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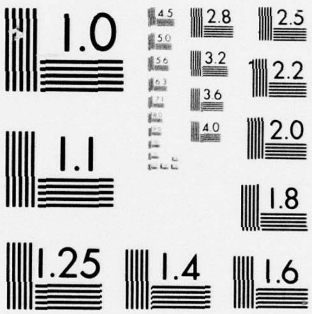

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(U) The objective of this study was to establish a comparative evaluation, to include economics, of using either carbon adsorption (with and without regeneration capacity), polymeric resin adsorption, or a series combination of the two techniques in effectively treating "pink" water. Load, assembly, and pack facilities and ammunition manufacture facilities discharge wastewater which is contaminated with explosives such as TNT, RDX, HMX, and tetryl. These

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20. ABSTRACT (Contd)

alpha
waters are referred to as pink water. Being photochemically active, the α-TNT in this wastewater chemically changes and forms toxic, colored compounds. To effectively treat this pink water, two different types of adsorption techniques are being considered: carbon and resin adsorption.

Several studies have been conducted on the laboratory-, pilot-, and plant-scale levels concerning the treatment of pink water. Results of these studies prove that both activated carbon and Amberlite XAD-4 are capable of treating pink water and thus are able to remove TNT and other nitrobodies such as RDX and HMX from munition waste streams to the target level of less than 1 ppm of *total nitrobodies.* These studies have generated the following conclusions:

(1) Amberlite XAD has greater capacity for TNT than has activated carbon,

(2) Activated carbon has a higher capacity for RDX, HMX, and tetryl and better color removal than has Amberlite XAD,

(3) Amberlite XAD is not completely effective in removing the color from a colored waste stream; if a waste stream were slightly colored, a carbon-polishing column placed after the resin column would remove the color, and

(4) Both adsorbents will provide similar nitrobody leakage for similar streams.

The economics of carbon and polymeric resin adsorption vary from plant to plant, since each plant has its own particular requirements on an adsorption system. The process that consistently had the lowest cost is carbon with regeneration capacity.

In view of the above, the recommended adsorption system is carbon with regeneration capabilities.

PREFACE

The work described in this report was funded by Environmental Technology Division of Chemical Systems Laboratory, Project Number 1L762720D048, Task 3, Work Unit S-17. This work was started in July 1976 and completed in August 1977.

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ANALYSIS OF CARBON VERSUS RESIN

I. INTRODUCTION.

The objectives of this study were: (1) to establish a comparative evaluation of using either carbon adsorption, polymeric resin adsorption, or a series combination of the two techniques in effectively treating "pink" water; (2) to determine the treatability of pink water and pink water containing other nonaromatic nitrobodies such as RDX and HMX; and (3) to compare the costs for using carbon adsorption only, with and without regeneration capacity, polymeric resin, and a combination of both techniques. This study will also examine the state of the art of carbon regeneration. Whenever possible, the above evaluations will be based on data obtained from experimental results using established practice.

II. GENERAL INFORMATION.

The operations of the munitions manufacture and load/assembly/pack (LAP) plants discharge varying quantities and qualities of wastewater which is contaminated with explosives. While munition pollutants have been a recognized problem for years, federal and state regulations now dictate that these materials be removed before the effluents can be discharged into local waters.

Wastewaters are produced during building washdown; within certain operations; and from scrubber blowdown.[1] These waters, referred to as pink water, are principally made up of α-TNT (2, 4, 6-trinitrotoluene), along with various concentrations of nitrobodies such as RDX (cyclotrimethylene-trinitramine), HMX (cyclotetramethylene tetranitramine), and tetryl. Being photochemically active, the α-TNT in this wastewater chemically changes and forms highly colored compounds. These compounds, whose identity and toxicity are not precisely known, pose a serious pollution problem to any receiving stream. Table 1 summarizes plants having pink-water waste.[2] Table 2 summaries available data on the nitrobody content of pink waters from various sources.[2]

Table 1. Plants with Pink-Water Waste

Army	Navy
Holston	Crane
Iowa	Hawthorne
Joliet	McAlester
Kansas	Yorktown
Lone Star	
Louisiana	
Milan	
Newport	
Radford	
Volunteer	

Table 2. Reported TNT Concentrations in Pink Wastewaters

Location	Evaporator condensate	Cleanup load/assembly/pack	Scrubber water	Laundry wastewater
		mg/l		
Joliet Army Ammunition Plant	1.4 – 16	178.3		2.9
Navy Ammunition Depot – Crane				
Rockeye		40.1		
Plant A		5.8 – 11.2		
Plant B		20.2		
Holston Army Ammunition Plant		3.9*	2 – 22	
Radford Army Ammunition Plant	7.3	90 – 175 75		
Navy Ammunition Depot – McAlester		30.6 – 38.4	30 – 80	
Iowa Army Ammunition Plant		86.9		25.4
Milan Army Ammunition Plant		<1		
Louisiana Army Ammunition Plant		80		
Cornhusker Army Ammunition Plant (inactive)		57		2.7

* From incorporation of TNT into composition B.

With increasing pressures from the Environmental Protection Agency and within the armed service organization themselves, plants are now being redesigned and updated to meet more stringent standards which go below the 1 milligram per liter (mg/l) concentration of α-TNT generally accepted for elimination of color developed.[1] The existing National Pollution Discharge Elimination System (NPDES) permit data for several Army Ammunitions Plants (AAP's) are listed in table 3.

The new standards also call for removal of other explosive contaminants, such as TNT, RDX, HMX and tetryl, which do not contribute to color. The new target value for wastewater effluent is 1 mg/l of *total nitrobodies.* At present, two different types of adsorption techniques are being considered as effective means for reducing the total nitrobody concentration in pink water to an acceptable level of 1 mg/l. These techniques are carbon and resin adsorption.

Table 3. Existing NPDES Permit Data[1]

Location	Contaminant	Allowable discharge	
		Average	Maximum
		mg/l	
Iowa Army Ammunition Plant	TNT RDX	0.5 15.0	1.0 25.0
Joliet Army Ammunition Plant	TNT	0.5	0.75
Radford Army Ammunition Plant	TNT	0.5	0.75
Volunteer Army Ammunition Plant	TNT	0.3	0.50
Milan Army Ammunition Plant	TNT RDX	– –	1.0 1.0

III. CARBON HISTORY.

Carbon adsorption has been and still is employed as a means of treating pink water at two Army ammunition plants: Joliet AAP and Iowa AAP. Both installations treat LAP wastewater. Joliet AAP uses a two-column series downflow system, and Iowa AAP uses a two-column expanded-bed parallel upflow system.[2] Iowa AAP is presently in the process of changing from a parallel to a series flow pattern, as well as expanding its number of carbon columns from 30 to 54.*,** In both installations, the carbon beds are preceded by sumps to remove settleable solids and diatomaceous earth filters to remove suspended solids carried over from the sumps.[2] The basic layout is the same for both plants, as represented in figure 1 which is a schematic of the Iowa installation. The exhausted carbon is destroyed by burning.

The successful use of carbon to treat TNT wastes can be traced back more than 20 years. C. C. Ruchhoft *et al.*, studied the treatment of both pure α-TNT (colorless) and TNT wastewaters in which color had developed.[2] For the colorless solution, at a TNT concentration of 121.8 mg/l, it was found that up to 99.5% removal of TNT was possible with powdered carbon; also, it was found that powdered carbon was more effective than granular carbon. With colored TNT wastewater, removal of TNT was less effective (40.0% to 48.7%). The effect of color development on carbon treatability has been confirmed by M. W. Nay *et al.*[2] Their studies demonstrated that as the waste-color intensity increased, the waste became more toxic to microorganisms and more refractory to biodegradation, and treatment by any process, including carbon adsorption, became more difficult.[2] While activated carbon was effective in removing color and TNT, the development of color significantly decreased the carbon adsorptive capacity for TNT.[2] These results are presented in figure 2.

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* Ms. Carol J. Paxton, Mason and Hanger–Silas Mason.

** Mr. James E. Leeper, Mason and Hanger–Silas Mason.

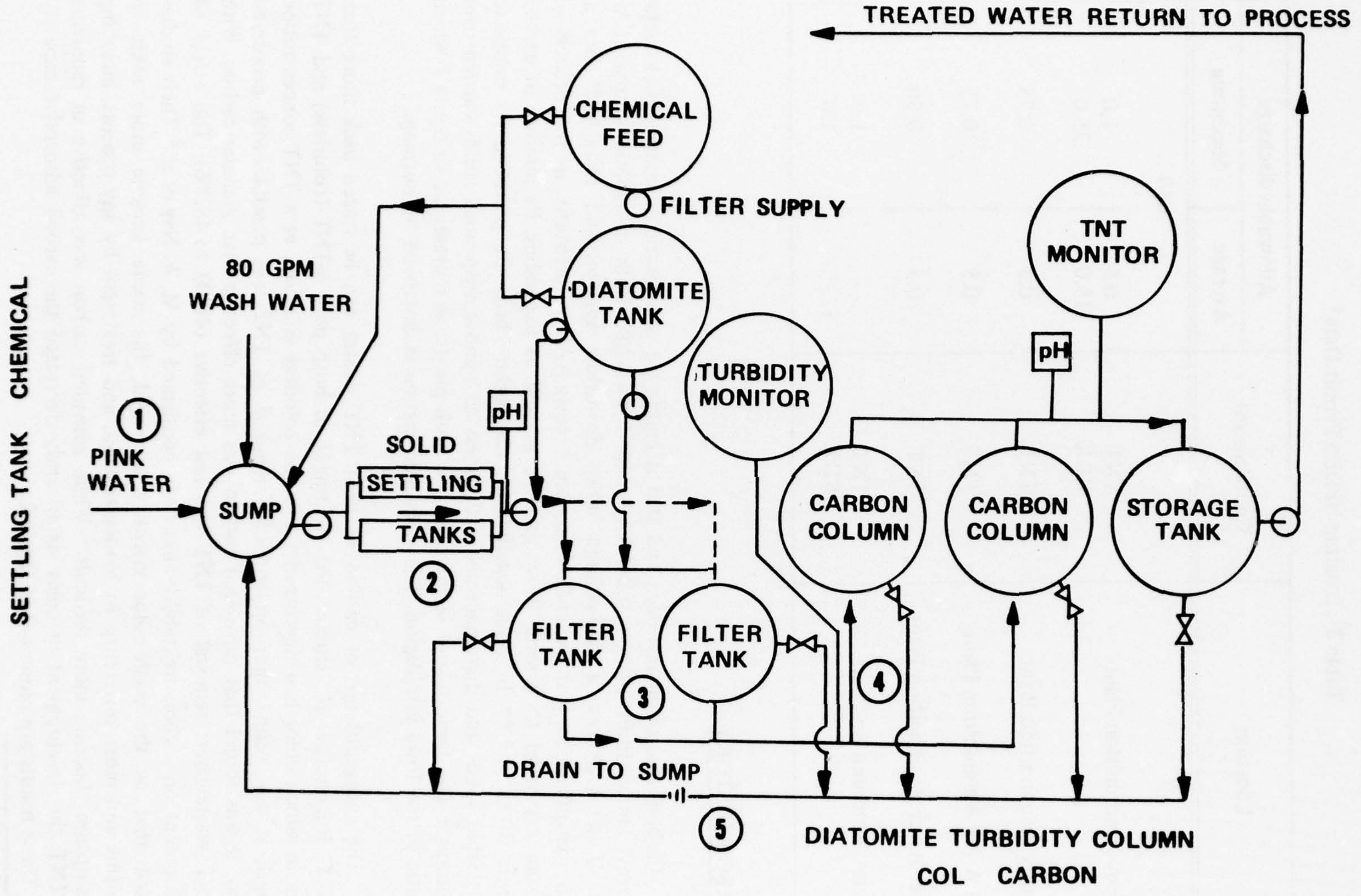

Figure 1. Pink-Water Treatment for Loading, Assembling, and Packing Operations

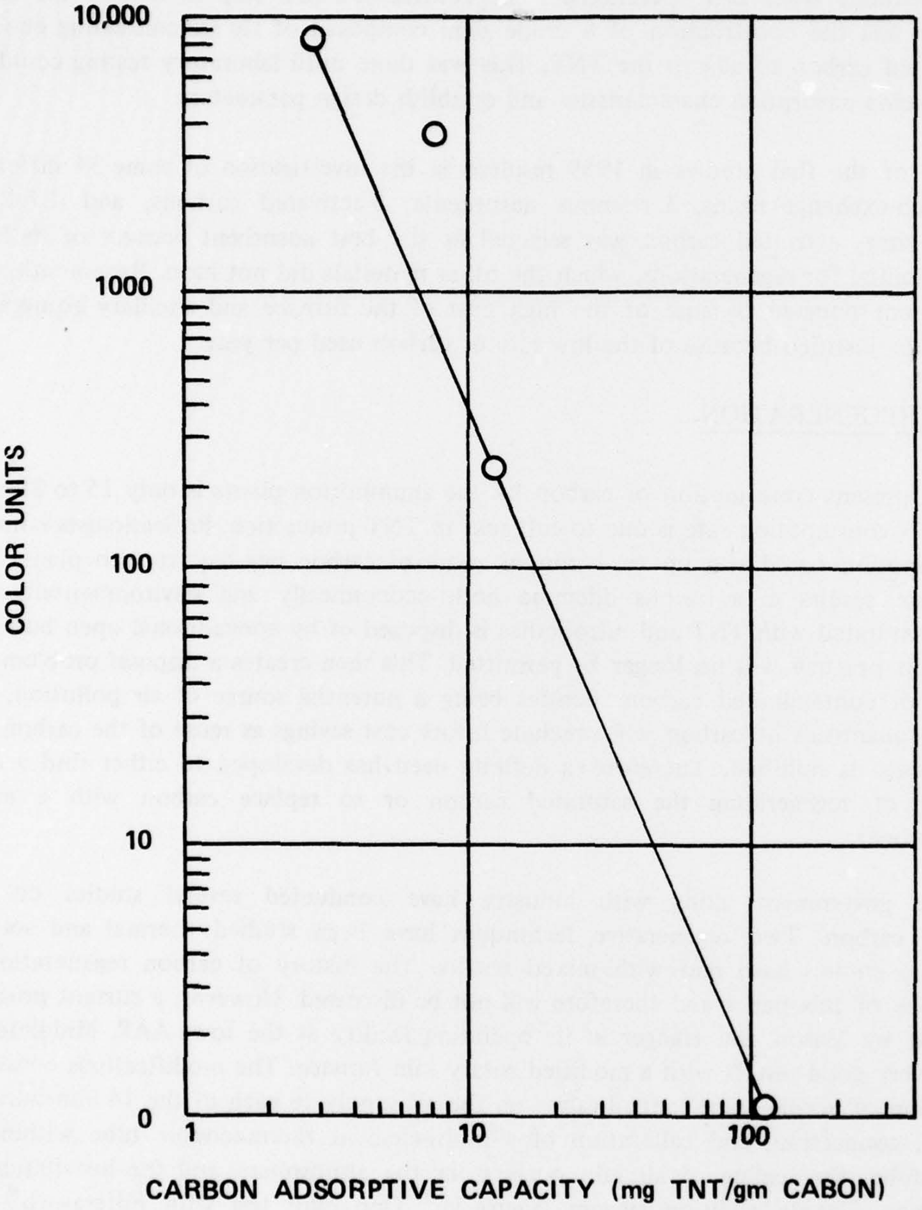

Figure 2. Relationship of Color and Carbon Adsorptive Capacity for TNT

Since the mid-1950's, Mason and Hanger–Silas Mason Co., Inc., the contractor at Iowa AAP, has been involved with the research, development, and use of activated carbon for cleanup of wastewaters from LAP operations.[1] The contractor's first step to remove the color from wastewater was the construction of a crude dam composed of fly ash containing enough unburned, activated carbon to adsorb the TNT. This was done until laboratory testing could be completed to develop adsorption characteristics and establish design parameters.

One of the first studies in 1959 resulted in the investigation of some 34 different materials: 27 ion-exchange resins, 3 resinous adsorbents, 3 activated carbons, and 1 fuller's earth.[1] At that time, activated carbon was selected as the best adsorbent because of its high capacity and potential for regenerations, which the other materials did not have. Regeneration of the carbon was not pursued because of the high cost of the furnace and ancillary equipment which could not be justified because of the low rate of carbon used per year.

IV. CARBON REGENERATION.

The present consumption of carbon by the ammunition plants is only 15 to 30 tons per year. This low consumption rate is due to cutbacks in TNT production. Projectionists estimate that this consumption could rise up to 1 ton or more of carbon per day at each plant. This projected increase results in a serious dilemma both economically and environmentally. At present, carbon saturated with TNT and nitrobodies is disposed of by conventional open burning. But by 1980, this practice will no longer be permitted. This then creates a disposal problem for large quantities of contaminated carbon. Besides being a potential source of air pollution, the burning of large quantities of carbon will preclude future cost savings as reuse of the carbon for adsorption purposes is nullified. Therefore, a definite need has developed to either find a cost effective means of regenerating the saturated carbon or to replace carbon with a more economical absorbent.

The government along with industry have conducted several studies on the regeneration of carbon. Two regenerative techniques have been studied: thermal and solvent extraction. These studies have met with mixed results. The history of carbon regeneration is beyond the scope of this paper and therefore will not be discussed. However, a current program being conducted by Mason and Hanger at its operating facility at the Iowa AAP, Middletown, Iowa, has had very good results with a modified rotary kiln furnace. The modifications consisted of the installation of needle-point control valves on the air supply to each of the 14 kiln burners; the installation, connection, and calibration of a multi-element thermocouple tube within the inner rotating tube; the sealing of all kiln ports from the atmosphere; and the installation of steam and carbon dioxide addition system (figure 3).[3] One pilot test with Filterasorb^{R} 300 carbon recovery rates of 85% to 95% and adsorbent capacities of 95% to 102% of virgin carbon has been reported.* In addition, these results have been maintained through successive regenerations.* Figure 4 is a laboratory-scale adsorption isotherm (obtained from Mason and Hanger) for comparing carbon regenerated by Mason and Hanger to virgin carbon. Figures 5 and 6 are the results of pilot-plant adsorbent capacity test (obtained from Mason and

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* Mr. Ronald Barron, Mason and Hanger–Silas Mason.

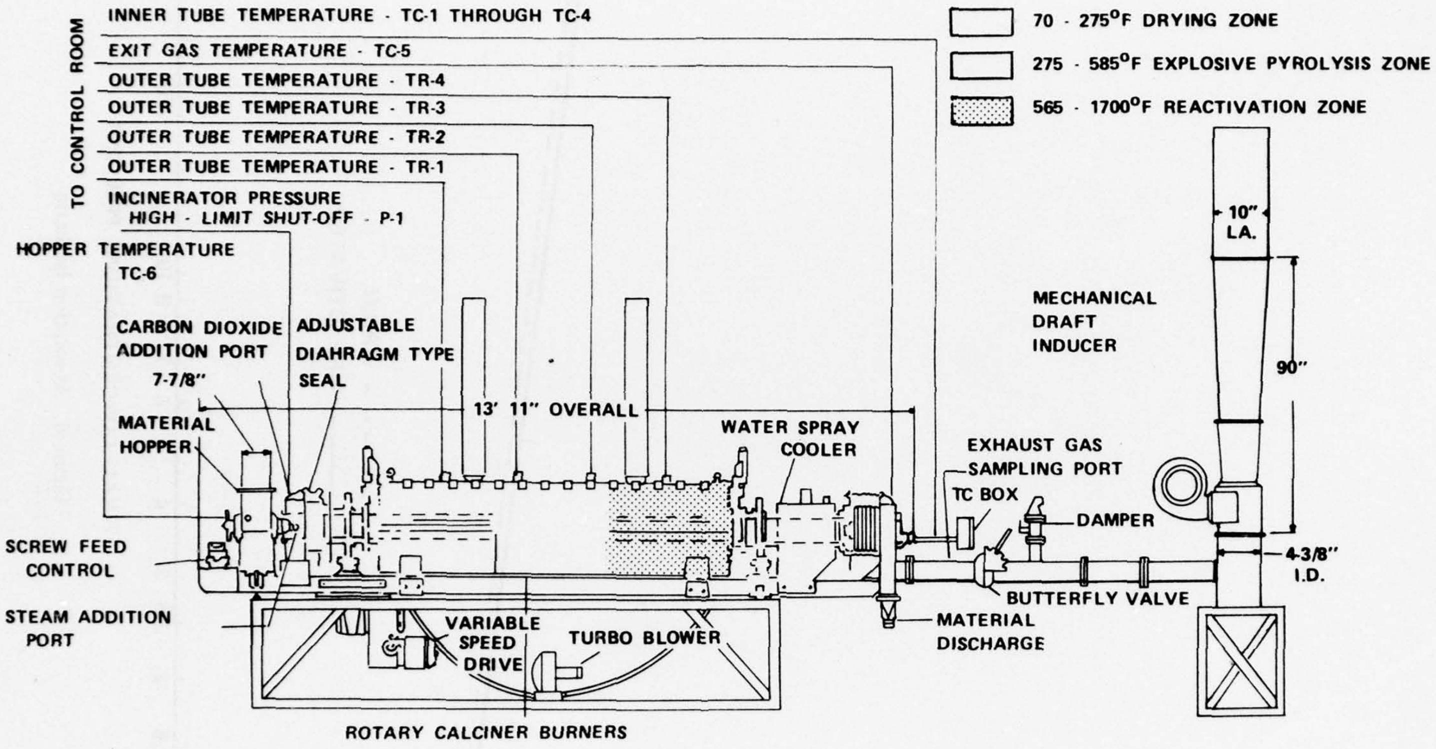

Figure 3. Indirect-Fired Carbon Regenerator

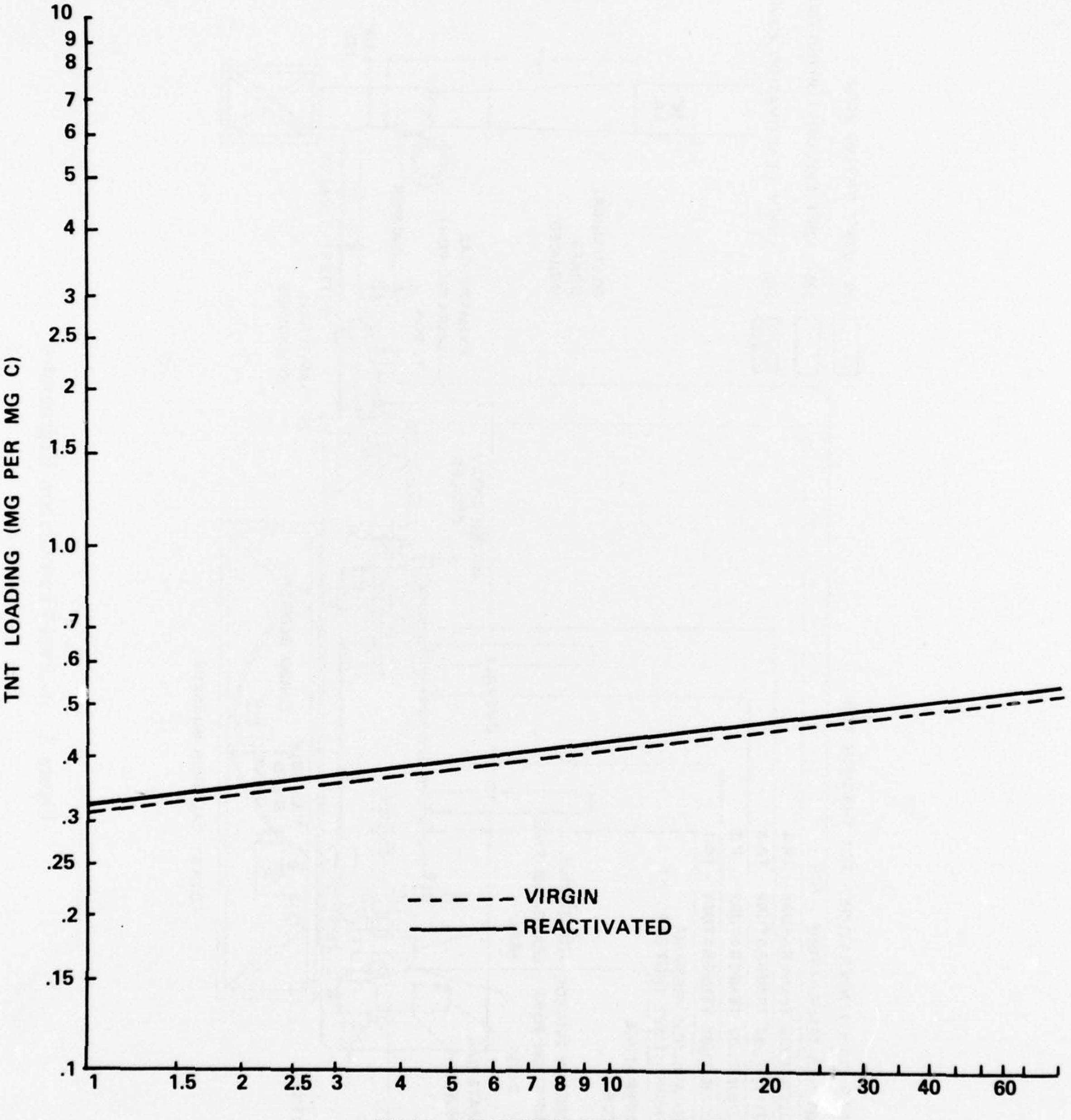

Figure 4. Absorption Isotherm

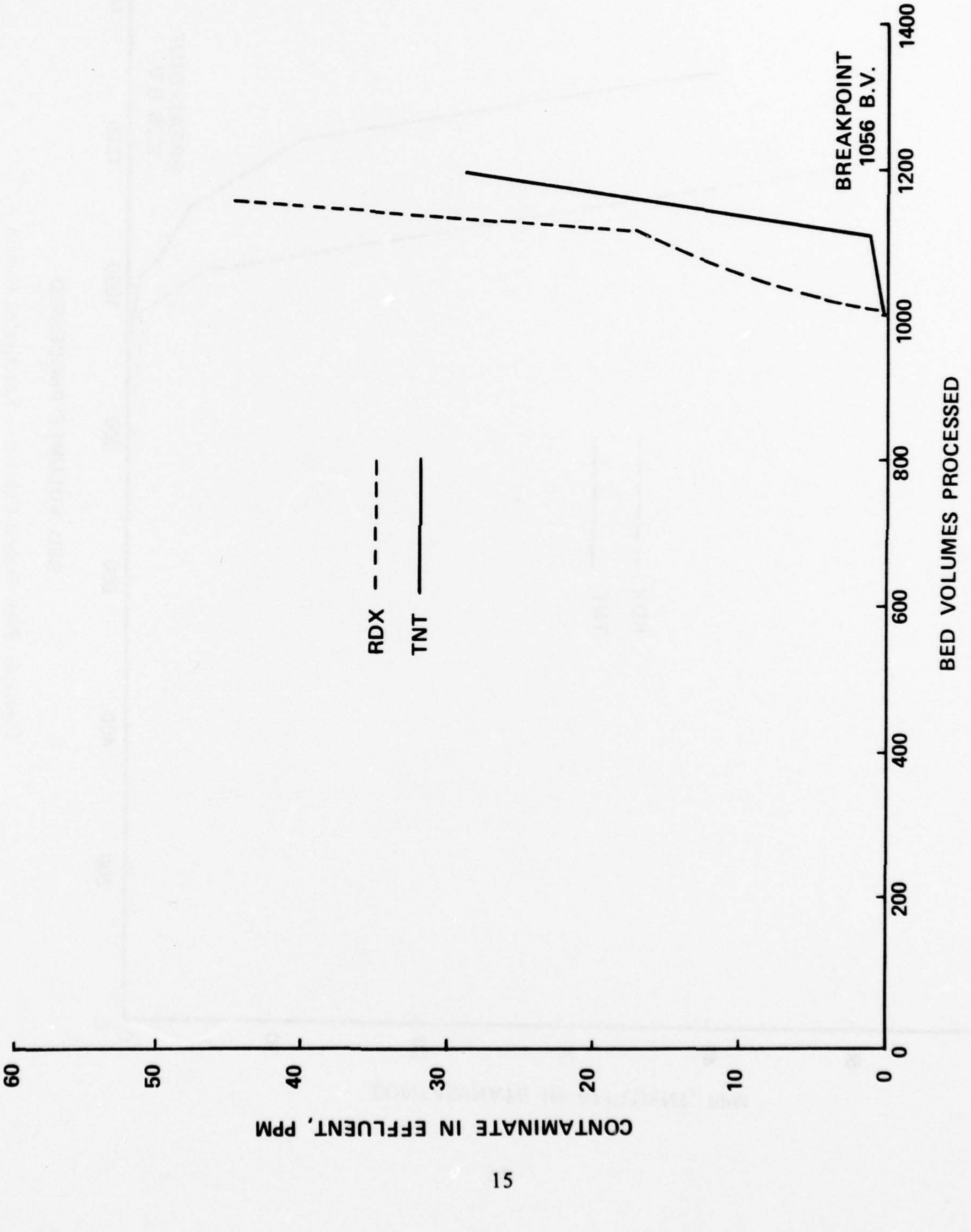

Figure 5. Pilot Carbon Column – Virgin Carbon

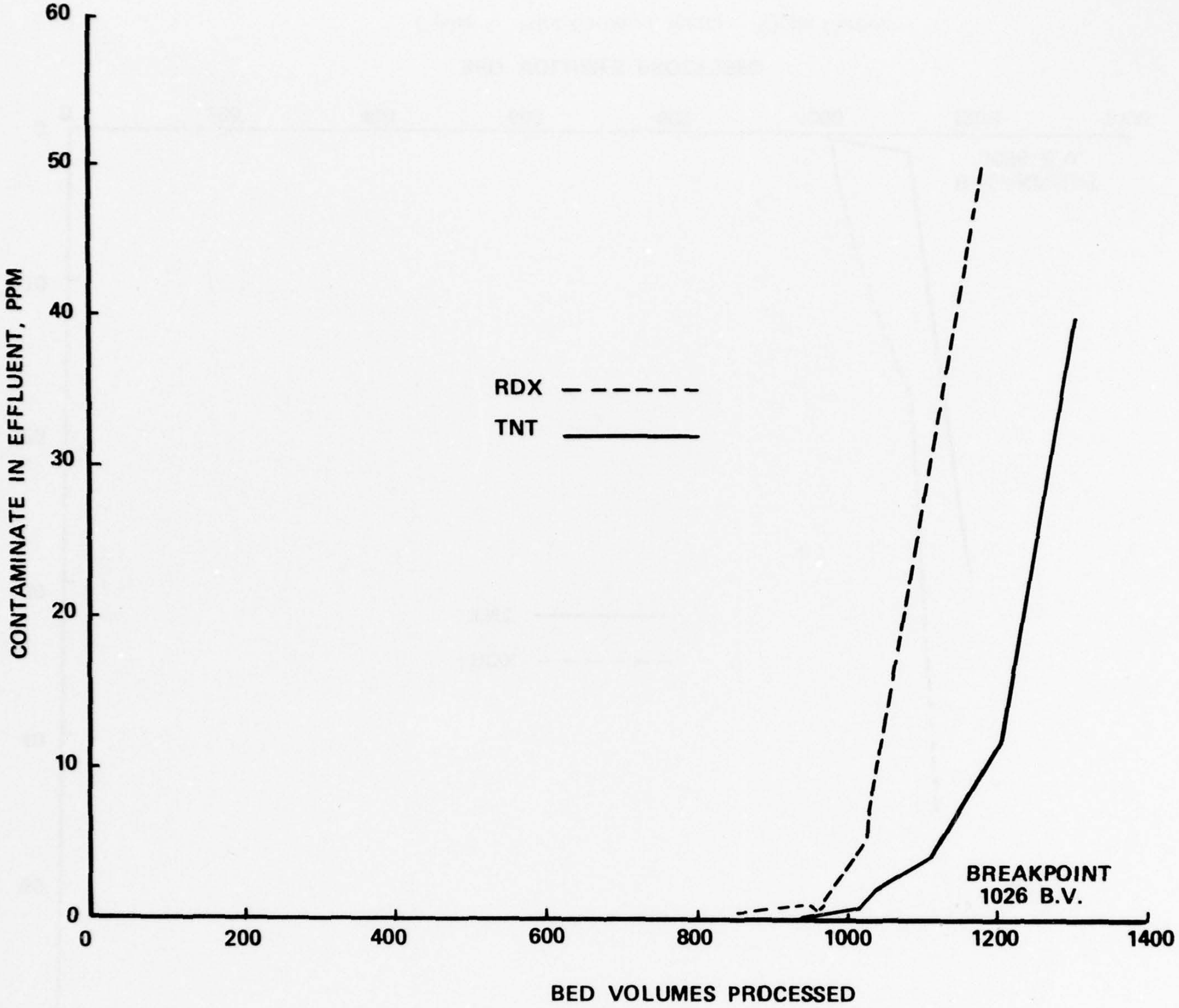

Figure 6. Pilot Carbon Column – Reactivated Carbon

Hanger) on virgin and regenerated carbon. Samples from the laboratory and pilot tests were analyzed by the use of liquid chromatography. The economics of carbon regeneration are discussed later in this paper.

V. POLYMERIC RESIN.

Polymeric resin adsorption is a comparatively new approach to the treatment of munition waste when compared to carbon adsorption. The polymeric resin adsorbents in question are manufactured by the Rohm and Haas Company under the trademark Amberlite^R. These polymers were developed during the late 1960's to remove organic compounds from water and concentrate them for recycle.[4] At the present time, there are at least 14 different commercially operating units employing Amberlite polymeric adsorbents. "One of these units has been operating for 22 months, removing 1/2% to 3% of phenol from waste streams. Two columns are employed with one on line while the other is being regenerated. Since this unit has been in operation, over 1100 cycles have been completed per resin column. The resin capacity for the phenols has been monitored and after these 1100 cycles, it is within 5% of the virgin-resin capacity measured in the laboratory."*

Natick Laboratories' involvement in the adsorption process began as a result of the use of Rohm and Haas' Amberlite XAD polymeric resins as a potential media to concentrate the nitrobodies in pink water for analytical purposes.[5] These studies indicated that the Rohm and Haas' polymeric resin not only is an effective adsorbent for aromatic nitrobodies such as TNT, but also can be easily chemically regenerated to restore its original capacity throughout many cycles of operation.[6] Figure 7 presents results from multiple regeneration experiments with this resin, using acetone.[2,5]

Natick's preliminary bench-scale experiments were performed with Amberlite XAD-2. Followup and pilot-plant studies used Amberlite XAD-4. The basic difference between these two resins is that XAD-4 is more absorbent. Both of these resins consisted of hard, insoluble, porous, resin beads formed from copolymers of styrene and divinylbenzene.[5] They are similar in physical structure to macroreticular ion-exchange resins, but exhibit no ionic functionality.[6] Having a high surface area to weight ratio the resin beads employ Van der Waals' forces to effectively adsorb many water soluble organics.[6] The process is reversible, and the adsorbed organics can be desorbed from the surface of the resin by a number of polar organic solvents.[6] Table 4 is a listing of some of the properties of Amberlite XAD-2 and XAD-4.

There are several common organic solvents (acetone, methanol, and toluene) that will successfully regenerate the resin. Of the three solvents, acetone is the most effective. Almost complete regeneration can be accomplished with only two bed volumes of acetone (figure 8). The residual solvent can be recovered by distillation with only a 3% loss. The recovered acetone is about 95% pure. Expected life of Amberlite XAD-4 is 5 years.

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* Mr. Chet Fox, Rohm and Haas Co.

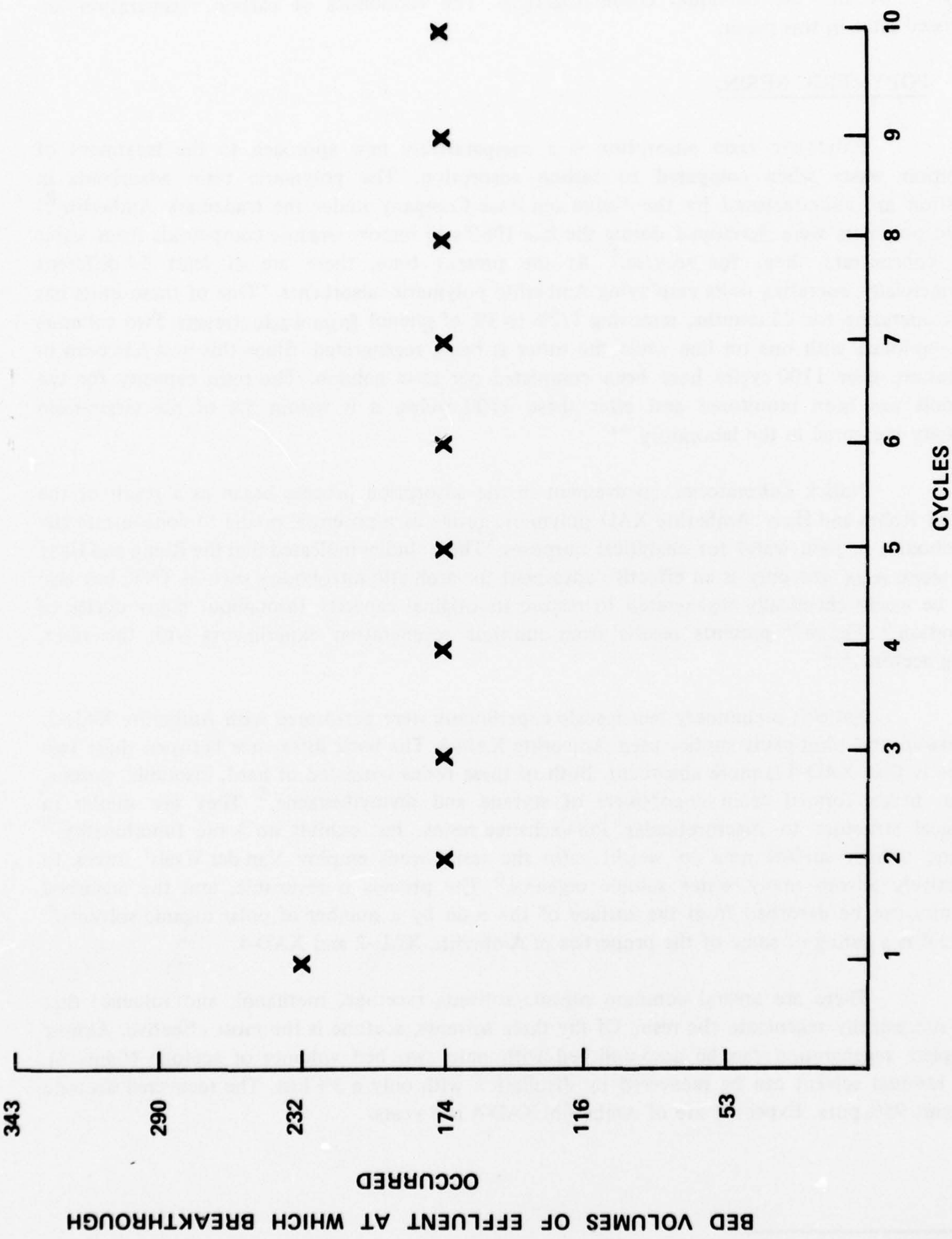

Figure 7. Results from Multiple Regeneration Experiments

Table 4. Amberlite XAD-2 and XAD-4

Parameter	XAD-2	XAD-4
Porosity, volume %	42	51
True wet density, gm/cc	1.02	1.02
Surface area, m^2/gm	330	750
Average pore diameter, Å	90	50
Skeletal density, gm/cc	1.07	1.08
Nominal mesh size	20 – 50	20 – 50

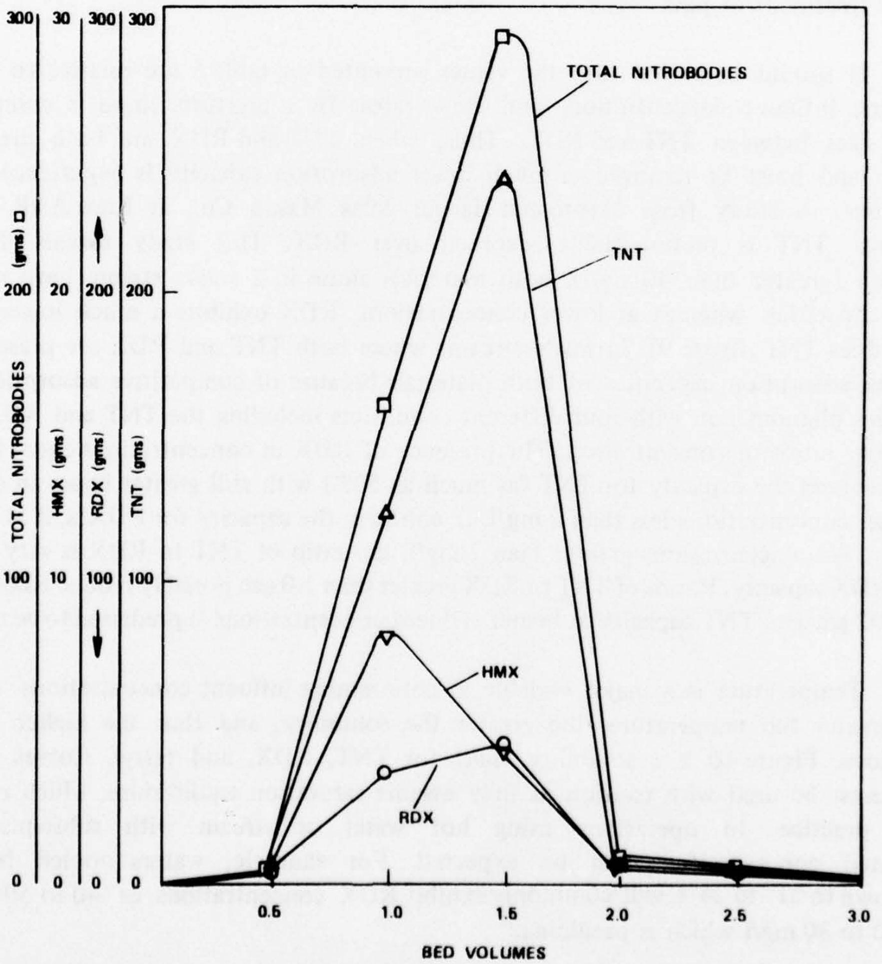

Figure 8. Acetone Regeneration of Amberlite XAD-4 (Cycle No. 3 "Nitrobodies")

VI. PERFORMANCE DATA.

As stated earlier, two of the three objectives of this paper were: (1) to establish a comparative evaluation of using carbon adsorption, polymeric resin adsorption, or a series combination of the two techniques in effectively treating pink water; and (2) to determine the treatability of pink water and pink water containing other nonaromatic nitrobodies such as RDX and HMX. The preceding sections dealt with these two objectives qualitatively. This section will deal with them quantitatively.

Numerous studies on the treatment of munition waste have been made on laboratory-, pilot-, and full-scale installations. Table 5 is a summary of adsorption capacities for activated carbon and polymeric resin Amberlite XAD-4. This table includes adsorbent nitrobody capacities for a variety of munition waste streams.

The performance data, listed in table 5, illustrate that both activated carbon and Amberlite XAD-4 have sufficient high adsorption capacity to provide a technically feasible solution for treatment of pink water.

It should be noted that the values presented in table 5 are relative to competitive contaminants, influent concentration, and flow rates. In a mixture, there is competition for adsorption sites between TNT and RDX. Thus, when TNT and RDX are both present in the waste stream and must be removed, a much lower adsorption capacity is experienced than that for TNT alone. A study from Mason and Hanger–Silas Mason Co., at Iowa AAP, by Layne[7] indicates that TNT is preferentially adsorbed over RDX. This study reveals that at high concentration (greater than 40 mg/l), both materials alone in a waste stream have nearly equal adsorption capacities, whereas at lower concentrations, RDX exhibits a much lower adsorption value than does TNT (figure 9). In waste streams where both TNT and RDX are present, one can expect lower adsorption capacities of both materials because of competitive adsorption. Figure 9 illustrates this phenomenon with four different conditions including the TNT and RDX alone and three different ratios of concentration. The presence of RDX in concentrations equal to or greater than TNT reduces the capacity for TNT (as much as 50%) with still greater losses in evidence for breakthrough concentrations less than 2 mg/l. In contrast, the capacity for RDX is, if at all, affected only slightly. At concentrations greater than 2 mg/l, the ratio of TNT to RDX is very much more critical for RDX capacity. Ratios of TNT to RDX greater than 1.0 can possibly reduce RDX capacity to less than 0.02 gm/gm. TNT capacity at higher effluent concentrations is predicted to be uneffected.[1]

Temperature is a major variable in determining influent concentrations. As a general rule, the greater the temperature, the greater the solubility, and thus the higher the influent concentrations. Figure 10 is a solubility chart for TNT, RDX, and tetryl. Curves for RDX in particular must be used with caution as they assume saturation equilibrium, which rarely occurs in actual practice. In operations using hot water or st/eam with subsequent cooling, supersaturated concentrations can be expected. For example, waters cooled from greater than 38° down to 21° to 24°C will commonly exhibit RDX concentrations of 40 to 50 mg/l rather than the 20 to 30 mg/l which is predicted.[8]

Table 5. Review of Available Munitions Waste Treatability Data*

Type of waste	Nitrobodies present	Concentration	Capacity, gm NB/gm Adsorbent			
			Breakthrough (1 ppm)		Saturation	
			Carbon	XAD-4	Carbon	XAD-4
		ppm				
TNT manufacturing waste, Radford Army Ammunition Plant^{5,9}	TNT	100	NA	0.236	0.55^{i}	0.240^{i}
Load, assemble, and pack waste, Burlington, Iowa Army Ammunition Plant^{9,10}	TNT	108	0.125	NE	0.181	NE
	RDX	89	0.074		0.090	
Load, assemble, and pack waste, Burlington, Iowa Army Ammunition Plant^{5,6}	TNT	114	NE	0.116	NE	0.278
	RDX	74		0.042		0.057
Contaminated ground water, Keyport, Washington^{9}	TNT	30.9	0.164	NE	NA	NE
	RDX	8.4	0.031		0.043	
	RDX	17.5	0.118	NE	0.125	NE
Load, assemble, and pack waste, Navy Ammunition Depot, Crane, Indiana^{9,10}	TNT	150	0.134	0.179	0.310	0.281
	HMX	4	0.006	0.002	0.009	0.009
Load, assemble, and pack waste, Milan Army Ammunition Depot^{1,8,11}	RDX	NA	0.098	0.020	0.125	0.050
	TNT	NA	0.300	0.236	0.550	0.882
	Tetryl	NA	NE	NE	0.030	0.005
	RDX	NA	0.008	0.003	0.048	0.019
	Tetryl		0.002	0.001	0.024	0.006

* These values are relative to flow rates, influent concentrations, and ratio of competitive contaminants.

NOTES: i – Isothermal capacity extrapolated from langmiur isotherms.

NB – Nitrobodies.

NA – Not available.

NE – Not evaluated.

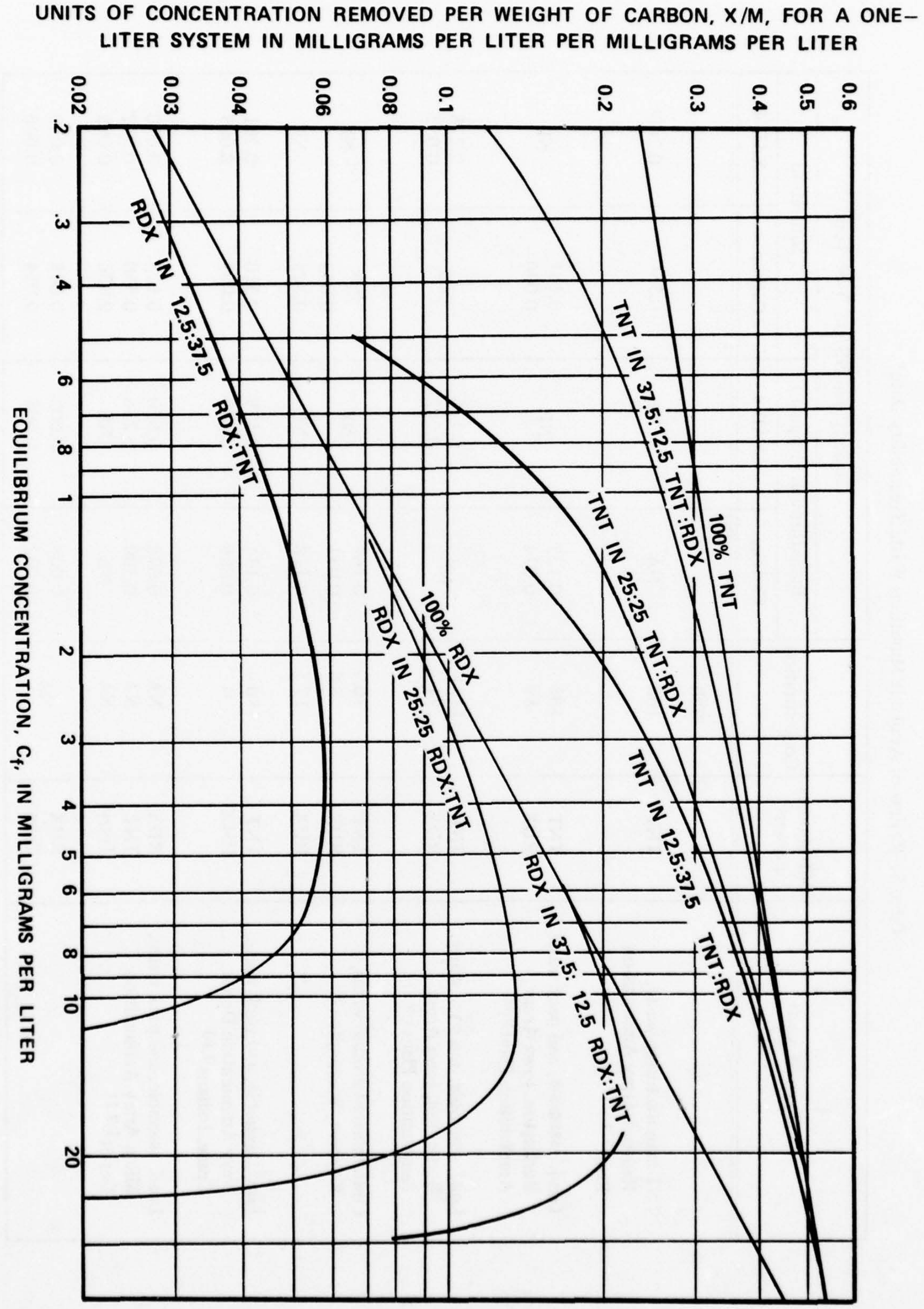

Figure 9. Freundlich Adsorption Isotherms of TNT and RDX Solutions

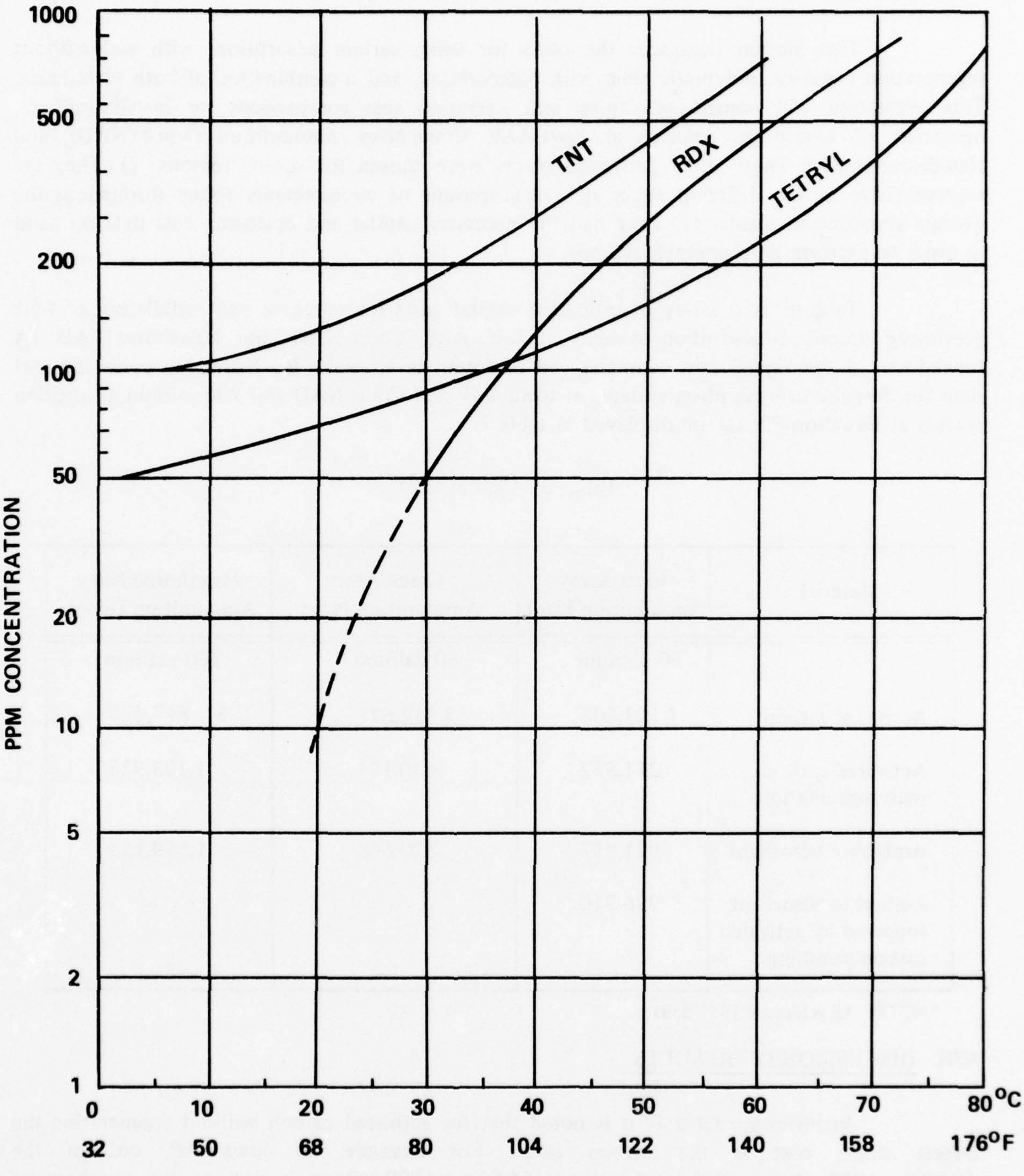

Figure 10. Solubility Chart

VII. ECONOMIC ANALYSIS.

This section compares the costs for using carbon adsorption, with and without regeneration capacity, polymeric resin with regeneration, and a combination of both techniques. This evaluation will consist of capital and operating cost comparisons for installation and operation of adsorption columns at Iowa AAP, Crane Navy Ammunition Depot (NAD), and Hawthorne NAD.* These three particular plants were chosen for several reasons: (1) They are representative of the different types of concentrations of contaminants found throughout the various ammunition plants. (2) They had the necessary capital and operating cost data on hand in order to perform an economic analysis.

Table 6 is a listing of estimated capital costs for purchase and installation of four previously described adsorption systems at Iowa AAP, Crane NAD, and Hawthorne NAD. (A breakdown of the capital cost estimates can be found in appendix B.) Estimated operating cost data for 80-gal/min adsorption systems at Iowa AAP and Crane NAD and 200-gal/min adsorption system at Hawthorne NAD are displayed in table 7.

Table 6. Capital Cost

Material	Iowa Army Ammunition Plant	Crane Army Ammunition Plant	Hawthorne Navy Ammunition Depot
	80 gal/min	80 gal/min	200 gal/min
Activated carbon	$ 193,802	$ 514,671	$ 847,425
Activated carbon with regeneration	251,552	630,171	1,193,925
Amberlite adsorbent	921,957	820,668	1,559,153
Amberlite adsorbent followed by activated carbon polishing	996,710	–	–

*NOTE: All values are 1977 dollars.

VIII. DISCUSSION OF RESULTS.

In reviewing table 8, it is noted that for activated carbon without regeneration the largest single cost is the carbon itself. For example, at Iowa AAP, out of the $7.08 per 1000 gallons of treated waters, $4.54 per 1000 gallons is due to the purchase of carbon, representing 64% of the total costs. A means of reducing this cost is to regenerate the

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* Cost data for these evaluations were obtained from the following sources: Carbon data from Iowa AAP and carbon regeneration data from Mason and Hanger–Silas Mason Co.; Crane and Hawthorne NAD data from Jerome Richardson at Crane NAD.

Table 7. Basis for Operating Cost Estimates

1. Raw material and utility costs.

Item	Cost
Electricity	$ 2.49/100 kw-hr
Processing water	$ 0.28/1,000 gal
Cooling water	$ 0.06/1,000 gal
Steam	$ 3.05/1,000 lb
Labor	$ 21.40/man hour
Nitrogen	$ 0.08/100 ft
Acetone	$ 0.12/lb
Amberlite XAD-4 resin	$ 4.50/lb (FOB, Philadelphia)
Shipping cost of resin	$ 4.34/100 lb (to Iowa)
Filterasorb 300 (carbon)	$ 0.63/lb (delivered)
Used carbon burning cost	$ 0.11/lb

2. Annual repairs, maintenance, and property overhead are 4% of the capital investment.
3. All equipment has a life of 15 years.
4. The LAP lines are run for 350 days/year
5. The resin life is 5 years.

Table 8. Operating Cost $/1,000 Gallons

	Iowa				Crane			Hawthorne		
	Carbon with regeneration	Resin	Resin and carbon	Carbon without	Carbon with regeneration	Resin	Carbon without	Carbon with regeneration	Resin	Carbon without
Resin replacement		0.42	0.42			0.54			0.54	
Carbon replacement	0.68		1.00	4.54	0.77		5.14	0.77		5.13
Labor–resin		1.53	0.92			4.36			1.78	
Labor–carbon	2.37		0.16	1.35	5.53		4.36	2.82		1.78
Acetone		0.25	0.13			0.46			0.46	
Steam		0.09	0.05			0.38			0.38	
Cooling water		0.02	0.01			0.06			0.06	
Process water					0.01	0.01	0.01	0.02	0.02	0.02
Nitrogen						0.01			0.02	
Electricity	0.14				0.15	0.01	0.01	0.33	0.16	
Carbon burning			0.08	0.60			1.11			0.15
Maintenance	0.29	0.91	0.95	0.22	0.69	0.93	0.69	0.61	1.13	0.61
Subtotal	3.48	3.22	3.72	6.71	7.16	6.76	11.32	4.55	4.55	7.69
Equipment depreciation	0.48	1.47	1.59	0.37	1.01	1.77	0.84	0.94	1.77	0.84
Total	3.96	4.69	5.31	7.08	8.17	8.53	12.16	5.49	6.32	8.53

NOTE: Iowa Army Ammunition Plant flow – 80 gal/min, 140 mg/l TNT and 70 mg/l RDX; Crane Navy Ammunition Depot flow – 80 gal/min, 140 mg/l TNT and 4 mg/l HMX; Hawthorne Navy Ammunition Depot flow – 200 gal/min, 150 mg/l TNT.

carbon. As previously mentioned, Mason and Hanger–Silas Mason Co. has had very good results with the regeneration of carbon in a modified rotary kiln furnace. They have had recovery rates of 85% to 95% and adsorbent capacities of 95% to 102% of virgin carbon.

Mason and Hanger personnel have just recently completed an economic analysis on carbon regeneration. This analysis is based on data obtained from Iowa's pilot regeneration system and the Calgon Corporation, the manufacturer of Filterasorb^{R} 300 and 400. The cost to purchase and install a thermal regeneration facility of sufficient size to handle mobilization requirements is $346,500 (table 9). This entails a 200-pound per hour rotary kiln furnace, process controls, exhaust scrubbers, feed and recovery systems.

The cost of virgin carbon is $0.63 per pound (June 1977 dollar values). In comparison, the cost of regenerated carbon is $0.17 per pound plus amortization cost. As a conservative estimate, if Iowa's adsorption system were to be composed of 85% regenerated carbon, it would cost only $3.96 to treat the same 1000 gallons. A savings of $3.12 per 1000 gallons of treated water is realized. By using regenerated carbon, in 1 year's time, the savings would be $109,200. Thus, it would take 3.17 years (346,000/109,200) to packback and amortize the regeneration equipment.

Referring back to table 8, one can observe a definite pattern. Throughout this table the adsorption systems with the lowest cost is carbon with regeneration capacity. Also, it should be pointed out that the makeup of the waste streams for each of the three listed facilities differs. The characteristics of these waste streams are as follows: Iowa–140 mg/l TNT and 70 mg/l RDX, Crane–140 mg/l TNT, and 4 mg/l HMX, and Hawthorne–150 mg/l TNT.

The economics of carbon and polymeric resin adsorption are not straightforward. As seen in tables 6 and 8, the capital and operating costs for the different plants and adsorption techniques vary considerably. This is due to several factors, of which the most important is the variation in types and concentrations of contaminants in waste streams of the various plants. This is shown in tables 2 and 3. Certain plants, like Joliet AAP, have just TNT; others, like Iowa AAP, have a combination of TNT and RDX; and then there is Milan AAP which has the distinction of having TNT, RDX, and tetryl. These waste streams all have one thing in common: they are colored in nature. Other factors that contribute to variations in capital and operating cost include flow rates, solid contaminants such as waxes and sludges, loading rates, wastewater temperatures, water requirements and restrictions. Since each plant has its own particular demand for an adsorption system, capital and operating costs must vary from plant to plant.

IX. CONCLUSIONS AND RECOMMENDATIONS.

A. Conclusions.

Numerous studies on the treating of munition wastewater, namely pink water, have been made on laboratory-, pilot- and full-scale installations. The results from these studies, summarized in this paper, establish that either activated carbon or Amberlite XAD-4 can provide a technically feasible solution to the pink-water problem. Both adsorbents are capable of removing TNT and other nitrobodies such as RDX and HMX from munition waste stream to the target level of less than 1 ppm of total nitrobodies.[11]

Table 9. Regeneration Equipment

Item	Cost
Equipment	$ 200,000
Installation	120,000
Land	10,000
Building	10,000
Instrumentation	5,000
Piping and electrical	1,500
Total	$ 346,500

The operating cost breakdown is as follows:

Utilities – mainly electricity	$ 0.02/lb carbon
Labor*	$ 0.15/lb carbon
Depreciation	$ 66.00/day at 15 years life

* Labor rate – $21.40 per hour.

In view of the findings of this report, the following conclusions can be drawn:

1. Amberlite XAD has greater capacity for TNT than has activated carbon.[8]

2. Activated carbon has a higher capacity for HMX than has Amberlite XAD-4.[8]

3. Activated carbon has a higher capacity than has Amberlite XAD for RDX and tetryl.[11]

4. Both adsorbents will provide similar nitrobody leakage for similar streams.[5]

5. Amberlite XAD is not completely effective in removing the color from a colored waste stream. If a waste stream is slightly colored, a carbon-polishing column placed after the resin column will remove the color.[8]

6. Operating at a lower feed pH (5.5) enhances color removal through both adsorbents.[8]

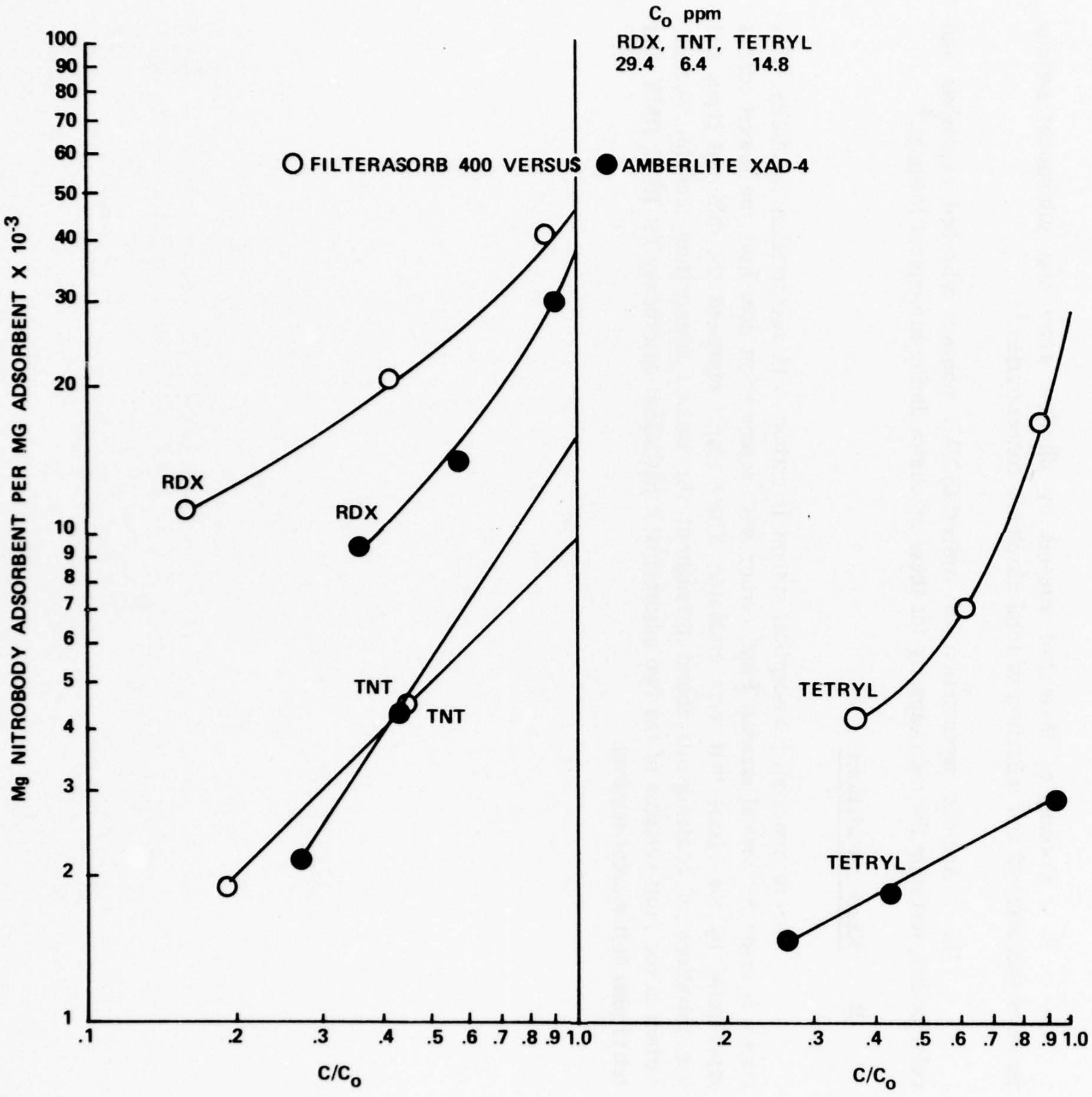

Figure 11. Isotherms for Composite

7. The effluents through both adsorbents when exposed to sunlight will not develop any additional color provided TNT concentration is less than 1 ppm.[8]

8. The highest nitrobody levels are common to those streams that originate from the contact of explosives by stream and/or hot water, i.e., kettle cleaning, tray washing, projectile steam-out, etc.[11]

9. Cooling of these hot streams by dilution water and subsequent settling provides wax removal and reduction of total nitrobody concentration.[11]

10. Acetone regeneration of Amberlite XAD removes adsorbed explosives and color bodies, restoring the resin capacity for these substrates during subsequent loadings.[8]

B. Recommendations.

The recommended adsorption system is carbon with regeneration capability. This choice is made for several reasons. First, carbon with regeneration does have the lowest cost as represented by the plants that were evaluated. These plants represent the different types and concentrations of contaminants found throughout the various ammunition facilities. Second, carbon is the most versatile of the two adsorbents; it has higher adsorbency for RDX, HMX, and tetryl plus better color removal.

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APPENDIX A

EQUIPMENT LAYOUT

Figures A-1 and A-2 illustrate the *major* piece of equipment required in a treatment building for carbon and resin-carbon system, respectively. These figures are intended only for descriptive purposes.

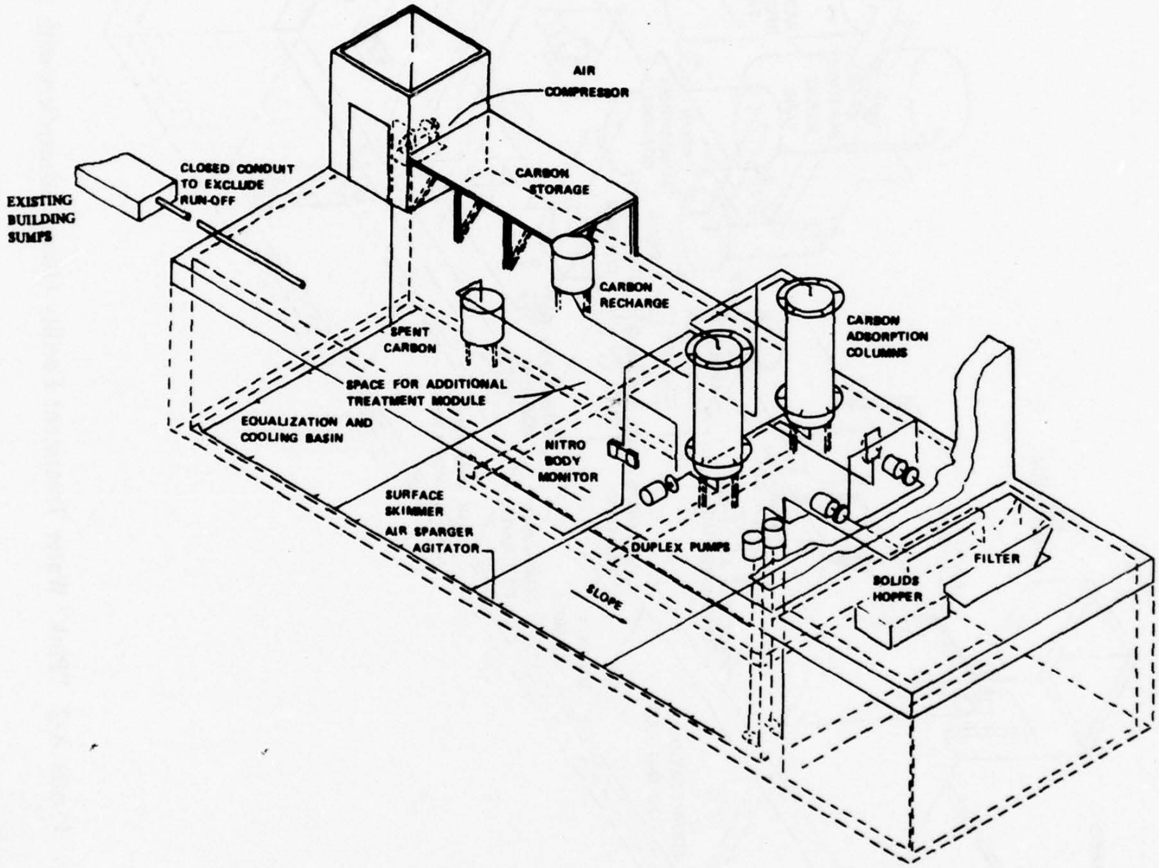

Figure A-1. "Pink" Water Treatment Facility (Carbon Adsorption)

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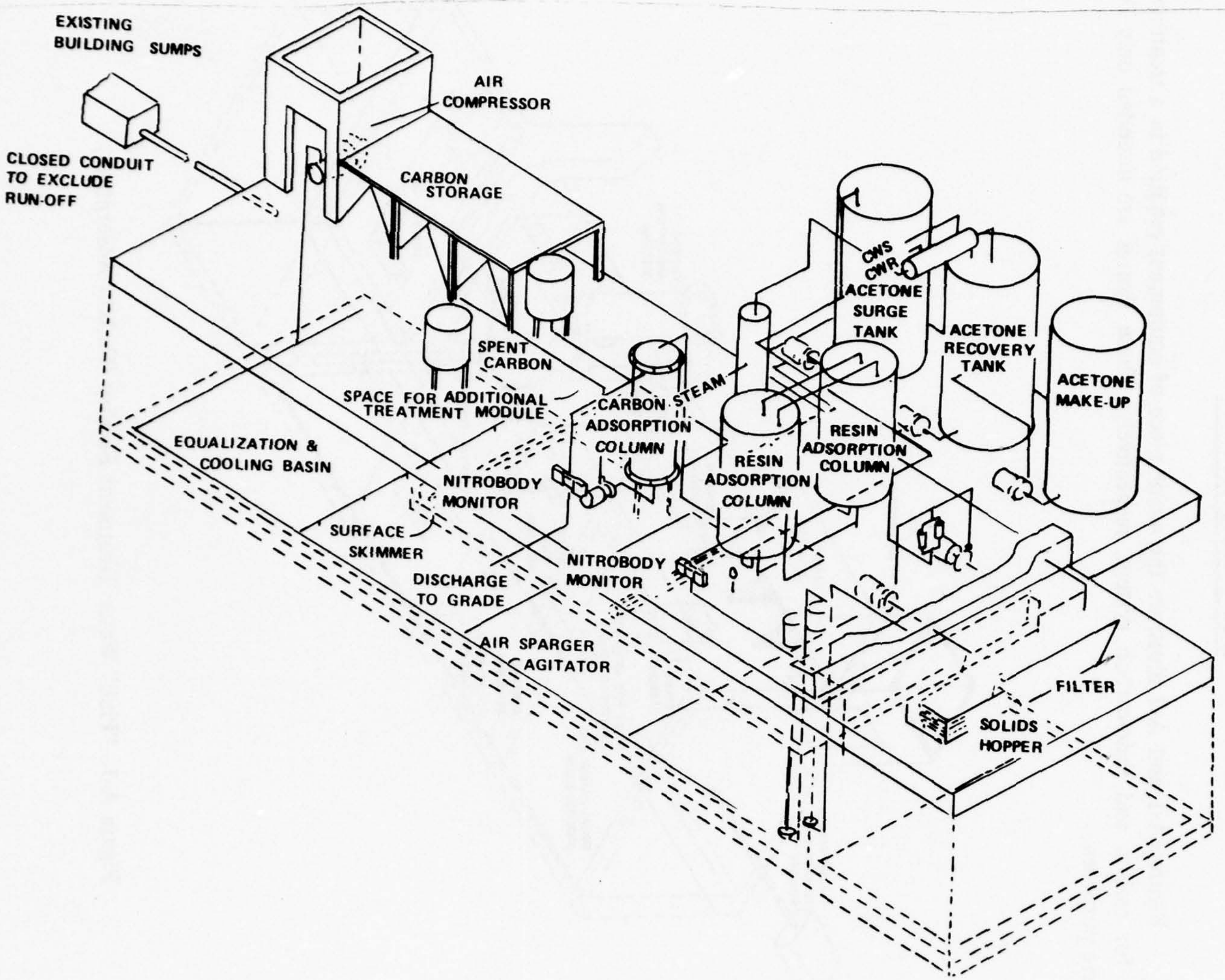

Figure A-2. "Pink" Water Treatment Facility (Resin Adsorption with Carbon Polishing)

Referring to figure A-1, wastewaters for the filter are pumped to the carbon columns which can operate in a downflow pressure condition. Further, the columns are to operate in a series mode which allows the primary columns to be fully saturated while the secondary acts as a polishing column. When the second column has reached the predetermined breakthrough concentration, the carbon from the first column is removed for disposal and is replaced with fresh carbon. The first then becomes the polishing column and the second column becomes the primary column.*

In the resin-carbon system (see figure A-2), the wastewaters from the filter are pumped to one of the two resin columns which are parallel. One is off stream, while the other is on. The carbon column acts simply as a polishing column in case one of the resin columns experiences an abnormal breakthrough. Once a resin column reaches breakthrough, it is automatically taken off line and the wastewaters are directed to the other column. The saturated column is then backwashed with approximately six bed volumes of acetone. Contaminated acetone is then distilled and condensed to 99 plus percent recovery.

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* Heck, R. Adsorption Technology Applied to Wastewaters of the Munitions Industry. Mason and Hanger–Silas Mason Co., Inc., presented at the 22nd Annual Technical Meeting of the Institute of Environmental Sciences, April 1976.

APPENDIX B

CAPITAL COST BREAKDOWN

CRANE NAVY AMMUNITION DEPOT CAPITAL COST – 80 gal/min

Item	Carbon	Resin
Adsorption units		
1. Installed equipment	$ 325,866	$ 372,583
2. Controls	75,992	78,782
Distillation units		
1. Recovery system	–	53,000
2. Building	–	26,100
3. Dikes and foundations	–	15,000
Total (material and labor)	$ 401,858	$ 627,227
Engineering (15%)	60,278	81,812
Technology license from Rohm and Haas and initial cost of Amberlite resin	–	32,000
Initial cost of Filterasorb	2,597	–
Total (1975 dollars)	$ 464,733	$ 741,039
Total (1977 dollars)	$ 514,671	$ 820,668

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HAWTHORNE NAVY AMMUNITION DEPOT CAPITAL COST – 200 Gal/min

Item	Carbon	Resin
Existing treatment plant	$ 765,200	$ 765,200
Resin regeneration and solvent reclamation system	–	545,543
Engineering and added charges	–	97,126
Total (1975 dollars)	$ 765,200	$ 1,407,869
Total (1977 dollars)	$ 847,425	$ 1,559,153

APPENDIX C

ECONOMIC ANALYSIS IN AR 11-28 FORMAT

SECTION 1

1. Title: Analysis of Carbon Versus Resin.

2. Objective: Determine the optimum technique to treat pink water generated from ammunition manufacture and LAP facilities.

3. Alternative 1. Activated carbon with regeneration capacity.

Alternative 2. Polymeric resin adsorption with regeneration capacity.

Alternative 3. Polymeric resin adsorption with regeneration followed by a polishing column of activated carbon.

Alternative 4. Activated carbon without regeneration capacity.

4. Assumptions and Constraints:

(a) As stated in the body of this report, each plant has its own particular requirements on an adsorption system, thus the economics must vary from plant to plant. To illustrate how the above alternatives are affected by the various plant demands, they will be evaluated for three different plants: Iowa AAP, Crane NAD, and Hawthrone NAD. These three plants were chosen because they are representative of the different types and concentrations of contaminants found throughout the various ammunition plants. Alternatives 1, 2, and 4 will be evaluated for all three plants. Because of the lack of data, alternative 3 will be evaluated only for Iowa AAP.

(b) The expected life of all equipment is 15 years. The expected technological life is 10 years.

(c) Depreciation will be calculated by using the straight-line method.

(d) The cost benefit ratio is defined as the uniform annual cost (with terminal value) divided by the number of thousand gallons of water treated per year, units of $/1000 gallons.

(e) All values are in 1977 dollars. All conversions were performed using CE plant cost index.

(f) The following assumed-general guidelines were used in distributing the nonrecurring cash flow: for year 1, 200,000 limit; for year 2, 300,000 limit; and remainder in year 3.

(g) Recurring cost will not start until year 4.

5. Not applicable.

6. Comparison of Alternatives and Recommendations:

Summary of Cost Benefit Ratio

	Iowa Army Ammunition Plant	Crane Navy Ammunition Depot	Hawthorne Navy Ammunition Depot
Alternative 1	4.45	10.65	7.28
Alternative 2	7.07	11.63	8.08
Alternative 3	7.84	–	–
Alternative 4	7.45	14.21	9.68

Summary of Uniform Annual Cost

Alternative 1	168,355	286,387	489,288
Alternative 2	267,336	312,718	542,744
Alternative 3	296,336	–	–
Alternative 4	281,523	381,906	650,435

Alternative 1, carbon with regeneration capacity, is the recommended alternative. As seen from the above data, it consistently had the lowest cost.

SECTION II

Alternative 1 – Iowa AAP Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	0	0	0	.954	0
2	38,000	0	38,000	.867	32,946
3	213,552	0	213,552	.788	168,278
4–13	0	131,544	131,544	4.844	637,199
Total				7.453	838,423

Total project cost (discounted)	$838,423
Less terminal cost (discounted)	22,911
Net total project cost (discounted)	815,512
Uniform annual cost (with terminal value)	168,355
Cost benefit ratio	4.45

Alternative 2 – Iowa AAP Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	300,000	.867	260,100
3	421,957	0	421,957	.788	332,500
4–8	0	121,716	121,716	2.988	363,687
9	12,900	121,716	134,606	.455	59,904
10–13	0	121,716	121,716	1.411	171,741
Total				7.453	1,378,372

Total project cost (discounted)	$1,378,732
Less terminal value (discounted)	83,971
Net total project cost (discounted)	1,294,760
Uniform annual cost (with terminal value)	267,292
Cost benefit ratio	7.07

Alternative 3 – Iowa AAP Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	200,000	.867	260,100
3	496,710	0	496,710	.788	391,407
4–8	0	140,616	140,616	2.988	420,160
9	6,450	140,616	147,066	.455	65,444
10–13	0	140,616	140,616	1.411	198.409
Total				7.453	1,526,320

Total project cost (discounted)	$1,526,320
Less terminal value (discounted)	90,800
Net total project cost (discounted)	1,435,520
Uniform annual cost *(with terminal value)*	296,336
Cost benefit ratio	7.84

Alternative 4 – Iowa AAP Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1–2	0	0	0	1.821	0
3	193,802	0	193,802	.788	152,715
4–13	0	253,638	253,638	4.844	1,228,622
Total				7.453	1,381,337

Total project cost (discounted)	$1,381,337
Less terminal value (discounted)	17,636
Net total project cost (discounted)	1,363,701
Uniform annual cost (with terminal value)	281,523
Cost benefit ratio	7.45

Alternative 1 – Crane NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	0	0	0	.954	0
2	200,000	0	200,000	.867	173,400
3	430,171	0	430,171	.788	338,974
4 - 13	0	192,460	192,460	4.844	932,280
Total				7.453	1,444,654

Total project cost (discounted)	$ 1,444,654
Less terminal cost (discounted)	57,395
Net total project cost (discounted)	$ 1,387,259
Uniform annual cost (with terminal value)	286,387
Cost benefit ratio	10.65

Alternative 2 – Crane NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	300,000	.867	260,100
3	320,668	0	320,668	.788	252,686
4 - 8	0	181,708	181,708	2.988	542,945
9	12,900	181,708	194,608	.455	86,600
10 - 13	0	181,708	181,708	1.411	256,378
Total				7.453	1,589,509

Total project cost (discounted)	$ 1,589,509
Less terminal value (discounted)	74,700
Net total project cost (discounted)	1,514,809
Uniform annual cost (with terminal value)	312,718
Cost benefit ratio	11.63

Alternative 4 – Crane NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	0	0	0	.954	0
2	200,000	0	200,000	.867	173,400
3	314,671	0	314,671	.788	247,960
4 - 13	0	304,281	304,281	4.844	1,473,940
Total				7.453	1,895,300

Total project cost (discounted)	$ 1,895,300
Less terminal value (discounted)	45,347
Net total project cost (discounted)	1,849,953
Uniform annual cost (with terminal value)	381,906
Cost benefit ratio	14.21

Alternative 1 – Hawthorne NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	300,000	.867	260,100
3	693,925	0	693,925	.788	546,812
4 - 13	0	305,760	305,760	4.844	1,481,101
Total				7.453	2,478,813

Total project cost (discounted)	$ 2,478,813
Less terminal value (discounted)	108,700
Net total project cost (discounted)	2,370,113
Uniform annual cost (with terminal value)	484,288
Cost benefit ratio	7.28

Alternative 2 – Hawthorne NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	300,000	.867	260,100
3	1,059,153	0	1,059,153	.788	834,612
4 - 8	0	305,760	305,760	2.988	913,610
9	12,900	305,760	318,660	.455	141,803
10 - 13	0	305,760	305,760	1.411	431,427
Total				7.453	2,772,352

Total project cost (discounted)	$ 2,772,352
Less terminal value (discounted)	143,298
Net total project cost (discounted)	$ 2,629,054
Uniform annual cost (with terminal value)	542,744
Cost benefit ratio	8.08

Alternative 4 – Hawthorne NAD Format 1 Equipment life 15 years

Project years	Nonrecurring cost	Recurring cost	Annual cost	Discount factors	Present values
1	200,000	0	200,000	.954	190,800
2	300,000	0	300,000	.867	260,100
3	347,425	0	347,425	.788	273,770
4 - 13	0	516,768	516,768	4.844	2,503,224
Total				7.453	3,227,894

Total project cost (discounted)	$ 3,227,894
Less terminal value (discounted)	77,183
Net total project cost (discounted)	3,150,711
Uniform annual cost (with terminal value)	650,435
Cost benefit ratio	9.68

DOCUMENTATION

General:

Cost data, capital and operating, for these evaluations were obtained from the following sources: carbon data from Iowa AAP and carbon regeneration data from Mason and Hanger–Silas Mason Co., Crane and Hawthorne NAD data from Jerome Richardson at Crane NAD.

Recurring Cost.

All Alternatives:

Operating cost breakdowns and estimates are listed in tables 7 and 8.

Waste stream flows are: Iowa – 80 gal/min X 22.5 hr/day = 108,000 gal/day, Crane – 80 gal/min X 16 hr/day = 76,800 gal/day, Hawthorne – 200 gal/min X 16 hr/day= 192,000 gal/day.

Example: Using the above waste stream flow and table 8 data the total operating cost per year for alternative 1 – Iowa is:

$$\frac{\$\,3.48}{1000\text{ gallons}} \times \frac{108{,}000\text{ gallons}}{\text{day}} \times \frac{350\text{ days}}{\text{year}} = \frac{\$\,131{,}544}{\text{year}}$$

Waste stream characteristics are: Iowa – 140, mg/l TNT and 70 mg/l RDX, Crane – 140 mg/l TNT and 4 mg/l HMX, Hawthorne – 150 mg/l TNT.

Nonrecurring Cost.

All Alternatives.

Capital cost data are listed in table 6 and in appendix B.

Alternative 2 – all plants.

$12,900 in year 9 to replace worn–out polymeric resin. Present value $12,900 X .445 = $5,740.

Alternative 3 – Iowa.

$6,450 in year 9 to replace worn–out polymeric resin. Present value $6,450 X .455 = $2,870.

Terminal Value.

All Alternatives

The expected life of the equipment is 15 years, after which time it will have an estimated salvage value of zero. The economic life of all the alternatives is 10 years. Using the straight-line method of depreciation after 10 years of service the equipment will be worth 1/3 of its original value. The equipment will be discounted in year 14.

Example: Alternative 1 – Iowa:

Total capital cost	$ 251,552
Net terminal values after 10 years	X .333
	83,776
Discount factor for 14 years	X .276
Net terminal value discounted	22,911

Summary of Net Terminal Value

	Iowa	Crane	Hawthorne	
Alternative 1	83,012	207,956	393,995	Net terminal value
	22,911	57,395	108,700	Terminal value discounted
Alternative 2	304,245	270,820	514,520	Net terminal value
	83,971	74,700	143,298	Terminal value discounted
Alternative 3	328,914	–	–	Net terminal value
	90,800	–	–	Terminal value discounted
Alternative 4	63,954	169,841	279,650	Net terminal value
	17,636	45,347	77,183	Terminal value discounted

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