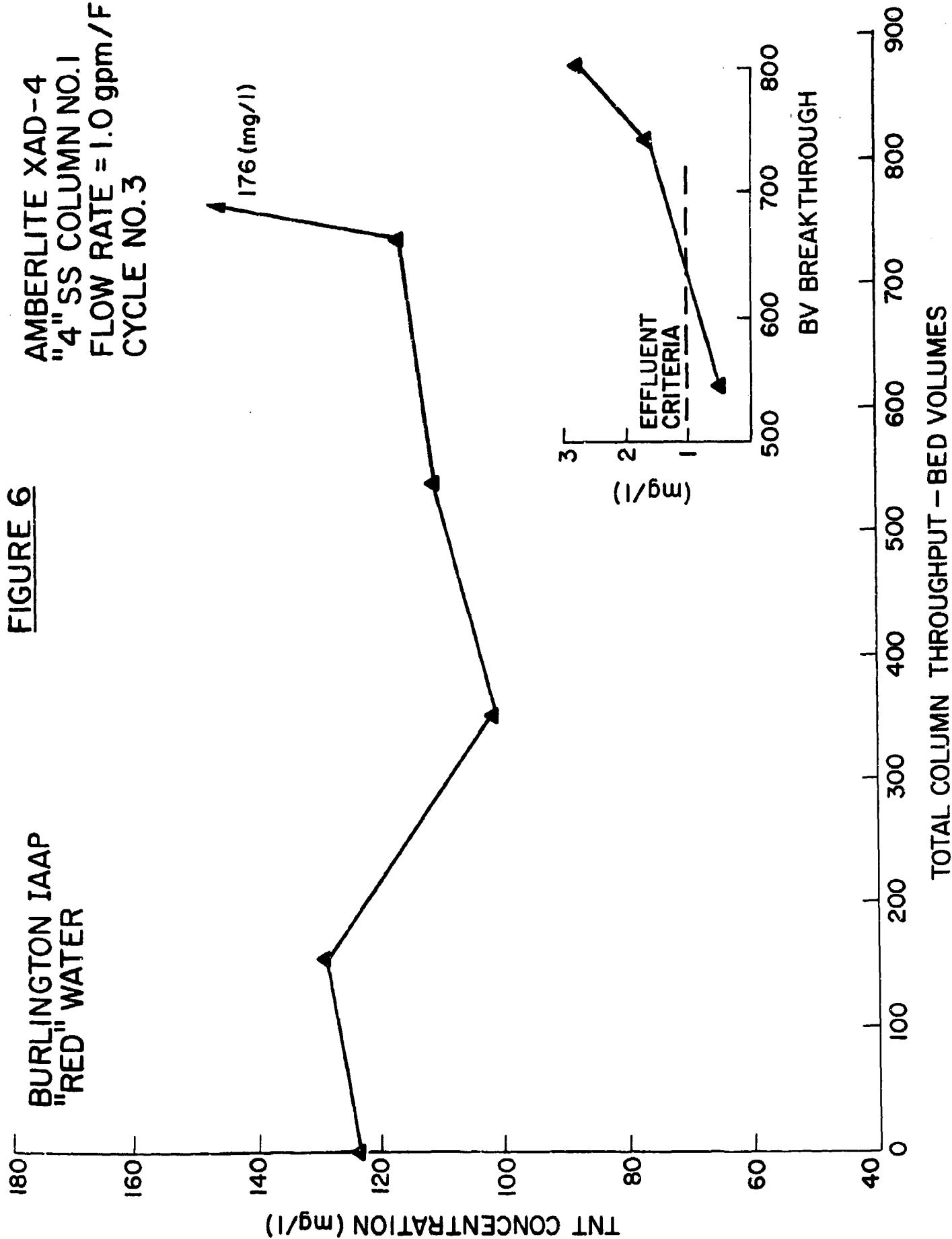
**FIGURE 5**



**FIGURE 6**

BURLINGTON IAAP  
"RED" WATER

AMBERLITE XAD-4  
"4" SS COLUMN NO.1  
FLOW RATE = 1.0 gpm / Ft<sup>3</sup>  
CYCLE NO.3



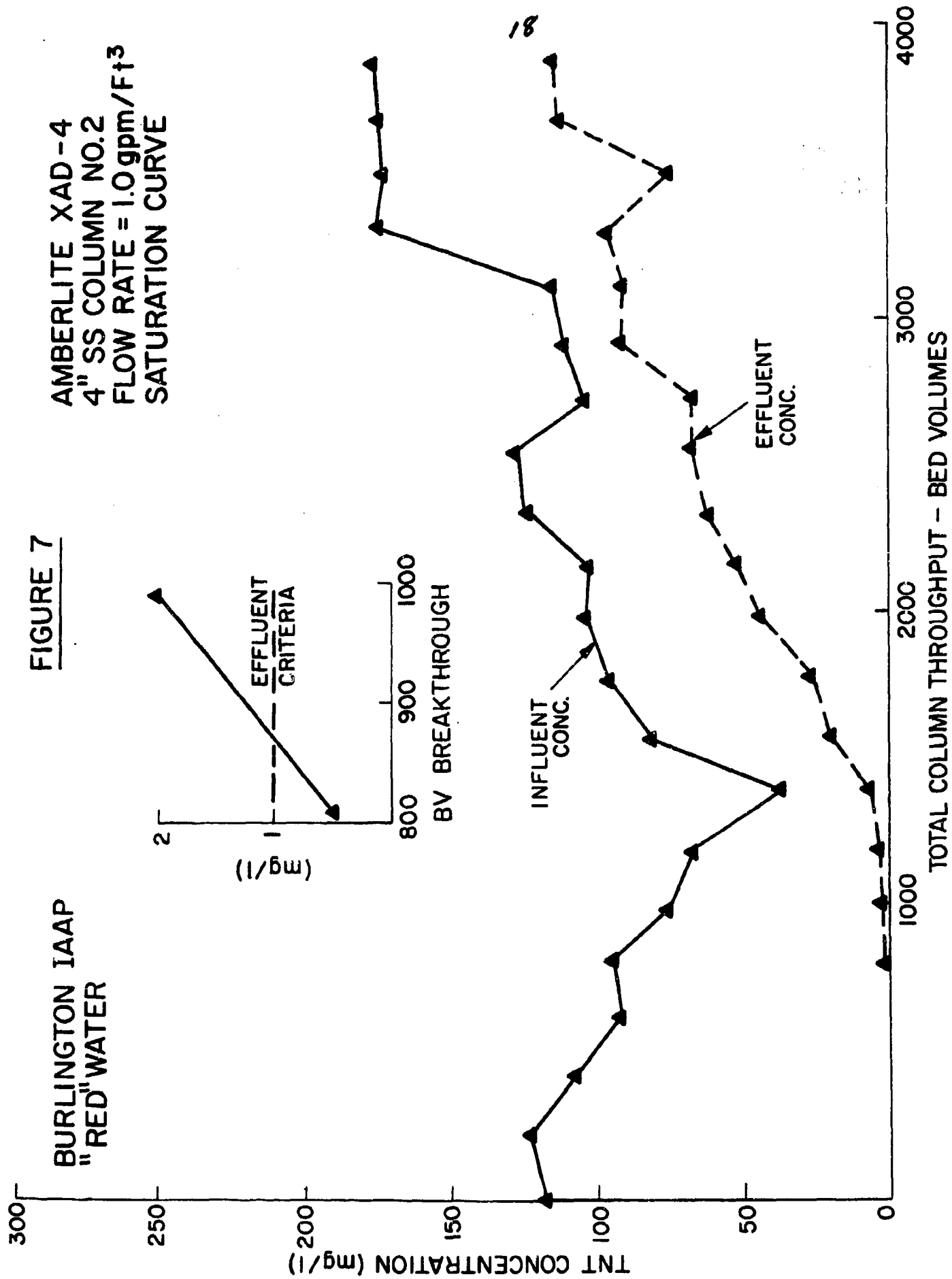
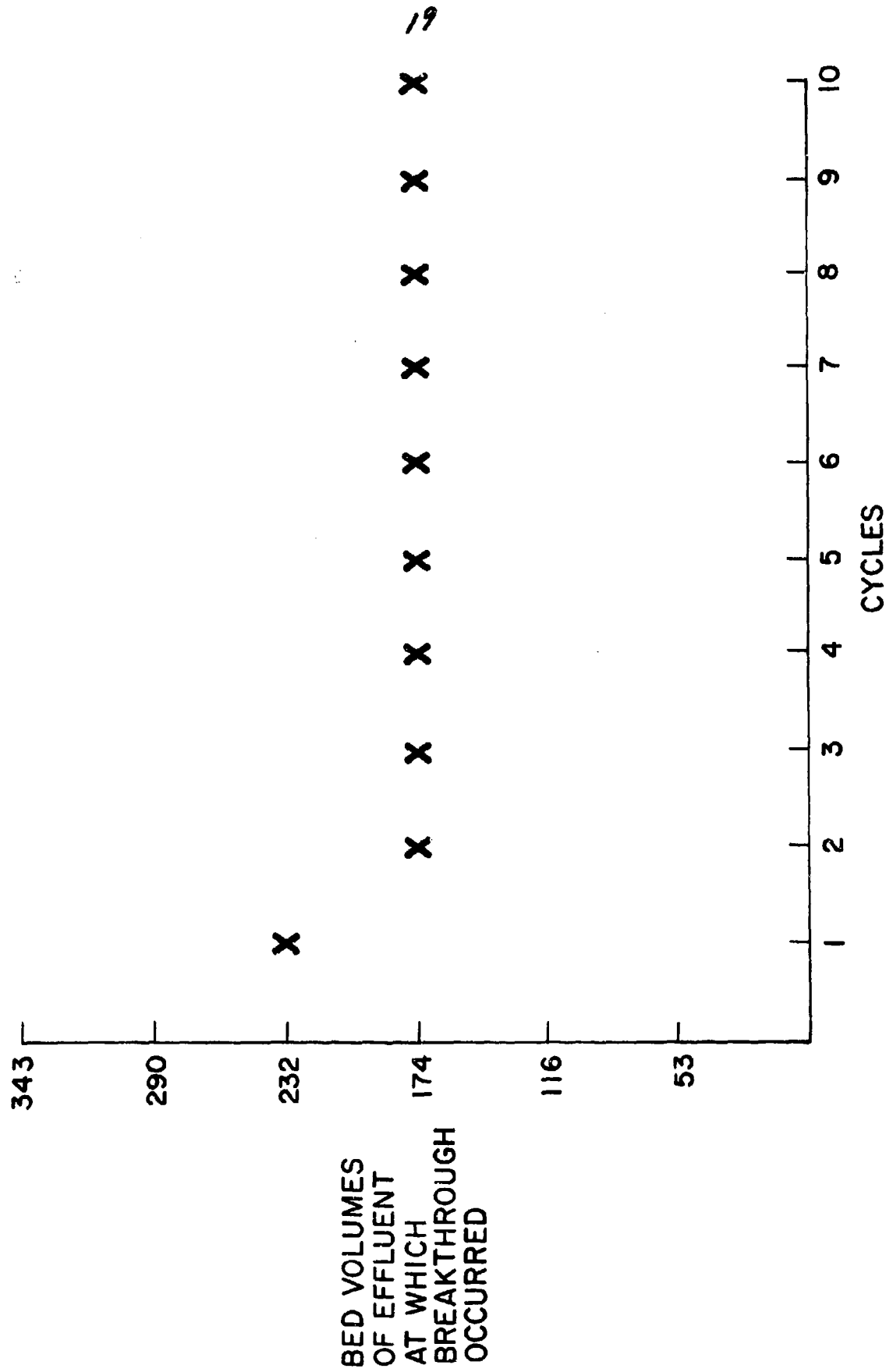


FIGURE 8

RESULTS FROM MULTIPLE  
REGENERATION EXPERIMENTS



**FIGURE 9**

BURLINGTON IAAP  
"RED" WATER

AMBERLITE XAD-4  
4" SS COLUMN NO.1  
FLOW RATE 1.0gpm/Ft<sup>3</sup>  
CYCLE NO. 1

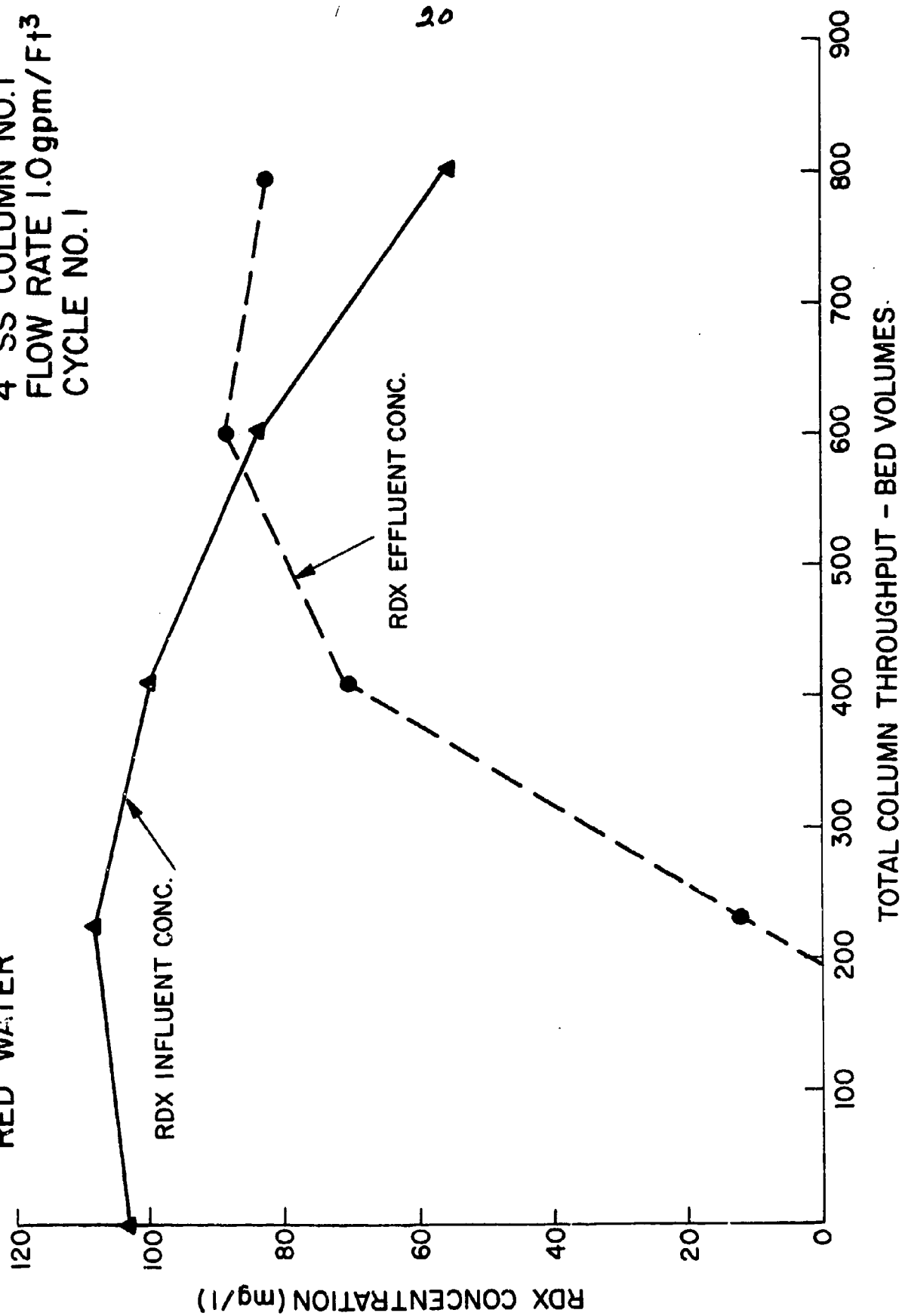


FIGURE 10

ACETONE REGENERATION OF AMBERLITE XAD-4

CYCLE NO. 3

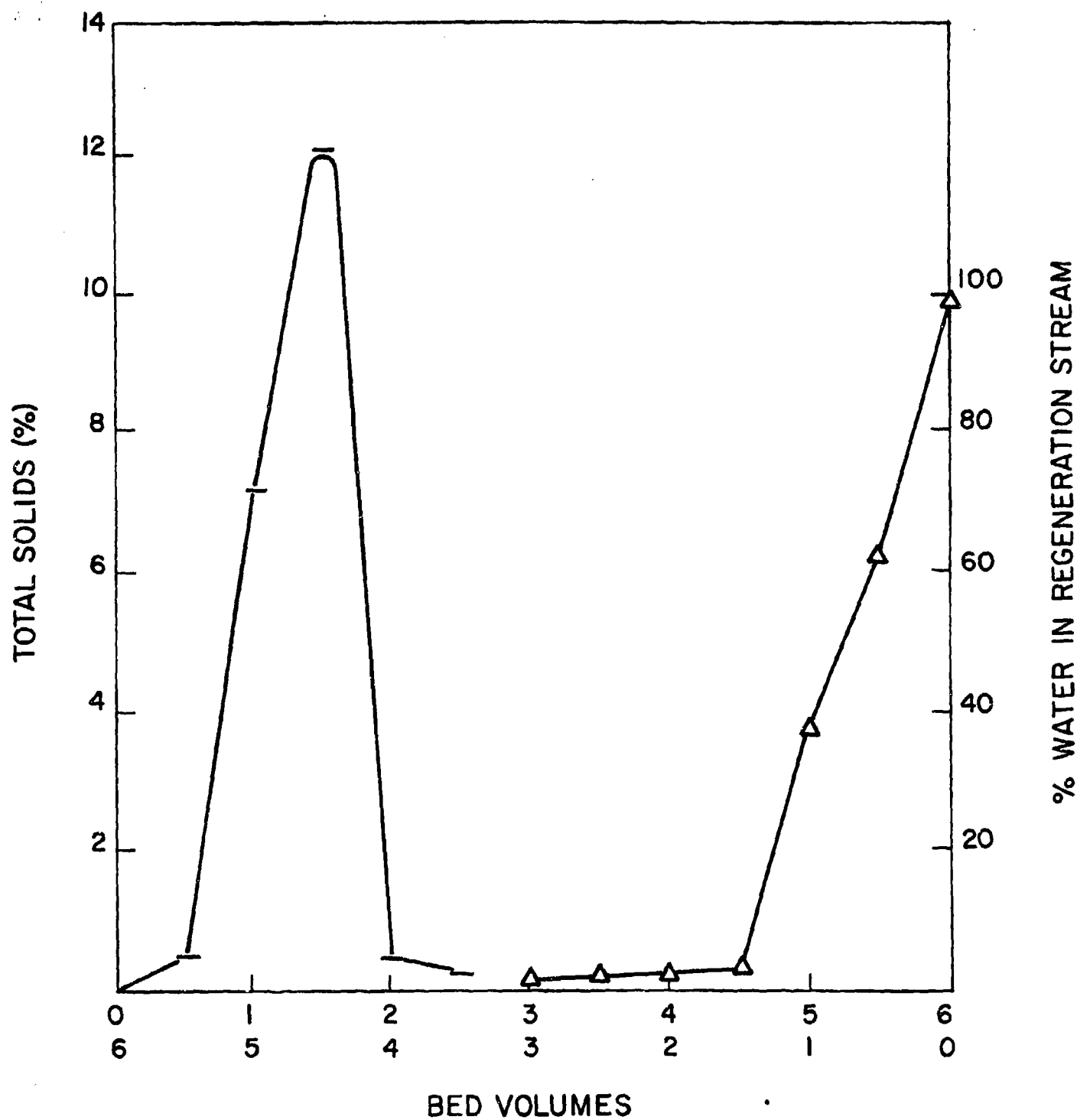
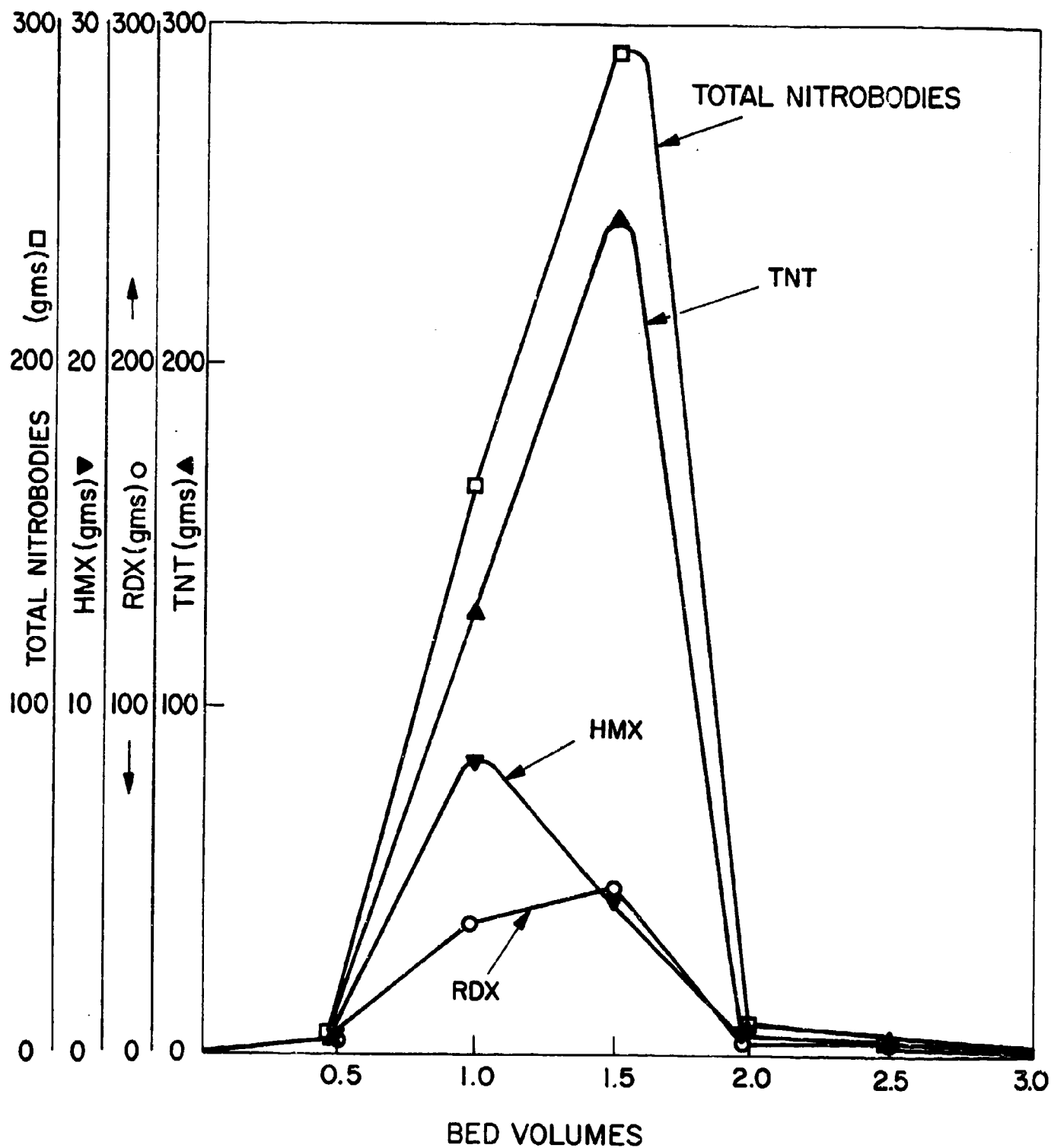


FIGURE II

ACETONE REGENERATION OF AMBERLITE XAD-4  
CYCLE NO. 3  
"NITRO BODIES"



SCHEMATIC OF NEW PROCESS TO REMOVE TOTAL NITROBODIES FROM WASTE STREAM

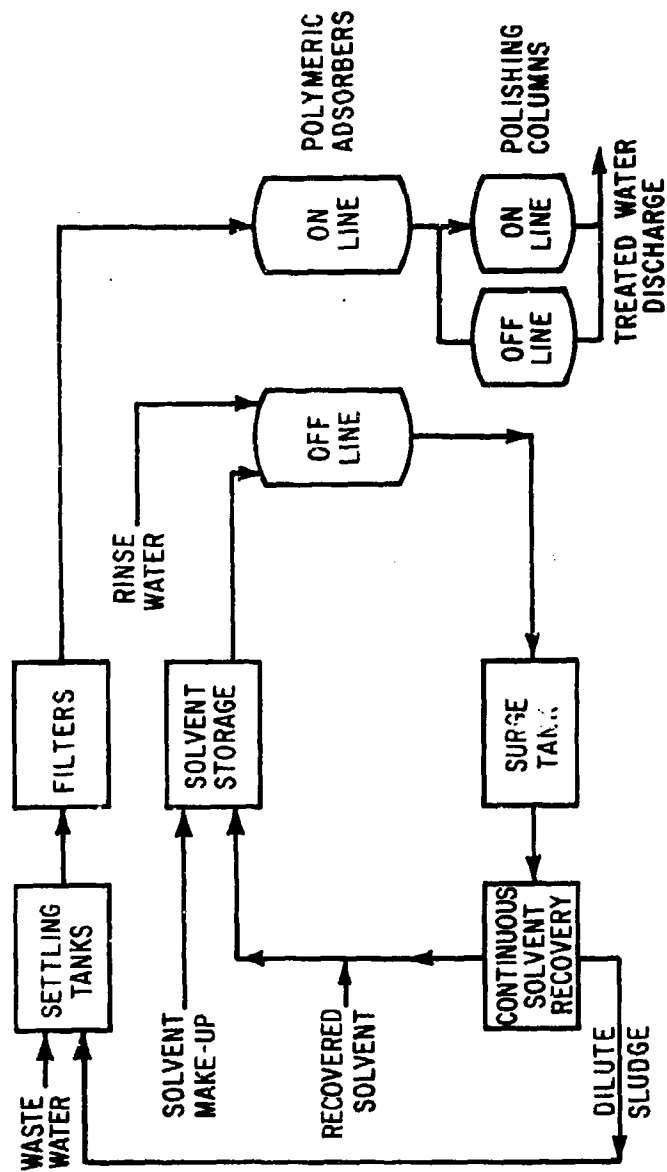


FIGURE 12

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3. R. K. Andren, J. M. Nystrom, R. J. Erickson, "Treatment of TNT Munitions Waste Waters Using Polymeric Adsorption Resins", U.S. Army Natick Laboratories, Pollution Abatement Division, Food Sciences Lab., January 1975.
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