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U.S. ARMY

Report

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on
CARBON
ADSORPTION TREATMENT
of
CONTAMINATED GROUNDWATER

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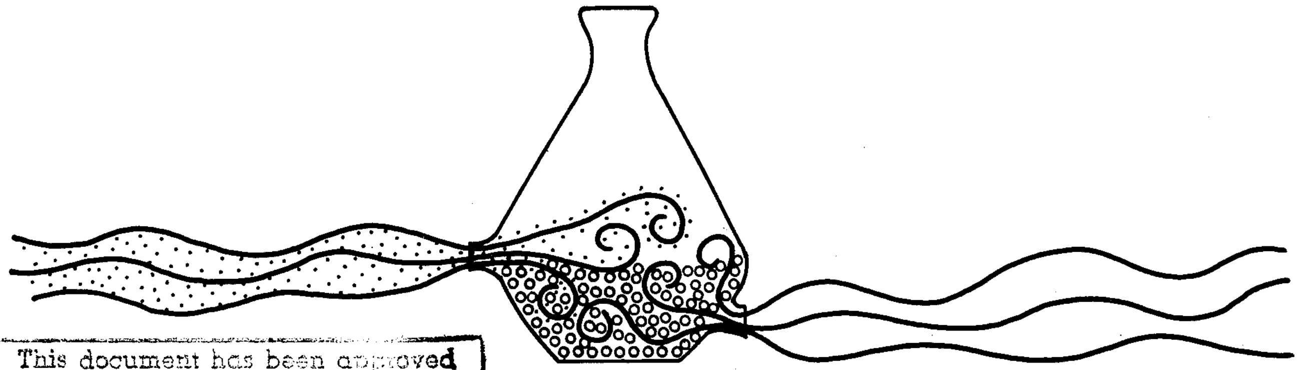

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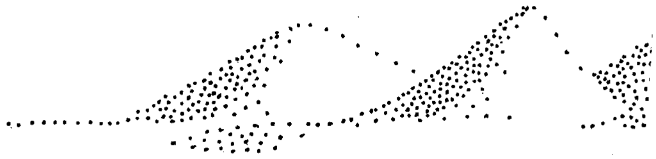

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AS A RESULT OF THE CEASE AND DESIST ORDERS A PROGRAM OF INSTALLATION RESTORATION WAS ESTABLISHED AND PLACED UNDER THE DIRECTION OF THE PROJECT MANAGER FOR CHEMICAL DEMILITARIZATION AND IR. THE PROGRAM OBJECTIVES AT RMA ARE TO STOP CONTAMINANTS MIGRATING OFF THE ARSENAL AND TO ACQUIRE TECHNOLOGY TO DEVELOP AND IMPLEMENT CONTAINMENT AND TREATMENT SYSTEMS. RMA, IN CONJUNCTION WITH WES AND MERADCOM DEVELOPED A PLAN OF STUDY TO DETERMINE THE MOST ECONOMICAL AND FEASIBLE INTERIM CONTAINMENT SYSTEM(S) FOR INSTALLATION AT RMA. IN LATE 1975, MANY STUDIES WERE INITIATED ON PROCESSES THAT WOULD BE APPLICABLE TO REMOVAL OF ORGANIC CONTAMINANTS. THIS REPORT DISCUSSES ONLY ONE PROCESS, CARBON ADSORPTION.

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15 October 1977

PREFACE

The carbon adsorption treatment of contaminated groundwater study was conducted at the Rocky Mountain Arsenal, Commerce City, Colorado, from September 1975 through July 1977 by Rocky Mountain Arsenal's Installation Restoration Directorate, in conjunction with Mobility Equipment Research and Development Command (MERADCOM) and Waterways Experiment Station (WES). The study was instituted as a result of the issuance of Cease and Desist Orders by the State of Colorado Department of Health on 7 April 1975.

Special acknowledgment is extended to the following individuals for their assistance during the course of this work: CPT Joe Kolmer and Mr. Dennis J. Wynne, Project Manager's Office for Installation Restoration; Messrs. Carl G. Loven, Edwin W. Berry, Wilfred R. Baca. Dr. Michael E. Witt, Richard Welling, Keith Reed, Michael J. French, Daryal L. Jones (RMA), MERADCOM and WES.

Colonel John P. Byrne, CmlC, was Commander of Rocky Mountain Arsenal during the preparation of this report. Mr. Irwin M. Glassman was Director of Installation Restoration.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

TABLE OF CONTENTS
(Continued)

LIST OF FIGURES

SECTION 1

INTRODUCTION

1.1 GENERAL

Industrial type operations have been conducted at Rocky Mountain Arsenal for over 35 years. During that time, wastes were disposed of in accordance with standard industrial practices. Although acceptable at the time, these practices have since been proven to contribute to surface and ground water contamination. Many studies have been conducted on ways to contain and/or treat contaminated water at RMA. This report discusses only the carbon adsorption studies.

1.2 ROCKY MOUNTAIN ARSENAL HISTORY

Rocky Mountain Arsenal was established in 1942 and originally encompassed 19,776 acres northeast of the City of Denver, Colorado. Since it was established RMA has either produced toxic chemicals and chemical filled munitions or demilitarized these same items upon obsolescense. In 1946, after World War II, a large portion of the manufacturing facilities was leased to private industry for the production of herbicides and insecticides. This production is currently continuing with the present lease due to expire in 1987.

1.3 CHRONOLOGY OF OFF-POST CONTAMINATION

From 1942 until 1953, all industrial wastes from Government and private industry operations were dumped into a natural ground basin called Basin A. With the production of nerve gas starting in 1953, it was apparent that Basin A would soon overflow. To handle this overflow, other natural basins located in the northwest surface water flow path were dammed and were labeled Reservoirs C, D and E (see Figure 1-1).

The first indication of off-post contamination occurred in the Summer of 1951 when some minor crop damage was observed on an irrigated farm northwest of RMA. At this time, the crop damage was not attributed to ground water contamination by RMA. In the Summer of 1954, several farmers complained that ground

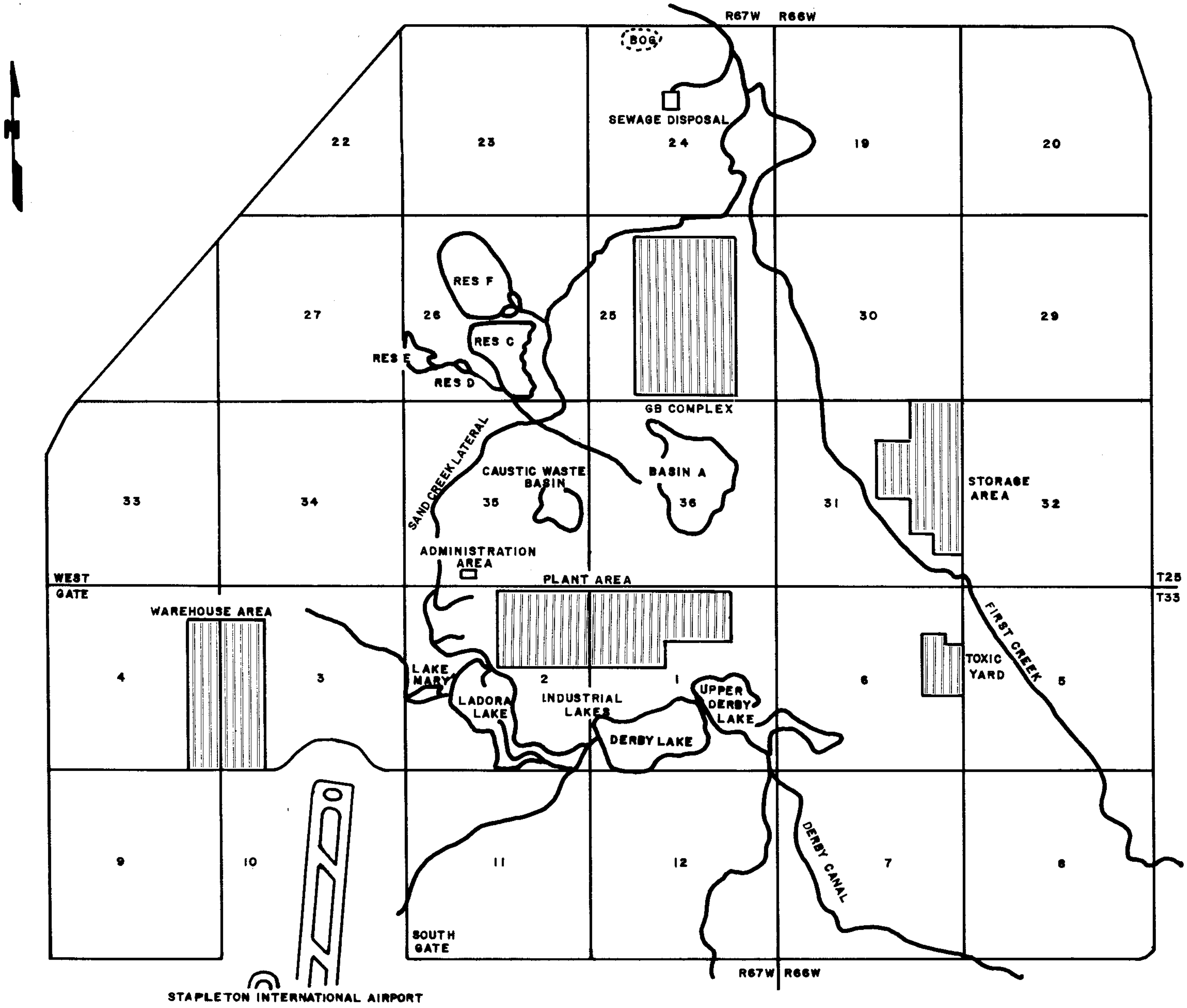

Figure 1-1. Rocky Mountain Arsenal Plan View

water used for irrigation had damaged their crops. (The precipitation in 1954 was considerably below average and increased pumping from shallow irrigation wells was required to produce crops). Due to the increase of complaints and subsequent damage claims, the Department of the Army initiated several studies.

As a result of these studies, Reservoir F was constructed and, since early 1957, all industrial wastes have been pumped to this reservoir. To preclude ground water contamination, the bottom of Reservoir F was lined with a waterproof membrane. Other studies indicated that the primary contaminants were sodium and chlorides and that the ground water flow patterns followed the general northwesterly surface water flow patterns.

In May 1974, diisopropyl methylphosphonate (DIMP) and dicyclopentadiene (DCPD), were detected in surface water draining from a marshy bog on the northern boundary of the Arsenal. DIMP is a persistent compound produced in small quantities (less than 3 per cent) during the manufacture of GB. DCPD is a chemical used in the production of insecticides (see Appendix, Pages A-2 through A-16). Detection of these two compounds resulted in the following action:

A. More wells were drilled and the well monitoring program was expanded to include tests for these and other compounds.

B. In September 1974, a dike was constructed north of the marshy bog to eliminate off-post surface drainage.

C. RMA and Ft. Detrick established programs to determine the effect of DIMP on wheat growth.

In December of 1974, the Colorado Department of Health detected DIMP in a well near the City of Brighton, Colorado. This data was published in "1974-75 Ground Water Study of the Rocky Mountain Arsenal and Some Surrounding Areas" and is based on comparison with synthesized DIMP rather than DIMP samples submitted by RMA to the Department of Health. Although the quantity of DIMP detected was extremely small (0.57 parts per billion), it indicates that ground water may travel in a northerly direction. A two year study by USGS tends to confirm this additional direction of ground water flow. The detection of DIMP and DCPD in the surface water off the Arsenal and DIMP in wells near Brighton led the State of Colorado Department of Health to issue three Cease and Desist Orders on 7 April 1975 against Shell Chemical Company (SCC) and Rocky Mountain Arsenal (RMA). In short, these Orders stated that SCC and RMA must:

A. Immediately stop the off-post discharge (both surface and subsurface) of DIMP and DCPD.

B. Take action to preclude future off-post discharge (both surface and subsurface) of DIMP and DCPD.
C. Provide written notice of compliance with Item A.
D. Submit a proposed plan to meet the requirements of Item B.
E. Develop and institute a surveillance plan to verify compliance with Items A and B.

1.4 PROGRAM HISTORY

As a result of the Cease and Desist Orders, a Program of Installation Restoration was established and placed under the direction of the Project Manager for Chemical Demilitarization and Installation Restoration. The program objectives at RMA are to stop contaminants migrating off the Arsenal and to acquire technology to develop and implement containment and treatment systems. Contaminated land areas on the Arsenal will be restored only when they are identified as sources of off-post contaminant migration at hazardous concentration levels.

RMA, in conjunction with Waterways Experiment Station (WES) and Mobility Equipment Research and Development Command (MERADCOM), developed a plan of study to determine the most economical and feasible interim containment system(s) for installation at RMA. This study was organized as follows:

A. Conduct literature research to review existing data.
B. Perform bench-scale studies on selected processes.
C. Perform field studies to develop design criteria.
D. Select full scale process based on:
    1. Efficiency of contaminant removal
    2. Process reliability
    3. Economic feasibility
    4. Compatibility with other processes
    5. Ease of expansion
E. Construct and operate the selected treatment system in compliance with the Cease and Desist Orders

In late 1975, many studies were initiated on processes that would be applicable to removal of organic contaminants. This report discusses only one process, carbon adsorption.

SECTION 2

BOG WATER STUDIES

2.1 GENERAL

A Corp of Engineers' Report and a U. S. Army Environmental Hygiene Agency Report were reviewed. Both reports contain water analyses from wells near the bog in Section 24. Comparisons between these well water analyses and bog water analyses show distinct similarity and tend to confirm that the north bog is a surface expression of groundwater (see Figure 2-1). Based on this, it was concluded that a successful bog water decontamination process would apply to groundwater treatment and would provide a basis for the groundwater reclamation program.

2.2 WATER CHARACTERIZATION

In September of 1975, one hundred gallons of bog water were delivered to the Mobility Equipment Research and Development Command (MERADCOM) at Ft. Belvoir, Virginia. Upon receipt, a water quality study was conducted to establish a baseline by identifying characteristics and quantifying contaminants as shown in Table 2-1. All analyses listed were conducted in accordance with procedures presented in the "13th Edition of Standard Methods for the Examination of Water and Wastewater" dated 1971. A Beckman Model 915 Total Carbon Analyzer was used to determine the total organic carbon (TOC) and the inorganic carbon (IC). Also, a water sample was fingerprinted by gas chromatographic methods using a Hewlett Packard Model 7620A gas chromatograph with a Ni 63 detector.

These analyses were repeated twice (Columns 4 and 5, Table 2-1) during preliminary investigations to insure that the water characteristics were not changing due to long term storage. The chemical oxygen demand (COD), TOC and alkalinity analyses showed reasonably good correlation and were used throughout the study as checks on laboratory analyses. Based on these correlations, the TOC analysis was selected for use in determining the efficiency of each process studied.

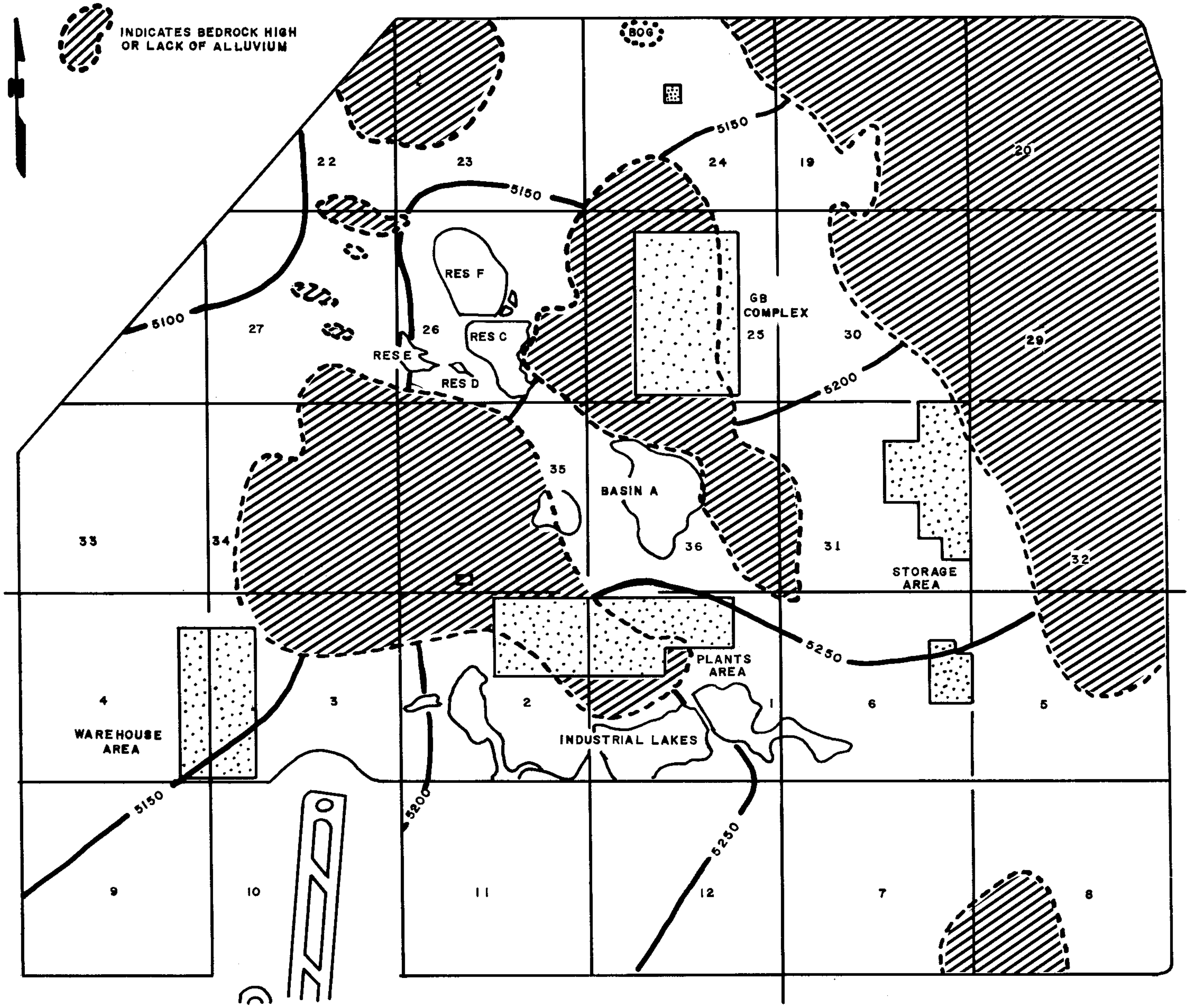

Figure 2-1. Groundwater Contours and Bedrock Highs

PARAMETER	UNITS	9/12/75	9/23/75	10/24/75
Turbidity	---	3.0	1.0	1.3
Color	---	19.0	18.0	18.0
TDS	mg/l	1300	1350	1300
Conductivity	u mhos/cm	1850	1850	1825
pH	---	7.6	7.9	8.0
Alkalinity	mg/l	252	256	240
Hardness	mg/l	488	498	466
Chlorides	mg/l	232	239	286
Sulfates	mg/l	627	540	620
Nitrates	mg/l	1.5	---	---
Copper	ppm	0.0	0.0	---
Chromium	ppm	0.0	0.0	---
Cadmium	ppm	0.01	0.02	---
Iron	ppm	0.40	0.46	---
TOC	mg/l	38.0	41.0	39.0
COD	mg/l	31.0	36.0	40.0
BOD	mg/l	<1.0	<1.0	---

Table 2-1. Bog Water Analyses at MERADCOM

2.3 BOG WATER BENCH STUDIES

Screening adsorption studies were conducted with granular and powdered carbon and polymeric and ion exchange resins. One gram of each adsorbant was added to a one liter sample of bog water. The resultant slurry was stirred continuously for thirty minutes and then allowed to stand for fifteen minutes to permit the adsorbant to settle. The water sample was then filtered, analyzed for TOC and the results compared with the baseline (see Table 2-2). Although XAD-2 and XAD-7 are specifically designed for the removal of organic carbon, the results showed that these resins and NCH did not have adequate capacity to warrant further studies. Based on these findings, more extensive studies were conducted on granular carbon, powdered carbon and the anionic exchange resin.

SYSTEM	ADSORBENT	CAPACITY IN mg/l TOC/gm ADS
Granular Carbon	Calgon 400	3.99
	NUCHAR 12 x 40	10.99
Powdered Carbon	Hydrodarco-C	26.00
	Darco G-60	25.00
Resin Exchangers	IRA - Anionic Resin	16.99
	NCH - Cationic Resin	7.98
	XAD-7 Poly Resin	9.01
	XAD-2 Poly Resin	7.99

Table 2-2. Preliminary Test Results

2.3.1 GRANULAR CARBON

The granular carbons exhibited a much lower capacity than expected as shown in Table 2-3. The resulting effluent TOC concentration was consistently higher than that obtained with other processes. Neither Calgon 400 nor Nuchar 12 X 40 had adequate specific sites to effectively reduce TOC. The granular carbon isotherm and kinetic study results are shown in Figure 2-2. To obtain maximum TOC reduction, the data indicates that a resident time of 30 minutes would be required at an adsorption capacity of 27.4 mg/l TOC gm carbon.

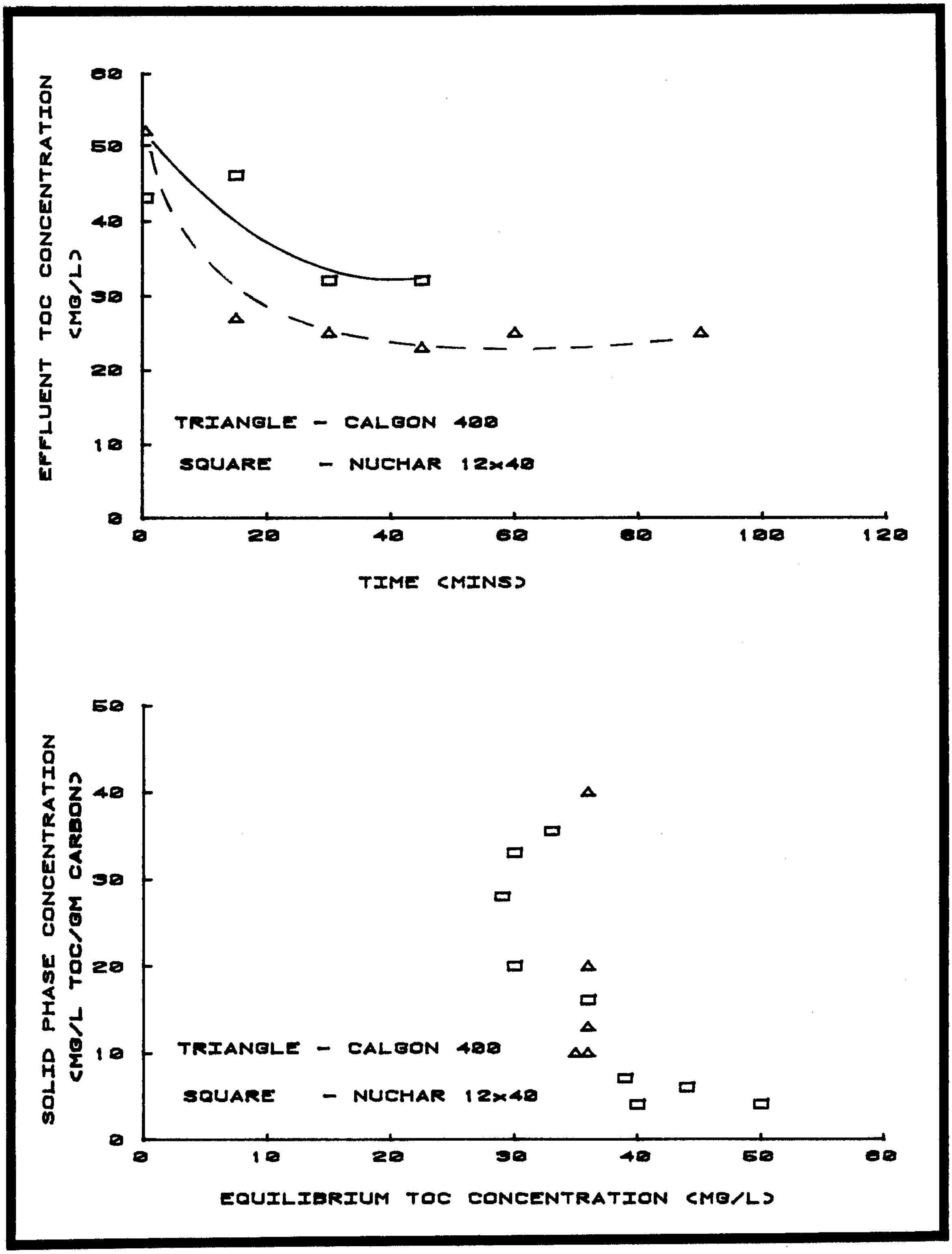

Figure 2-2. Granular Carbon Isotherm

This data also indicated that TOC was leaching from granular carbon; however, after washing the carbon in distilled water and drying it, this was minimized. Still, it is unknown as to the amount of leachable organics that may be expected from granular carbon. Due to the low capacity of granular carbon, it was recommended that it should only be considered as a pretreatment process.

SAMPLE VOLUME (ml)	WT. OF CARBON (mg)	CALGON 400		NUCHAR 12 x 40	
		FINAL TOC (mg)	CAPACITY mg/l TOC/gm ADS	FINAL TOC (mg)	CAPACITY mg/l TOC/gm ADS
1000	0	39		39	
	100	36	40.0	33	70.0
	200	36	20.0	33	35.5
	300	36	13.3	30	33.3
	400	36	10.0	29	27.5
	500	35	10	30	20.0

Table 2-3. Granular Carbon Adsorption Capacity

2.3.2 POWDERED CARBON

The powdered carbons exhibited high adsorption capacities and excellent efficiency. The adsorption isotherm for Darco G-60 is presented in Figure 2-3. Regression analyses showed that the adsorption could be predicted with a correlation coefficient ($\sqrt{R^2}$) of ± 0.95 by the equation

$$X/_{m}=1.76\ (C_{TOC}) + 5.62$$

where the C is TOC concentration remaining in milligrams per liter. The removal may be expressed by

$$\%R = -2.23\ (C_{TOC}) + 97.22$$

with a correlation coefficient of ± 0.98 where C_{TOC} is the concentration remaining. The adsorption isotherm for Hydrodarco-C is presented in Figure 2-4. Adsorption capacity using this carbon may be predicted by

$$X/_{m} = 1.30\ (C_{TOC}) + 7.60$$

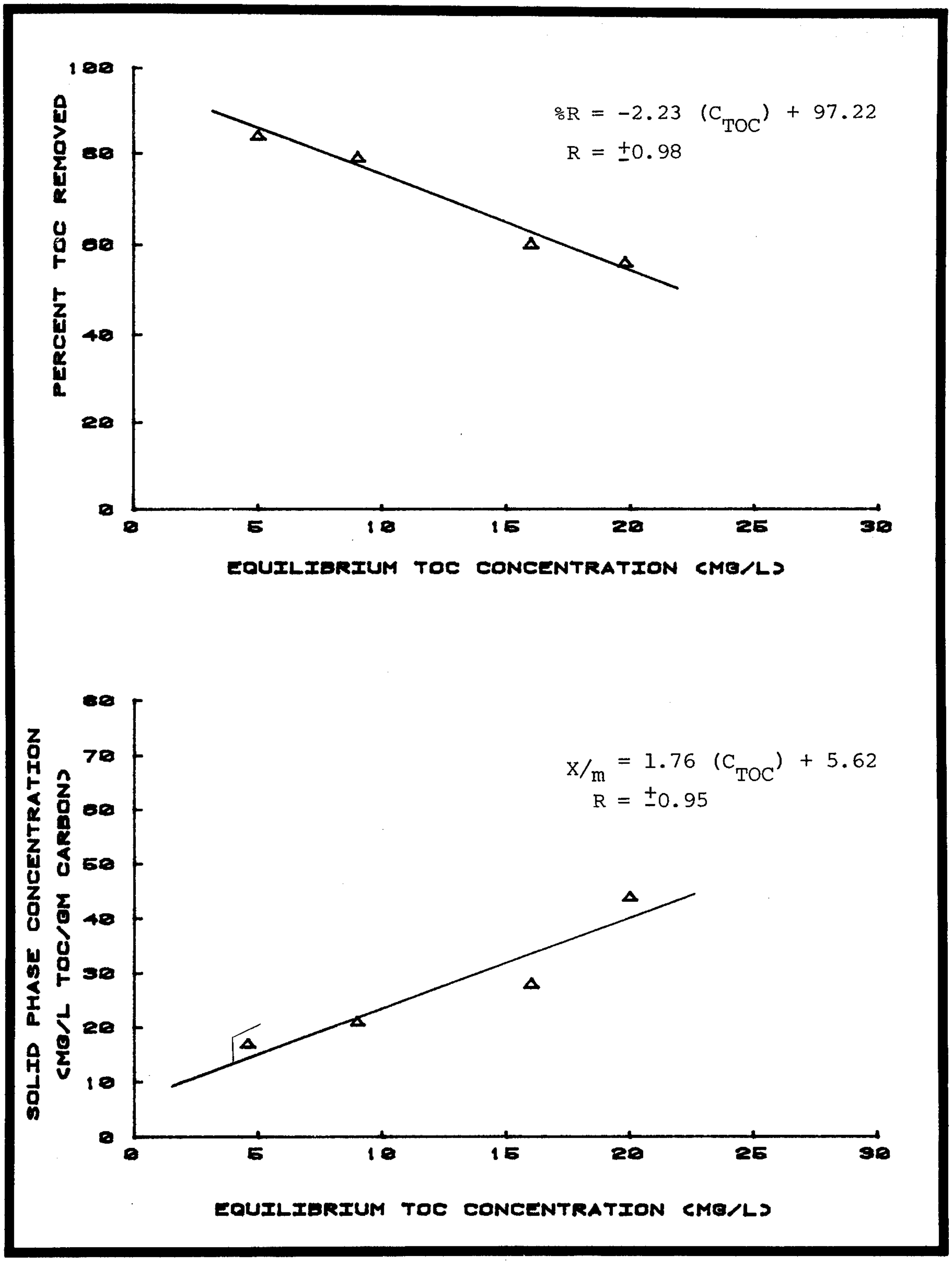

Figure 2-3. Darco G-60 Isotherm

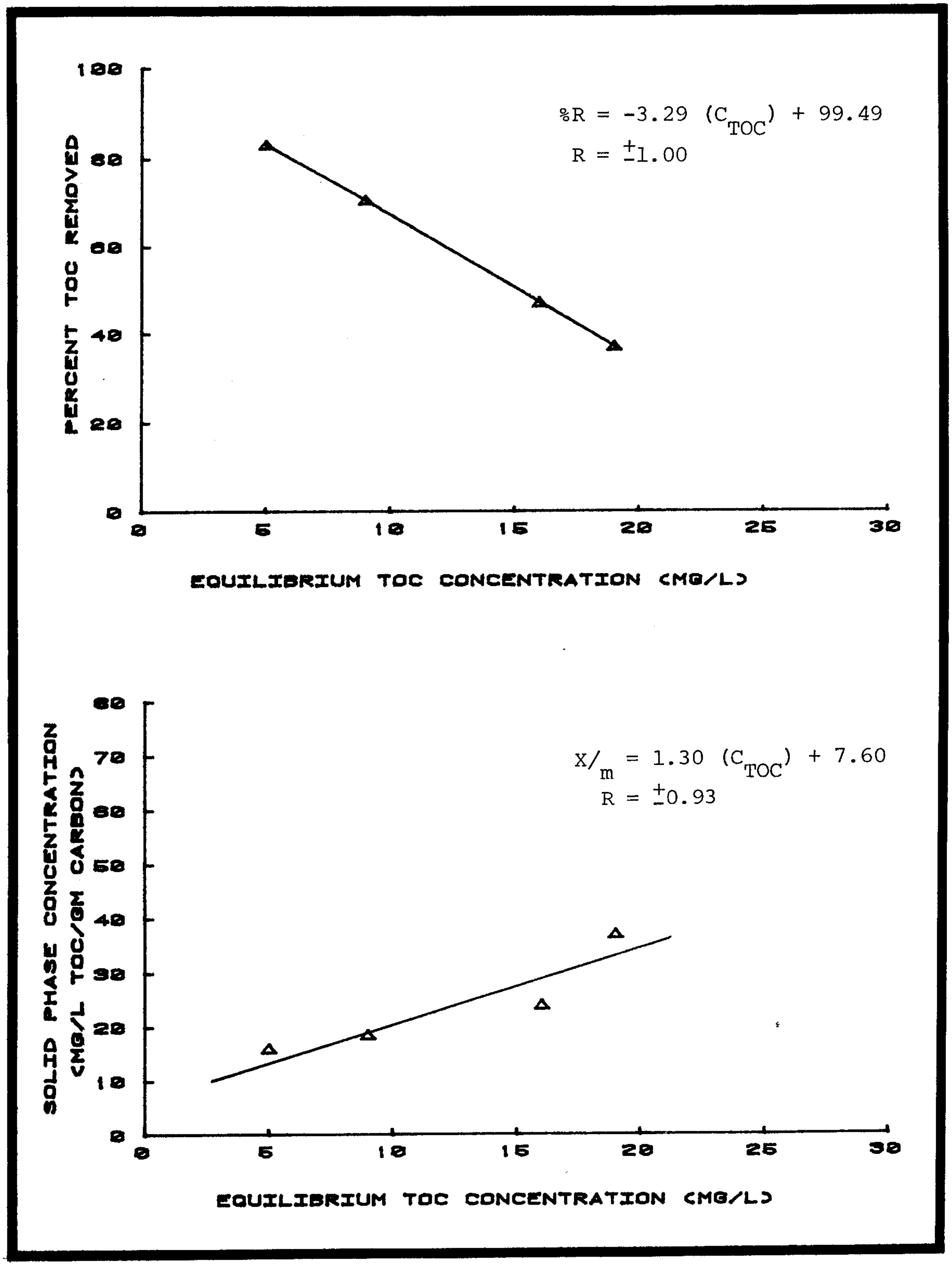

Figure 2-4. Hydrodarco-C Isotherm

with a correlation coefficient of ±0.93. The efficiency of this carbon may be expressed by

$$\%R = -3.29 (C_{TOC}) + 99.49$$

with a correlation coefficient of ±1.00. Analysis of the limited data available shows little difference in the performance of the two powdered carbons; however, Hydrodarco-C does appear to be slightly more adsorptive.

It was discovered that some coagulant was necessary to effectively separate the carbon phase from the fluid. Adsorption and coagulation studies were conducted using a cationic coagulant, Catfloc, with both powdered carbons (see Table 2-4) and using an anionic coagulant, Drewfloc, with Hydrodarco-C (see Table 2-5). The results showed that the anionic coagulant and Hydrodarco-C was the most effective mixture. It was determined that a dosage of 2 grams/liter of carbon and 1 milligram/liter of coagulant would reduce TOC from 40 mg/liter to 5 mg/liter as shown in Figure 2-5. Based on these results, it seems that the anionic coagulant/powdered carbon process offers the greatest flexibility and control.

CATFLOC DOSE mg/l	DARCO G-60			HYDRODARCO-C		
	FINAL TOC mg/l	CAPACITY mg/l TOC/ gm ADS	PERCENT REMOVAL	FINAL TOC mg/l	CAPACITY mg/l TOC/ gm ADS	PERCENT REMOVAL
5	25	3.0	10.7	21	7.0	25.0
10	16	12.0	42.9	20	8.0	28.6
20	11	17.0	60.7	24	4.0	14.3
30	15	13.0	47.4	19	9.0	32.1
40	18	10.0	35.7	19	9.0	32.1
50	11	17.0	60.7	14	14.0	50.0

Table 2-4. Cationic Coagulant Test Results

DREWFLOC DOSE mg/l	HYDRODARCO-C		
	FINAL TOC mg/l	CAPACITY mg/l TOC/ gm ADS	PERCENT REMOVAL
0.2	23	7.0	23
0.5	12	18.0	60
5.0	11	19.0	63
8.0	11	19.0	63
10.0	16	14.0	47
15.0	28	2.0	7
20.0	26	4.0	13

Table 2-5. Anionic Coagulant Test Results

IRA DOSE gm/l	FINAL TOC mg/l	CAPACITY mg/l TOC/ gm RESIN	PERCENT REMOVAL
0	50	0	0
0.25	40	40	20
0.5	30	40	40
1.0	46	4	8
1.5	28	14.66	44
2.0	31	14.55	38

Table 2-6. Anion Resin Adsorption Test Results

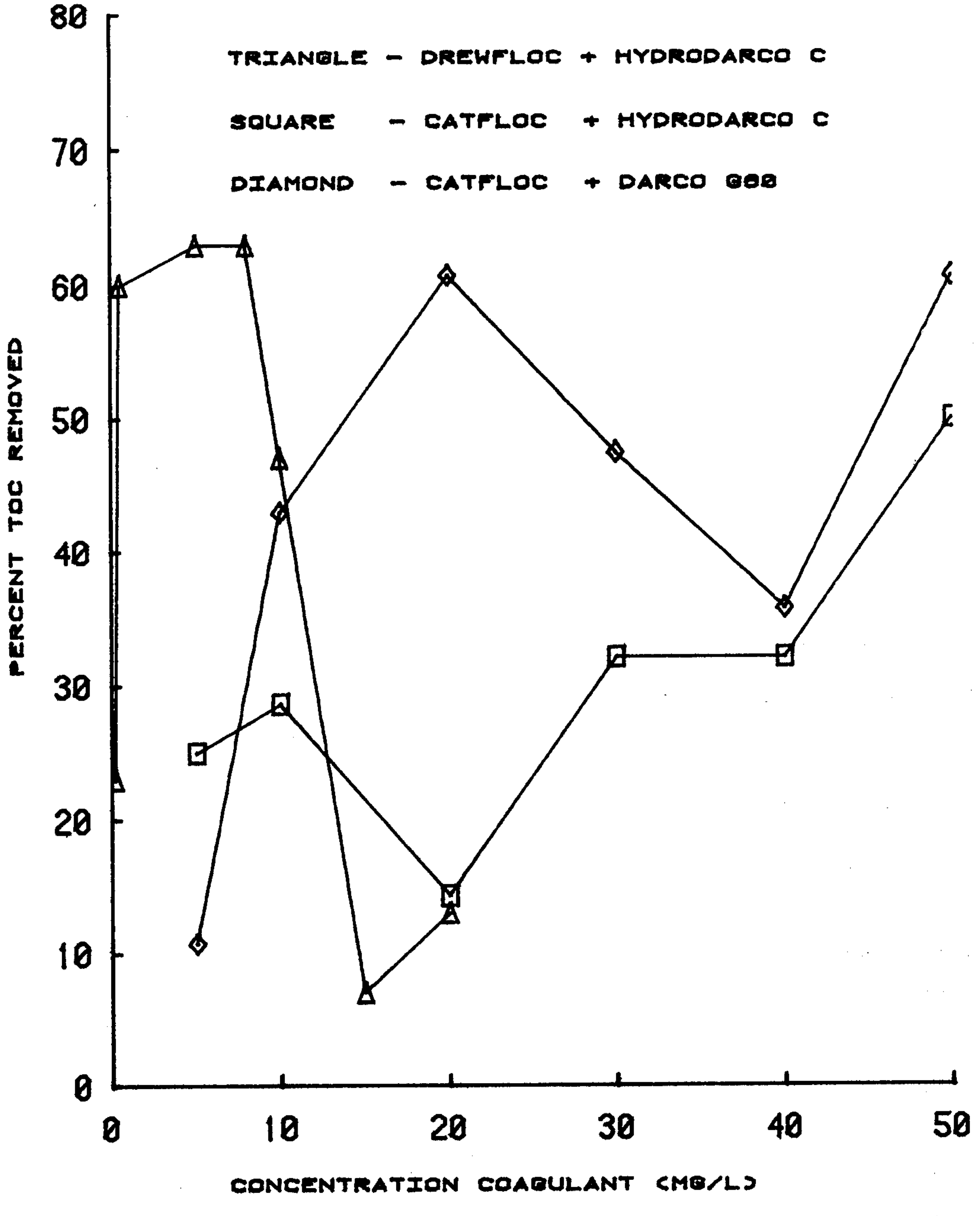

Figure 2-5. TOC Removal With Coagulant

2.3.3 ANION EXCHANGE RESIN

The only resin that showed promise for treating bog water was an intermediate strength anion exchange resin, IRA. This is comparable to the anionic coagulant test result. The results of the anion resin adsorption tests are presented in Table 2-6 and a capacity curve is presented in Figure 2-6. Based on this data, an ion exchange bed of approximately 100 cubic feet would be required to treat 125 gallons of water per minute. The economics of this process must be evaluated before further studies are conducted.

2.4 BOG WATER FIELD STUDIES

Even though bench studies conducted at MERADCOM indicated that the powdered carbon process was much more promising than the granular carbon process, it was decided to conduct field studies at Rocky Mountain Arsenal to evaluate both processes within the confines of available technology and equipment. The bench studies also indicated that the adsorptive capability and organic removal efficiency of powdered carbon was enhanced by the addition of a polymeric coagulant. Therefore, it was decided to conduct field studies on the powdered carbon/coagulation and the equipment selected was a 420 gallon per hour Erdlator. Equipment selected for the granular carbon study was a five column Filtrasorb system manufactured by Calgon Corporation.

2.4.1 ERDLATOR PROCESS DESCRIPTION

The Erdlator is a 420 gallon per hour water purification unit designed to field treat water for use by military personnel. The system consists of a dry-carbon feeder, chemical feeder, mix tank, clarifier, sludge concentrator and diatomite filter (see Figure 2-7). Feed water passes through a 0-10 gallon per minute flow meter into a mixing pot on the side of the dry-carbon feeder where a regulated amount of carbon is injected to produce a carbon slurry. The carbon slurry flows to the mix tank where coagulant (anionic, cationic or a combination) is added and the slurry is thoroughly mixed by a paddle-wheel stirrer. This slurry is pumped from the bottom of the mix tank to the clarifier.

The slurry enters the clarifier at the top of the downcomer tube where the carbon, coagulant and developing floc are further agitated by a stirrer consisting of three flat metal disks mounted on a drive shaft (see Figure 2-8). This stirrer can be adjusted to rotate at four different speeds (200, 240, 300

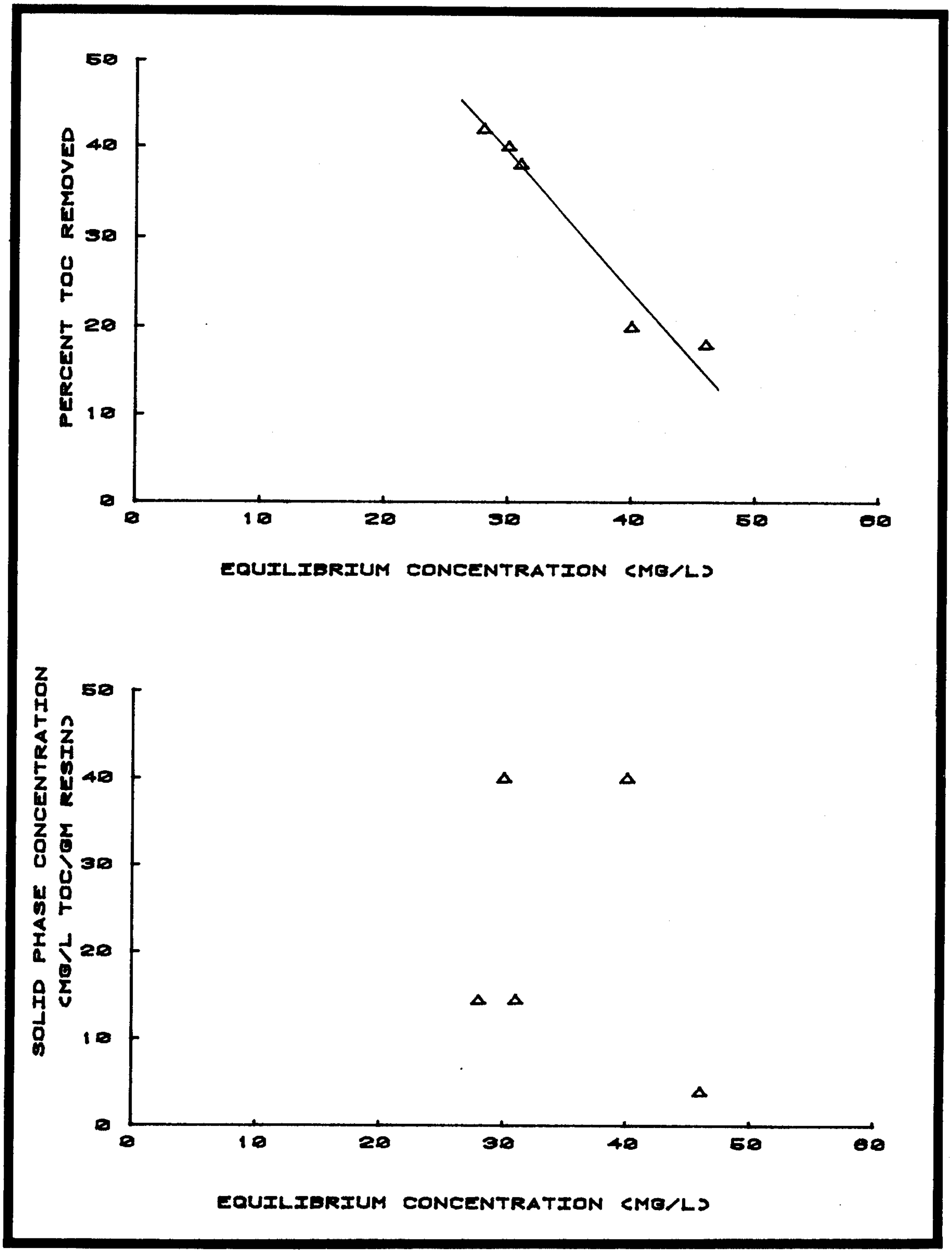

Figure 2-6. Anion Resin Capacity Curve

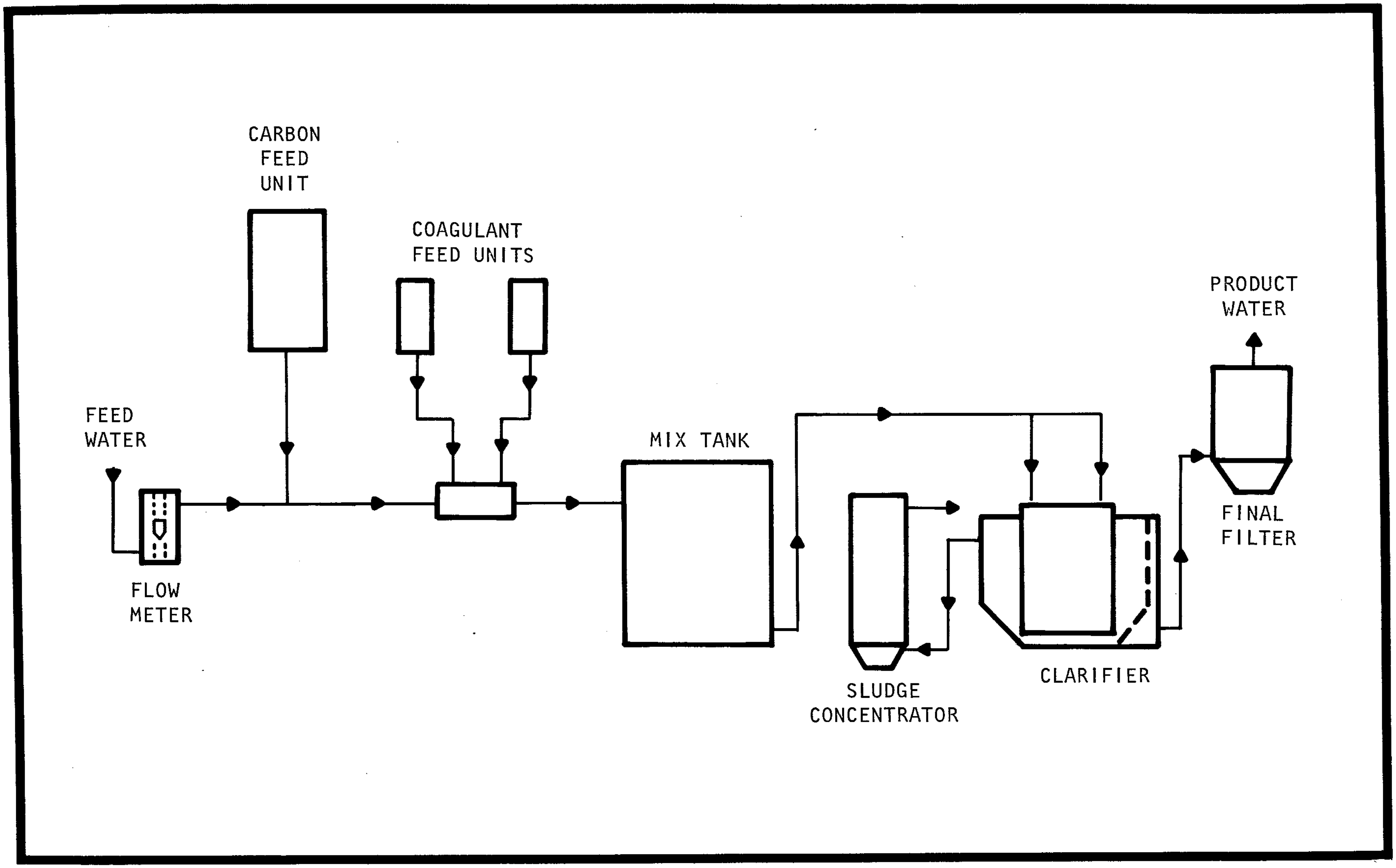

Figure 2-7. Erdlator Process Flow Diagram

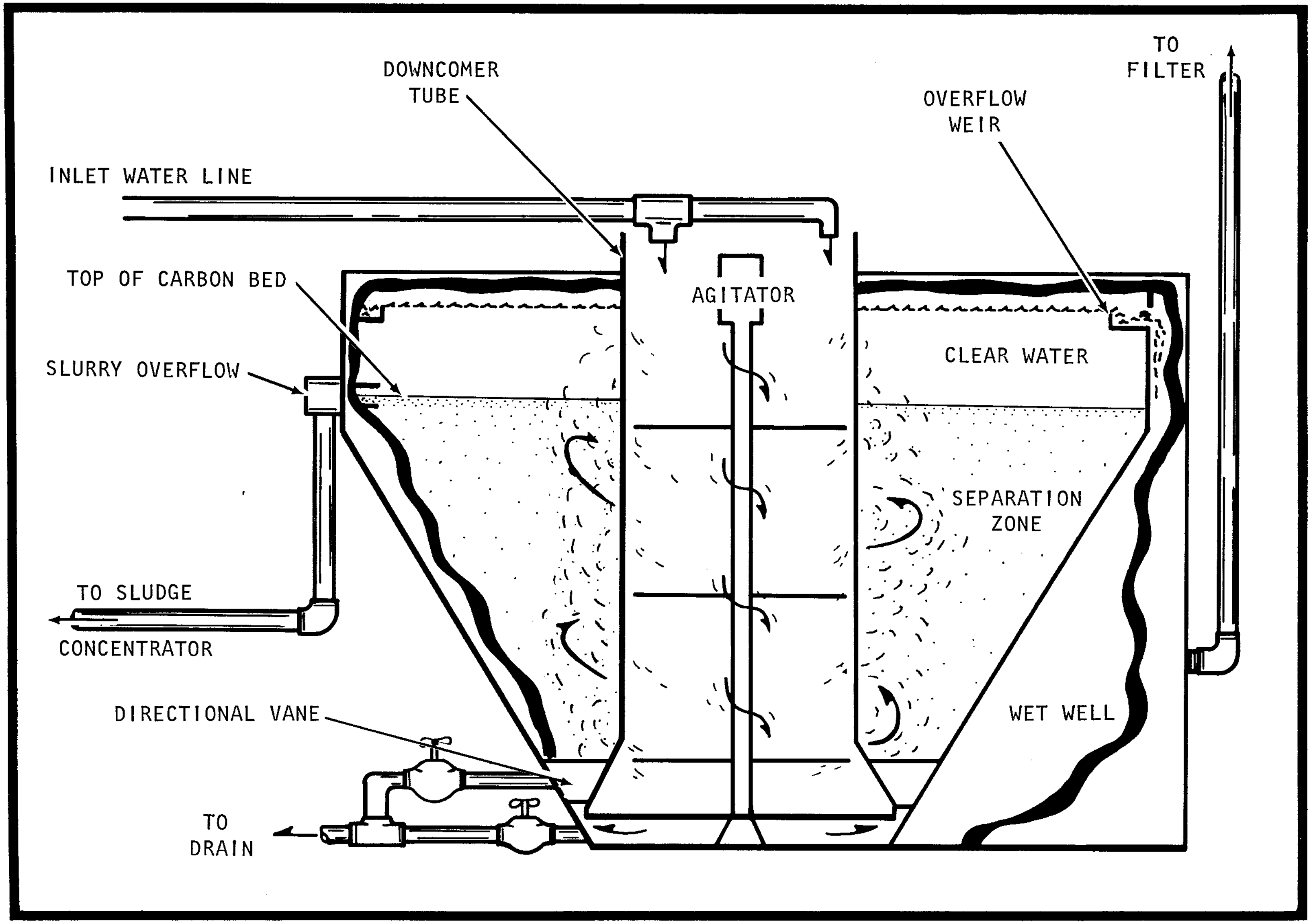

Figure 2-8. Clarifier Details

and 350 rpm). The direction of slurry rotation imparted by the stirrer is reversed by baffles at the bottom of the downcomer tube. After passing through the baffles, the slurry flows upward in the separation zone which is the annular space between the downcomer tube and the outer shell. The separation zone is designed so that, at a maximum feed rate of 7 gpm, the water has a retention time of 20 minutes with an upflow velocity of 1.1 gallons/minute/ft.^{2}. The upward revolving flow maximizes the residence time to provide effective contact between feed water, carbon, coagulant, developing floc and established floc. The separation zone, where hydraulic separation of carbon and water occurs, is characterized by a well-defined horizontal plane below which is the established carbon bed and above which is the clear water effluent. The clear water is collected around the outer shell in a weir which in turn discharges to the wet well. The wet well provides water storage and sufficient head for the final filter pump.

The sludge concentrator is a 30 gallon cylindrical tank which accepts the slurry overflow from the carbon bed in the clarifier. The carbon bed height and slurry withdrawal rate are regulated by adjusting a ball valve which controls the amount of slurry flowing from the clarifier to the sludge concentrator. The slurry is withdrawn from the clarifier through a horizontal slit located twelve inches below the weir on the outer shell. Since the flow in the separation zone is upward and the slurry is withdrawn from the top of the carbon bed, carbon in the withdrawn slurry has had the most residence time . The sludge concentrator acts as a small clarifier because the clear effluent from the top of the concentrator is returned to the wet well. The spent slurry is intermittently drained from the bottom of the concentrator to prevent restriction of slurry flow from the clarifier.

The final product filter is a domed cylindrical shell which contains four cylindrical filter columns (see Figure 2-9, Pg. 2-17). Each filter column has seven inverted porous plastic cups and is covered by a metal screen. Water from the clarifier wet well is pumped into the bottom of the filter and is mixed with diatomaceous earth. As the mixture flows upward, diatomaceous earth is applied to the filter cups to provide the filter medium. When water starts to flow out of an air release valve at the top of the filter, this valve is closed and trapped air is compressed in each of the inverted cups and in the filter dome. Water discharge from the top of each column is piped to a three-way valve which can be positioned to "RECIRCULATE," "PRODUCT" or "BACKWASH". Upon startup, the water is recirculated to the wet well until it becomes clear as determined by viewing it

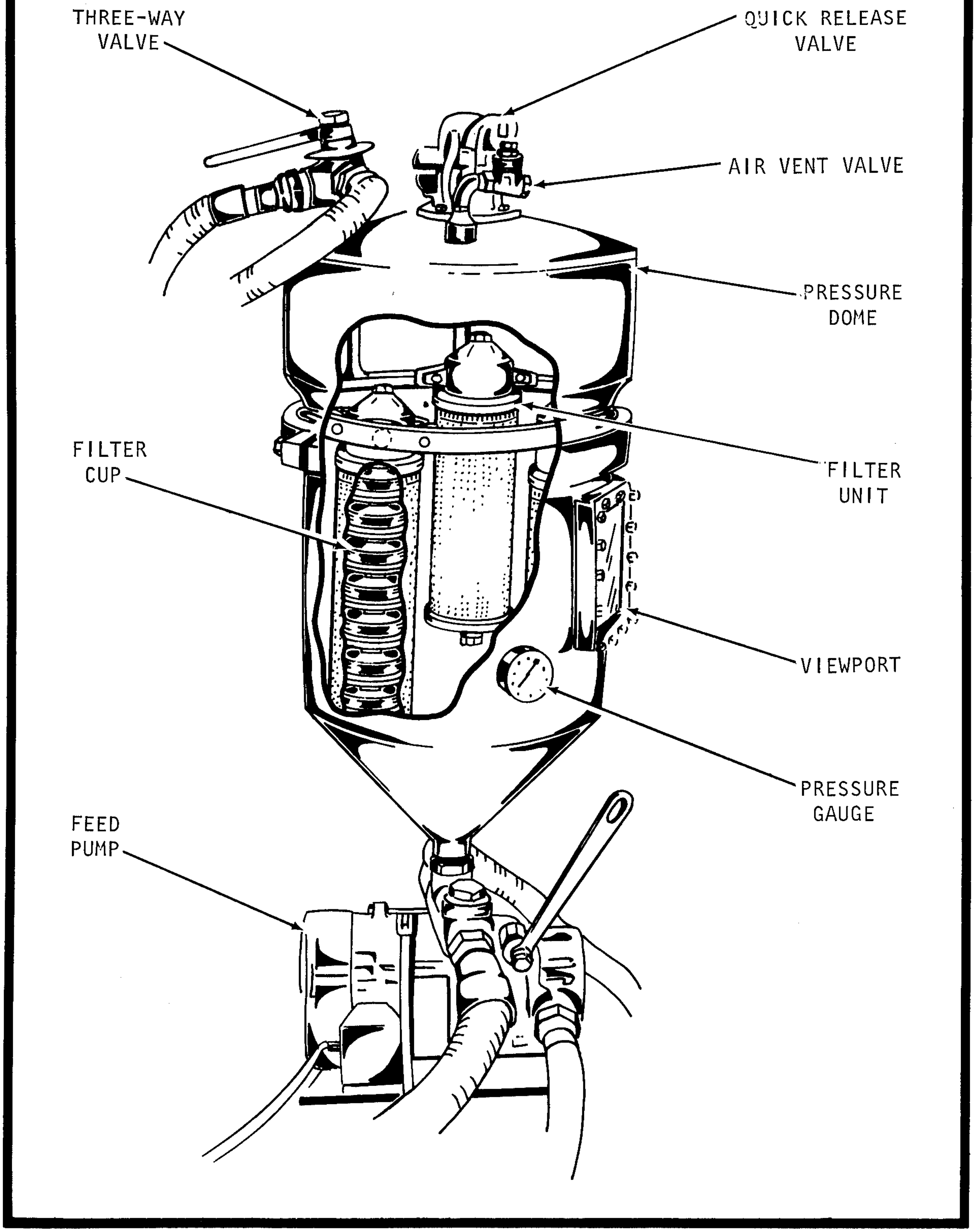

Figure 2-9. Final Filter Details

through a glass port in the bottom of the filter. When the water becomes clear, the three-way valve is positioned to "PRODUCT" and the water is ready for personnel use.

During normal operation, the filter pressure will vary between 25 and 40 psi. As the filter cups become clogged, the pressure will increase. When the pressure reaches 50 psi, it is considered the end of a filter run and the filter is shutdown and cleaned. To clean the filter, a quick release valve at the top of the dome is opened. This sudden reduction in pressure allows the trapped air in the inverted cups to expand very rapidly and, in effect, blow the clogged cake off of the filter cups. The three-way valve is then set to "BACKWASH" the filter is backwashed and drained, and the filter is ready for another cycle.

The equipment just described was provided by MERADCOM and installed at RMA for field testing. Equipment setup and the first two test runs were supervised by MERADCOM personnel. The remaining test runs were conducted by RMA personnel and all water analyses were conducted in RMA laboratories. The field test program was conducted to; (1) determine the feed rates of coagulants and powdered carbon that would optimize DIMP removal and (2) determine the raw water feed rate that would produce the most stable carbon bed.

2.4.2 COAGULANT FEED STUDIES

In the first field test, it was determined that the addition of both coagulants (anionic and cationic) was necessary to obtain a stable carbon bed. Neither the omission of both coagulants nor the addition of a single coagulant produced an acceptable bed. Only one anionic coagulant and one cationic coagulant were used throughout all field test runs. The anionic coagulant was Hercufloc 836.2 manufactured by Hercules, Inc. The cationic coagulant was Catfloc manufactured by Calgon Corporation.

During the first two test runs which were conducted by MERADCOM, the anionic mixture and feed rate was 0.556 gm/l at 1000 cc/min., and the cationic mixture and feed rate was 4 mg/l at 26.5 cc/min. It is acknowledged that these concentrations and feed rates were excessive; however, the objective of the test runs was not optimization of coagulant feed.

After the completion of MERADCOM's two test runs, RMA personnel conducted several short test runs to optimize the coagulant mixture and feed rates. These studies were hampered by three constraints. First, there were operating limitations of the metering equipment; secondly the feed rates had to be compatible with overnight, unmonitored operation; and thirdly, too high a concentration would increase the viscosity beyond pumpable limits. Within these limitations, the optimum anionic concentration and feed rate was set at 0.13 gm/l at 120 cc/min. Concentration was the limiting factor since a higher concentration would create a mixture too viscous to be pumped. If desired, a lower concentration could be used in conjunction with a higher feed rate. The optimum cationic concentration and feed rate was set at 1.59 gm/l at 25 cc/min. Metering was the limiting factor since 25 cc/min was a minimum available setting. Again, a lower concentration could be used in conjunction with a higher feed rate. In both cases, a higher feed rate would necessitate more frequent filling of the chemical feeders. Both rates are an absolute minimum because the carbon bed starts to deteriorate at lower concentrations and/or feed rates. These concentrations and feed rates were used throughout the remaining field tests.

2.4.3 INFLUENT WATER FEED STUDIES

The feed rate of influent water directly affects the fluidization of the powdered carbon bed. The purpose of these tests was to determine the sensitivity of the carbon bed height to fluctuations in water feed rates using different carbons and different dosages. These tests had to be conducted by using a one-time carbon dosage and eliminating the constant carbon replacement feed. Otherwise the bed would always stabilize at the design height of 26 inches or would overflow. Three test runs were conducted using a constant coagulant feed rate and variable water feed rates of 1, 3, 5, 6, 7 and 7.5 gpm.

The first test was conducted using a 20 pound bed of Hydrodarco-C powdered carbon manufactured by Atlas Chemical Industries, Inc. In this test, the bed showed a uniform increase in height up to the 7 gpm rate and stayed within the design height of 26 inches (see Figure 2-10). When the water feed rate was increased to 7.5 gpm (0.5 gpm over maximum design rate), the bed height dropped 3.5 inches and a carbon carryover was observed in the product water.

The second test was conducted using a 30 pound bed of Hydrodarco-C. In this test, the bed showed a uniform increase in height up to the 6 gpm rate. When the water feed rate was increased to 7 gpm, the bed height increased rapidly but still stayed within design limits. The drop in bed height at 7.5 gpm was negligible but the product water still contained carbon carryover.

The third test was conducted using a 20 pound bed of Aqua Nuchar powdered carbon manufactured by Westvaco Chemical Co. In this test, the bed showed a uniform but very rapid height increase up to 6 gpm. At 5 gpm, the bed height exceeded design height by 5 inches and at 7 gpm, the bed overflowed into the weir and could not be measured. A fourth test was originally scheduled using a 30 pound bed of Aqua Nuchar; however, based on the results of the third test, this test was cancelled.

The results of this test indicate that Aqua Nuchar can only support a water feed rate of 3 gpm or less; therefore, the carbon feed studies were conducted with Hydrodarco-C powdered carbon. The results also showed that Hydrodarco-C would support a water feed rate of 6 gpm. However, a water feed rate of 5 gpm was selected for further studies since this rate would accommodate feed rate fluctuations while maintaining a stable carbon bed.

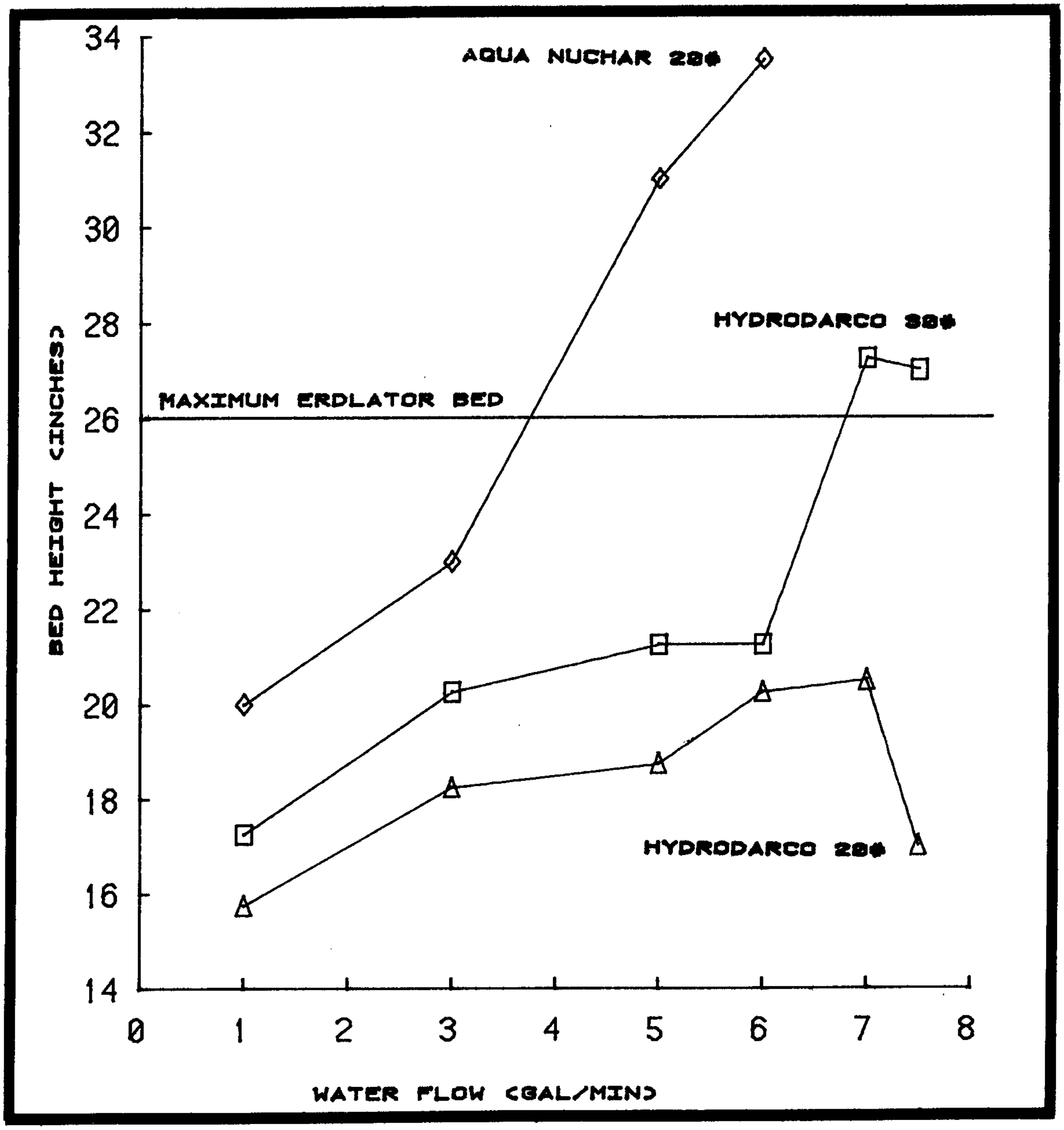

Figure 2-10. Influent Water Feed Studies

2.4.4 CARBON FEED STUDIES

The carbon feed studies were conducted to determine the optimum carbon feed rate while maintaining an acceptable effluent DIMP concentration. Hydrodarco-C powdered carbon was used for all the carbon feed rate test runs. All carbon feed rates are expressed as milligrams per liter of feed water. Test run one was conducted by MERADCOM under the following operating parameters:

Water feed rate	7 gpm (26.5 liters)
Anionic conc.	0.556 gm/l
Anionic feed rate	1000 cc/min.
Cationic conc.	4 mg/l
Cationic feed rate	26.5 cc/min.
Carbon feed rate	1649 mg/l

The test run was started on 23 March 1976 and terminated on 25 April after processing 28,600 gallons of bog water. The results from test run one are presented in Figure 2-11. DIMP concentrations in the feed water varied from 210 ppb to 430 ppb. The highest effluent DIMP concentration was 1.9 ppb accompanied by the lowest DIMP removal rate of 99.4 percent. The average DIMP removal rate was 99.75 percent.

Based on the data from test run one, test run two was conducted using a reduced carbon feed rate of 1000 mg/l; all other operating parameters remained the same. Test run two was started 26 April and terminated on 20 May after processing 22,000 gallons of bog water. The results from test run two are presented in Figure 2-12. DIMP concentrations in the feed water varied from 290 ppb to 470 ppb. The highest effluent DIMP concentration was 6.4 ppb accompanied by the lowest DIMP removal rate of 98.7 percent (and the highest influent concentration of 470 ppb). The average DIMP removal rate was 99.72 percent; however, if the one data point of 98.7 percent is eliminated, the average DIMP removal rate is 99.77 percent. This indicates that the carbon feed rate is still above the optimum feed rate.

After the completion of these two test runs, RMA personnel optimized both the coagulant concentrations and feed rates and the influent water feed rate. Based on the results of these tests, test run three was conducted under the following operating parameters:

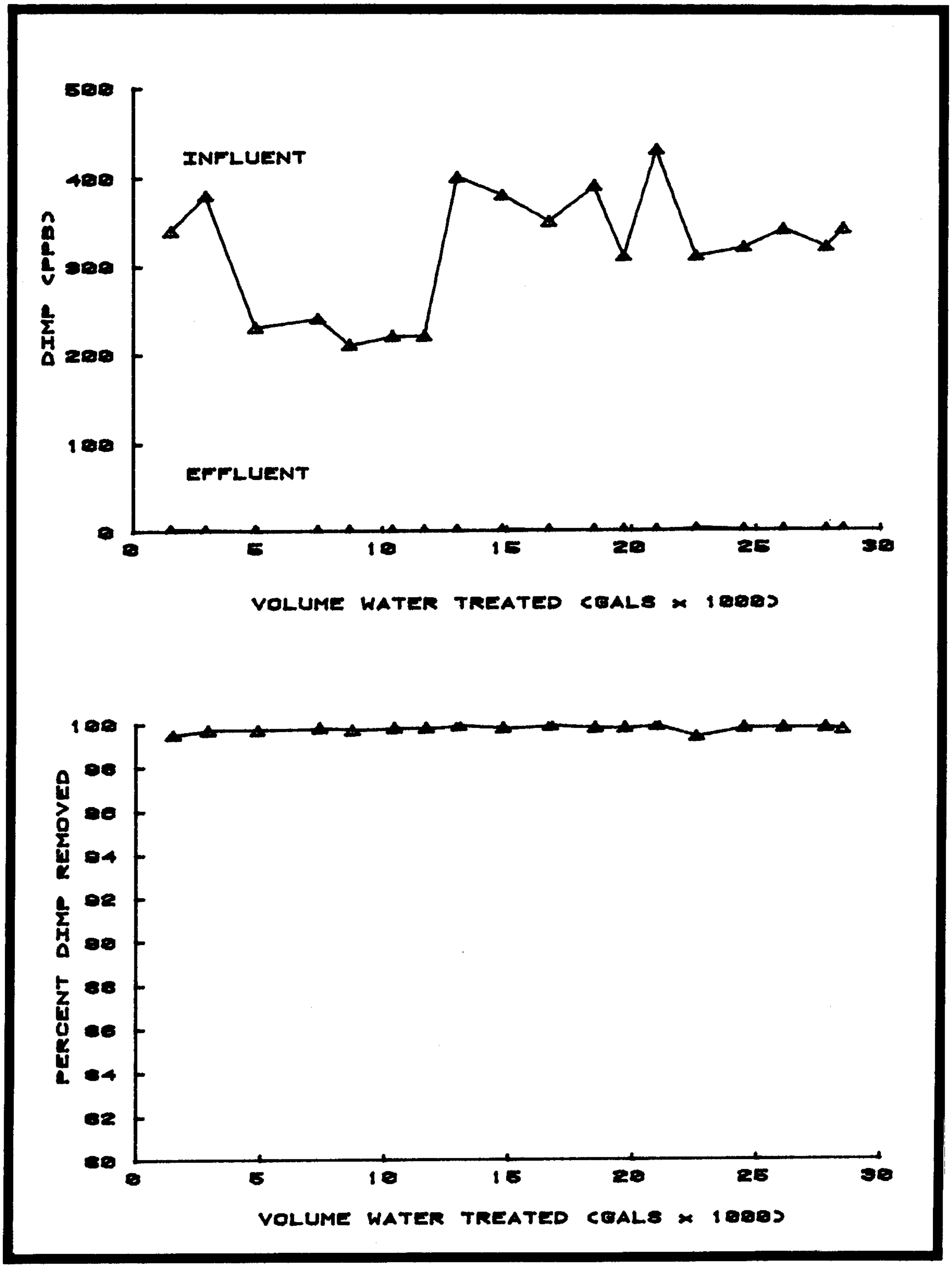

Figure 2-11. DIMP Removal - Test Run One

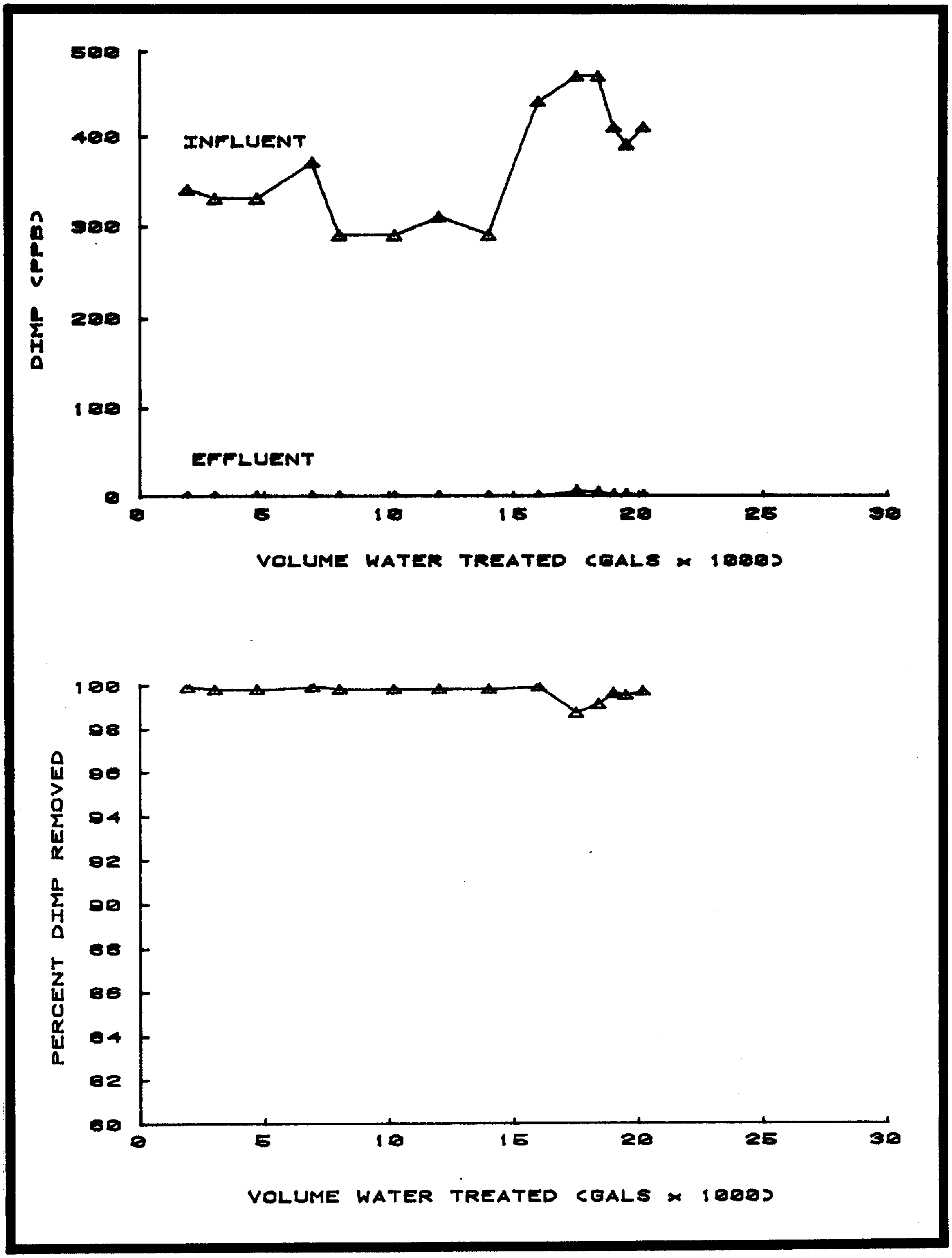

Figure 2-12. DIMP Removal - Test Run Two

Water feed rate	5 gpm (18.9 liters)
Anionic conc.	0.13 gm/l
Anionic feed rate	120 cc/min.
Cationic conc.	1.59 gm/l
Cationic feed rate	25 cc/min.
Carbon feed rate	350/250 mg/l

The test run was started on 27 October 1976 and after processing 3,790 gallons of water, a steady-state DIMP removal of 99 percent was achieved (see Figure 2-13). The 350 mg/l feed rate was continued through 4 November and after processing 25,480 gallons of water, the carbon feed rate was reduced to 250 mg/l without changing the bed. Although DIMP removal dropped below 99 percent during part 1 of the test run, an average DIMP removal of 99.02 percent was achieved. Within 24 hours after reducing the carbon feed rate the DIMP removal percentage dropped to 96.62 percent. Part 2 of the test run was terminated on 12 November due to high turbidity and excessive foreign material in the bed. An average DIMP removal of 96.33 percent was achieved during part 2 of test run three.

Test run four was conducted to evaluate adsorption efficiency at lower (more economical) carbon feed rates. Except for a carbon feed rate of 175 mg/l, the operating parameters were the same as in test run three. The test run was started on 18 November and after processing 19,360 gallons of water, the carbon feed rate was increased to 220 mg/l. The data from both parts of the test run are presented in Figure 2-14. This data shows that a feed rate of 175 mg/l produces an effluent of widely varying quality, 92.50 to 97.50 percent DIMP removal. After the feed rate was increased to 220 mg/l, the percentage of DIMP removal quickly stabilized at 97.50 percent and gradually increased to 98.72 percent 24 hours before the run was terminated. After processing 52,000 gallons of water, test run four was terminated on 8 December due to high turbidity and carbon bed breakdown. Data from this test run indicates that the optimum carbon feed rate (for treating bog water) is between 175 and 220 mg/l.

Test run five was conducted to confirm that the optimum carbon feed rate is more than 175 mg/l. The test run was started on 9 December using a carbon feed rate of 100 mg/l. The system maintained steady-state conditions through the first 10,000 gallons processed and then gradually decreased in adsorption efficiency (see Figure 2-15). After 20,000 gallons, a very rapid decrease in efficiency occurred and continued to a point of ultimate bed breakdown. This test run was terminated on 23 December after processing 47,850 gallons of water.

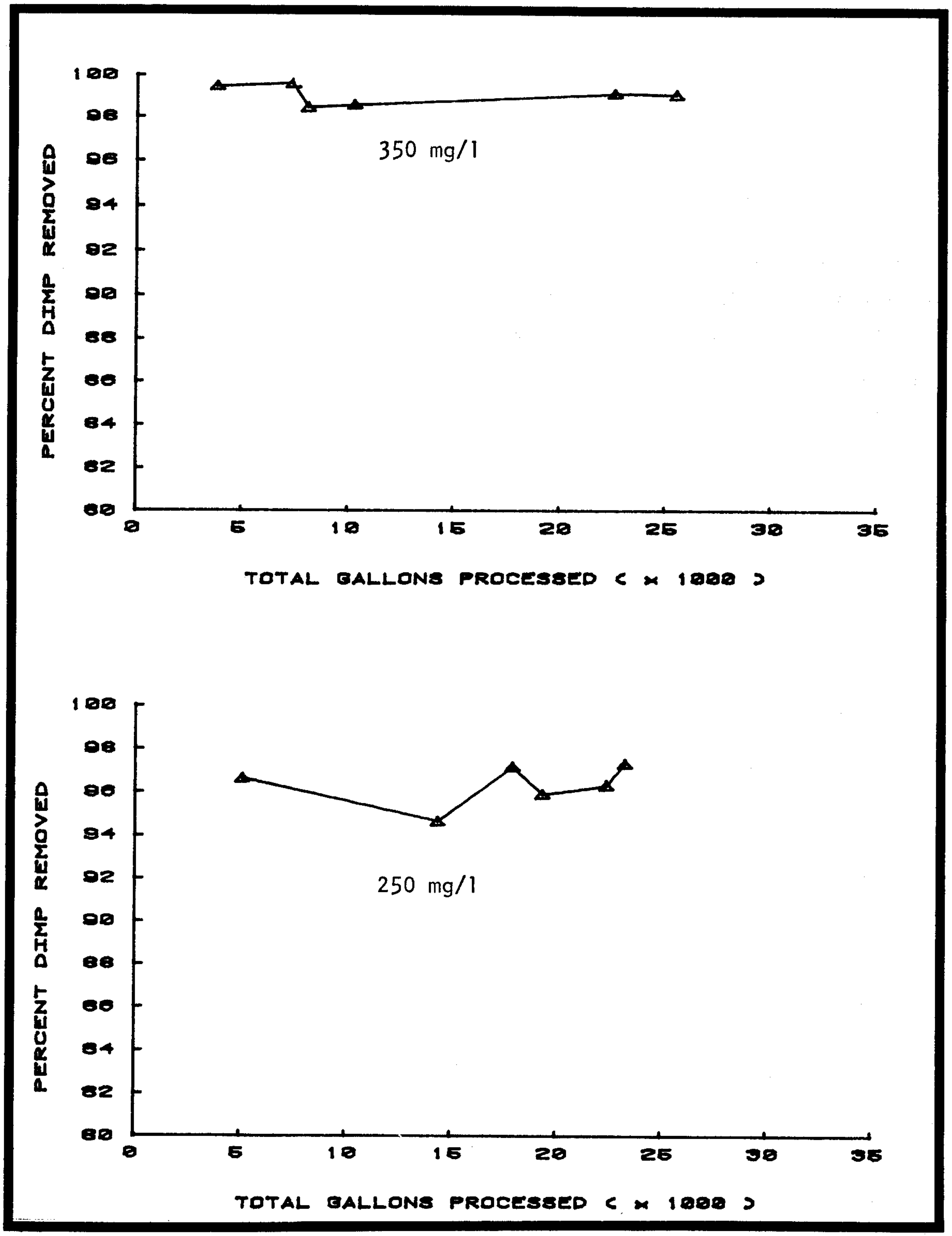

Figure 2-13. DIMP Removal - Test Run Three

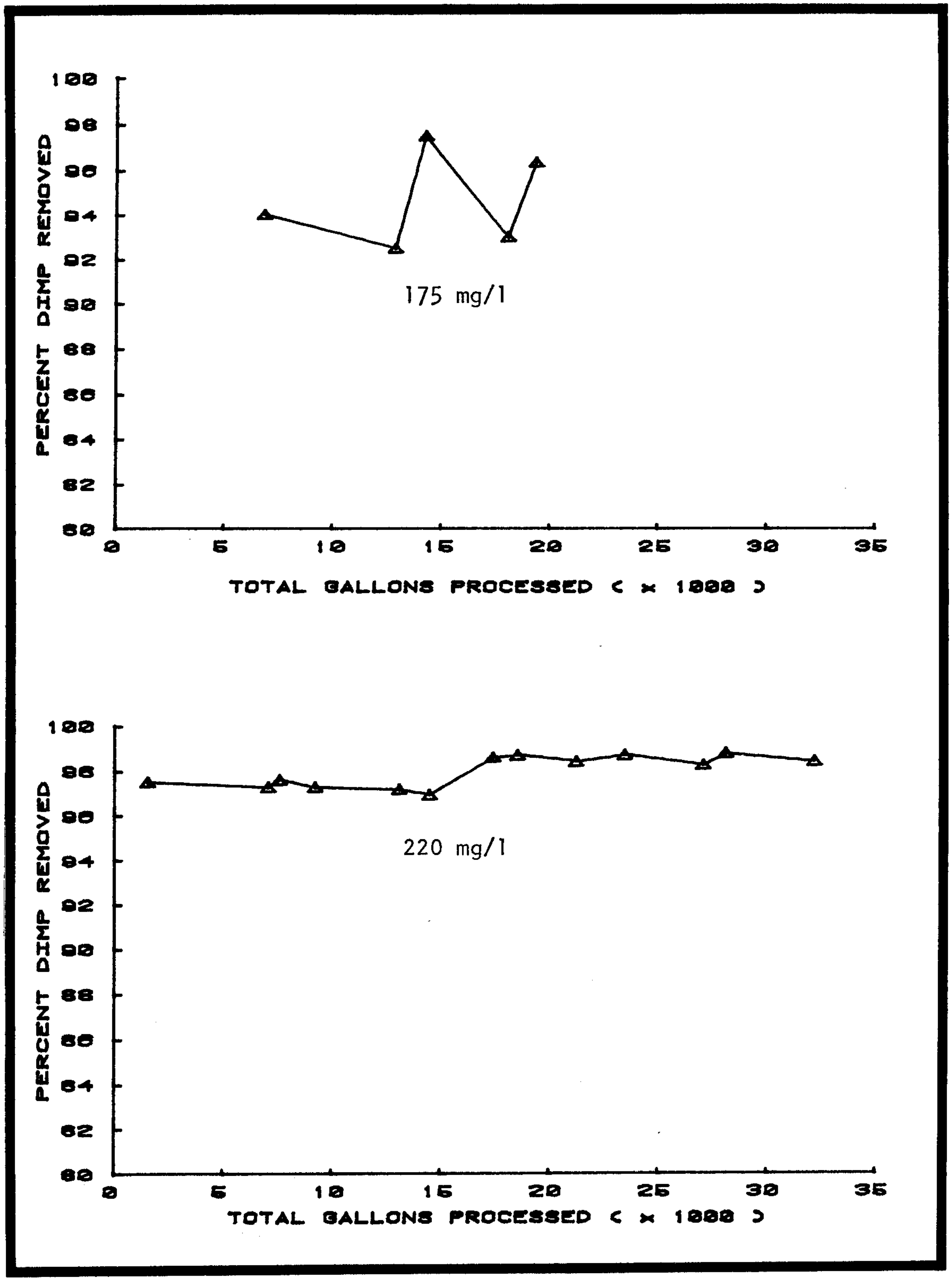

Figure 2-14. DIMP Removal - Test Run Four

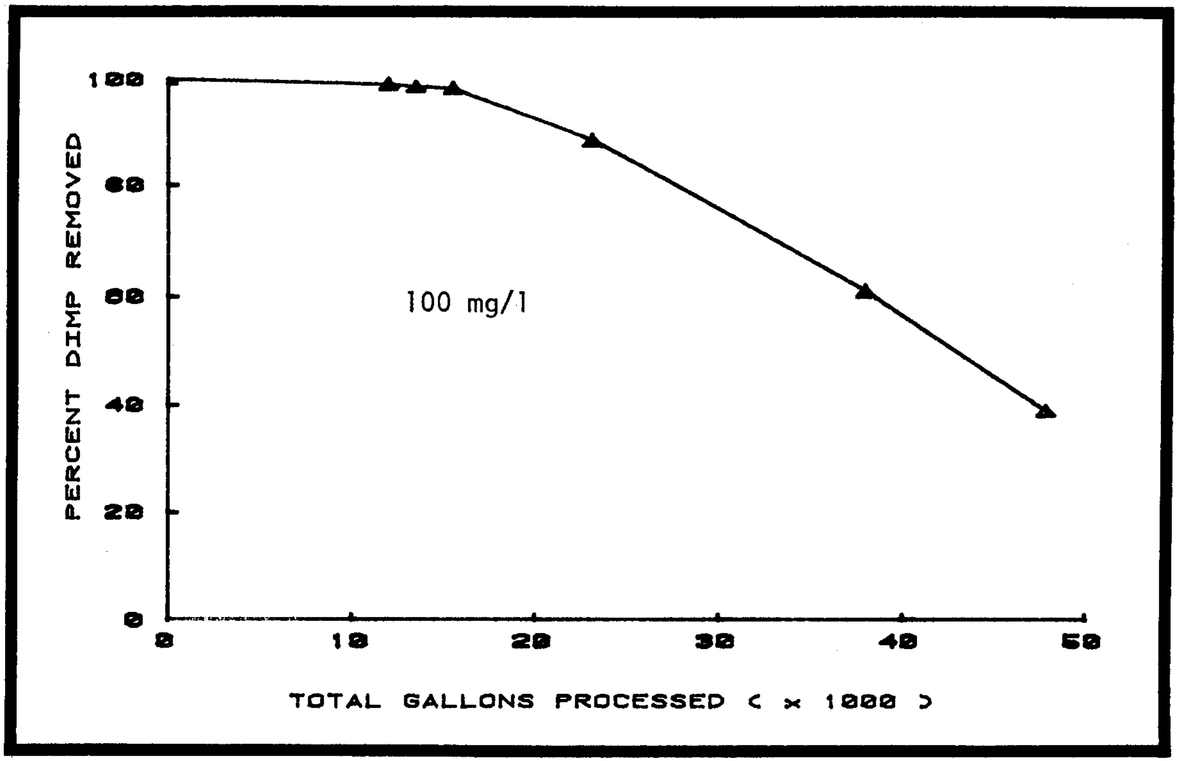

Figure 2-15. Dimp Removal - Test Run Five

Two important variables, influent DIMP concentration and influent water temperature, were considered constant throughout test runs three, four and five. DIMP concentrations fluctuated from 390 to 450 ppb; however, the variance in the average DIMP concentrations for each run was less than 15 ppb. The water temperature remained constant since the tests were conducted indoors and the bog water was transported sufficiently ahead of time to permit the temperature to stabilize before processing.

This study shows that under field conditions a minimum dosage of 220 mg/l is necessary to maintain a 95 percent removal of DIMP from bog water over a sufficient period of time to make the process controllable. A dosage of 350 mg/l was required to maintain over 98 percent removal of DIMP. Even higher degrees of removal can be achieved by increasing the carbon dosage, as exemplified by the 1,649 and 1,000 mg/l dosages with over 99 percent removal rates in earlier experimental runs. No consideration should be made for carbon feed rates of less than the 220 mg/l as noted by the erratic DIMP removal rates at 175 mg/l and 100 mg/l.

2.4.5 SCALE-UP ERDLATOR

In October and November of 1976, a 10,000 gph water treatment plant was installed at RMA. This plant was basically a scale-up of the 420 gph Erdlator. Since the scale-up factors are not linear, some experimentation was required to establish the carbon and coagulant feed rates. The first scheduled test run was started 22 November and a stable carbon bed was established with little difficulty. The system was operated for two days using an influent flow rate of 165 gpm (9900 gph). Analysis of product water showed that the DIMP content was less than the detectable limit of 0.5 ppb. Over the Thanksgiving Holiday, below freezing temperatures resulted in extensive system damage. Due to large repair costs, limited personnel, and some doubt as to system capability, the plant was not repaired for further tests.

Although test data obtained during the two day run was encouraging, longer test runs are necessary to obtain data for valid conclusions. Also, when extrapolating test data from the influent water feed studies, it appears doubtful that operational stability could be attained over extended periods even at a reduced feed rate of 8000 gph.

2.4.6 FILTRASORB PROCESS DESCRIPTION

Even though bench study results using granular carbon were not encouraging, it was decided to field test granular carbon using the Calgon Corporation Filtrasorb system (see Figure 2-16). An attractive advantage of this system is that it eliminates the problem of sludge disposal. The Filtrasorb system consists of five plexiglass columns connected in series. Each column is six feet long and five inches in diameter and is piped to permit down-column process flow and up-column backwash flow. Each column is equipped with a sample valve and a pressure gauge. The first column contains 0.25 cubic feet of sand (size 0.5 mm, uniformity coefficient 1.7) covered by 0.25 cubic feet of anthracite coal (size 0.7 mm, uniformity coefficient 1.7) and is used as a pretreatment filter. The four remaining columns contain three to four inches of commercial grade shot gravel covered by 15 pounds of granulated carbon. Influent water is pumped down-ward through the pretreatment filter at a rate of 0.25 gallons per minute (1.84 gpm/ft^2) to remove suspended solids which would clog the carbon beds. At the designated flow rate of 0.25 gpm, each one of the columns provides an empty bed contact time of 15 minutes. Therefore, the complete system (four columns) represents a total contact time of 60 minutes. Empty bed contact time is a combination of flow rate and empty bed volume. Empty bed volume refers to the volume within one column that is occupied by both the granular carbon and the voids between individual granules.

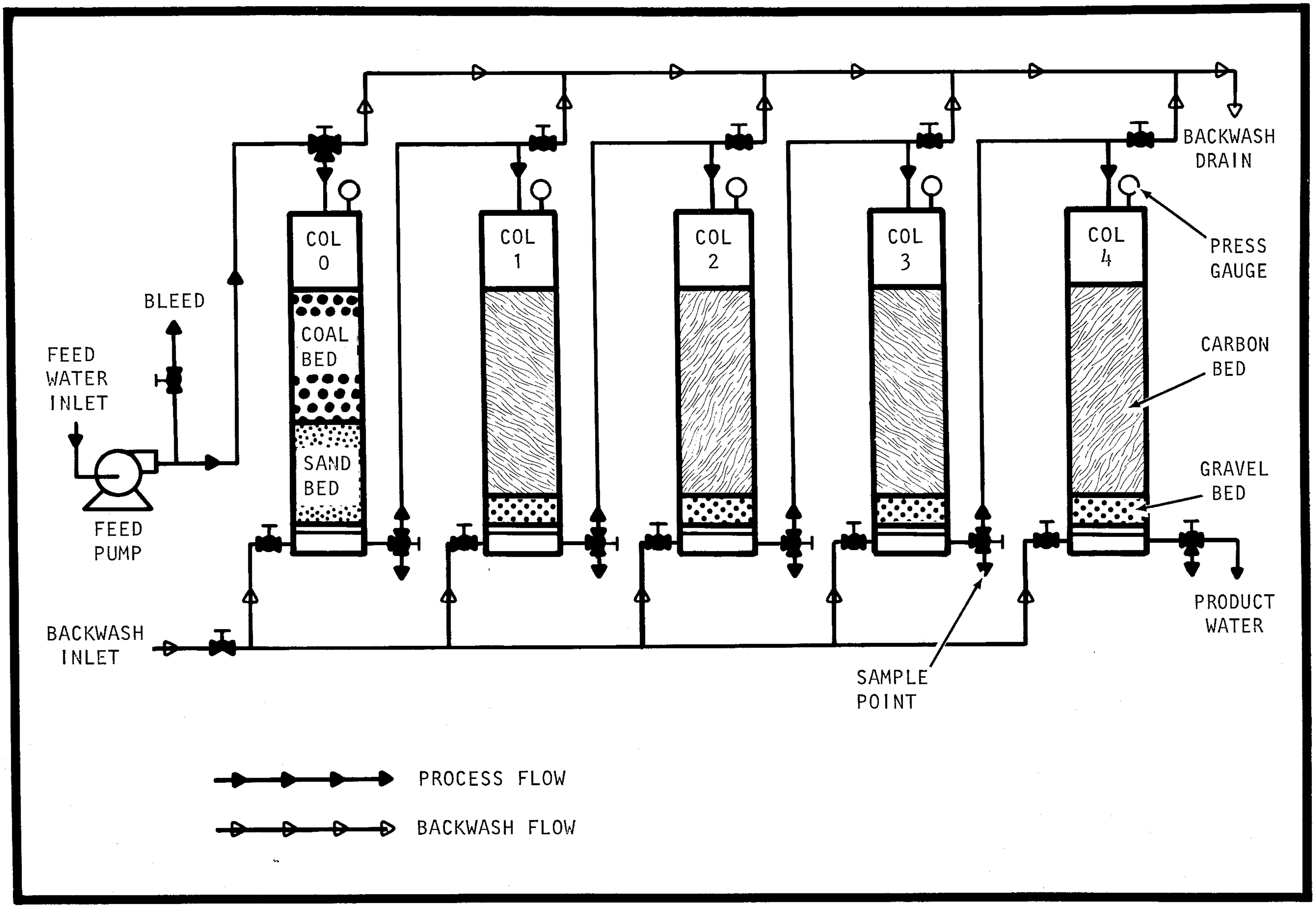

Figure 2-16. FILTRASORB Process Flow Diagram

2.4.7 GRANULAR CARBON ADSORPTION STUDIES

The adsorption studies were conducted to evaluate the adsorptive capacity of Calgon's service reactivated carbon versus the adsorptive capacity of Calgon's virgin activated carbon. Therefore, Calgon Corporation was contracted by RMA to provide two Filtrasorb systems. Calgon personnel installed and tested both units in November of 1976. The test run was started on 26 November 1976 and continued through 10 January 1977. RMA personnel operated and maintained the equipment and conducted all analyses throughout the test run. Bog water was used for feed water and DIMP removal was the basis for adsorption evaluation. Since a common source provided feed water for both units, water temperature and DIMP concentrations were identical for both units.

During this study, samples were collected from both units and analyzed for five parameters in the Material Analysis Laboratory. Since DIMP was the first compound that exhibited breakthrough characteristics, these analyses are presented in Table 2-7. A breakthrough characteristic is defined as an increasing contaminant in the effluent as the treatment period increases. Data from the other analyses are shown on Pages A-17 through A-21 in the Appendix. When reading Table 2-7, note that column "0" is the pretreatment filter effluent, column "1" is the first carbon column effluent, etc. A graphical presentation of DIMP data is shown in Figure 2-17 in the form of breakthrough curves. These curves were plotted using data from column "0" and column "1" versus volume treated; therefore, the curves represent an adsorption treatment time or contact time of 15 minutes.

The DIMP breakthrough curves indicate that both types of granular carbon are capable of reducing DIMP concentrations from influent levels of 400 ppb to effluent levels of <50 ppb. However, reactivated carbon outperformed virgin carbon in that reactivated carbon treated 17,000 gallons of water before breakthrough occured as compared to 9,600 gallons of water using virgin carbon. A specific explanation of this phenomenon is not available, but it is probable that reactivated carbon performs better because of its larger pore size. Since DIMP is a large molecule (molecular weight 180.17), there would be more activation sites available in reactivated carbon than in virgin carbon.

The capacity of carbon to adsorb organics is frequently expressed in milligrams of adsorbate (DIMP) removed per gram of carbon. The carbon capacity was calculated by integrating the area between the influent and effluent DIMP curves (Figure 2-17) and dividing this quantity by the weight of carbon in a single column. Using an average influent DIMP concentration of 415 ppb and an effluent breakpoint concentration of 50 ppb, the capacities were calculated to be 3.8

	COLUMN 'A' REACTIVATED CARBON						COLUMN 'B' VIRGIN CARBON					
DATE	Feed	#0	#1	#2	#3	#4	Feed	#0	#1	#2	#3	#4
11/26/76	400	313	1.1	--	--	--	400	406	0.7	--	--	--
11/29/76	--	370	0.7	--	--	--	--	390	0.4	--	--	--
11/30/76	--	370	2.0	--	--	--	--	420	3.2	--	--	--
12/01/76	410	390	13.0	--	--	--	410	408	3.3	--	--	--
12/02/76	--	410	3.1	--	--	--	--	420	2.4	--	--	--
12/03/76	420	420	3.4	--	--	--	420	400	2.5	--	--	--
12/06/76	430	430	2.4	<0.5	--	--	430	420	3.9	<0.5	--	--
12/07/76	--	400	2.2	<0.5	--	--	--	410	3.4	<0.5	--	--
12/09/76	410	410	4.7	1.7	--	--	410	460	4.2	1.1	--	--
12/10/76	--	170	2.7	1.9	--	--	--	430	9.4	1.0	--	--
12/14/76	420	370	3.9	0.8	--	--	420	390	16.0	<0.5	--	--
12/15/76	400	370	3.4	<0.5	--	--	400	400	17.0	1.9	--	--
12/16/76	--	410	1.0	5.1	--	--	--	460	24.0	14.0	--	--
12/17/76	400	200	9.3	<0.5	<0.5	--	400	400	19.0	<0.5	1.2	--
12/20/76	390	420	1.6	<0.5	1.2	--	390	390	27.0	<0.5	1.5	--
12/21/76	410	390	2.2	<0.5	<0.5	--	410	440	36.0	<0.5	<0.5	--
12/23/76	--	460	0.5	<0.5	<0.5	--	--	450	67.0	<0.5	<0.5	--
12/27/76	--	420	6.8	<0.5	<0.5	5.4	--	410	93.0	<0.5	<0.5	1.0
12/28/76	--	450	7.4	2.4	<0.5	1.4	--	420	76.0	<0.5	<0.6	<0.5
12/29/76	--	440	7.9	<0.5	<0.5	8.1	--	440	102.0	<0.5	<0.5	<0.5
12/30/76	400	400	7.1	<0.5	<0.5	8.1	400	420	120.0	<0.5	<0.5	<0.5
1/03/77	424	415	8.6	<0.5	<0.5	<0.5	424	400	76.0	<0.5	<0.5	<0.5
1/05/77	490	490	6.4	<0.5	<0.5	<0.5	490	420	370.0	110.0	<0.5	<0.5
1/07/77	427	415	6.7	<0.5	<0.5	<0.5	--	--	--	--	--	--
1/10/77	426	352	41.0	<0.5	<0.5	<0.5	426	352	155.0	1.8	<0.5	<0.5

Table 2-7. Dimp Removal With Granular Carbon

milligrams DIMP per gram of reactivated carbon and 2.3 milligrams DIMP per gram of virgin carbon. The quantity of carbon required to provide a given effluent DIMP concentration is expressed as a usage rate. Again, using the data in Figure 2-17 and a breakpoint concentration of 50 ppb DIMP, the usage rates were calculated to be 0.9 pounds of reactivated carbon per 1000 gallons (108 mg/l) and 1.4 pounds of virgin carbon per 1000 gallons (168 mg/l). Although the carbon capacity and usage rates were calculated from a relatively short test run, the results indicate that treatment in a granular reactivated carbon bed is practical and warrants further study.

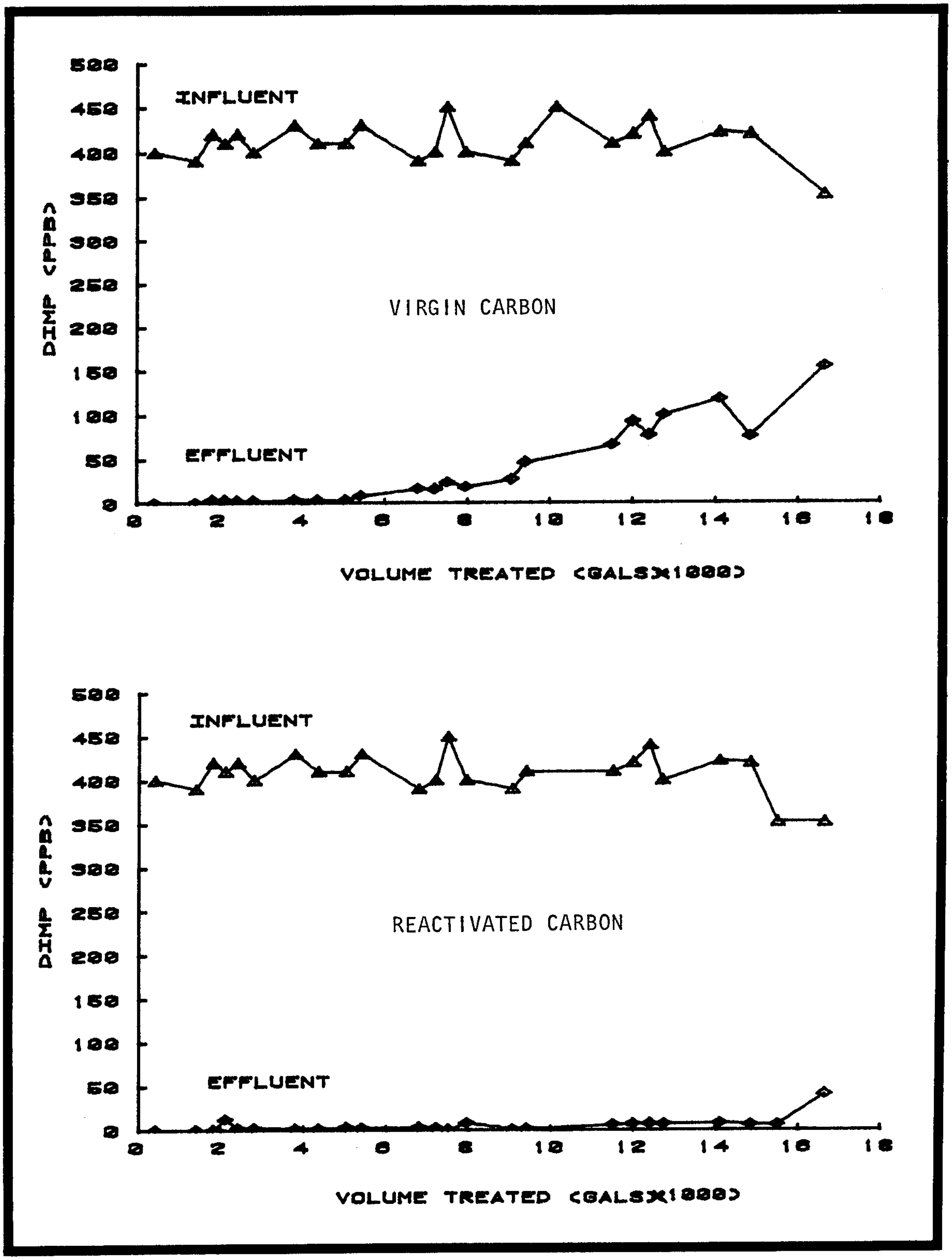

Figure 2-17. DIMP Breakthrough Curves for Granular Carbon

SECTION 3

WELL WATER STUDIES

3.1 GENERAL

A review of well water analyses obtained from the monitoring program (required by the Cease and Desist Orders) shows that the concentration of DIMP in certain well waters is considerably higher than the concentration of DIMP in bog waters. Since the treatment of bog water by carbon adsorption was very encouraging, more field studies were conducted using well water as the influent. Pump wells PW2 and PW3 were selected because of their alignment with the interim containment/treatment system (see Figure 3-1). Water samples were collected from each well and analyzed with a gas chromatograph. These analyses (Table 3-1) show that both wells had high concentrations of organic compounds and would be suitable feed water for the field studies.

COMPOUND	UNIT	PW #2	PW #3
Aldrin	ppb	<2.0	<2.0
Dieldrin	ppb	4.5	<2.0
DCPD*	ppb	1000.0	82.0
DIMP*	ppb	530.0	2800.0
p-Chlorophenylmethyl-			
sulfide	ppb	68.3	<10.0
sulfoxide	ppb	53.3	<10.0
sulfone	ppb	40.5	<10.0
Endrin	ppb	8.6	<2.0
Nemagon*	ppb	7.6	<1.0
* - Average			

Table 3-1. Well Water Analyses

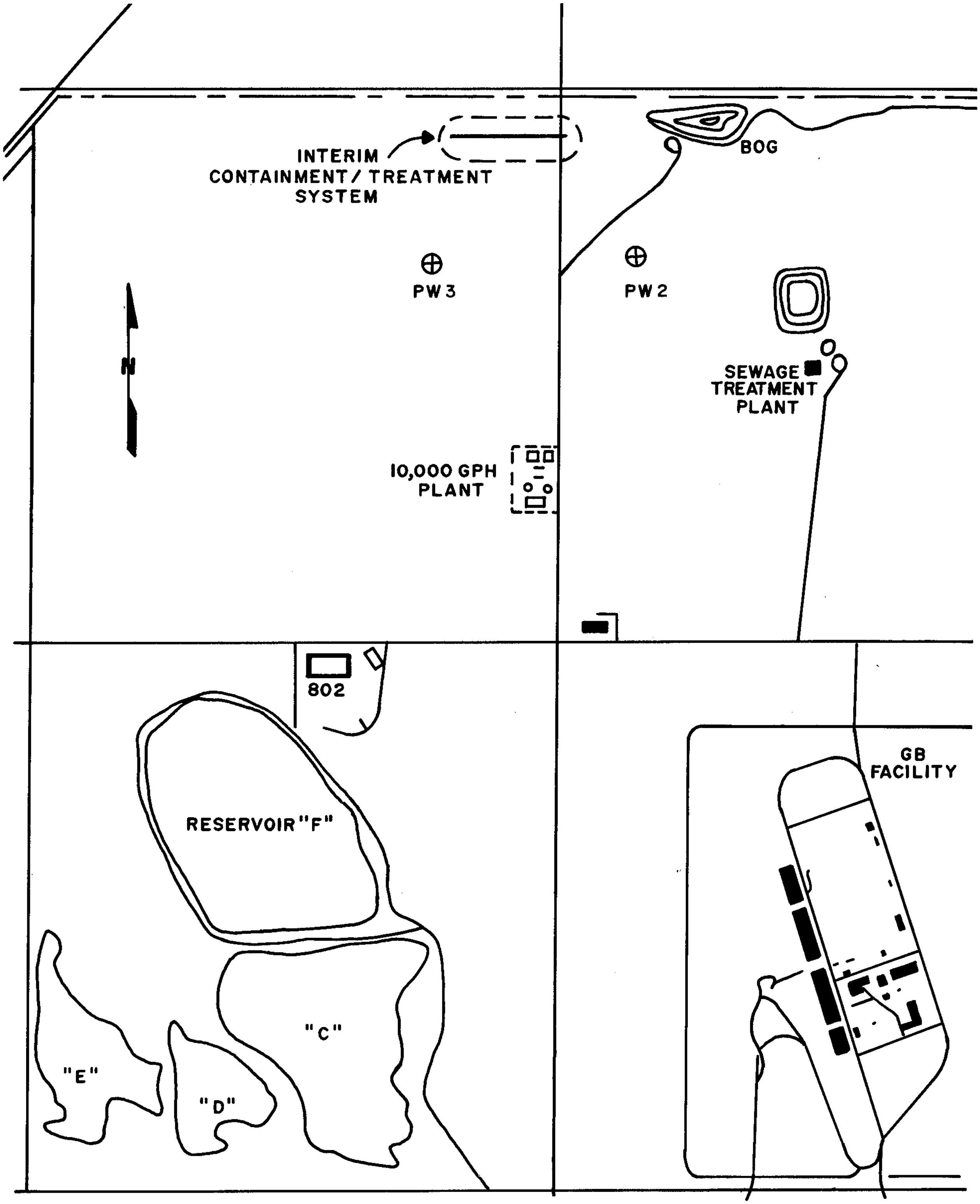

Figure 3-1. North Boundary Plan View

3.2 ADSORPTION ISOTHERMS

Prior to conducting the field studies, adsorption isotherms were developed for seven activated carbons to reconfirm that the most promising carbons would be utilized. The granular carbons selected were Calgon's virgin and reactivated carbons. The powdered carbons selected were Aqua Nuchar, Hydrodarco-C, -HDH, -KV and -XPC. An adsorption isotherm was developed for each carbon as follows:

A. Into each of five Erlenmeyer flasks, measure 200 ml of well water.
B. Measure four samples (10, 20, 40 and 60 milligram) of the carbon to be tested.
C. Place each sample into a flask. The fifth flask is the control and contains no carbon.
D. Agitate the solutions for 60 minutes and immediately filter all five samples. Agitation time and temperature must be identical for all samples.
E. Analyze the filtrate for residual DIMP and express as percent of original concentration.
F. Plot results on log-log graph paper. The horizontal axis is percent of contaminant remaining, the vertical axis is the inverse of the relative carbon loading.

This procedure was followed for each of the seven carbons tested and the results are presented in Figure 3-2. Contrary to the tests conducted by MERADCOM, these tests show that granular carbon has a higher capacity than powdered carbon. This could possibly be explained in that MERADCOM's isotherms were based on TOC removal whereas RMA's isotherms are based on DIMP removal. Based on the isotherms, both granular carbons, Aqua Nuchar powdered carbon, and Hydrodarco-C powdered carbon were selected for well water field studies.

3.3 POWDERED CARBON STUDIES

The purpose of the powdered carbon studies was to optimize both coagulant and carbon feed rates while processing well water so that valid cost comparisons could be made with the granular carbon process. On the possibility that the higher concentrations of organic contaminants might change the coagulant requirements, several short test runs were conducted using the optimum and increased coagulant feed rates. These studies showed that the optimum coagulant

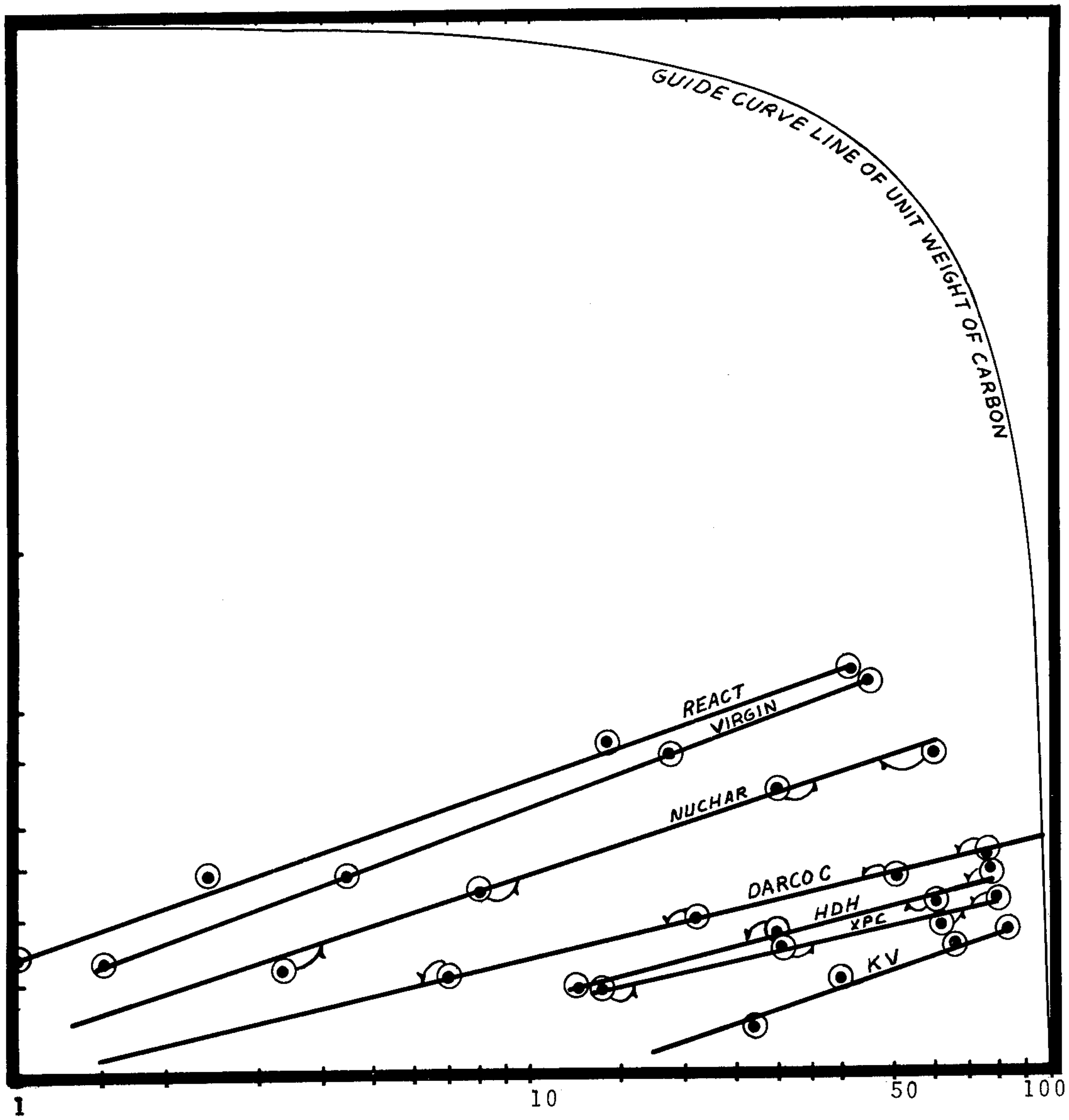

Figure 3-2. Adsorption Isotherms

concentrations and feed rates established during the bog water studies were applicable to treatment of well water. Therefore, these coagulant concentrations and feed rates were used throughout the powdered carbon studies.

The first test run was started on 14 February 1977 using the 420 gph Erdlator and Hydrodarco-C at a feed rate of 252 mg/l. After processing 3,740 gallons of well water, a steady state of 99 percent DIMP removal was achieved (see Figure 3-3). The average influent DIMP concentration was 2690 ppb. After processing 13,110 gallons of well water, the percentage of DIMP removal had dropped to 98 with an average influent DIMP concentration of 2680 ppb. On 16 February, the carbon feed rate was reduced to 200 mg/l until the end of the test run on 23 February. Even though the influent DIMP concentration had decreased to 2400 ppb,

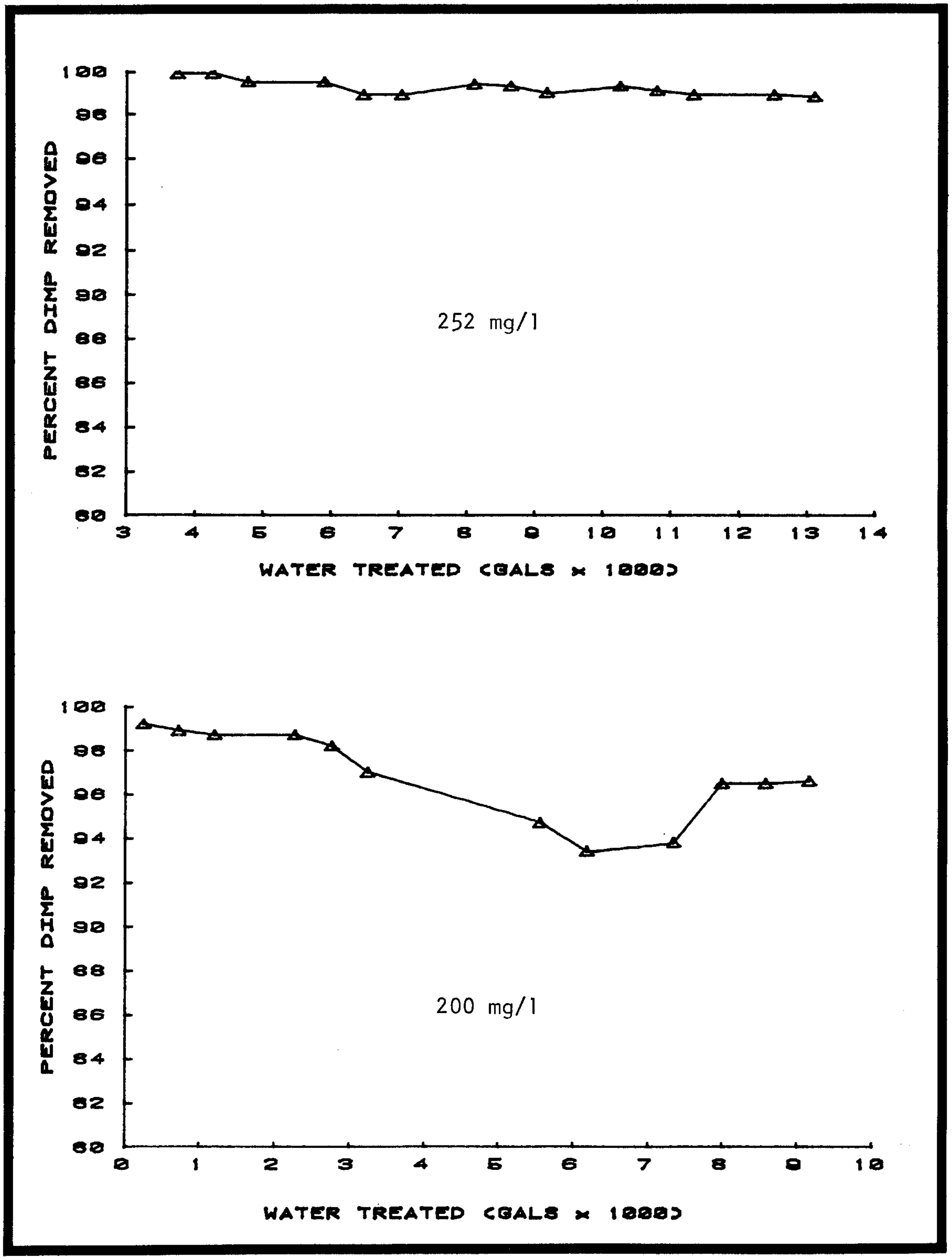

Figure 3-3. Hydrodarco-C DIMP Removal

the graph in Figure 3-3 shows that the 200 mg/l feed rate is unacceptable.

The Erdlator clarifier was cleaned and filled with Aqua Nuchar powdered carbon. On 29 April, a test run was started using a carbon feed rate of 252 mg/l. After processing 15,250 gallons, the test was terminated on 11 May due to the erratic DIMP removal percentage (see Figure 3-4). Although the influent DIMP concentration was high (2546 ppb), the important fact is that a steady-state removal percentage could not be achieved. Aqua Nuchar has a lower density than Hydrodarco-C and, even with additional coagulant, an Aqua Nuchar bed starts to deteriorate at an influent feed rate of 225 gal/hr (see Figure 2-10) versus the design feed rate of 420 gal/hr. Therefore, even though the isotherm for Aqua Nuchar shows a greater adsorption capacity, this carbon is not recommended because a stable bed and steady-state removal cannot be obtained with high influent feed rates.

Results of this study show that a minimum feed rate of 252 mg/l Hydrodarco-C powdered carbon is required for acceptable treatment of well water. This feed rate is considered an absolute minimum since the DIMP removal percentage was gradually decreasing (see Figure 3-3) when the influent DIMP concentration was 2680 ppb as compared to later concentrations up to 3400 ppb.

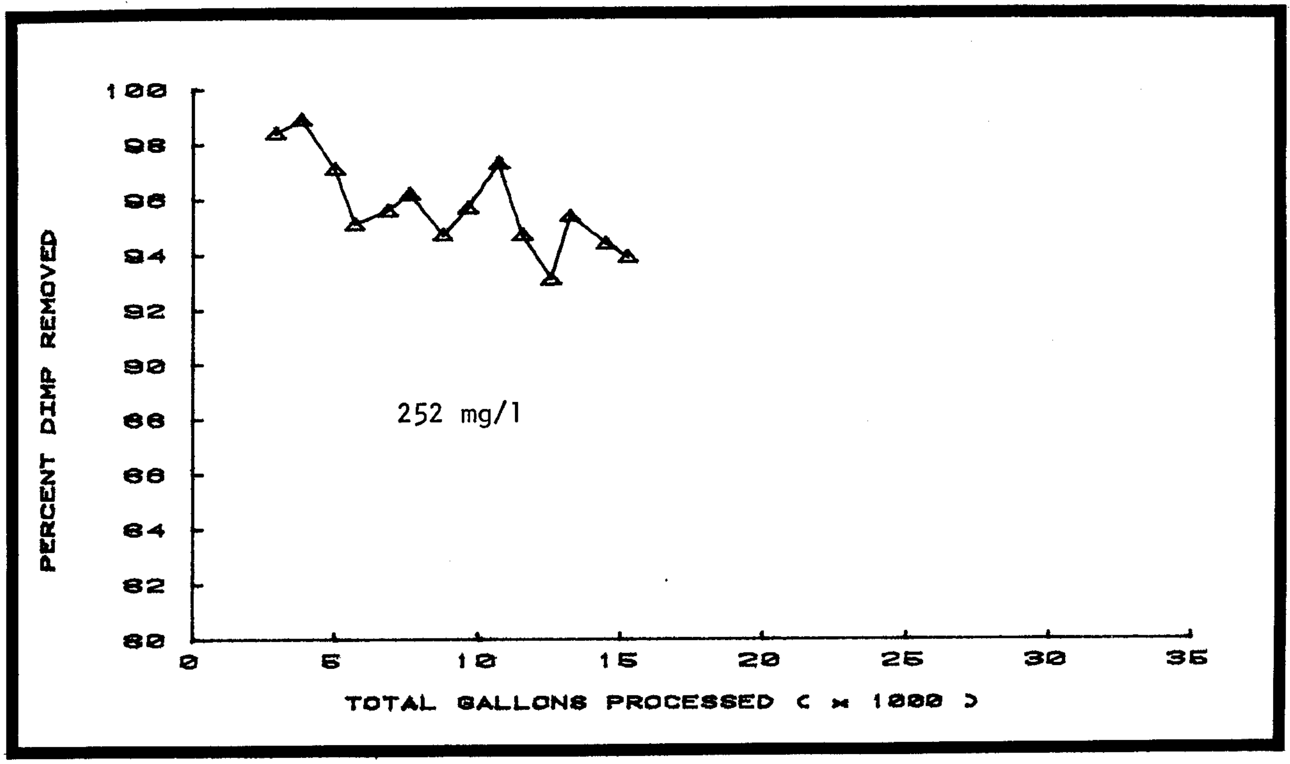

Figure 3-4. Aqua Nuchar DIMP Removal

3.4 GRANULAR CARBON STUDIES

The Erdlator unit can utilize either powdered or granular carbon as a filter medium. Since a 10,000 gph Erdlator is installed at RMA, it was considered appropriate to evaluate the performance of granular carbon in the Erdlator. Therefore, granular carbon was evaluated in both the 420 gph Erdlator and the Filtrasorb units. When evaluating granular carbon in the Erdlator, neither coagulant nor replacement carbon feed was utilized.

3.4.1 ERDLATOR WITH GRANULAR CARBON

The Erdlator was cleaned of all powdered carbon and then filled with well water. One hundred pounds of virgin carbon was placed in the separation zone of the clarifier and the influent water feed rate was set at 7 gpm until the bed stabilized. After the bed became stable, DIMP removal was tested for 3, 5 and 7 gpm water feed rates. Percentage DIMP removal was 62 percent at 3 gpm, 45 percent at 5 gpm and 37 percent at 7 gpm. After four days, the Erdlator was shut down and the test results considered invalid because water in the downcomer was overflowing through access slots into the separation zone. The slots were sealed and the Erdlator was restarted. Very quickly, the water level rose and water poured over the top of the downcomer into the separation zone. Again, the system was shut down and the clarifier was drained and cleaned. When the clarifier was drained it was noted that approximately 30 pounds of carbon had migrated into the downcomer. To prevent this from reoccurring, a screen was placed around the downcomer on top of the directional vanes.

Granular carbon was replaced and the tests were rerun. With the carbon bed supported by the screen, no blockage was observed and the DIMP removal efficiency improved considerably. Tests were run with water influent feed rates of 0.5, 1, 3, 5 and 7 gpm. Bed height and DIMP removal percentage were measured for each feed rate and are presented in Figure 3-5. These results show that the flow rate had very little influence on the bed height. It was also noted during the tests that the directional vanes imparted no rotational movement to the carbon bed. The relatively small variations in carbon bed height and the lack of rotational bed movement are probably due to the higher density of granular carbon versus powdered carbon. It is also assumed that the supporting screen probably impeded the rotational flow imparted by the directional vanes.

Based on the volume of the separation zone, it was determined that the clarifier would hold a 275 pound granular carbon bed. Using the average cross-sectional area, increased residence times were calculated for the 275 pound bed at flow rates

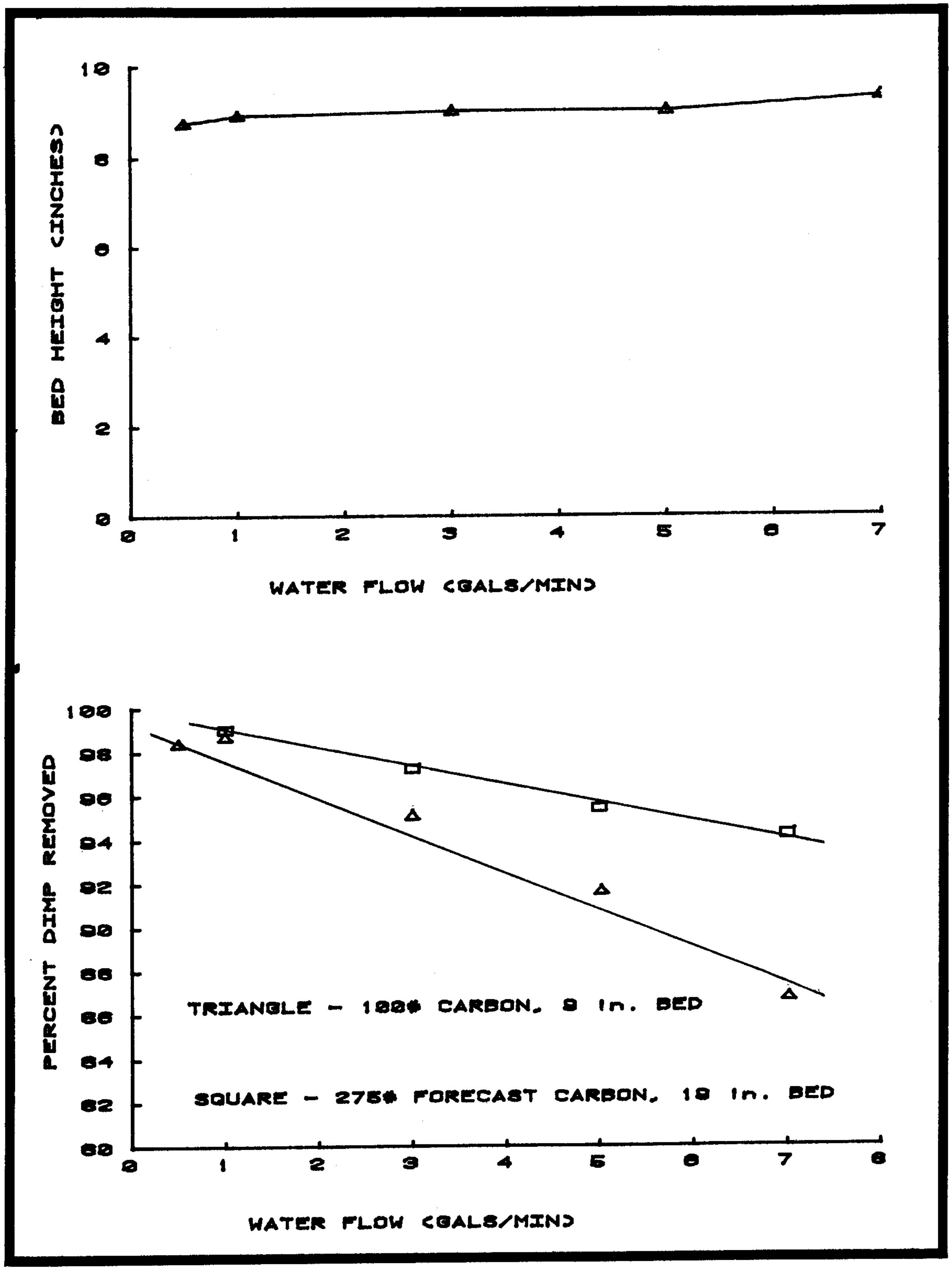

Figure 3-5. Performance of Granular Carbon in Erdlator

of 1, 3, 5 and 7 gpm. The increased residence time was then used in conjunction with the 100 pound bed test results to determine DIMP removal efficiency for the 275 pound bed (see Figure 3-5). Based on this prediction and the average influent DIMP concentration of 825 ppb during the test, it was determined that granular carbon in the Erdlator would be inadequate to treat well water (2000 to 3000 ppb DIMP) at acceptable flow rates of 5 to 7 gpm.

3.4.2 FILTRASORB WITH GRANULAR CARBON

The same two Filtrasorb units used for the bog water studies were utilized for the well water studies. Before the well water studies were conducted, both units were emptied, cleaned and filled with fresh filter media and carbon. Column set "A" was filled with reactivated granular carbon and Column set "B" was filled with virgin granular carbon. At the start of the studies, feed water consisted of a mixture of PW2 and PW3 well water. PW2 was selected because of the high DCPD content and PW3 was selected because of the high DIMP content (the two compounds addressed in The Cease and Desist Orders). Use of PW2 water was discontinued after one month because DCPD was apparently evaporating during pumping, transportation and storage.

Well water studies were started on 25 January 1977 and continued through 25 July 1977. During this study, samples were collected from all four carbon columns of both units and analyzed for five parameters in the Material Analysis Laboratory. Since DIMP was the first compound to exhibit breakthrough characteristics, these analyses are presented in Table 3-2. Data from the other analyses are presented in the Appendix (Pages A-22 through A-26). The data in Table 3-2 were used to plot DIMP breakthrough curves for reactivated carbon, Figure 3-6, and virgin carbon, Figure 3-7. Since each carbon column represents a contact time of 15 minutes, the breakthrough curves should represent the treatment results which can be obtained with contact times of 15, 30, 45 and 60 minutes. After processing approximately 11,500 gallons of water, the discontinuance of PW2 well water caused a significant increase (1000 to 3000 ppb) in influent DIMP concentration. This increase in DIMP concentration also accompanied the DIMP breakthrough in column 1; therefore, column 1 breakthrough is based on 1000 ppb DIMP while the breakthrough in columns 2, 3 and 4 is based on 1000 and 3000 ppb DIMP.

Based on data obtained from both the bog and well water studies, breakthrough characteristics and carbon capacities were calculated and are presented in Table 3-3. The "DIMP loading @ breakthrough" entry shows the weight of DIMP adsorbed by the carbon when the effluent exceeded 50 ppb DIMP. Although it is a common

DATE	COLUMN 'A' REACTIVATED CARBON						COLUMN 'B' VIRGIN CARBON					
	#0	#1	#2	#3	#4	CUML. FLOW (GAL)	#0	#1	#2	#3	#4	CUML. FLOW (GAL)
1/25/77	1510	0.5	0.5			360	1490	0.5	0.5			360
1/26/77	1250	0.5	0.5			720	1240	0.5	0.5			720
1/28/77	1300	0.5	0.8			1440	1090	0.8	0.8			1440
1/31/77	930	0.9	0.5			2520	870	0.8	0.5			2520
2/1/77	906	1.0				2880	900	0.6	0.5			2880
2/2/77	850	1.3	1.3			3240	850	2.2	0.5			3240
2/3/77	762	0.8	0.8			3600	793	0.8	0.8			3600
2/4/77	737	0.6	0.5			3960	733	2.1	0.5			3960
2/7/77	678	1.5	0.5			5040	636	17.3	0.5			5040
2/8/77	705	2.0	1.1			5400	662	4.7	5.0			5400
2/9/77	681	1.0	0.8			5760	643	4.7	0.5			5760
2/10/77	678	0.8	0.5			6120	693	11.1	0.5			6120
2/11/77	680	1.4	0.5			6480	658	20.3	0.6			6480
2/14/77	1149	3.1	0.7			7560	1168	18.9	0.5			7560
2/15/77	1158	3.3	0.5			7920	1140	27.2	1.5			7920
2/16/77	1202	4.1	0.5			8280	1193	47.6	0.6			8280
2/17/77	2067	4.7	0.5			8640	2183	52.1	0.5			8640
2/18/77	2229	5.0	0.7			9000	2198	75.1	0.5			9000
2/22/77	885	5.8	1.2			10440	850	185	1.0			10440
2/23/77	1591	7.4	2.2			10800	1629	236	1.6			10800
2/24/77	1585	8.1	0.8			11160	1660	280	1.3			11160
2/25/77	1656	11.2	0.5			11520	1649	278	1.0			11520
2/28/77	2413	58.0	12.7			12600	2510	555	1.0			12600
3/1/77	2361	65.1	3.1			12960	2450	682	4.6			12960
3/2/77	3109	103	4.2			13320	2682	958	5.1			13320
3/3/77	2317	137	1.3			13680	3434	1123	1.2			13680
3/4/77	2589	215	2.1			14040	2578	1115	1.6			14040
3/7/77	2941	442	1.3			15120	2917	1417	0.4			15120
3/8/77	3434	582	1.9			15480	3249	1655	0.8			15480
3/9/77	3198	648	2.4			15840	3211	1580	0.8			15840
3/10/77	3065	801	0.3			16200	3034	1624	2.4			16200
3/14/77	2800	419	1.2			16560	3187	1238	1.3			16560
3/15/77	2713	701	0.4			16920	2788	1558	1.9			16920
3/16/77	3005	937	1.3			17280	3283	2060	3.1			17280
3/17/77	3070	1318	1.2			17640	3280	2208	3.9			17640
3/18/77	3227	1471	1.5			18000	3142	2310	7.1			18000
3/21/77	3106	1623	2.2			19080	3183	2266	12.9			19080
3/22/77	3230	1885	1.3			19440	3169	2155	24.5			19440
3/23/77	3098	1889	1.7			19800	3107	2271	20.6			19800
3/24/77	3080	2053	1.2			20160	3095	2497	35.1			20160
3/25/77	3068	2100	1.2			20520	3048	2337	34.3			20520
3/28/77	3092	2166	2.1			21600	3022	2343	98.3			21600
3/29/77	2994	2015	5.4			21960	3079	2151	254			21960
3/30/77	2807	1933	7.3			22320	2874	2200	231			22320
3/31/77	2734	2331	19.4			22680	3357	2594	252			22680

Table 3-2. Granular Carbon Test Results (Sheet 1 of 2)

DATE	COLUMN 'A' REACTIVATED CARBON						COLUMN 'B' VIRGIN CARBON					
	#0	#1	#2	#3	#4	CUML. FLOW (GAL)	#0	#1	#2	#3	#4	CUML. FLOW (GAL)
4/1/77	3035	2421	37.0			23040	3014	2422	278			23040
4/4/77	LACK OF WATER					23960	UNIT 'B' IMPELLER REPLACED					23960
4/5/77	NO SAMPLE					24210	NO SAMPLE					24210
4/6/77	2991	2327	31.4			24570	3092	2608	308			24570
4/7/77	2908	2689	96.6	8.7		24930	3051	2795	450	8.4		24930
4/8/77	3199	2935	127	5.4		25290	3253	2935	554	5.3		25290
4/11/77	3323	3125	284	5.2		26340	NO SAMPLE (UNIT DOWN)					26340
4/12/77	2957	2770	312	16.1		26700	2787	2611	490	2.6		26670
4/13/77	2919	2632	326	1.0		27060	3085	2665	476	2.2		27030
4/14/77	3143	2873	438	3.3		27400	NO SAMPLE (UNIT DOWN)					27100
4/15/77	3044	2895	510	0.9		27760	3044	NO SAMPLE				27100
4/18/77	3180	2651	290	3.4		28840	3209	3188	358	16.3		28090
4/19/77	3080	2766	391	2.3		29190	3257	2751	445	0.6		28440
4/20/77	NO SAMPLE					29520	NO SAMPLE (UNIT DOWN)					28710
4/21/77	2783	2559	546	2.6		29820	NO SAMPLE (UNIT DOWN)					28710
4/22/77	2820	2976	693	1.2		30180	NO SAMPLE (UNIT DOWN)					28710
4/25/77	2737	2565	1043	3.8		31260	2915	2512	699	9.4		29790
4/26/77	3149	2901	1338	7.3		31620	2917	2865	948	15.1		30150
4/27/77	3039	3147	1489	1.2		31980	3152	2997	1112	0.5		30510
4/28/77	2611		1743	7.7		32340	2667		1304	1.2		30870
5/2/77	2711		1213	11.9		33780	2602		1167	16.6		32310
5/5/77	2992		2008	1.0		34860	2935		1986	10.7		33390
5/6/77	UNITS SHUT DOWN AT 1500 HOURS -- LACK OF WATER											
5/12/77	2514		997	3.9		35310	2722		966	5.7		33840
5/16/77	2874		2141	0.5		36750	3032		2127	41.2		35280
5/19/77	3014		2354	2.4		37830	3235		2227	122		36360
5/24/77	2920		1504	186		38980			1495	312		37270
5/26/77	3086		1518	199		39700	3223		1513	406		37990
5/31/77	3312		3327	521		41500	3275		2879	811		39790
6/2/77	3037		3058	638		42220	2955		2788	944		40510
6/6/77	2954			1108	1.8	43660	3031			1199	4.3	41950
6/16/77	NO SAMPLE					45190	3078			1649	23	45520
6/20/77	NO SAMPLE					46270	2989			1743	55.8	46960
6/23/77	2592			1553	33.5	47350	2639			1692	76.3	48040
6/27/77	NO SAMPLE					48460	3189			2159	199	49480
6/29/77	2861			1964	19.0	49180	2838			2141	249	50200
7/5/77	2512			1815	19.5	51340	2577			2012	422	52360
7/11/77	NO SAMPLE					52090	2962			2306	660	54520
7/14/77	NO SAMPLE					53350	2753			2317	766	55600
7/18/77	NO SAMPLE					54510	2863			2794	1151	57040
7/21/77	2494			2343	377	55410	2852			2783	1175	58120
7/25/77	2394			2524	721	56850	2528			2527	1155	59560

Table 3-2. Granular Carbon Test Results (Sheet 2 of 2)

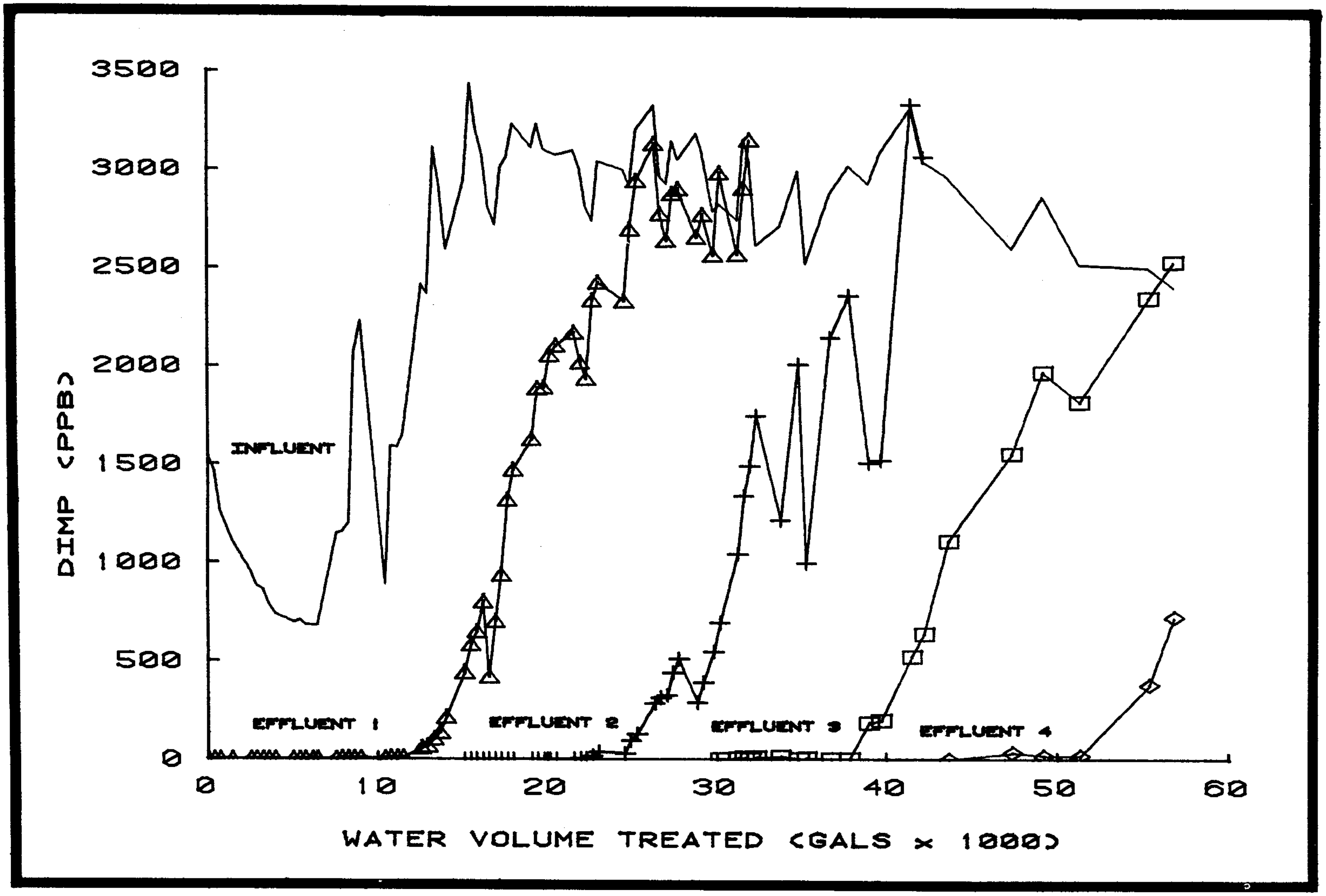

Figure 3-6. DIMP Breakthrough Curve for Reactivated Carbon

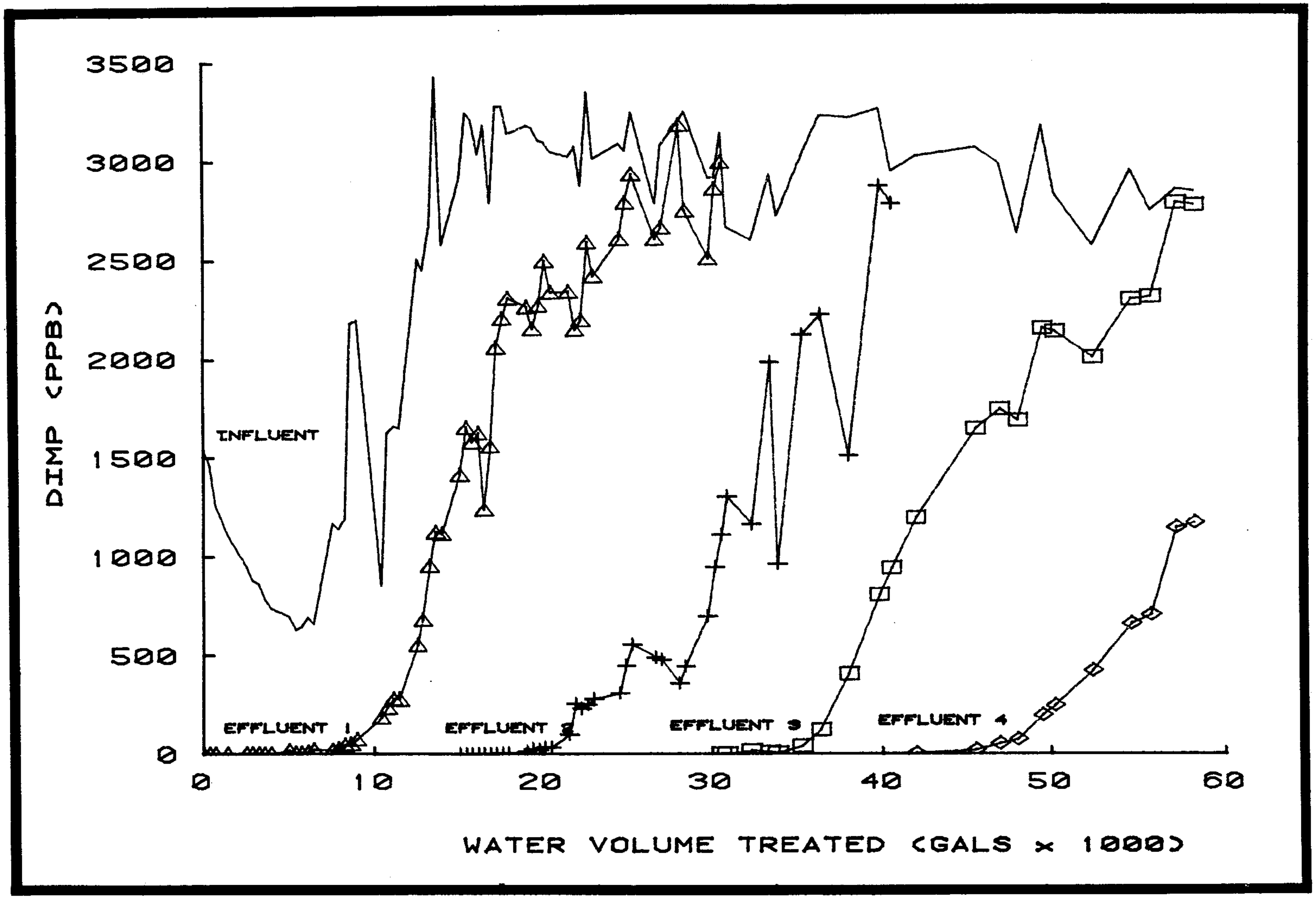

Figure 3-7. DIMP Breakthrough Curve for Virgin Carbon

CHARACTERISTIC	REACTIVATED CARBON	VIRGIN CARBON
DIMP Loading @ Breakthrough -		
15 min. contact time (bog water w/415 ppb)	25.9 gm	15.6 gm
15 min. contact time (well water w/1000 ppb)	53.4 gm	33.4 gm
30 min. contact time (well water w/1000-3000 ppb)	177.6 gm	138.0 gm
Volume Throughput @ Breakthrough -		
15 min. contact time (bog water w/415 ppb)	17,000 gal.	10,800 gal.
15 min. contact time (well water w/1000 ppb)	11,520 gal.	7,560 gal.
30 min. contact time (well water w/1000-3000 ppb)	22,680 gal.	19,080 gal.
Carbon Capacity -		
15 min. contact time (bog water w/415 ppb)	3.8 mg/gm	2.3 mg/gm
15 min. contact time (well water w/1000 ppb)	7.8 mg/gm	4.9 mg/gm
30 min. contact time (well water w/1000-3000 ppb)	13.0 mg/gm	10.0 mg/gm

Table 3-3. Granular Carbon Characteristics

occurrence in carbon adsorption processes, it is interesting to note that carbon's capacity for DIMP increases as the influent concentration of DIMP increases. No data is available for a 30 minute contact time treating bog water since column 2 exhibited no breakthrough during the bog water tests. The 15 minute contact time data for well water is based on 1000 ppb influent DIMP concentration and the 30 minute contact time data is based on a combination of 1000 and 3000 ppb influent DIMP concentration. Since column 1 was not exposed to 3000 ppb DIMP throughout the test, breakthrough characteristics are not available for a 15 minute contact time with this concentration. Also, had column 1 been exposed to 3000 ppb DIMP from the start of the test, the DIMP breakthrough curves for columns 2, 3 and 4 would probably be different. Due to the large fluctuations in influent DIMP concentrations, it is difficult to derive meaningful breakthrough characteristics; but, the data is considered acceptable for process comparison purposes.

The well water study shows that granular carbon is very effective for DIMP removal over a wide range of influent concentrations. Although a contact time of 15 minutes was effective for DIMP removal at 400 to 1000 ppb influent concentrations, a 30 minute contact time with reactivated carbon is recommended for a full scale system. The longer contact time will accommodate higher influent concentrations and still provide a safety margin while producing effluent water of acceptable quality.

SECTION 4

CONCLUSIONS & RECOMMENDATIONS

4.1 GENERAL

The bench and field studies evaluated several different carbon adsorption materials in one of two systems, the Erdlator or Filtrasorb units. Based on the results of these studies, only one comparison will be made; the 10,000 gph Erdlator using Hydrodarco-C powdered carbon with a single-bed Filtrasorb unit using a 20,000 pound bed of reactivated granular carbon. Many times a decision is made solely on the basis of cost comparison; however, to present a valid comparison, other factors such as efficiency, reliability and safety should also be considered.

4.2 OPERATING COMPARISON AND CONCLUSION

During operation, the Erdlator must be constantly monitored for eight operating conditions. The influent water feed rate must be kept constant to prevent carbon bed overflow and effluent turbidity. The influent DIMP concentration must be determined since field tests have shown that as the DIMP concentration increases the carbon feed rate must be increased. The feed rates and concentrations of both coagulants must be monitored; too much coagulant increases operating costs and too little coagulant will result in disintegration of the carbon bed. And, the effluent must be frequently analyzed for DIMP to verify proper system operation. The Filtrasorb unit is a totally enclosed automatic system (including pretreatment filter backwash) which requires intermittent monitoring. Only the effluent water needs to be analyzed for DIMP to determine when the carbon is saturated. The Erdlator consists of six separate units which require two water pumps, two coagulant feed pumps, two mixer motors and a motorized carbon feed screw. The Filtrasorb consists of two units which require a water pump and two pressure-activated valves for filter backwash. Comparing operating parameters and equipment of the two processes, basic statistics will prove that the reliability of the Filtrasorb is far better than that of the Erdlator.

The first Erdlator field tests using carbon feed rates of 1649 and 1000 mg/l of feed water showed that a DIMP removal efficiency of almost 100 percent could be obtained. However, during these tests, the influent DIMP concentration only averaged 415 ppb. For the well water studies, with a carbon feed rate of 252 mg/l and an influent DIMP concentration of 2700 ppb, a DIMP removal efficiency of 98 percent was obtained. This efficiency would be inadequate for an influent concentration of 3000 ppb (60 ppb effluent) and the carbon feed rate would have to be increased. All field studies using the Filtrasorb unit show a DIMP removal efficiency of almost 100 percent until just before breakthrough regardless of the influent DIMP concentration. Based on this, the Filtrasorb unit is more efficient than the Erdlator and will more readily accommodate fluctuating DIMP concentrations.

The 10,000 gph Erdlator has several open tanks and an open clarifier 12 feet in diameter all serviced by access catwalks. The Erdlator requires two full time operators per shift. The Filtrasorb unit is totally enclosed and requires one intermittent operator per shift. Comparing equipment and personnel for both systems, it is apparent that the Filtrasorb unit provides the greatest margin of safety.

When evaluating any process, the waste products and disposal methods must be addressed to comply with environmental requirements. The Erdlator waste product is a concentrated sludge consisting of saturated powdered carbon and overflow coagulant. This sludge must be disposed of by landfill, incineration or reactivation. Landfill is the least desirable because the contaminant (DIMP) has not been destroyed. Incineration consumes large amounts of energy, requires complex combustion gas scrubbing equipment and permits only a one-time use of powdered carbon. Reactivation requires a significant equipment investment but does permit reuse of the carbon. The Filtrasorb waste product is saturated granular carbon. Granular carbon is more conducive to reactivation than powdered carbon; therefore, the granular carbon is reactivated for reuse. During reactivation, DIMP apparently undergoes thermal destruction (see Calgon Corp. reports in the Appendix, Pages A-27 through A-35). When comparing waste products and disposal methods, Filtrasorb is the superior system.

4.3 COST COMPARISON AND CONCLUSION

All costs for the Erdlator (see Appendix, Pages A-36 through A-39) and sludge disposal are based on studies conducted by the Department of The Army. All costs for the Filtrasorb are based on firm quotes from Calgon Corporation. Annual operating costs for both units (see Table 4-1) are based on processing 10,000 gallons of water per hour, 24 hours per day, 330 days per year even though field tests indicate that the Erdlator cannot maintain a stable bed at 10,000 gph. Material costs for the Erdlator are based on the optimum carbon and coagulant feed rates established during the well water studies. A maximum operating period of six years is anticipated so only routine maintenance is listed for the Erdlator. The annual service contract for Filtrasorb includes maintenance and reactivation of three carbon beds. The $8,000.00 listed for material is a contingency fund in the event a fourth carbon bed must be reactivated. The $10,000 for the Filtrasorb is for utilities installation and operation.

ITEM	ERDLATOR	FILTRASORB
Service Contract[1]	-0-	125,000.00
Material	41,621.00	8,000.00
Labor	266,240.00	40,000.00
Maintenance, Utilities, etc.	34,400.00	10,000.00
TOTAL	342,261.00[2]	183,000.00

1. The Erdlator requires an initial capital investment of $84,000.00; The Filtrasorb requires an initial capital investment of $140,000.00
2. Does not include sludge disposal costs

Table 4-1. Annual Operating Costs Less Inflation

Operation of the Erdlator requires some method of sludge disposal. Since there are four options, the annual costs have not been listed in Table 4-1. Figures 4-1 and 4-2 graphically depict the total costs for the three and six year programs respectively. These bar graphs present all four sludge disposal options and include an annual inflation rate of 6.5 percent. Figure 4-3 also includes the inflation rate and shows the cost per 1000 gallons treated for both

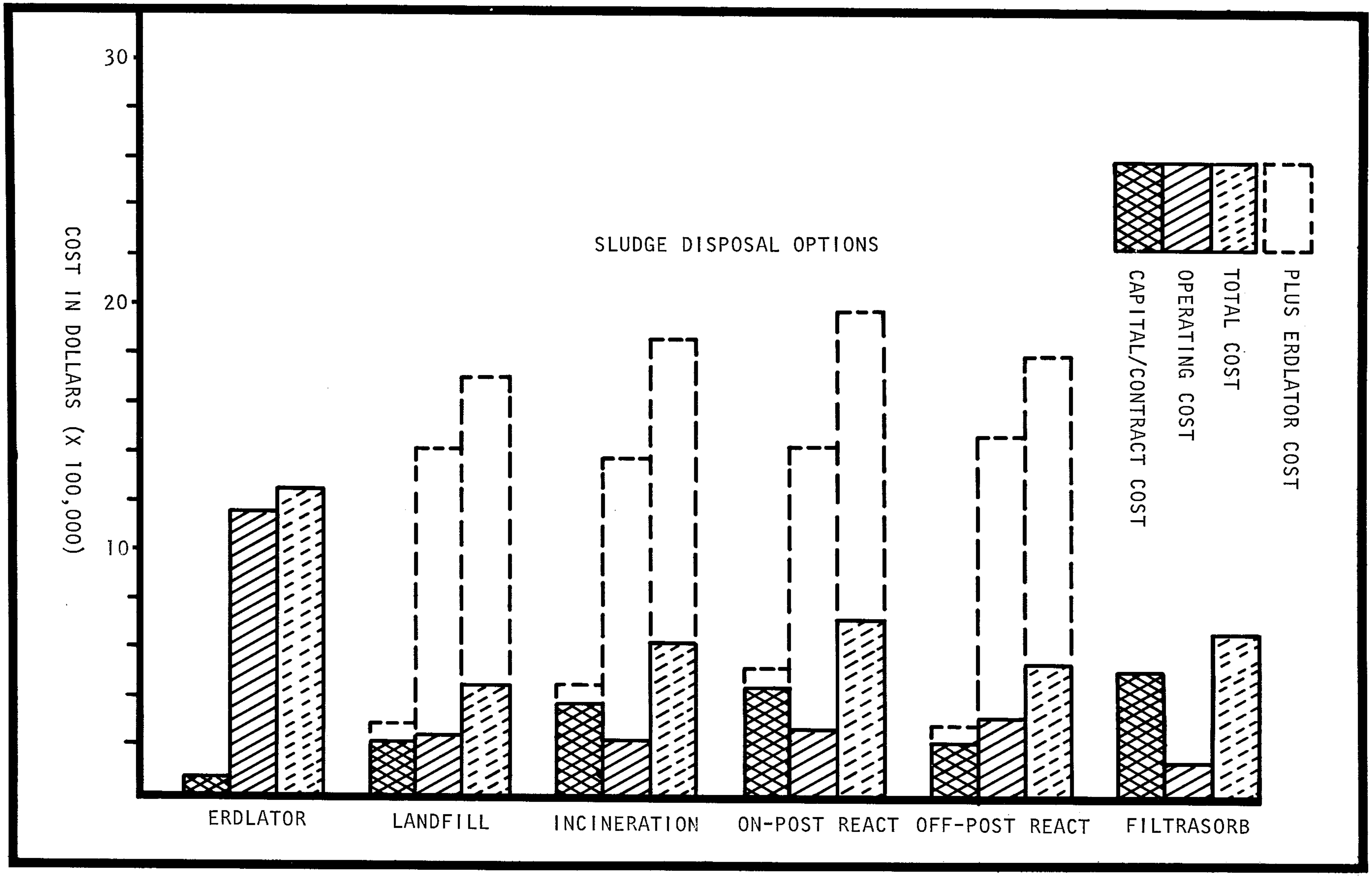

Figure 4-1. Total Costs for Three Year Program

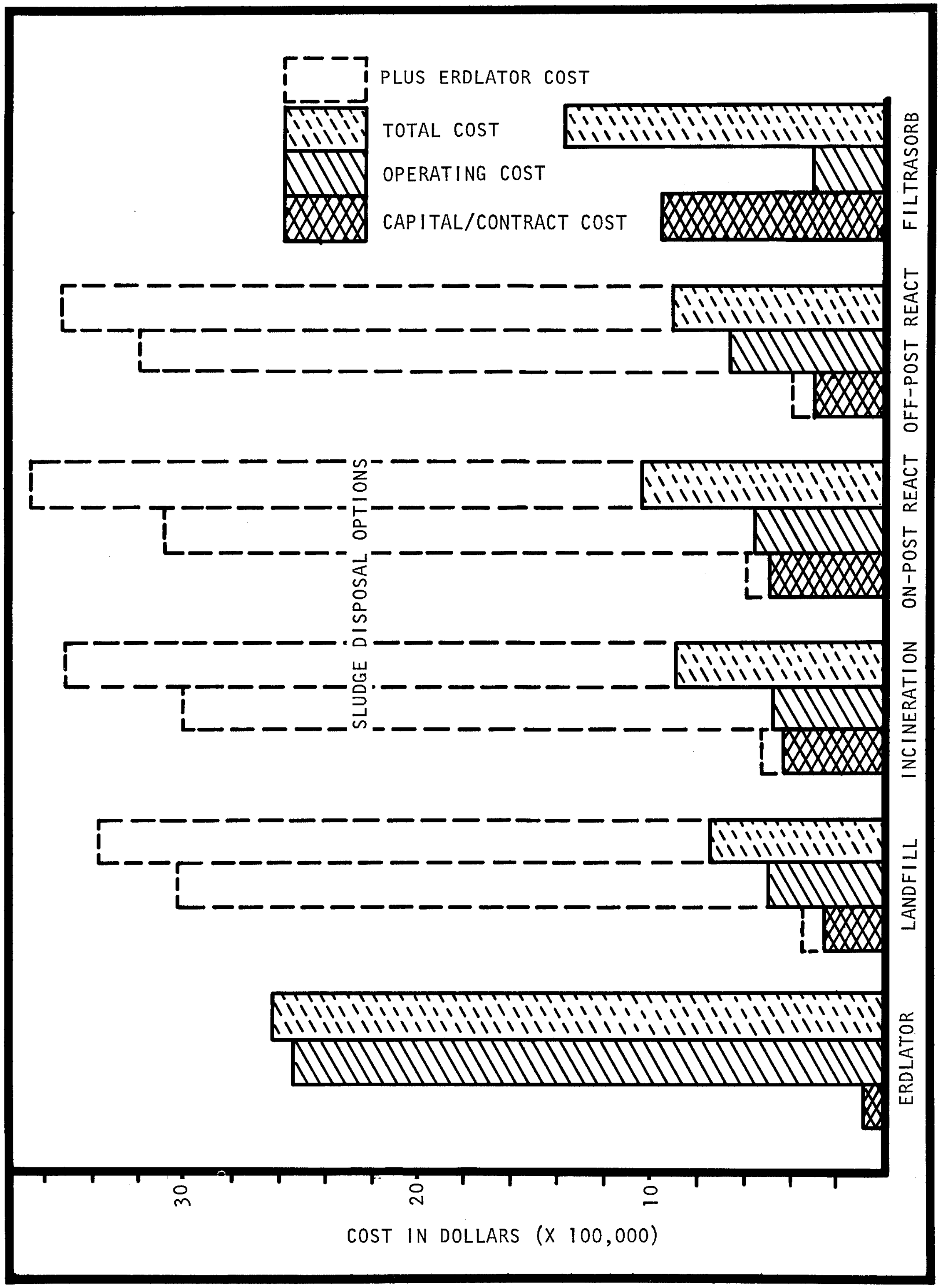

Figure 4-2. Total Costs for Six Year Program

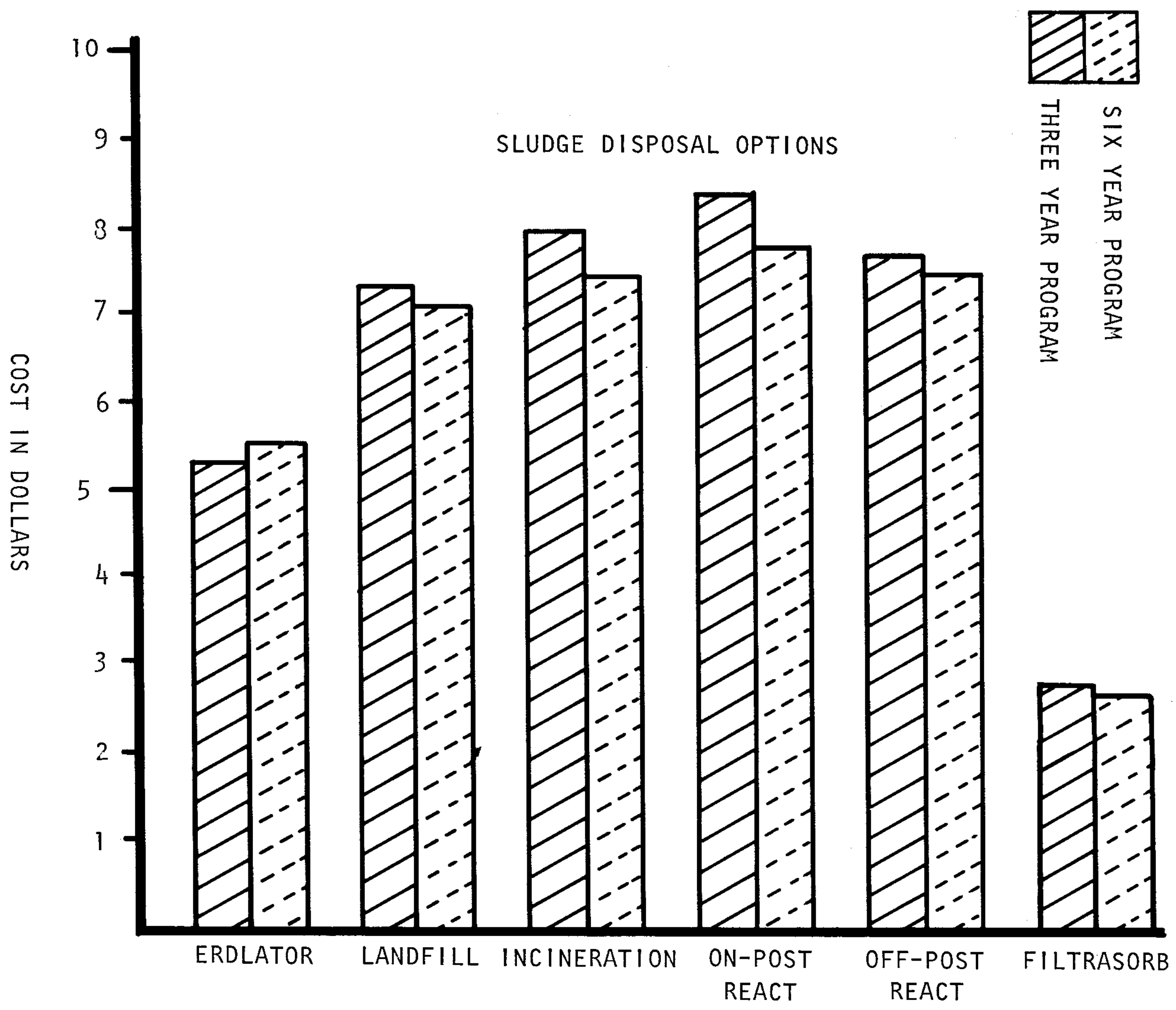

Figure 4-3. Costs per 1000 Gallons for Three and Six Year Programs

the three and six year programs. Except for the Erdlator, amortization of the original capital costs over six years instead of three years reduces the cost per 1000 gallons for six years. Since labor is the primary expense for the Erdlator operation, labor inflation costs exceed equipment amortization gains and increases the cost per 1000 gallons over six years. Any cost comparison between the two processes show the Filtrasorb unit to be economically advantageous.

4.4 RECOMMENDATION

Evaluation of both processes with respect to the full scale process guidelines (see Page 1-4) dictates that the Calgon Corporation Filtrasorb unit be selected for the Interim Containment/Treatment System.

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APPENDIX

Following is an index of material in the Appendix which is referenced in the report. This material is arranged in order of reference.

BOG WATER STUDIES

WELL WATER STUDIES

REACTIVATION STUDIES

DIISOPROPYL METHYLPHOSPHONATE

ALTERNATIVE NAMES

Diisopropyl methylphosphonate; DIMP; phosphonic acid, methyl-, bis-(1-methylethyl) ester (Chem. Abstr. after 1971); phosphonic acid, methyl-, diispropyl ester (1947-1971); methanephosphonic acid, diisopropyl ester.

PHYSICAL AND CHEMICAL PROPERTIES

CAS Reg. No. 1445-75-6
Toxic Substances List: Not listed
Edgewood Arsenal Number: EA 1250
Wiswesser Line Notation: TY&0P0&1&0Y
Molecular formula: $C_7H_{17}O_3P$

Structural formula: $((CH_3)_2CHO)_2(CH_3)P=O$

DIMP is a liquid at room temperature with $n_D^{20}=1.4112$ (1), a bulk density at 25°C of 0.976 g/cc and a boiling point of 174°C (2,3). Its vapor pressure-temperature behavior is closely approximated by the following empirical relationship (2, 3).

$$\text{Log } P \text{ (mm of Hg)} = 9.8571 - 3105/T(^\circ K)$$

DIMP is best synthesized through the reaction of methyl iodide with triisopropyl phosphite (4, 5). Other methods are mentioned in the patent literature (6, 7, 8).

Very little is known of DIMP solubility in water. In studies of DIMP hydrolysis in acidic and basic solutions (9), 0.12 N or higher DIMP was used at temperatures above 80°C, indicating solubilities of above 11 g/liter in that temperature range. In DIMP studies at Southeast Research Institute (10), the solubility in water at 25°C was between 1 and 2 g/liter.

DIMP hydrolysis rates in water at 98, 90 and 80°C have been reported as 2×10^{-6}, 0.88×10^{-6} and $0.31\times10^{-6}\,\text{sec}^{-1}$ respectively (11). The hydrolysis activation energy was estimated to be 26.9 Kcal/mole. These reaction rates can be used to predict hydrolytic behavior at 10°C, a temperature more representative of ground water in a temperate climate. The estimated rate is $3.2\times10^{-11}\,\text{sec}^{-1}$, corresponding to a hydrolysis half-life of about 687 years. In studies cited previously (9), DIMP was among a series of alkylphosphonate esters whose hydrolysis characteristics were measured. In 1N HCl solution, rate constants of 1.74×10^{-4}, 2.81×10^{-4}, 4.78×10^{-4}, 8.53×10^{-4} and $8.56\times10^{-4}\,\text{sec}^{-1}$ were determined at 88.9, 94.4, 99.7, 104.8 and 105.9 C, respectively (9). The acid hydrolysis appears to proceed by the S_N1 mechanism, since the rate of DIMP hydrolysis is greater than that of the lower alkyl phosphonate esters. Basic hydrolysis appears to proceed by the S_N2 mechanism, since the DIMP hydrolysis rate is less than that of the lower alkylphosphonate esters. Typical rate constants for 0.12 N DIMP in 0.2N NaOH solution were 1.53×10^{-4}, 2.29×10^{-4}, and 4.82×10^{-4} M sec^{-1} at 80, 90 and 100°C respectively. Basic hydrolysis at elevated temperatures is a convenient way to prepare the monoester, isopropyl methylphosphonate. In DIMP studies at Southeast Research Institute (10), the mono-sodium salt of DIMP was prepared by dissolving DIMP in 2N NaOH, heating to 50°C, followed by slow cooling to room temperature, with stirring applied throughout the process. About four days were required for completion of the hydrolysis reaction. It would appear that at room temperature and mildly basic conditions, hydrolysis of DIMP would be quite slow. DIMP is formed from sodium isopropyl methylphosphonate at 270°, but DIMP is also converted, in part, to trimethylphosphine oxide at this temperature (12). DIMP is decomposed almost entirely on short residence in a microwave plasma discharge (13); among the products are methylphosphonic acid, isopropyl methylphosphonate, phosphoric acid, isopropyl alcohol, and propylene.

DIMP forms a number of metal complexes in the absence of moisture (14, 15, 16).

DIMP does not appear to be a cholinesterase inhibitor (17).

ANALYTICAL METHODS

DIMP analysis by infrared and Raman spectra was reported by Meyrick and Thompson in 1950 (18). Strong infrared bands occur at 504, 983, 1008, 1248 (phosphonyl), and 2983 cm^{-1}, while strong Raman bands occur at 710, 1445, 2930 and 2985 cm^{-1}. Christol, Levy and Marty listed infrared absorptions at 987, 1015 and 1244 (phosphonyl) cm^{-1}. Moores (19) reported absorptions at 899, 1239 and 1314 cm^{-1}. The spectrum of DIMP was also studied by Lorquet and Vassart (20). Unfortunately, other alkylphosphonate esters have similar absorption bands.

Thin-layer and paper chromatography methods for DIMP have been studied (21). A 2:1:1 v/v solution of hexane-benzene-methanol or a 6:1:1 v/v solution of hexane-methanol-diethyl ether was used to develop the paper chromatogram. Spots were made visible with a spray of 1% cobalt chloride in anhydrous acetone, which detected DIMP and other phosphorous esters. These esters appeared at room temperature as blue spots, which could be distinguished by their relative R_f values. DIMP detection levels were not given.

Gas chromatography has been used to analyze DIMP in water with a flame ionization detector. Two methods are known; one developed by Shell Chemical Company (22) and adopted by the Colorado Department of Health (23) and one developed at Edgewood Arsenal (12). The Colorado Department of Health methodology (23) involves extraction of DIMP from water with chloroform. Three ml of chloroform suffices to extract 85-90% of DIMP from 200 ml of water. The glass chromatographic column was 5 ft long, ¼ inch in diameter, and filled with OV-17/Reoplex on 400 CRG. A 1 ppm solution of DIMP in chloroform was used as a standard.

The Edgewood Arsenal work (12) was oriented towards determining components of waste from demilitarized methyl isopropylphosphonofluoridate (GB). The waste is extracted with methylene chloride. The chromatography column was of glass, 6 ft long x ¼ inch in diameter and filled with QF-1 in 60-80 mesh Gas Chrom Q. GB could be detected by phosphorus flame photomety as 20 ppb (12); no limits were mentioned for DIMP or other compounds. Field ionization mass spectrometry (24) can be used to detect as little as 0.2 ppb (mole ratio), i.e., 10^{-9} g/liter.

The nuclear magnetic resonance spectrum of DIMP at 25 MHz was studied by Mavel and Martin (25).

MAMMALIAN TOXICOLOGY

No published information is available on the toxicity of DIMP to humans or experimental animals. Unpublished acute toxicity data (LD50) on experimental animals were obtained from the files at Edgewood Arsenal, and are summarized in Table E-1.

TABLE E-1
Summary of Acute Toxicity of DIMP

Animal Species	Route of Administration	LD50 (mg/kg)	Remarks	References
Mouse	Intraperitoneal	>250		26
Rat	Subcutaneous	>200		27
Rabbit	Subcutaneous	>100 <200		27
Rabbit	Intravenous	224	Local irritation 179-280 (19/20 confidence limits)	28
Rabbit	Dermal	>200	No irritation at application site	28

The toxicology of DIMP, including acute data, phytotoxicity and detoxification studies have been summarized in a fact sheet (2). No evidence was found that DIMP has been studied for carcinogenic, mutagenic or teratogenic activity <u>in vitro</u>. One report (17) stated that DIMP does not inhibit the enzyme cholinesterase, although no experimental evidence was given for the statement.

It is concluded from the data presented above, that DIMP is fairly toxic to experimental animals and could be irritating or corrosive to the eyes. The lack of complete data indicates the need for further studies to accurately evaluate the potential toxicity of DIMP. Recommendations for further toxicological studies were made (2) and these have been implemented through a USAMRDC contract with

Litton Bionetics, Inc., Falls Church, Virginia 22046.

An additional study on DIMP has been initiated (May 1975) in the Toxicology Division, Biomedical Laboratory, Edgewood Arsenal, APG, MD (29). This work includes a 26 week subacute study and a reproduction study in rats only.

ENVIRONMENTAL CONSIDERATIONS

No information was found as to DIMP behavior in soil and water, its effect on animals in the environment, or its transmittal in food chains. A USAMRDC contract study to determine the toxicity of DIMP to aquatic vertebrates and invertebrates has been initiated through Bionomics, E. G. & G., Inc., Wareham, MA 02571.

PLANTS

Evaluation of DIMP at Ft. Detrick during 1974-1975 indicated that DIMP could injure wheat and beans (Witchita wheat and Black Valentine beans) (30). In one test, treatment of wheat and beans (water solution to soil) with 10 ppm DIMP produced no effect on wheat, but gave a burning on edges of bean leaves. In a second test, treatment with 10 ppm or 40 ppm levels of DIMP resulted in tip burn of leaves on both wheat and beans at both levels. In other tests where DIMP and dicyclopentadiene (DCPD) were used together, there was an indication of additive or synergistic effects due to DCPD. DIMP may also be phytotoxic to sugar beets (31). In herbicidal screening tests at Ft. Detrick, rice, morning glory, bean, oat and soybean plants growing in pots in a greenhouse and sprayed with DIMP at 0.1 and 1.0 pounds per acre exhibited no injurious effects from the DIMP (32). A USAMRDC contract study to determine plant uptake and effects and soil retention of DIMP has been initiated through Aerojet Ordinance and Manufacturing Co., Downey, CA 90241.

EXISTING STANDARDS

No information available.

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DICYCLOPENTADIENE

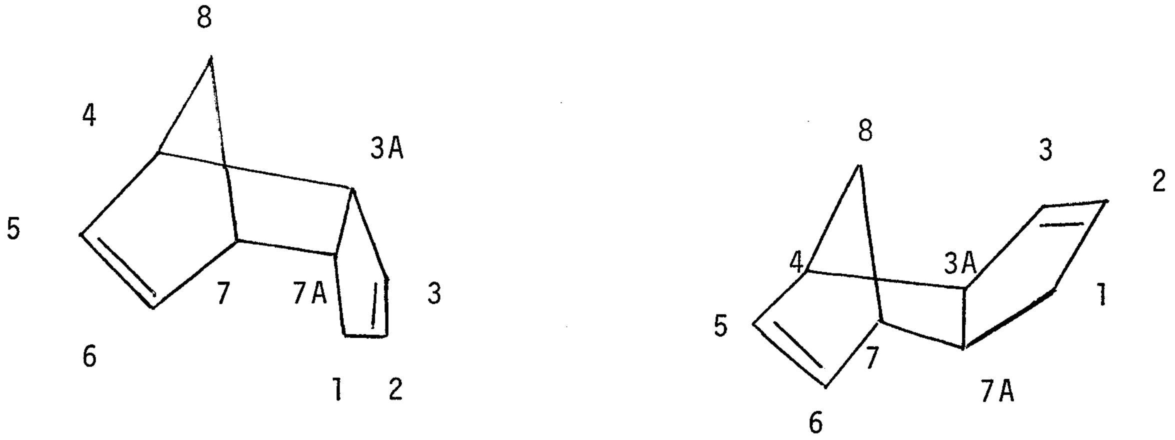
ALTERNATIVE NAMES

Dicyclopentadiene; Bicyclopentadiene; Biscyclopentadiene; 3a,4,7,7a-Tetrahydro-4,7-methanoindene

PHYSICAL AND CHEMICAL PROPERTIES

CAS Reg. No. 0077-73-6
Toxic Substances List: PC 10500
Molecular formula: $C_{10}H_{12}$

Dicyclopentadiene (DCPD) is a waxy solid at room temperature with a strong camphor-like odor. The structures of DCPD appear in Figure J-1. The isomers may be considered as cis- and trans- in terms of the 2- and 8- carbons. Trans-DCPD is the usual form, (and where DCPD is cited the trans- form is understood). The cis- form has been prepared from the trans- form by a method described by Schröder (1). A 20% solution of DCPD in CS_2 was heated for 2 to 4 hours at 180°-200°C under 50 atmospheres pressure. The solvent was then distilled, and the products separated by *in vacuo* distillation with a 30% yield of *cis*-DCPD.



"Trans"

"Cis"

Figure J-1. *Cis*- and *Trans*- Isomers of Dicyclopentadiene

According to an article by Waring and co-workers (2), crude DCPD was distilled, and 40°-44°C range distillate (probably monomer) collected and allowed to stand overnight. The *cis*- isomer reportedly crystallized when the distillate was placed in vacuum, had a melting point of 27.8°C, and only a faint odor.

Table J-1 summarizes physical properties of <u>trans</u>-DCPD.

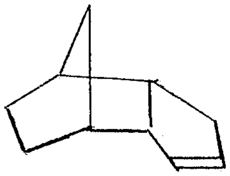
TABLE J-1

Physical properties of <u>Trans</u>-Dicyclopentadiene

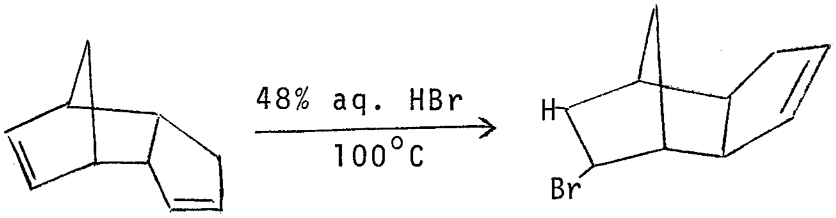
Property	Value	References
Density at 20°C, g/cc	0.982	(3)
Melting Point, °C	32.9	(4)
n_D^{35} (Refractive Index)	1.5050	(5)
Temp, °C for cited Vapor Press, mm Hg		
20°	1.4	(3)
47.6°	10.0	(6)
105°	100.0	(3)
166.6° (boiling point)	760.0	(4)
Solubility in Water (ppm)	Considered insoluble Estimated 40*	(6) (6a)

*-Estimation on basis of solubility of diolefins of similar molecular volume (6a).

Dicyclopentadiene can be prepared by dimerizing cyclopentadiene. Harkness et al. (7) reported that the second-order rate constant for the reaction in liquid cyclopentadiene was $8.5 \times 10^7 e^{-14900/RT}$ cc/mole-sec. Thus, if one cc of cyclopentadiene is allowed to stand at 25°C for one day, 52% conversion to the dimer should occur. This result is approximate since the liquid phase changes density as dimerization proceeds. DCPD in turn can break down to the monomer. These authors (7) determined the breakdown to be a first-order reaction in the vapor phase with rate constant $10^{13} e^{-33,700/RT}$ sec^{-1}. In 1936, Khambata and Wassermann (8) reported the liquid phase rate constant as $3 \times 10^{13} e^{-35400/RT}$ sec^{-1}. At 30°C, the half-lives of DCPD breakdown in the vapor and liquid phases are calculated at 4,315 and 24,200 years, respectively. This means that the equilibrium between the monomer and dimer of cyclopentadiene lies strongly on the side of the dimer at ambient temperatures. The 584A photoelectron spectrum of DCPD was measured by Baker et al. (9). DCPD undergoes reactions involving its double bonds; some of these were studied in a thesis by Donaldson in 1958 (10). If addition is made across one double bond, it is inevitably the 5,6-bond. DCPD can be hydrogenated in the presence of Raney nickel to



However, typical addition reactions such as hydrohalogenation, hydration or esterification yield rearranged structures which are _cis_-oriented. For example:



Donaldson (10) found that 99% of the saturated analogue of DCPD, _trans_-4, 7-methanoindan, could be isomerized to the _cis_-4,7-methanoindan, in sharp contrast to DCPD. He presented the infrared spectrum of DCPD (identified as Spectrum #46) and spectra of the other compounds studied. Although he did not investigate the reaction of HOCl with DCPD, he indicated that addition occurs across the 5,6-bond to form a chlorohydrin (10).

ANALYTICAL METHODS

Until recently, analysis for DCPD as a trace pollutant was not well developed. According to a 1967 article by Szewczyk (11), DCPD absorbs in the infrared at 677 and 1344 cm^{-1} sufficiently distinct from the cyclopentadiene peaks of 644 and 1369 cm^{-1} to permit analysis of DCPD in the presence of cyclopentadiene. Raman spectrum frequencies are found at 1571 and 1613 cm^{-1} (12). Miskalis (13) used gas chromatograph to detect DCPD in coke-oven gas. Gas chromatography of mixtures containing DCPD was reported as early as 1958 (14). Kinkead, et al. (3) used flame ionization gas chromatographic analysis (at 135°C, with a 10 ft column of 15% Tergitol NP-44 on Gas Chrom Q) to measure DCPD concentrations as low as 1 ppm in air. In work done for the Colorado State Department of Health, headspace analysis by gas chromatography was performed on water containing DCPD (15). Details of the analysis are not available, though it is claimed to detect DCPD at 0.28 ppb in water (16). DCPD in a benzene-acetic acid mixture gives a color text with bromine at a sensitivity of about 60 ppm (17). DCPD exhibits a fluorescence that might be useful for analysis (18).

DCPD was found to be an irritant when subjected to the standard rabbit eye irritation test but was not found to be a primary skin irritant (20). No TLV has been established for DCPD, but Gerarde (6) suggested "a value of 100 ppm seems reasonable based on the limited toxicity date available and extrapolation from similar chemicals." Kinkead et al. (3) have suggested a hygienic standard for man of 5 ppm. The TLV for DCPD recommended by Russian workers (24, 25), is 0.185 ppm (1 mg/m^3). Russian workers (26) have also recommended a permissible concentration of 0.0001 mg/l for DCPD in water supply systems. Man can detect 0.003 ppm DCPD vapor by odor (3).

The carcinogenicity of DCPD by intramuscular injection in the rat was investigated under an NCI contract at the Institute of Chemical Biology, San Francisco University (Dr. A. Furst, 1975) (27). The compound was not considered to be carcinogenic under the conditions of the experiment.

The toxicology of DCPD, including phytotoxicity, has been summarized in a fact sheet (28). The pathological effects in rats were typical of irritating hydrocarbons when administered orally in large doses; it is slightly to moderately toxic by the dermal route; and highly toxic by the oral and intraperitoneal routes in single dose studies. The lack of complete data indicates the need for further studies for an accurate evaluation of the toxic potential of DCPD. Recommendations for further toxicological studies have been made (28), and the implementation of these recommendations has already been undertaken through a USAMRDC contract with Litton Bionetics, Inc., Falls Church, Virginia 22046.

ENVIRONMENTAL CONSIDERATIONS

No information is available as to DCPD behavior in soil and water, its effects on animals in the environment, or its transmission through food chains. A USAMRDC contract study to determine the toxicity of DCPD to aquatic vertebrates and invertebrates has been initiated through Bionomics, E. G. & G., Inc., Wareham, MA 02571.

PLANTS

Tests conducted at Ft. Detrick during 1974-1975, in which wheat (Wichita) and beans (Black Valentine) were treated with diisopropyl methylphosphonate (DIMP) and DCPD combined (water solution to soil), showed a greater effect on test plants than treatments with DIMP alone. Thus an additive, or possible synergistic, effect due to DCPD was suggested. Tests conducted with DCPD alone at 10 and 40 ppm caused tip burning of leaves (29). A USAMRDC contract study to determine plant uptake and effects and soil retention of DCPD has been initiated through Aerojet Ordnance and Manufacturing Co., Downey, CA 90241.

EXISTING STANDARDS

No information available.

MAMMALIAN TOXICOLOGY

There is no published information on the toxicity of DCPD to humans. Information on the mammalian toxicity of DCPD is summarized in Tables J-2 and J-3.

TABLE J-2

Summary of Acute Toxicity of DCPD

Animal Species	Route of Administration	LD50 (mg/kg)	Range Value	References
Rat	Oral	353	262-478	3
		410	310-530	19
Rat (male)	Oral	435	361-523	20
Rat (female)	Oral	396	343-458	20
Rat	Intraperitoneal	200		21
		310		3
Mouse	Intraperitoneal	200		21
Rabbit	Dermal	5080*	3110-8290	3
		4460*	2440-8150	19
		6720*	3150-14360	22

* - LC50 values.

TABLE J-3
Inhalation Toxicity of DCPD

Animal Species	Dose (ppm) & Exposure (hr)	LC50 (ppm)	Remarks	References
Rat	4	660	Range 553-817	3
Rat		359		3
Rat		385		3
Rat	Saturated vapor	1*		3
Mouse (male)	4	145		3
Rabbit (male)	4	771		3
Rat	2500/1		1/4 killed	23
Rat	2000/4		4/6 killed	23
Rat	1000/4		4/4 killed	23
Rat	500/4		1/6 killed	23
Rat	250/6 x 10		1/4 killed	23
Rat	100/6 x 15		4/4 killed	23

* - LT 50 (hr.)

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GENERAL

Before starting the field studies, continued water analyses detected the presence of three additional contaminants; p-chlorophenyl methyl sulfide, sulfone and sulfoxide. Therefore, these compounds were included in the analytical parameters for the Filtrasorb unit and are presented on Pages A-22 through A-24 for well water. As previously discussed, DIMP was the first compound to exhibit breakthrough characteristics. It follows that, if water is satisfactorily treated for DIMP removal, the sulfur compounds will be removed to an acceptable level.

Temperature and pH are parameters which affect the evaluation of carbon adsorption. Therefore, pH was also included in the analytical parameters for the Filtrasorb unit (temperature was constant) and is presented on Page A-21 for bog water and Page A-25 for well water. Decreasing pH below 9.0 increases the adsorptive characteristics and adsorption is adversely affected above 9.0. During both the bog and well water tests, the maximum pH detected was 8.71.

ROCKY MOUNTAIN ARSENAL

p-chlorophenyl methyl sulfide (μg/1)

	Column "A" React						Column "B" Virgin					
Date	Feed	#0	#1	#2	#3	#4	Feed	#0	#1	#2	#3	#4
11/26/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
11/29/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
11/30/76	-	<10	<10	-	-	-	-	11.3	<10	-	-	-
12/01/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/02/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
12/03/76	13.8	<10	<10	-	-	-	13.8	<10	<10	-	-	-
12/06/76	12.2	<10	<10	-	-	-	12.2	<10	<10	-	-	-
12/07/76	-	<10	<10	-	-	-	-	11.2	<10	-	-	-
12/08/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
12/09/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/10/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
12/14/76	<10	<10	<10	-	-	-	-	<10	<10	-	-	-
12/15/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/16/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/17/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/20/76	<10	<10	<10	-	-	-	<10	<10	<10	-	-	-
12/21/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
12/23/76	-	<10	<10	-	-	-	-	<10	<10	-	-	-
12/27/76	13.7	11.8	<10	-	-	-	13.7	13.8	<10	-	-	-
12/28/76	13.5	<10	<10	-	-	-	13.5	12.0	<10	-	-	-
12/29/76	46	50	<10	-	-	-	46	72	<10	-	-	-
12/30/76	28	28	<10	-	-	-	28	26	<10	-	-	-
01/03/77	-	53	<10	-	-	-	-	-	-	-	-	-
01/05/77	63	58	<10	-	-	-	63	58	<10	-	-	-
01/07/77	31.4	<10	<10	-	-	-	31.4	-	-	-	-	-
01/10/77												

ROCKY MOUNTAIN ARSENAL

p-chlorophenyl methyl sulfone ($\mu g/l$)

	Column "A" React						Column "B" Virgin					
Date	Feed	#0	#1	#2	#3	#4	Feed	#0	#1	#2	#3	#4
11/26/76	81.6	27.6	<10				81.6	64.6	<10			
11/29/76	-	49.3	<10				-	76.9	<10			
11/30/76	-	52.8	<10				-	77.8	<10			
12/01/76	78.7	53.4	<10				78.7	75.9	<10			
12/02/76	-	70.4	<10				-	79.7	<10			
12/03/76	74.8	89.2	<10				74.8	66.1	<10			
12/06/76	91.6	76.1	<10				91.6	82.1	<10			
12/07/76	-	77.8	<10				-	102.0	<10			
12/08/76	-	71.6	<10				-	90.7	<10			
12/09/76	92.7	58.5	<10				92.7	83.1	<10			
12/10/76	-	10	<10				-	79.2	<10			
12/14/76	74.2	47.0	<10				74.2	64.8	<10			
12/15/76	63.4	50.2	<10				63.4	69.4	<10			
12/16/76	-	56.3	<10				-	65.0	<10			
12/17/76	56.5	16.0	<10				56.5	57.3	<10			
12/20/76	44.9	76.7	<10				44.9	52.1	<10			
12/21/76	-	65.8	<10				-	78.6	<10			
12/23/76	-	65.5	<10				-	69.4	<10			
12/27/76	52.5	52.7	<10				52.5	50.1	<10			
12/28/76	48.0	60.0	<10				48.0	63.0	<10			
12/29/76	55.0	50.0	<10				55.0	51.0	<10			
12/30/76	28.0	28.0	<10				28.0	26.0	<10			
01/03/77	-	53.0	<10				-	-	-			
01/05/77	63.0	58.0	<10				63.0	58.0	10			
01/07/77	74.3	77.3	<10				74.3	down				
01/10/77												

ROCKY MOUNTAIN ARSENAL

p-chlorophenyl methyl sulfoxide ($\mu g/l$)

	Column "A" React						Column "B" Virgin					
Date	Feed	#0	#1	#2	#3	#4	Feed	#0	#1	#2	#3	#4
11/26/76	215	85.2	<10	-	-	-	215	211	<10	-	-	-
11/29/76	-	127	<10	-	-	-	-	236	<10	-	-	-
11/30/76	-	138	<10	-	-	-	-	235	<10	-	-	-
12/01/76	238	139	<10	-	-	-	238	230	<10	-	-	-
12/02/76	-	178	<10	-	-	-	-	200	<10	-	-	-
12/03/76	235	215	<10	-	-	-	235	168	<10	-	-	-
12/06/76	241	196	<10	-	-	-	241	203	<10	-	-	-
12/07/76	-	181	<10	-	-	-	-	260	<10	-	-	-
12/08/76	-	221	<10	-	-	-	-	253	<10	-	-	-
12/09/76	261	223	<10	-	-	-	261	226	<10	-	-	-
12/10/76	-	23.7	<10	-	-	-	-	258	<10	-	-	-
12/14/76	213	164	<10	-	-	-	213	218	<10	-	-	-
12/15/76	218	177	<10	-	-	-	218	216	<10	-	-	-
12/16/76	-	181	<10	-	-	-	-	219	<10	-	-	-
12/17/76	170	41.8	<10	-	-	-	170	170	<10	-	-	-
12/20/76	167	184	<10	-	-	-	167	187	<10	-	-	-
12/21/76	-	194	<10	-	-	-	-	209	<10	-	-	-
12/23/76	-	184	<10	-	-	-	-	200	<10	-	-	-
12/27/76	177	182	<10	-	-	-	177	173	<10	-	-	-
12/28/76	155	187	<10	-	-	-	155	190	<10	-	-	-
12/29/76	181	180	<10	-	-	-	181	185	<10	-	-	-
12/30/76	75	78	<10	-	-	-	75	78	<10	-	-	-
01/03/77	-	127	<10	-	-	-	-	-	-	-	-	-
01/05/77	203	198	<10	-	-	-	203	195	<10	-	-	-
01/07/77	209	213	<10	-	-	-	209	down				
01/10/77												

ROCKY MOUNTAIN ARSENAL

pH

	Column "A" React						Column "B" Virgin					
Date	Feed	#0	#1	#2	#3	#4	Feed	#0	#1	#2	#3	#4
11/26/76	8.11	8.15	8.18	-	-	-	8.11	8.11	1.12	-	-	-
11/29/76	-	8.07	8.09	-	-	-	-	8.08	8.05	-	-	-
11/30/76	-	8.13	8.13	-	-	-	-	8.10	8.09	-	-	-
12/01/76	8.15	-	-	-	-	-	8.15	-	-	-	-	-
12/02/76	-	8.50	8.62	-	-	-	-	8.42	8.59	-	-	-
12/03/76	8.31	8.43	8.45	-	-	-	8.31	8.42	8.44	-	-	-
12/06/76	8.15	8.23	8.19	8.13	-	-	8.15	8.15	8.13	8.10	-	-
12/07/76	-	8.26	8.27	8.26	-	-	-	8.23	8.33	8.21	-	-
12/08/76	-	8.19	8.19	8.16	-	-	-	8.15	8.15	8.16	-	-
12/09/76	8.24	8.15	8.28	8.26	-	-	8.24	8.30	8.19	8.23	-	-
12/10/76	-	8.12	8.14	8.16	-	-	-	8.16	8.16	8.16	-	-
12/14/76	8.54	8.56	8.55	8.57	-	-	8.54	8.55	8.57	8.66	-	-
12/15/76	8.55	8.22	8.40	8.52	-	-	8.55	8.44	8.63	8.53	-	-
12/16/76	-	8.42	8.52	8.58	-	-	-	8.52	8.40	8.42	-	-
12/17/76	8.45	8.40	8.18	7.99	7.75	-	8.45	8.52	7.94	7.90	8.13	-
12/20/76	8.06	8.10	8.12	8.14	8.14	-	8.06	8.09	8.10	8.11	8.11	-
12/21/76	-	-	-	-	-	-	-	-	-	-	-	-
12/23/76	-	8.60	8.49	8.53	8.38	-	-	8.60	8.29	7.93	8.49	-
12/27/76	8.13	8.12	8.03	8.01	8.04	8.02	8.13	8.11	8.06	8.06	8.03	8.03
12/28/76	-	8.65	8.68	8.63	8.59	8.64	-	8.67	8.71	8.71	8.60	8.63
12/29/76	-	8.62	8.63	8.61	8.61	8.45	-	8.47	8.61	8.56	8.58	8.59
12/30/76	8.57	8.46	8.68	8.59	8.60	8.44	8.57	8.49	8.49	8.38	8.52	8.40
01/03/77	8.29	8.33	8.20	8.27	8.31	8.22	8.29	8.33	8.29	8.28	8.28	8.30
01/05/77	8.03	8.04	8.07	8.09	8.16	8.22	8.03	8.07	8.07	8.11	8.08	8.00
01/07/77	8.23	8.35	8.35	8.14	8.12	8.19	-	-	-	-	-	-
01/10/77	7.90	7.98	7.65	7.80	8.02	8.04	7.90	7.98	7.97	7.94	7.98	8.04

ROCKY MOUNTAIN ARSENAL

P-CHLOROPHENYL METHYL SULFIDE (ug/l)

	Column "A" React			Column "B" Virgin	
Date	#0	#1	Cumulative Flow (gal)	#0	#1
2/16/77	31.4	<10	8280	29.8	<10
2/24/77	10.6	<10	11160	10.7	<10
3/2/77	< 10	<10	13320	< 10	<10
3/9/77	< 10	<10	15840	< 10	<10
3/16/77	< 10	<10	17280	< 10	<10
3/23/77	< 10	<10	19800	< 10	<10
3/30/77	< 10	<10	22320	< 10	<10
4/6/77	< 10	<10	24570	< 10	<10
4/13/77	< 10	<10	27060	< 10	<10
4/19/77	< 10	<10	29190	< 10	<10

ROCKY MOUNTAIN ARSENAL

P-CHLOROPHENYL METHYL SULFONE (ug/l)

Date	Column "A" React #0	Column "A" React #1	Cumulative Flow (gal)	Column "B" Virgin #0	Column "B" Virgin #1
2/16/77	68.8	< 10	8280	67.2	< 10
2/24/77	38.8	< 10	11160	38.1	< 10
3/2/77	15.3	< 10	13320	11.6	< 10
3/9/77	< 10	< 10	15840	< 10	< 10
3/16/77	< 10	< 10	17280	< 10	< 10
3/23/77	< 10	< 10	19800	< 10	< 10
3/30/77	< 10	< 10	22320	< 10	< 10
4/6/77	< 10	< 10	24570	< 10	< 10
4/13/77	< 10	< 10	27060	< 10	< 10
4/19/77	< 10	< 10	29190	< 10	< 10

ROCKY MOUNTAIN ARSENAL

P-CHLOROPHENUL METHYL SULFOXIDE (ug/l)

Date	Colume "A" React #0	#1	Cumulative Flow (gal)	Column "B" Virgin #0	#1
2/16/77	97.6	<10	8280	102.6	< 10
2/24/77	63.5	<10	11160	54.7	< 10
3/2/77	27.5	<10	13320	25.3	< 10
3/9/77	< 10	<10	15840	< 10	< 10
3/16/77	< 10	<10	17280	< 10	< 10
3/23/77	< 10	<10	19800	< 10	< 10
3/30/77	< 10	<10	22320	< 10	< 10
4/6/77	< 10	<10	24570	< 10	< 10
4/13/77	< 10	<10	27060	< 10	< 10
4/19/77	< 10	<10	29190	< 10	< 10

ROCKY MOUNTAIN ARSENAL

pH

Date	Colume "A" React #0	Colume "A" React #1	Colume "A" React #2	Colume "A" React #3	Cumulative Flow (gal)	Column "B" Virgin #0	Column "B" Virgin #1	Column "B" Virgin #2	Column "B" Virgin #3
2/14/77	7.56	7.54	7.53		7560	7.56	7.59	7.61	
2/15/77	7.47	7.49	7.61		7920	7.55	7.59	7.56	
2/16/77	7.63	7.67	7.69		8280	7.65	7.72	7.67	
2/17/77	7.58	7.68	7.66		8640	7.60	7.69	7.69	
2/18/77	7.32	7.48	7.45		9000	7.44	7.41	7.48	
2/22/77	7.50	7.57	7.57		10440	7.59	7.58	7.60	
2/23/77	7.30	7.40	7.44		10800	7.40	7.39	7.45	
2/24/77	7.34	7.42	7.39		11160	7.46	7.44	7.48	
2/25/77	7.24	7.37	7.41		11320	7.37	7.39	7.40	
2/28/77	7.49	7.54	7.69		12600	7.64	7.56	7.50	
3/1/77	6.95	7.61	7.57		12960	7.61	7.57	7.54	
3/2/77	7.40	7.44	7.41		13320	7.41	7.39	7.47	
3/3/77	7.39	7.46	7.50		13680	7.47	7.50	7.53	
3/4/77	7.45	7.47	7.45		14040	7.46	7.45	7.47	
3/7/77	7.63	7.70	7.65		15120	7.72	7.70	7.68	
3/8/77	7.53	7.64	7.59		15480	7.58	7.59	7.63	
3/9/77	7.59	7.44	7.60		15840	7.65	7.67	7.66	
3/10/77	7.30	7.40	7.43		16200	7.47	7.43	7.46	
3/14/77	7.63	7.40	7.41		16560	7.64	7.54	7.42	
3/15/77	7.36	7.78	7.70		16920	7.45	7.76	7.73	
3/16/77	7.37	7.44	7.46		17280	7.44	7.46	7.51	
3/17/77	7.54	7.55	7.57		17640	7.62	7.60	7.57	
3/18/77	7.34	7.36	7.34		18000	7.39	7.42	7.44	
3/21/77	7.55	7.56	7.50		19080	7.55	7.63	7.54	
3/22/77	7.58	7.60	7.56		19440	7.54	7.56	7.59	
3/23/77	7.36	7.40	7.42		19800	7.54	7.56	7.59	
3/24/77	7.41	7.44	7.44		20160	7.45	7.47	7.47	
3/25/77	7.37	7.41	7.40		20520	7.41	7.44	7.43	
3/28/77	7.73	7.77	7.75		21600	7.75	7.81	7.74	

ROCKY MOUNTAIN ARSENAL

PH

Date	Column "A" React #0	#1	#2	#3	Cumulative Flow (gal)	Column "B" Virgin #0	#1	#2	#3
3/29/77	7.65	7.68	7.66		21960	7.70	7.68	7.66	
3/30/77	7.54	7.59	7.64		22320	7.63	7.58	7.61	
3/31/77	7.43	7.47	7.49		22680	7.48	7.52	7.48	
4/6/77	7.31	7.45	7.59		24570	7.38	7.44	7.59	
4/7/77	7.37	7.40	7.39	7.48	24930	7.44	7.50	7.51	7.50
4/8/77	7.39	7.45	7.45	7.46	25290	7.42	7.47	7.45	7.50
4/11/77	7.29	7.34	7.33	7.39	26340	No Sample			
4/12/77	7.62	7.66	7.65	7.61	26700	7.73	7.72	7.69	7.66
4/13/77	7.66	7.65	7.66	7.69	27060	7.69	7.69	7.67	7.67
4/14/77	7.58	7.68	7.67	7.63	27400	No Sample			
4/15/77	7.35	7.39	7.36	7.35	27760	No Sample			
4/18/77	7.66	7.57	7.41	7.30	28840	7.66	7.61	7.48	7.43
4/19/77	7.84	7.76	7.75	7.69	29190	7.88	7.87	7.81	7.72
4/20/77	No Sample				29520	No Sample			
4/21/77	7.29	7.41	7.49	7.60	29820	No Sample			
4/22/77	7.28	7.32	7.35	7.40	30180	No Sample			
4/25/77	7.34	7.57	7.51	7.40	31260	7.39	7.66	7.51	7.42
4/26/77	7.20	7.35	7.32	7.32	31620	7.43	7.48	7.46	7.36
4/27/77	7.28	7.40	7.37	7.37	31980	7.46	7.41	7.43	7.43
4/28/77	7.38		7.34	7.29	32340	7.33		7.40	7.33
4/29/77	7.34		7.30	7.23	33780	7.29		7.30	7.26

GENERAL

The reactivation process for contaminated granular carbon is subject to environmental air quality standards. To demonstrate that reactivation of DIMP contaminated carbon complies with these standards, Calgon Corporation conducted a reactivation off-gas analysis. The methods and analytical results for bog water contaminated carbon are presented on Pages A-28 through A-31. Methods and analytical results for well water contaminated carbon are presented on Pages A-32 through A-35.

CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

INTEROFFICE CORRESPONDENCE
CALGON CORPORATION
Research & Development

March 3, 1977

TO: S. D. Cifrulak

FROM: R. F. Devine

COPY
~~File~~ 61087-00 Rocky Mt. Arsenal
D. Bassett
E. Henn
R. Devine
E. Froelich
W. Siderewicz

SUBJECT: GC/MS Analysis of Off-Gases from TGA of Carbon from Rocky Mountain Arsenal - Lab. #C2172-75

Objective

To measure the concentration of diisopropyl methyl phosphonate in off-gases from TGA collected in methanol.

Conclusions

Diisopropyl methyl phosphonate was not detected in any of the samples as received or after concentrating 50X.

The estimated detection limit for DIMP was 5 ppm in the original solutions and 100 ppb in the concentrated solution.

No other compounds were detected.

Discussion

These samples were analyzed to determine if DIMP is destroyed during carbon reactivation. About 1 gram of carbon was reactivated using TGA equipment. The off-gases were collected in methanol. The carbon was known to hold about 4 mg of DIMP/gram.

Procedure

A portion of the methanol blank solution submitted was spiked with DIMP and chromatographed using the conditions listed on Page A-30. The area of the DIMP peak was obtained for use in quantifying the DIMP concentration in the samples. When the samples were analyzed however, no GC peaks were obtained.

To determine if DIMP were present at low concentrations the air dried #1 sample and the oven dried #1 sample were evaporated to provide 50 concentrations. The blank methanol was also concentrated 50X and spiked with DIMP. Several peaks were seen in the chromatogram of the blank, due to impurities in the methanol however these did not interfere with the detection of the added DIMP. The same impurity peaks were detected in the concentrated sample chromatograms but DIMP or other compounds were not detected.

R. F. Devine
R. F. Devine
E. L. Henn
E. L. Henn

/vid

GC/MS OPERATING CONDITIONS

Column:	10 ft. x 2.0 mm glass, packed with 3% OV-225
Column Temperature:	80°C-220°C at 6°C/min.
Injector Temperature:	240°C
MS Inlet Temperature:	240°C
MS Analyzer Pressure:	5 x 10^{-5} Torr
Mass Range:	20-450 AMU
Scan Rate:	6 msec/AMU
Preamp Sensitivity:	10^{-7} Amps/volt
Multiplier Voltage:	1800 volts
Electron Energy:	70 eV
Emission Current:	0.5 ma

ROCKY MOUNTAIN ARSENAL

Thermal Reactivation Data

Parameter	Column A Spent	Column A React	Column B Spent	Column B React
Activity				
A.D. air dried	0.567	-	0.542	-
A.D. dried @150°C	0.551	-	0.518	-
A.D. react.	-	0.503	-	0.499
Iodine No.	721	870	849	964
CCl_4 No.	39.0	50.4	54.1	59.3
Molasses No.	209	231	204	189
Ash (%)	3.75	4.50	4.70	4.68
Na (%)	0.24	0.28	0.024	0.028
Screening				
CAS pH	7.1	10.8	7.2	10.0
Flammability	>150°F	-	>150°F	-
Total Sulfur %	1.06	1.03	1.02	0.97
Volatile Sulfur %	-	0.11	-	0.09
Total Halides %	0.44	< 0.10	0.25	< 0.10
Volatile Halides %	-	0.44	-	0.25
Corrosive	-	No	-	No
React				
Yield (%-Vol)	-	98.5	-	99.5
Time, minutes	-	15.8	-	1.8

CALGON
CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

INTEROFFICE CORRESPONDENCE
CALGON CORPORATION
Research and Development

DATE: June 1, 1977

TO: B. Pillmore

FROM: J. D. Sember

SUBJECT: ROCKY MT. ARSENAL - OFF-GAS ANALYSIS

KEYWORDS: Rocky Mt. Arsenal/Off-Gas Analysis
Diisopropyl Methyl Phosphonate

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PROJECT NO.:
29-130-00

TSR NO.:
C477-4
(8/172.00)

INTRODUCTION

A sample of spent FS-300 taken from Column No. 1 at Rocky Mt. Arsenal was submitted for an off-gas collection and analysis for the presence of Diisopropyl Methyl Phosphonate (DIMP). The request was made to determine whether this material is released upon reactivation.

SUMMARY AND CONCLUSION

The off-gas analysis was performed according to procedures previously reported. (JDS/RBN to RHZ, April 1, 1977)

Approximately 3.0 grams of spent FS-300 carbon was used for the collection at 1750°F. The off-gases were condensed in 100 ml of methanol. A GC/MS analysis of the methanol solution failed to detect the presence of DIMP. The estimated detection limit for this compound is 0.1 mg/l.

RECOMMENDATIONS

The information obtained in this study and in that of a previous study (JFA/WJH to WS 2/21/77) shows that DIMP is not emitted in the off-gases upon reactivation of this carbon. Based on recent reactivations of samples from Rocky Mt. Arsenal, it appears that the material is an acceptable react candidate which can be handled satisfactorily.

DISCUSSION

Approximately 3.0 grams of air dried spent FS-300 carbon was enclosed in the sample cell. Steam was pumped through the cell at the rate of 3cc/min. The off-gases and steam were condensed in 100 ml of pure methanol. The carbon was maintained at 1750°F for a total residence time of 15 minutes. The methanol solution was submitted to Calgon Laboratores for the analysis of DIMP by GC/MS. A copy of the report is attached, showing no detectable amount of DIMP. The estimated detection limit of this compound in solution is 0.1 mg/l. Based on the volume of methanol used (100ml), the actual minimum detectable quantity of DIMP is 10 ug in the off gases.

J. D. Sember - 989

JDS:gah
Attachments

GC/MS OPERATING CONDITIONS

Column	10 Ft. X 2.0 mm glass, packed with 3% OV-25
Column Temperature	$80^{o}C - 220^{o}C$ at $10^{o}C$/minute
Injector Temperature	$240^{o}C$
MS Inlet Temperature	$240^{o}C$
MS Analyzer Pressure	5×10^{-5} Torr
Mass Range	20 - 450 AMU
Scan Rate	7 msec/AMU
Preamp. Sensitivity	10^{-7} AMPS/Volt
Multiplier Voltage	1800 Volts
Electron Energy	70 eV
Emission Current	0.5 ma

ROCKY MOUNTAIN ARSENAL

THERMAL REACTIVATION DATA

Parameter	Column Set "A" Spent	Column Set "A" React	Column Set "B" Spent	Column Set "B" React
A.D. Air Dried	0.631		0.652	
A.D. Dried @ 150°C	0.548		0.550	
A.D. React		0.492		0.500
Iodine No.	603	799	771	1000
CCl_4 No.	27.9	34.4	43.3	60.8
Molasses No.	214	221	193	197
Ash %	6.37	6.80	5.74	6.44
Na%	0.21	0.23	0.10	0.105
Screening				
CAS pH	7.8	10.0	7.8	10.8
Flammability	>150 °F		>150 °F	
Total Sulfur %	1.14	0.91	0.98	0.82
Volatile Sulfur %		0.32		0.24
Total Halides %	<0.1	<0.1	<0.1	<0.1
Volatile Halides %		<0.1		<0.1
Corrosive		No		No
React				
Yield (% - Vol.)		98.5		98.5
Time, Minutes		3.3		8.8

ERDLATOR COST ANALYSIS

Annual Operating and Maintenance Costs for the Interim Treatment/Containment System at RMA.

Operational Assumptions: Interim system will work at capacity (10,000 gal/hr) for 24 hours/day (3 shifts), 7 days a week, 330 days/ year. The present carbon dosage of 252 mg of carbon per liter of treated water will remain at this level in the future. The same applies for the present anionic and cationic polymer dosages, .13 and 1.59 mg/l respectively. It is assumed that one full time supervisor and one operator per shift will be needed to operate the treatment unit. Once the containment system is operational, only periodic inspection will be needed.

Maintenance Assumptions: Due to the limited length of time the treatment unit is to operate, possibly up to six years, it is speculated that only routine repair and maintenance will be required. However, this statement is complicated by the fact that this unit has been inoperative for an extended period of time. Therefore, a moderate cost will be assumed.

Other Assumptions: It has been assumed that the laboratory at RMA will continue to be in direct support of the Installation Restoration Program. The quality control costs can therefore be considered part of overhead and have been included in the manpower costs.

COST CALCULATIONS

Raw Materials

Total Yearly Capacity:

10,000 gal/hr x 24 hrs/day x 330 days/year = 7.92×10^7 gal = 79,200,000 gal.

Carbon Costs (1)*:

At 24 cents per pound (truck load quantity),

(7.92×10^7 gal)(252 mg/l)(3.78 l/gal)(1 gms/1000 mg)(1 # /454 gms)
($.24/#) = $39,900

Polymer Costs (1):

At $1.50 per pound for either coagulant,

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* - Number in parenthesis refers to a corresponding reference

Cationic
(7.92×10^7 gal)(1.59 mg/l)(3.78 l/gal)(1 gm/1000 mg)(1 #/454 gms)
($1.50/#) = $1580

Anionic
(7.92×10^7 gal)(.13 mg/l)(3.78 l/gal)(1 gm/1000 mg)(1 #/454 gms)
(41.50/#) = $130

TOTAL RAW MATERIALS = $41,600/yr

Operating Labor: Assume the treatment unit will operate 3 shifts per day for 7 days per week. This equals 21 shifts/week. Each operator can handle 5 shifts/week, therefore, there is a need of 5 men. This total amount of manpower covers sickness, leave, etc. All overhead costs such as administrative expenses and arsenal costs are included in the manpower rates.

At a rate of $20 per hour for a technician at RMA (1), the operating labor cost equals; (this cost may be under estimated)

5 ($20/hr x 40 hrs/week x 52 weeks/yr) = $208,000/yr

Operating Supervision:

At a rate of $28 per hour for an engineer (1), the operating supervision cost equals;

$28/hr x 40 hrs/week x 52 weeks/yr = $58,240

TOTAL MANPOWER = $266,240/yr

Power & Utilities: For the treatment/containment system at RMA, no steam, fuel, refrigeration or municipally treated water is required for operation. Of the electricity to be used, the majority will go for the containment aspect. Pumping of groundwater to and from the treatment unit, intermediate pumping at the erdlator and the necessity of mixing, heating and lighting make-up the electrical requirements.

Only an estimate can be made of the containment utility costs due to the fact the pump tests have not been completed. WES (2) puts this estimate at approximately $1,000 per month or $12,000 per year.

Utility costs for the treatment unit have been estimated at 20% of the containment power costs. An alternate technique (9) is that of estimating utilities at 3% of the overall equipment costs. For the sake of comparison, both techniques have been used.

a. 20% of $12,000/year = $2400

b. A phone conversation (4) sets the cost of the 10K Erdlator at $42,000 as of 1960. Applying the Marshall and Stevens' equipment cost inflation factors (9) to the Erdlator brings the present worth of the unit to $84,000.

(474/237)($42,000) = $84,000

Three per cent of $84,000 is

(.03)(84,000) = $2520/year

TOTAL UTILITY COSTS = $14,400/year

Maintenance and Repairs:

Four sources have been utilized to obtain a realistic cost estimate for this section.

a. Carbon Adsorption Manual (6) states that maintenance and repairs total about half of the raw material costs.

(.5)(41,600) = $20,800

b. WES (2) commonly uses a figure of 37 cents per 1000 gallons of treated water for maintenance, repairs and utilities.

($.37/1000 gal)($7.92 \times 10^7$ gal) = $29,300

c. Rohm & Haas (8) has calculated a figure of $62.15 per day from past experience.

($62.15/day)(330 days) = $20,500

d. Popper (9) again uses a percentage of capital (equipment) costs to estimate maintenance and repair costs.

Repair is 5.2% of capital (.052)($84,000) = $4368

Supplies are 6% of operating labor (.06)(166,400) = $9984

TOTAL $14,352

TOTAL MAINTENANCE & REPAIR COSTS = $20,000/year

Laboratory Charges:

Previously included in manpower overhead costs.

REFERENCES

Phone Conversations:

	Person Called	Date	Subject of Conversation
1.	Carl Loven (RMA)	16 Aug	Received information on costs of materials, manpower requirements and typical hourly rates for the interim 10K water treatment unit.
2.	Britt Mitchel (WES)	17 Aug	Received estimates on maintenance and utility cost for both the treatment and containment processes.
3.	Ron Rhea (EWA)	18 Aug	Received information on inflating rates as per DF-SAREA-OC-C dated 14 May 76; Subject: "Guidance for inflation of cost estimates". Army document concerning Operation & Maintenance (OMA) costs.
4.	COL Carnahan (MERADCOM)	18 & 19 Aug	Received the purchase price for the 10K Erdlator as of 1960.

Literature Sources:

5. Dustin, Donald F., "Economic Evaluation of the Solvent and Thermal Regeneration of TNT-Laden Activated Carbon", 1 April 1975. Waste Treatment Section, Chemical Process Technology Branch, Chemical and Plants Division, Manufacturing Technology Directorate, EWA.

6. Environmental Protection Agency, "Process Design Manual for Carbon Adsorption", 1 Oct 1971. Contracted to Swindell-Dressler Co., a division of Pullman, Inc., 441 Smithfield St., Pittsburg, PA 15222.

7. Hutchins, R. A., Chemical Engineering Progress, "Thermal Regeneration Costs; Activated Carbon", May 1975. Vol. 71, No. 5.

8. Rohm and Haas Co., "The Removal of Nitrobodies from the Waste Water of Munition Plants", March 17, 1976. Contract No. DAAK03-75-C-0021 with the US Army Natick Development Center, Natick, MA.

9. Popper, H., "Modern Cost-Engineering Techniques", 1970. Compiled from the publication Chemical Engineering by McGraw-Hill Book Company.

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