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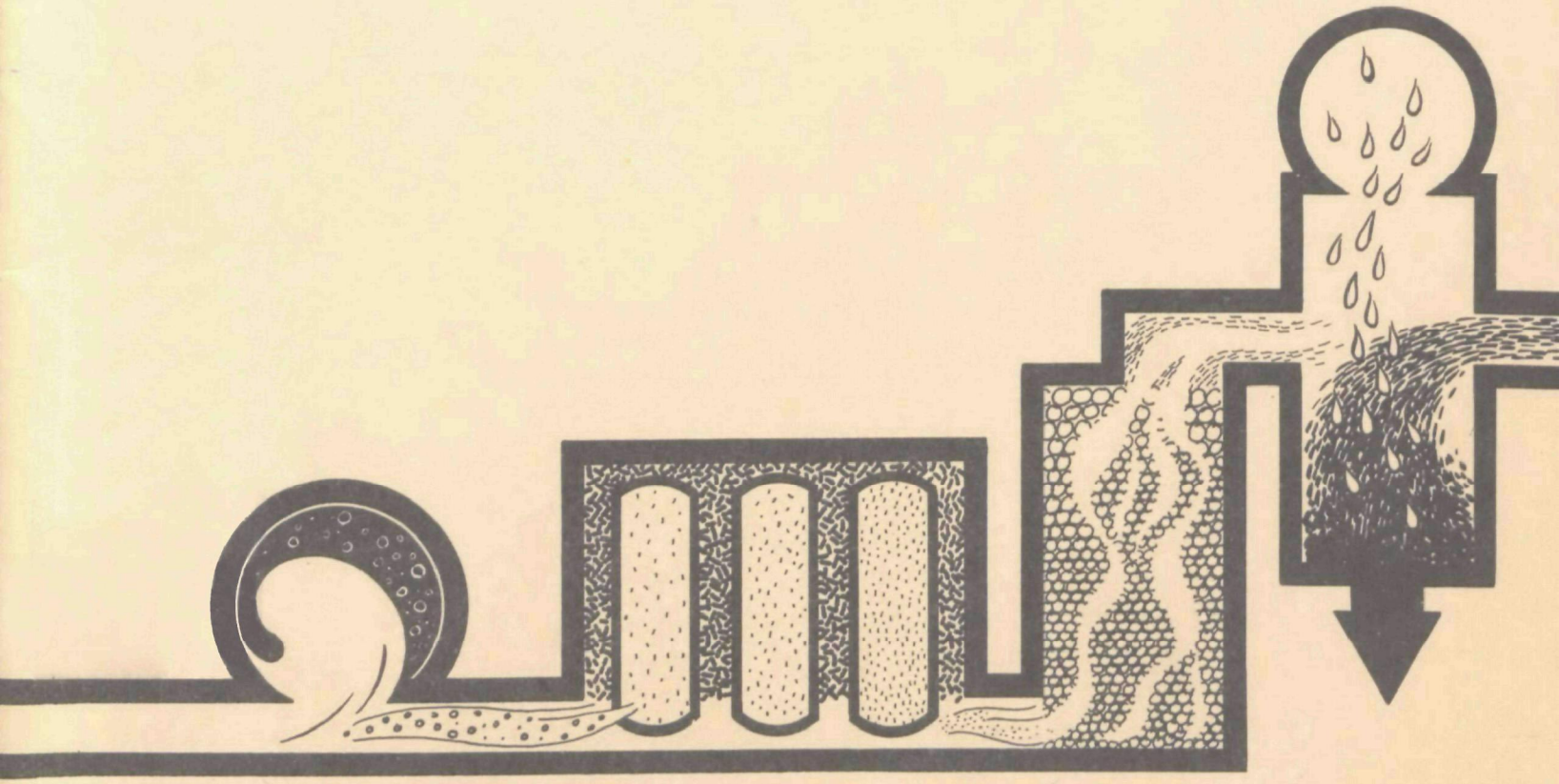
ADVANCED WASTEWATER TREATMENT USING POWDERED ACTIVATED CARBON IN RECIRCULATING SLURRY CONTACTOR-CLARIFIERS



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ABSTRACT

In this investigation, high-rate solids-contact treatment units embodying internal slurry recirculation were operated singly and in series as powdered activated carbon adsorption systems. Secondary (activated sludge) sewage treatment plant effluent was treated in a 30,000-gpd pilot plant using a slurry of activated carbon and a cationic polyelectrolyte flocculation agent.

Practical operating parameters of the system are developed for different activated carbon dosage levels for two contact-clarifiers operated in series with countercurrent carbon advance. Similar parameters are developed for a single unit and one carbon dosage. Adsorption system results, expressed as COD reduction, are evaluated by comparison with laboratory generated single-stage adsorption isotherms.

In a practical sense, effluent COD for series adsorption was equivalent to that expected from consideration of two-stage adsorption theory. Possible modification of the process to improve efficiency is discussed.

Contactor-clarifier effluent was filtered through a gravity sand unit and development of operational difficulties with respect to biological growth and polyelectrolyte-flocculated carbon-sand agglomerates are noted. At a 3-gpm/ft^2 operating rate, no carbon passed through the filter. Backwash water requirements increased to 5 per cent of the filtered water volume as the filter condition deteriorated.

Supplemental investigations conducted during the pilot plant program include evaluation of the influence of temperature variation on system performance and its analysis; consideration of adsorption theory; the influence of the treatment process on nutrients, color, and surfactants; and comparison of the results of two methods of turbidity measurement.

The total operating cost of a 10-mgd system based on the pilot plant process and 90 per cent reuse of carbon recovered by regeneration is estimated as 15¢/1000 gal. at a carbon dosage of 2 lb/1000 gal., or 9.7¢/1000 gal. if in terms of effluent quality objectives the carbon requirement can be reduced to 1 lb/1000 gal. A similar system rated at 100 mgd is estimated to produce treated wastewater for 12.7¢/1000 gal. at a 2-lb/1000 gal. carbon requirement, or 7.4¢/1000 gal. at half this dosage.

This report was submitted in fulfillment of Contract No. 14-12-400, Program No. 17020 FKB, between the Federal Water Quality Administration and Infilco Company.

INTRODUCTION

Background

Adsorption is a proven process for separating relatively small quantities of organic impurities or valuable products from dilute solutions. Activated carbon is one of the more efficient and better known adsorbents.

Activated carbon adsorption has long been applied to industrial purification processes, many times successfully competing with other purification systems. Its use in water purification dates back to the late 1920's.[1] It is only natural that activated carbon adsorption is receiving serious attention as a candidate for advanced wastewater treatment as water pollution and water shortage problems augment.

Performance of traditional single-stage powdered activated carbon contacting systems is controlled by two different aspects of adsorption: kinetics and adsorption equilibrium.[2] Carbon feed rates sufficient to improve the quality of sewage plant effluents to acceptable levels for reuse may be very high because of the equilibrium adsorption aspect. As a result, treatment cost is high. Until now, cost factors have favored the use of granular activated carbon in columnar systems. Practical granular carbon regeneration systems are in operation now, so that carbon reuse results in further treatment cost reduction.[3]

Powdered activated carbon should be more efficient and thus more economical than granular carbon by virtue of its greater surface area. However, powdered carbon is unsuitable for columnar flow schemes. Regeneration of this type of carbon on an economical basis is still under study. As powdered activated carbon is readily slurried, hydraulic transfer to and from process equipment is practicable.

The authors' company sponsors continuing advanced waste treatment research and a few years ago reported the results of a brief investigation of the use of powdered activated carbon in a model ACCELATOR clarifier, a high-rate solids-contact unit embodying internal slurry recirculation.[4]

The model test was conducted on chemically treated sewage plant effluent and the recirculating slurry was developed from feeds of powdered activated carbon and coagulant. The results provided evidence that the single ACCELATOR contactor-clarifier functioned as a compound contact system producing lower residual COD and more efficient carbon utilization than theoretically predictable for a continuously operating single adsorption stage.

If a single treatment unit could be shown to produce some of the process advantages of a multiple-stage adsorption system, the cost of treating wastewater with finely divided activated carbon would be reduced. Two such process stages could markedly lower treatment cost.

Process Description

A two-stage countercurrent system is visualized. Application of the process involves series operation of two solids-contact clarifiers of a type used widely for water treatment. Carbon is fed to the second unit and first-stage slurry is developed from carbon advanced from the second contact-clarifier. Spent carbon is withdrawn from the system by blowdown from the first unit. To protect the receiving stream from carbon lost during process disruption, post filtration is indicated.

Objectives of this Investigation

The primary objective of the present investigation was a performance and cost evaluation of such a system for treatment of municipal sewage activated-sludge plant effluent. Brief performance evaluation of single-stage treatment was a corollary objective.

Experimental Approach

Initially, a commercially available powdered activated carbon and a polymer flocculation agent to improve slurry settleability were selected on the basis of laboratory study.

These materials were then used during six consecutive pilot plant studies under various conditions. The first and second studies were intended to determine physical and hydraulic capabilities of the system. The third, fourth and fifth experiments utilized different activated carbon feed dosages in the complete system. For the sixth study, one of the solids-contact clarifiers was operated alone to evaluate single-stage treatment.

During all experiments, data were collected from the pilot plant and single-stage adsorption isotherms were developed for the various feed streams. These data were then compared by application of adsorption theory.[5]

Peripheral laboratory analyses of 24-hr composite samples plus auxiliary grab samples were used to disclose operational parameters other than those directly associated with the adsorption process. These data, together with the pilot plant control records, reveal important practical operating requirements and results in other areas of interest.

Analytical Procedures

With certain exceptions, methods used in this study conformed to those in "Standard Methods."[6]

A modification to "Standard Methods" developed especially for low-level COD values was used. The complete procedure appears in the Appendix. Except as noted, all samples for which COD is reported were filtered through 0.45-micron Millipore filter discs prior to the COD determination. This was necessary in the case of powdered activated carbon treated samples as residual carbon particles contribute to the COD value. In order to provide a usable COD relationship between carbon treated samples and untreated samples, most of the untreated samples were filtered in a like manner.

Certain ACCELATOR clarifier control tests performed at the pilot plant site are discussed hereinafter.

PREPARATORY LABORATORY INVESTIGATION

Objectives

A suitable adsorption system had to be developed if the pilot plant was to produce data of sufficient scope to develop the objectives. The feed stream was to be effluent from a secondary sewage treatment plant. The characteristics of the available stream had to be determined. The adsorbent, activated carbon in powdered form, is available from different sources. It is manufactured from various raw materials by a number of different processes and may be specialized in its application.[7] Activated carbons were tested with aliquots of feed stream to assure selection of a material that would perform within the time limitations and hydraulic conditions imposed by the pilot plant. A flocculation system using this carbon in the feed stream had to be found. Inorganic coagulation agents were ruled out as they could be cumulative in the carbon where reactivation and reuse are concerned. The flocculated slurry must settle rapidly, leaving little if any residual carbon particles in the supernatant; and it would be advantageous if the slurry dewatered well on standing.

For the purposes of this study, the COD of the feed stream is the adsorbate concentration indicator. Some impurities present may be adsorbed which do not exhibit a COD while others having a COD may not be readily adsorbed. Sewage plant effluent contains an everchanging combination of these materials, many of them not identified; so the COD determination is a useful but incomplete pollution indicator.

Sewage Plant Effluent Quality

The City of Tucson commissioned a new activated sludge sewage treatment plant in 1968 parallel to two existing treatment systems. Secondary clarifier overflow from this plant was selected as the feed stream source for the pilot plant.

The new plant was observed to experience infrequent difficulties as the result of the usual new equipment shakedown process. It was still considered the most reliable source of feed stream, however, as the two older installations were undergoing various repair and maintenance operations. Sections of them would be down from time to time. When in difficulty, the new plant effluent contained appreciable amounts of activated sludge. During these periods of several hours duration, it was observed that the solids appeared first, occurred in heavier concentration, and persisted longer in the outer of the two concentric take off launders in the final clarifiers. Therefore, the inner launder was selected as the take off point that would best minimize solids input to the pilot plant.

Physical and chemical characteristics of several of the grab samples collected at random from this location are presented in Table 1.

TABLE 1

Final-clarifier Effluent Characteristics, mg/l
Tucson Sewage Treatment Plant

Date	7/17/68	7/18/68	8/12/68	8/26/68	10/14/68
Time	7:00 A.M.	3:00 P.M.	7:00 A.M.	3:00 P.M.	3:00 P.M.
Calcium (as Ca)	68	62	48	65	54
Magnesium (as Mg)	3	8	8	8	10
Sulfate (as SO_4)	138	179	131	150	153
Chloride (as Cl)	84	74	58	81	69
Nitrate (as NO_3)	1	6	1	10	-
Iron (as Fe)	0.1	0.2	-	0.1	0.3
Manganese (as Mn)	0.05	0.05	0.05	0.05	0.05
Silica (as SiO_2)	41	42	34	48	47
Alkalinity (as $CaCO_3$)	220	216	224	198	254
Hardness (as $CaCO_3$)	184	190	150	195	178
Color (SU)	16	14	15	15	17
Turbidity (JTU)	9	11	10	9	90
Suspended Solids	4	6	3	10	65
COD (unfiltered)	-	33	33	35	125
COD (filtered)	28	26	28	27	25
BOD_5	4	-	-	-	-
pH	7.4	7.2	7.6	6.5	7.5

Adsorption Uptake Rate Study

Three powdered activated carbon products were selected for evaluation against project requirements. These were Darco S-51, a product of Atlas Chemical Industries, Inc., and Aqua Nuchar A and Filtchar, both products of the Westvaco Corporation.

Darco S-51 was used in our earlier experiments. Aqua Nuchar A was utilized in an FWQA pilot plant at Lebanon, Ohio. Filtchar is not a standard commercial grade product, but was furnished by the manufacturer for experimentation.[8] Carload quantities could be produced for certain tonage situations.

For each uptake-rate comparison study, sufficient effluent sample was prefiltered through 0.45-micron Millipore filter discs for the entire procedure. Five aliquots of one grade of dry powdered activated carbon were weighed and wetted with demineralized water. One was added to each of five 250-ml aliquots of effluent while mixing with a gang stirrer at preselected speeds. A sixth 250-ml effluent aliquot was stirred as a control. The five treated jars were stirred for 5, 10, 20, 45 and 60 min, respectively. At the end of its stirring time each aliquot was immediately filtered through a 0.45-micron filter disc and filtrate COD was determined. The process was repeated for the remaining two grades of carbon.

The foregoing procedure was repeated three times at stirring speeds of 50, 150 and 400 rpm. At the highest speed, the activated carbon dosage was changed from 200 mg/l to 400 mg/l to increase the range of COD results and to provide a more definitive picture of uptake-rate differences between carbon grades.

All three activated carbons exhibit a rapid initial adsorbate uptake rate (Figure 1). Equilibrium had not been reached after 60 minutes of contact, but the rate at which adsorption was continuing at this time was very low. At 400-rpm stirring speed, all three grades achieved essentially 95% of their respective 60-min COD removals at 30 min of contact. Aqua Nuchar A approached the 95% level after only 10 min compared with 87% for the Darco S-51 and 85% for the Filtchar.

Adsorption Isotherm Study

Equilibrium adsorption isotherms were used to study the relative adsorptive capacities of the three activated carbons under consideration.

Sufficient sewage plant final clarifier effluent was prefiltered through 0.45-micron filter discs to perform each comparison study. A stock solution of each grade of carbon was prepared with special low-COD distilled water (Appendix). The activated carbons were added to sets of five 250-ml aliquots of the prepared effluent at concentrations of 40,

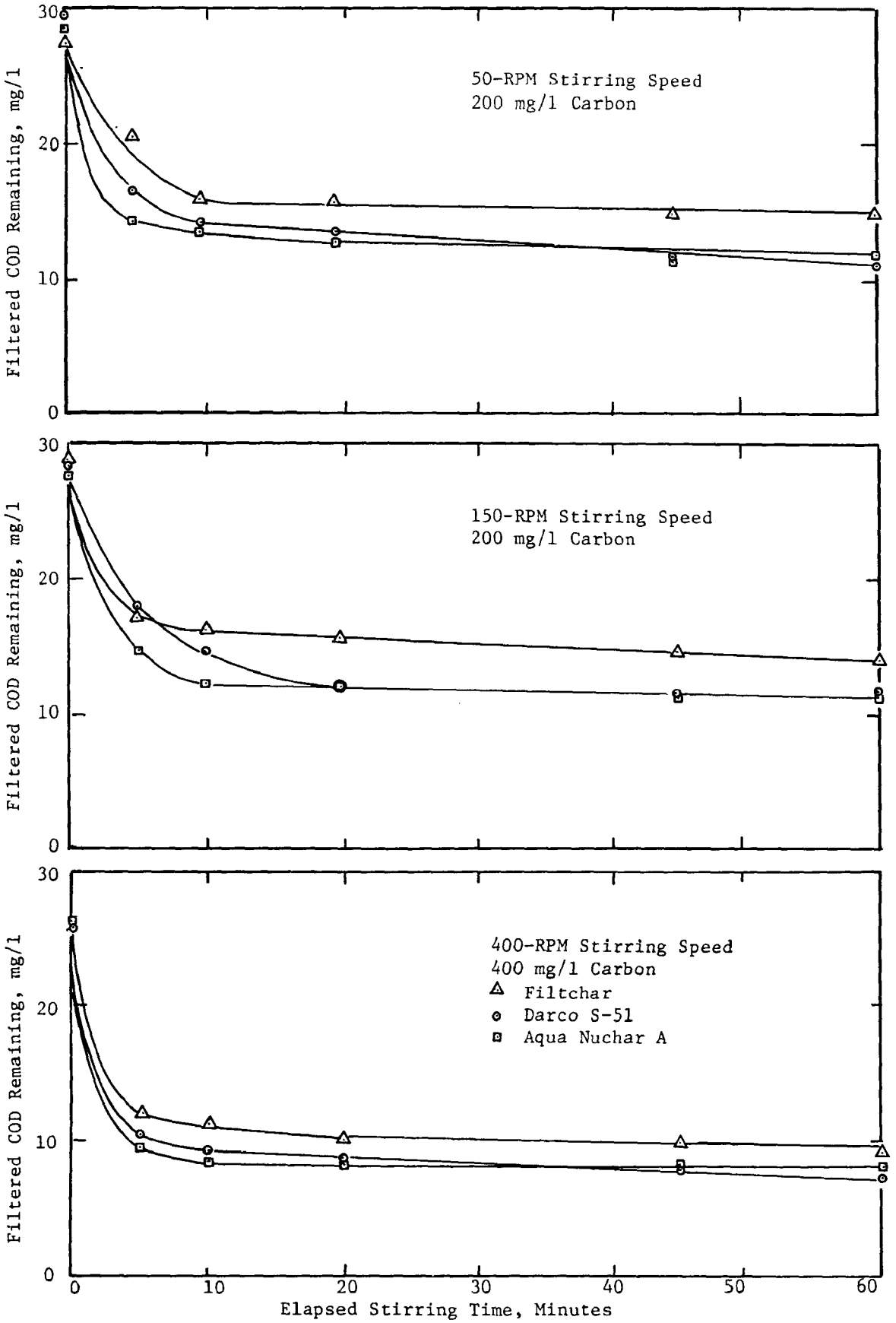


FIGURE 1: Uptake Rate Study

200, 400, 800, and 1600 mg/l. A sixth aliquot in each set was left untreated as a control. The jars were stirred at 100 rpm for 60 min, their contents were then filtered through 0.45-micron filter discs, and filtrate COD determined.

Preliminary work had shown the feasibility of handling the carbons as stock suspensions rather than individually weighed dry aliquots. The stock suspensions provided greater handling ease by minimizing problems associated with wetting the carbon. Additional work had shown that low stirring speed influenced loading achieved and the shape of the isotherm plot. A stirring speed of 100 rpm was selected as the result of this work.

Freundlich curves of the data (Figures 2 and 3) were developed. The Freundich equation is empirical but widely used because of its simplicity. It is generally written: $X/M = KC_t^{1/n}$, where X is the mg/l of adsorbate taken up by M mg/l of adsorbent applied. C_t is the mg/l of adsorbate remaining unadsorbed at equilibrium and K and 1/n are constants specific for the materials and conditions of test. When X/M is plotted against C_t on logarithmic paper, a straight line is commonly obtained which has a slope of 1/n and an intercept K at $C_t = 1$.

Slight variations in the original concentration of COD (C_o), perhaps caused by the passage of time, between the individual carbon test sets were retained in plotting the Freundich curves. However, for positioning the curves of constant carbon dosage, an average C_o value was utilized.

For the activated carbons tested, the plots show Darco S-51 to be superior. Higher loading (X/M) and lower residual COD (C_t) are evident at each carbon dosage.

The manufacturer states Darco S-51 is made from lignite. After activation by heat and steam, it is thoroughly washed with mineral acids and then with water to remove extractable inorganic constituents. The ash content, being generally inert and insoluble, has no adverse influence on the adsorptive capacity. The carbon wets readily with a minimum of dusting and goes into suspension quickly.

According to the manufacturer, Darco S-51 has the following properties:

Moisture content (Max., as packed)	12%
Water-solubles (Max., determined by 4 leachings with boiling water)	1%
Acid-solubles (approx., determined by leaching with 1:1 hydrochloric acid)	3%
Ash (normal range)	17-24%
pH of water extract (normal range)	5.0-7.0

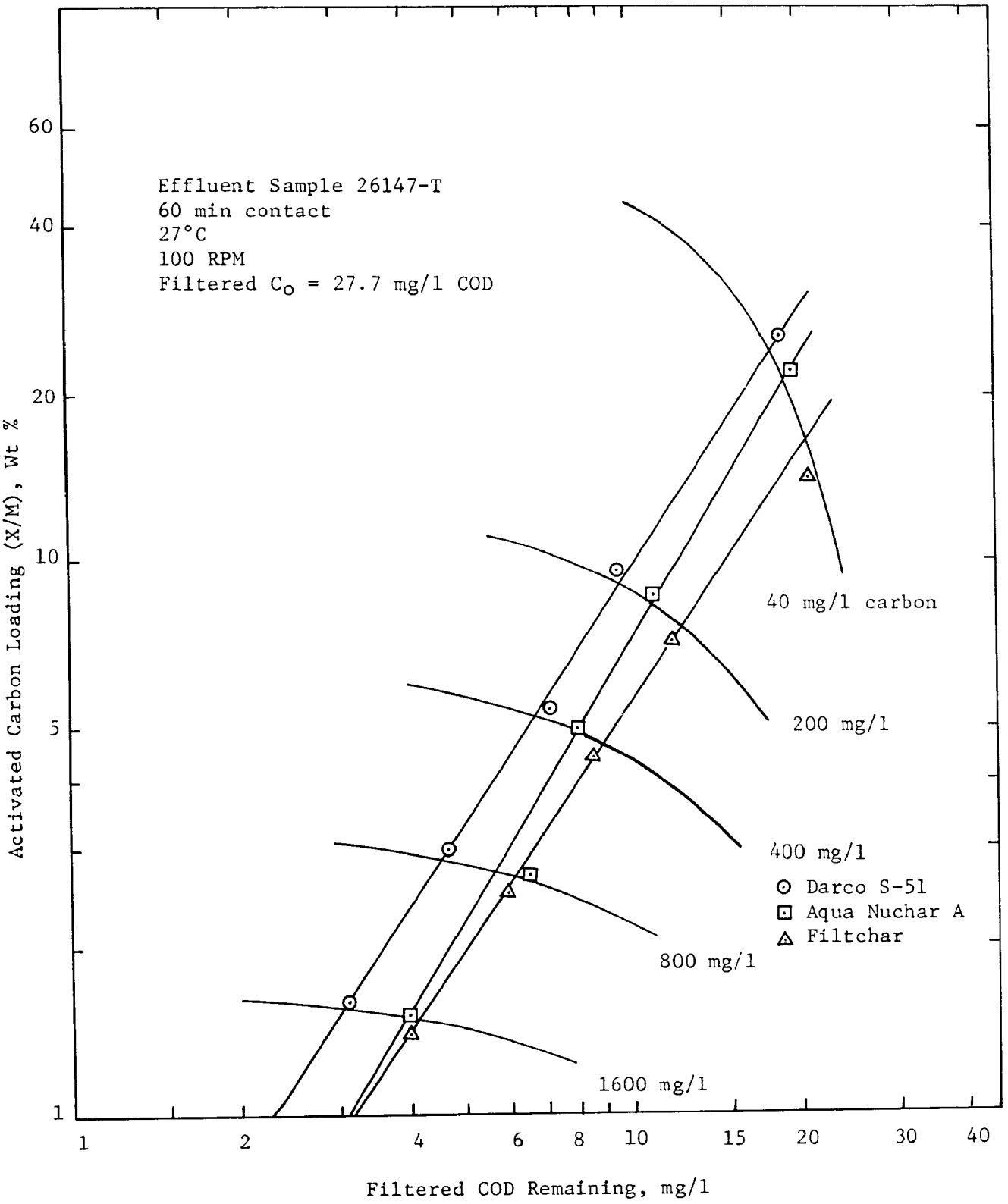


FIGURE 2: Adsorption Isotherm Carbon Comparison

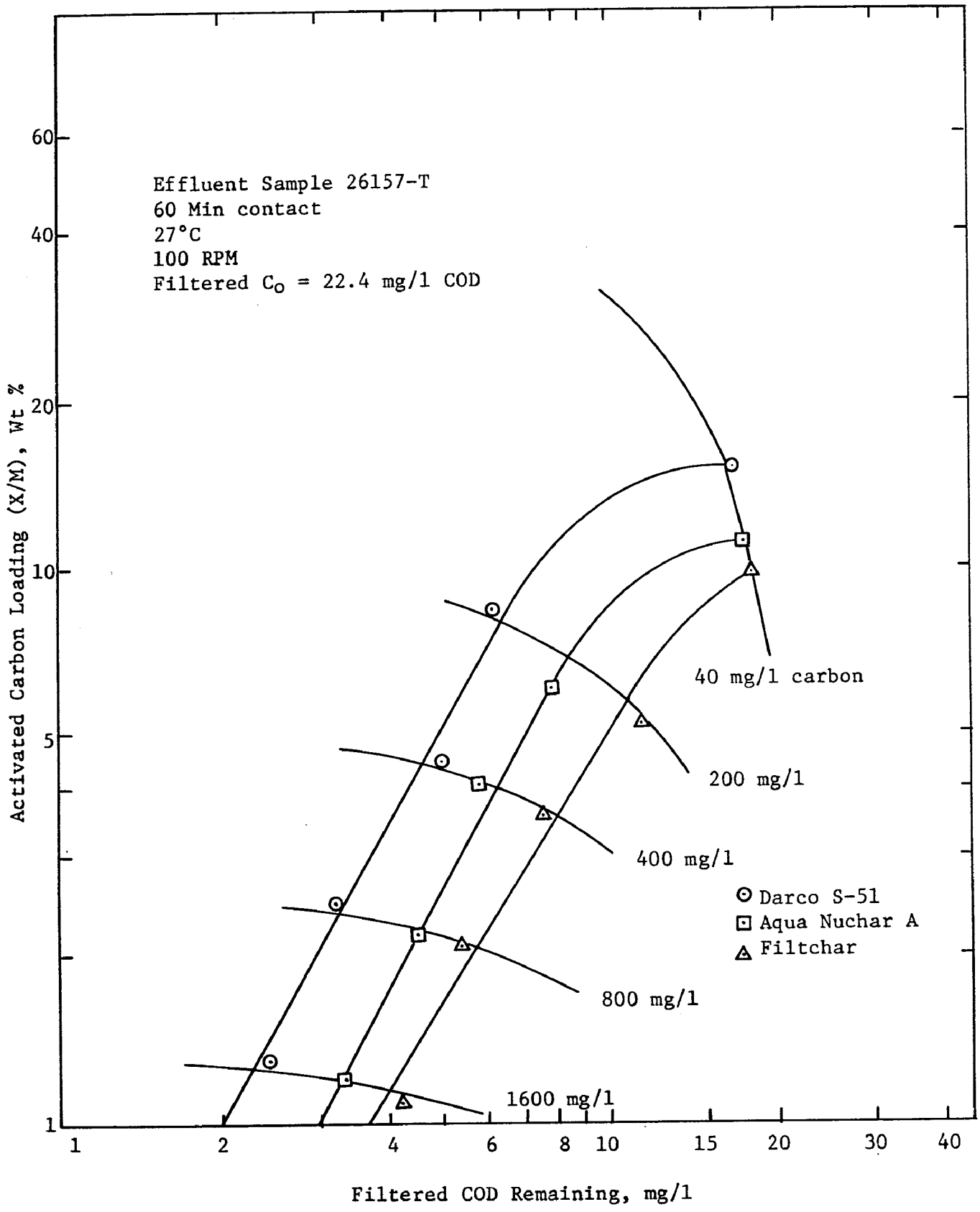


FIGURE 3: Adsorption Isotherm Carbon Comparison

Bulk density, lb/ft^3 (determined by 30-minute tamping test)	27-33
Mesh size (approx.) % through 100-mesh screen	95
% through 325-mesh screen	70
Filterability (max.) ..... 1.0 sec./ml/cm. depth (water)	
Storage space needed (ft^3/ton, approx.)	80

Coagulation Studies

For successful operation of the high-rate clarification units to be used in the pilot plant, it was essential that an efficient and effective coagulation system be developed. The floc particles had to settle rapidly, be strong enough to withstand the repeated cycling through the flocculation paddles, entrap a high percentage of the carbon particles, and dewater readily. In addition, inorganic chemicals were to be avoided as the resulting carbon slurry had to be amenable to thermal regeneration. Repeated regeneration and reuse of carbon flocculated with the common iron or aluminum salts or clay-coagulant mixtures would result in progressive contamination of the carbon with inert solids.

Organic polyelectrolytes were used, with rare exception, in all of the laboratory coagulation studies. These materials would contribute carbon residues, along with the organic materials flocculated and adsorbed from solution, to the activated carbon undergoing thermal reactivation.

The emphasis for much of the coagulation investigation was directed at cationic polyelectrolytes. When those on hand failed to produce the results desired, anionic and nonionic products were tested individually and in combination with cationic products and each other. Additional cationic products were secured and some products subject to deterioration with time were replaced with fresh material. In all, 26 different products were involved. Those few which are weighting agents or contain weighting agents or inorganic primary coagulants improved flocculation, but could not be applied in the pilot plant for reasons mentioned earlier. Supplementary use of a quaternary ammonia compound and two wetting agents did not improve the effectiveness of the polyelectrolytes tested.

The products tested and their respective manufacturers were as follows:

1. Aquafloc 412 - Dearborn Chemical
2. Cab-O-Sil - Cabot Corporation
3. Cat-Floc - Calgon Corporation
4. CMC - Hercules Powder Company
5. Claracel CO-980 - North American Mogul Products Co.
6. Guar Gum
7. Hyamine 3500 - Rohm & Haas

8. Mud Gel - Baroid Div., National Lead Co.
9. Nalco 600 - Nalco Chemical Company
10. Nalco 650 - " " "
11. Nalcolyte 110 - Nalco Chemical Company
12. Polyfloc 4D - Betz Laboratories
13. Primafloc XA-10 - Rohm & Haas
14. " C-3 - " "
15. " C-7 - " "
16. Purifloc A21 - The Dow Chemical Company
17. " A22 - " " " "
18. " C31 - " " " "
19. " C32 - " " " "
20. Reten 205 - Hercules Powder Company
21. Separan AP30 - The Dow Chemical Company
22. " NP20 - " " " "
23. Superfloc 16 - " " " "
24. Triton QS-15 - Rohm & Haas
25. " X-40 - " "
26. Wisprofloc 20 - Ionac Chemical (Permutit)

A total of 180 individual jar tests were conducted on unfiltered secondary clarifier effluent with variations in mixing speed, mixing time, carbon dosage, coagulating agent(s), order of coagulating agent and carbon addition, and the use of floc from previous tests.

Aliquots, generally 200 ml, of final clarifier effluent were treated first with activated carbon stock solution to either 150-mg/l or 200-mg/l dosages. While being stirred at test speed, the coagulating agent(s) were added, generally in the range of 2 to 5 mg/l. This range was broadened to between 1 to 10 mg/l if results seemed promising. Stirring time was normally 10 min; however, this was shortened to 5 min if floc breakup was observed during the longer period. Flash mixing at 400 rpm for less than 1 min after addition of the coagulating agent was evaluated and discontinued as ineffective. Also discontinued as having no desirable effect was a variation wherein the activated carbon was introduced at a timed interval after introduction of the coagulating agent. Supernatant turbidities were determined on most jars showing promise. A 5-min settling period was allowed before sampling the supernatant for turbidity measurement. Notes were made on the time required for the prominent floc particles to settle the 3-1/2" liquid depth to the jar bottom.

Early results were discouraging. The majority of well known polyelectrolytes tested showed no promise. Supernatant turbidities ranged from 18-58 JTU except when bentonite-bearing compounds or polyelectrolytes were used with bentonite. Rohm and Haas' Primafloc C-7, used at Lebanon, Ohio, was marginally effective; but at the required dosages of 5 to 10 mg/l it was considered too costly. It performed better at lower concentrations, 2 to 5 mg/l, if the pH of the jar was adjusted to 8.5 to 9.0 with caustic soda. Calgon's Cat-Floc and Dow's C-31 were tested at length with results

slightly inferior to C-7. Supernatant turbidities remained in the range of 8 to 14 mg/1.

Fresh stocks of Dow's C-31 and C-32 were obtained and additional work indicated C-31 was as effective as C-7. The C-32 was found to produce a supernatant turbidity of 8-10 JTU at dosages ranging from 1-3 mg/1.

The optimum coagulation results recorded for the several polyelectrolytes showing promise was achieved using a solids recycle procedure. The settled solids (floc) produced in one reaction were retained by decanting the supernatant to waste. A fresh aliquot of effluent was introduced to these solids along with carbon and coagulant. The jar stirring and settling were repeated and the solids again retained. This procedure was continued through as many as seven cycles during which the floc characteristics change and coagulant dosage changes may be evaluated. The solids recycle procedure is particularly applicable to the type of solids-contact units used in the pilot plant.

Typical data reporting (Table 2) for jar studies of this type indicates the amounts and types of materials used, as well as notes on floc formation, quiescent settling ability, and clarification results as being poor, fair, or good. The resultant slurry volume existing at the end of the settling period, as well as the number of previously formed slurry volumes returned to each jar, are also recorded.

Even though the cationic polyelectrolyte, C-32, left a marginal 8 mg/1 supernatant turbidity, the low dosage level and potential cost were acceptable and time did not permit further investigation in this direction. Experience indicates that better coagulation can frequently be achieved in a plant-scale continuous operation than in jars. So C-32 was selected for the pilot plant operation.

Little information was available concerning the effect of polyelectrolyte flocculation on the adsorptive capacity of powdered activated carbon. It was desirable to learn if the adsorption system selected would be adversely affected by the C-32.

Pairs of adsorption isotherms were developed using Darco S-51. One isotherm of each pair was produced using the procedure described previously. The other incorporated a 3-mg/1 C-32 dosage applied immediately after the carbon addition to each of the five jars and at zero time to the sixth or control jar. Optimization of the coagulant dosage was not attempted.

Comparison plots of these isotherms (Figures 4 and 5) show displacement of points for the polymer-treated samples downward and to the left of those of the control. Note, also, that the differences are greater for effluent samples having a higher original suspended solids content. A speculative explanation for this shift is that coagulation of colloidal

TABLE 2

Partial Coagulation Study Report

Evaluation of New Shipment of Purifloc C-31, and Purifloc C-32 Polyelectrolytes with Cat-Floc

Effluent Sample 26151-T, pH 7.4
Temperature 26°C
200 rpm stir speed
Stir 10 min, Settle 5 min Date: 9-12-68

TEST	S-51 mg/l	Poly mg/l	Coag.	Sett.	Clar.	JTU	%SV	SVR
A	New Purifloc C-31							
1	200	3	F	P	many fines		<1	0
2	"	3	F-G	P	improved		1	1
3	"	3	G	F-P	"	15	1	2
4	"	3	G	F	"	10	2	3
5	"	2	G	F		12	3	4
6	"	2	G	F-G		12	4	5
B	New Purifloc C-32							
1	200	3	F	P	many fines		<1	0
2	"	3	F-G	P	improved		1	1
3	"	3	G	F-P	"	11	1	2
4	"	3	G	F		8	2	3
5	"	2	G	F		8	3	4
6	"	2	G	F		8	3	5
	C-32 slightly better than C-31, also settling is slightly improved							
7	200	1	G	F		9	4	6
C	Cat-Floc							
1	200	3	F-P	P	many fines		<1	0
2	"	3	G	P	improved		1	1
3	"	3	G	F	"	12	1	2
4	"	2	G	F		9.5	2	3
5	"	2	G	F		12	3	4
	Cat-Floc and C-31 very comparable. C-32 better							

G-Good, F-Fair, P-Poor, %SV-percent of volume occupied by slurry after 5 min settling, SVR-Slurry Volumes Returned, to subject test from previous reactions.

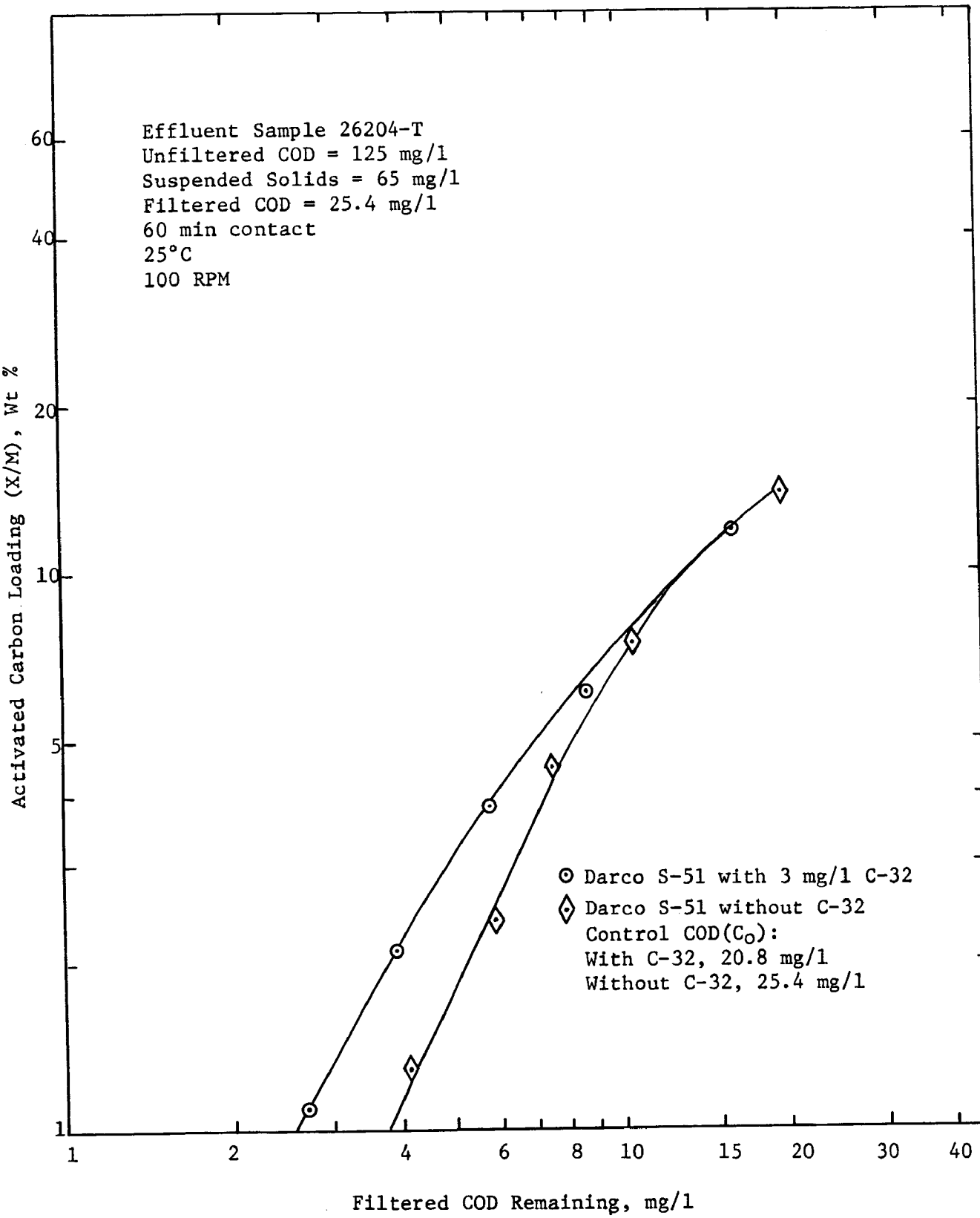


FIGURE 4: Effect of polyelectrolyte on an adsorption isotherm when the original sample contains a substantial suspended solids concentration.

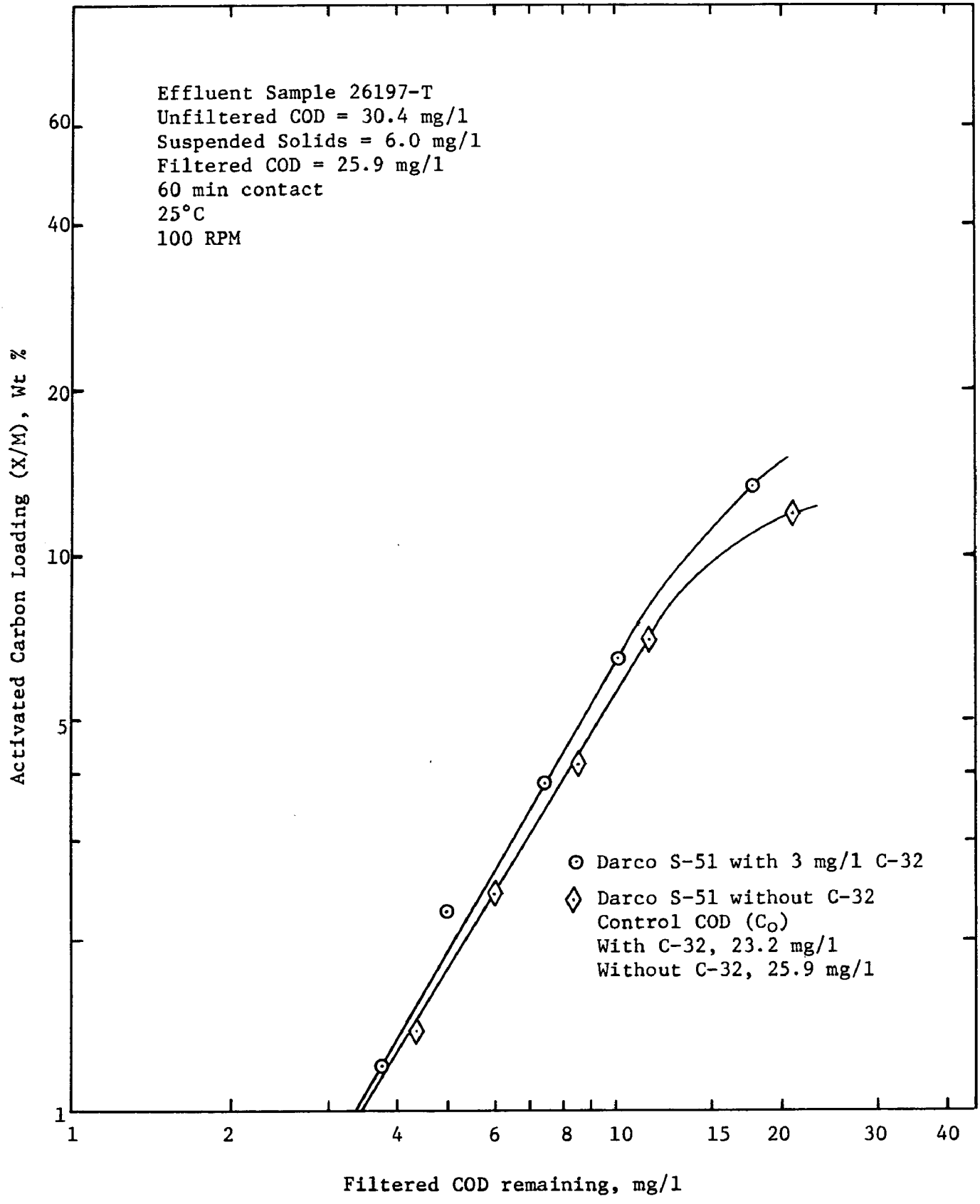


FIGURE 5: Effect of polyelectrolyte on an adsorption isotherm when the original sample contains a low suspended solids concentration.

organic solids not removed by filtration of the original clarifier effluent in the polymer-dosed series enabled removal of some of this material in the final filtration step of the test procedure. This would not occur to the same extent in the control series. The resultant isotherm points plotted lower in both residual COD and carbon loading. If adsorption had been adversely affected, these points would have plotted at higher residual COD and lower carbon loading.

However, on the basis of this work, it was decided that control isotherms should be developed using the same polymer dosage as in the pilot plant to obtain the closest correlation between them and plant performance.

Having now selected a suitable powdered activated carbon, Darco S-51, and a coagulant, Dow C-32, operation of the pilot plant was initiated.

PILOT PLANT PROGRAM

Apparatus and Procedure

A constant-rate pilot plant was constructed at the INFILCO Test Facility adjacent to the Municipal Sewage Treatment Plant serving the City of Tucson, Arizona.

The plant included two series-operated JBAS ACCELATOR^R clarifiers, a type of recirculating-slurry, solids-contact unit which is the principal component of a pre-engineered water treatment system used extensively in the beverage industry. As depicted in Figure 6, the pilot plant schematic flowsheet, the JBAS ACCELATOR clarifier contains an inlet-mixing chamber, flocculators and a slurry recycle impeller on a common shaft, a slurry concentrator, and a clarified water zone with effluent take off system.

Certain features of the standard JBAS unit were modified for this application. A submerged-orifice peripheral launder was substituted for the normal low-rate effluent collection system and the concentrator rim was extended in the form of a sloped trough to enable extraction of solids from the recirculating carbon slurry independent of the slurry-pool level.

Operation at throughput rates as high as 30,000 gpd was visualized, resulting in an overflow rate of 1.6 gpm/ft^2 of clarification area based on the 12.9-ft^2 cross-section of the annular clarification zone.

Each of the 730-gal JBAS clarifiers (4.5 ft diameter x 7.5 ft side-sheet) included a recirculation zone volume of 225 gal. which provided carbon contact times of 32, 16, and 11 min at operating rates of 10,000, 20,000, and 30,000 gpd, respectively.

In a solids-contact unit of this type, the throughput rate cannot exceed the pumping capacity of the recirculation system if short-circuiting to the solids separation zone is to be avoided. The estimated pumping capacity of the slurry recirculation impeller in the pilot units was five times the maximum operating rate. The recirculation flow also prevents deposition of solids on the tank floor. Except for material isolated in the slurry concentrator, all of the carbon inventory was maintained in suspension during operation.

The pilot plant (Figure 7) was erected out-of-doors in an orientation which differed only slightly from that shown in Figure 6. The feed stream, pumped from the inner launder of one of the final clarifiers of the adjacent activated sludge plant, was brought to the center front of the layout through a rotameter after which it was split into two streams. One of these operated a slurry-advance ejector and the other was throttled as needed to set the combined flow to the inlet chamber of the first-stage contactor-clarifier to the feed rate desired.

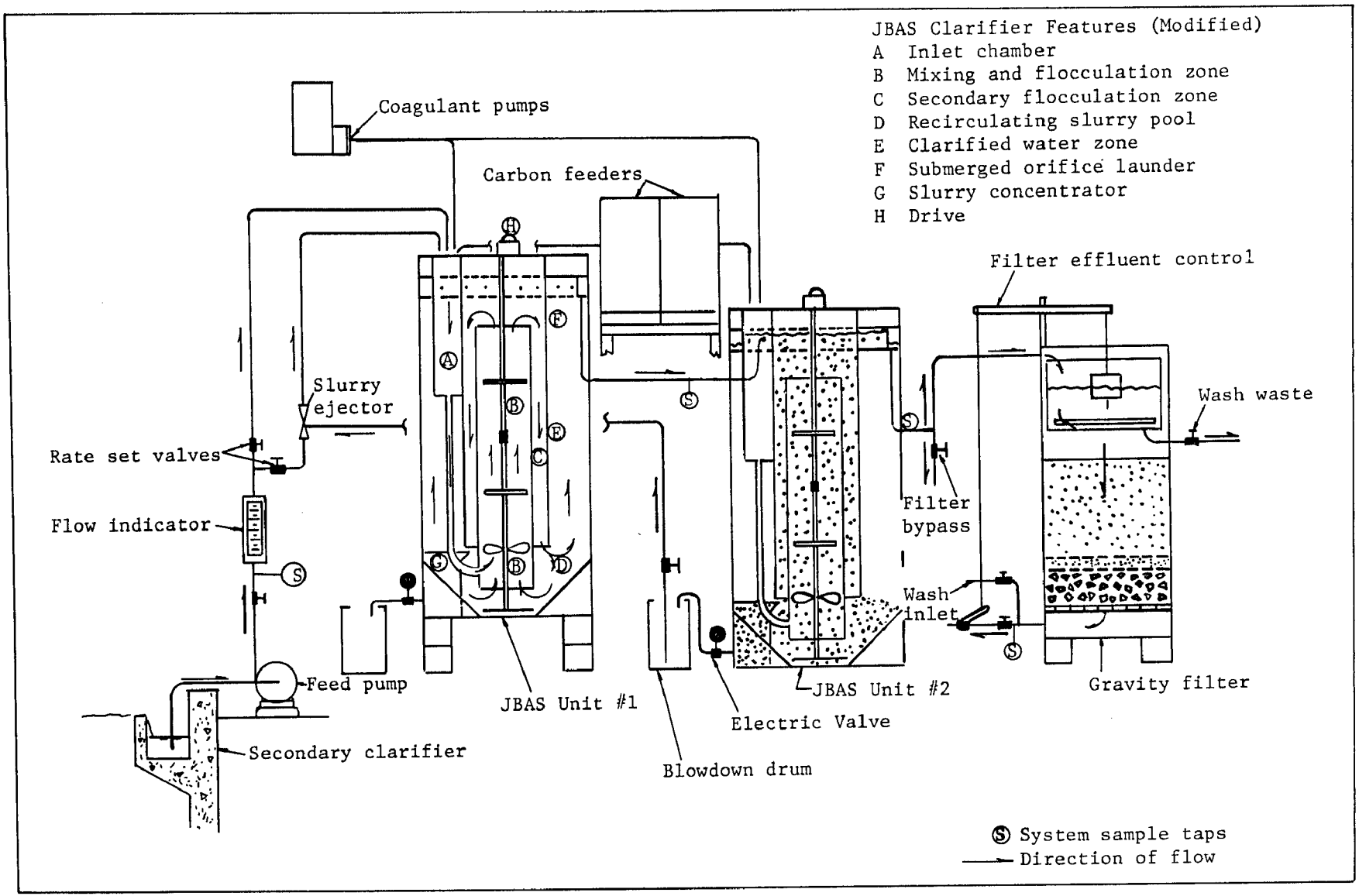


FIGURE 6: Schematic, Pilot Plant System

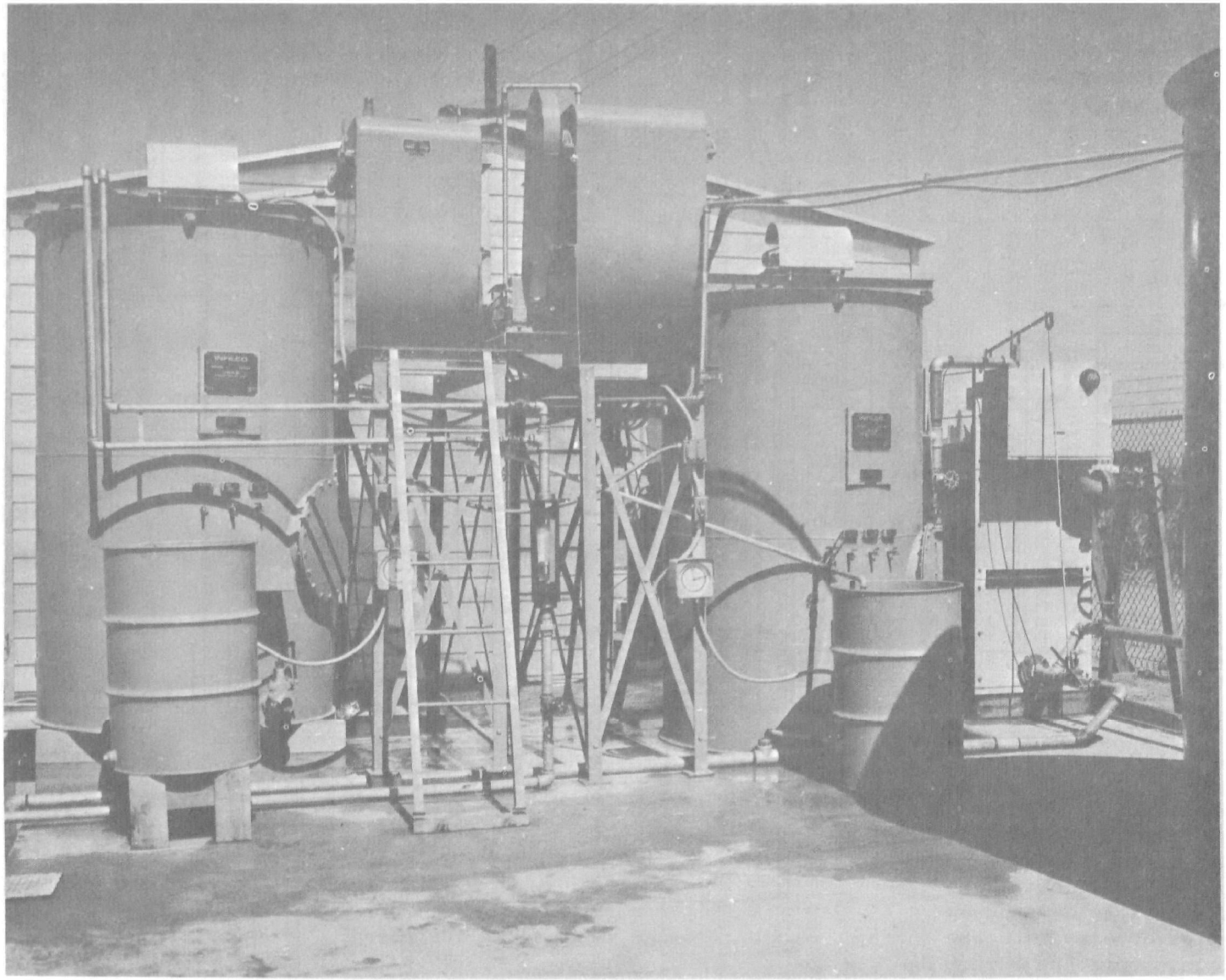


FIGURE 7: Photograph of 30,000 gpd pilot plant.

First-stage effluent flowed by gravity to the second-stage JBAS unit and thence to a gravity sand filter for final treatment.

Carbon feed was countercurrent to the throughput flow. Fresh powdered activated carbon was gravity fed by a volumetric slurry feeder to the inlet chamber of the second-stage JBAS unit, along with a separate feed of polymer flocculant. A second carbon feeder (the left-hand unit above the ladder in Figure 7) was used during initial start-up to permit simultaneous development of slurry in both contactor-clarifiers and to provide standby for the other feeder.

Flocculated carbon slurry recirculated within the second-stage JBAS unit was permitted to accumulate to a manageable concentration which was controlled by timer-actuated blowdown from the internal concentrator. The Flexopulse repeating-cycle timer used afforded independent adjustment of both the valve-open and valve-closed portions of the blowdown cycle from one minute each up to a 2-hr total cycle time.

Used-carbon blowdown from this unit was collected in the right-hand drum shown in pilot plant photograph and, together with a small flushing stream of treated wastewater, transferred continuously to the inlet chamber of the upstream contactor-clarifier by a Penberthy hydraulic ejector operated with a portion of the feed stream. A secondary flocculant dosage was also fed separately to this point.

Blowdown from the first-stage JBAS unit was to waste, except when being measured. Both 55-gal. blowdown collection drums soon proved to be too large and were replaced with 10-gal. polyethylene tanks.

Second-stage contactor-clarifier effluent could be divided so that any portion or all of it could be wasted or flowed to a 2-ft square by 6-ft high sand filter. This gravity research unit, manufactured by Filtration Equipment Corporation, was constructed of Transite and Lucite with two opposing transparent sidewalls, allowing visual observation of the contents. It included a FRE-FLO extruded asbestos-cement underdrain system supporting 11 inches of graded gravel and 22 inches of filter sand with a specified effective size between 0.45 and 0.55 mm and a maximum uniformity coefficient of 1.75.

A float-operated effluent control valve was added to this unit to pace filtration with plant flows up to 12 gpm. During higher plant operating rates, effluent from the second-stage JBAS unit was wasted to limit the filtration rate to 12 gpm (3 gpm/ft^2 of filter area). A transparent plastic hose tapped into the underdrain and extended to the top of the filter enabled loss-of-head measurement during filtration.

As a matter of convenience, locally available well water pumped from a 2000-gal. storage tank was used for filter backwashing. The wash rate was set manually while observing the extend of sand expansion and computed from the duration of wash and drawdown in the storage tank.

Sample taps were provided on each contactor-clarifier unit for slurry withdrawal and determination of the slurry-clear water interface elevation.

A specially designed, multiple-dipper sampler to which streams of plant feed, first- and second-stage contactor-clarifier effluents, and filter effluent were conveyed continuously was used to obtain daily composite samples collected at 1-min intervals over 24 hours. These samples were accumulated in polyethylene containers refrigerated to a temperature between 1° and 3°C.

The pilot plant program was conducted in six consecutive phases:

1. Brief operation of the two-stage system at 7 gpm and a carbon dosage of 140 mg/l for equipment shakedown and operator training. This flow was selected as a practicable minimum dictated by the water flow required to operate the slurry-advance ejector plus a minimum manageable ejector bypass flow.

2. Limited operation at the same carbon dosage over a range of flow rates to define the hydraulic capacity of the system.

3. Operation for ten event-free days at a 14-gpm flow selected on the basis of data generated during Phase 2 and a carbon dosage of 140 mg/l.

4. Operation over a similar period at the same flow and a 280-mg/l carbon dosage.

5. Operation as in Phases 3 and 4 at a carbon dosage of 70 mg/l.

6. Operation of a single contactor-clarifier and the filter for the same period at 14 gpm and a carbon dosage of 140 mg/l to evaluate performance of a single-stage system for comparison with that of the two-stage system operated under closely similar conditions.

During each of these runs, composite and grab samples were collected for development of laboratory isotherms and analysis sufficient to define process performance; i.e., pH, suspended solids, turbidity, COD, BOD_5, and slurry and blowdown solids concentrations. Other data recorded comprised quantities and types of treatment chemicals; plant flow; rate and volume of blowdown; slurry volume after five minutes of settling; slurry level; filter head loss; and the filter backwash frequency, rate, and duration. Records were also made of events which interfered with or otherwise affected plant operation or performance.

Ten-day runs at each of the various operation conditions were adopted to define mean system performance under the variable loading imposed by the inconstant feed characteristics anticipated. And 24-hr operation was undertaken to minimize the potential influences of biological activity on BOD, COD, turbidity, and suspended solids.

Experimental Results

Phase 1 - Initial operation of the pilot plant at 7 gpm for four days provided an opportunity for equipment shakedown and operator training. After certain minor equipment repairs and revisions, this was followed by five days of similar operation. Sampling and record keeping procedures were initiated and analytical laboratory programming established during this start-up period.

Performance of the carbon slurry feeders was excellent and no special measures to wet the carbon were required.

It was established that powdered activated carbon slurry could be produced in the contactor-clarifiers and controlled as desired. Operation for 23 hours at a carbon feed of 140 mg/l to the second-stage unit was required for development of slurry to an extent such that blowdown and carbon advance to the first-stage could be initiated. However, the single 4.7-gal. blowdown per hour produced at the minimum setting of the original control system was deemed unsatisfactory and an adjustable 1-min resetting timer triggered by the existing timer was added to the system. This permitted limitation of blowdown duration to a fraction of a minute while retaining the primary timer's flexibility for determining the interval between blowdowns and reduced the unit discharge volume to 0.85 gal.

Slurry concentration and its control were two important additional operational factors receiving attention during this program. When activated carbon is loaded with adsorbate to equilibrium, further removal is impossible. Indeed, should the system equilibrium change, desorption may occur. In a practical sense, the equilibrium loading is attained within a relatively short time, but to blow down the carbon after this time would result in an unmanageably low solids inventory. It was therefore necessary to operate with slurry concentrations that were manageable physically without regard to sludge age.

In this connection, brief comment on operation of ACCELATOR units is pertinent. Recirculating slurry discharges as a moving stream into the lower portion of the clarification region. The upper surface of the slurry stream is the solids-liquid separation interface. Clarified liquid rises to the effluent collection system, while solids carried in the recirculating stream are drawn downward and re-enter the mixing and flocculation zones. If the volume occupied by the slurry exceeds the available volume, the interface rises into the clarification zone and a so-called slurry pool forms above the streaming slurry. Treated liquid escapes by filtering up through the slurry pool and slurry- or sludge-blanket operation results. Solids in the blanket are non-uniform in size and are not readily available for recovery and reuse by recirculation.

To establish the limiting slurry solids relationship which avoids sludge-blanket operation at a particular installation, the unit is

initially operated with little or no blowdown and the increase in solids inventory is conveniently monitored by a simple 5-min slurry settling test. When a limit is reached beyond which a slurry pool forms, the per cent floc volume after five minutes of settling is noted and used as a continuing operating datum.

Early operation of the pilot plant demonstrated superior settling characteristics for the second-stage slurry and revealed that sludge-blanket operation was not encountered in the first-stage unit until the 5-min settled slurry volume reached 30%. To provide margin for the influence of variable floc quality, to permit operation at greater flow rates, and for operator convenience, an operating range of 10-15% was selected for both contactors.

The relationship between the suspended solids content and 5-min settled volume of draft-tube slurry samples collected at intervals throughout the pilot plant operating period is shown in Figure 8. Except for a few occasions when feed suspended solids (activated sludge carry-over) were abnormally high, good correlation was noted. The second-stage unit was affected only once when slurry with an appreciable content of activated sludge was not wasted rapidly enough from the first-stage contactor and carry-over resulted.

Filter sand was adequately cleaned by backwashing. However, inasmuch as the pilot plant feed was unchlorinated sewage plant effluent, it was not unexpected to note development of a rather heavy growth of algae and slime in the filter underdrain, supporting gravel, and on the Lucite sidewalls. Following the initial 4-day run, cover plates extending from the sand-gravel interface to the filter floor were installed over the Lucite to exclude light and thus inhibit algae growth. This was not completely effective, however, and growth of algae and slime below the sand was to influence filter effluent quality throughout the study.

Phase 2 - Performance of the pilot plant at different flow rates was studied over a 10-day period. Two 24-hr sampling runs at 7 gpm were followed by four days at 10.5 gpm, two days at 14 gpm, and two days at 20 gpm. Carbon feed to the second-stage contactor was 136 mg/l and 3 mg/l of polyelectrolyte were fed to each unit, except for a brief period when a feeder recharging error raised it to 4.3 mg/l.

The analytical data developed during this phase (Table 3) and the COD results graphed in Figure 9 show that while over-all plant performance was affected by variations in feed quality, any influence due to increased flow rate is not evident.

On the final day of the 20-gpm run, settling rates of 8.4 and 13.0 in./min were observed for draft-tube samples from the first- and second-stage contactors, respectively. The equivalent overflow rates of 5.2 and 8.1 gpm/ft^2 are far above conventional clarifier loadings and several

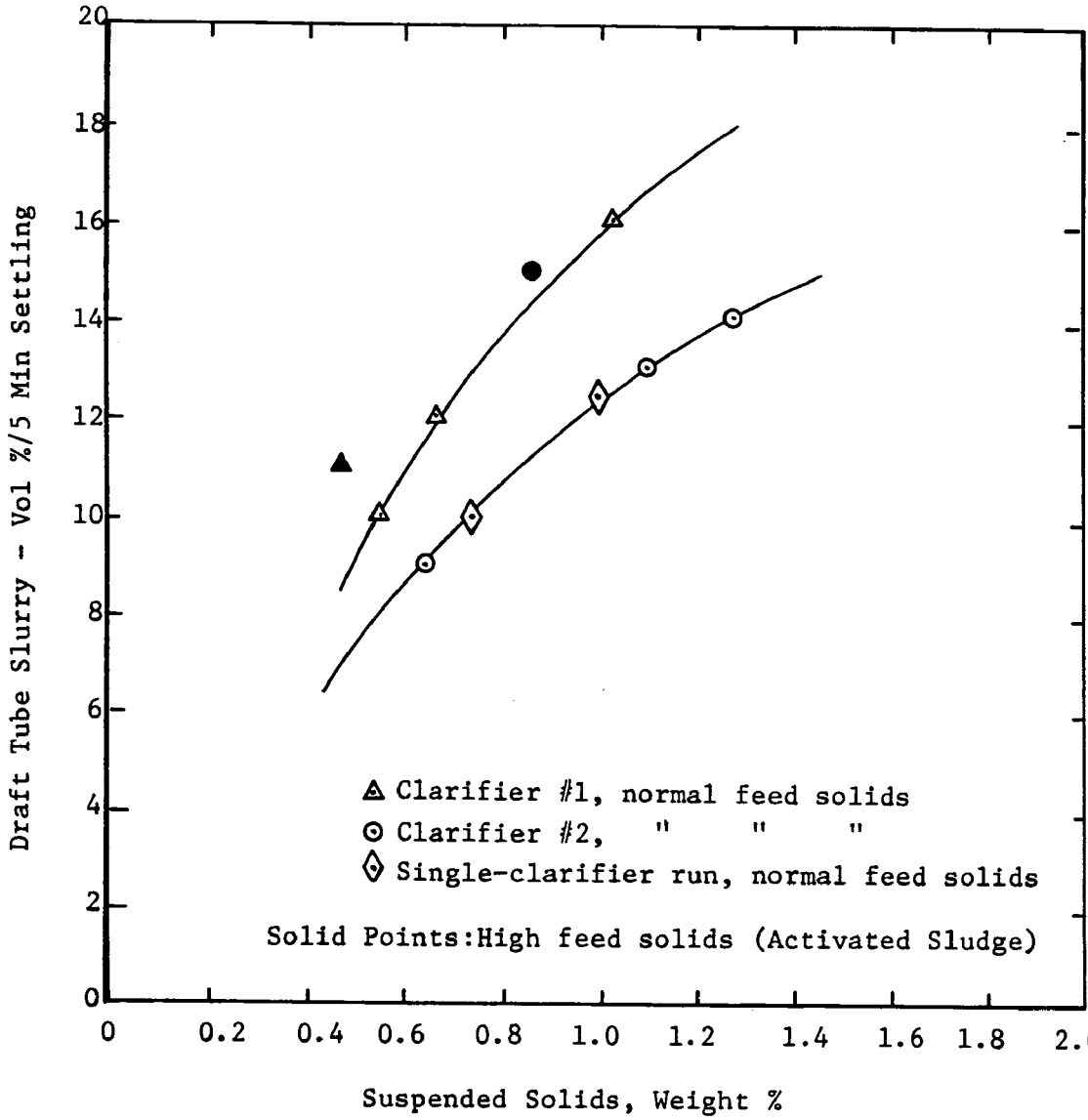


FIGURE 8: Relationship between draft tube slurry 5 min settled volume and suspended solids content.

TABLE 3

Phase 2, 24-hour Composite Sample Analyses

DATE - 1968	10-6,7	10-7,8	10-8,9	10-10,11	10-11,12	10-12,13	10-13,14	10-14,15	10-15,16
Rate of Flow, gpm	7.0	7.0	10.5	10.5	10.5	14.0	14.0	20.0	20.0
Feed Stream									
pH	7.7	7.5	7.5	7.8	7.6	8.0	8.0	8.0	8.1
Turb., JTU	11	17	12	22	14	12	4	25	13
Sus. Solids, mg/l	10	12	13	20	11	8	5	20	15
COD filtered, mg/l	25.0	26.7	25.8	27.2	24.5	28.2	24.6	33.6	24.6
BOD, mg/l	10.2	-	8.0	19.0	10.1	8.4	9.1	-	16.1
Clarifier #1 Eff.									
pH	7.8	7.7	7.7	7.9	7.7	8.0	8.0	8.1	8.1
Turb., JTU	16	14	12	13	9	5	2	8	15
Sus. Solids, mg/l	17	11	18	16	10	6	4	15	27
COD filtered, mg/l	13.4	12.7	14.3	16.6	13.6	16.2	14.7	17.0	13.8
BOD, mg/l	4.7	-	4.7	7.9	3.6	5.2	5.5	-	8.3
Clarifier #2 Eff.									
pH	7.9	7.7	7.8	7.9	7.8	8.0	8.0	8.1	8.2
Turb., JTU	4	4	3	2	2	2	1	4	2
Sus. Solids, mg/l	6	4	7	3	3	2	2	5	4
COD filtered, mg/l	5.4	6.7	8.5	8.8	5.2	7.9	7.5	8.3	6.9
BOD, mg/l	4.0	-	2.4	4.0	3.4	2.6	2.6	-	5.4
Sand filter Eff.									
pH	7.9	7.7	7.8	7.9	7.8	8.0	7.9	8.1	8.1
Turb., JTU	1	2	2	2	2	3	2	3	2
Sus. Solids, mg/l	4	2	2	2	2	2	1	3	4
COD unfilt, mg/l	6.3	7.6	9.0	9.6	6.6	8.8	7.9	10.1	7.4
COD filtered, mg/l	5.8	6.2	8.5	8.8	5.2	8.3	7.5	8.3	6.9
BOD, mg/l	-	-	2.8	2.3	2.2	2.6	3.5	-	5.2
COD Red'n, %	78	77	67	68	79	72	70	75	72
BOD Red'n, %	61	-	66	88	78	69	72	-	68
Carbon loading %	14.0	14.6	12.3	13.1	13.8	14.5	12.2	18.1	12.6

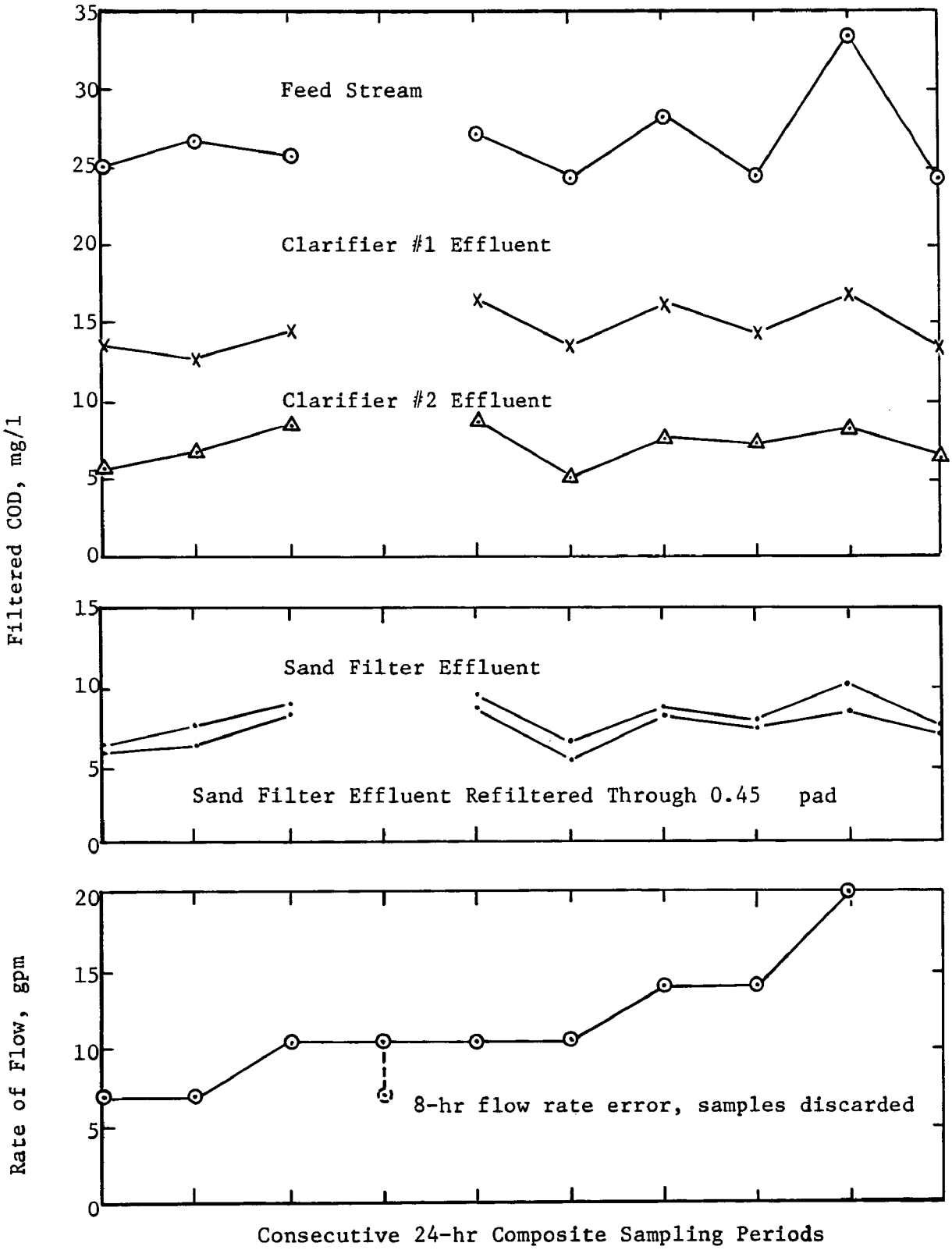


FIGURE 9: Filtered COD versus plant operating rate, Phase 2.

times those of high-rate water treatment units. Understandably, the pilot plant operating at 20 gpm (overflow rate 1.6 gpm/ft^2) could contain the carbon slurry even during periods when it was substantially degraded by a large content of activated sludge solids.

The influence of solids carry-over from the sewage plant on operation during this phase is shown in Figure 10. Control of the second-stage solids inventory was not difficult; but the first-stage contactor was more sensitive, as expected.

Filtered COD removal through the pilot plant for the 10-day period averaged 73 per cent. A COD loading of 19.4 mg on 136 mg of carbon was attained, or 14.3 per cent by weight. Limited isotherm data generated during this program indicated that achievement of this much COD reduction by single-stage treatment would require about 750 mg/l of carbon and loading would drop to 3.5 per cent by weight.

Filter operating records (Figure 11) revealed progressively shorter runs as the rate increased, as well as production of less finished water per run as the pilot plant operating rate increased. Several events producing significant head loss deviations are indicated as having been operator induced. Other deviations of from 1-4 inches are attributed to mechanical friction in the rate controller which did not provide precise modulation.

A total of 172,000 gal. of treated wastewater was filtered during five filter runs, the first of which started prior to initiation of this operating phase. The rate and duration of backwash were determined by observing sand expansion and cleaning effectiveness. An expansion of 8 inches or 36 per cent was achieved at wash rates of from 18 to 25 gpm/ft^2, depending on wash water temperature. A carbon penetration of several inches below the sand surface was observed at times and the top inch of sand retained a black cast throughout the study. Carbon floc was occasionally observed migrating in the bed during backwash; but this appeared to break up satisfactorily. Backwash duration evolved from an initial and inadequate five minutes to 10 minutes with manual surface agitation and freeboard brushing. Wash water consumption was less than two per cent of the filtered water volume.

The turbidity and suspended solids content of filter effluent are not readily evaluated. The visual appearance of filter influent and effluent was markedly dissimilar. The influent had a characteristic black cast, with small carbon floc visible on occasion. Effluent was clear, but the slight residue after Millipore filtration was brown or green rather than black, evidently a result of biological activity in the lower portions of the filter.

Phase 3 - This first constant-rate study followed the preceding program without interruption. Without shutting down the pilot plant, chemical

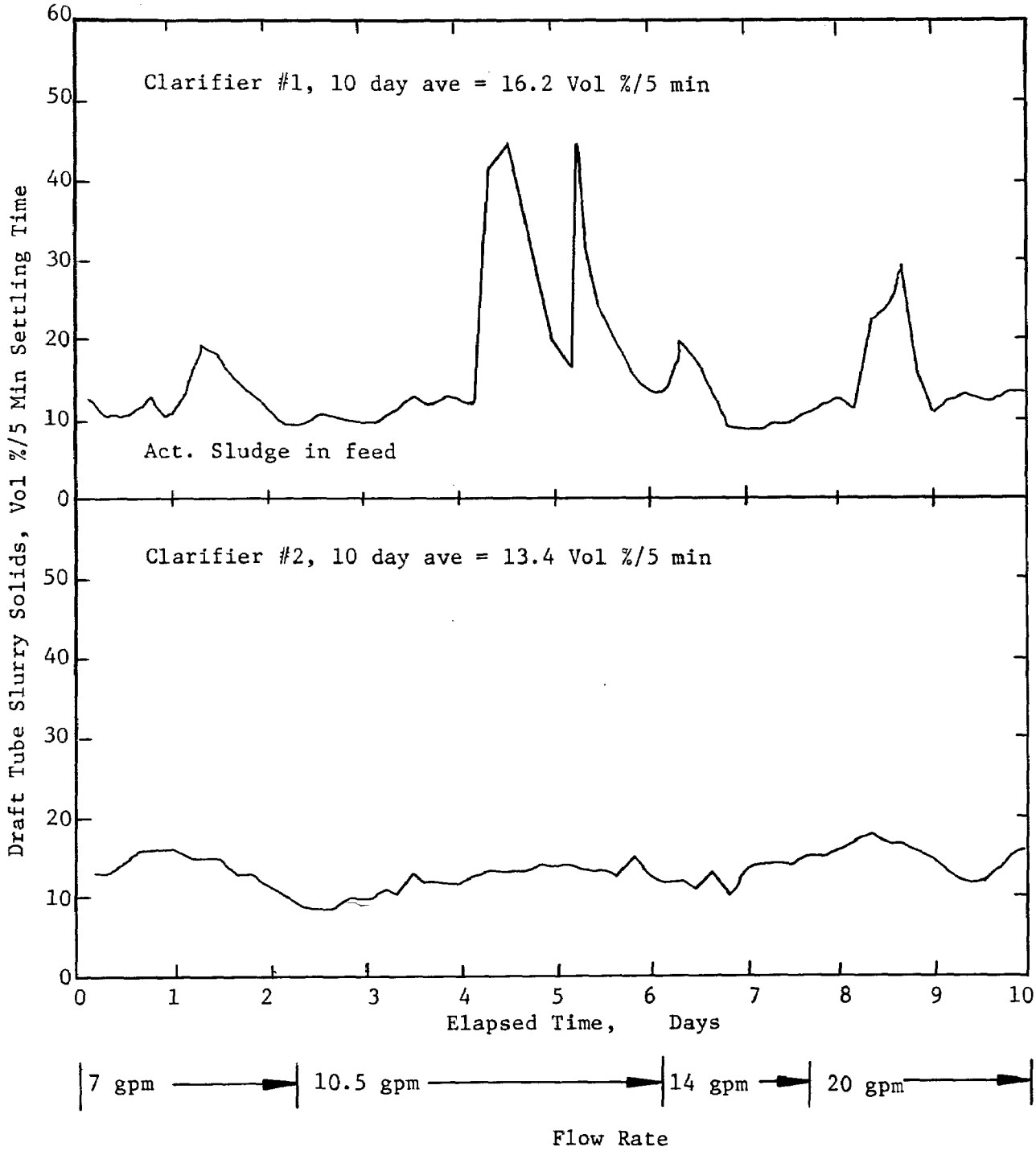
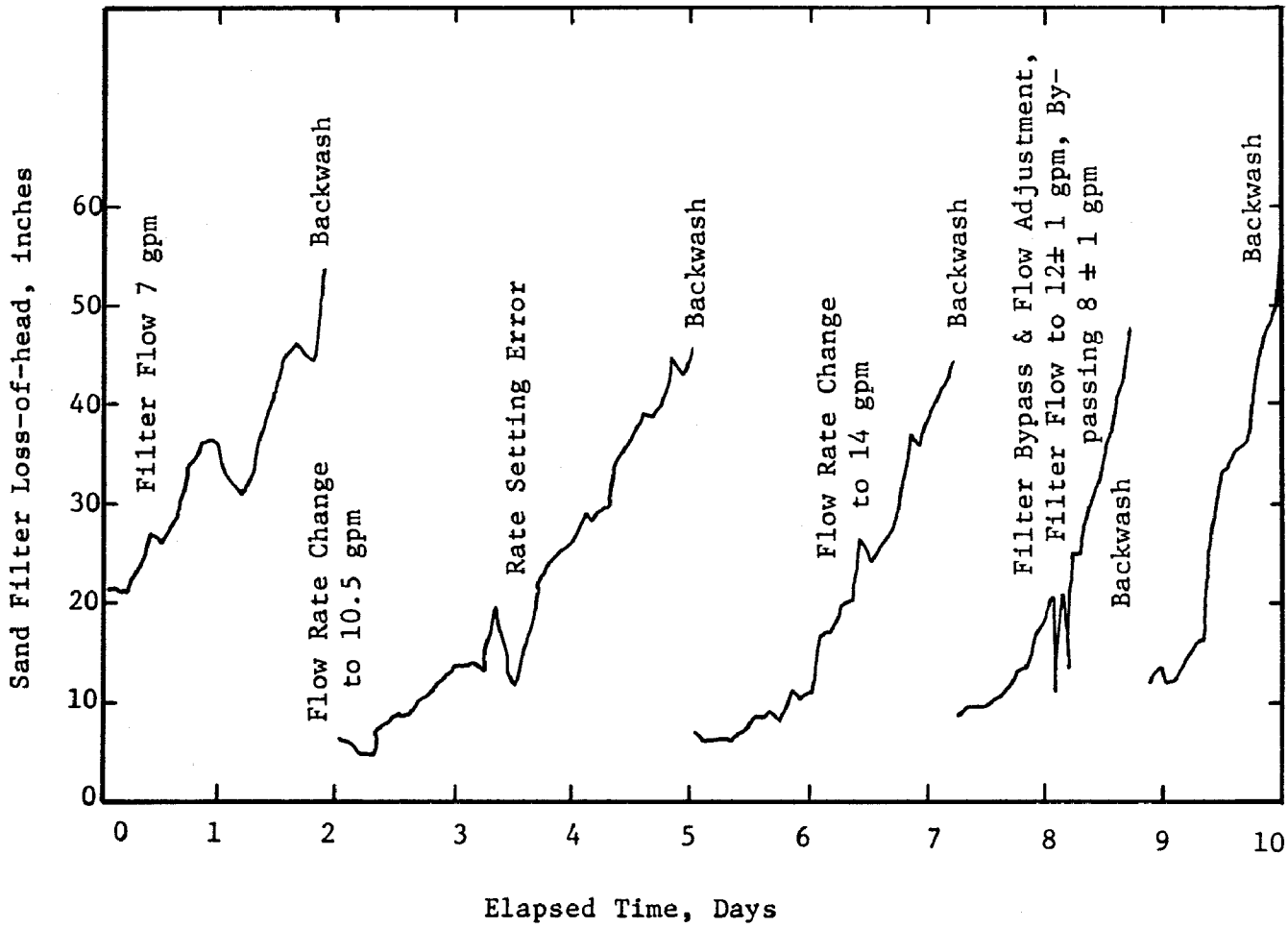


FIGURE 10: Settled slurry volume versus pilot plant throughput rate, Phase 2.



Performance Data

Run	1st	2nd	3rd	4th	5th
Duration, hr	91*	71	25+28	20+18	28
Filter rate, gpm	7	10.5	10.5/14	14/12	12
Surface loading, gpm/ft^2	1.75	2.63	2.63/3.50	3.50/3.0	3.0
Volume filtered, gal	38,000	44,700	39,300	29,800	20,200
Pilot plant flow rate, gpm	7	10.5	10.5/14	14/20	20
Clarifier overflow rate, gpm/ft^2	0.55	0.74	0.74/1.1	1.1/1.6	1.6

*Run #1 was in progress at time zero.

FIGURE 11: Gravity Sand Filter Operating Data, Phase 2.

feeders were reset and recharged and flow was set at 14 gpm, a rate selected to avoid hydraulic gradient limitations encountered within the pilot plant at the maximum operating rate of the previous study.

A target carbon dosage to the second-stage contactor of 140 mg/l, chosen as a medium dosage level, was tested first in the constant-flow series of programs because the plant was operating at this dosage and no transition period would be required. Calculated from carbon consumption over the 10-day run, the actual dosage was 146 mg/l.

Initially, 2.5 mg/l of C-32 polyelectrolyte was fed to the inlet chamber of each contactor and this concentration of coagulant was fed to the second-stage unit throughout the run. Because of a noticeable increase in effluent turbidity and suspended solids from the first-stage contactor during the first day, C-32 feed to this unit was then increased to 3.0 mg/l and, although not particularly effective, maintained at this level until the last day when it was again increased to 3.5 mg/l as a result of continuing slurry deflocculation.

No unusual events were encountered during the 10-day study. Operators were able to control blowdown from each contactor to maintain reasonable draft-tube slurry conditions. There was some time lag in the blowdown system which produced cyclic increases and decreases in results of the 5-min settled volume test, but averages for the run were close to the target value (Figure 12).

Filter operation (Figure 13) at 3 gpm/ft^2 was good with runs in excess of 60 hours when the filter was not backwashed prematurely. Occasional dips in loss-of-head vs. time curves were not fully investigated. These frequently occured within the first four hours of a sampling period. Operator maintenance such as a 15-min flow interruption to clean the rate of flow indicator or brushing algae from launders or the filter freeboard may have contributed. Characteristically during this period, wastewater temperature rose 4-6°F and a change in clarifier performance may have been occuring. Whatever the causes, a collapse of and slight penetration of material on the filter surface appeared to be occuring periodically.

Analytical data (Table 4) for this run show that uniform performance was characteristic. Of interest is the decided increase in first-stage contactor effluent turbidity and suspended solids over the feed levels. This was counteracted in the second-stage contactor which delivered an effluent of uniformly low turbidity and suspended solids. For the first five days of the run, filter effluent solids were undesirably high. Following a filter backwashing, suspended solids decreased for the balance of the run. Filter effluent BOD shows a similar trend. Prior to the mid-period backwash, final BOD exceeded filter influent BOD, whereas after this backwash the reverse was true.

BOD reduction through the system averaged 69 per cent and mean COD reduction was 72 per cent. The cumulative frequency distribution curves

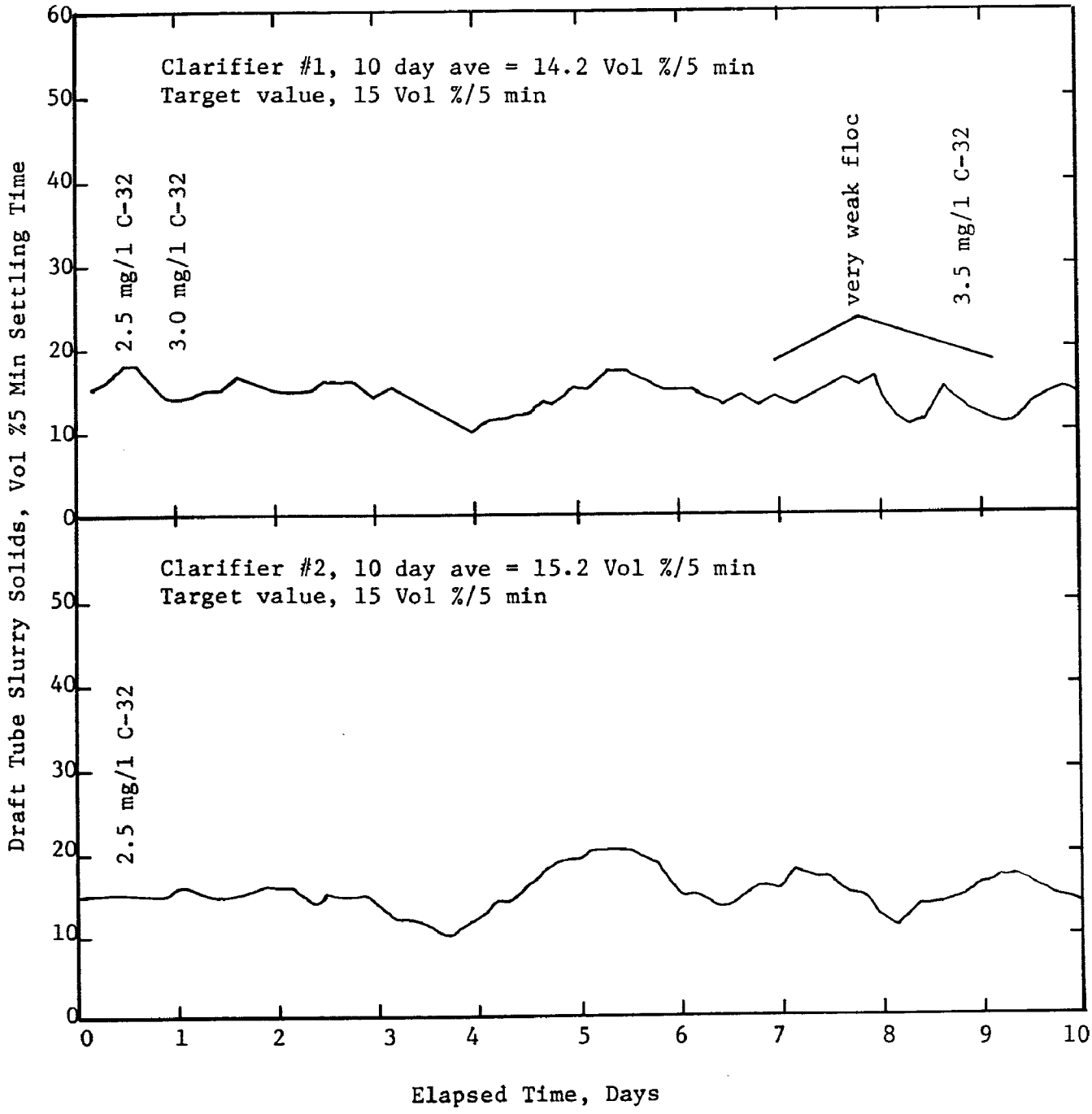
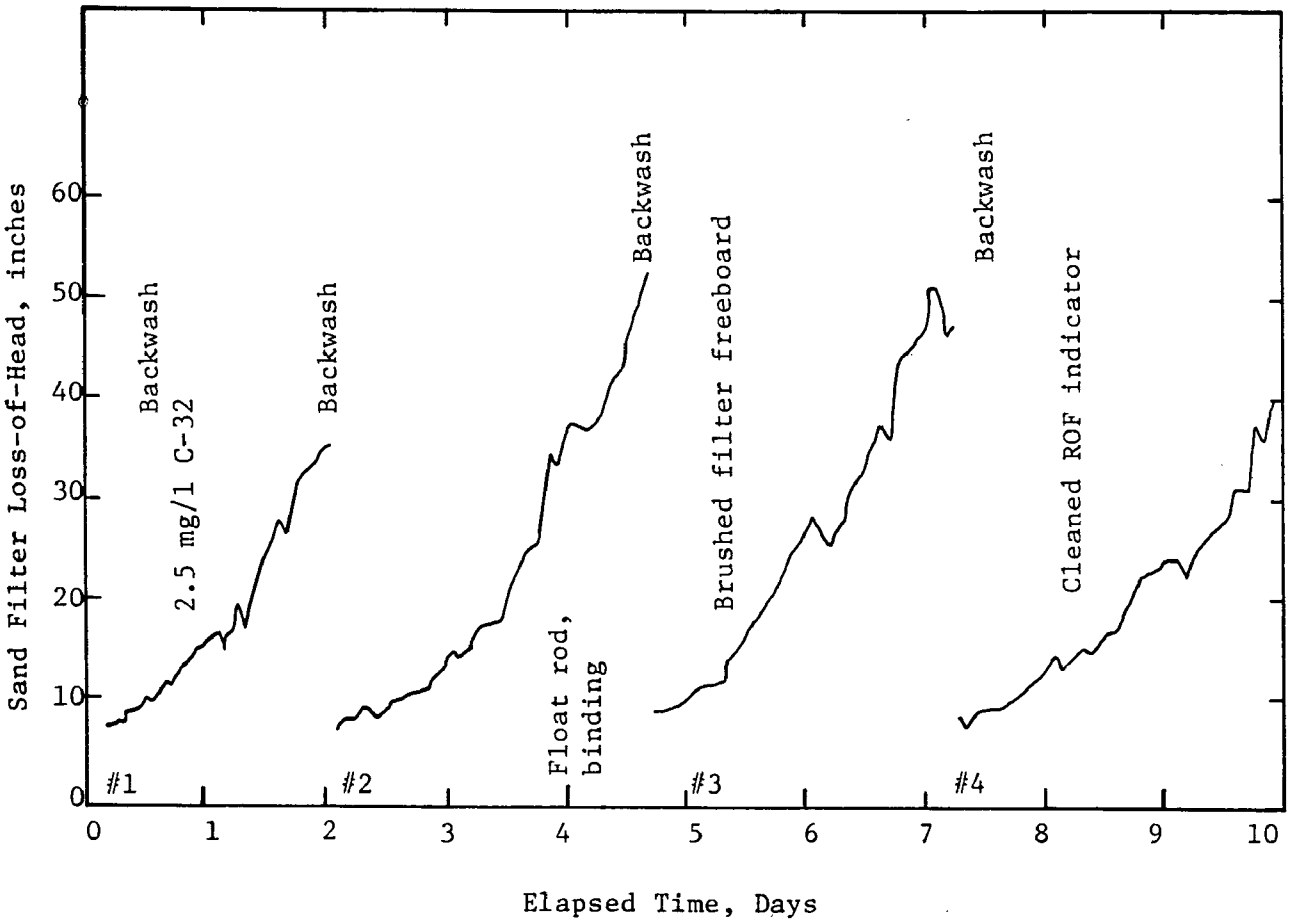


FIGURE 12: Settled slurry volume, Phase 3.



Performance Data

Run	#1	#2	#3	#4
Duration, hr	49	63	60	72
Filter rate, gpm	12	12	12	12
Surface loading, gpm/ft^2	3.0	3.0	3.0	3.0
Volume filtered, gal	36,300	45,300	43,200	51,800
Pilot plant flow rate, gpm	14	14	14	14
Clarifier overflow rate, gpm/ft^2	1.1	1.1	1.1	1.1

Total wash water used, 2160 gal = 1.2% at ave. rate of 20.7 gpm/ft^2

FIGURE 13: Gravity Sand Filer Operating Data, Phase 3.

TABLE 4

Phase 3, 24-hour Composite Sample Analyses

DATE - 1968	10-16,17	17,18	18,19	19,20	20,21	21,22	22,23	23,24	24,25	25,26
Feed stream										
pH	7.7	7.9	7.7	8.0	7.9	7.9	7.9	7.7	7.9	7.9
Turb., JTU	8	9	14	7	8	8	9	9	9	9
Sus. Solids, mg/l	13	7	11	8	9	8	11	6	7	6
COD filtered, mg/l	24.6	24.0	25.6	28.5	25.4	28.8	26.1	25.6	26.6	27.2
BOD, mg/l	12.7	11.2	8.6	5.5	10.2	-	14.0	12.5	10.9	9.5
Clarifier #1 Eff.										
pH	7.8	8.1	7.8	8.1	8.0	8.0	8.0	7.9	8.0	8.0
Turb., JTU	19	23	26	22	28	30	27	30	28	27
Sus. Solids, mg/l	25	22	21	32	40	44	34	34	31	27
COD filtered, mg/l	14.7	13.0	14.6	14.4	16.3	15.1	13.6	12.5	13.6	13.1
BOD, mg/l	8.8	10.9	5.6	3.3	8.2	-	10.0	8.4	10.2	7.1
Clarifier #2 Eff.										
pH	7.8	8.1	7.9	8.1	8.1	7.9	7.9	7.9	8.0	8.0
Turb., JTU	3	2	3	5	4	4	2	2	3	2
Sus. Solids, mg/l	4	3	5	7	5	5	3	2	3	3
COD filtered, mg/l	7.7	7.4	6.4	9.9	9.1	7.8	7.3	5.7	7.3	6.8
BOD, mg/l	3.6	5.4	3.3	2.2	2.8	-	7.0	6.5	4.5	4.2
Sand filter Eff.										
pH	7.8	8.0	7.9	8.1	8.1	7.9	7.9	7.9	7.9	7.9
Turb., JTU	2	2	2	2	1	2	1	2	2	2
Sus. Solids, mg/l	3	3	2	4	2	1	1	1	2	1
COD unfilt, mg/l	9.1	8.2	7.7	10.7	9.9	9.5	7.8	7.3	7.8	7.2
COD filtered, mg/l	7.7	7.4	6.4	10.4	8.6	7.8	6.8	5.7	6.9	6.3
BOD, mg/l	4.6	6.1	4.5	1.8	2.3	-	2.2	2.6	3.2	2.7
COD Red'n, %*	69	69	75	65	66	73	74	78	74	77
BOD Red'n, %*	72	52	62	67	77	-	84	79	71	72
Carbon loading %	11.6	11.4	13.2	12.8	11.5	14.4	13.3	13.7	13.6	14.3

*Computed from lowest effluent value attained, disregards increases if any occuring in sand filter.

of Figure 14 show the COD of samples collected during the run from various points throughout the treatment system.

These COD data are also portrayed in the adsorption isotherm analysis of Figure 15, the construction of which requires explanation.

The 24-hr feed samples varied in COD (C_o) and individual isotherms varied significantly in slope (1/n) and carbon loading (X/M) achieved at equilibrium. Taken separately, they are unsatisfactory for evaluation of mean pilot plant performance.

Individual Freundlich isotherm data were accumulated throughout the pilot plant operating period, after which all were transferred to a composite data array (Figure 16). The points on this array were obtained by selecting a specific COD remaining value (C_t), reading the carbon loading (X/M) achieved at this C_t on each individual isotherm curve, calculating the mg/l activated carbon dosage indicated by each, and then plotting the dosage against the respective C_o values. A curve approximating the mean carbon dosage versus C_o for that C_t was then drawn through the points. This procedure was repeated for six C_t levels. The array of points discloses the magnitude of variation in raw data encountered and emphasizes the impracticality of attempting to evaluate a pilot plant run directly with individual isotherms.

The C_t curves (Figure 16) determine six points for which loading (X/M) versus COD remaining (C_t) can be derived and plotted as an isotherm for any C_o value. While this procedure is not absolute with respect to accuracy it provides a basis for comparative run evaluation common to all pilot plant studies. The performance of one study at a specific mean C_o can be evaluated against one or more other studies at their respective mean C_o conditions.

The mean-value single-stage isotherm for the Phase 3 study (Figure 15) was derived in this fashion, as were others for the balance of the field studies. From the slope and percentage of COD remaining at various points on the single-stage isotherm, a two-stage countercurrent isotherm was developed and added to the graph. Since published information for two-stage countercurrent systems did not cover the entire range of adsorbate-remaining values of interest[5], available data were extrapolated graphically.

The isotherm analysis graphs also include mean performance paths which were calculated and plotted from the mean C_o value and actual activated carbon feed utilized, and in the case of two clarifiers operated in series, for the intermediate COD value (C_i) and the carbon feed. The intermediate COD being the filtered COD in the effluent of the upstream clarifier which is the feed to the downstream clarifier. For any given feed COD and activated carbon feed, the carbon loading achieved when plotted against COD remaining must fall on the performance path.

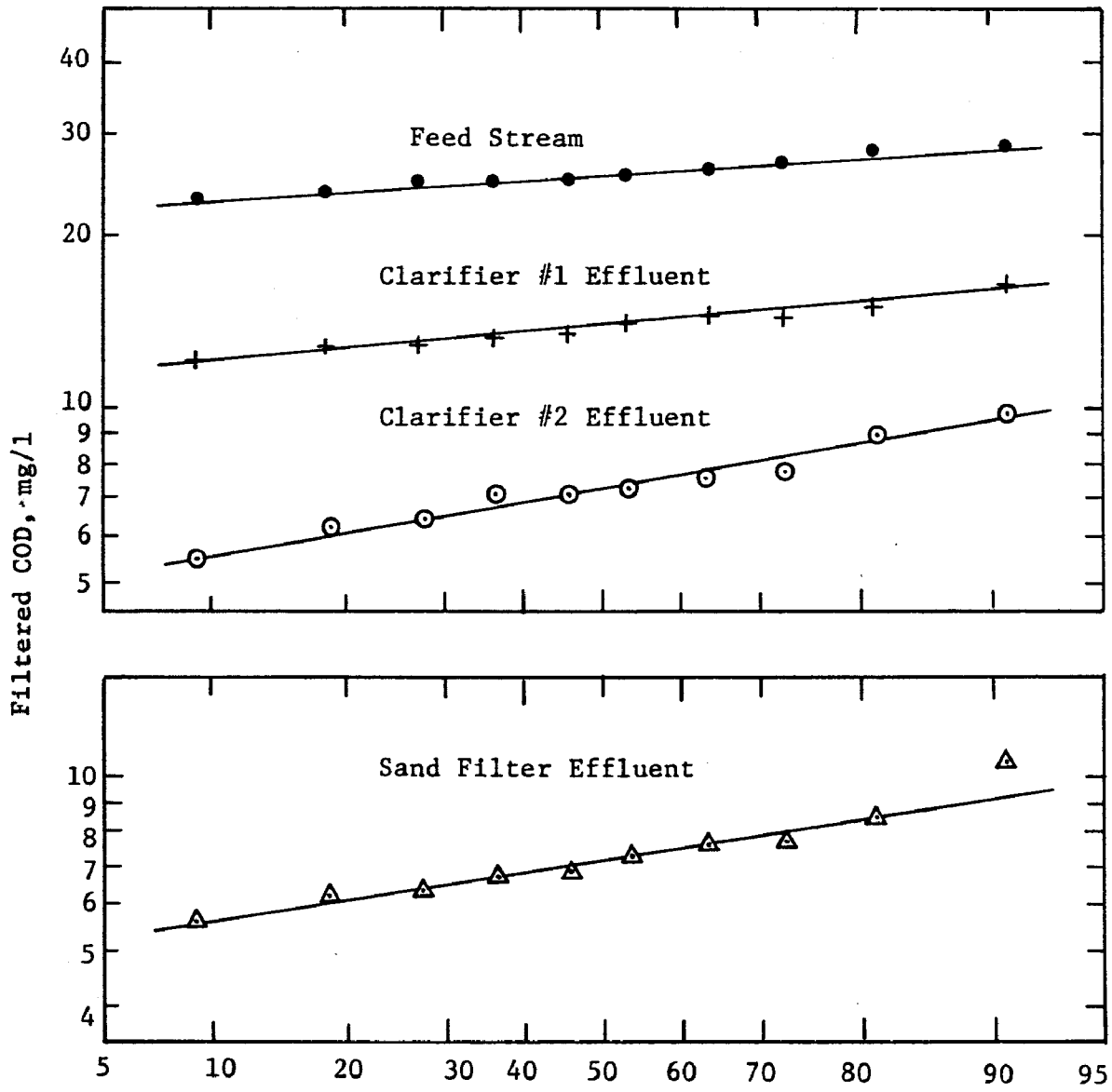


FIGURE 14: Composite-sample COD, Phase 3.

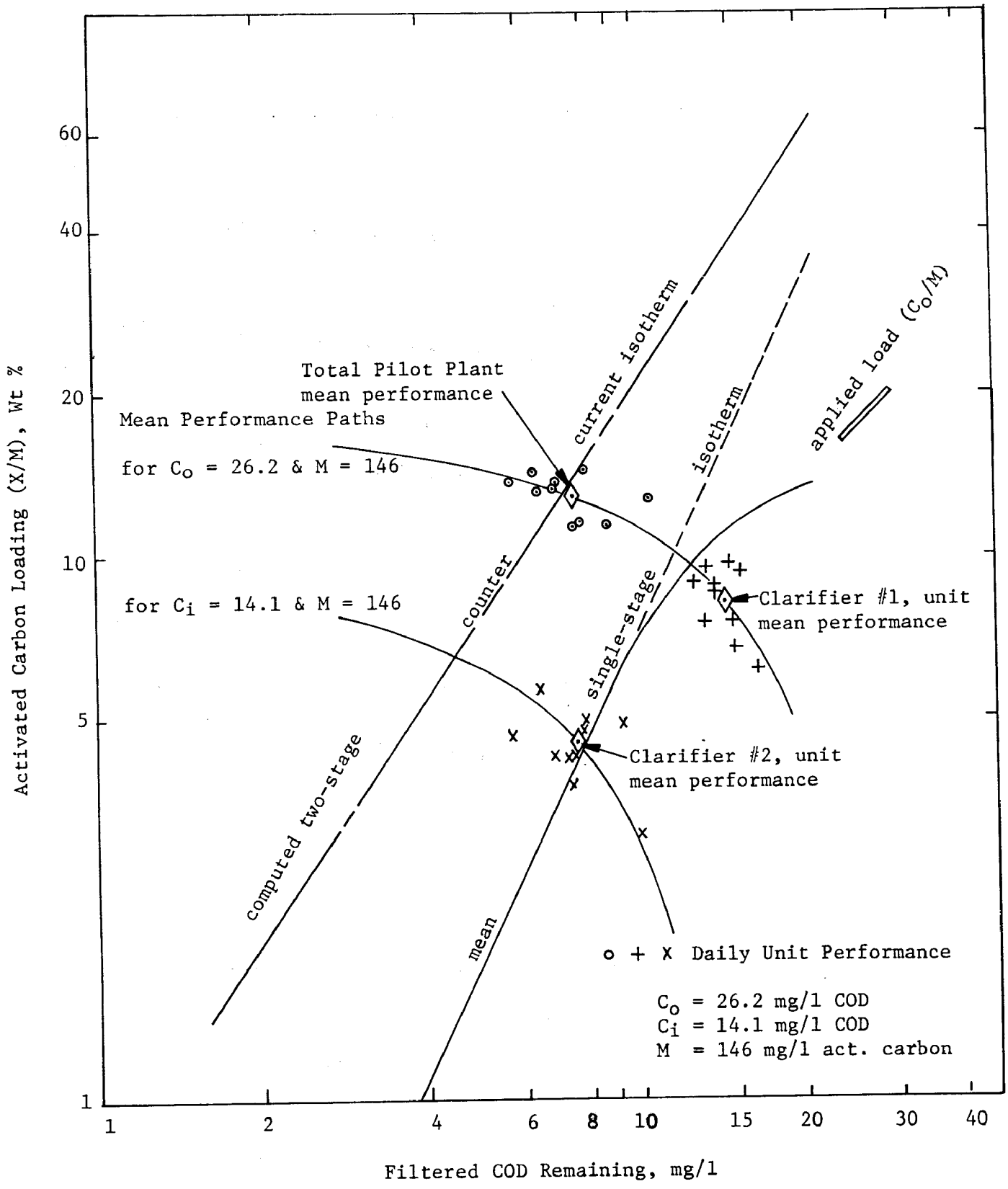


FIGURE 15: Adsorption Isotherm Analysis, Phase 3.

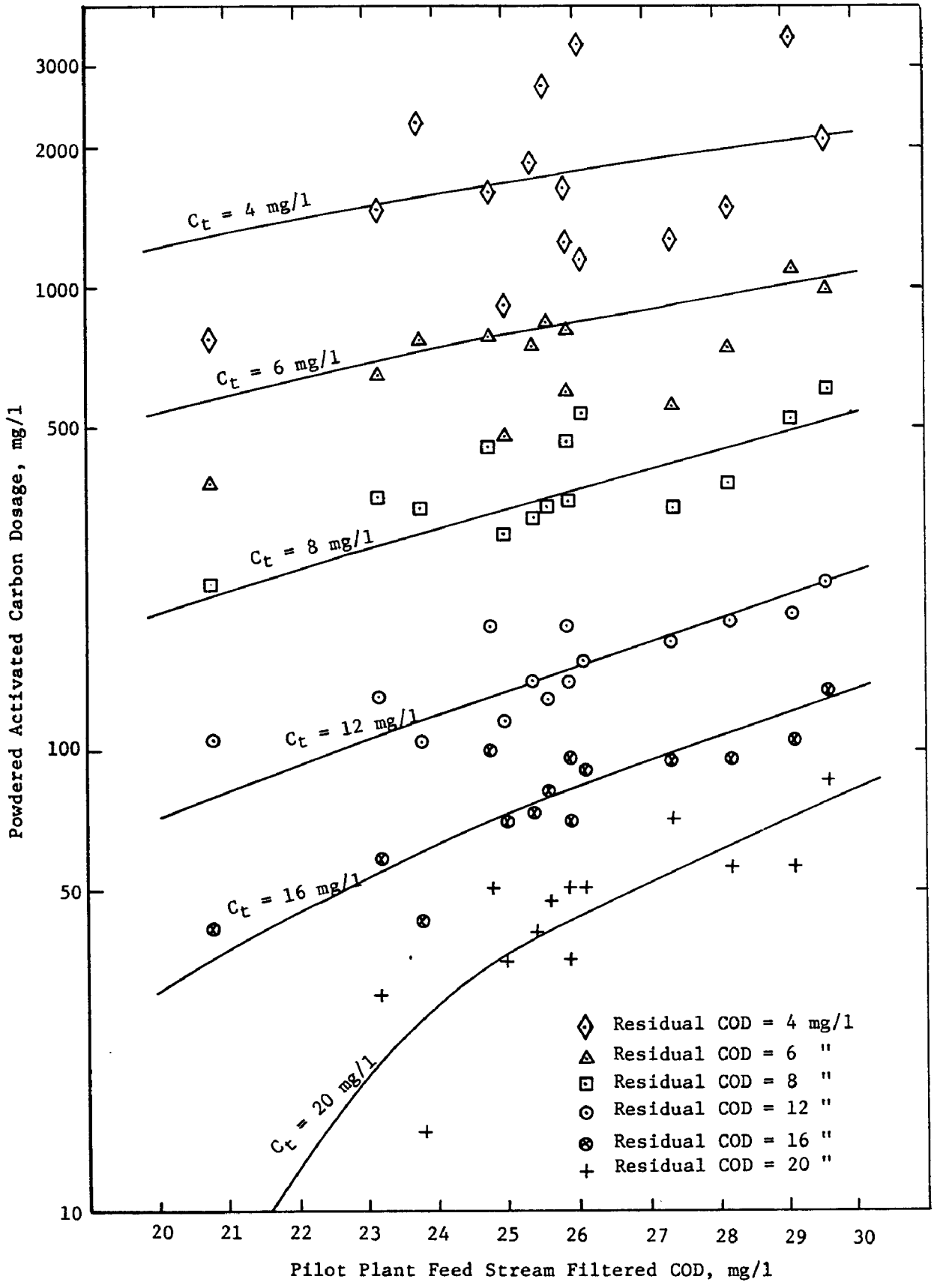


FIGURE 16: Single-stage adsorption isotherm data array.

The performance paths intersect the isotherms and the intersections can be considered predicted performance points for true single-stage or two-stage countercurrent processes.

A box labeled "applied load" appears on each analysis curve. The ratio of applied COD to carbon feed for each day of operation was plotted. The box encompasses these points and contributes some understanding of the limitation on the magnitude of carbon loadings achieved.

Figure 15 includes the daily unit and total system performances attained. These points deviate slightly from the mean performance paths because they are calculated from daily C_o and C_i values. Diamond-shaped points designate mean unit and total performance for specific runs.

Observed mean and computed system performances were essentially equal. COD loading on the carbon was 12.9 per cent by weight as compared to 9.6 per cent predicted for single-stage adsorption.

First-stage contactor effluent, produced with carbon already partially loaded with COD from the second-stage unit, was slightly inferior to that predicted for a single-stage process using new carbon. Carbon loading added in this unit was 8.3 per cent by weight as compared to 9.6 per cent predicted for use of new carbon.

The second-stage unit, operating with a feed COD (C_i) of 14.1 mg/l, loaded the new carbon to 4.5 per cent of its weight. A single-stage loading was not predicted for this unit as insufficient isotherms were generated to permit development of a mean-value curve. Performance in this stage was sufficiently good to compensate for the first-stage deficiency and bring the total system efficiency up to that predicted for two-stage countercurrent adsorption.

Phase 4 - System performance at the same flow rate and a carbon target dosage of 280 mg/l, double the previous concentration, was determined during this 11-day program. Calculated from carbon consumption over this period, the actual dosage was 266 mg/l, excluding a period of six hours near the end of the run when the feeder clogged.

Polyelectrolyte feed to both units was increased to flocculate the higher carbon dosage. A dosage of 5.0 mg/l to the first-stage contactor was maintained throughout the run. The initial 4.0 mg/l fed to the second-stage unit was increased first to 4.5 mg/l on the second day and then to 5.0 mg/l on the fifth day to cope with carryover. During the last day of the run, the point of application for each unit was changed from the inlet chamber to the bottom of the inner draft tube to overcome a head-loss problem occasioned by clogging of the 2-in. transfer lines between the inlet chambers and the draft tubes.

Draft-tube slurry control was excellent for Contactor #2 but variable for Unit #1 (Figure 17). The solids content of system blowdown of 19 per cent by weight made blowdown management difficult and this problem persisted throughout the run. Blowdown volume was on the order of 0.1 per cent of the throughput.

In spite of the decreased suspended solids carryover to the filter which characterized this run, filter runs shortened significantly (Figure 18) and wash water consumption increased to 2.1 per cent.

Analytical results for the run (Table 5) are consistent with the exception of two occurences. When polyelectrolyte feed to Unit #2 was increased at the beginning of the fifth sampling period there was a slight reduction in the turbidity and suspended solids content of final effluent and the filter began discharging BOD at concentrations above those in its influent.

The COD of samples collected during the run from various points in the treatment system is presented in Figure 19. Mean COD reduction through the plant was 84 per cent and BOD reduction, disregarding the filter problem, was 78 per cent.

The isotherm analysis for this run (Figure 20) indicates that plant performance exceeded two-stage countercurrent adsorption. The first-stage unit very nearly equalled single-stage new carbon efficiency by picking up 6.6 per cent more COD loading on carbon already loaded to 2.1 per cent in Unit #2. COD equivalent to an additional 0.1 per cent load was removed in the filter for a mean total loading of 8.8 per cent.

The predicted carbon requirement to achieve 84 per cent COD reduction by two-stage countercurrent adsorption is 360 mg/l, or 34 per cent more than was actually used.

Phase 5 - The final series study for 11 days at 14 gpm using two JBAS clarifiers with countercurrent carbon advance was initiated without plant shutdown. This investigation, using a low-level carbon dosage of 67 mg/l (target dosage: 70 mg/l or 25 per cent of the high-level concentration) and an appropriate reduction in polyelectrolyte, was subject to numerous difficulties.

Initial polyelectrolyte feed rates were inadequate and were increased several times (Figure 21). High solids carryover and poor floc formation are thought to be the result of the reduced ratio of activated carbon to the normal organic solids input. The existing carbon slurry inventory in the contactors which was brought forward to this study took 48 hours to reach equilibrium at the new conditions. This transition was accelerated on the third sampling day by reducing draft-tube slurry concentrations to the target range of 10 vol %/5 min (Figure 21). With the much lower rate of slurry production, the concentration was dropped too far in Unit #1

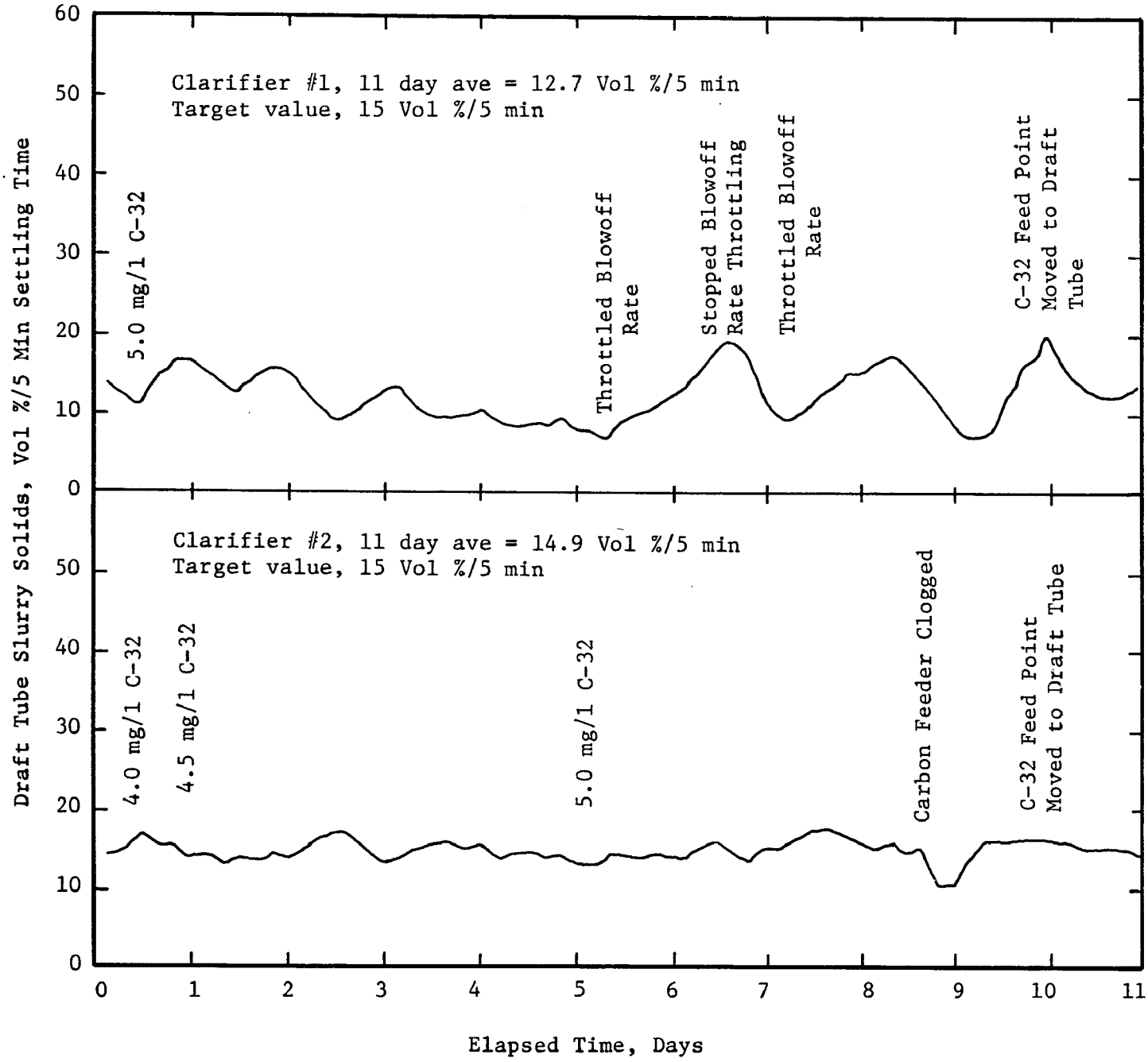
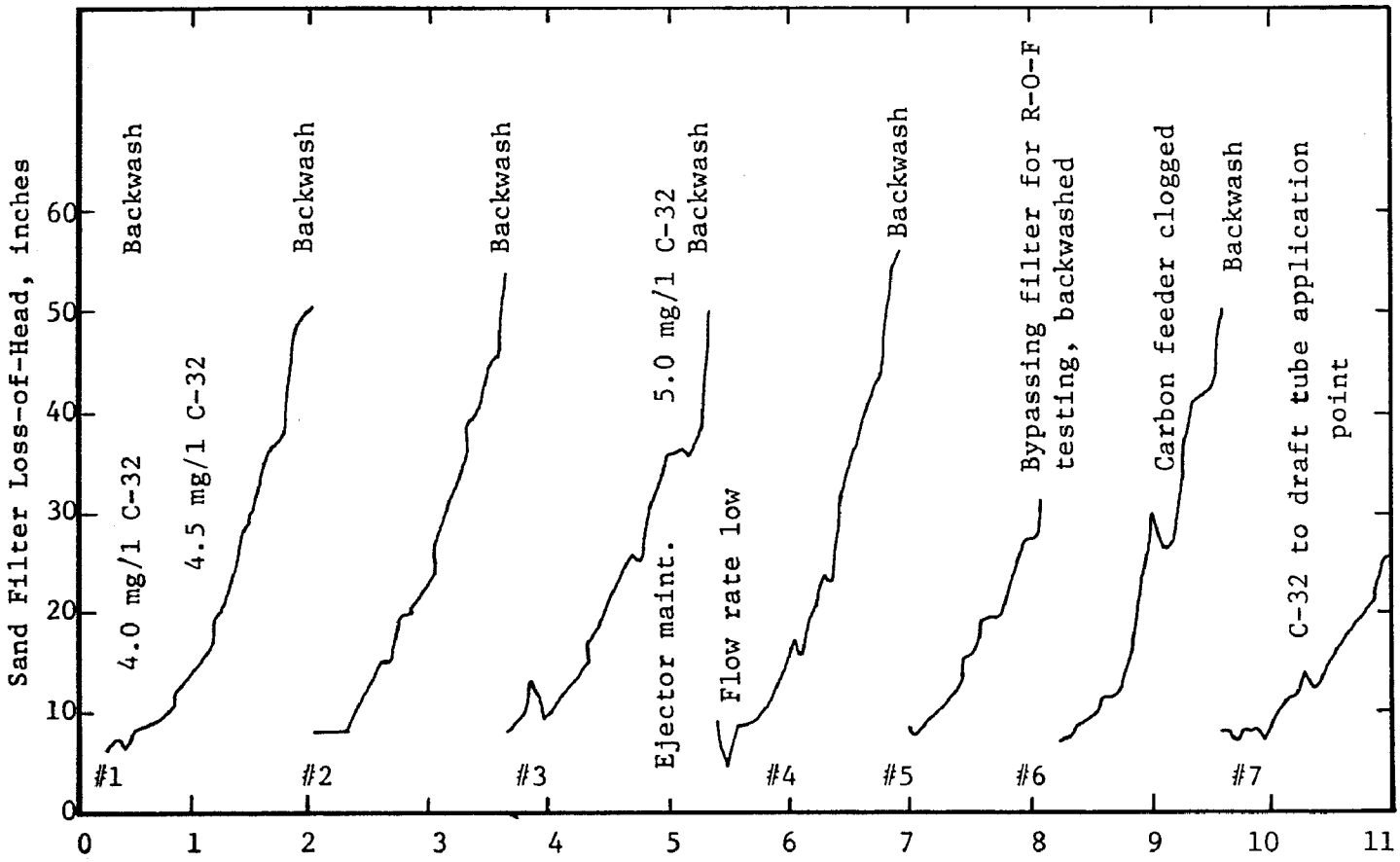


FIGURE 17: Settled slurry volume, Phase 4.



Performance Data

Run	#1	#2	#3	#4	#6	#7
Duration, hr	42	39	40	38	33	52
Filter rate, gpm	12	12	12	12	12	12
Surface loading, gpm/ft^2	3.0	3.0	3.0	3.0	3.0	3.0
Volume filtered, gal	30,200	28,100	28,800	27,400	23,800	37,400
Pilot plant flow rate, gpm	14	14	14	14	14	14
Clarifier overflow rate, gpm/ft^2	1.1	1.1	1.1	1.1	1.1	1.1

Total wash water used, 3690 gal or 2.1% at ave. rate of 22 gpm/ft^2

Note: Incomplete Run #5 ommitted from data table

FIGURE 18: Gravity Sand Filter Operating Data, Phase 4

TABLE 5

Phase 4, 24-hour Composite Sample Analyses

DATE - 1968	10-26,27	27,28	28,29	29,30	30,31*	31,11-1	1,2	2,3	3,4	4,5	5,6
Feed stream											
pH	7.9	7.8	8.0	7.9	7.9	8.0	8.0	7.8	7.8	7.8	7.9
Turb., JTU*	10	9	12	11	10/3.2	11/3.1	10/2.4	8/2.3	8/2.3	9/2.6	8/2.2
Sus. Solids, mg/l	10	6	9	11	7	7	11	5	7	7	12
COD filtered, mg/l	28.5	23.4	29.6	28.0	27.5	25.4	31.2	29.3	26.4	29.6	26.4
BOD, mg/l	10.6	10.6	-	10.8	13.3	12.3	11.4	6.4	9.1		11.7
Clarifier #1 Eff.											
pH	8.0	7.9	8.0	7.9	7.9	8.0	8.1	7.9	7.9	7.9	8.0
Turb., JTU*	15	9	12	9	9/1.2	7/1.1	8/0.66	10/1.2	7/1.4	13/1.1	9/1.1
Sus. Solids, mg/l	12	7	9	12	5	11	7	7	8	13	15
COD filtered, mg/l	10.9	9.4	9.4	9.8	9.8	9.4	10.4	11.4	9.8	11.3	10.8
BOD, mg/l	9.9	9.6	-	7.5	7.6	8.1	6.6	4.3	5.4	-	6.1
Clarifier #2 Eff.											
pH	8.0	7.9	8.0	7.9	7.8	8.0	8.0	7.9	7.9	7.9	7.9
Turb., JTU*	5	4	6	4	3/0.5	4/0.7	4/0.62	4/0.67	4/0.68	4/0.67	3/0.45
Sus. Solids, mg/l	3	3	4	3	2	4	4	3	4	3	4
COD filtered, mg/l	4.2	3.1	3.6	4.2	4.7	4.7	5.2	5.7	5.7	5.2	5.2
BOD, mg/l	6.9	2.8	-	2.5	1.4	1.6	1.8	1.5	1.7	-	1.6
Sand filter Eff.											
pH	7.9	7.9	7.9	7.8	7.8	7.9	8.0	7.8	7.8	7.8	7.8
Turb., JTU*	2	2	4	3	2/0.4	3/0.35	2/0.10	2/0.58	1/0.65	1/0.28	2/0.60
Sus. Solids, mg/l	3	2	2	2	2	2	1	2	1	2	3
COD unfilt., mg/l	5.7	4.7	5.2	5.7	5.7	5.2	5.7	6.1	6.6	6.1	5.7
COD filtered, mg/l	4.2	3.1	3.1	3.6	4.2	4.7	4.7	5.7	5.2	4.7	4.7
BOD, mg/l	3.3	4.5	-	4.8	5.4	6.3	7.2	4.0	5.4	-	6.1
COD Red'n, %**	85	87	90	87	85	82	85	81	80	84	82
BOD Red'n, %**	69	74	-	77	90	87	84	77	81	-	86
Carbon loading %	9.1	7.6	10.0	9.2	8.7	7.8	10.0	8.8	8.0	9.4	8.2

* Starting 10/30, Hach Model 2100 turbidimeter readings appear at the right of spectrophotometer determinations.
**Computed from lowest effluent value attained, disregards increases if any occuring in sand filter.

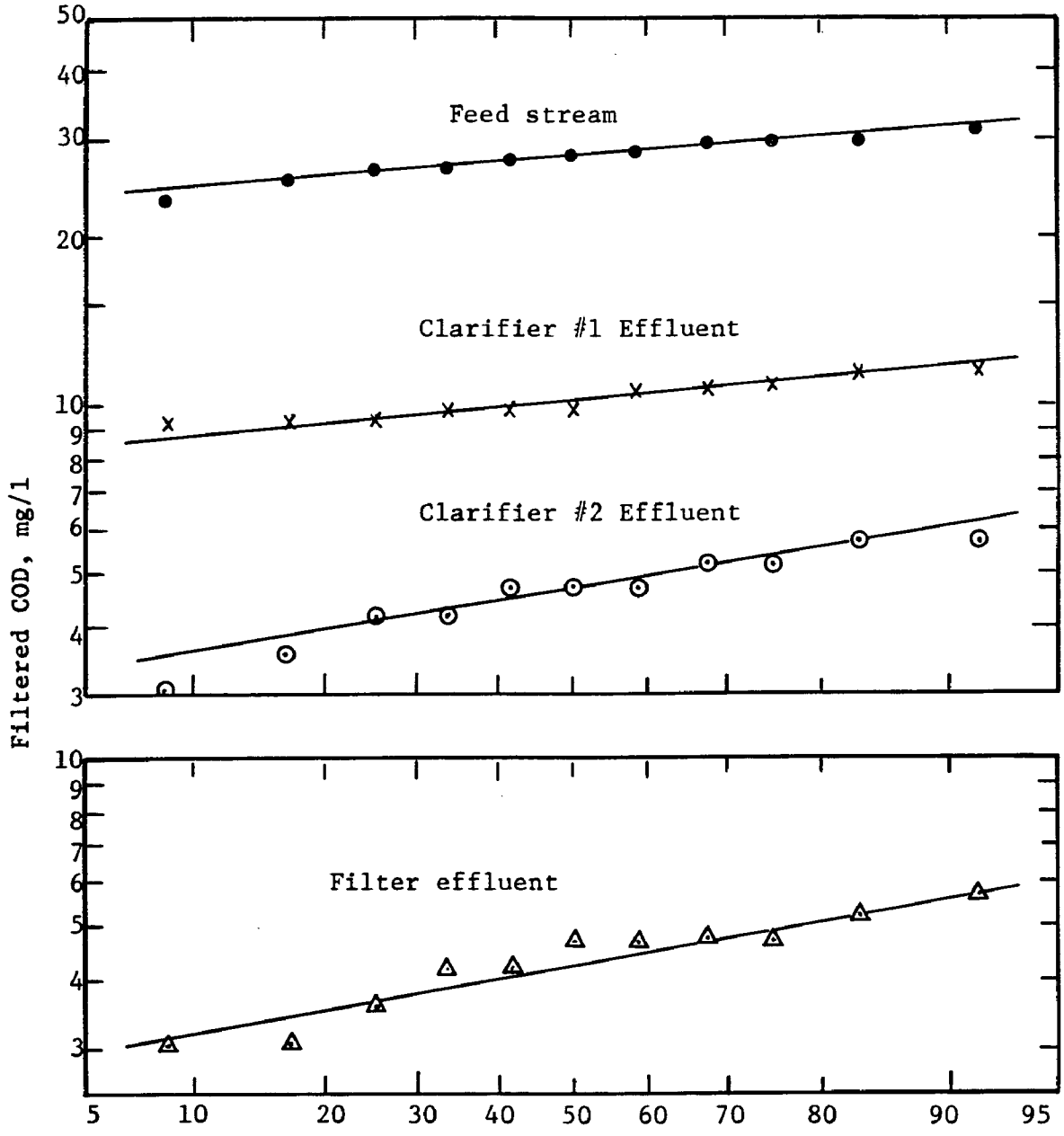


FIGURE 19: Composite sample COD, Phase 4.

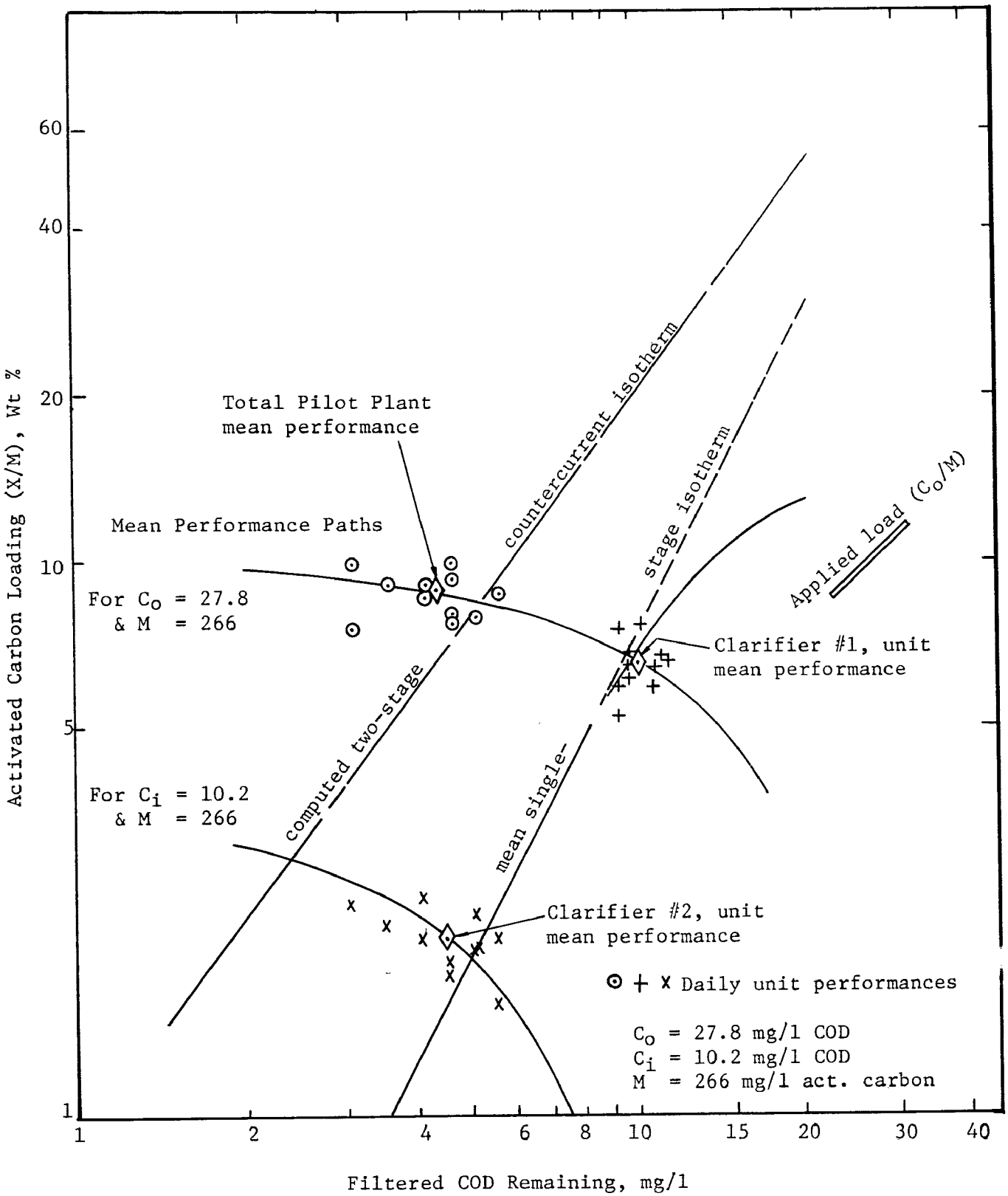


FIGURE 20: Adsorption Isotherm Analysis, Phase 4.

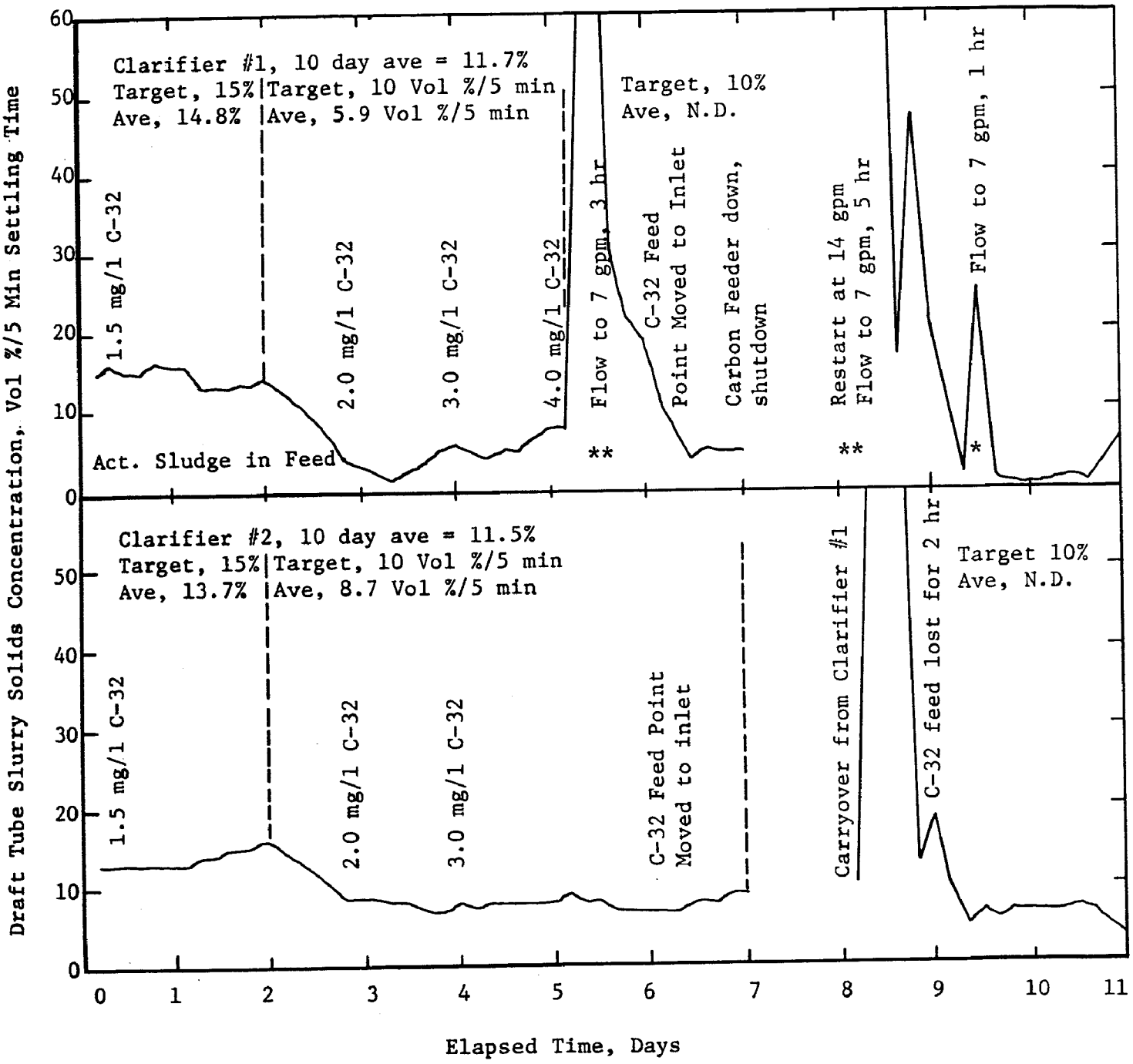


FIGURE 21: Settled slurry volume, Phase 5.

and took nearly two days to restore. The blowdown discharge pipes of both units were equipped with 5/16" drilled orifices to further reduce the volume per blowdown and permit more frequent cycling.

On the sixth sampling day activated sludge appeared in the feed stream for six hours, shooting the draft tube slurry in Unit #1 up to 92 vol %/5 min in 4.5 hours elapsed time. The unit was filling up with this poor floc and if the flow had not been cut to 7 gpm to reduce the solids input, slurry would have decanted to the second-stage unit. Extensive manually triggered blowdowns wasted much of this sludge volume and two hours after the feed stream cleared, the flow rate was restored to 14 gpm.

The seventh sampling period was uneventful with plant operation substantially restored to normal.

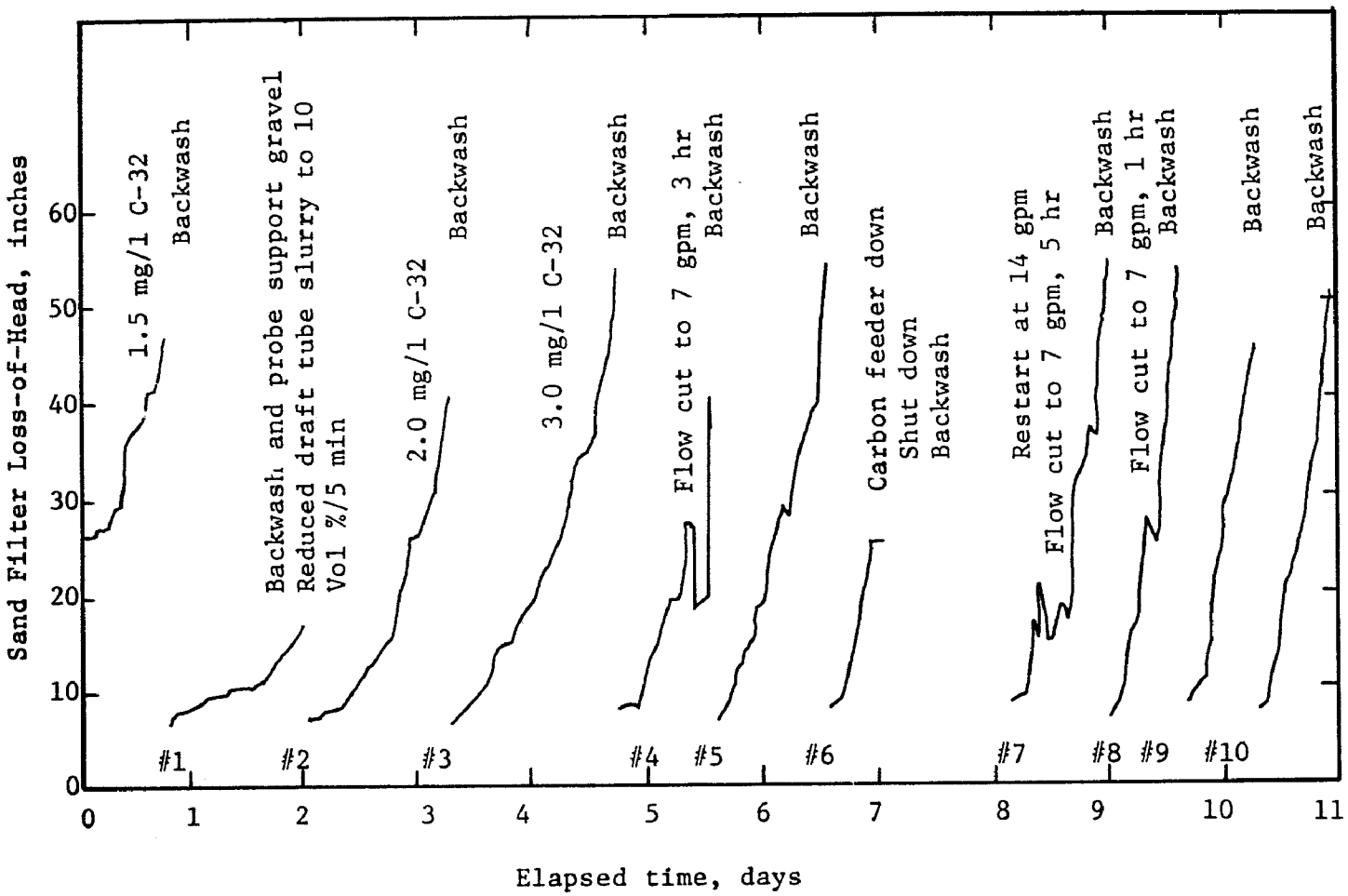
The eighth day started with a mechanical failure of the carbon feeder supplying Unit #2 which shut down the pilot plant. Start-up on the ninth day coincided with the reappearance of activated sludge in the feed stream which continued for nine hours. Within 2.5 hours, the poorly conditioned floc in Unit #1 had lost its characteristic black color due to dilution by the organic solids and started decanting into Unit #2. Unit #1 draft-tube slurry went up to 95 vol %/5 min and Unit #2 increased to 94 vol %/5 min.

Overflow of slurry continued until the flow rate was reduced to 7 gpm (for 5 hours) just one hour before the feed stream cleared. The slurry immediately settled down in Unit #2 but it required 1.5 hours of heavy blowdown to lower the slurry in Unit #2 at this flow rate. No draft tube slurry escaped from Unit #2 to the sand filter. Considering that all activated sludge solids carried over to Unit #2 had to be removed from the system by blowdown to Unit #1 (to maintain the carbon feed to Unit #1) and then be wasted from here, it is understandable that recovery of the system took 14 hours from the time the feed stream cleared. Recovery was not seriously affected by another short slug of sludge received on the tenth sample day.

The pilot plant was operated through one more 24-hr sampling period to compensate for the day lost by mechanical problems.

Sand filter performance (Figure 22) during this period was poor. Runs were short and wash water consumption jumped to 4.9 per cent.

Analytical data for the run (Table 6) reveal that the reduction in polyelectrolyte feed was accompanied by deterioration of the effluents of both clarifiers. The reduced coagulant dosage was inadequate to maintain the condition of floc brought forward from the preceding run, as well as the 67 mg/l of new carbon feed. Improvement was noted after the dosage was increased to 4.0 mg/l to Unit #1 on the sixth day. Unit #2 coagulant dosage was 3.0 mg/l at this time and this rate was maintained throughout the balance of the run.



Performance Data

Run	#2	#3	#4	#5
Duration, hr	30	35	20	24
Filter rate, gpm	12	12	12/7	12
Surface loading, gpm/ft^2	3.0	3.0	3.0/1.75	3.0
Volume filtered, gal	21,600	25,200	13,500	17,300
Pilot plant flow rate, gpm	14	14	14/7	14
Clarifier overflow rate, gpm/ft^2	1.1	1.1	1.1/0.55	1.1

Run	#7	#8	#9	#10
Duration, hr	21	15	14	16
Filter rate, gpm	12/7	12/7	12	12
Surface loading, gpm/ft^2	3.0/1.75	3.0/1.75	3.0	3.0
Volume filtered, gal	13,600	10,500	10,100	11,600
Pilot plant flow rate, gpm	14/7	14/7	14	14
Clarifier overflow rate, gpm/ft^2	1.1/0.55	1.1/0.55	1.1	1.1

Total wash water used, 6070 gal or 4.9% at ave. rate of 20.5 gpm/ft^2

Note: Incomplete Runs #1 and #6 omitted from data table.

FIGURE 22: Gravity Sand Filter Operating Data, Phase 5.

TABLE 6

Phase 5, 24-hour Composite Sample Analyses

DATE - 1968	11-6,7	7,8	8,9	9,10	10,11	11,12	12,13	14,15	15,16	16,17
Feed stream										
pH	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
Turb., JTU*	10/2.8	10/3.0	9/2.5	9/2.4	8/2.0	70/23	8/2.5	95/29	35/12	10/3.5
Sus. Solids, mg/l	9	9	14	8	7	69	6	72	25	8
COD filtered, mg/l	24.8	25.9	25.9	26.4	24.2	27.7	25.6	28.6	27.4	29.0
BOD, mg/l	12.3	10.1	9.7	8.2	11.5	-	13.3	30	28.4	18.4
Clarifier #1 Eff.										
pH	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Turb., JTU*	34/2.5	50/2.8	40/2.6	43/3.0	38/2.7	13/3.1	17/2.8	115/21	34/5.7	11/2.2
Sus. Solids, mg/l	23	51	53	29	40	13	24	131	28	12
COD filtered, mg/l	12.2	14.6	16.3	18.7	16.5	17.9	19.0	17.7	16.6	21.6
BOD, mg/l	9.8	8.0	8.1	6.4	9.5	-	10.3	23	16.3	14.5
Clarifier #2 Eff.										
pH	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Turb., JTU*	5/1.1	6/0.86	5/1.0	6/1.0	4/0.90	5/1.0	3/0.90	10/2.3	11/1.5	31/5.4
Sus. Solids, mg/l	6	5	11	7	5	7	5	11	6	26
COD filtered, mg/l	6.8	10.0	10.5	12.5	10.7	11.2	12.0	10.8	9.6	13.6
BOD, mg/l	3.0	3.2	2.5	3.6	2.3	-	2.1	5.7	2.1	3.1
Sand filter Eff.										
pH	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Turb., JTU*	2/0.71	3/0.81	3/0.76	2/0.76	2/0.75	2/0.74	2/0.82	6/2.0	2/1.6	3/1.0
Sus. Solids, mg/l	3	2	6	3	2	4	4	5	4	4
COD unfilt., mg/l	7.7	10.5	10.9	13.0	11.2	12.1	12.4	15.0	14.1	14.0
COD filtered, mg/l	5.9	9.1	10.0	12.1	10.3	10.7	11.0	9.6	9.1	13.6
BOD, mg/l	4.4	3.9	4.6	4.8	4.9	-	6.5	6.9	2.3	5.4
COD Red'n, %**	76	65	61	54	57	61	57	66	67	53
BOD Red'n, %**	76	68	74	56	80	-	84	-	93	83
Carbon loading %	28.2	25.1	23.7	21.3	20.8	25.4	21.8	28.4	26.2	22.0

* Hach Model 2100 Turbidimeter readings appear at the right of spectrophotometer determinations.
**Computed from lowest effluent value attained, disregards increases if any occuring in sand filter.

Results for the first two sample days are considered transitional and have been discarded in evaluating performance. The COD of samples collected from various points in the system is given in Figure 23. Mean reduction through the plant was 60 per cent. Based on limited representative data, BOD removal was about 83 per cent.

The isotherm analysis of Figure 24 for this run shows a system performance equivalent to that computed for two-stage countercurrent adsorption..

First-stage performance equivalent to single-stage treatment with fresh carbon was achieved, even though partially loaded carbon was used here. The COD loading obtained on the carbon in this unit was 13.1 per cent by weight in addition to the 10.0 per cent achieved in the second-stage contactor. Including the small removal across the filter, total carbon loading was 24.0 per cent by weight.

The solids content of blowdown from Units #1 and #2 was 21.5 and 16.7 per cent by weight, respectively, and system blowdown approximated 0.05 per cent of the throughput volume.

Phase 6 - In this investigation, a single contactor-clarifier and the filter were operated for ten days at 14 gpm and a carbon dosage of 140 mg/l to enable comparison of single- and two-stage treatment under closely similar conditions.

Polymer dosage was 4.0 mg/l initially, but was increased to 4.5 mg/l during the first day. Continuing solids carry-over prompted an increase to 5.0 mg/l on the sixth day. On the last day, exploratory reduction of the dosage to 3.0 mg/l resulted in rapid deterioration of floc quality and the feed was increased again to the end of the run.

Slurry control (Figure 25) was complicated by clogging problems which were finally overcome by removal of the blowoff orifice. Sampled near the end of the run, the solids content of system blowdown was 12.6 per cent by weight and blowdown volume was about 0.1 per cent of the wastewater treated.

Settling rates of 10-12 in./min for the fragile and readily deflocculated draft-tube slurry were measured on the sixth day, equivalent to overflow rates of 6.2-7.5 gpm/ft^2.

Filter runs (Figure 26) averaged 28 hr. The relatively high wash water consumption of 4.8 per cent is at least partially attributable to modified procedure instituted during this run when the presence of mud balls was noted. The latter most likely represented material accumulated over the entire period of plant operation rather than being unique to this run.

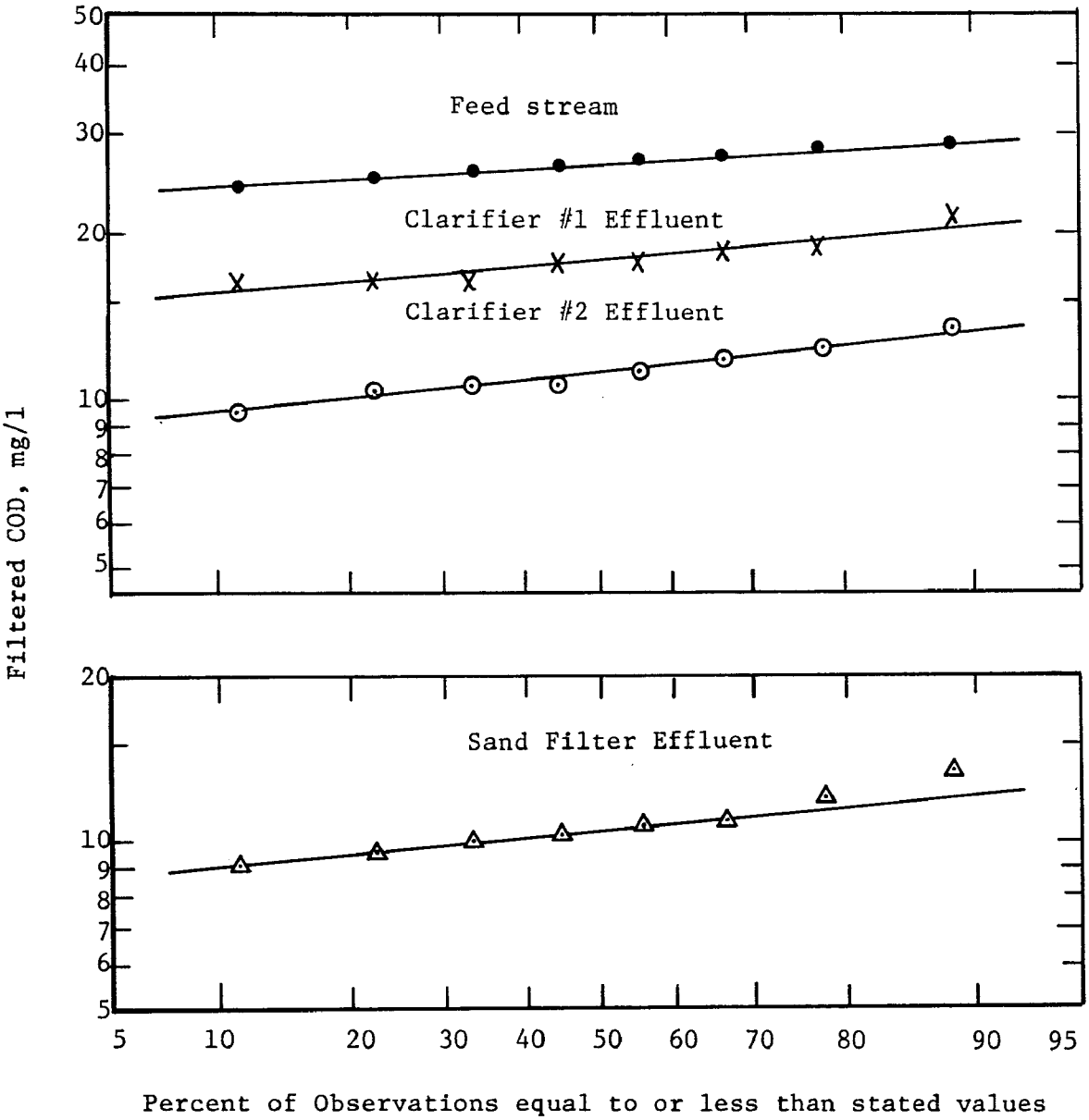


FIGURE 23: Composite-sample COD, Phase 5.

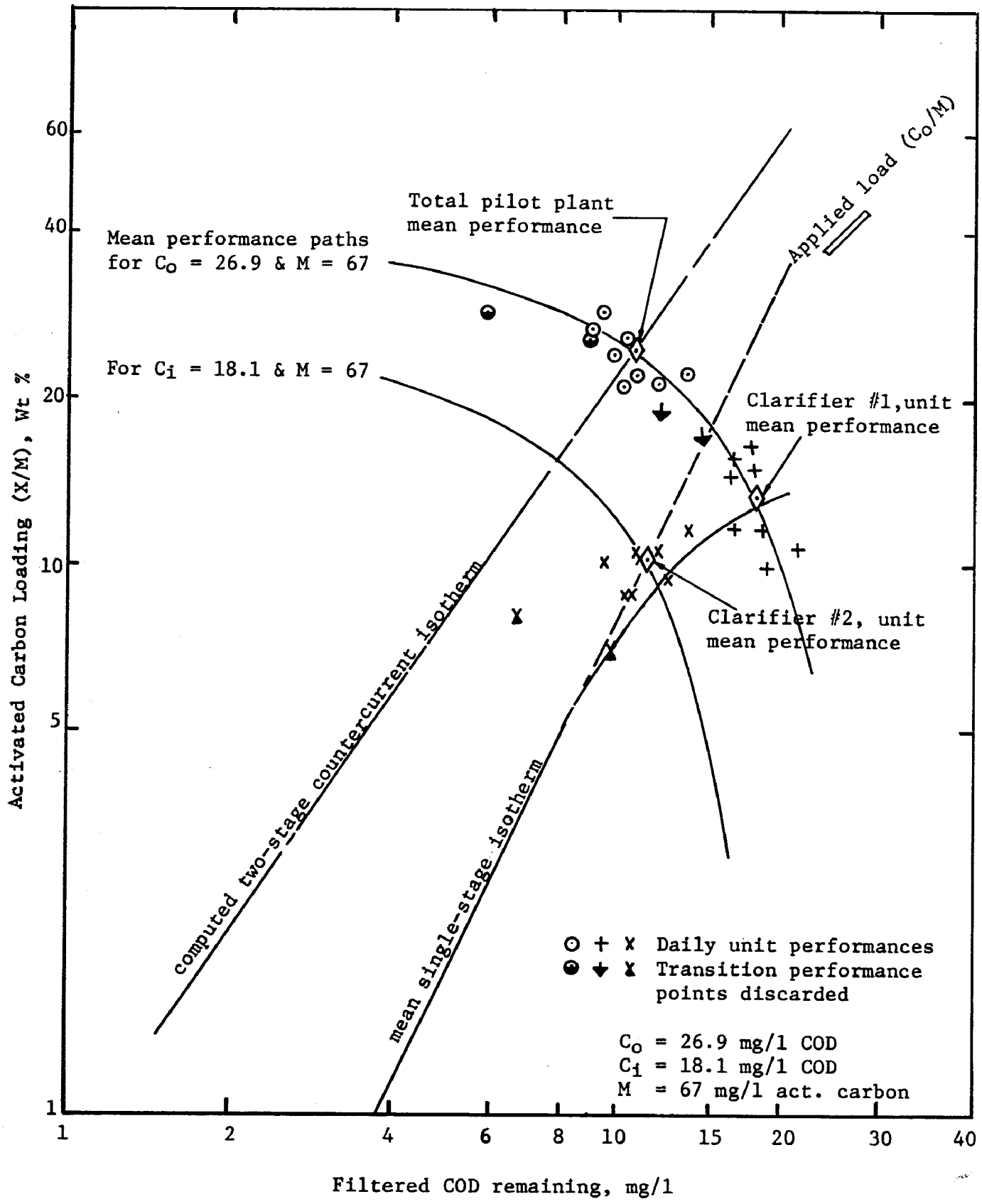


FIGURE 24: Adsorption Isotherm Analysis, Phase 5

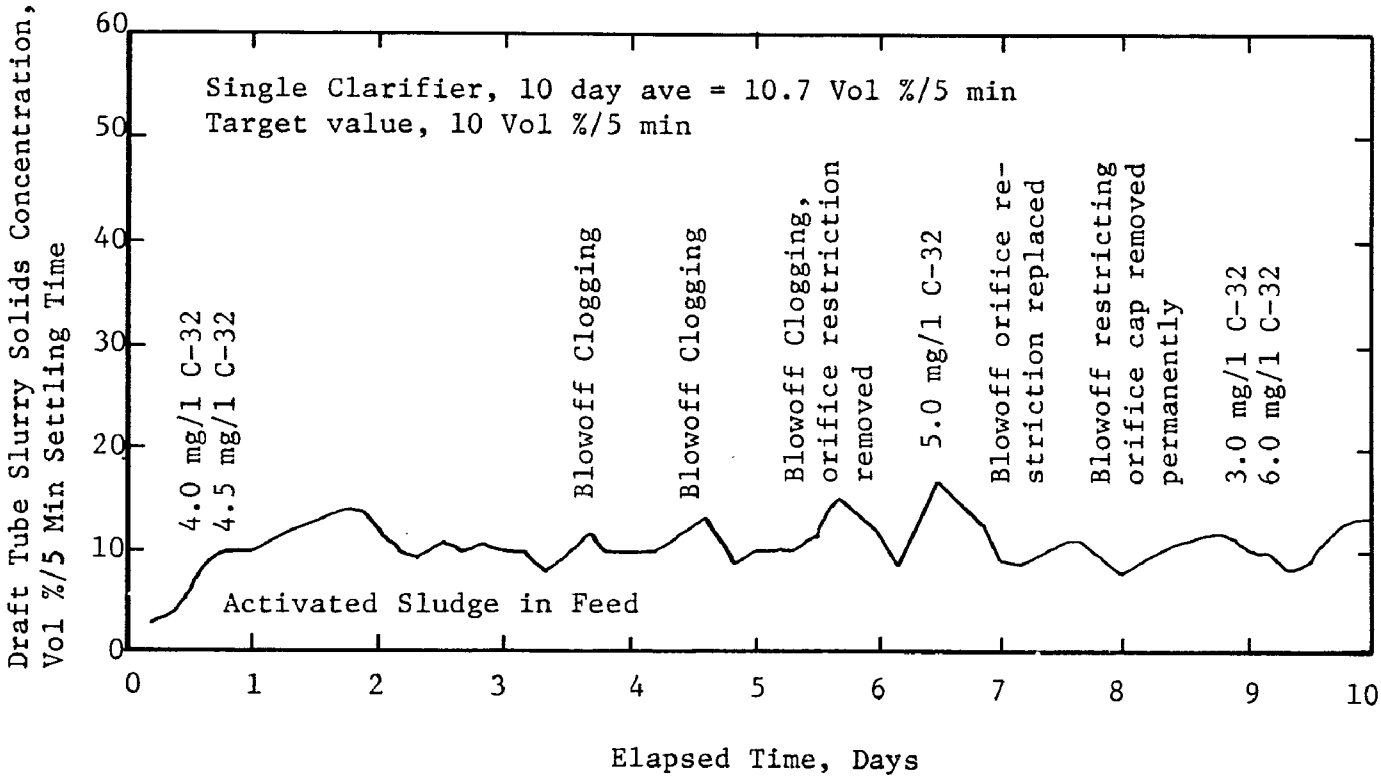
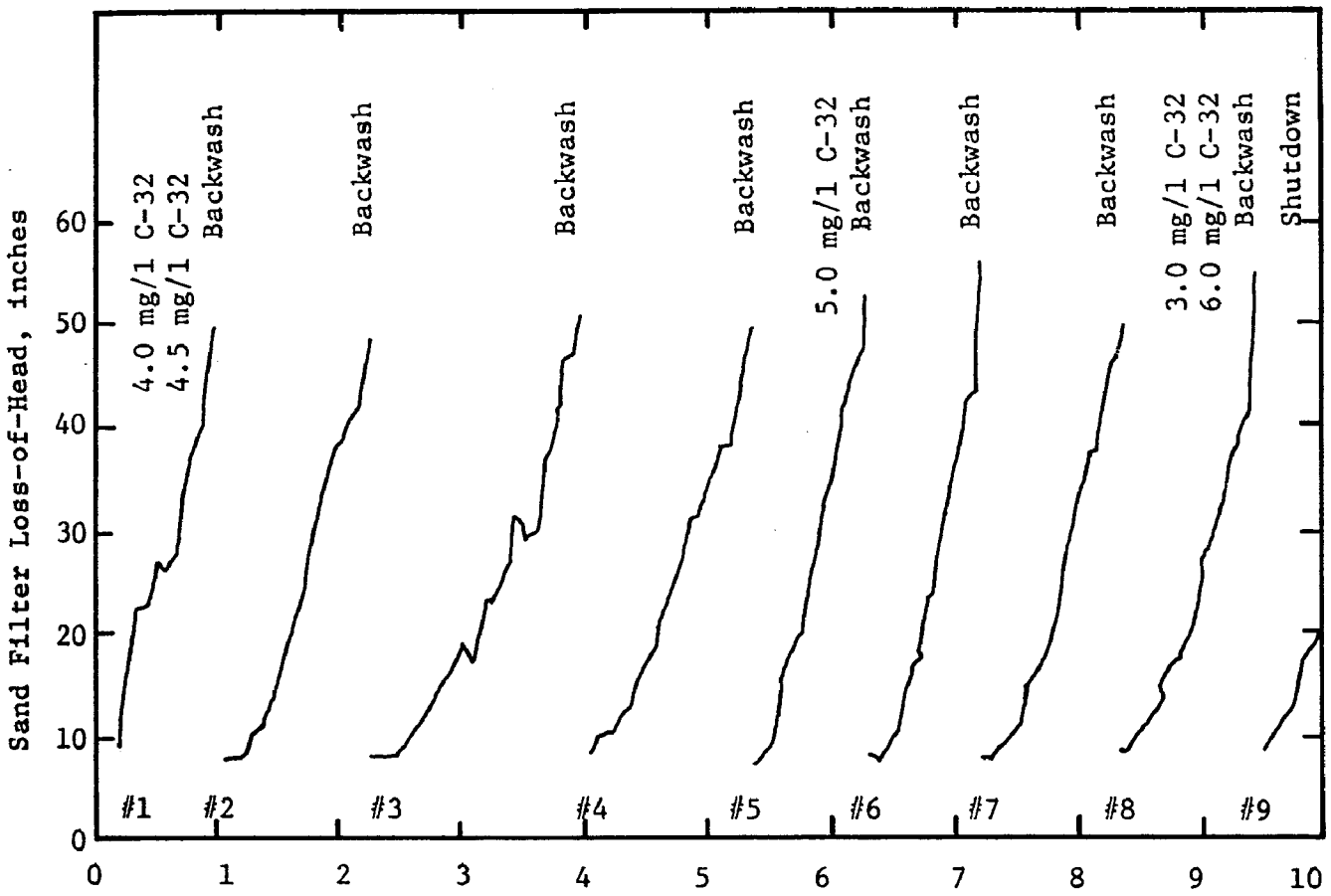


FIGURE 25: Settled Slurry Volume,
Phase 6



Performance Data

Run	#1	#2	#3	#4
Duration, hr	20	29	41	32
Filter rate, gpm	12	12	12	12
Surface loading, gpm/ft^2	3.0	3.0	3.0	3.0
Volume filtered, gal	14,400	20,900	29,500	23,000
Pilot plant flow rate, gpm	14	14	14	14
Clarifier overflow rate, gpm/ft^2	1.1	1.1	1.1	1.1

Run	#5	#6	#7	#8
Duration, hr	23	23	28	26
Filter rate, gpm	12	12	12	12
Surface loading, gpm/ft^2	3.0	3.0	3.0	3.0
Volume filtered, gal	16,600	16,600	20,200	18,700
Pilot plant flow rate, gpm	14	14	14	14
Clarifier overflow rate, gpm/ft^2	1.1	1.1	1.1	1.1

Total wash water used, 7,700 gal or 4.8% at ave. rate of 23.5 gpm/ft^2

Note: Incomplete Run #9 omitted from data table.

FIGURE 26: Gravity sand filter operating data, Phase 6.

Analytical data for the run (Table 7) disclosed that filter performance was little changed from the previous study. Effluent suspended solids were relatively high and BOD increased significantly across the unit.

Clarifier effluent suspended solids averaged 14 mg/l up to the sixth sampling period when the polymer dosage was increased. The average dropped to 8 mg/l for the balance of the run which included a 2-hr influx of activated sludge in moderate concentration which was handled without difficulty.

COD at various points in the treatment system is given in Figure 27. Mean overall reduction was 65 per cent and a BOD removal of 79 per cent was achieved across the clarifier.

The isotherm analysis of Figure 28 places the mean plant performance well above that predicted. The observed carbon loading was 13.1 per cent by weight, 130 per cent of that predicted for single-stage treatment and 89 per cent of that calculated for a two-stage system. The 9.7 mg/l of residual COD represents a 30 per cent improvement over the effluent quality predicted by the mean-value isotherm and approaches the theoretical effluent concentration of 7.5 mg/l for two-stage countercurrent treatment.

Supplemental Investigations

Additional studies conducted during the pilot plant program included evaluation of the effect of observed temperature variation on system performance and its analysis; consideration of adsorption theory; limited review of the influence of the treatment process on nutrients, color, and surfactants; and a comparison of the results of two methods of turbidity measurement.

Temperature - Feed-stream temperature was measured hourly during much of pilot plant program. Data presented in Figure 29 for two 60-hr periods separated by four weeks show appreciable differences in range and mean temperature. Although the adsorption process is temperature sensitive, it was not expected that the observed temperature changes over the period of plant operation would significantly affect the results.[9] However, the validity of this assumption was assessed by a simple laboratory experiment.

Using procedure for determination of equilibrium COD described previously, feed-stream samples were contacted with carbon at temperatures of 75, 80, and 85°F. Observed differences in equilibrium COD concentration in jars of identical makeup were within experimental error and no influence of temperature over the range studies was evident. It was concluded, therefore, that adjustment of the equilibrium adsorption data of this study for temperature was not indicated.

TABLE 7

Phase 6, 24-hour Composite Sample Analyses

DATE - 1968	11-17/18	18,19	19,20	20,21	21,22	22,23	23,24	24,25	25,26	26,27
Feed stream										
pH	7.7	7.7	7.8	7.7	7.7	7.7	7.7	7.7	7.8	7.6
Turb., JTU*	10/3.3	9/3.0	12/3.7	9/3.6	11/3.8	10/2.9	17/6.7	10/2.6	12/3.7	11/3.1
Sus. Solids, mg/l	9	10	10	11	11	10	16	7	9	8
COD filtered, mg/l	27.0	27.7	29.0	26.9	27.4	28.2	28.2	27.7	31.2	31.2
BOD, mg/l	14.7	-	11.6	15.2	14.2	13.2	17.9	12.1	-	12.8
Clarifier #1 Eff.										
pH	7.8	7.8	7.9	7.8	7.8	7.8	7.8	7.8	7.9	7.8
Turb., JTU*	14/2.6	10/1.6	15/1.9	12/2.6	10/2.0	7/1.6	10/2.0	9/1.5	11/2.0	6/2.0
Sus. Solids, mg/l	11	17	16	18	10	8	8	6	9	11
COD filtered, mg/l	10.6	9.9	9.9	9.5	10.4	10.4	9.4	9.9	6.0+	11.4
BOD, mg/l	2.7	-	3.7	4.2	2.7	2.8	2.9	1.6	-	2.2
Sand filter Eff.										
pH	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.9	7.8
Turb., JTU*	3/1.1	3/1.5	3/1.0	2/1.4	3/1.4	3/1.2	3/1.3	3/1.1	3/1.5	3/1.5
Sus. Solids, mg/l	3	5	4	4	3	3	2	3	4	8
COD unfilt., mg/l	11.4	12.0	10.4	9.9	11.2	10.8	9.9	10.4	6.4+	12.9
COD filtered, mg/l	10.2	9.9	9.1	8.7	9.5	10.4	8.4	9.4	5.5+	11.4
BOD, mg/l	4.5	-	5.7	6.4	6.0	6.3	7.2	7.7	-	7.8
COD Red'n, %**	62	64	69	68	65	63	70	66	82+	64
BOD Red'n, %**	82	-	68	72	81	79	84	87	-	83
Carbon loading, %	12.0	17.8	14.2	12.9	12.8	12.7	14.1	13.1	18.4	14.1

* Hach Model 2100 Turbidimeter readings appear at the right of spectrophotometer determinations.
**Computed from lowest effluent value attained, disregards increases if any occuring in sand filter.
+ Data discarded, analytical problem.

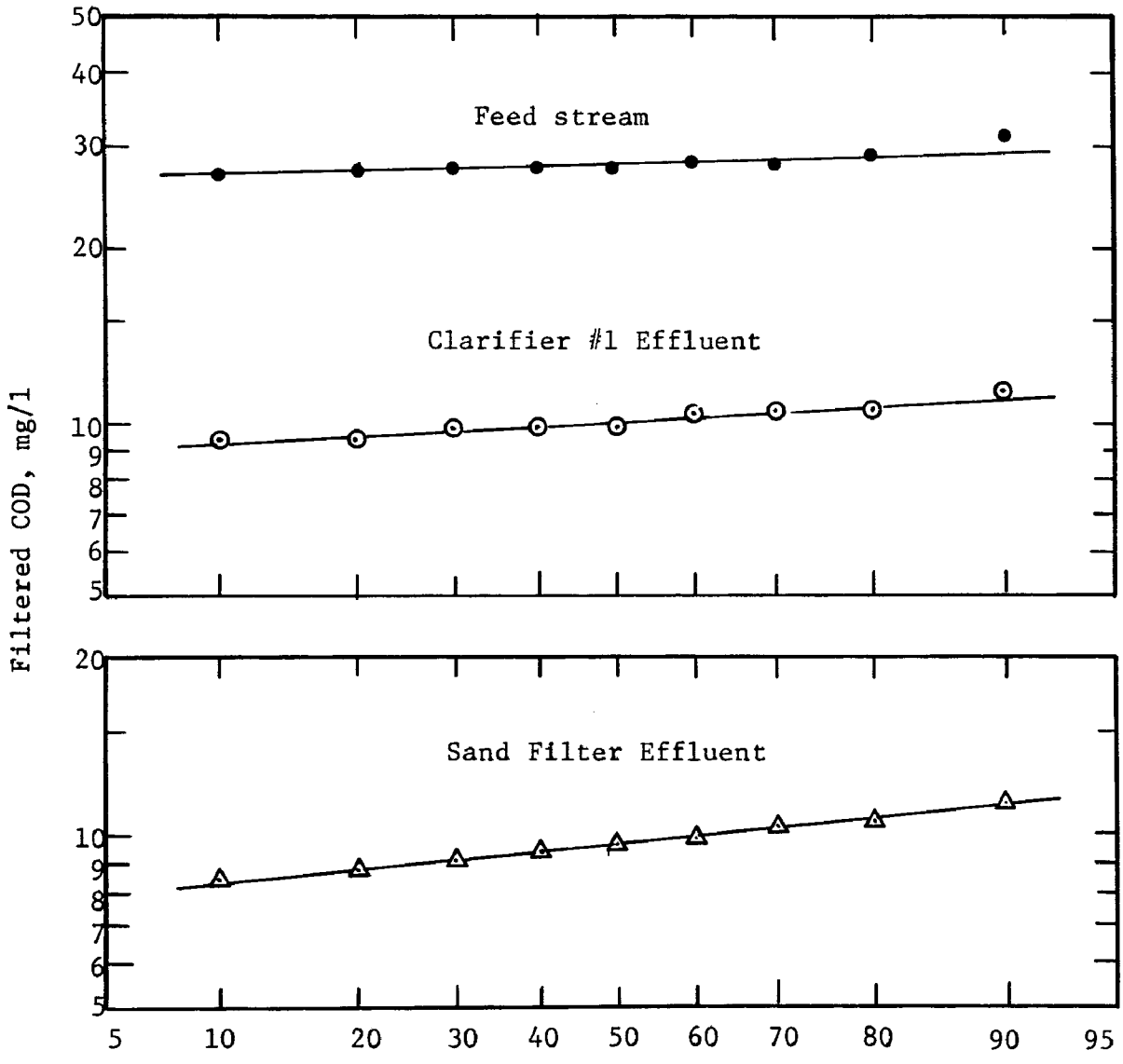


FIGURE 27: Composite sample COD, Phase 6.

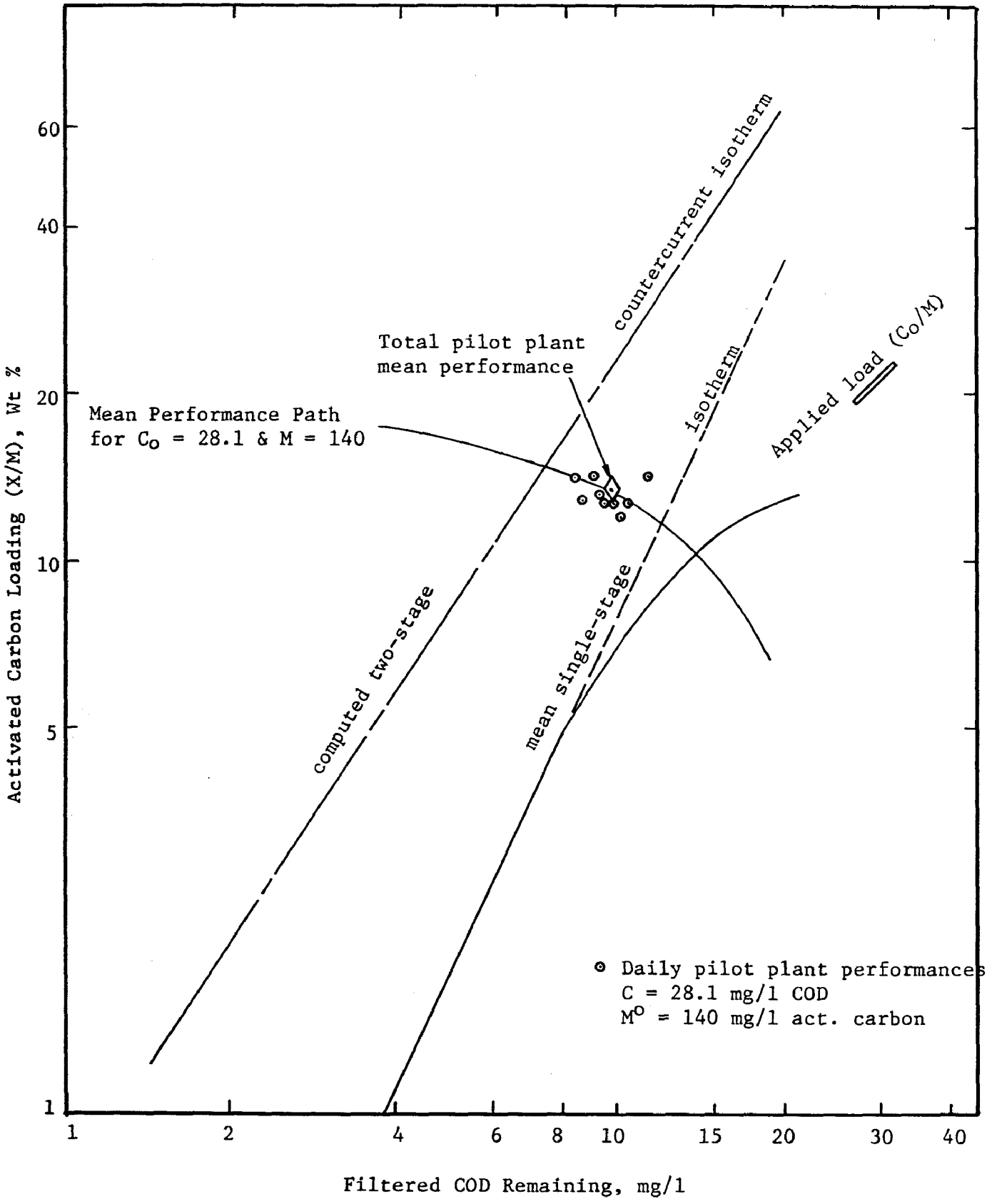
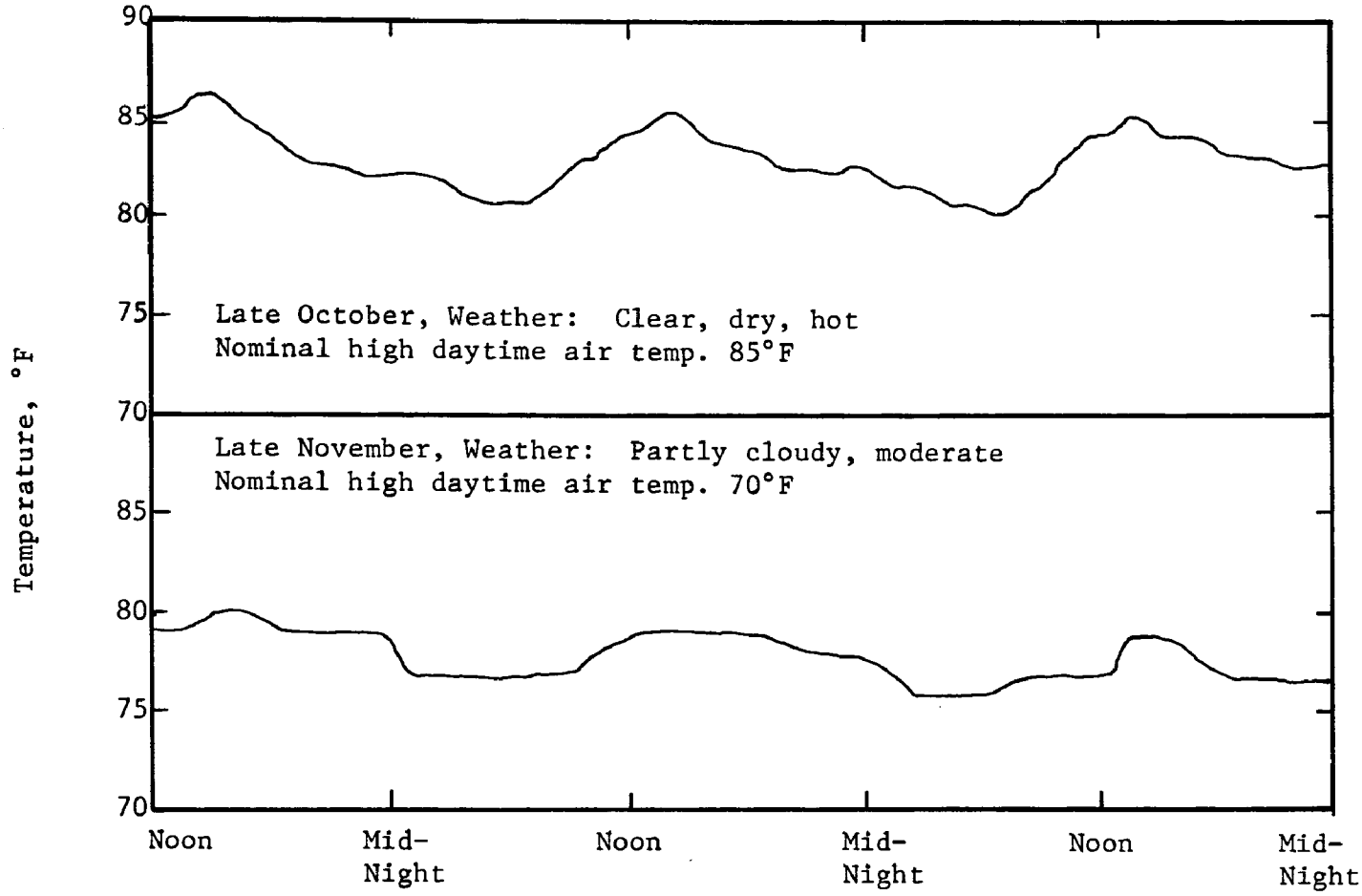
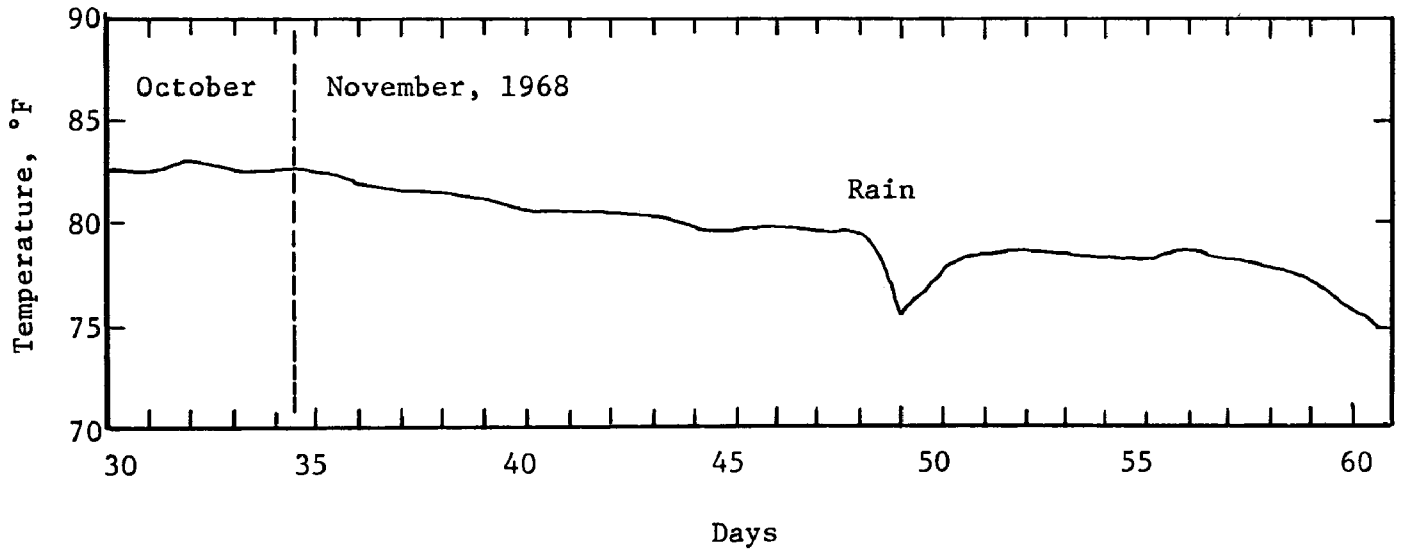


FIGURE 28: Adsorption Isotherm Analysis,
Phase 6.



Representative diurnal feed stream temperature variations



Daily average feed stream temperature, partial record

FIGURE 29: Feed-stream temperature variation.

Adsorption Theory - With rare exception, single-stage laboratory batch isotherms developed on the sewage plant effluent showed a COD/carbon load limit of 15 per cent by weight. The data of Figure 2 are an exception and more typical isotherms are portrayed in Figures 3, 4, and 5. Most of the individual isotherms leveled off on the low carbon dosage end of the curve at or just under 15 per cent load. This limitation is also evident in the mean single-stage isotherms used in evaluating pilot plant performance.

Only the low-level dosage study (Phase 5) was characterized by a carbon feed low enough to determine if loading in the pilot system could surpass the limit implied by the single-stage isotherms. The results (Figure 24) show conclusively that higher loading was possible. Mean loading was 24 per cent by weight, with daily performance ranging between 21 and 28.5 per cent.

A laboratory generated isotherm featuring several points for low carbon dosage (Figure 30) confirms the 15 per cent load limit.

The empirical Freundlich equation used in this work is not a preferred model for basic adsorption research because it is not based upon theory and is unable to cope with limitations such as encountered here. Its practical usefulness, however, is evidenced in the present study.

The Langmuir and the Brunauer-Emmett-Teller (B.E.T.) adsorption models are used in basic studies. The Langmuir equation is valid only for single-layer adsorption and assumes that maximum loading is reached when a single complete layer of adsorbate molecules is formed on the surface of the adsorbent. It is

$$X = \frac{X_m bC}{(1+bC)}$$

in which X is the adsorbate loading per unit weight of carbon at the equilibrium concentration C in solution. X_m is the ratio of adsorbate to carbon when the former has formed a complete monolayer on the carbon surface and b is a constant related to the energy of adsorption.

The B.E.T. equation assumes multilayer adsorption and further that a given layer need not be completed prior to initiation of subsequent layers. In one form it is written

$$X = \frac{ACX_m}{[C_s-C][1+(A-1)\frac{C}{C_s}]}$$

where X, X_m, and C are as defined above; A is an energy constant; and C_s is the adsorbate saturation concentration. As this work deals with a mixture of unidentified adsorbate compounds of unknown saturation concentration, application of the B.E.T. model was not attempted.

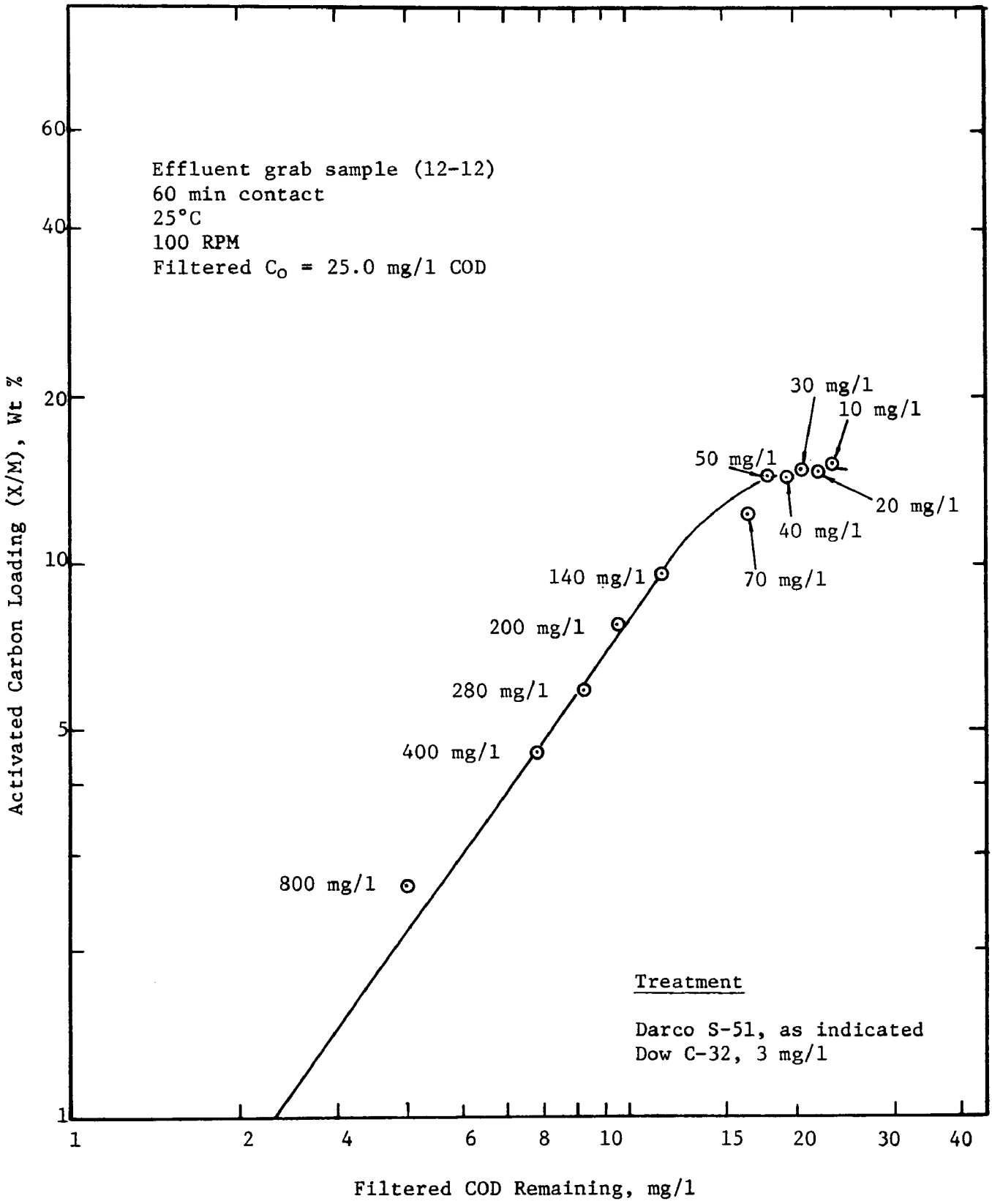


FIGURE 30: Freundlich adsorption isotherm with emphasis on the low carbon dosage end of the curve.

The Langmuir equation may be linearized as follows:

$$\frac{C}{X} = \frac{C}{X_m} + \frac{1}{bX_m}$$

Figure 31, a graphical presentation of the eleven data points of Figure 30 in this form, indicates that only the low-dosage values are described by this type of adsorption isotherm. The monolayer COD capacity, X_m, calculated from the slope of the dashed line of Figure 31 is 14.5 per cent by weight, a value confirmed by several other similar low-dosage isotherms and implied closely by the Freundlich model.

Also plotted in Figure 31 are the mean pilot plant results. The original COD concentration for the various studies varied slightly, invalidating direct comparison, but the relationships shown are informative. Pilot plant performance at carbon dosages of 140, 146, and 266 mg/l (including the single-clarifier study) all approach the apparent monolayer load capacity at equilibrium conditions unobtainable in batch laboratory experiments. Of interest is the fact that plant performance at a carbon dosage of 67 mg/l, a more favorable original COD-to-carbon ratio, falls in the region of multilayer adsorption to the right of the dashed line.

Nutrients - Feed-stream phosphorus and ammonia nitrogen concentrations were expected to be unaffected by the treatment process. These were monitored for one week during the pilot plant program and the results (Table 8) confirm this expectation as concerns phosphorus. Ammonia nitrogen, on the other hand, increased an average of 2.7 mg/l. A clear explanation for this is lacking and the point was not pursued. The sewage plant can chlorinate at various points in the treatment process. It is possible that the pilot plant feed contained unsuspected chloramines which affected analysis by direct Nesslerization.

Chemical feeder dilution water from the test facility well contains as much as 7 mg/l of nitrate nitrogen. However, the dilution factor of 160 to 1 in the pilot plant reduces nitrogen contribution from this source to an inconsequential level. Biological reduction of nitrate or nitrite from whatever source is a possibility.

The polymer coagulant used is a polyamine, but tests indicated it was not directly responsible for the observed results.

Color and Surfactants - During the pilot plant program, a limited number of grab samples were analyzed for color. The apparent color of the feed stream averaged 18 units, Clarifier #1 effluent averaged 4 units, and the average color of effluents from Clarifier #2 and the filter was 2 units.

The surfactant removal capabilities of activated carbon are well known and this subject was not investigated quantitatively in this work.

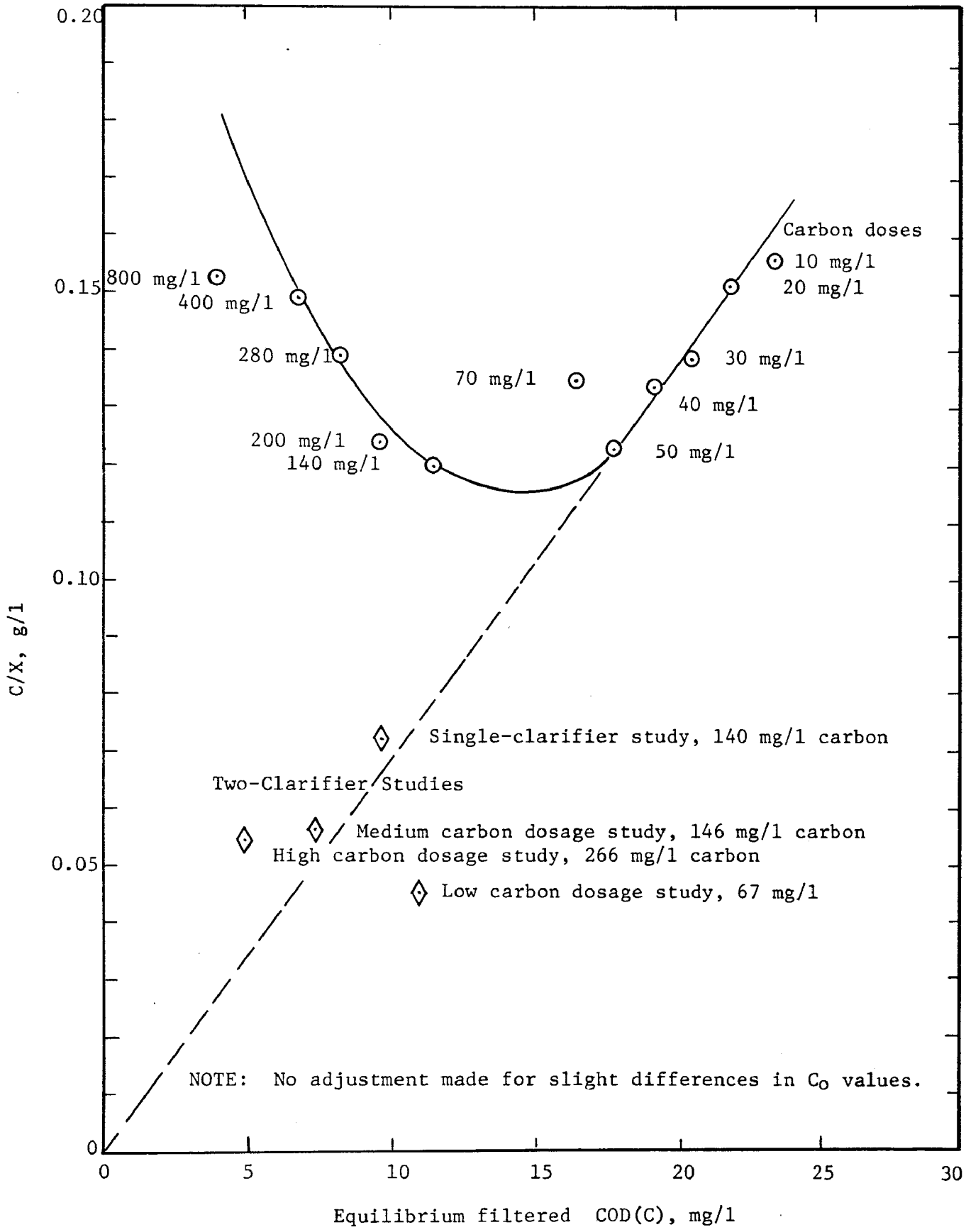


FIGURE 31: Langmuir single-stage adsorption isotherm.

TABLE 8

Phosphorus and Ammonia Nitrogen

Content of 24-hr composite samples collected during the Phase-6 (single-stage) pilot plant program.

DATE: Nov. 1968	20-21	21-22	22-23	23-24	24-25	25-26	26-27	Ave.
P, mg/l								
Feed stream	10.1	11.3	12.1	10.8	10.8	12.3	12.4	11.4
Clarifier Eff.	9.5	11.1	11.7	11.7	10.7	12.4	10.6	11.1
Filter Eff.	9.1	11.1	11.7	11.7	10.7	11.7	10.2	10.9
NH_3-N, mg/l								
Feed stream	18.0	12.8	18.5	17.3	16.3	18.0	12.4	16.2
Clarifier Eff.	18.7	15.3	30.5*	18.8	17.0	19.3	18.8	18.0
Filter Eff.	20.0	15.8	19.3	18.8	16.3	21.6	20.2	18.9

*Questionable value, discarded.

Foam to a depth of 2-3 inches existed much of the time in the inlet chamber of the first-stage clarifier with the ejector and feed lines jetting into it constantly. This trapped amounts of feed-stream solids and recycled carbon floc but was easily dissipated by occasional brushing. No other point in the treatment system foamed. Filter effluent shaken vigorously in a stoppered bottle did not foam. It was concluded from these indications of very low surfactant concentrations that quantitative study of this point was of no practical value.

Turbidity Measurement - When the project was initiated it was decided to use a standardized spectrophotometer for turbidity analysis. Part way through the program it was requested that turbidity also be determined with a Hach Model 2100 Laboratory Turbidimeter because this instrument had been used during other FWQA treatment studies with powdered activated carbon and it was recognized that results from the two methods of analysis would undoubtedly differ.

The Hach instrument was used at the pilot plant site for determining the turbidity of the four principal streams every two hours and that of the composite samples each day before they were taken to the laboratory where spectrophotometer turbidities were then measured. Data for the composites are reported in Tables 5, 6, and 7. Inasmuch as they contribute nothing to data comparison, the bihourly results are not reported here.

Feed-stream and filter effluent turbidities were produced by suspended matter containing no activated carbon, whereas clarifier-effluent turbidities resulted primarily from the presence of black flocculated carbon. Initially, it was felt that light absorption by the carbon floc would result in low light transmittance and turbidity readings as determined by spectrophotometer. However, it developed that spectrophotometer turbidities were of the same order of magnitude as the suspended solids content of all four sample streams. Both values were reported to the nearest whole unit and frequently were in exact agreement.

The Hach instrument measures scattered light and is standardized against a solidified Formazin suspension of known turbidity; hence its readings may be quite different from those obtained by light transmittance or absorption. Hach JTU readings ranged from 29 to 32 per cent of the spectrophotometer turbidities for feed-stream samples and 23 to 45 per cent for filter effluent. Carbon-bearing samples, however, produced readings only 12 to 19 per cent of the spectrophotometer turbidities. Thus, Hach readings were reduced by about 50 per cent when carbon floc was present.

Comparison of the two sets of readings based on mean values for each pilot plant run (Table 9) also shows a trend of increasingly higher Hach readings as time elapsed which might have resulted from dust accumulating in the instrument's optical system and increasing light scatter.

TABLE 9

Ratio of Spectrophotometer to Hach Turbidities

Pilot Plant Program	Feed Stream	1st-stage Clarifier Effluent	2nd-stage Clarifier Effluent	Filter Effluent
Phase 4	3.5	8.5	6.1	4.4
Phase 5	3.3	8.2	5.4	2.7
Phase 6	3.1	5.3	-	2.2

DISCUSSION

General Considerations

Inspection of the filter following completion of the pilot plant program disclosed the presence of a few 1/4-inch carbon-sand mud balls in the sand bed and larger aggregations of this material up to 1-1/2 inches in diameter were found on top of the supporting gravel. These large balls, not visible through the transparent filter sidesheets, were 2-3 inches deep against the Transite sides. It is probable that this material was the principal source of BOD and COD contributed by the filter.

COD and BOD reductions through the pilot plant are summarized in Table 10. In a practical sense, effluent COD for series adsorption was equivalent to that expected from consideration of two-stage adsorption theory. Mean residual COD for the high carbon dosage run (Phase 4) was 0.9 mg/l lower than that predicted for two-stage countercurrent adsorption and, while this may appear insignificant, it is noteworthy that a further reduction of only 0.6 mg/l represents the predicted achievement of a three-stage system.

Residual COD for the single-clarifier study was 9.8 mg/l versus predicted concentrations of 14 mg/l and 7.5 mg/l for single- and two-stage treatment, respectively. The observed carbon loading of about 13 per cent by weight for this run was close to that predicted for a two-stage system. In general, however, performance was below that indicated by the earlier single-stage model study during which carbon was fed directly in the recirculating slurry.[4]

Throughout the present field program, carbon was fed to the inlet chamber of each solids-contact unit. At the 14-gpm plant operating rate, each of these chambers provided a holding time of one minute during which the principle of countercurrent adsorption was violated by concurrent flow of the wastewater and carbon. As much as 50 per cent of the equilibrium COD loading on the carbon may be obtained in this short time and although the concurrent condition was not overlooked, its importance with respect to the overall process was perhaps underestimated. The significance of the brief concurrent contact merits further investigation.

Single- and two-stage countercurrent adsorption treatment has been mentioned frequently. The greater the slope of the single-stage isotherm, the greater the carbon economy in utilizing countercurrent systems. This economy may extend to three- and even to four-stage processes, provided extremes of treatment are required and cost and complexities can be justified. However, the saving in carbon dosage is not nearly as great between two-stage and three-stage as it is between single-stage and two-stage systems, etc.

TABLE 10

Mean Pilot Plant Performance

Adsorption System	Carbon Dosage mg/l	Filtered COD Inf mg/l	Filtered COD Eff mg/l	Filtered COD Red'n %	BOD* Inf mg/l	BOD* Eff mg/l	BOD* Red'n %
Two-stage	67	26.9	10.8	60	14.9	2.6	83
Two-stage	146	26.2	7.4	72	10.6	4.4	59
Two-stage	266	27.8	4.4	84	10.7	2.4	78
Single-stage	140	28.1	9.7	65	14.0	2.9	79

*Exclusive of sand filter

For example, using data from the single-stage pilot plant study (Figure 28) and assuming an objective of 80 per cent COD reduction, it can be determined that a carbon dosage of 1,000 mg/l is required for single-stage treatment. The residual COD is 5.6 mg/l and carbon loading is only 2.2 per cent by weight. Two-stage treatment requires only 24 per cent of the single-stage carbon dosage, or 240 mg/l. And the dosage for a three-stage system would approximate 14 per cent of the single-stage dosage, or 140 mg/l.

The solids-contact clarifier offers certain simplifications and economy for powdered activated carbon adsorption system design by combining in one vessel the functions of mixing, flocculation, and solids separation. Power use per stage is minimized and multiple tankage within each stage is eliminated, thus reducing space requirements and piping complexity.

An ACCELATOR clarifier produces a dense carbon slurry blowdown suitable for direct transfer to a regeneration system. Should its internal slurry concentrator prove troublesome due to polymer gelling of the slurry as experienced at times in the pilot plant studies, external thickening is practicable. Slurry at a concentration of about one per cent by weight would be blown down to a thickener where it would concentrate to 10-20 per cent or more.

Process Economics

Based upon the design approach noted below, cost estimates have been developed for 10-mgd and 100-mgd treatment systems of the type studied.

Plant Design - Each plant incorporates complete water recovery, eliminating any requirement for separate disposal. All process water needs are met with filter wash water which is pumped from storage to operate carbon-slurry transfer ejectors, to fill slurry makeup tanks, and to dilute polymer in day tanks. Excess backwash water is pumped to the second-stage adsorption units for recovery.

Chemical feed systems are sized to provide maximum dosages of 400 mg/l and 10 mg/l of carbon and polyelectrolyte, respectively. Carbon recovery via regeneration is visualized and 10 per cent loss per cycle is assumed.

The site requirement for the 10-mgd plant is an area 110 ft x 150 ft. Two ACCELATOR mechanisms in basins 62 ft square x 17.5 ft deep handle the adsorption duties of this plant and three 4-cell gravity sand filters with GREENLEAF Filter Controls (a unique siphon valve system for controlling the functions of multiple rapid-sand gravity filters) provide effluent polishing at 3 gpm/ft^2. These concrete structures, as well as a two-story metal building housing the carbon regeneration system, polyelectrolyte feed tanks and pumps, carbon makeup and polyelectrolyte storage, office, and laboratory are constructed above grade.

Agitated covered concrete tanks located below grade between the ACCELATOR basins and the filters include three 6000-ft^3 carbon-slurry day tanks. During operation, one tank is in use, a second is being readied with water plus carbon from regeneration and/or storage, and the third is ready and on standby for use the following day. Two 3,400-ft^3 mixed tanks provide up to 12 hr of holding time for blowdown from the respective clarifiers, one supplying partially spent carbon to the first-stage unit and the other furnishing fully spent carbon to regeneration.

The type of filter visualized requires no wash water storage. A 21,000-ft^3 unmixed basin for backwash wastewater catchment completes the below-grade tankage for this plant.

At a feed rate of 240 mg/1 (2 lb/1000 gal.), the daily carbon requirement is 20,000 lb. The plant requires an in-service carbon inventory of 100,000 lb and storage for two carloads of bagged carbon. A 36,000-lb carload will meet maximum makeup requirements for 12 days. Drum delivery of coagulant is assumed, since a 500-lb drum is sufficient for about a week of operation.

A 100-mgd plant of similar general design occupies an area 450 ft by 450 ft. To provide appropriate flexibility and emergency operating capability, five 20-mgd ACCELATOR units operate in parallel as the first contact stage, with five similar parallel units as the second stage. These mechanisms are installed in common-wall concrete basins, each 88 ft square x 21 ft deep. Fourteen 43-ft square, 4-cell filters with GREENLEAF Filter Controls are required.

A two-story building covers two below-grade agitated blowdown and three carbon slurry day tanks and houses the carbon regeneration system, two polyelectrolyte day tanks, carbon feed systems, service pumps, offices, and laboratory. Unit capacities of the blowdown and carbon slurry tanks are 18,000 ft^3 and 60,000 ft^3, respectively.

In this plant, a conventional 67-ft diameter clarifier is used for filter wash water recovery. The overflow furnishes all plant process water and underflow solids are transferred by gravity to the first-stage blowdown tank unroute to regeneration. As before, excess filter backwash goes to the second contact stage for recovery.

The design also includes a 1-million gal. covered storage reservoir to receive blowdown during periods of first-stage upset when the regular holding tank could be totally inadequate. Carbon slurry so collected is returned at a low rate to the first-stage contact-clarifiers to recover both carbon and partially treated water. Carbon salvaged in this fashion could amount to many thousands of pounds per occurence.

The in-service carbon inventory for this plant is about one million pounds. At 240 mg/1, daily carbon use is 200,000 lb and a make-up

requirement of 20,000-30,000 lb/day is indicated. Bulk storage is not included. Rail delivery of bulk carbon is visualized with cars unloading makeup quantities into the day tanks as required.

Polyelectrolyte coagulant is delivered by tank car to a 20,000-gal. storage tank from where it is pumped as required to either of two day tanks for dilution to feed strength. The diluted material is then pumped to each contact-clarifier through variable-orifice rate control devices installed along a distribution header serving all units.

Both plant designs assumed a mild climate location with weatherproof equipment installed in the open. Carbon handling equipment is either of corrosion resistant material or is protected with suitable coatings. Essential instrumentation for flow metering and control and low-lift process and service pumps are included. Treated water storage and high-service pumps are not included.

Treatment Cost - The estimated construction cost of the 10-mgd plant, including land but exclusive of the capital cost of a carbon regeneration system, is as follows:

Equipment delivered ($268,200) and installed	$333,000
Plant structures	215,200
Total plant cost	$548,200
Engineering (10% of total plant cost)	54,800
Contractor's fee (10% of total plant cost)	54,800
Land aquisition (2% of total plant cost)	11,000
Contingencies and omissions (15% of total plant cost)	82,200
Total capital cost	$751,000

Annual operating cost breaks down as follows:

Capital ($751,000 for 20 years @6%)	$ 65,500
Maintenance (3% of equipment + 1% of structures)	12,150
Labor	66,600
Power (1¢/KWH)	21,400
TOTAL	$165,650

equivalent to 4.5¢/1000 gal. treated, exclusive of chemical costs. The latter are influenced by the feed-stream quality and treatment objectives associated with specific applications. Assuming a polyelectrolyte dosage of 8 mg/l and a carbon feed of 240 mg/l (2 lb/1000 gal.), 90 per cent

supplied by regeneration and 10 per cent by fresh makeup, and modifying the total carbon regeneration costs of Bloom, et al., [10] to reflect increased interest rates, 90 rather than 95 per cent recovery, and 25 rather than 50 per cent increased production predicted for processing 15 rather than 10 per cent by weight slurry, chemical costs are:

	¢/1000 gal.
Regenerated carbon (2 lb/1000 gal.) (2¢/lb) (0.90)	3.6
Makeup carbon (2 lb/1000 gal.) (13¢/lb + 3¢/lb freight) (0.10)	3.2
C-32 Polyelectrolyte (0.067 lb/1000 gal.) (52.5¢/lb + 3¢/lb freight)	3.7
	10.5

On this basis, the total cost of producing low-COD water on this scale is 15¢/1000 gal.

Using the same approach, the estimated construction cost of the 100-mgd installation is as follows:

Equipment delivered ($1,927,600) and installed	$2,158,700
Plant structures	1,155,100
Total plant cost	$3,313,800
Engineering (10% of total plant cost)	331,400
Contractor's fee (10% of total plant cost)	331,400
Land aquisition (2% of total palnt cost)	66,300
Contingencies and omissions (15% of total plant cost)	497,100
Total capital cost	$4,540,000

The breakdown for annual operating cost exclusive of chemical cost is:

Capital ($4,540,000 for 20 years @6%)	$ 395,800
Maintenance (3% of equipment + 1% of structures)	76,300
Labor	199,800
Power (1¢/KWH)	122,500
TOTAL	$ 794,400

equivalent to 2.2¢/1000 gal. treated. The unit chemical costs noted above remain unchanged, making the total cost of producing low-COD water on this scale 12.7¢/1000 gal.

The significance of carbon dosage in establishing treatment cost is most evident. For example, if 120 mg/l (1 lb/1000 gal.) proves adequate, unit costs for regenerated carbon, makeup carbon, and coagulant decrease to 1.8, 1.6, and 1.8¢/1000 gal., respectively. Plant-scale total treatment cost reduces to 9.7¢/1000 gal. for the 10-mgd installation and 7.4¢/1000 gal. for the 100-mgd facility.

Less costly activated carbons are available and if they perform suitably their use would lower the cost of makeup carbon still further. However, the 13¢/lb carbon for makeup constitutes only 17 per cent of the total cost for the 10-mgd plant at the 2-lb/1000 gal. feed rate and 13 per cent at the 1-lb/1000 gal. dosage. These figures for the 100-mgd plant are 20 and 17 per cent, respectively. Use of 8¢/lb carbon would reduce total cost by 1¢/1000 gal. for 2-lb/1000 gal. treatment and by 0.5¢/1000 gal. for the 1-lb/1000 gal. dosage.

The projected total operating cost of a 10-mgd granular activated carbon adsorption system using multiple downflow contact columns is 8.3¢/1000 gal.[3] A plant of this type might require as much as 133,000 lb of in-service carbon inventory for each 1000 gpm of system capacity. The powdered activated carbon system described is conservatively estimated to require only 14,300 lb of in-service carbon inventory for each 1000 gpm of capacity. These inventories represent an initial carbon cost of $293,000 (31.5¢/lb) for a 10-mgd granular carbon plant as compared to only $13,000 (13¢/lb) for a powdered carbon plant of the same capacity, or $8,000 (8¢/lb) if less costly carbon can be used. Both systems require facilities to warehouse and handle 10-15 per cent makeup carbon.

Powdered carbon plant makeup requirements would commence within five days of plant startup as compared to several months later for the granular system. Powdered carbon utilization would range from 25-33 per cent of the top utilization reported for granular systems, thus requiring regeneration 3-4 times more frequently. Three or four times as much makeup carbon is required, but this factor could be offset by the unit price differential between powdered and granular carbons.

The cost of powdered carbon regeneration has been projected as 2¢/lb on a large scale. Considering that granular activated carbon has been reactivated on a moderate scale for 1.5¢/lb, the recycle and regeneration frequency for powdered carbon therefore results in a cost burden that must be offset by lower capital, operating, and maintenance costs, reduction in carbon loss, and eventually by lower regeneration cost and improved carbon utilization.

SUMMARY

Powdered activated carbon treatment of activated-sludge sewage plant effluent in recirculating-slurry solids-contact clarifiers was evaluated in this pilot-scale investigation. A single unit achieved 30 per cent greater carbon efficiency than a conventional single-stage adsorption system. Two such clarifiers operated in series with countercurrent carbon transfer performed as well or better than conventional two-stage countercurrent adsorption systems requiring multiple agitated tanks, clarifiers and filters. Series operation provided substantial process protection during periods of gross deterioration of feed-stream quality.

Preliminary laboratory study of three powdered activated carbons resulted in selection of Atlas Chemical Industries' Darco S-51 for the pilot plant program and it was found that polyelectrolyte flocculation was required to produce floc which settled well. For the system involved, a study of 26 compounds disclosed that Dow Chemical Company's Purifloc C-32 was the most effective and it was used throughout the pilot plant work. A polyelectrolyte dosage of 6-7 mg/l was required for effective flocculation at carbon feed rates up to 140 mg/l. For a series study using 266 mg/l of carbon, 10 mg/l of C-32 were required.

Slurry settling rates far exceeded requirements of the pilot plant which was operated at hydraulic loads from 0.4 to 1.6 gpm/ft^2 of clarification area. In spite of this, it was necessary to reduce the pilot plant throughput when influent suspended solids were high because of an inability to remove solids as rapidly as they were accumulated within the system during these periods.

The volume of system blowdown ranged from 0.05-0.1 per cent of the throughput and its solids content of 13-22 per cent by weight would enable economical recovery of carbon for reuse by reactivation without further concentration.

A gravity sand filter operated at 3 gpm/ft^2 on the downstream end of the pilot plant was not completely successful. Shortly after initiation of the pilot plant program, it was noted that effluent COD and BOD occasionally exceeded the filter influent concentrations and this situation worsened with the passage of time. There was no evidence that carbon fines were passed, but biological growth in the filter underdrain was observed and at the conclusion of the program carbon-sand mudballs were found at the gravel-sand interface. Wash water requirements ranged from 1.2 per cent of the filtered water volume to a high of 4.9 per cent when extremes in backwash rate and duration were used in an effort to correct the filter condition.

Carbon was fed by a slurry feeder which provided continuous horizontal agitation and wetting was never a problem.

Pilot plant influent filtered COD averaged 27.2 mg/l and ranged from 23-34 mg/l during the study program. Two-stage countercurrent treatment with 67, 146, and 266 mg/l of carbon achieved respective reductions of 60, 72, and 84 per cent. Residual COD concentrations observed were 10.8, 7.4, and 4.4 mg/l.

A COD reduction of 65 per cent was obtained across a one unit contactor system with a carbon dosage of 140 mg/l. This compares with a predicted single-stage removal of 50 per cent. Residual COD concentration observed was 9.7 mg/l.

Carbon loadings for the two-stage systems ranged from 9-24 mg of COD/100 mg of carbon and a loading of 13.1 per cent by weight was obtained during single unit treatment. There is reason to believe that modification of the system as operated will improve carbon efficiency.

BOD removals for the respective systems, exclusive of the sand filter, were 83, 59, 78, and 79 per cent. Considering the low average feed BOD of 12 mg/l and the substantial removals through the pilot plant, only order-of-magnitude removals should be inferred here.

On a 10-mgd scale, assuming respective carbon and polyelectrolyte dosages of 240 and 8 mg/l, the total estimated cost of treatment by the pilot plant process is 15¢/1000 gal. If chemical feed requirements in terms of effluent quality objectives could be reduced to 120 and 4 mg/l, respectively, the total cost decreases to 9.7¢/1000 gal.

A 100-mgd plant of similar design would produce treated water at a cost of 12.7/1000 gal. at the higher chemical feed rates and 7.4¢/1000 gal. at the lower chemical dosages. Both plants feature 90 per cent carbon recovery by regeneration and 10 per cent fresh carbon makeup. Solid and liquid waste handling and disposal problems for either plant are minimal.

REFERENCES

1. Anon., "Taste and Odor Control in Water Purification." West Virginia Pulp and Paper, Chemical Division, 1966.

2. Morris, J. C. and Weber, W. J., Jr., "Removal of Biochemically Resistant Compounds by Adsorption." U. S. Department of Health, Education and Welfare, Public Health Service Publication No. 999-WP-11, AWTR-9.

3. "Summary Report, Advanced Waste Treatment Research Program, July 1964-July 1967," U. S. Department of the Interior, Water Pollution Control Research Series Publication No. WP-20-AWTR-19.

4. Beebe, R. L. and Stevens, J. I., "Activated Carbon System for Wastewater Renovation." Water and Wastes Engineering, Jan. 1967, pp 43-45.

5. "Measuring Adsorptive Capacity of Activated Carbons for Liquid Purification," Bulletin D-87, Atlas Chemical Industries, Inc., 1966.

6. "Standard Methods for the Examination of Water and Wastewater," 12th Ed., American Public Health Assn., Inc., 1965.

7. Rinehart, T.M., Scheffler, G. H., Helbig, W. A., and Truemper, J. T., "A Symposium on Activated Carbon," Atlas Chemical Industries, Inc., 1968.

8. Private communication, Cunningham, A. W., 1968 (Letter 7-16-68).

9. Weber, Walter, Jr., and Morris, J. Carrell, "Equilibria Capacities for Adsorption on Carbon," Jour. ASCE San. Eng. Div., Vol. 90, No. SA3, pp 79 (June 1964).

10. Bloom, R., Jr., Joseph, R. T., Friedman, L. D., and Hopkins, C. B., "New Technique Cuts Carbon Regeneration Costs," Environmental Science and Technology, March 1969, pp 214-217.

APPENDIX

Low-Level COD Determination

The procedure is essentially that given in the 12th Edition of "Standard Methods for the Examination of Water and Waste Water," p. 513, par. 4.6.

Attention is directed to the precaution concerning contaminated glassware or contamination from atmospheric dust.

It has been found that ordinary laboratory grade distilled or demineralized water used for pre-reflux dilution, blanks, rinsing, or final dilution leads to highly erratic results. Therefore, this laboratory has developed a special distillation procedure for producing suitable water.

A further source of error is in preparation of Ag_2SO_4-H_2SO_4 solution. Every effort must be made to avoid contamination. It is essential that all determinations and blanks in a single set be run with the same batch of silver-acid. In this way any small contamination of the solution is automatically corrected for by the blanks.

No significant error is introduced by the use of a polyethylene wash bottle for rinsing down condenser tubes and tips.

The apparatus described is effective in preventing dust contamination and in protecting the analyst from injury by bumping which may occasionally occur during refluxing. It differs slightly from that described in "Standard Methods."

1. Apparatus

   1.1 500-ml short-necked round bottom boiling flasks. ST joint 24/40, Corning #4320 or equal.

   1.2 Allihn type condensers, 500-ml jacket, drop tip inner ST joint 24/40, top outer ST joint 24/40, Corning #2480 or equal.

   1.3 Connecting tubes 75°, both ends inner ST joints 24/40, Corning 8920 or equal.

   1.4 Tube stoppers, cap type, full length outer ST joint 24/40, 2 required per condenser.

   1.5 Heaters, Precision Catalog #61560 or equal.

1.6 Running water cooling bath large enough for required number of flasks. The apparatus is assembled in such a way that the complete glass assembly consisting of flask, condenser, and upper connecting tube may be raised from or lowered to the heater as required. The connecting tube is placed in the upper end of the condenser pointed away from any work or chemical storage area. The cap type stoppers are placed on condenser tip and connecting tube tip when the apparatus is not in use, to prevent entrance of dust particles. Both caps are, of course, removed when the apparatus is in use.

2. Reagents

2.1 0.025N potassium dichromate, as per "Standard Methods" except made up in special water (2.6).

2.2 0.01N ferrous ammonium sulfate. (For routine work this laboratory uses approximately 0.025N solution with reproducible results).

2.3 Ferroin indicator as per "Standard Methods."

2.4 Silver sulfate-sulfuric acid solution.

Prepare as follows: Place 31 grams reagent grade silver sulfate in a scrupulously clean dry 2-liter beaker. Add about 1 liter conc. reagent grade H_2SO_4 from a newly opened standard 9-lb bottle. With a flat tipped large diameter glass stirring rod, carefully crush lumps of Ag_2SO_4 and stir thoroughly, repeating as often as necessary. Complete dissolution may be obtained in 20 minutes or less as compared with 1-2 days in "Standard Methods." Return the solution to the 9-lb bottle. Cap securely and mix thoroughly by inversion. Caution: Avoid exhaling directly toward the beaker during dissolution step. Such exhalation can obviously lead to particulate contamination.

2.5 Mercuric sulfate, reagent grade.

2.6 Blank water. Redistill a high quality distilled or demineralized water from an all-glass ST joint apparatus. An activated carbon purifier from which most of the chloride has been leached may be used ahead of the redistillation. Proceed as follows:

Place in a 3-liter R.B. distilling flash containing several boiling chips or beads, 500 ml water, 200 ml 0.25N (approx) potassium dichromate, 200 ml Ag_2SO_4-H_2SO_4 solution, (2.4), and about 1 gram $HgSO_4$. Swirl to mix and dissolve the $HgSO_4$. Mark level of this mixture on flask. Add about 1.5

liters of water and mix. Bring to a boil on electric heater. If a short-necked ST flask is used, a long glass stirring rod may be kept in the flask while mixture is heating. This helps to prevent bumping. Stir occasionally until boiling starts. Allow to boil for 10 minutes wasting steam to the atmosphere. Place connecting tube and condenser, and waste steam through uncooled condenser for 2 or 3 minutes. Start cooling water and waste enough condensate to rinse condenser.

Collect distillate in a glass bottle rinsed several times with a little distillate. A 9-lb acid bottle, well cleaned with chromic acid, makes a good container. Use an adapter from condenser tip into bottle. The adapter tip should enter the receiver bottle through a hole in a loose fitting foil dust cap. Distill until level in flask drops to the mark. A larger still should be used where the COD determination load is heavy. Keep mixture proportions the same.

Keep water storage bottles tightly capped when not in use.

The oxidizing mixture in the flask may be used repeatedly until there is obvious discoloration.

3. Procedure

3.1 Two blanks should be run with each set of samples.

3.2 Place 50-ml blanks and samples in identified 500-ml boiling flasks containing about 7 glass beads. Keep flasks capped with small glass beakers at all times except when placing samples and reagents.

3.3 Add 5 ml conc. H_2SO_4 (not 2.4), swirling to avoid local heating.

3.4 Add approx. 0.5 gram $HgSO_4$ and swirl to mix until $HgSO_4$ is dissolved.

3.5 Add exactly 25 ml 0.025N potassium dichromate solution swirling to mix during addition.

3.6 Remove caps from reflux condensers and top connecting tubes. Start cooling water through condenser jackets. Turn heaters to "high."

3.7 To each flask, add without mixing 70 ml Ag_2SO_4-H_2SO_4 solution (2.4).

3.8 It is convenient to have a tray to hold flasks upright during this and preceding steps. Carry tray to reflux bank and taking each flask in turn swirl to mix contents quickly but thoroughly and connect immediately to condenser. Clamp and lower apparatus to heater. Boiling will start immediately without bumping. When vigorous boiling is established, turn heater down to a point to maintain boiling (about 75 on Precision heater scale). Reflux for 2 hours.

3.9 At end of reflux time, taking each unit in turn, in the same order as in 3.8, turn off heater and raise apparatus several inches above heater. Place an asbestos square over heater top. Cool 15 minutes.

3.10 Now remove connecting tube and rinse down condenser with a little blank water (2.6) Allow to drain for about 10-15 seconds and holding flask by the neck lower it from condenser. Rinse condenser tip into flask with a little blank water. Place capped flask in cooling bath immediately. Replace condenser and connecting tube caps.

3.11 While flasks are cooling, prepare a ferrous ammonium sulfate standardization. Place 25 ml of 0.025N dichromate solution and about 200 ml blank water in a 500-ml erlenmeyer flask. Add with swirling, 30-35 ml conc. H_2SO_4 (not 2.4). Cover and place in water bath to cool. Note: If using 0.01N ferrous ammonium sulfate, 10 ml of 0.025 dichromate solution is sufficient for the standard.

3.12 When reflux flasks have cooled for about 15 minutes (cool to the touch), add 200 ml blank water (2.6) carefully to each. Mix and return to water bath.

3.13 When all flasks, including standard, have cooled, replace in tray. Add 2-3 drops of ferroin indicator to each. Titrate with ferrous ammonium sulfate directly in the boiling flask. Do not transfer. This may require a little manipulative practice, but is essential for consistent results.

3.14 Empty flasks without removing beads. Rinse flasks and beads thoroughly 3 times with ordinary distilled water and 3 times with small portions (about 10 ml) of blank water. Replace caps immediately.

4. General Notes

4.1 Blanks should titrate within 0.2 ml of the standard if there is no contamination. Different lots of Ag_2SO_4-H_2SO_4 reagent

will produce different blank titrations. With careful attention to cleanliness there will be less than 0.2 ml difference in blanks. Within this limit use the highest blank, not the average of two. For very precise work (non-routine) the two blanks should agree.

4.2 All glassware must be kept clean and dust free. Use cleaning acid followed by distilled water and finally blank water (2.6). To illustrate the sensitivity of the method to contamination, calculation indicates that in a 50 ml sample a speck of cellulose dust weighing 0.05 milligrams would contribute about 1 mg/l COD.

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