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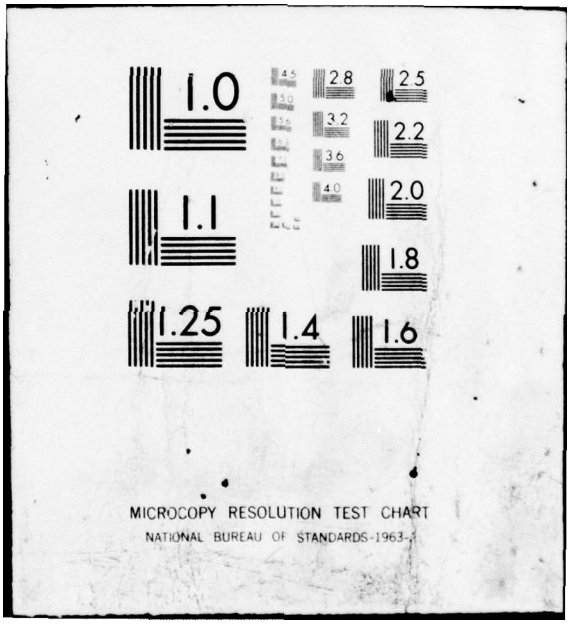
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Calspan Report No. ND-5296-M-2

FEASIBILITY STUDY OF TREATING FIELD MILITARY WASTEWATER BY A PROCESS INCLUDING POWDERED CARBON ADSORPTION, POLYMER COAGULATION, AND DIATOMITE FILTRATION

Second Interim Report
for the Period 16 April - 15 June 1973

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By

Lawrence K. Wang
Project Engineer

June 1973

Prepared for

Department of the Army
U. S. Army Mobility Equipment
Research and Development Center

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Contract No. DAAK02-73-C-0206

Prepared by

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P. O. Box 235
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FEASIBILITY STUDY OF TREATING FIELD MILITARY WASTEWATER BY A PROCESS INCLUDING POWDERED CARBON ADSORPTION, POLYMER COAGULATION, AND DIATOMITE FILTRATION.

(9)

Second Interim Report, no. 2,
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CALSPAN CORPORATION
Buffalo, New York 14221

FEASIBILITY STUDY OF TREATING FIELD MILITARY WASTEWATER BY A PROCESS SYSTEM INCLUDING POWDERED CARBON ADSORPTION, POLYMER COAGULATION, AND DIATOMITE FILTRATION

CALSPAN INTERIM REPORT NO. ND-5296-M-2

June 1973

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ABSTRACT

Previous investigations of the use of powdered carbon and organic coagulants for treating wastewaters having characteristics similar to those generated at military bases were surveyed and assessed

Synthetic wastewater consisting of tap water, dishwashing detergent, laundry detergent, soap, clay, oil and food constituents, was prepared for the feasibility and mechanism studies of treating the wastewater by a proposed adsorption/coagulation/filtration system. Operational parameters selected for laboratory optimization studies of the treatment system were: initial pH and temperature of wastewater; contact time of carbon adsorption; types and dosages of powdered carbons; types and dosages of polymers; feed time and feed order of carbon and polymer; retention time of polymer coagulation; and the efficiency of diatomite filtration. Based on the experimental results, the technical feasibility of the proposed treatment system was positively demonstrated, the suitable types of carbon and polymer were selected, and the controlling parameters were optimized.

The standard U. S. Army mobile water purification plant, described in Army Report No. TM5-4610-208-14, has two feeders, an upflow clarifier, a pressure diatomite filter and a sludge thickener. The basic concept of this program was to use the same mobile water purification plant (with an additional mixing tank) for wastewater treatment by the proposed adsorption/coagulation/filtration process. Actual wastewaters from the field shower, laundry and kitchen units had been collected and treated by the proposed treatment technique with a standard mobile plant of 420 GPH. Their treatabilities by the proposed treatment technique and the mobile plant were confirmed to be promising.

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1.0 INTRODUCTION

Calspan Corporation (formerly Cornell Aeronautical Laboratory, Inc., Cornell University) was authorized by the U. S. Army Mobility Equipment Research and Development Center (USAMERDC) to investigate a carbon-polymer system designed for treating the wastewaters generated at military field bases. Initially, previous investigations on the use of powdered carbon and organic coagulants for treating wastewaters with characteristics similar to those generated at military bases were surveyed and assessed. It was believed that the existing Army standard mobile water purification units (Ref. 1) could be used as basic components of the carbon-polymer waste treatment system.

Subsequently, a synthetic wastewater with characteristics similar to the military field wastewaters was then formulated with detergents, soap, clay, oil and food constituents for an extensive laboratory investigation. A number of specific controlling parameters relating to the adsorption of dissolved pollutants onto the carbon, and the flocculation of the suspended matter (including spent carbon) by the polymer were researched. A summary of experimental results and conclusions are presented in Section 6.0, SUMMARY AND CONCLUSIONS.

Full scale treatment of actual field kitchen, laundry, and shower wastewaters by the carbon-polymer technique with a standard mobile water purification unit was conducted concurrently by USAMERDC personnel for the purpose of comparison and demonstration. The technical feasibility of treating field military wastewater by the carbon-polymer was positively confirmed.

2.0 WASTEWATERS TO BE TREATED

Treatment of field military wastewaters was the broad objective of this investigation. A compilation of the physical, chemical and biological characteristics of various wastewater streams generated in field military installations was one of four research tasks conducted under this program. The first project report, No. ND-5296-M-1, summarized the available data on the quantities and characteristics of laundry wastewater, kitchen and dining room wastewaters, shower and lavoratory wastewaters, human wastes, hospital wastewaters, photographic wastewaters, washrack wastewaters, and combined wastewaters (Ref. 2). Although the nature and characteristics of almost all field military wastewaters were surveyed, special emphasis of this research was placed on the treatment of field kitchen, laundry and shower wastewaters. The characteristics of these three waste streams and their associated tap waters are indicated in Table 1.

Synthetic wastewater was prepared with tap water, detergents, soap, clay, oil and food constituents according to the formulation described in Section 4.1.a., Synthetic Wastewater Preparation. Characteristics of the synthetic wastewater can be seen from Appendix I.

Data for the treatability tests for both synthetic wastewater and actual field wastewaters are reported in Section 5.0, RESULTS AND DISCUSSIONS OF LABORATORY OPTIMIZATION STUDIES AND PRELIMINARY FULL SCALE PLANT OPERATION.

TABLE 1

CHARACTERISTICS OF WASTEWATERS GENERATED FROM FIELD SHOWER, LAUNDRY, AND KITCHEN UNITS

PARAMETERS mg/l except as noted	SHOWER		LAUNDRY		KITCHEN	
	TAP	WASTEWATER	TAP	WASTEWATER	TAP	WASTEWATER
Turbidity, JTU	0.3	59.0	0.6	3800.0	0.5	440.0
pH, Unit	7.0	6.8	7.7	7.6	7.5	6.3
Total Dissolved Solids	135.0	175.0	140.0	290.0	145.0	430.0
Detergent	0.0	1.8	0.0	6.5	0.0	8.4
Total Phosphate	20.0	35.0	5.0	48.0	2.0	52.0
Ortho Phosphate	12.0	28.0	5.0	45.0	2.0	36.0
Poly Phosphate	8.0	7.0	0.0	3.0	0.0	16.0
Sulphate	7.2	22.0	12.0	175.0	35.0	--
Silicate	36.0	55.0	37.0	150.0	35.0	170.0
Total Hardness, $CaCO_3$	12.0	18.0	20.0	30.0	14.0	28.0
Calcium, $CaCO_3$	12.0	16.0	16.0	22.0	12.0	26.0
Magnesium, $CaCO_3$	0.0	2.0	4.0	8.0	2.0	2.0
Alkalinity, $CaCO_3$	108.0	136.0	194.0	116.0	118.0	120.0
Chloride	10.0	10.0	--	--	--	35.0
BOD	--	0.5	--	339.0	--	--
TOC	--	15.0	--	258.0	--	214.0

SOURCE: U. S. Army Mobility Equipment Research & Development Center.

3.0 PROCESS SELECTION AND LITERATURE REVIEW

3.1 General Discussion

The methods of field wastewater treatment depend largely on the characteristics of the wastes, level of treatment required, and the mobility of the treatment facility. Figure 1 gives an overall view of the hierarchy of treatment processes available for treating military field wastewaters and their associated sludges and residuals. The methods of treatment are diverse and can be broadly categorized as either biological or physicochemical processes. Chemical reagents, adsorbents and mechanical separation processes are used for physicochemical treatment, whereas microorganisms are used to accomplish the treatment in biological processes. All processes shown in Figure 1 have been defined in environmental engineering text books. Appendices II to IV summarize most of the processes shown in Figure 1. Their capabilities, treatment efficiencies, and their approximate operating costs are also given in the appendices. This report, however, reviews only the processes which are suitable for use with the mobile standard water purification unit (Ref. 1), shown in Figure 2.

It is hypothesized that the combined field wastewater, shown as the top bulk line in Figure 1, can be treated by one or more unit processes from Nos. 1 through 53. The end product can be either potable water or nonpotable water (i.e., Nos. 54 and 55, respectively). The associated sludges and/or residuals can be treated by one or more unit processes from Nos. 39 to 48.

Field military wastewaters generated from the lavatory and photographic units contain hazardous viruses and heavy metals. Such hazardous waste streams, shown as the bottom bulk line in Figure 1, can be treated separately by one or more unit processes from Nos. 32 through 49, or treated in combination with all other wastewaters together.

This program, however, considers only the treatment of nonhazardous kitchen, shower and laundry wastewaters by a mobile treatment plant having two chemical feeders, an upflow clarifier, a diatomite filter and a sludge concentrator (Figure 2). Although there are still many treatment system

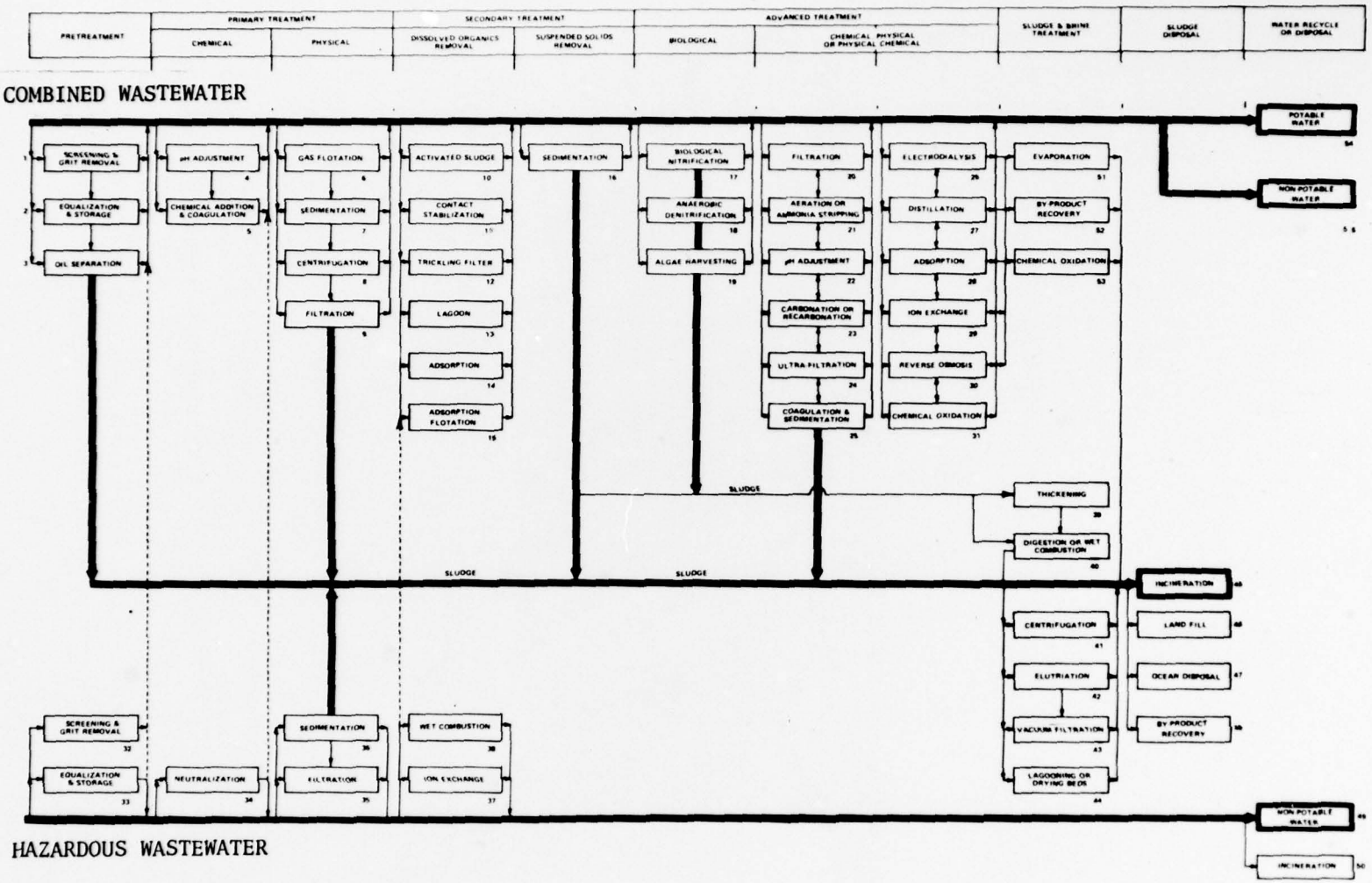

FIGURE 1. WASTEWATER TREATMENT PROCESSES SEQUENCE AND SUBSTITUTION DIAGRAM

Revised and Expanded by Calspan Corporation, Buffalo, N. Y.
Based on EPA Report No. 12020 GND 07/71

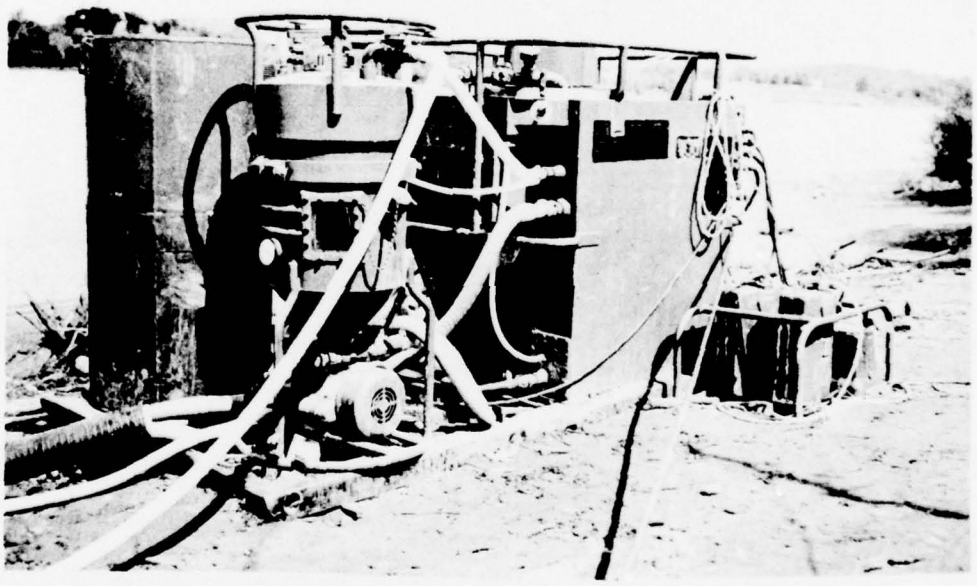

FIGURE 2. 420 GPH WATER PURIFICATION PLANT

alternatives, a powdered carbon adsorption system, shown as either Nos. 2-4-14-25-20-55 or Nos. 2-14-25-20-55 in Figure 1, seems feasible and adaptable. The equalized wastewater can be mixed with chemicals in a mixing tank, coagulated by the upflow clarifier and then further purified by the diatomite filter. The spent carbon sludges can be thickened in the provided sludge concentrator (i.e., the process No. 39 in Figure 1).

3.2 State-of-the-Art Review of Adsorption/Coagulation/Filtration Process

The proposed powdered carbon adsorption system is termed the adsorption/coagulation/filtration process in this program on the basis of its processing mechanisms. A search was made for available literature covering this process. Relevant literature is summarized in this section.

References 3 to 27 relate to water and wastewater treatment by the powdered carbon adsorption process. The basic principle of carbon treatment is adsorption of dissolved pollutants at water-carbon interfaces. Powdered carbons are those materials which are smaller in particle size than approximately 150 mesh. There are at least two systems of pores of distinctly different sizes existing in every carbon particle. Macropores in activated carbon are larger in diameter than 1000 Angstroms. These macropores contribute relatively little to the surface area for adsorption. Micropores in activated carbon are smaller in diameter than 1000 Angstroms and generally are in the order of 10 to 100 Angstroms. These micropores contribute about 600 to 1,000 square meters of surface area per gram of carbon, and are mainly responsible for the adsorptive action (Ref. 7).

Powdered activated carbon was first used in this country by New Milford Purification Plant of Hackensack Water Company, New Jersey, for removing taste-and-odor-causing substances from water in 1930. Now it is widely used for water purification. Wastewater treatment with powdered activated carbon became popular since 1963 (Refs. 3 to 26). Of major value is the removal of dissolved organics from wastewater by activated carbon adsorption. In general, the spent carbons are removed by coagulation

and filtration (Refs. 4 to 23). In other words, a process system of adsorption/coagulation/filtration is used. The spent powdered carbon can also be separated from a treated water by ultrafiltration (Ref. 25) and flotation (Ref. 26) techniques.

References 28 to 72 relate to water and wastewater treatment by polymer coagulation. There is a wide variety of types and sizes of polymers that are presently offered to the areas of water and wastewater treatments. However, there are only three types of general materials being used. The first type consists of some non-ionic polymers that are useful in forming a link between two or more solid particles by the so-called "bridging effect". The second type consists of anionic polymers which are those carrying a negative charge in solution. The third type includes cationic polymers which are positively charged in solution. Both anionic and cationic polymers are also termed polyelectrolytes due to their ionizable groups (i.e., charge sites). Polyelectrolytes can be responsible for both charge neutralization and particle bridging in a coagulation or flocculation process (Refs. 32-34, 65-68, 70).

The majority of water or wastewater treatment plants use polymers as coagulation aids in conjunction with alum or ferric chloride as primary coagulants (Refs. 32, 54-58). The use of polymers as primary coagulants was first suggested by Pressman in 1967 (Ref. 31), and accepted by many other environmental scientists (Refs. 7, 23, 30, 36). Calspan Corporation's research in the use of powdered activated carbons for wastewater treatment (Refs. 7 and 23) showed that the cationic organic coagulants would be essential for proper coagulation of spent powdered carbons. Nonionic and anionic polymers would be of little value for this purpose.

Coagulation of spent powdered carbons and other suspended matter with polymer materials can be accomplished in either a rectangular sedimentation unit or an upflow clarifier. Since the upflow clarifier (i.e., Erdlator) is included in the standard Army mobile treatment plant

(Figure 2), it was considered for use in this program. References 73 to 76 introduce the function and applications of the upflow clarifier. Polymer coagulation can remove not only suspended matter but also pathogenic bacteria and viruses. References 37 to 42 demonstrate the disinfection effects achieved by polymer coagulation.

The tertiary wastewater treatment unit in the proposed adsorption/coagulation/filtration system is a diatomite filter. References 75 to 89 relate to the function, applications and improvements of diatomite filtration. In this filtration process, a filter cake or precoat of diatomeceous earth is used as a filter medium. The precoat of diatomaceous earth is formed over a permeable base or septum by adding a slurry of diatomite to the filter shell and recirculating the slurry until the precoat is formed. The unit is then ready for the filtering operation. Diatomaceous earth filtration is employed primarily where the utmost clarity of the effluent is required or where space and weight limitations are quite stringent. The use of polyelectrolyte to improve the efficiency of the diatomite filter has been demonstrated by many researchers (Refs. 77, 80, 81, 85 and 86). It is conceivable that polyelectrolyte coagulation prior to diatomite filtration would improve the overall treatment efficiency because the slightly overdosed polyelectrolyte in the coagulated water would serve to improve the efficiency of the filtering process.

References 90 to 93 present the pollution effects of and the current physicochemical treatment methods for detergent type wastewater. Note that operation of a diatomaceous earth filtration system for the purification of a laundromat waste has been conducted by Aulenbach et al. (Ref. 93).

4.0 PERFORMANCE OF LABORATORY INVESTIGATIONS

The objective of the laboratory investigations are to demonstrate the feasibilities of treating the military field wastewater with an adsorption/coagulation/filtration process and to determine the suitable types of carbons and polymers to be used, the optimum chemical dosages, and the optimum operational conditions.

Experimental materials, apparatus, analytical methods, and test procedures are fully described in this section. All experimental results are reported and discussed in the next section, RESULTS OF LABORATORY OPTIMIZATION STUDIES AND PRELIMINARY FULL SCALE PLANT OPERATION.

4.1 Materials Used

4.1.a Synthetic Wastewater Preparation

Synthetic wastewater was prepared with tap water, biodegradable laundry detergent, automatic dishwasher detergent, military bar soap, Bentonite clay, lubricating oil, and canned dog food according to the formulation indicated in Table 2. The sources of these materials are described briefly as follows:

- Tap water -- Laboratory tap water at Calspan Corporation, Buffalo, New York.
- Biodegradable laundry detergent --"Cold Power", manufactured by Colgate-Palmolive Co., New York, New York.
- Automatic dishwasher detergent -- "Cascade, Detergent", manufactured by Proctor & Gamble, Cincinnati, Ohio.
- Military bar soap -- U. S. military bar soap, "Floating Soap", received from the U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia.

TABLE 2

FORMULATION OF SYNTHETIC WASTEWATER

	MATERIALS USED	QUANTITY
F_1	LABORATORY TAP WATER: (CALSPAN CORPORATION)	1000.0 GAL.
F_2	BIODEGRADABLE LAUNDRY DETERGENT: COLD POWER (COLGATE-PALMOLIVE CO.)	2.0 LB.
F_3	DISHWASHER DETERGENT: CASCADE DETERGENT (PROCTER & GAMBLE)	2.0 LB.
F_4	GROUND BAR SOAP: MILITARY SOAP (USAMERDC)	0.3 LB.
F_5	CLAY: BENTONITE SPV (AMERICAN COLLOID CO.)	0.4 LB.
F_6	SAE-10 LUBRICATING OIL: HEAVY DUTY (HD) OIL (PENN. CORP.)	0.1 LB.
F_7	CANNED DOG FOOD: BLUE RIBBON RECIPE (RIVAL PET FOODS)	3.7 LB.

- Clay -- Powdered Volclay Bentonite SPV supplied by American Colloid Company, Skokie, Illinois.
- Lubricating Oil -- Heavy Duty (HD) oil, Grade SAE-10 supplied by Penn Corporation, Butler, Pennsylvania.
- Canned dog food -- Blue Ribbon Recipe (balanced and complete nutrition), packaged by Rival Pet Foods, A Division of Associated Products, Inc., Bridgeview, Illinois.

4.1.b Powdered Activated Carbons

Six powdered activated carbons evaluated in this program were Hydrodarco H, Hydrodarco C, Darco S-51, Darco KB, Nuchar A, and Nuchar C-190N. Hydrodarco and Darco carbons were received from ICI America, Inc., Wilmington, Delaware; while Nuchar carbons were received from Westvaco, Covington, Virginia.

4.1.c Organic Coagulants

Fifteen organic coagulants (or flocculants) were evaluated and scrutinized in this program. Hercofloc 832.1, Hercofloc 829, Hercofloc 813, Hercofloc 824, Hercofloc 817, Hercofloc 833, and Hercofloc 819 were supplied by Hercules Incorporated, Environmental Services Division, 910 Market Street, Wilmington, Delaware. Arquad 2HT-75 and Arquad 18-50 were supplied by Armak Chemicals Division, 300 South Wacker Drive, Chicago, Illinois. WT-2870, Cat-Floc and Cat-Floc B were manufactured by Calgon Corporation (Subsidiary of Merck & Co., Inc.), 101 Inwood Drive, Syracuse, New York. Nalcolyte 607 was received from Nalco Chemical Company, Industrial Division, 354-B Waverly St., Framingham, Mass. Natron 88 was received from National Starch and Chemical

Corporation, 750 Third Ave., New York, N. Y. Another organic coagulant, Swift X-100, was provided by Swift Chemical Co., 115 W. Jackson Blvd., Chicago, Ill.

4.1.d Filter Media and Filter Aid

Whatman No. 3 filter paper, made in England by W & R Balston Ltd., was used as the filter medium for most of the laboratory tests. It is a thick, medium speed paper with high retention.

A simulated laboratory-scale diatomite filter was constructed of a rubber screen and a layer of uniformly precoated filter aid. The rubber screen and the filter aid used in this program were actual filter sleeve and diatomaceous earth (Celite 545) used in the Army standard water purification unit (described in Army Report TM-5-4610-208-14). Both materials were supplied by the USAMERDC.

4.1.e Other Chemical Reagents and Standards

Sodium hydroxide and sulfuric acid solutions in appropriate concentrations (1N. and 0.1 N.) were used for the pH adjustment. Both chemicals used were reagent grade.

Reference standards for total organic carbon (TOC) analysis were received from the U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268.

4.2 Analytical Methods and Apparatus Used (Figures 3, 4-a and 4-b)

The turbidity of samples was measured by a Delta Scientific Model 260 Water Analyzer, manufactured and distributed by Delta Scientific Corporation, Lindenhurst, N. Y. (Ref. 96).

FIGURE 3. ORGANIC CARBON ANALYZER

FIGURE 4-a.

DELTA PHOTOMETER, Model 260

To assure maximum accuracy, each instrument is individually calibrated and the tests cells are optically ground and polished. A clear, step-by-step Procedure Handbook is provided with each instrument. The tests require only a minimum of ordinary labware such as beakers, pipets, etc.

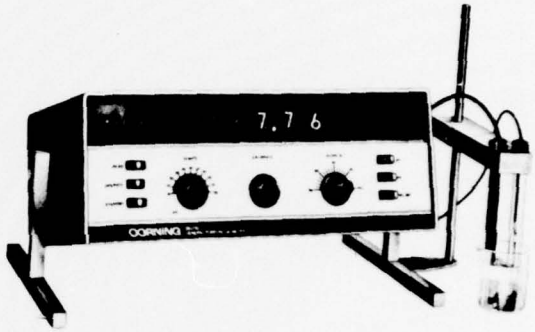

FIGURE 4-b.

CORNING DIGITAL pH METER, Model 111

A versatile instrument with electronic digital display system, for pH or millivolt measurements. Reads directly from pH 0.00 to pH 14.00, to nearest 0.01 pH, and from -1800 to +1800 mv, to nearest 1 mv.

pH was measured by a Corning Digital 111 General Purpose pH Meter, manufactured by Corning Scientific Instruments, Medfield, Mass., according to Standard Methods (Ref. 94).

Total carbon (TC) and total inorganic carbon (TIC) were analyzed following the methods and procedures given by the U. S. Environmental Protection Agency (Ref. 95). A Beckman Model 915 Total Organic Carbon Analyzer was used to analyze TC and TIC. The TC reading substracted by the TIC reading gives the total organic carbon (TOC) reading.

4.3 Experimental Apparatus (Figures 5-a and 5-b)

An Osterizer blender and a Lightnin mixer (Model 10, manufactured by Mixing Equipment Co., Rochester, N. Y.) were used for the preparation of synthetic wastewater.

All mixing and flocculation operations, except that for the wastewater temperature studies, were stirred with a Six-Unit Multiple Stirring Apparatus, manufactured by Phipps & Bird, Inc., Richmond, Virginia.

For the investigations of temperature effect on carbon adsorption and coagulation, the test samples were stirred magnetically with a Corning Stirrer-Hot-Plate, distributed by Arthur H. Thomas Co., Philadelphia, Pa.

The filtration unit used in general tests consisted of a seamless Buchner funnel (4 inches I.D., porcelain), a filtering flask, and a vacuum pump. A piece of Whatman No. 3 filter paper was placed in the Buchner funnel as the filter medium.

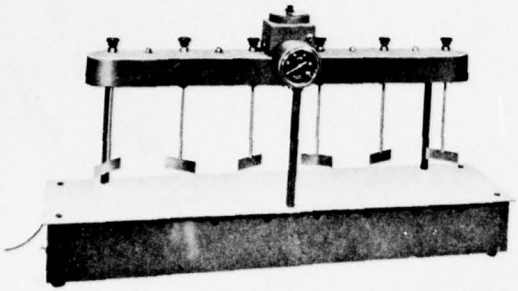

FIGURE 5-a.
MULTIPLE STIRRING APPARATUS
Phipps & Bird

Variable transformer provides speeds from 10 to 100 rpm. Stirrers are driven by 1/30 hp universal motor with gear train. Entire unit is mounted in elongated, cast aluminum housing, supported 9-1/2 inches above bench on three posts. Tachometer on front has 3-inch dial reading from 0 to 100 rpm in 20 divisions.

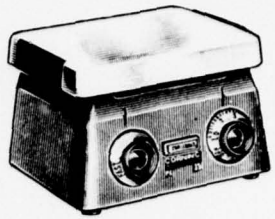

FIGURE 5-b.
MAGNETIC STIRRER-HOT PLATE
Corning PC-351

Temperature adjustable up to 520°C; stirring speed variable from approximately 250 to 1000 rpm. Glazed white 5 X 7 inch top plate is as corrosion-resistant as glass. Spilled or spattered materials can be easily wiped away to preserve the original fine appearance of the unit.

For the diatomite filtration experiments, the same vacuum filtration assembly as described in the last paragraph was used. However, the rubber screen and the precoated diatomaceous earth described in Section 4.1.d were substituted as filter medium in place of the filter paper. The amount of diatomaceous earth precoated was 0.1 lb per sq. ft.

4.4 Experimental Procedures

4.4.a Preparation of Synthetic Wastewater Samples

According to the formulation of synthetic wastewater listed in Table 2, the measured amounts of canned dog food, SAE-10 lubricating oil, and clay were first thoroughly mixed with one liter of tap water in an Osterizer blender at the fastest speed for about two minutes. This one-liter mixture was then transferred to a twenty-five-liter glass bottle containing nineteen liters of tap water and the measured amounts of laundry detergent, dishwasher detergent, and ground bar soap. The overall twenty-liters of mixture in the big glass bottle was again mixed with a Lightnin mixer at the fastest speed for at least 15 minutes. The final liquid solution/suspension mixture was used as the synthetic wastewater for the laboratory experiments.

For certain experiments, initial pH adjustment or initial temperature adjustment to the synthetic wastewater was required. pH adjustment for the initial synthetic wastewater sample was made by adding either sulfuric acid solution or sodium hydroxide solution to the wastewater sample which was continuously mixed with a magnetic stirrer and continuously monitored with a pH meter until the desired pH value was reached. The

temperature adjustments for the wastewater samples were made simply by keeping the samples in a freezer, a refrigerator, a room, and a Corning Stirrer-Hot-Plate for an appropriate period of time before conducting the temperature effect studies.

4.4.b Preparation of Organic Coagulants

Care must be taken for the preparation of organic coagulants. In general, the polymer solutions were prepared with distilled water in accordance with procedures provided in the manufacturer's technical bulletins (Refs. 97 to 100).

4.4.c Polymer Coagulation Experiments

Synthetic wastewater and coagulant solutions were prepared following the methods described in Sections 4.4.a and 4.4.b, respectively. For each coagulation test, one liter of the prepared synthetic wastewater was placed in a one-liter glass beaker. The prepared coagulant solution of specified volume was pipetted to the beaker containing the wastewater sample. The mixture was stirred with a jar-test apparatus (i.e., Six Unit Multiple Stirring Apparatus) at 100 RPM for one minute, and subsequently flocculated at 20 RPM for 10 minutes. The flocculated sample was allowed to stand undisturbed for 60 minutes. Thirty ml of the settled liquid sample (supernatant) was then taken near the middle of the one-liter beaker and analyzed for its turbidity and total organic carbon, as required.

4.4.d Carbon Adsorption Experiments

For each test, one liter of the prepared synthetic wastewater was placed in a one-liter glass beaker. Powdered activated carbon of

specified quantity was then added to the synthetic wastewater sample, and thoroughly mixed with a jar-test apparatus, or a Corning Stirrer-Hot-Plate, at the fastest speed for a specific contact time. The mixed sample was immediately filtered with a Whatman No. 3 filter paper. Finally the filtrate was analyzed for its percent transmittance, turbidity and total organic carbon.

4.4.e Adsorption/Coagulation Experiments

Synthetic wastewater and coagulant solutions were prepared following the methods described in Sections 4.4.a and 4.4.b, respectively. For each adsorption/coagulation test, powdered activated carbon and organic coagulant of specific quantities were added to and rapidly mixed with one liter of the prepared synthetic wastewater in a desired order. The mixture of wastewater, carbon and polymer was continuously and rapidly mixed with a stirrer at a fast speed ($\backsim$100 RPM) for a specific mixing time, then gently stirred with the same stirrer at about 20 RPM for a specific flocculation time. Finally, the flocculated sample was allowed to stand undisturbed for a selected period of settling time. 30 ml of the settled liquid sample (supernatant) was then taken near the middle of the one-liter beaker and analyzed for its percent transmittance, turbidity and total organic carbon.

4.4.f Adsorption/Coagulation/Filtration Experiments

The same procedures described in Section 4.4.e were followed. The mixed, flocculated and settled liquid sample was then filtered with a vacuum filtration unit described in Section 4.3. The filtrate was finally analyzed for its percent transmittance, turbidity and total organic carbon.

5.0 RESULTS AND DISCUSSIONS OF LABORATORY OPTIMIZATION STUDIES AND PRELIMINARY FULL SCALE PLANT OPERATION

5.1 General Description of Research Approach

The proposed treatment system for the removal of dissolved and suspended pollutants from the field military wastewater consists of powdered carbon adsorption, polymer coagulation and diatomite filtration. The specific research task for the period of April 16 through June 15, 1973 was aimed at studying the mechanisms and controlling parameters of the proposed treatment system, demonstrating the system's feasibility for treating military wastewater, and concurrently selecting the suitable types and dosages of chemicals to be used in the treatment system.

First of all, the capabilities of carbon adsorption, polymer coagulation, and filtration for treating the target wastewater were researched with several specific questions in mind: (1) Can any one of these three unit processes satisfactorily treat the field military wastewater? (2) If not, do we need all three unit processes to achieve our treatment goal? and (3) What will the order of these unit processes be arranged in series in the proposed treatment system?

Based on the preliminary investigation data, the aforementioned questions were partially answered, and the processing mechanisms of the adsorption/coagulation/filtration system were hypothetically established.

Detailed laboratory experiments were then conducted to demonstrate the proposed processing mechanisms, to optimize the controlling parameters of the proposed treatment system, and to select the suitable types and amounts of chemicals to be used in the system.

Finally, the feasibility of the proposed treatment system was confirmed by both laboratory jar tests and full-scale plant operation.

5.2 Preliminary Investigations

5.2.a Polymer Coagulation without Powdered Carbon

Experiments of polymer coagulation (involving no addition of powdered activated carbon) were conducted according to the procedures described in Section 4.4.c.

A cationic polyelectrolyte, Cat-Floc, was first selected as primary coagulant for the treatment of synthetic wastewater which was described in Sections 4.1.a and 4.4.a. Results in Appendix V indicate that as the Cat-Floc dosage is increased from 0 to 100 ppm, the residual turbidity of coagulated water decreases toward a minimum point at optimum Cat-Floc dosage, then increases as the optimum polymer dosage is exceeded. About 75% to 85% of turbidity in the synthetic wastewater can be removed by this cationic polymer coagulation at a pH range of 9.4 to 11.0.

Total organic carbon (TOC) data in Appendix V are scattered due to the suspended matter of various sizes in the coagulated wastewater samples and due to the needle sampling technique used in TOC analysis. Nevertheless, the TOC data demonstrate that the cationic Cat-Floc is incapable of removing organic matter from the target wastewater if no other coagulant aid is added to the treatment unit. Over the wide pH range and the wide polymer dosage range investigated, the lowest TOC result (obtained at pH = 9.4 and Cat-Floc dosage = 50 ppm) was 64 ppm which is considered to be unsatisfactory.

Additional polymer coagulation tests were conducted by the same test procedures except using a nonionic polymer (Hercofloc 824) and an anionic polymer (Hercofloc 819) as primary coagulants. Systematic investigations with these two polymers were conducted at five different polymer dosages ranging from 0 to 100 ppm and at four different initial pH conditions ranging from 3 to 11. The coagulated samples from all tests were found to be extremely turbid. Therefore, no effort was made to analyze these treated samples in order to obtain quantitative but negative data.

The synthetic wastewater contains mainly anionic surfactants and other negatively charged colloids. In the coagulation process, these negatively charged colloids and solutes are required to be neutralized so that their charge is not strong enough to prevent particle collisions and floc formation. When the nonionic and anionic polymers were used as primary coagulants for the wastewater treatment, the negative surface charge on the polluted particles and colloids could not be neutralized. Thus, these negative charges repelled each other; and poor coagulation performance resulted.

When cationic polymer, Cat-Floc, was added to the wastewater treatment unit as primary coagulant, the negative surface charge on the pollutants was nearly neutralized at the optimum Cat-Floc dosage. Those neutralized particles which were close together thus agglomerated by the so called Vander Wall's attraction. The bridging mechanism of the polymer further brought two or more neutralized particles together to become flocs. At optimum Cat-Floc dosage, the residual turbidity of the treated water was reduced when the flocs settled (Appendix V). The performance of this cationic polymer coagulation, however, was seriously affected and limited by the high concentrations of detergents in the wastewater. Apparently, the negatively-charged detergent solutes (Note: not particles) could not form flocs even after they were neutralized by the positively-charged Cat-Floc.

The remedy for improving cationic polymer coagulation is the addition of an appropriate coagulation aid, such as clay or adsorbent. Adding powdered activated carbon certainly would serve such purpose.

5.2.b Powdered Carbon Adsorption without Polymer

It is well-known that activated carbon is an excellent adsorbent for removing detergents (Ref. 103) and many other dissolved organics from water. Nevertheless, the most suitable type of powdered carbon for removing the specific types of dissolved pollutants in the field military wastewater should be selected through research.

Preliminary carbon adsorption experiments were conducted using six different powdered carbons and following the test procedures outlined in Section 4.4.d. Each carbon was tested for its ability to treat the synthetic wastewater at six different carbon dosages ranging from 0 to 1,200 mg/l. The adsorption tests were run at room temperature for one hour with mixing. The filtrate TOC of carbon-treated samples are reported in Table 3, where the low remaining filtrate TOC is interpreted as high dissolved organic removal.

It is seen from Table 3 that of six carbons evaluated for treating the synthetic wastewater without pH adjustment, Nuchar C-190N, Nuchar A, Darco KB, Hydrodarco C, and Darco S-51 have excellent or fair adsorption capabilities for treating the target wastewater. The feasibility of using powdered carbon to adsorb the dissolved organics from the wastewater is thus confirmed.

Powdered carbon, however, is incapable of removing suspended pollutants. In fact, the spent powdered carbon itself is suspended matter which has to be removed by one of several liquid-solid separation methods, such as coagulation (Refs. 3-21, 24 and 27), flotation (Refs. 22 and 26), or filtration (Refs. 23-25). Coagulation is the conventional method for the removal of spent carbons.

Using powdered carbons in conjunction with polymer coagulation for treating the wastewater would have the following advantages:

1. Dissolved organic solutes, such as detergents, could be removed by the powdered carbon, and would not affect the performance of polymer coagulation;

2. The spent powdered carbon could act as a nucleus for causing and/or enhancing the floc formation; and

3. The spent powdered carbon could act as a weighting agent for increasing the floc's settling rate.

TABLE 3

REMOVAL OF DISSOLVED POLLUTANTS FROM SYNTHETIC WASTEWATER BY VARIOUS POWDERED ACTIVATED CARBONS AT VARIOUS CARBON DOSAGES

CARBON DOSAGE mg/l	TOTAL ORGANIC CARBON (TOC) OF FILTRATE, mg/l					
	Darco KB	Darco S-51	Hydrodarco H	Hydrodarco C	Nuchar C-190N	Nuchar A
0	75.0	75.0	75.0	75.0	75.0	75.0
200	46.5	53.5	63.2	57.0	42.0	46.5
450	27.0	40.5	49.0	42.0	27.5	29.0
700	18.0	33.0	40.5	29.2	16.0	20.5
950	14.5	23.0	36.0	20.0	11.0	14.0
1200	12.5	18.5	33.2	14.2	8.5	12.5

EXPERIMENTAL CONDITIONS:

NO pH ADJUSTMENT; ROOM TEMPERATURE; ONE HOUR MIXING.

INITIAL TOC WITHOUT FILTRATION 165 mg/l

5.2.e Filtration

A simple vacuum filtration test was conducted to determine the upper limit of organic removal that could be achieved by filtration alone. A synthetic wastewater having an initial TOC of 114 ppm was filtered through a 0.45 micron Millipore filter paper. The residual TOC of the filtrate was analyzed to be 36 ppm. In other words, the suspended organic matter in the synthetic wastewater is about 68.5% in terms of TOC. Since the porosity of the diatomaceous earth layer in a diatomite filter is much coarser than 0.45 micron, the TOC removal would be lower than 68.5% if the wastewater is simply physically filtered with a diatomite filtration unit.

Diatomite filtration is conventionally used for the separation of trace suspended matter from low turbidity water. When the powdered carbon is used for the dissolved organics removal, the majority of spent powdered carbons can be logically removed by polymer coagulation or its equivalent; and the trace amount of residual spent carbon, as well as suspended pollutants, are expected to be removed by diatomite filtration. Besides, a certain amount of excess polyelectrolyte could precoat the diatomite filter, thereby allowing further polishing of the final treated effluent.

Five tentative conclusions can be drawn from the preliminary investigations:

1. If no carbon is added to the synthetic wastewater, even at appropriate pH condition and optimum cationic polymer dosage, the polymer coagulation can achieve turbidity removal only to a limited degree, and cannot achieve a satisfactory TOC removal.

2. With or without the pH adjustment to the wastewater, neither nonionic polymer nor anionic polymer is suitable for use as primary coagulant for the clarification of detergent-type wastewater if no carbon and/or other chemicals are added to the polymer coagulation system.

3. Certain powdered activated carbons can effectively remove the specific types of dissolved pollutants from the target field military wastewater; however, the powdered carbon is incapable of removing any suspended pollutants. The spent powdered carbon, as well as the suspended pollutants, should be separated from water by an effective liquid-solid separation process or system.

4. Membrane filtration (with 0.45 micron Millipore filter paper) can remove almost all suspended organics from the synthetic wastewater. The suspended organics which can be physically filtered out, however, only represent 68.5% of TOC in the synthetic wastewater. Since the porosity of the precoated diatomaceous earth layer in a diatomite filter is much coarser than 0.45 micron, it is expected that a 68.5% TOC removal would be the upper limit which a diatomite filter can achieve.

5. None of the carbon adsorption, polymer coagulation, and diatomite filtration processes alone can adequately treat the field military wastewater. However, the combination of all three unit processes in an optimized arrangement and operation would satisfactorily purify the wastewater.

5.3 Mechanisms of Adsorption/Coagulation/Filtration Treatment System

The capabilities of polymer coagulation, powdered carbon adsorption, and filtration for treating the field military wastewater have been preliminarily evaluated in Section 5.2. Although none of the three unit processes alone can treat the wastewater, the combination of the three, in optimum arrangement and operation, was expected to be effective and will produce an acceptable effluent.

The removal of dissolved and suspended pollutants from the wastewater by the proposed adsorption/coagulation/filtration treatment system can be generally divided into the following six steps:

1. Transport of the dissolved and colloidal pollutants (i.e., adsorbates) to the exterior surface of the powdered activated carbon (i.e., adsorbent) by mixing and diffusion.

2. Adhesion of the dissolved and colloidal pollutants on the exterior and the interior surfaces of the powdered activated carbon by physical adsorption, chemical adsorption, and electrostatic adsorption.

3. Destabilization and agglomeration of the spent powdered carbons and the residual colloidal particles by the addition of primary coagulant (and coagulant aid, if necessary) to the wastewater and carbon mixture. Mutual repulsion by electrostatic surface charges of the solid particles (i.e., the Zeta potential) is initially counteracted by charge neutralization, so that the Van der Waal forces (i.e., the inherent cohesive forces) will cause the spent carbons and the residual colloidal particles to adhere to the coagulant (i.e., polymer) and agglomerate.

4. Bridging of two or more small destabilized particles at active sites of the polymer's huge and long molecule to effect flocculation (i.e.,floc formation with gentle mixing).

5. Settling of the heavy carbon-pollutants-polymer agglomerates by gravity in a clarifier.

6. Removal of residual fine suspended pollutants and spent carbons from the clarified supernatant by filtration.

The above tentative mechanisms for the adsorption/coagulation/filtration system suggest that the adsorption of dissolved pollutants on powdered carbon should take place first; the coagulation and settling of most of spent carbons and suspended pollutants should take place next; and the filtration of residual fine suspended matter from the clarified water would be considered to be final polishing. Therefore, the order of the three unit processes in the proposed treatment system would be adsorption, coagulation, and filtration. This proposed treatment order is further confirmed by the experimental data presented in the subsequent sections. The mechanisms and controlling parameters of carbon adsorption, polymer coagulation, and diatomite filtration were investigated and discussed in Sections 5.4-5.7, Sections 5.8-5.9, and Section 5.9, respectively.

5.4 Carbon Dosage, Adsorption Capacity, and Adsorption Isotherm

Hydrodarco H, Hydrodarco C, Darco S-51, Darco KB, Nuchar A, and Nuchar C-190N were the six powdered activated carbons evaluated in this program. All carbon adsorption experiments (Sections 5.4-5.7) were conducted in accordance with the procedures outlined in Section 4.4.d.

Original evaluation data in Table 3 are also illustrated in Figure 6 for ease of comparison and for economic dosage selection. The figure clearly shows that at any carbon dosage (except zero ppm), Nuchar C190-N is always most effective; Darco KB and Nuchar A are the second best; Hydrodarco C and Darco S-51 are the third best; and Hydrodarco H is the worst, provided that the synthetic military wastewater is treated without pH adjustment (Initial pH = 9.4).

Activated carbon is known to be technically feasible for adsorbing organic pollutants from an aqueous solution; theoretically the higher the carbon dosage, the higher will be the percent organic removal. Nevertheless for a specific type of carbon, there will be a dosage beyond which the increase in organic removal becomes insignificant with further increases in carbon. Figure 6 shows that 750 ppm seems to be the most economical carbon dosage for Nuchar C-190N, Darco KB, Nuchar A and Hydrodarco H. Darco S-51 and Hydrodarco C, however, can be dosed higher than 750 ppm and still significantly reduce the residual TOC of the treated water.

The adsorbability of carbon (i.e., the adsorbent) is termed adsorption capacity having a unit of:

Gram Adsorbate Removed/Gram Adsorbent Used

The adsorption capacity of a specific adsorbent relative to a specific adsorbate is a function of the adsorption contact time (i.e., mixing time) between carbon and wastewater, the initial pH condition of wastewater, the temperature of the wastewater, and the foreign constituents present in the

wastewater. A term, ultimate adsorption capacity, is generally used if a sufficiently long contact time is maintained (assuming all other conditions are held constant) so that the adsorbent's adsorption capacity can reach its steady equilibrium state. It should be noted that whenever the ultimate adsorption capacity of a specific adsorbent relative to a specific adsorbate is stated, all processing conditions except the contact time must be specified. The ultimate adsorption capacity of the carbon for uptake if dissolved pollutants determines, to a large extent, the useful life of the carbon. However, practical environmentalists prefer to compare the adsorbabilities of powdered carbons on the basis of their utilized adsorption capacities at a contact time of about one hour. This is due to the fact that the one-hour utilized adsorption capacity of powdered carbon is practically close to the carbon's ultimate adsorption capacity. Thus, most waste wreatment plants control the retention time of their powdered carbon reactors to be equal to or less than one hour.

All powdered carbon adsorption tests in this program were conducted at a mixing period equal to or less than one hour. The utilized adsorption capacity of exactly one hour mixing is used to select the suitable powdered carbons to be used in the proposed adsorption/coagulation/filtration system. The plots of utilized adsorption capacity versus the remaining TOC of treated sample, shown in Figure 7, are termed adsorption isotherms. For a desired residual TOC of 20 ppm, the six carbons evaluated are listed below in order of decreasing adsorption capacity if no pH adjustment is made: Nuchar C-190N, Darco KB, Nuchar A, Hydrodarco C, Darco S-51, and Hydrodarco H.

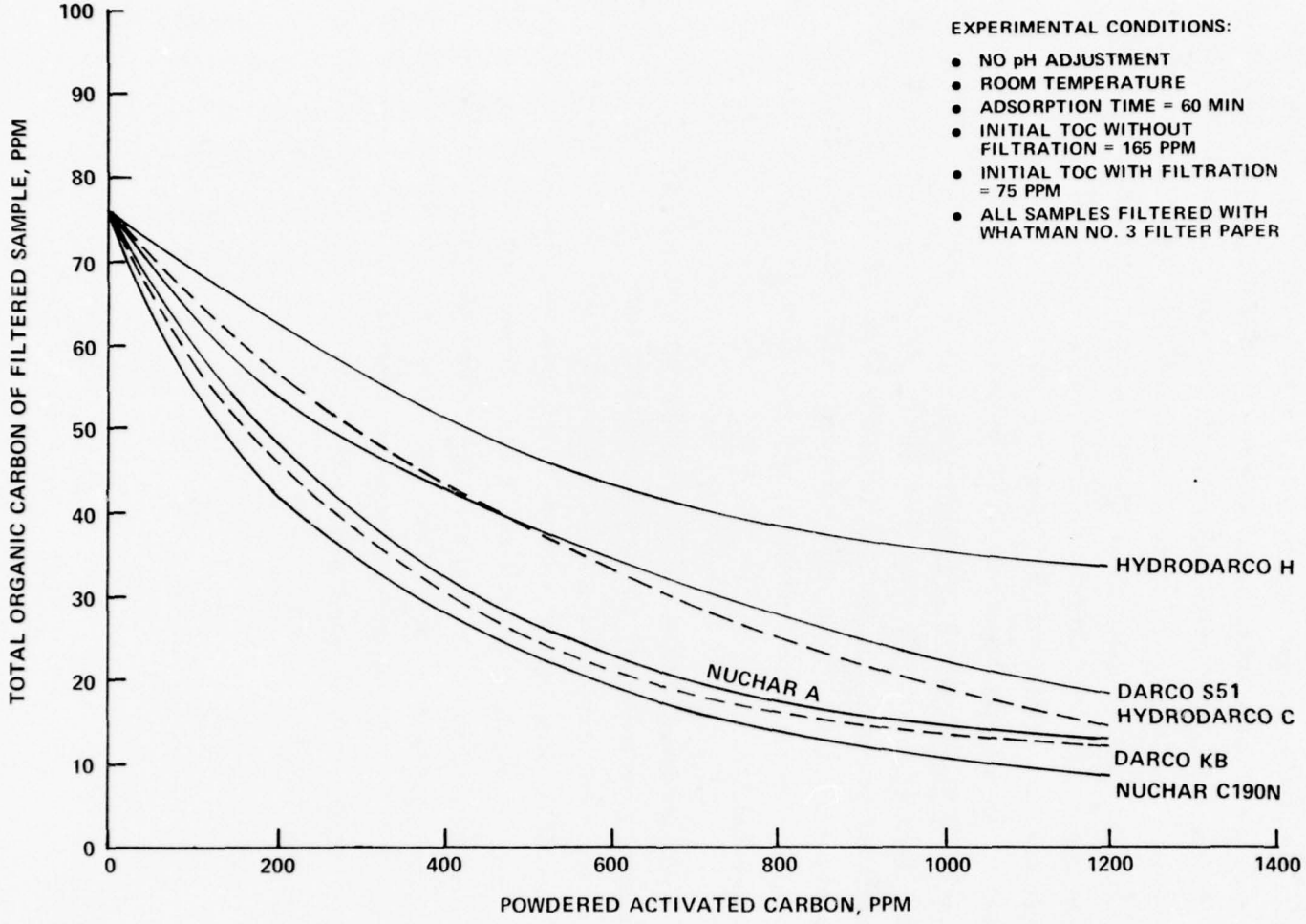

Figure 6 REMOVAL OF DISSOLVED ORGANICS FROM SYNTHETIC WASTEWATER BY VARIOUS CARBONS AT VARIOUS CARBON DOSAGES

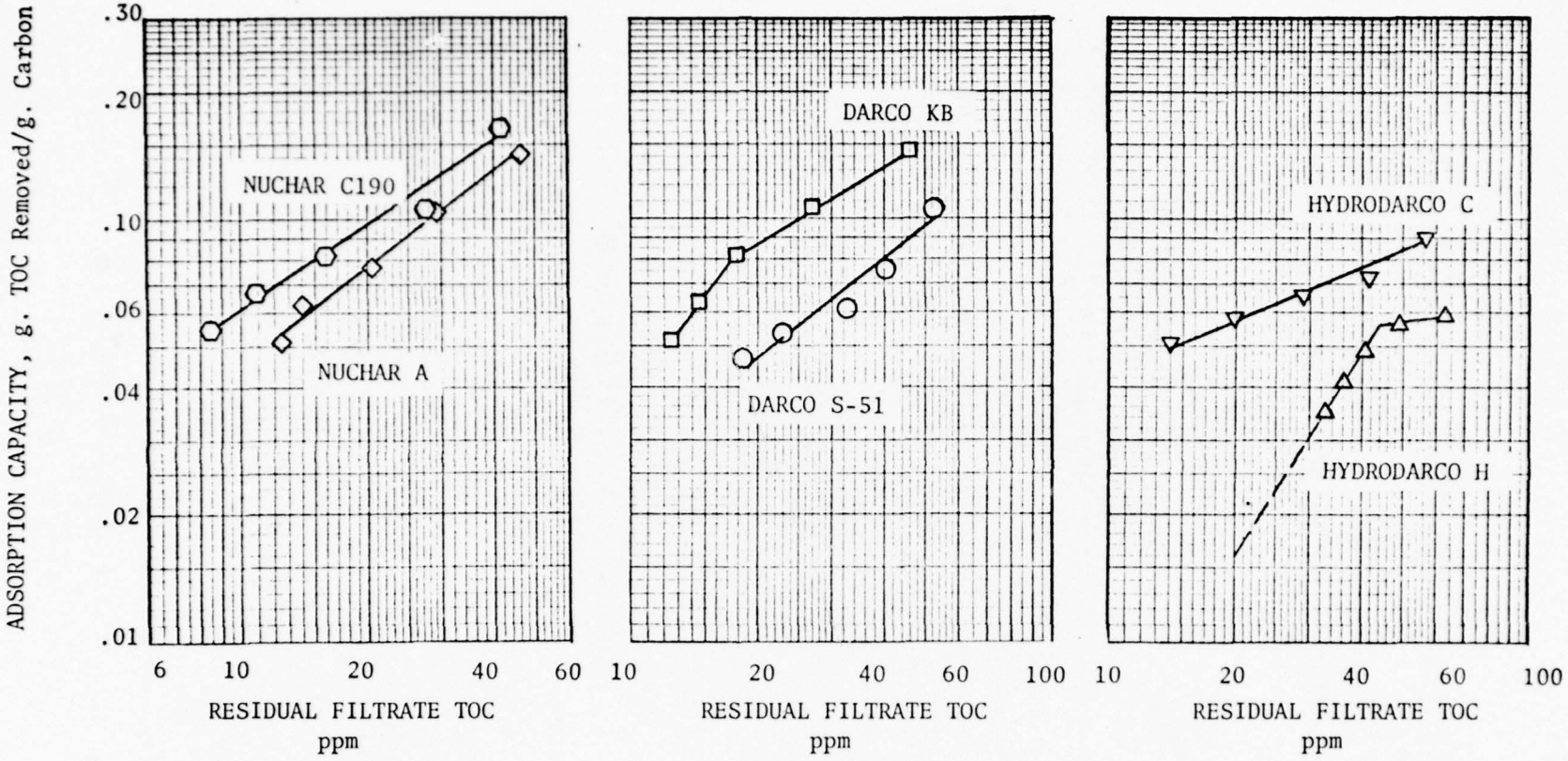

FIGURE 7. ADSORPTION ISOTHERM

(Experimental Conditions: No pH Adjustment; Room Temperature; Adsorption Time = 60 min; Initial TOC without Filtration = 165 ppm; Initial Filtrate TOC = 75 ppm; All Treated Samples Filtered with Whatman No. 3 Filter)

5.5 Contact Time, Wastewater Temperature, and Adsorption Rate

The tentative carbon dosage of 750 ppm given in the previous section was selected for the remainder of the carbon adsorption experiments.

Two powdered activated carbons, Nuchar A and Darco S-51, were used to determine the effect of contact time on carbon adsorption at various pH conditions. Figures 8 and 9 show the remaining filtrate TOC of the Nuchar A system and the Darco S-51 system, respectively. Additional related turbidity data can be found from Tables 4 and 5. Both figures and both tables demonstrate that at least 5 minutes retention is required for the powdered carbon adsorption under any pH conditions. Although the longer the retention time the better, 15 to 20 minutes of adsorption contact time will generally give satisfactory adsorption results (i.e., the utilized adsorption capacity is close to the ultimate adsorption capacity at a specific pH condition).

The aforementioned contact time studies were conducted at four different pH conditions with two different carbons, and at room temperature. Further contact time studies were conducted with 750 ppm of Darco S-51, at an initial pH of 9.4 (i.e., no pH adjustment), and under four different wastewater temperatures, 35, 45, 72, and 110 degrees Fahrenheit. The test data are listed in Table 6 and partially illustrated in Figure 10. As shown in the table and the figure, decreasing the wastewater temperature does not significantly affect the carbon adsorption capacity if about 70 minutes of adsorption contact time can be maintained. However, the required contact time for a desired utilized adsorption capacity increases significantly with decreasing wastewater temperature. Figure 10 shows that if the desired remaining TOC is 45 ppm (i.e., the desired utilized adsorption capacity = 0.0586 g. TOC/g. carbon), the required adsorption contact time will be 5 minutes at $110^{o}F$, 15 minutes at $72^{o}F$, 40 minutes at $45^{o}F$, and 50 minutes at $35^{o}F$, provided that the initial pH of the wastewater is 9.4 (i.e., no pH adjustment).

It is then clear that the required contact time for carbon adsorption is governed mainly by the wastewater temperature, not by the initial pH of the wastewater. Scientifically speaking, carbon adsorption rate is governed by the wastewater temperature, and carbon adsorption capacity is governed by the initial pH of wastewater.

Four tentative conclusions relative to adsorption contact time and adsorption rate are drawn in this section:

1. At room temperature ($72 \pm 5^{o}F$) and optimum carbon dosage (750 ppm of Nuchar A or Darco S-51), adsorption of dissolved organics from wastewater would require a contact time of at least 5 minutes, or a sufficient contact time of 20 minutes.

2. Initial pH of wastewater has little or no effect on the required contact time or on the relative adsorption rate.

3. If an adsorption contact time of about 70 minutes is maintained, decreasing the wastewater temperature results in an insignificant decrease in the carbon's utilized adsorption capacity.

4. When the carbon-wastewater contact time is as short as 5 minutes, the available adsorption capacity (for a specific pH condition) can be almost fully utilized at $110^{o}F$, but only about 50% utilized at $35^{o}F$. The remedy for using the carbon adsorption process in cold weather areas is simply to increase the carbon-wastewater contact time, because the longer the contact time, the higher the fraction of available adsorption capacity that can be used for pollution control.

TABLE 4

EFFECT OF CONTACT TIME ON CARBON ADSORPTION
OF DISSOLVED ORGANICS FROM SYNTHETIC WASTEWATER
(750 PPM OF NUCHAR A)

CONTACT TIME minutes	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF CARBON-TREATED AND FILTERED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
2	27.5	30.0	25	36.0	--	--	--	--
3	--	--	--	--	21	47.0	23.5	54.5
5	15	15.5	21	25.0	19	46.0	22	51.5
10	8	12.0	17	20.0	17	41.0	22.5	46.0
15	6	10.5	15	18.0	15	(42.5)	22.5	45.5
20	5	10.5	12.5	16.0	12.5	35.5	23	45.5
30	4	9.5	12.5	15.0	12	33.0	22	44.0
60	4	9.5	11	12.5	10	28.0	22	42.5

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF NUCHAR A
NO POLYMER; ALL SAMPLES WERE FILTERED WITH WHATMAN NO. 3 PAPER;
INITIAL TOC (FILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 96.5 PPM

TABLE 5

EFFECT OF CONTACT TIME ON CARBON ADSORPTION OF DISSOLVED ORGANICS FROM SYNTHETIC WASTEWATER

(750 PPM OF DARCO S-51)

CONTACT TIME minutes	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF CARBON-TREATED AND FILTERED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
2	34	39.0	30	46.5	--	--	--	--
3	--	--	--	--	27.5	60.5	27	81.5
5	28	28.0	28	36.0	25	56.0	26	73.5
10	23	27.0	26	32.0	24	54.5	24	73.5
15	20	17.0	25	29.5	23	57.0	24	73.5
20	17	19.0	25	27.5	23	47.5	24	73.5
30	12	14.5	22.5	25.0	22	47.0	24	73.0
60	9	14.0	22.0	22.5	23	44.0	26	70.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF DARCO S-51; NO POLYMER; ALL SAMPLES WERE FILTERED WITH WHATMAN NO. 3 PAPER; INITIAL TOC (FILTERED) OF SYNTHETIC WASTEWATERS WITHOUT pH ADJUSTMENT = 96.5 PPM.

TABLE 6

EFFECT OF WATER TEMPERATURE ON CARBON ADSORPTION

CONTACT TIME minutes	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF CARBON-TREATED & FILTERED SAMPLES AT DIFFERENT TEMPERATURES							
	TEMP = 110°F		TEMP = 72°F		TEMP = 45°F		TEMP = 35°F	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
5	22	46.5	30	52.5	32	61.5	32	66.0
10	17	41.0	28	47.0	32	--	35	--
15	14	40.0	25	47.5	34	58.5	33	59.0
30	10	34.0	19	38.5	31	52.0	31	55.0
60	10	30.5	15	33.5	22	(43.0)	28	36.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; 750 PPM OF DARCO S-51; NO POLYMER ADDED. ALL CARBON TREATED SAMPLES WERE FILTERED BY WHATMAN NO. 3 PAPER; NO pH ADJUSTMENT; INITIAL TOC (FILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 96.5 PPM

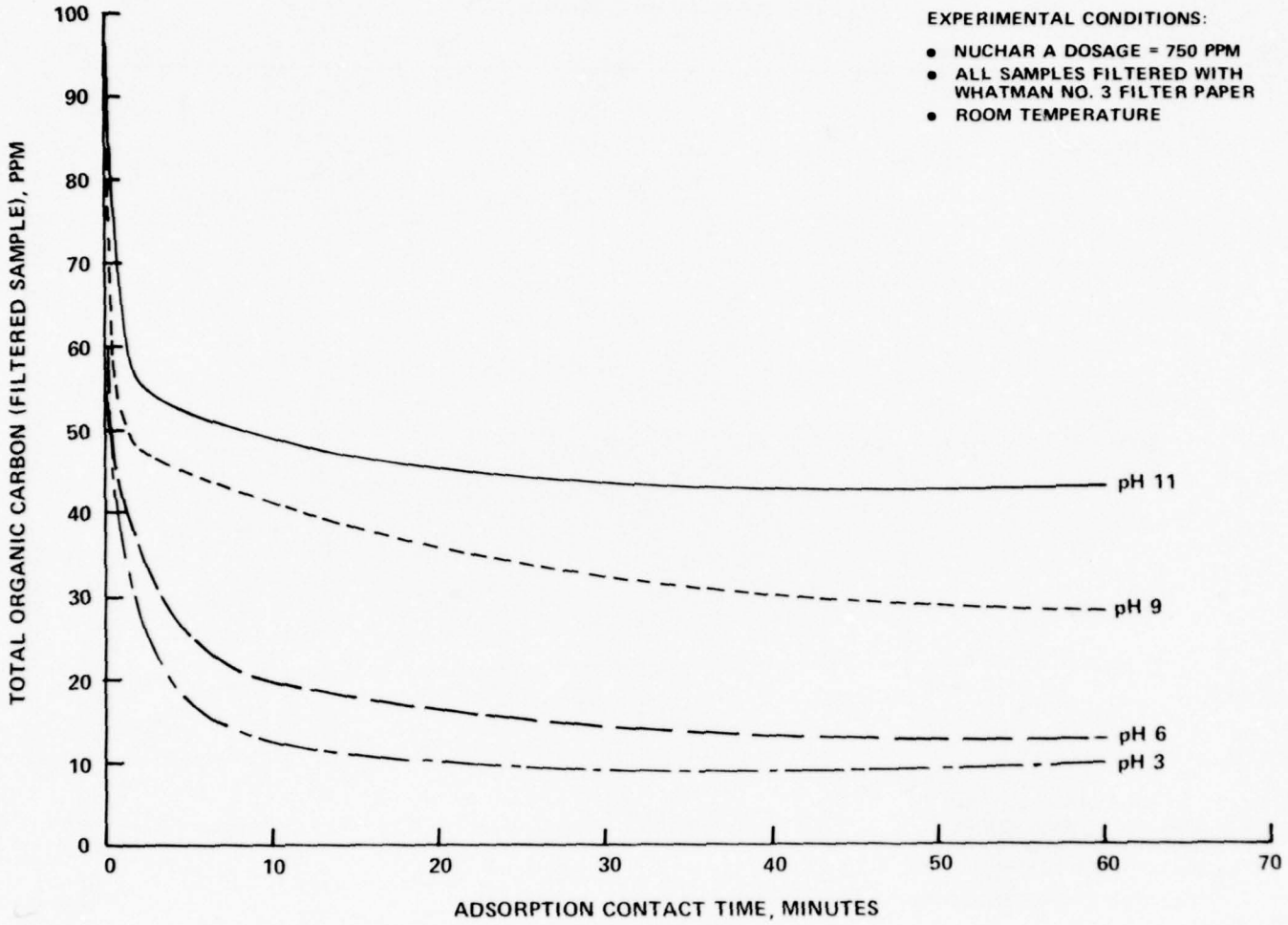

Figure 8 EFFECTS OF pH ADJUSTMENT AND CONTACT TIME ON CARBON ADSORPTION (NUCHAR A SYSTEM)

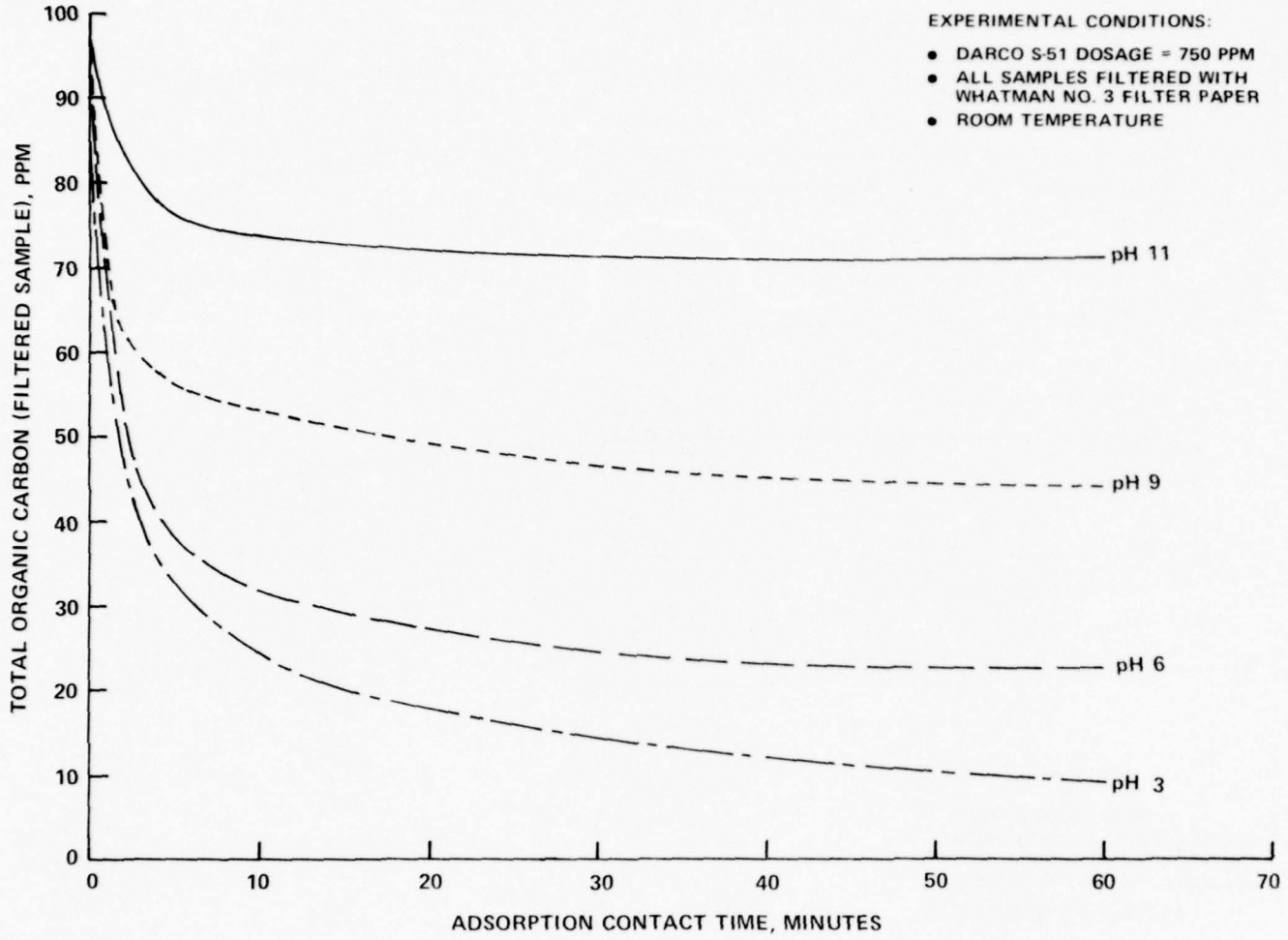

Figure 9 EFFECTS OF pH ADJUSTMENT AND CONTACT TIME ON CARBON ADSORPTION (DARCO S-51 SYSTEM)

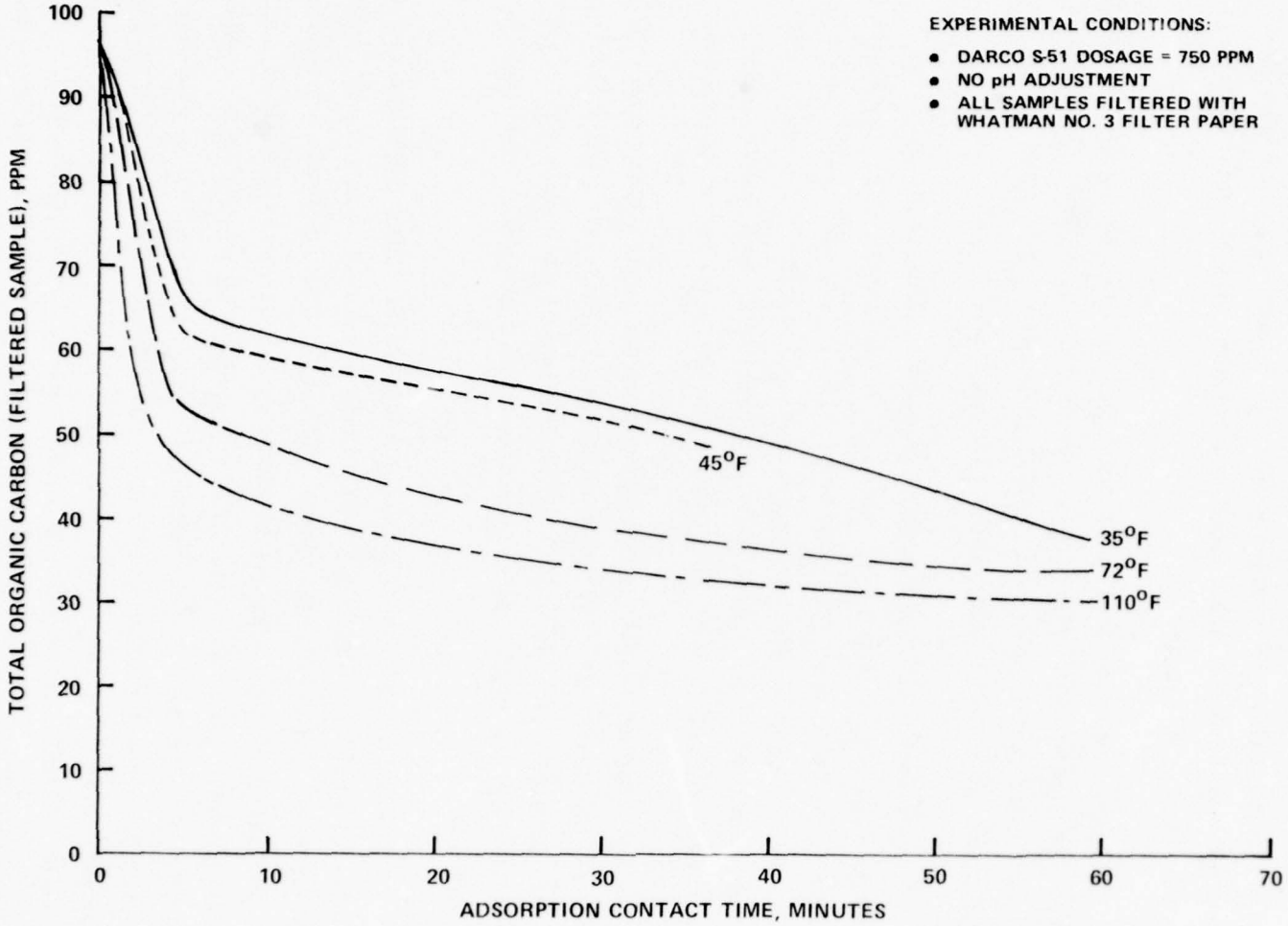

Figure 10 EFFECTS OF WATER TEMPERATURE AND CONTACT TIME ON CARBON ADSORPTION

5.6 Effect of pH Adjustment on Carbon Adsorption

The initial pH of synthetic wastewater was 9.4. Its pH was adjusted with either 0.1 N sodium hydroxide or 0.1 N sulfuric acid for pH adjustment studies.

Figures 8-9 show that decreasing the initial pH of the wastewater will have significant effect on increasing the available adsorption capacities of Nuchar A and Darco S-51. However, the effect of pH adjustment on relative adsorption rate is insignificant.

In addition to Nuchar A and Darco S-51, four other powdered carbons were also evaluated at various pH conditions. It was found from Tables 4, 5 and 7 that the ranking of all six carbons evaluated is as follows, in order of decreasing adsorption capacity: Nuchar C-190N, Nuchar A and Darco KB, Darco S-51, Hydrodarco C, and Hydrodarco H. The two hydrodarco carbons are relatively insensitive to pH adjustment.

The true mechanisms of pH adjustment on carbon adsorption have been researched in 1971 by Calspan personnel (Ref. 104) under an internally funded project (W/A 86-294). The phenomenon of pH adjustment might be explained by the electrical adsorption forces between carbon and the adsorbates.

Activated carbon is generally accepted as being negatively charged (Refs. 105-106). This may be partially due to the presence of carboxyl and hydroxyl groups on the carbon surfaces. The synthetic wastewater investigated in this progrmm is known to contain mainly anionic surface active agents (Section 4.1.a). Decreasing pH by adding acid to the wastewater increases the hydrogen ion concentration, which probably neutralizes the negative charges at the surface of the activated carbon, thereby decreasing the electrical repulsion for anionic surface active species. Diffusion of anionic surfactant to active surfaces of the carbon is then enhanced. However, as the initial pH of the synthetic wastewater (i.e., anionic surfactant solution) was increased by adding alkaline solution, adsorption decreased because of increasing electronegative repulsion.

In summation, the increase in adsorption observed at lower pH's may be due to alterations in the carbon surface, particularly its electrokinetic character, with changing hydrogen-ion concentration.

TABLE 7

REMOVAL OF DISSOLVED POLLUTANTS FROM SYNTHETIC WASTEWATER BY VARIOUS POWDERED ACTIVATED CARBONS AT VARIOUS pH CONDITIONS

INITIAL pH	TOTAL ORGANIC CARBON (TOC) OF FILTRATE, mg/l					
	NO CARBON (0 ppm)	Darco KB (750 ppm)	Hydrodarco H (750 ppm)	Hydrodarco C (750 ppm)	Nuchar C-190N (750 ppm)	Nuchar A (750 ppm)
3	76.0	4.5	27.5	26.5	0.0	4.0
5	82.7	18.6	30.5	23.0	10.0	12.5
7	78.5	24.0	37.5	27.5	13.0	17.4
9	75.0	26.5	47.3	26.5	20.5	28.6
11	75.5	42.5	50.0	34.5	32.5	38.5

EXPERIMENTAL CONDITIONS:

pH ADJUSTED WITH 0.1N SULFURIC ACID OR 0.1N SODIUM HYDROXIDE; ROOM TEMPERATURE; ONE HOUR MIXING; ORIGINAL pH (NO ADJUSTMENT) OF SYNTHETIC WASTEWATER = 9.4;

INITIAL TOTAL ORGANIC CARBON WITHOUT FILTRATION 184 mg/l

5.7 Suitable Types and Dosages of Powdered Activated Carbons

The properties and prices of the six powdered carbons investigated are presented in Table 8. Based on the technical evaluations described in Sections 5.1 to 5.6, these carbons are assessed as follows:

1. Nearly 100% dissolved organics removal can be achieved if 750 ppm of prewetted Nuchar C-190N is dosed to the synthetic wastewater at pH = 3 (Table 7). The major disadvantage of Nuchar C-190N is its low density and poor wettability (Table 8). When Nuchar C-190N is fed in dry powdered form, a significant portion of the unwetted carbon will float on the wastewater surface causing a loss in the available carbon. Nuchar C-190N could be a potential candidate carbon for treating the field military wastewater if a feeder is commercially available or can be developed which has a built-in mixer for rapidly preparing a carbon slurry.

2. Although Darco KB has satisfactory adsorpability for the treatment of field military wastewater at a wide initial pH range (Figure 6 and Table 7), its cost is too high to make it practical (Table 8).

3. Hydrodarco H is the most inexpensive one among all six carbons evaluated (Table 8); however, its poor adsorpability at any pH conditions limits its application (Figure 6 and Table 7).

4. Hydrodarco C is a dense carbon with medium price (Table 8). Due to its insensitivity to changing pH (Table 7), it could be considered as a candidate carbon only if initial pH of wastewater is above 7. However, in most cases, the actual wastewater's pH is lower than 7 (Ref. 2).

5. Nuchar A and Darco S-51 would be the possible candidate powdered carbons for the carbon adsorption/polymer coagulation process regardless of initial pH conditions. Comparing these two carbons, Nuchar A is cheaper (Table 8) and has better adsorpability at variable carbon dosages (Figure 7) and at any pH condition (Table 7) than does Darco S-51; while Darco S-51 is denser and has better wettability (Table 8).

TABLE 8

PROPERTIES AND PRICE INFORMATION OF POWDERED ACTIVATED CARBONS INVESTIGATED

INFORMATION	TYPES OF CARBON					
	Darco KB	Darco S-51	Hydrodarco H	Hydrodarco C	Nuchar C-190N	Nuchar A
TL/CL Price, cents/lb	35.25	16.50	8.00	11.00	17.50	9.50
Origin	Wood	Lignite	Lignite	Lignite	Wood	Wood
Particle Size,						
%-100 mesh	95	95	--	--	80-95	99
%-300 mesh	50	70	75	65	40-65	90
Apparent Density, lb/ft^3	26-32	27-33	30.8	30.8	12.7	15-25
Surface Area, M^2/g	--	--	475	550	841	754
pH	4.5-6.5	5.0-7.0	10.5	10.5	--	--
Molasses RE, dry basis	185	100	40	95	199	80
Water Solubles, %	1.0	1.0	3.5	5.5	--	--
Wettability	Excellent	Excellent	Superior	Superior	Poor	Good

5.8 Evaluation of Various Organic Coagulants Used in Adsorption/Coagulation System

The information of various organic coagulants investigated or assessed in this program are presented in Table 9. Nuchar A, Darco S-51, and Hydrodarco C were further evaluated in the adsorption/coagulation experiments. All tests discussed in this section were conducted following the procedures outlined in Section 4.4.e. Detail experimental conditions are listed in each presented figure or table.

Seven Hercoflocs with different charge conditions were tested first for their feasibility of being used as primary coagulants in treating military wastewater by adsorption/coagulation system. The initial form of an organic coagulant can be either powdered or liquid (Table 9). The coagulant concentrations are expressed as ppm by weight if the organic coagulant was initially in powdered form, and are expressed as ppm by volume if the coagulant was initially in liquid form. Figure 11 and Table 10 indicate that the high cationic Hercofloc 832.1, the medium cationic Hercofloc 829, and the low cationic Hercofloc 813 gave better performance for wastewater clarification at pH = 9 as compared to any anionic or nonionic Hercoflocs.

Anionic Hercofloc 817 and nonionic Hercofloc 824 were further evaluated under different pH conditions. Data in Table 11 indicate that both Hercoflocs are able to produce the coagulated effluents of low TOC (but extremely high turbidity) when no pH adjustment was made (pH = 9.4). They do not function well as primary coagulant at any other pH conditions.

Cationic polymer is, therefore, definitely superior to nonionic and anionic polymers as the primary coagulant for the treatment of field military wastewater. Accordingly, seven other cationic organic coagulants in addition to cationic Hercolfocs were selected for added evaluations (Tables 9 and 12). Of ten cationic organic coagulants tested, Swift X-100, Natron 88, Arquad 18-15 and Arquad 2HT do not perform well as primary coagulant compared to others. (Figures 11 -13, Tables 10 and 12). Hercofloc 832, Hercofloc 829, Hercofloc 813, Nalcolyte 607, Cat-Floc, and Cat-Floc B, however, exhibit different degrees of success in the coagulation (Figures 11-13 and Tables 10 and 12) of synthetic wastewater at pH $\tilde{=}$ 9.

The cationic, liquid-type Cat-Floc was found to be the best polymer compared to other evaluated polymers for treating the synthetic wastewater at pH = 9.4 (Figures 11-15). The Cat-Floc's effective polymer dosage range is wide (Figure 14). At optimum carbon dosage of 750 ppm, the optimum Cat-Floc dosage is always 50 ppm regardless of the types of carbon used (Table 13) and regardless of the initial pH conditions (Table 14).

Three different carbon-polymer combinations were tested under various pH conditions. Experimental results are reported in Tables 14 through 16. It was found that the effect of pH adjustment on adsorption/coagulation is very significant for the Nuchar A/Nalcolyte 607 system (Table 16), somewhat less significant for the Darco S-51/Hercofloc 813 system (Table 15), and very insignificant for the Darco S-51/Cat-Floc system (Table 14, and Figure 14). When the initial pH of wastewater is lower than 7, the Darco S-51/Cat-Floc system cannot compete with the Nuchar A/Nalcolyte 607 system (Tables 14 and 16).

The following are four tentative conclusions drawn in this section:

1. Hercofloc 832 is in liquid form (Table 9), with extremely high viscosity. It works well (Table 10), but is not recommended for use due to the difficulty in polymer feeding.

2. Cat-Floc and Cat-Floc B are similar liquid cationic polymers, both manufactured by Calgon Corp. The latter is cheaper in truck load price (Table 9), but requires a much higher polymer dosage (Table 12, Figures 12 and 13) than does the former. Therefore, Cat-Floc B will not be considered for use as the primary coagulant.

3. Candidate cationic polymers for the treatment of field military wastewater by adsorption/coagulation will be Hercofloc 829, Hercofloc 813, Nalcolyte 607, and Cat-Floc. Each has its specific advantages and disadvantages. Hercoflocs 829 and 813 are powdered polymers, having ease of shipment and handling, but difficulty in solution preparation and feeding. These two Hercoflocs generally require dose of only about 15 to 25 ppm for

effective coagulation (Tables 10 and 15; Figure 11); however, their clarification capabilities cannot compete with Cat-Floc under normal pH conditions (pH = 6-9).

4. Nalcolyte 607, a liquid cationic polymer, has the lowest viscosity among all liquid polymers tested, and a lower cost ($159/drum) compared to that of Cat-Floc ($180/drum). It functions well over a wide polymer dosage range (Figure 12), and a wide pH range (Table 14). Nalcolyte 607 cannot compete with Cat-Floc in the clarity of coagulated water when the initial pH of wastewater is higher than or equal to 9 (Figure 12, Tables 14 and 16). However, when the pH is close to or lower than 6, Nalcolyte works the best as a primary coagulant.

TABLE 9

INFORMATION ON ORGANIC FLOCCULANTS

FLOCCULANT	MANUFACTURER	IONIC NATURE	PHYSICAL FORM	TL PRICE*
Hercofloc 832.1	Hercules	Very High Cationic	Liquid	$0.35/lb (500 lb/drum)
Hercofloc 829	Hercules	Medium Cationic	Powder	$1.50-2.10/lb
Hercofloc 813	Hercules	Low Cationic	Powder	$1.15-1.80/lb
Hercofloc 824	Hercules	Nonionic	Powder	$1.15-1.50/lb
Hercofloc 817	Hercules	Low Anionic	Powder	$1.10-1.50/lb
Hercofloc 833	Hercules	Medium Anionic	Powder	$1.10-1.50/lb
Hercofloc 819	Hercules	High Anionic	Powder	$1.10-1.50/lb
Arquad 2HT-75	Armak	Cationic	Gelatin	$0.335/lb (390 lb/drum)
Arquad 18-50	Armak	Cationic	Liquid	$0.565/lb (301 lb/drum)
WT-2870	Calgon	Cationic	Liquid	$200/drum (450 lb/drum)
Cat-Floc	Calgon	Cationic	Liquid	$180/drum (450 lb/drum)
Cat-Floc B	Calgon	Cationic	Liquid	$130/drum (450 lb/drum)
Nalcolyte 607	Nalco	Cationic	Liquid	$0.300/lb (530 lb/drum)
Natron 88	National	Cationic	Liquid	$23.25/drum (8.9 lb/gal)
Swift X-100	Swfit	Cationic	Powder	$1.70/lb.

*NOTE: PRICE IN MAY 1973; 1 DRUM = 55 GAL.

TABLE 10

SELECTION OF SUITABLE TYPE(S) OF POLYMER BASED ON CHARGE CONDITIONS OF POLYMERS

POLYMER DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) OF SYNTHETIC WASTEWATER COAGULATED BY VARIOUS HERCOFLOCS						
		CATIONIC 8321	CATIONIC 829	CATIONIC 813	NONIONIC 824	ANIONIC 817	ANIONIC 833	ANIONIC 819
5	5	56	17	22	102	82	60	67
	15	56	17	20	91	82	60	65
	35	54	17	19	79	73	60	64
	60	52	17	19	78	71	60	64
15	5	47	15	11	91	96	52	79
	15	44	15	11	91	85	50	73
	35	41	15	10	85	78	49	73
	60	40	15	10	78	74	49	73
25	5	44	28	10	91	96	49	92
	15	38	28	9	85	91	44	79
	35	32	27	8	82	79	42	78
	60	32	25	8	74	74	40	77

TABLE 10 (CONT'D)

SELECTION OF SUITABLE TYPE(S) OF POLYMER BASED ON CHARGE CONDITIONS OF POLYMERS

POLYMER DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) OF SYNTHETIC WASTEWATER COAGULATED BY VARIOUS HERCOFLOCS						
		CATIONIC 8321	CATIONIC 829	CATIONIC 813	NONIONIC 824	ANIONIC 817	ANIONIC 833	ANIONIC 819
35	5	39	45	35	195	110	54	98
	15	36	45	34	82	96	49	79
	35	33	45	28	82	85	47	79
	60	33	42	28	71	78	44	79
50	5	15	49	40	95	114	64	107
	15	15	49	39	79	98	49	88
	35	14	49	36	76	91	49	86
	60	12	48	35	73	80	45	82
100	5	25	49	44	91	174	67	102
	15	24	49	41	79	136	54	91
	35	22	49	40	74	115	52	89
	60	22	49	38	69	98	49	83

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 mg/l DARCO S-51; ADSORPTION TIME = 15 MIN; NO pH ADJUSTMENT

TABLE 11

EFFECT OF pH ADJUSTMENT ON CARBON ADSORPTION/POLYMER COAGULATION FOR NONIONIC AND ANIONIC POLYMERS

TYPE & DOSAGE OF POLYMER	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
ANIONIC HERCOFLOC 817, 5 ppm	32	65	72	46	74	21	88	83
NONIONIC HERCOFLOC 824, 5 ppm	37	64	65	42	72	23.5	79	57.5

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF NUCHAR A; SETTLING TIME = ONE HOUR; HERCOFLOCS; INITIAL TOC OF SYNTHETIC WASTEWATER WITHOUT FILTRATION AND pH ADJUSTMENT = 184 PPM

TABLE 12

SELECTION OF SUITABLE TYPE(S) OF CATIONIC ORGANIC FLOCCULANTS

POLYMER DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) OF SYNTHETIC WASTEWATER COAGULATED BY VARIOUS CATIONIC ORGANIC FLOCCULANTS						
		ARQUAD 2 HT	ARQUAD 18-15	CAT FLOC	CAT FLOC B	NALCO 607	NATRON 88	SWIFT X-100
5	5	--	157	63	88	102	122	59
	15		95	59	65	85	118	59
	35		88	55	65	76	95	59
	60		88	52	61	74	89	59
15	5	152	136	29	57	67	110	47
	15	110	89	28	52	59	102	32
	35	105	85	26	48	57	88	23
	60	105	82	26	48	55	88	23
25	5	152	123	20	47	13	105	50
	15	102	95	17	42	10	89	39
	35	102	85	15	42	10	88	25
	60	102	82	15	40	9	82	23

TABLE 12 (CONT'D)

SELECTION OF SUITABLE TYPE(S) OF CATIONIC ORGANIC FLOCCULANTS

POLYMER DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) OF SYNTHETIC WASTEWATER COAGULATED BY VARIOUS CATIONIC ORGANIC FLOCCULANTS						
		ARQUAD 2 HT	ARQUAD 18-15	CAT FLOC	CAT FLOC B	NALCO 607	NATRON 88	SWIFT X-100
35	5	132	118	8	32	8	110	67
	15	100	85	8	30	8	89	62
	35	95	79	7	28	8	85	53
	60	95	79	7	27	8	85	47
50	5	88	114	7	14	9	95	67
	15	79	90	7	12	9	82	63
	35	76	85	6	12	9	79	61
	60	74	83	6	12	8	79	59
100	5	23	27	25	12	13	105	70
	15	22	25	25	10	12	102	70
	35	22	22	23	10	12	95	65
	60	22	21	22	10	12	89	63

TABLE 12 (CONT'D)

SELECTION OF SUITABLE TYPE(S) OF CATIONIC ORGANIC FLOCCULANTS

POLYMER DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) OF SYNTHETIC WASTEWATER COAGULATED BY VARIOUS CATIONIC ORGANIC FLOCCULANTS						
		ARQUAD 2 HT	ARQUAD 18-15	CAT FLOC	CAT FLOC B	NALCO 607	NATRON 88	SWIFT X-100
125	5	22	21	--	10	--	--	--
	15	20	20		9			
	35	18	14		9			
	60	18	12		9			
150	5	29	20	--	40	--	--	--
	15	27	15		39			
	35	25	12		36			
	60	25	10		33			
175	5	45	30	--	82	--	--	--
	15	41	26		79			
	35	38	23		79			
	60	38	20		79			

EXPERIMENTAL CONDITIONS:

NO pH ADJUSTMENT; ROOM TEMPERATURE; 750 mg/l DARCO S-51; ADSORPTION TIME = 15 MIN.; SYNTHETIC WASTEWATER

TABLE 13

EVALUATION OF THREE POWDERED ACTIVATED CARBONS
THROUGH COAGULATION WITH CAT-FLOC

CAT-FLOC DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES HAVING DIFFERENT CARBONS					
		DARCO S-51 750 ppm		HYDRODARCO C 750 ppm		NUCHAR A 750 ppm	
		TURB	TOC	TURB	TOC	TURB	TOC
0	60	--	78	--	83.0	--	67.5
5	5	63	--	143	--	88	--
	15	59	--	79	--	63	--
	35	55	--	76	--	55	--
	60	52	57.0	74	72.0	55	65.5
25	5	20	--	70	--	42	--
	15	17	--	63	--	35	--
	35	15	--	63	--	35	--
	60	15	27.0	63	71.0	35	50.0
35	5	8	--	37	--	15	--
	15	8	--	35	--	13	--
	35	7	--	35	--	13	--
	60	7	21.0	35	53.0	13	31.0

TABLE 13 (CONTINUED)

EVALUATION OF THREE POWDERED ACTIVATED CARBONS THROUGH COAGULATION WITH CAT-FLOC

CAT-FLOC DOSAGE ppm	SETTLING TIME minutes	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES HAVING DIFFERENT CARBONS					
		DARCO S-51 750 ppm		HYDRODARCO C 750 ppm		NUCHAR A 750 ppm	
		TURB	TOC	TURB	TOC	TURB	TOC
50	5	7	--	12.5	--	9	--
	15	7	--	12	--	9	--
	35	6	--	12	--	9	--
	60	6	16.0	12	30.0	8	23.0
100	5	25	--	18	--	30	--
	15	25	--	15	--	28	--
	35	23	--	15	--	27	--
	60	22	24.5	15	29.5	26	35.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; NO pH ADJUSTMENT; ROOM TEMPERATURE; CARBON DOSAGE = 750 PPM; ADSORPTION TIME = 15 MIN; FLOCCULATION TIME = 1 MIN.; CAT-FLOC; INITIAL TOC OF SYNTHETIC WASTEWATER WITHOUT FILTRATION = 184 PPM.

TABLE 14

EFFECT OF pH ADJUSTMENT ON CARBON ADSORPTION/POLYMER COAGULATION AT VARIOUS CATIONIC POLYELECTROLYTE DOSAGES (NUCHAR A AND NALCOLYTE 607 SYSTEM)

NALCOLYTE 607 DOSAGE ppm	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
5	7	11.0	24	23.0	12	32.0	28	50.5
15	10	10.0	22	23.0	8	24.5	10	38.5
25	14	11.5	28	19.5	8	(38.5)	7	34.0
35	14	19.5	27	39.0	10	26.5	7	33.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF NUCHAR A; ADSORPTION TIME = 60 MIN; SETTLING TIME = 30 MIN; NALCOLYTE 607; INITIAL TOC (UNFILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 184 PPM.

TABLE 15

EFFECT OF pH ADJUSTMENT ON CARBON ADSORPTION/POLYMER COAGULATION AT VARIOUS CATIONIC POLYELECTROLYTE DOSAGES (DARCO S-51 AND HERCOFLOC 813 SYSTEM)

HERCO-FLOC 813 DOSAGE mg/l	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
2.5	22	15.0	105	43.5	32	41.0	40	49.5
5.0	15	12.5	75	33.0	19	33.5	15	37.5
15.0	15	16.5	64	32.5	10	28.5	10	35.5
25.0	14	19.5	55	36.5	8	27.0	9	38.0
35.0	35	46.0	62	54.5	28	48.0	35	66.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF DARCO S-51; SETTLING TIME = 35 MIN; HERCOFLOC 813; INITIAL TOC (UNFILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 184 PPM

TABLE 16

EFFECT OF pH ADJUSTMENT ON CARBON ADSORPTION/POLYMER COAGULATION AT VARIOUS CATIONIC POLYELECTROLYTE DOSAGES (DARCO S-51 AND CAT-FLOC SYSTEM)

CAT-FLOC DOSAGE mg/l	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED SAMPLES AT DIFFERENT pH CONDITIONS							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
5	44	35.5	87.5	56.0	67.0	71.0	110.0	89.5
25	44	19.0	82.5	37.5	22.5	42.0	70.0	73.0
50	41.5	21.5	68.0	25.5	7.0	19.5	10.0	28.0
100	42.5	22.5	69.5	25.5	14.0	21.0	17.0	24.0

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF DARCO S-51; SETTLING TIME = ONE HOUR; CAT-FLOC; INITIAL TOC (UNFILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 184 PPM

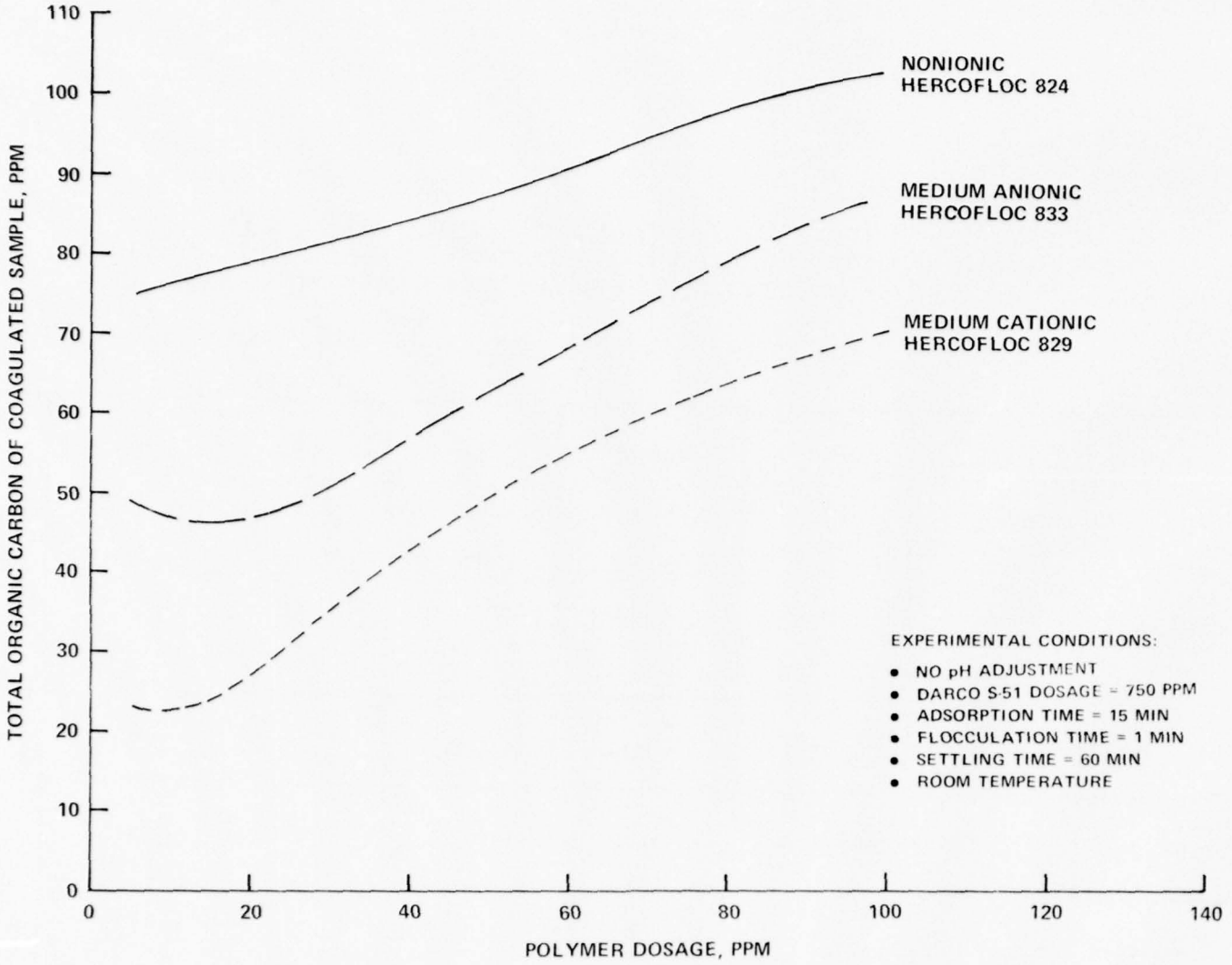

Figure 11 EFFECT OF POLYMER DOSAGE ON ADSORPTION/COAGULATION (HERCOFLOC SYSTEMS)

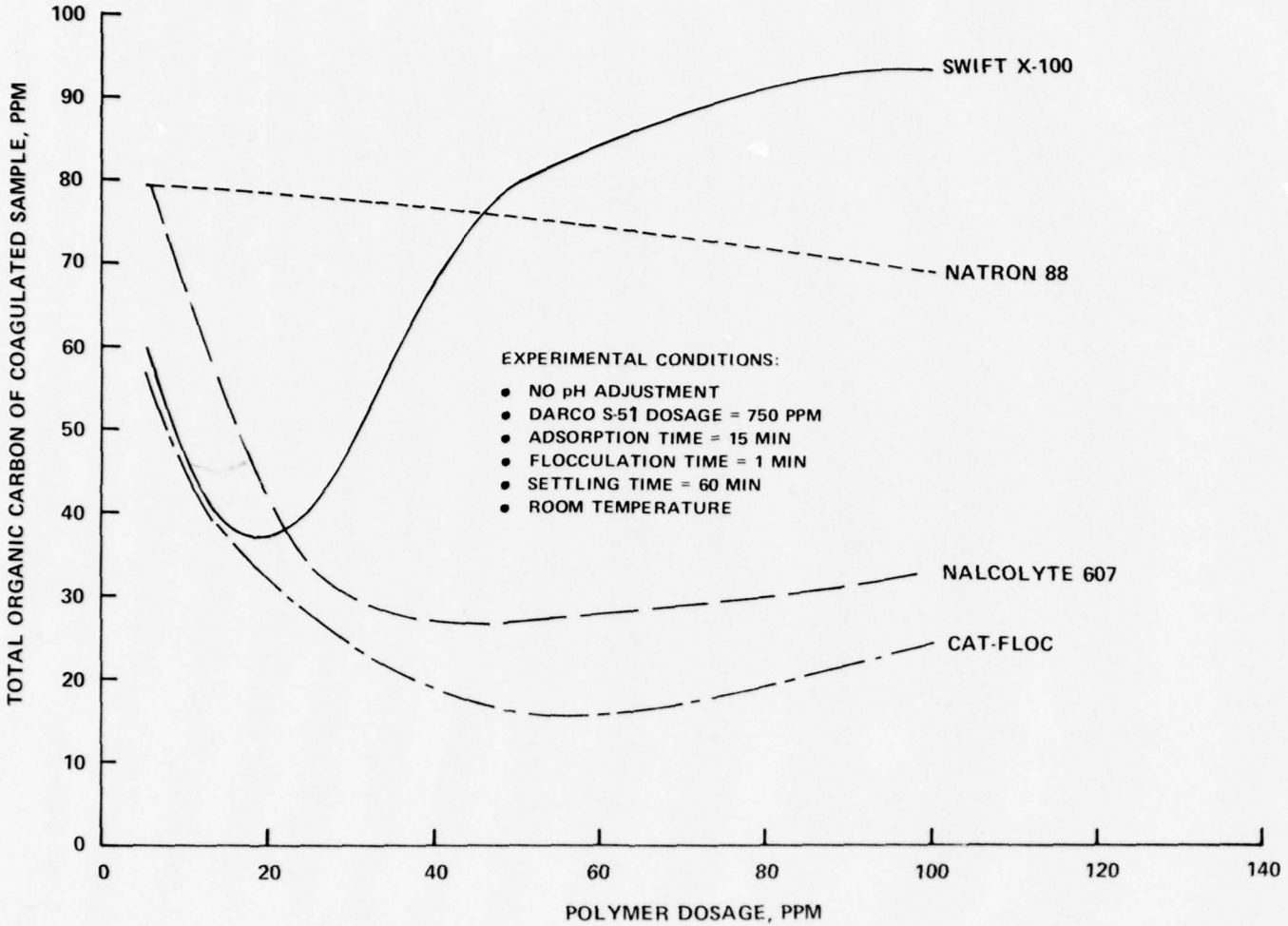

Figure 12 EFFECT OF POLYMER DOSAGE ON ADSORPTION/COAGULATION (SWIFT X-100, NATRON 88, NALCOLYTE 607 AND CAT-FLOC SYSTEMS)

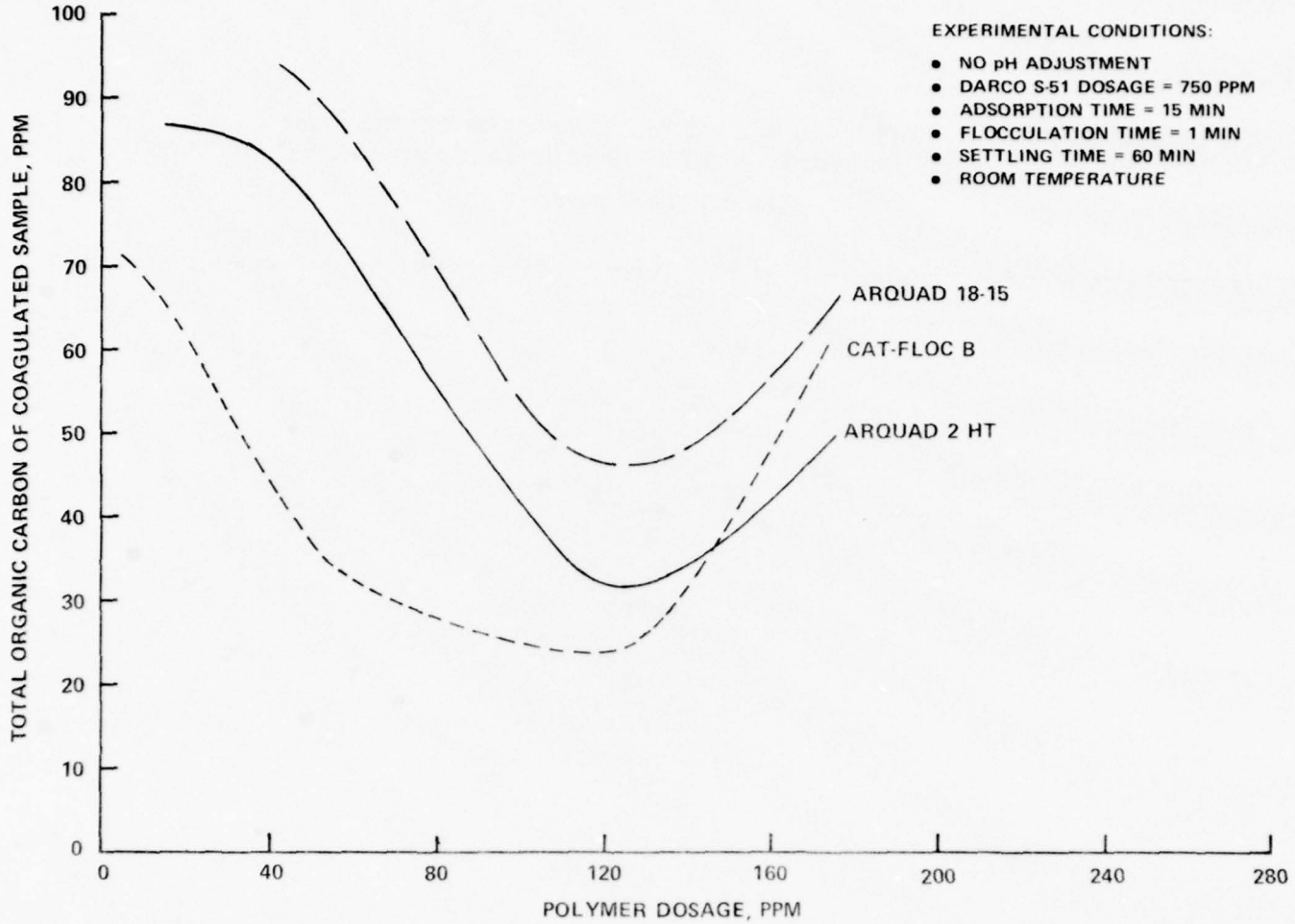

Figure 13 EFFECT OF POLYMER DOSAGE ON ADSORPTION/COAGULATION (ARQUAD 18-15, CAT-FLOC B, AND ARQUAD 2 HT SYSTEMS)

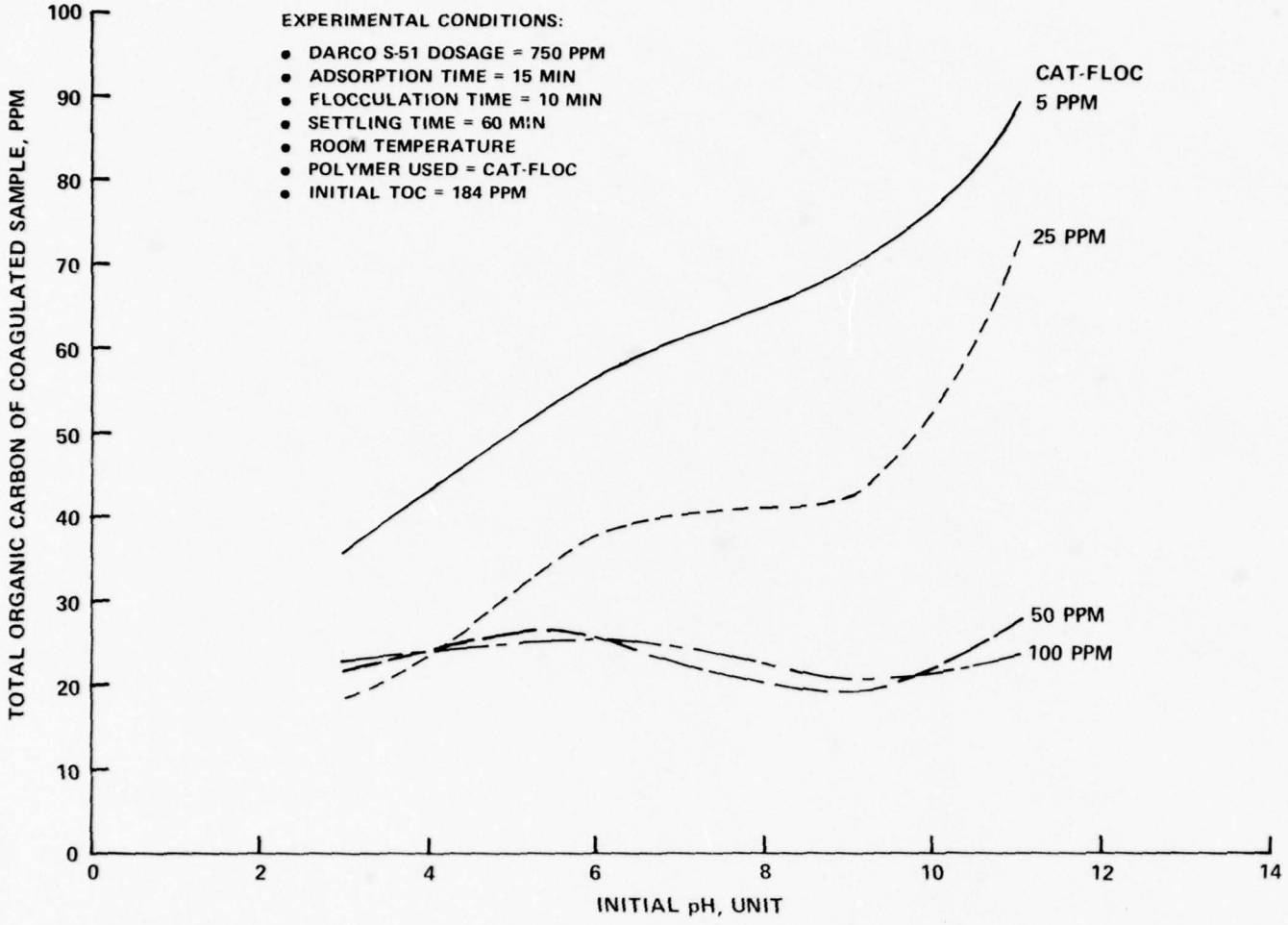

Figure 14 EFFECT OF pH ADJUSTMENT ON RESIDUAL TOTAL ORGANIC CARBON OF COAGULATED SAMPLES

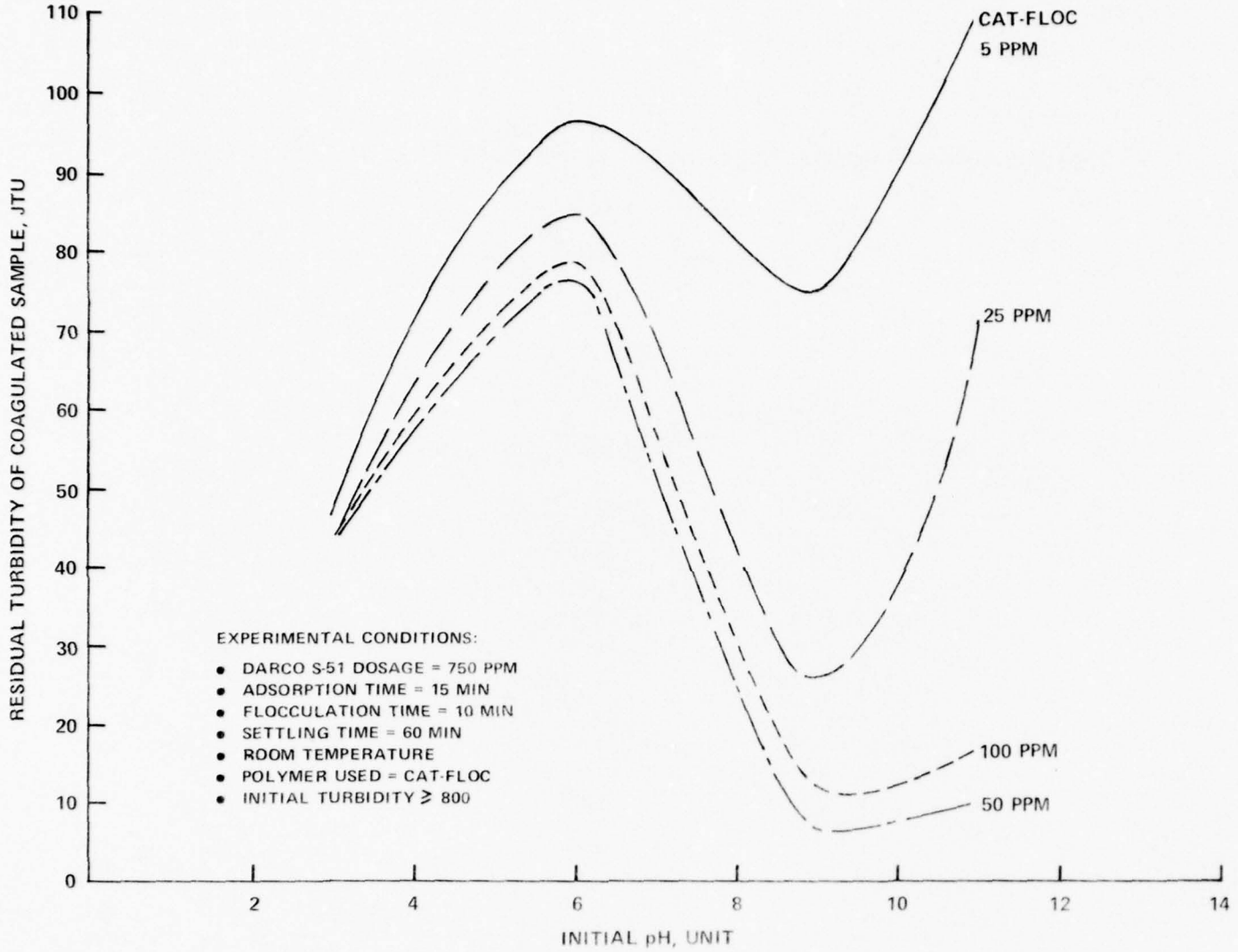

Figure 15 EFFECTS OF pH ADJUSTMENT AND POLYMER (CAT-FLOC) DOSAGE ON RESIDUAL TURBIDITY OF COAGULATED SAMPLES

5.9 Operational Parameters of Adsorption/Coagulation/Filtration System

Controlling parameters of the adsorption/coagulation/filtration system include: the types and dosages of chemicals; initial pH of wastewater; initial temperature of wastewater; retention time; chemical feed order and feed time; and filter operation. This section summarizes the parameters which have been investigated earlier in Sections 5.2 to 5.8, and also presents new technical data on polymer coagulation and diatomite filtration.

Types and Dosages of Chemicals Used

Both the Darco S-51/Cat-Floc system and the Nuchar A/Nalcolyte 607 system were found to be promising for treating the simulated military wastewater. The two carbons and two polymers will be evaluated further in another task of this program.

When the Darco S-51/Cat-Floc system is used for the treatment of synthetic wastewater, Darco S-51 and Cat-Floc dosages should be 750 ppm and 50 ppm, respectively. Note that the concentration of field military wastewater changes from time to time. Establishing the chemical dosage requirements for the treatment of wastewaters of fluctuated concentrations is the major task of this program. Its accomplishment will be reported in Project Report No. ND-5296-M-5, entitled "Investigation of Methods for Determining Optimum Powdered Carbon and Polyelectrolyte Dosages in Military Wastewater Treatment Systems".

Initial pH of Wastewater

Initial pH of wastewater will affect carbon adsorption and polymer coagulation. Since the investigated system involves both adsorption and coagulation, the chemicals used and their dosages will govern the overall performance of the combined treatment system.

The military wastewater encountered in a field base contains mainly anionic detergents; therefore, in all cases, carbon adsorption capacity increases with decreasing initial pH of wastewater (Section 5.6).

Although this fact is independent of the type of carbon used, the degree of sensitivity to the initial pH of wastewater is different from carbon to carbon. The carbon's sensitivity to increasing adsorption capacity by decreasing pH is rated in a decreasing order of: Nuchar C-190N, Nuchar A, Darco KB, Darco S-51, Hydrodarco C, and Hydrodarco H (Tables 5 and 7).

In a combined carbon-polymer system, the pH effect on the waste treatment will be mainly governed by carbon if the amount of polymer is insufficient for coagulating the spent carbon. In other words, poor quality of treated effluent is expected for a wastewater having high initial pH (Figure 14).

If the cationic polymer is in sufficient amount or overdosed for coagulating the spent carbon in a carbon-polymer system, the combined pH effect on waste treatment depends on the types of carbon and polymer used. For instance, the optimum pH conditions are 3 and 9 for the Darco S-51/ Cat-Floc system (Figure 14).

Multiple pH Adjustments

Different multiple pH adjustments to the same systems containing 750 ppm of Darco S-51 and 50 ppm of Cat-Floc yielded completely different coagulation results. Table 17 indicates that best coagulation results (turbidity = 3 JTU, and TOC = 9.5 ppm) were obtained for the Darco S-51/ Cat-Floc system by adjusting pH's from 8.0 to 9.5 and again to 6.0 with additions of sodium hydroxide and sulfuric acid solutions in the described sequence. Further investigations are required in order to obtain an understanding of the mechanism involved.

Feed Order and Feed Time of Chemicals

Powdered carbon and cationic polymer can be fed to the adsorption/ coagulation processing unit under different feed times and feed orders. A series of tests was conducted and all data are listed in Table 18. The table indicates that preparing a carbon-polymer slurry and feeding it by

means of one chemical feeder (Test D in Table 18) will result in the loss of some of the carbon's active surface area, and in turn, provide unsatisfactory treatment. Repeated agitation and sedimentation will increase the contact time and improve the quality of the coagulated effluent.

The use of two separate feeders for the cationic polymer and powdered carbon simultaneously to an adsorption/coagulation unit (Test C in Table 18) was found to produce better coagulated effluent than that of the use of one feeder for the two chemicals (Test D in the same table). Repeated agitation and sedimentation also improved the performance, probably due to an increase in retention time.

Adding the cationic polymer 2 to 10 minutes before adding the powdered carbon to an adsorption/coagulation unit (Tests A and B in Table 18) by means of two separate feeders was found to yield results similar to those obtained by adding the two chemicals at the same time but separately (Test C).

In adsorption/coagulation operation, feeding powdered carbon 10 or 15 minutes before feeding cationic polymer (Tests E and F in Table 18) was found to produce treatment results more promising than those of any other feeding scheme (Tests A through D in the same table). Following the rapid mixing and the flocculation, a thirty-minute setting time was sufficient for effective solids removal. The quality of coagulated effluent could be reporudced without being affected by any additional rapid or gentle agitations.

Wastewater Temperature and Retention Time

In the adsorption/coagulation process operated at room temperature, longer than 15 minutes is generally required for settling the coagulated suspended solids if the cationic polymer is under dosed. Less than 15 minutes is sufficient if the cationic polymer dosage is at optimum amount or overdosed (Tables 12-13).

Decreasing the wastewater temperature has significant effect on decreasing the settling rate of coagulated (suspended) flocs (Figure 16; Table 19). For the cold weather operation, possible remedies include one or more of the following methods: (1) increasing the retention time of the upflow clarifier (i.e., using a clarifier of higher capacity); (2) decreasing the influent flow rate; (3) using two-stage coagulation (i.e., two upflow clarifiers connected in series); (4) backwashing the diatomite filter more frequently; (5) using the two or more diatomite filters connected in parallel; and (6) increasing the wastewater temperature.

Filter Operation

A bench-scale diatomite filter was assembled in accordance with the descriptions in Section 4.3, Experimental Apparatus. The same rubber sleeve and diatomaceous earth used in the Army standard water purification unit (Ref. 1) were selected for use in the the bench-scale filter. The amount of diatomaceous earth precoated on the rubber sleeve was 0.1 lb per sq. ft.

A group of experiments conducted under varying wastewater temperatures were reported in Table 19. The 60-min. coagulated water was filtered by a Whatman No. 3 filter paper and by the bench-scale diatomite filter, separately. In general, the filtrate from the diatomite filter had lower TOC compared to that from Whatman No. 3 paper. It is then clear that diatomite filtration is a feasible method for removing most of the residual fine suspended solids in the coagulated supernatant. A complete adsorption/coagulation/filtration treatment system can generally remove from the wastewater about 90 percent of organic pollutants in terms of total organic carbon by an optimized single-stage operation.

TABLE 17

EFFECT OF MULTIPLE pH ADJUSTMENT ON CARBON ADSORPTION/POLYMER COAGULATION

TEST NO.	pH ADJUSTMENT	QUALITY OF COAGULATED SAMPLES			
		NATURE OF FLOC	PERCENT TRANSM.	TURBIDITY JTU	TOC ppm
1	3.2	small	55	55	27.5
2	6.7	small	42	85	55.5
3	8.0	large	72	30	32.0
4	10.0	large	68	35	48.5
5	3.2 - 10.5	small	95	5	13.0
6	8.0 - 9.5	small	95	5	26.5
7	3.2 - 10.5 - 6.3	large	93.5	6	10.5
8	8.0 - 9.5 - 6.0	large	97	3	9.5

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; 750 PPM OF DARCO S-51; 50 PPM OF CAT-FLOC; 35 MIN. OF SETTLING TIME; INITIAL TOC OF SYNTHETIC WASTEWATER WITHOUT FILTRATION = 184 PPM AND pH ADJUSTMENT

TABLE 18

CHEMICALS FEED TIME STUDIES FOR CARBON ADSORPTION/POLYMER COAGULATION

SETTLING TIME minutes	SAMPLE	RESIDUAL TURBIDITY (JTU) AND TOC (PPM) OF CLARIFIED SAMPLES											
		A. Dose polymer 10 minutes before dosing carbon		B. Dose polymer 2 minutes before dosing carbon		C. Dose polymer & carbon at same time separately		D. Dose polymer & carbon at same time combined		E. Dose carbon 10 minutes before dosing polymer		F. Dose carbon 15 minutes before dosing polymer	
		TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
		Samples rapid mixed for 2 min. gentle mixed for 10 min. and then settled											
30	coagul.	25	59.5	30	65.0	28	55.5	74	93.0	4	22.0	4	18.5
60	coagul.	25	64.5	30	74.0	30	74.5	74	85.0	4	21.5	4	22.5
60	filtrate*	13	40.5	15	42.0	15	41.0	33	51.5	4	20.0	4	19.0
		Samples rapid mixed again for 5 min., and then settled											
2	coagul.	23	--	17	--	23	--	61	--	14	--	14	--
5	coagul.	10	--	10	--	13	--	37	--	12	--	8	--
10	coagul.	10	--	10	--	11	--	34	--	4	--	5	--
15	coagul.	10	--	9	--	10	--	30	--	4	--	3	--
15	filtrate*	4	35.0	4	24.5	4	25.0	10	28.0	2	17.0	2	19.0

EXPERIMENTAL CONDITIONS:
SYNTHETIC WASTEWATER; 750 PPM OF DARCO S-51; 50 PPM OF CAT-FLOC; NO pH ADJUSTMENT; ROOM TEMPERATURE; INITIAL TOC OF SYNTHETIC WASTEWATER WITHOUT FILTRATION = 184 PPM

* NOTE: SAMPLES FILTERED WITH WHATMAN NO. 3 FILTER PAPER.

TABLE 19

EFFECT OF WATER TEMPERATURE ON THE PROCESS OF CARBON ADSORPTION/ POLYMER COAGULATION/DIATOMITE FILTRATION

SETTLING TIME minutes	RESIDUAL PERCENT TRANSMITTANCE AND TOTAL ORGANIC CARBON (PPM) OF TREATED SAMPLES AT DIFFERENT TEMPERATURES							
	TEMP = 110°F		TEMP = 72°F		TEMP = 45°F		TEMP = 35°F	
	TRANS %	TOC ppm	TRANS %	TOC ppm	TRANS %	TOC ppm	TRANS %	TOC ppm
	COAGULATED SUPERNATNAT SAMPLES (UNFILTERED)							
0	2	--	2	--	2	--	2	--
5	87	31.5	73.5	52.0	48	90.5	45	78.5
10	88.5	--	79.5	--	64	--	--	--
15	90	--	83.5	--	69	--	70	--
30	92	--	87	--	79	--	--	--
60	93.5	23.5	89	33.5	85.5	24.0	83	29.5
	60 MIN-SETTLED SAMPLES FILTERED WITH WHATMAN NO. 3 PAPER							
60	95.5	23.0	94.5	27	93.5	20.5	93	21.0
	60 MIN-SETTLED SAMPLES FILTERED BY DIATOMITE FILTER							
60	--	15.0	--	21	--	15.5	--	21.5

EXPERIMENTAL CONDITIONS:
SYNTHETIC WASTEWATER; 750 PPM OF DARCO S-51; 60 MIN. OF CARBON ADSORPTION TIME; NO pH ADJUSTMENT; 50 PPM OF CAT-FLOC; INITIAL TOC OF SYNTHETIC WASTEWATER WITHOUT FILTRATION = 184 PPM; INITIAL TOC OF SYNTHETIC WASTEWATER WITH WHATMAN-PAPER FILTRATION = 96.5 PPM

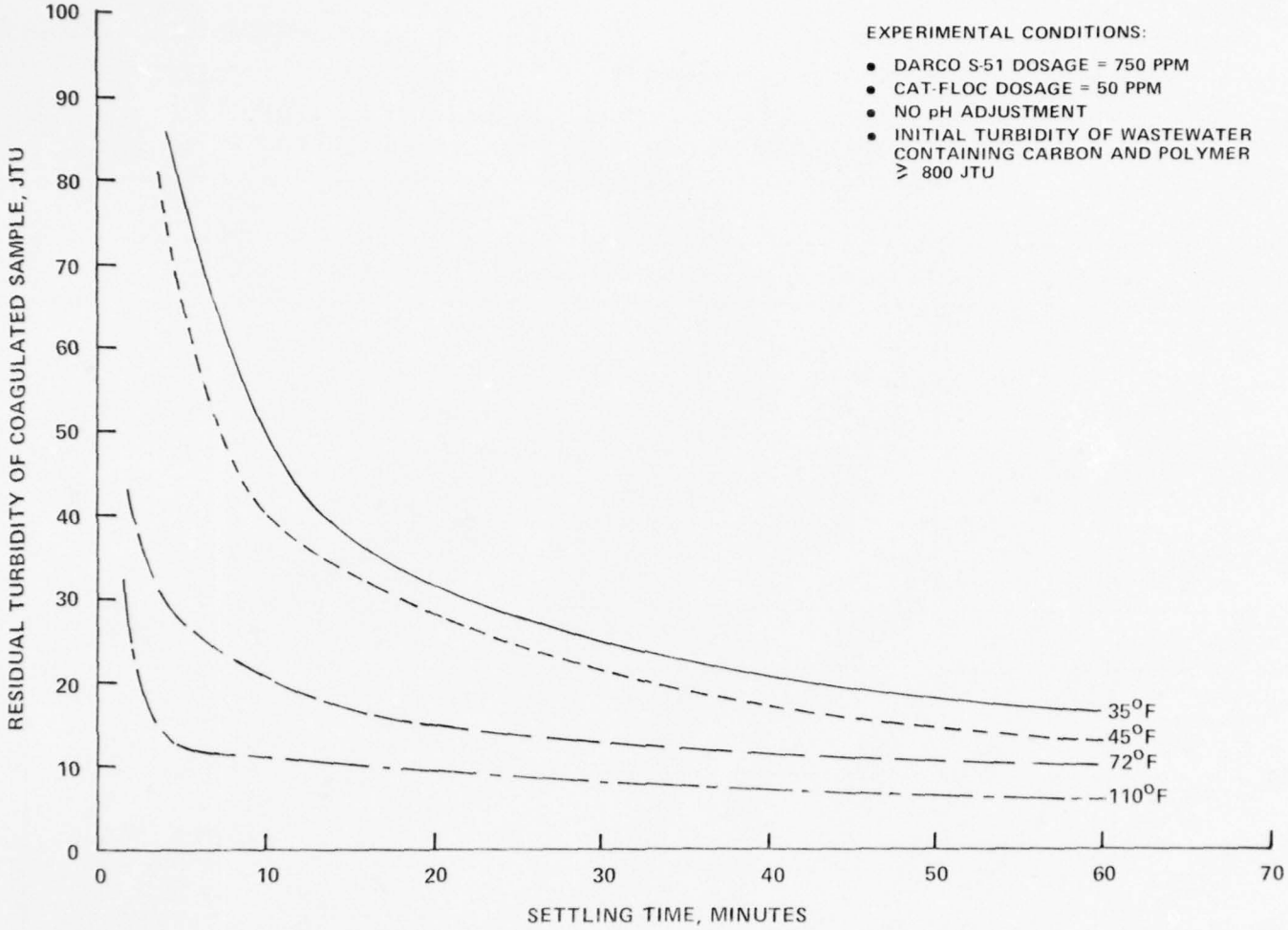

Figure 16 EFFECTS OF WATER TEMPERATURE AND SETTLING TIME ON ADSORPTION/COAGULATION

5.10 Preliminary Full-Scale Plant Operation

Full-scale treatment of field shower, laundry and kitchen wastewaters was conducted by the USAMERDC personnel. The wastewaters indicated in Table 1 were treated by a 420 GPH mobile plant (Figure 2).

Tables 20 to 23 indicate the data for full-scale wastewater treatment. The plant was operated following the Operator, Organizational, Direct Support and General Support Maintenance Manual, Army TM5-4610-208-4 (Ref. 1). The filter unit was backwashed when its filter pressure reached 50 psi. The bottom portion of Tables 20 through 23 present both the treatment data and the experimental conditions.

Preliminary full-scale plant operation was found to be successful. Shower wastewater, laundry wastewater and kitchen wastewater either separately (Tables 20-22) or in combination (Table 23) could be satisfactorily treated by the adsorption/coagulation/filtration process.

TABLE 20.

FULL SCALE TREATMENT OF SHOWER WASTEWATER

PLANT OPERATIONAL DATA				
Elapsed Time (Hrs:Mins)	Turbidity (JTU)		Filter Pressure (PSI)	Filter Cycle Length (Hrs:Mins)
	Coagulated	Filtrate		
0:10 start	--	--	0	
0:15	*	0.37	0	
0:45	*	0.22	50	
0:48 backwash	--	--	50	0:38
1:13 start	--	--	0	
1:25	*	0:41	10	
1:35 backwash	--	--	50	0:22
2:28 start	--	--	0	
2:30	*	4.2	1	
2:56 backwash	--	--	50	0:28
3:07 start	--	--	0	
3:15	*	--	9	
3:28 backwash	--	--	50	0:21
3:35 start	--	--	0	
3:40	8	0.11	2	
5:30	0.85	0.03	20	
6:00	0.38	0.03	22	
6:30	0.30	0.01	10	
7:00	0.22	0.01	20	
7:30	0.16	0.01	15	
8:00	0.22	0.01	18	
8:30	0.10	0.01	22	
9:00	0.30	0.01	22	
9:30	.10	0.01	18	
9:35	--	--	18	

TREATMENT DATA		
Parameter mg/l except noted	Raw Wastewater	Filtrate
Turbidity (JTU)	59.0	.03
pH (Units)	6.8	7.3
TDS	175.0	170.0
Total PO_4	35.0	25.0
Total Hardness ($CaCO_3$)	18.0	24.0
Alkalinity ($CaCO_3$)	136.0	124.0
Chloride (Cl)	10.0	11.5
BOD	51.0	3.0
TOC	15.0	4.0

NOTE: Dose = Initial dose 425 mg/l Darco S-51 & 50 mg/l Cat Floc; After 3 hours dose changed to 425 mg/l Darco S-51 & 12 mg/l Polymer.
Filtrate = Sampled at 5 hrs. and 30 min. elapsed time.

TABLE 21

FULL SCALE TREATMENT OF LAUNDRY WASTEWATER

PLANT OPERATIONAL DATA

Elapsed Time (Hrs:Mins)	Turbidity (JTU)		Filter Pressure (PSI)	Filter Cycle Length (Hrs:Mins)
	Coagulated	Filtrate		
0:10 start	--	--	0	
0:20	5.4	0.18	0	
0:50	32.0	0.65	20	
1:20 backwash	--	--	50	1:10
1:35 start	--	--	0	
1:45	89.0	30.0	--	
2:15	95.0	6.0	20	
2:45 backwash	92.0	6.0	50	1:10
3:08 start	--	--	0	
3:15 backwash	160.0	--	50	0:07
3:30 start	--	--	0	
3:55	160.0	32.0	30	
4:05 backwash	--	--	50	0:35
4:20 start	--	--	0	
4:30	160.0	120.0	12	
4:45 backwash	--	--	50	0:25
5:04	--	--	--	

TREATMENT DATA

Parameter mg/l except noted	Raw Wastewater	Filtrate
Turbidity (JTU)	3800.0	140.0
pH (Units)	7.6	7.1
TDS	290.0	310.0
Total PO_4	48.0	28.0
Total Hardness ($CaCO_3$)	30.0	24.0
Alkalinity ($CaCO_3$)	116.0	184.0
Chloride (Cl)	--	--
BOD	339.0	55.0
TOC	258.0	42.0

NOTES:

Dose = 425 mg/l Darco S-51 and 50 mg/l Cat Floc;

Filtrate = Sampled at 4 hours and 25 minutes elapsed time.

TABLE 22

FULL SCALE TREATMENT OF KITCHEN WATER

PLANT OPERATIONAL DATA				
Elapsed Time (Hrs:Mins)	Turbidity (JTU)		Filter Pressure (PSI)	Filter Cycle Length (Hrs:Mins)
	Coagulated	Filtrate		
0:29 start	--	--	0	
0:55	74	21	29	
1:01 backwash	--	--	50	0:32
1:10 start	--	--	0	
1:25	86	81	10	
1:45 backwash	--	--	50	0:35
1:57 start	--	--	0	
2:10	85	81	7	
2:25	82	59	20	
2:38 backwash	--	--	50	0:41
2:46 start	--	--	0	
2:55	60	78	4	
3:25	64	64	38	
3:27 backwash	--	--	50	0:41
3:35 start	--	--	0	
4:10	57	37	28	
4:15 backwash	--	--	50	0:40
4:20 start	--	--	0	
4:25	54	81	0	
4:55	48	48	10	
5:11 backwash	--	--	22	0:51
5:17	--	--	--	

TREATMENT DATA		
Parameter mg/l except noted	Raw Wastewater	Filtrate
Turbidity (JTU)	440.0	80.0
pH (Units)	6.3	7.1
TDS	430.0	450.0
Total PO_4	52.0	28.0
Total Hardness ($CaCO_3$)	28.0	24.0
Alkalinity ($CaCO_3$)	120.0	254.0
Chloride (Cl)	35.0	80.0
TOC	214.0	45.0

NOTES: Dose = 750 mg/l Darco S-51 and 60 mg/l Cat Floc;
Filtrate = Sampled at 2 hours 15 minutes elapsed time.

TABLE 23

FULL SCALE TREATMENT OF FIELD COMBINED WASTEWATER

PLANT OPERATIONAL DATA				
Elapsed Time (Hrs:Mins)	Turbidity (JTU)		Filter Pressure (PSI)	Filter Cycle Length (Hrs:Mins)
	Coagulated	Filtrate		
0:35 start	--	--	0	
0:50	5.2	3.5	0	
1:10	1.9	0.6	0	
1:40	0.49	0.2	0	
2:10	0.44	0.08	0	
2:40	0.05	0.02	1	
3:10	0.08	0.01	1	
4:10	0.08	0.01	2	
4:40	0.25	0.01	-	
5:10	0.18	0.01	2	
5:24 back-wash	0.18	0.01	2	4:50

TREATMENT DATA		
Parameter mg/l except noted	Raw Wastewater	Filtrate
Turbidity (JTU)	220.0	0.1
pH (Units)	6.7	7.0
TDS	190.0	200.0
Total PO_4	48.0	28.0
Total Hardness ($CaCO_3$)	17.0	21.0
Alkalinity ($CaCO_3$)	135.0	106.0
Chloride (Cl)	11.3	34.5
BOD	100.0	19.0
TOC	146.0	12.0

NOTE:

Combined Wastewater = 50% shower, 40% field laundry, and 10% kitchen.

Dose = Initial dose 750 mg/l Darco S-51 and 50 mg/l Cat Floc; After 4 hours dose changed to 425 mg/l Darco S-51 and 50 mg/l Cat Floc.

Filtrate = Sampled at 2 hours and 15 minutes elapsed time.

6.0 SUMMARY AND CONCLUSIONS

Results of the research performed during the period of 16 April to 15 June 1973, have been evaluated and the following conclusions are derived.

1. If no carbon is added to the synthetic wastewater, even at appropriate pH condition and optimum cationic polymer dosage, the polymer coagulation can achieve turbidity removal only to a limited degree, and cannot achieve a satisfactory TOC removal (see Appendix V).

2. With or without the pH adjustment to the wastewater, neither nonionic polymer nor anionic polymer is suitable for use as primary coagulant for the clarification of surface-active type wastewater if no carbon and/or other chemicals are added to the polymer coagulation system (only qualitative tests were conducted).

3. Certain powdered activated carbons can effectively remove the specific types of pollutants from the target field military wastewater (Tables 3 and 7); however, the spent powdered carbon cannot settle rapidly in the absence of an added coagulant (Appendix VI).

4. The six powdered carbons evaluated are listed below in order of decreasing ability to adsorb dissolved organics from wastewater if no pH adjustment is made: Nuchar C-190N, Nuchar A, Darco KB, Hydrodarco C, Darco S-51, and Hydrodarco H (Figure 6 and Table 3). Optimal carbon dosages for all tested carbons were found to be about 750 mg/l (Figure 6).

5. When pH adjustment is made by adding acid to the wastewater, the ranking of the six carbons evaluated becomes as follows, in order of decreasing adsorption capacity: Nuchar C-190N, Nuchar A and Darco KB, Darco S-51, Hydrodarco C, and Hydrodarco H. (Tables 4, 5, 7)

6. For wettability, the six carbons evaluated rank as follows in order of decreasing wettability: Darco KB and Darco S-51, Hydrodarco H and Hydrodarco C, Nuchar A, and Nuchar C-190N. (Table 8) The carbons with excellent wettability can be fed to the wastewater in dry powdered form; while the ones with poor wettability have to be wetted in slurry form before being fed to the wastewater.

7. The ranking of the six carbons evaluated in order of increasing truck load prices is as follows: Hydrodarco H and Nuchar A, Hydrodarco C, Darco S-51 and Nuchar C-190N, and Darco KB (Table 8).

8. Decreasing the initial pH of the wastewater will have significant effect on increasing the available adsorption capacities of Nuchar A (Figure 8, Tables 4 and 7), Darco S-51 (Figure 9 and Table 5), Nuchar C-190N (Table 7) and Darco KB (Table 7). However, the two hydrodarco carbons are relatively insensitive to pH adjustment (Table 7).

9. When the wastewater temperature is about 72 ^{o}F, the available adsorption capacity of powdered carbons (e.g., Nuchar A and Darco S-51) can be fully utilized within 60 minutes of contact time at any initial pH conditions. (Figures 8-9; Tables 4-5)

10. At room temperature (72^{o}F), more than 90% of the available adsorption capacity of powdered carbons (which varies with the initial

pH of wastewater) will be utilized within 15 minutes. Minimum contact time between uncoagulated carbon and the wastewater should be, however, at least 5 minutes at room temperature under any pH conditions (Figures 8-9).

11. Increasing the wastewater temperature has an insignificant effect on increasing the available adsorption capacity of powdered carbons when carbon and wastewater are thoroughly mixed for at least 60 minutes (Figure 10 and Table 6).

12. Decreasing the wastewater temperature has a very pronounced effect on decreasing the powdered carbon's adsorption rate. When the carbon-wastewater contact time is as short as 5 minutes, the available adsorption capacity (for a specific pH condition) can be almost fully utilized at 110°F, but only about 50% utilized at 35°F (Figure 10). The remedy for using the carbon adsorption process in cold weather areas is simply increasing the carbon-wastewater contact time, because the longer the contact time, the higher the fraction of available adsorption capacity that can be used for pollution control. Other possible remedies for cold weather operation include increasing the carbon dosage, adjusting the initial pH of wastewater with acid, or, of course, increasing the wastewater temperature.

13. Nearly 100% dissolved organics removal can be achieved if 750 ppm of prewetted Nuchar C-190N is dosed to the synthetic wastewater at pH = 3 (Table 7). The major disadvantage of Nuchar C-190N is its low density and poor wettability (Table 8). When Nuchar C-190N is fed in dry powdered form, a significant portion of the unwetted carbon will float on

the wastewater surface causing a loss in the available carbon. Nuchar C-190N could be a potential candidate carbon for treating the field military wastewater if a feeder is commercially available or can be developed which has a built-in mixer for rapidly preparing a carbon slurry.

14. Although Darco KB has satisfactory adsorptabiity for the treatment of field military wastewater at a wide initial pH range (Figure 6 and Table 7), its cost is too high to make it practical (Table 8).

15. Hydrodarco H is the most inexpensive one among all six carbons evaluated (Table 8); however, it's poor adsorptability at any pH conditions limits its application (Figure 6 and Table 7).

16. Hydrodarco C is a dense carbon with medium price (Table 8). It could be considered as a candidate carbon only if initial pH of wastewater is above 7 (Table 7). However, in most cases, the actual wastewater's pH is lower than 7 (Ref. 2). Further coagulation tests (Table 13) show that Hydrodarco C is not a suitable type of carbon compared to Darco S-51 and Nuchar A, provided that adsorption time is 15 minutes and Cat-Floc is used as primary coagulant.

17. Nuchar A and Darco S-51 would be the possible candidate powdered carbons for the carbon adsorption/polymer coagulation process regardless of initial pH conditions. Comparing these two carbons, Nuchar A is cheaper (Table 8) and has better adsorptability at variable

carbon dosages (Figure 6) and at any pH conditions (Table 7) than does Darco S-51; while Darco S-51 is denser and has better wettability (Table 8).

18. Seven Hercoflocs with different charge conditions (Tables 9 and 10) have been tested for feasibility of being used as primary coagulants in treating field military wastewater by adsorption/coagulation system. The high cationic Hercofloc 832.1, the medium cationic Hercofloc 829, and the low cationic Hercofloc 813 gave better performance for wastewater clarification at pH = 9 as compared to any anionic or nonionic Hercoflocs (Table 10 and Figure 11).

19. Anionic Hercofloc 817 and nonionic Hercofloc 824 are able to produce coagulated effluents of low TOC at pH = 9.4. They do not function well as primary coagulant at any other pH condition (Table 11).

20. Cationic polymer is definitely superior to nonionic and anionic polymers as the primary coagulant for the treatment of field military wastewater. Accordingly, seven other cationic organic coagulants in addition to cationic Hercoflocs were selected for added evaluations (Tables 9 and 12). Of ten cationic organic coagulants tested, Swift X-100, Natron 88, Arquad 18-15 and Arquad 2HT do not perform well as primary coagulant as compared to others (Figures 11-13, Tables 10 & 12). Hercofloc 832, Hercofloc 829, Hercofloc 813, Nalcolyte 607, Cat-Floc, and Cat-Floc B, however, exhibit different degrees of success in the coagulation (Figures 11-13 and Tables 10 and 12) of synthetic wastewater at pH $\simeq$ 9.

25. The cationic, liquid-type Cat-Floc is the best polymer compared to other evaluated polymers for treating the synthetic wastewater at pH = 9.4 (Figures 11-15). The Cat-Floc's effective polymer dosage range is wide (Figure 14). At optimum carbon dosage of 750 ppm, the optimum Cat-Floc dosage is always 50 ppm regardless of the types of carbon used (Table 13) and regardless of the initial pH conditions (Table 14).

26. Effect of pH adjustment on adsorption/coagulation is very significant for the Nuchar A and Nalcolyte 607 system (Table 16), somewhat less significant for the Darco S-51 and Hercofloc 813 system (Table 15), and very insignificant for the Darco S-51 and Cat-Floc System (Table 14, and Figure 14). When the initial pH of wastewater is lower than 7, the Darco S-51 and Cat-Floc system cannot compete with the Nuchar A and Nalcolyte 607 system (Tables 14 and 16).

27. Under the same experimental conditions, the pattern of pH effect on residual TOC of coagulated water (Figure 14) is different from that on residual turbidity of coagulated water (Figure 15). Turbidity data, indeed, are closely related to the TOC data (Tables 4-6, 13-16, and 18-19; Appendix V), and can be used as one of the important process controlling parameters. The turbidity-to-TOC ratio, however, varies significantly with varying pH conditions. For a specific carbon-polymer system (such as Darco S-51 and Cat-Floc), the turbidity-to-TOC ratio at different pH levels can be established for the ease of process control.

21. Hercofloc 832 is in liquid form (Table 9), with extremely high viscosity. It works well (Table 10), but is not recommended for use due to the difficulty in polymer feeding.

22. Cat-Floc and Cat-Floc B are similar liquid cationic polymers, both manufactured by Calgon Corp. The latter is cheaper in truck load price (Table 9), but requires a much higher polymer dosage (Table 12, Figures 12 and 13) than does the former. Therefore, Cat-Floc B will not be considered for use as the primary coagulant.

23. Candidate cationic polymers for the treatment of field military wastewater by adsorption/coagulation will be Hercofloc 829, Hercofloc 813, Nalcolyte 607, and Cat-Floc. Each has its specific advantages and disadvantages. Hercoflocs 829 and 813 are powdered polymers, having ease of shipment and handling, but difficulty in solution preparation and feeding. These two Hercoflocs generally require doses of only about 15 to 25 ppm for effective coagulation (Tables 10 and 15; Figure 11); however, their clarification capabilities cannot compete with Cat-Floc under normal pH conditions (pH = 6-9).

24. Nalcolyte 607, a liquid cationic polymer, has the lowest viscosity among all liquid polymers tested, and a lower cost ($159/drum) compared to that of Cat-Floc ($180/drum). It functions well over a wide polymer dosage range (Figure 12), and a wide pH range (Table 14). Nalcolyte 607 cannot compete with Cat-Floc in the clarity of coagulated water when the initial pH of wastewater is higher than or equal to 9 (Figure 12, Tables 14 and 16). However, when the pH is close to or lower than 6, Nalcolyte works the best as a primary coagulant.

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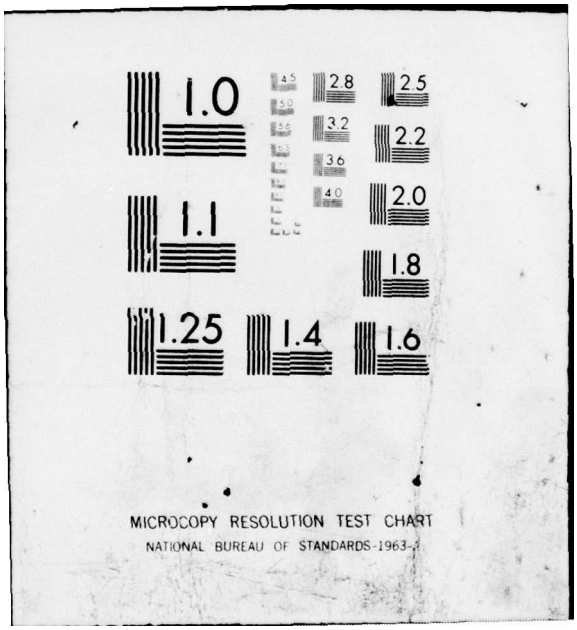
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28. Different multiple pH adjustments to the same systems containing 750 ppm of Darco S-51 and 50 ppm of Cat-Floc yielded completely different coagulation results (Table 17). Best coagulation results (turbidity = 3 JTU, and TOC = 9.5 ppm) were obtained for the Darco-Cat-Floc system by adjusting pHs from 8.0 to 9.5 and again to 6.0 with additions of sodium hydroxide and sulfuric acid solutions in the described sequence. Further investigations are required in order to obtain an understanding of the mechanism involved.

29. Powdered carbon and cationic polymer can be fed to the adsorption/coagulation processing unit under different feed times and feed orders. (Table 18) Preparing a carbon-polymer slurry and feeding it by means of one chemical feeder (Test D in Table 18) will result in the loss of some of the carbon's active surface area, and in turn, provide unsatisfactory treatment. Repeated agitation and sedimentation will increase the contact time and improve the quality of the coagulated effluent.

30. The use of two separate feeders for the cationic polymer and powdered carbon simultaneously to an adsorption/coagulation unit (Test C in Table 18) will produce better coagulated effluent than will the use of one feeder for the two chemicals (Test D in the same table). Repeated agitation and sedimentation will also improve the performance, probably due to an increase in retention time.

31. Adding the cationic polymer 2 to 10 minutes before adding the powdered carbon to an adsorption/coagulation unit (Tests A and B in Table 18) by means of two separate feeders yields results similar

to those obtained by adding the two chemicals at the same time but separately (Test C).

32. In adsorption/coagulation operation, feeding powdered carbon 10 or 15 minutes before feeding cationic polymer (Tests E and F in Table 18) will produce treatment results more promising than those of any other feeding scheme (Tests A through D in the same table). Following the rapid mixing and the flocculation, a thirty-minute of setting time will generally be sufficient for effective solids removal. The quality of coagulated effluent can be reproduced without being affected by any additional rapid or gentle agitations.

33. In the adsorption/coagulation process operated at room temperature, longer than 15 minutes is generally required for settling the coagulated suspended solids if the cationic polymer is under dosed. Less than 15 minutes is sufficient if the cationic polymer dosage is at optimum amount or overdosed (Tables 12-13).

34. Decreasing the wastewater temperature has significant effect on decreasing the settling rate of coagulated (suspended) flocs (Figure 16; Table 19). For the cold weather operation, possible remedies include one or more of the following methods: (1) increasing the retention time of the upflow clarifier (i.e., using a clarifier of higher capacity); (2) decreasing the influent flow rate; (3) using two-stage coagulation (i.e., two upflow clarifiers connected in series); (4) backwashing the diatomite filter more frequently; (5) using two or more diatomite filters connected in parallel; and (6) increasing the wastewater temperature.

35. Diatomite filtration is a feasible method for removing most of the residual fine suspended solids in the coagulated supernatant. A complete adsorption/coagulation/filtration treatment system can generally remove from the wastewater about 90 percent of organic pollutants in terms of total organic carbon by an optimized single-stage operation.

7.0 PROPOSED FURTHER INVESTIGATIONS

Under Contract No. DAAK 02-73-C-0206, Calspan will continue to develop test methods, techniques, and/or devices to be used for determining the optimum carbon-polymer dosages in the adsorption/coagulation/filtration system designed for the treatment of various wastewaters generated in such field military facilities as laundry, shower and kitchen units. Possible improvements to the adsorption/coagulation/filtration systems, or possibly better treatment system alternatives will also be proposed and/or conceptually designed.

For the control and monitoring of the adsorption/coagulation/filtration systems, the following investigations will be completed:

- Evaluation of Hydroscan Streaming Current Detector as a field process control device;
- Evaluation of Zeta Potential Meter as a process control device;
- Determination of the dosage requirements of a selected powdered activated carbon and a selected cationic polyelectrolyte for treating the synthetic wastewater at different initial concentration levels;
- Establishment of the TOC/COD ratio and the TOC/turbidity ratio for the synthetic wastewater at different pH conditions;
- Evaluation of the two-phase titration method (Ref. 102) for analyzing the detergent content and, in turn, for determining the TOC/LAS ratio;

- Development of a colorimetric method for determining the carbon dosage, and controlling the process efficiency.

The results obtained from investigations completed to the current research stage have demonstrated that only about 90% of organic pollutants in the wastewater can be removed by the adsorption/coagulation/filtration process system at normal pH conditions, a nearly zero-pollution discharge still cannot be achieved. This is accounted in part by the following two factors: (1) single-stage powdered carbon adsorption cannot remove all dissolved organic pollutants from the wastewater without appropriate pH adjustment; and (2) using cationic polyelectrolyte as the primary coagulant cannot remove phosphate from the wastewater (Ref. 29). The residual organic pollutants can be removed, if desired, by one of the following ways:

- Adjusting the initial pH of the wastewater to 3 with acid, and using the most efficient powdered carbon, Nuchar C-190N;
- Placing granular activated carbon in the pressure diatomite filtration unit, or simply using an additional granular carbon column for tertiary treatment;
- Using metal electrolyte(s) and organic polyelectrolyte as coagulant for treating the field military wastewater;
- Improving the treatment system by multiple pH adjustment; or

- Using an added reverse osmosis unit to further convert the effluent to reusable water.

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APPENDIX I

ANALYSIS OF SYNTHETIC WASTEWATER

PARAMETER (mg/ℓ EXCEPT AT NOTED)	SAMPLES*, $\sum_{i=1}^{N} F_i$						
	TAP WATER	+ LAUNDRY DETERGENT	+ DISHWASHER DETERGENT	+ SOAP	+ CLAY	+ OIL	+ DOG FOOD
	N = 1	N = 2	N = 3	N = 4	N = 5	N=6	N = 7**
TURBIDITY, JTU	~0	10	12	20	55	60	110
RESISTIVITY, OHM-CM	975	600	450	400	400	400	400
TOTAL ALKALINITY($CaCO_3$)	114	142	164	164	158	164	166
TOTAL HARDNESS($CaCO_3$)	127	123	104	98	97	98	96
CHLORIDE	27	31	36	34	34	32	34
SULFATE	34	120	193	185	193	180	200
SILICATE (SILICA)	1	22	26	26	24	26	47
TOTAL SOLIDS	206	428	647	674	718	728	876
DISSOLVED SOLIDS	204	326	494	472	466	428	478
SUSPENDED SOLIDS	2	102	153	202	252	300	398
DISSOLVED PROTEIN	<15	<15	<15	<15	<15	<15	30
COD, TOTAL	16	92	112	184	188	188	236
COD, DISSOLVED	12	80	88	116	109	124	124
TC, TOTAL	23	63	68	95	92	97	136
TC, DISSOLVED	25	50	57	64	61	53	58
TOC, TOTAL	1	41	46	73	70	75	114
TOC, DISSOLVED	3	28	35	42	39	31	36
5-DAY BOD, TOTAL	0.9	78	79	102	144	120	162
DISSOLVED OXYGEN(25°C)	9.5	8.5	8.3	8.3	8.2	8.2	8.0
IDOD (25°C)	0.0	1.0	1.2	1.2	1.3	1.3	1.5
TOTAL PHOSPHATE	0.03	0.07	28.0	27.6	29.2	29.2	30.0
OIL AND GREASE	< 3.0	17.4	20.8	28.0	24.0	26.0	47.4
pH, UNIT	7.3	9.3	9.5	9.5	9.5	9.4	9.4

*F_1, F_2, F_3, F_4, F_5, F_6 AND F_7, AS INDICATED IN TABLE 2, ARE THE MATERIALS USED FOR THE PREPARATION OF THE SYNTHETIC WASTEWATER

**SYNTHETIC WASTEWATER

APPENDIX II

EFFICIENCIES AND COSTS OF PRELIMINARY, PRIMARY AND SECONDARY TREATMENTS

WASTE CONSTITUENT	TREATMENT PROCESSES	PERCENT REMOVAL	COST, ¢/1000 gal
COARSE SOLIDS	SCREENING	90	0-5
	GRINDING AND COMMINUTING	–	0-5
	CENTRIFUGATION	90	20-40
SUSPENDED SOLIDS	SEDIMENTATION	60	0-5
	FLOTATION	60-90	5-20
	COAGULATION	80	5-20
	MICROSTRAINING	60	0-5
DISSOLVED ORGANICS	ACTIVATED SLUDGE	60	5-20
	TRICKLING FILTER	60	5-20
	ANAEROBIC CONTACT	50	20-40
	AERATED LAGOON	50	20-40
	CARBON ADSORPTION	70	20-40
	ADSORPTION FLOTATION	95	>40
REFRACTORY SURFACTANTS	FOAM SEPARATION	90	5-20
OIL	GRAVITY SEPARATION	95	0-5
	DISSOLVED AIR FLOTATION	90	5-20
	ABSORPTION	30-80	5-20
	ADSORPTION FILTRATION	99	20-40
	CONVENTIONAL FILTRATION	30-90	0-5
	ADSORPTION FLOATATION	99	>40
NEUTRALIZATION	ACID OR BASE TREATMENT	99	5-20
BACTERIA, VIRUSES	CHLORINATION	99	0-5
	IRRADIATION	99	5-20
	OZONATION	90	0-5

APPENDIX III

EFFICIENCIES AND COSTS OF ADVANCED TREATMENTS

WASTE CONSTITUENT	TREATMENT PROCESSES	PERCENT REMOVAL	COST ¢/1000 gal.
FINE SUSPENDED SOLIDS TURBIDITY	SAND FILTRATION	70	1-5
	MICROSTRAINING	60	1-5
	DIATOMACEOUS EARTH FILTRATION	70-90	5-20
	ULTRAFILTRATION	100	>40
AMMONIA-NITROGEN	BIOLOGICAL NITRIFICATION	90	3-20
	ION EXCHANGE	90	5-20
	AMMONIA STRIPPING	85	5-20
	BREAKPOINT CHLORINATION	99	5-20
NITRATE-NITROGEN	ANAEROBIC DENITRIFICATION	85	2-20
	ION EXCHANGE	90	5-20
	ALGAE HARVESTING	50-80	5-20
	CARBON ADSORPTION	20-80	20-50
PHOSPHORUS	CHEMICAL PRECIPITATION	95	5-20
	ION EXCHANGE	90	5-20
	BIOLOGICAL UPTAKE	30	5-20
	CARBON ADSORPTION	20-80	20-50
TASTE AND ODOR, TRACE DISSOLVED ORGANICS	CARBON ADSORPTION	95	20-40
TRACE REFRACTORY SURFACTANTS	BUBBLE FRACTIONATION	95	5-20
SOLUBLE INORGANICS (HEAVY METALS RADIOACTIVITY, SALTS, HARDNESS)	ION EXCHANGE	90	> 40
	DISTILLATION	95	> 40
	REVERSE OSMOSIS	90	> 40
	CHEMICAL PRECIPITATION	20-95	5-20
	FREEZING	80	> 40
	ELECTRODIALYSIS	90	> 40
	CARBON ADSORPTION	5-90	20-40
	PRECIPITATE FLOTATION	90	20-40
COLOR	CHEMICAL CLARIFICATION	80-90	5-20
	CARBON ADSORPTION	95	10-40
BACTERIA VIRUSES	CHEMICAL OXIDATION	90-99	0-5
	REVERSE OSMOSIS	90	> 40

APPENDIX IV

COSTS OF BRINE AND SLUDGE TREATMENTS*

FUNCTION	TREATMENT PROCESSES	COST, ¢/1000 gal
BRINE TREATMENT	EVAPORATION	0-5
	CHEMICAL OXIDATION	5-20
	BY-PRODUCT RECOVERY	----
SLUDGE PRETREATMENT	SCREENING AND GRIT REMOVAL	0-5
	ELUTRIATION	0-5
SLUDGE DEWATERING	GRAVITY SETTLING	0-5
	CHEMICAL COAGULATION	5-20
	FLOTATION	1-5
	EVAPORATION	0-5
	CENTRIFUGATION	0-5
	VACUUM FILTRATION	0-5
	IRRADIATION	----
	MAGNETIC COAGULATION	5-20
	ABSORPTION	0-5
SLUDGE REDUCTION	WET OXIDATION	0-5
	ANAEROBIC DIGESTION	0-5
	AEROBIC DIGESTION	0-5
	INCINERATION	5-20
	CALCINATION	5-20
	SLUDGE RECOVERY	----
ULTIMATE DISPOSAL	LAND	0-5
	MARINE	0-5
	AIR	0-5

*TREATMENT EFFICIENCIES ARE DEPENDENT ON THE NATURE AND ORIGIN OF THE SLUDGE.

APPENDIX V

COAGULATION OF SYNTHETIC WASTEWATER WITH CATIONIC POLYELECTROLYTE (CAT-FLOC) ALONE

CAT-FLOC DOSAGE ppm	RESIDUAL TURBIDITY (JTU) AND TOTAL ORGANIC CARBON (PPM) OF COAGULATED & SETTLED SAMPLES							
	INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9.4		INITIAL pH = 11	
	TURB	TOC	TURB	TOC	TURB	TOC	TURB	TOC
0	131	--	132	--	130	--	130	--
1	95	98	91	93	30	--	81	120
5	98	100	91	88	33	90	50	102
15	122	99	85	97	34	92	18	82
25	151	99	91	104	38	96	18	83
50	168	85	91	85	33	64	18	83
100	165	94	134	85	48	66	29	83

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; NO CARBON ADDED; SETTLING TIME = ONE HOUR; INITIAL TOC (UNFILTERED) OF SYNTHETIC WASTEWATER WITHOUT pH ADJUSTMENT = 184.0 PPM

APPENDIX VI

SETTLING OF SPENT POWDERED ACTIVATED CARBONS WITHOUT USING ANY FLOCCULANT

TYPE & DOSAGE OF CARBONS	SETTLING TIME min.	RESIDUAL PERCENT TRANSMITTANCE AND TURBIDITY (JTU) OF SETTLED SAMPLES AT VARIOUS pH CONDITIONS							
		INITIAL pH = 3		INITIAL pH = 6		INITIAL pH = 9		INITIAL pH = 11	
		TRANS %	TURB JTU	TRANS %	TURB JTU	TRANS %	TURB JTU	TRANS %	TURB JTU
DARCO S-51	0	2	--	2	--	2	--	2	--
750 ppm	5	68.5	34	18	202	56	54	26	152
	15	76	25	20	187	60	46	33	118
	35	78	22	21	180	61	45	36	105
	60	79.5	20	26	152	64	40	39.5	93
	0	2	--	2	--	2	--	2	--
NUCHAR A	5	79	21	64	40	70	32	40	91
750 ppm	10	82	18	73	28	76	24	51	63
	15	89	10	75	26	77	23	52	61
	35	91	9	77	23	82	18	57	52
	60	95	5	80	20	87	12	60	47

EXPERIMENTAL CONDITIONS:

SYNTHETIC WASTEWATER; ROOM TEMPERATURE; NO POLYMER ADDED; COMPLETE MIXING FOR ONE HOUR BEFORE SETTLING

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13. ABSTRACT

Previous investigations of the use of powdered carbon and organic coagulants for treating wastewaters having characteristics similar to those generated at military bases were surveyed and assessed.

Synthetic wastewater consisting of tap water, dishwashing detergent, laundry detergent, soap, clay, oil and food constituents, was prepared for the feasibility and mechanism studies of treating the wastewater by a proposed adsorption/coagulation/filtration system. Operational parameters selected for laboratory optimization studies of the treatment system were: initial pH and temperature of wastewater; contact time of carbon adsorption; types and dosages of powdered carbons; types and dosages of polymers; feed time and feed order of carbon and polymer; retention time of polymer coagulation; and the efficiency of diatomite filtration. Based on the experimental results, the technical feasibility of the proposed treatment system was positively demonstrated, the suitable types of carbon and polymer were selected, and the controlling parameters were optimized.

The standard U. S. Army mobile water purification plant, described in Army Report No. TM5-4610-208-14, has two feeders, an upflow clarifier, a pressure diatomite filter and a sludge thickener. The basic concept of this program was to use the same mobile water purification plant (with an additional mixing tank) for wastewater treatment by the proposed adsorption/coagulation/filtration process. Actual wastewaters from the field shower, laundry, and kitchen units had been collected and treated by the proposed treatment technique with a standard mobile plant of 420 GPH. Their treatabilities by the proposed treatment technique and the mobile plant were confirmed to be promising.

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