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A STUDY OF THE REMOVAL OF FLOCCULENT AND DISCRETE PARTICULATE MATTER IN A RAPID SAND FILTER

by

Gerald William Foess

A dissertation submitted in partial fulfillment
of the requirements for the degree of
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Doctoral Committee:

Professor Jack A. Borchardt, Chairman
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Professor Lloyd L. Kempe
Professor Walter J. Weber, Jr.

A B S T R A C T

A STUDY OF THE REMOVAL OF FLOCCULENT AND DISCRETE PARTICULATE MATTER IN A RAPID SAND FILTER

by

Gerald William Foess

Chairman: Jack A. Borchardt

The process of water filtration has been, and continues to be, one of the most thoroughly investigated unit operations in the field of sanitary engineering. Nevertheless, advances in filtration technology have resulted primarily from trial and error procedures rather than from a fundamental understanding of the filtration mechanism. Because of the present disproportionately-high cost of rapid sand filters in comparison to other water treatment units, it is becoming increasingly imperative that filters be designed rationally and operated under optimum conditions. To accomplish these aims the basic mechanisms of particle removal must be known and understood.

Investigators of filtration have recently delineated two broad categories of removal mechanisms: (1) those that control particle transport of a suspended particle to the vicinity of the media surface, and (2) those that control particle attachment at or near the surface of the media. Most previous studies have focused on particle transport

mechanisms; the few investigations that have directed their attention to the attachment step have displayed considerable disagreement. The current research has been aimed, therefore, at evaluating the significance of various particle attachment mechanisms in sand filtration with the objective of clarifying some of the prevailing discordance.

The experimental work employed both flocculent (hydrous ferric oxide particles) and discrete (the green algae Chlorella and Scenedesmus) particulate matter. Physical filtration parameters such as sand size, flow rate, bed depth and water temperature were maintained constant and in close conformity to standard plant practice.

The results indicate that the filtration behavior of ferric-floc dispersions is largely controlled by the flocculability of these dispersions--hence by floc-to-floc interactions within the filter. Such parameters as aging time, pH, ionic strength, and phosphate ion concentration, which have a demonstrable effect on the flocculation process, were shown to also affect filtration. Additionally, some correspondence has been obtained between the flocculation properties of iron(III) dispersions and their subsequent filterability by means of jar tests. An exception to the foregoing may occur in the filtration of positively charged ferric-flocs, whose flocculation and filtration characteristics seem to

indicate that an electrokinetic mechanism based on floc-sand interactions may be operative in the filtration process under certain conditions.

Floc size was observed in these studies to be markedly affected by the pH and the type and concentration of anions in the dispersion. In this connection it was concluded that laboratory filtration investigations conducted using deionized water may not be representative of many practical systems.

The attachment mechanism for algae has been demonstrated to involve a surface interaction between the organism and the sand which can be chemically controlled. By means of micro-electrophoresis it was found that both algae and sand, when suspended in Ann Arbor tap water, possess a negative surface charge which decreases in magnitude with decreasing pH. Reducing the repulsive energy between algae and sand by precoating the latter particles with Fe(III) or Th(IV) resulted in increased filter removal efficiencies. Accordingly, removal percentages were also demonstrated to be directly dependent upon the pH of the influent suspension; nearly complete removals were achieved in runs operated near the isoelectric points of the sand and algae (pH 2-3) while progressively decreasing efficiencies were obtained as the pH was increased. Concurrent studies of the flocculation characteristics of algae showed that the organisms studied were completely resis-

tant to agglomeration over the pH range 2 to 10. By means of precise size measurements with an electronic particle counter and sizer, straining was virtually eliminated as a significant removal mechanism for the sizes of algae utilized (2 to 11 microns).

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CHAPTER 1

INTRODUCTION

The separation of suspended impurities from water supplies by filtration through sand has been carried out with varying degrees of success for more than 4,000 years (4). Modern filtration practice, however, bears little resemblance to that of past centuries. The most significant turning point in its evolution occurred during the latter part of the nineteenth century, with the development of the "rapid" sand filter. This advancement took place currently with the introduction of chemical pretreatment. It was found that the addition of chemical coagulants to the water in a pretreatment unit, allowing some carryover of gelatinous floc to the filter, permitted the use of significantly higher filtration rates. The rapid sand filter was also distinguished from previous "slow" sand filters by the practice of cleansing it by fluidization of the bed with reversed flow.

Design criteria for rapid sand filters have changed relatively little since their inception, despite demands for increased production of high quality water brought about by

the rapid expansion of urban centers and increasing industrialization along water courses. George W. Fuller and his associates, who pioneered the changeover from slow sand filters to rapid sand filters, quite early established design parameters (40) such as flow rate (2 gpm/sq ft), sand size (0.35 mm effective size), and bed depth (30 in) which are still being used today. Ironically, Fuller's classic experimental work was not even aimed at establishing fixed design criteria. By a fortuitous sizing of his experimental apparatus, Fuller was limited to application rates less than 2 gpm/sq ft. He made it clear that this was not to be considered a limiting rate.

In contrast to the design criteria and operating practice, suspensions treated in rapid sand filters show a wide variation. Some suspended impurities are due to pretreatment of the water, while others are naturally occuring. Examples of the former group are iron or aluminum coagulant, calcium carbonate precipitates, and activated carbon. The latter group typically includes silt, clay, organic colloids, and a wide variety of microorganisms. Broadly speaking, the aforementioned particles may be classified either as flocculent or discrete. Investigations in recent years have focused attention on the markedly different filtering properties of the two groups.

Borchardt and O'Melia (11), for example, investigated the filtering properties of uncoagulated algal suspensions using sand sizes ranging from 0.316 to 0.524 mm and flow rates ranging from o.15 to 2.16 gpm/sq ft, and found significant numbers of algae in every effluent sample collected; removal efficiencies of less than 10 per cent were not uncommon. Suspensions containing algae of the genera Ankistrodesmus, Anabaena, or Scenedesmus were used; these algae averaged 15-60 microns in size, depending upon the genus. Similarly, Ghosh (44) investigated the filtering properties of uncoagulated diatomaceous-earth suspensions of mean size 20 microns and found turbidity penetrated the entire depth of media under almost all conditions of flow. The filter sands tested ranged in size from 0.46 to 0.77 mm, and flow rates from 1 to 3 gpm/sq ft were used.

On the other hand, several excellent investigations of the filtering properties of ferric-floc suspensions have concluded unanimously that most of the applied suspended material was removed in the upper portion of the bed (22,34, 97,116). All of these studies used flow rates and sand sizes similar to those mentioned above. Furthermore, the suspended particle sizes used by Borchardt and O'Melia (11) and by Ghosh (44) were actually larger than the ferric floc used by Eliassen (34), Stanley (116) and O'Melia and Crapps (97).

In view of the diverse filtering properties of particles which the rapid sand filter is called upon to remove, the conclusion must be reached that standardized filter designs are not capable of providing both efficient and economical facilities for a wide variety of waters. Fortunately this conclusion has been reached in recent years by a number of researchers and filter designers and considerable progress has been made in applying improvements in filtration technology to practical situations. It is unfortunate, however that most of the advances have developed from past plant experiences and trial and error procedures, rather than from a clear comprehension of the filtration mechanism. Despite the fact that water filtration is among the most widely used and extensively investigated unit operations in the field of sanitary engineering, a clear understanding of the processes by which particle removal from water is accomplished in a sand filter is not yet available. Such an elucidation of particle removal mechanisms, however, would help greatly in the development of rational design criteria for the process, and would also be valuable in seeking the optimum conditions for filtration as well as in predicting the effects of changes in operating conditions.

While a complete understanding of particle removal mechanisms has not been attained, some progress has indeed

been made. The current status of knowledge regarding removal mechanisms will be discussed in detail in Chapter 3. For purposes of an introduction these mechanisms can be put into two general groups as suggested by O'Melia (96): (1) those that control movement of the suspended particle from the bulk of the liquid in a filter pore to the surface of a sand grain, i.e., particle transport, and (2) those that control removal at the surface of a sand grain, i.e., particle attachment. Particle transport mechanisms are basically physical-hydraulic in nature and are not removal mechanisms in the strict sense--they merely control removal. Nevertheless, most investigators of water filtration have surprisingly restricted their studies to these, to the neglect of particle attachment mechanisms. O'Melia and Stumm (98) suggest that this may be one reason for the remarkable disagreement that exists in filtration literature. Recently, however, an increasing number of workers have been directing their attention to the particle attachment step, hence to the effects of chemical parameters on the filtration process (72,86, 97,98). This is not to say that concordance has been reached. Indeed, chemical, or particle attachment, theories show as much disagreement among themselves as do their physical counterparts.

The areas of disagreement may be summarized briefly as

follows. Mackrle and Mackrle (86) consider that the attachment of a suspended particle to the surface of the filter media is controlled by van der Waals forces and assume that electrostatic forces are insignificant. Ives and Gregory (72) propose that particle attachment is determined by the combined energies of interaction between particle and sand grain, these being calculated by combining the electrostatic effects of the diffuse layer interactions with the attractive energy resulting from van der Waals forces. Where interaction energies are not favorable for attachment, Ives and Gregory propose that removal mechanisms which are independent of surface forces forces (e.g., intersitial straining) may be operative. O'Melia, et al. (97,98) consider that electrokinetic-van der Waals interactions are only one of many types of colloid-chemical reactions which can occur at the water-filter interface, other possibilities being ion exchange, hydrogen bonding, and the formation of coordinative bonds and linkages. Finally, there is wide disagreement as to whether particle attachment is accomplished primarily through interactions between the suspended particle and the sand grain, or whether interactions between one suspended particle and another particle previously removed are of prime importance.

Proposed Research. The research reported herein has been directed toward a clarification of some of the disagree-

ments mentioned above. It has thus involved an evaluation of the mechanisms of particulate removal during the attachment step in water filtration. Both flocculent (hydrous ferric oxide particles) and non-flocculent (algae) particulate matter have been investigated because of the different filtering properties previously observed--but not yet fully explained--for these two types of materials. It has also been an objective of the research to amplify and elucidate the works of O'Melia (95) and Davis (29) which have previously been carried out in the University of Michigan laboratories. These investigators have provided an excellent background of information on the filtration properties of flocculent and non-flocculent particulate matter.

The insights into the filtration mechanism gained in this work ultimately will aid the engineer in designing filter plants on a more rational basis. They should also allow him to be better able to specify the operating conditions necessary for maximum filter efficiency. Further, they could provide impetus for development of synthetic media with more optimal filtration characteristics.

CHAPTER 2

EXPERIMENTAL MATERIALS AND PROCEDURES OF INVESTIGATION

General

The experimental apparatus employed in this research was a modification of the system originally utilized by O'Melia (95) and Davis (29). It had proven satisfactory for these workers in the filtration of suspensions of algae and ferric-flocs. The main feature of the design was the use of open-ended filters which were capable of maintaining a constant water level and flow rate against a varying head loss in the sand bed. This resulted in close conformity to actual plant practice while permitting the flexibility and precision of operation of a laboratory filter. A schematic diagram of the entire filter apparatus and appurtenances is shown in Figure 2-1.

Filter Sand

The sand used in the experiments was obtained from the Ottawa Silica Company in two U. S. Standard sieve size ratings, 20/30 and 30/50. The former was used directly, after washing, for the algal filtration runs, while the latter

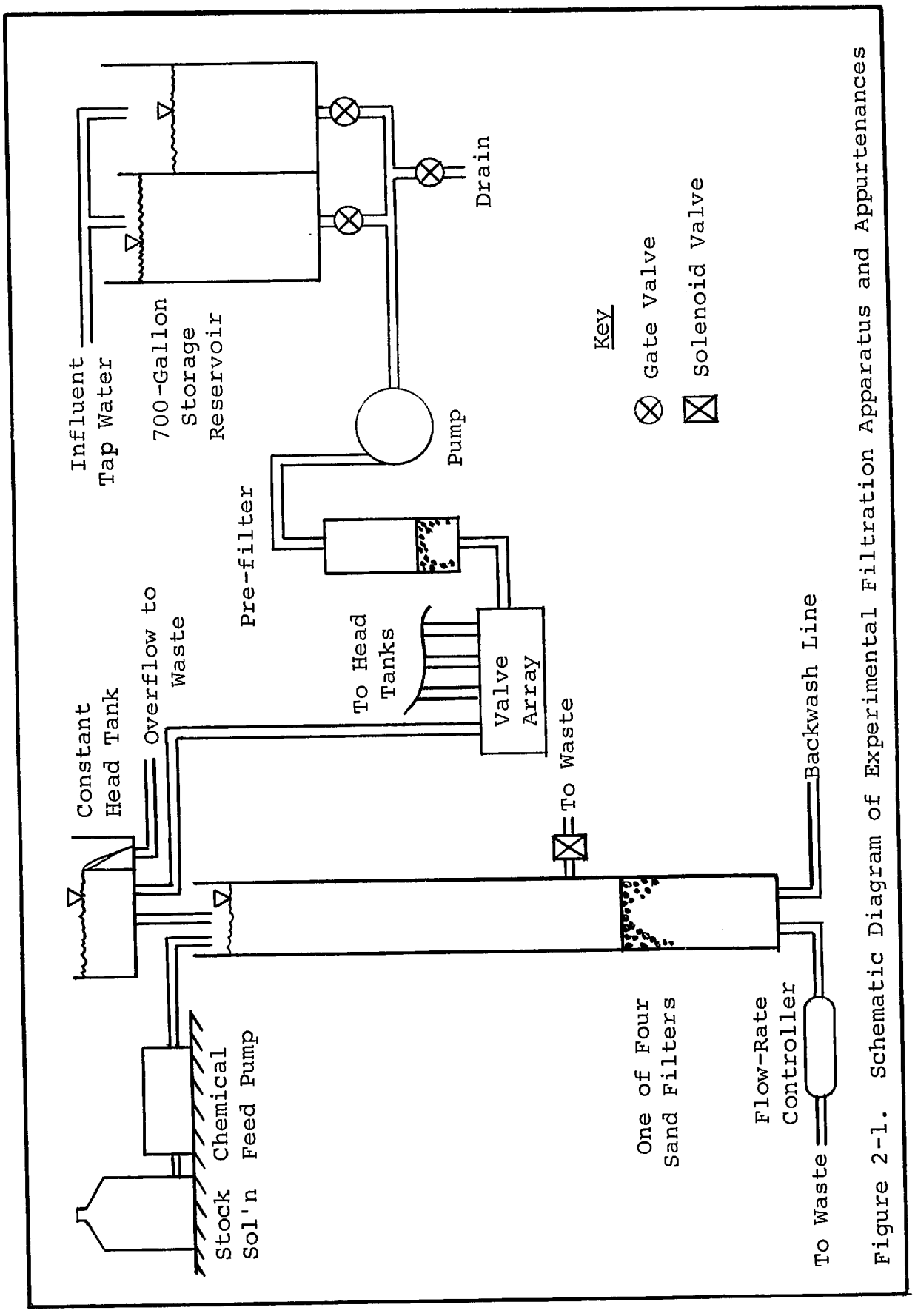


Figure 2-1. Schematic Diagram of Experimental Filtration Apparatus and Appurtenances

was further sieved in the laboratory to 30/40 for use in the runs employing iron-floc. For purposes of obtaining a more complete physical description of the sands, their equivalent diameter was also found by Hazen's count and weigh method (50). This procedure resulted in diameters of 0.756 mm for the 20/30 sand and 0.515 mm for the 30/40 sand. In this work sand sizes are expressed in terms of their arithmetic mean diameters, these being 0.503 and 0.711 mm for the 30/40 and 20/30 sieve sizes, respectively.

Initially, sand beds were prepared after the manner of O'Melia (95) and Davis (29). This method consisted of adding 14.60 pounds of dry sand to each filter, backwashing the filters to remove entrapped air, and, finally, compacting the sand bed to 24-1/2 inches by gently tapping the sides of the filters. The use of 14.60 pounds of sand with a specific gravity of 2.65 in a column 3-5/8 inches in diameter and 24-1/2 inches deep produced sand beds with an overall porosity of 40.0 per cent.

After several preliminary runs failed to yield completely reproducible results, two additional methods of filter media placement were tried. The first consisted of adding 15.33 pounds of sand to each filter and following the procedures given above. This resulted in a porosity of 37.0 per cent. It was felt that the additional tapping required to compact

the sand to a 24-1/2 inch depth for this amount of sand would result in a more uniform bed.

In the third method of sand bed preparation, dried sand was applied to each empty filter through an orifice approximately four feet above the bottom of the filter, and allowed to compact naturally as it fell. Preliminary studies had shown that if the rate of sand discharge from the orifice was sufficiently small, uniform porosities would be attained. Water was applied to the bed through the bottom of the filter; the rate of filling was kept small enough to prevent bed expansion and to allow all of the interstitial air to be removed. The results of runs conducted at all three bed porosities are presented in Chapter 4.

Algae

Culturing

Algae were chosen as the non-flocculent particulate matter to be filtered in this research because of their size, their surface charge characteristics, and their proven filter-penetrating ability. Stock cultures of *Chlorella* and *Scenedesmus* were grown in batch systems consisting of fifteen liter clear glass carboys. The light energy source was provided by four forty-watt fluorescent lamps. Mixing of the organisms in the containers was accomplished by air diffusers suspended in the cultures. The air also

served as a supplementary carbon source.

No provisions were installed to insure a pure culture or to provide a constant temperature. It was found that these preparations were not necessary, as cultures exceeding 95 per cent purity were always obtained in open jars at the prevailing laboratory temperature. The composition of the synthetic algal media used is given in Table 1.

Counting and Sizing

All of the algae samples taken in this research were subjected to counting of the organisms, and, on certain pre-selected samples, size distributions were also performed. These measurements were made electronically with a Model B Coulter Counter. Details of the instrument can be obtained from the instruction and service manual and from the literature (e.g. 12,15,103). However, because of the unique importance of the instrument in this research, a brief description of the instrument and its operation is pertinent.

The Coulter principle consists of forcing the particulate suspension to flow through a small aperture (100 microns in diameter) having an immersed electrode on each side. As each particle passes through the aperture, it replaces its own volume of electrolyte within the aperture, momentarily changing the resistance value between the electrodes. This change produces a voltage pulse of short

TABLE 1

Composition of Synthetic Algal Media

Chemical	Concentration in Culture (mg/l)
1. $MgSO_4 \cdot 7\ H_2O$	450
NH_4Cl	75
$NaHCO_3$	250
K_2HPO_4	14
2. $FeSO_4 \cdot 7\ H_2O$	5
+ KOH Aerated	15
+ EDTA	26
3. $MnSO_4 \cdot H_2O$	1.55
$ZnSO_4 \cdot 7\ H_2O$	0.22
H_3BO_3	2.86
MoO_3	0.02
$CuSO_4 \cdot 5\ H_2O$	0.08

duration having a magnitude proportional to particle volume, and the resultant series of pulses is electronically amplified, scaled and counted. Particle shape and structure have but little effect on response.

The Coulter Counter has the remarkable capability of counting particles in any pre-selected size range, rendering it useful for both total counts and for size distributions. However, since the noise limitations of electronic amplification prevent measurement below 1 to 2 per cent of the aperture diameter, particles smaller than 1 to 2 microns could not be counted.

Samples for counting and sizing were withdrawn from the influent line and from the effluent streams of each filter in 1/2 gallon jars. From these, 95 ml was taken and diluted to 100 ml with a 20 per cent sodium chloride solution. The resulting 1 per cent saline suspension was then counted in accordance with instrument procedures. According to investigations reported by Salle (107), a 1 per cent salt solution should not be sufficient to cause any significant changes in cell volume as a result of osmotic effects.

In order to perform size measurements of algae, it was first necessary to calibrate the instrument. This was done following procedures given in the operating manual with human blood cells (90 cubic-microns mean cell volume) and

verified with pollen grains (3620 cubic-microns mean cell volume). The results of these calibrations for the amplification gains used in this research are presented in Appendixes I and II.

Chemical and Influent Suspensions

Chemicals

When it was desired to feed chemicals directly to the top of the filters, they were delivered by means of positive displacement syringe pumps. The pumps consisted of disposable plastic syringes with 2-way valves driven by a variable speed motor through a gear box and an arrangement of hinged brass rods.

The discharge of the syringes was dependent upon their placement in the syringe holder and on the rotational speed of the gear box wheel, both of which could be varied. Once set, the discharge of the syringes remained constant indefinitely, although they were usually re-calibrated prior to each run. The calibration was achieved by measuring the discharge over a thirty minute period. Throughout the experimental runs, the chemical pumping assembly operated in completely satisfactory fashion, producing highly accurate discharges and remaining trouble-free.

Stock solutions of the chemicals to be fed were pre-

pared in concentrations that varied according to the rate at which they were delivered. Generally, syringe discharges were about 1/25 of the liquid feed, requiring the concentration of chemical in the stock solutions to be approximately 25 times those desired in the filters, i.e., about 0.002 M for the iron(III) solutions. Except where noted, stock solutions of iron were made up one day prior to each run in 5 gallon glass containers by dissolving suitable quantities of $FeCl_3 \cdot 6H_2O$ in 0.1 M HCl. Thus, all were undersaturated with respect to ferric hydroxide.

Influent Suspensions

Water used in the experiments was treated Ann Arbor city water, a representative chemical composition of which is shown in Table 2. The water was adjusted to the desired pH with $NaHCO_3$ and/or HCl. It was hoped at first to store enough water in two 5000 gallon tanks to last for several runs. However, these tanks were under repair for much of the research and it was necessary to use a 700 gallon tank, filling before each run. The possible effects of using "different" water for each run were evaluated and the results are presented in Chapter 4. Throughout the series of filtration runs the water temperature was found to vary between 21 and 24 degrees Centigrade.

For filter runs employing algae, stock cultures were

TABLE 2

Representative Composition of Ann Arbor Tap Water

Component	Concentration (mg/l)
Methyl Orange Alkalinity	45 as $CaCO_3$
Phenophthaline Alkalinity	50 "
Total Hardness	80 "
Non-Carbonate Hardness	35 "
pH	10.3
Ca^{2+}	25
Mg^{2+}	5
F^-	0.9
Cl^-	65
Fe	0.1
Total Dissolved Solids	146

introduced into the 700 gallon tank in sufficient quantity to provide the desired concentration in the filter influent. The resulting suspension was mixed by means of diffusers for a period of one hour prior to the start of each run and was continued throughout the run. Growth of the algae in this tank was not significant according to counts and size distributions taken during runs.

From the 700 gallon tank, water was pumped to constant head tanks located directly above the filters. Liquid was fed to the filters from these through orifices calibrated to yield a filter flow rate of 2 gpm/sq ft. The head on each orifice was 8 inches and the overflow weirs were 11 inches in length.

Microelectrophoresis

Cell

Electrophoretic mobility measurements were performed with the flat horizontal cell designed by Briggs (13) and discussed in detail by Black and coworkers (8-10). A few features of the original Briggs design were sources of trouble and inconvenience leading Rock and Burbank (104) to suggest improvements. Some of their suggestions were implemented in this research. These consisted of (1) providing flexible rubber connections on either side of the cell to

provide for easy replacement of damaged cells and interchangeability of glassware components, (2) partial straightening of the curve in the right-hand glassware section to remove an inherent bubble trap, and (3) use of a porous material fitted to the open end of each electrode to lengthen electrode life by preventing entry of settling particles while permitting passage of electric current; the porous material used was glass wool.

The entire cell assembly was mounted on an aluminum frame. The frame could be easily secured to or removed from the microscope stage, as desired. Some additional information about the cell, as well as the relationship used in calculating electrophoretic mobilities, is given in Table 3.

Power Supply

An electrophoresis power supply, manufactured by A. H. Thomas Company, was used as a constant current source. This unit is also capable of supplying a constant voltage, although this feature is not useful in working with a Briggs cell.

Microscope and Accessories

The microscope used was a Spenser model provided with standard oil immersion and water immersion objectives, a quadruple revolving nosepiece and a graduated mechanical stage. A 10x objective and 25x occular were employed for the mobility work. For the concentration and size of particulate matter dealt with, this 250-magnification was the most

TABLE 3

Microelectrophoresis Constants

Cell Depth (viewed full of water)	780 μ
Cell Depth (actual)	1040 μ
Lower Stationary Layer (distance from bottom)	156 μ
Cell Width	20.2 mm
Cell Cross-Section	0.210 cc
Micrometer Calibration	4.8 μ/Div.

$$\Omega = \frac{10 \times 4.8 \times 0.210}{t \times I \times R_s}$$

In which Ω = electrophoretic mobility (μ/sec/v/cm)

t = time for particle to migrate 10 micrometer divisions (sec)

I = applied current (amps)

R_s = specific resistance (ohm-cm^2)

satisfactory in terms of providing sufficient viewing area for ease of timing.

A saturated copper sulfate solution contained in a plexiglass vessel was placed in front of the microscope illuminator. The solution served to absorb heat rays from the light source, preventing density currents due to differential heating in the cell.

Mobility Measurements

Electrophoretic mobilities of algae and particles of silica were determined according to the methods of Black and coworkers (8-10). The silica particles used in these measurements were obtained by washing the fines from fresh sand as it was received from the manufacturer. All particles were suspended in tap water, the pH being adjusted in the same manner as in the filtration runs so that representative mobilities would be obtained.

Data Collection and Analytical Methods

Data Collection

The filtration properties of the suspensions dealt with in this research were determined either by removal efficiency data or by head loss and penetration readings, depending on whether the suspended material was algae or iron, respectively. These parameters have been used with success pre-

viously (e.g. 29,95,97). The frequency at which samples or readings were taken was determined by the nature and anticipated length of the filter run. Analysis of the filter samples was, in all cases, conducted immediately after collection.

Iron Determination

Analyses for ferric iron were made, with few exceptions, only on filter influent samples. Procedures followed were those for the Phenanthroline method, as set forth in Standard Methods (116). The calibration curve utilized is given in Appendix III.

Jar Tests

When the flocculation characteristics of a suspension to be filtered were desired, jar tests were run utilizing a 100 rpm rapid mix for 2 minutes, a 20 rpm slow mix for 10 minutes and a 15 minute settling period. Samples for analysis were withdrawn from a point 1-1/2 inches below the surface of the liquid.

Filters

Filter Columns

Four filters were constructed of plexiglass tubes having an inside diameter of 3-5/8 inches and a wall thickness of 3/16 inch. Each filter was fabricated from two plexiglass sections four feet in length, the two sections being flanged

and bolted together with 4 brass bolts and wing nuts. A watertight seal was achieved with a 4 inch by 1/8 inch rubber o-ring seated in a groove on the lower flange. This arrangement permitted rapid and easy dismantling of the two filter sections between runs.

Piezometer Ports

For the studies involving the filtration of flocculent material, it was felt that head loss readings afforded the best measure of the rate of clogging of the sand bed. In some studies it was desired to measure not only the total head loss but also the losses in various layers of the bed. For this purpose, eight piezometer ports were placed at various distances below the sand surface as shown in Figure 2-2. The piezometer taps were constructed of 1/4 inch I. D. acrylic tubing which was threaded to engage holes tapped in the filter tube. A watertight seal was provided by placing a strip of plastic film around the tap before screwing it into the filter.

Several designs of piezometer ports were tried, the simplest design emerging as the most satisfactory. This consisted simply of wedging a disc of brass mesh into a 1 inch piece of the acrylic tubing. The mesh openings were of such a size as to restrict passage of sand into the manometer tubes, yet allow rapid response of the piezometer tubes

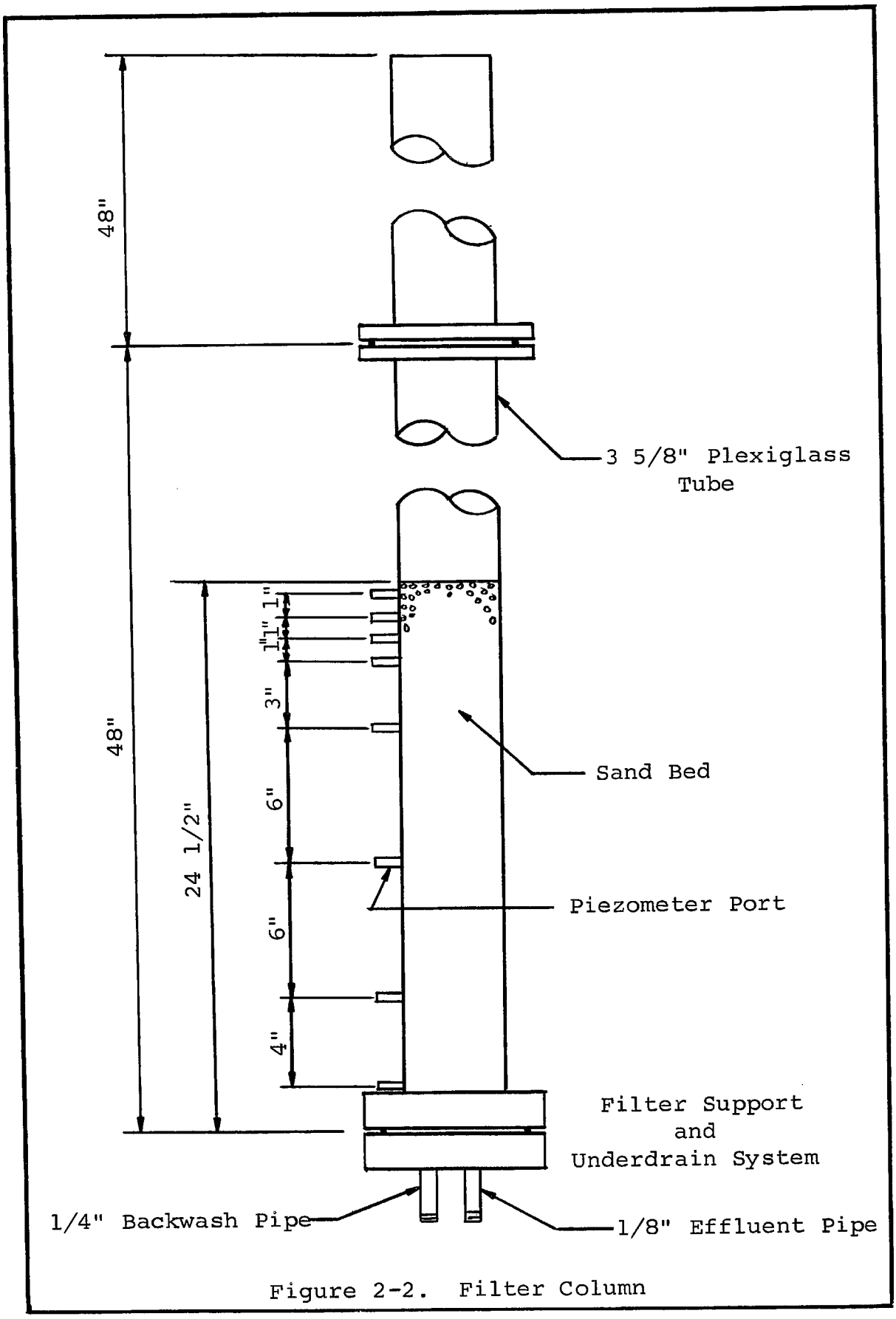


Figure 2-2. Filter Column

to changes of head in the filters.

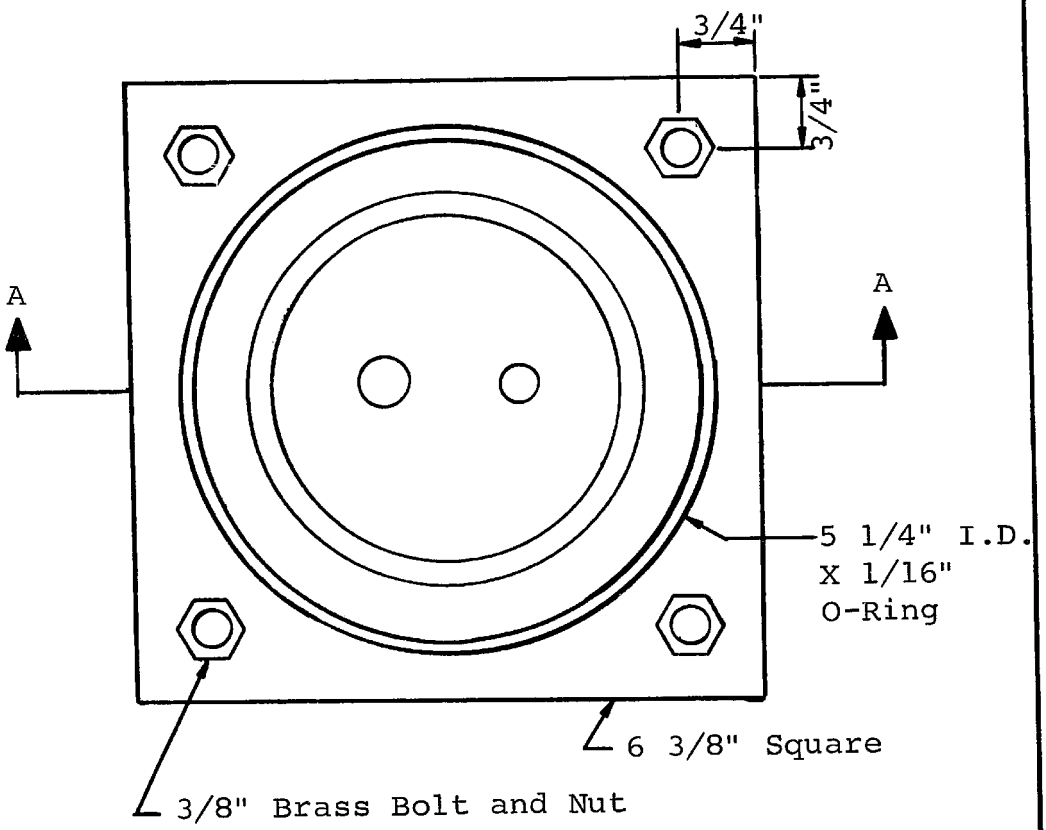
The piezometer ports were connected by means of rubber tubing to piezometer tubes. The latter were made of sections of 11 mm glass tubing and secured to a sheet of 1/2 inch plywood located behind the filters. The piezometer board was covered with profile paper marked into feet, inches, and tenths of inches and the paper, in turn, was protected from water spillage by a sheet of transparent acetate.

Filter Bottom and Underdrain System

Previous workers (29, 95) utilizing plexiglass filters with bottoms consisting of square, plastic-coated wooden blocks indicated leakage to be a persistent problem. This led to the adoption of a plexiglass design which is shown in Figure 2-3.

The bottom was constructed from two 6-3/8 inch square plexiglass blocks each 1-1/2 inches thick. The upper block served as a flange for the filter column while the lower one provided a support for the porous underdrain, as well as an effluent and backwash flow transition zone. The two blocks were fastened together with four 3/8 inch brass bolts and nuts placed at each corner; a rubber o-ring placed between the blocks prevented leakage.

The underdrain system consisted of a porous polyethylene sheet which separated the sand bed from the flow transition region and the effluent- and backwash-pipes. The synthetic



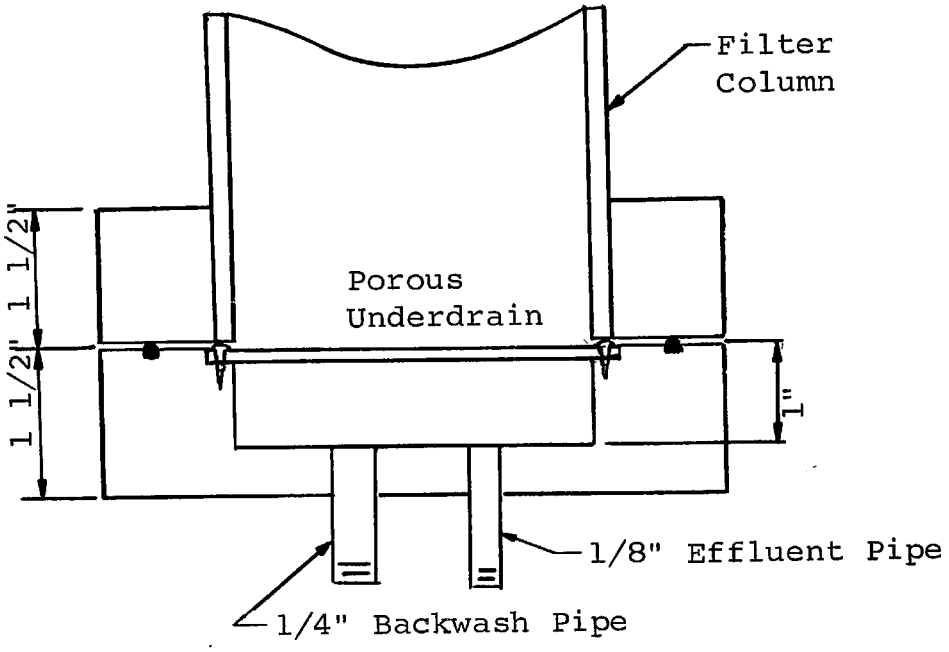


Figure 2-3. Filter Bottom and Underdrain

porous underdrain added negligible head loss to the system and served well in preventing passage of the sand during filtration.

The filter bottom blocks produced a stable and leak-free base and could be readily dismantled when the need arose.

Flow-Controlling Mechanism

In the hydraulic design of the filter system it was desired to simulate the operation of an actual plant filter as closely as possible. Thus, two requirements had to be met: (1) the rate of filtration had to be maintained constant at a predetermined level against a variable head loss in the filter bed, and (2) the water level above the sand bed had to be kept at a precise level throughout a filter run. Fulfillment of these requirements meant that the overall head loss through the sand bed and the effluent needle valve had to be held constant, the proper distribution of head loss between the bed and the valve being achieved by opening the valve as the bed became clogged.

The control apparatus consisted of a motor-driven needle valve; the action of the motor was governed by the level of water in the filter column. Thus, when the water level would rise, due to head loss build-up in the filter, a plastic ball float would activate a micro-switch. This

action would result in current being fed to the motor, causing it to turn in the direction appropriate to open the valve. If, on the other hand, the water level fell due to overcorrection of the valve, the float would activate a second micro-switch which would complete the circuit to the motor, causing it to close the valve. Of course, if the water level remained constant neither micro-switch was activated and the valve position remained constant.

Using this same type of rate-controlling mechanism, Davis (29) found that the motors were not rapid enough in their response to prevent wandering of the water level. Following his correctional procedure, a "normally closed" solenoid valve was connected to the filter column above the sand bed and wired in parallel across the "open" motor line. Thus, whenever the upper micro-switch was activated, due to a rise in water level, the valve would withdraw water from above the filter. This rapid response in lowering the water level prevented over-opening of the effluent needle valve and allowed water levels to be maintained within 1/2 inch of the desired level. The amount of water withdrawn through the solenoid valves was less than 1 per cent of the total water filtered in all runs tested. A schematic diagram of the the rate-controller circuit is presented in Figure 2-4. It might be mentioned that the purpose of the

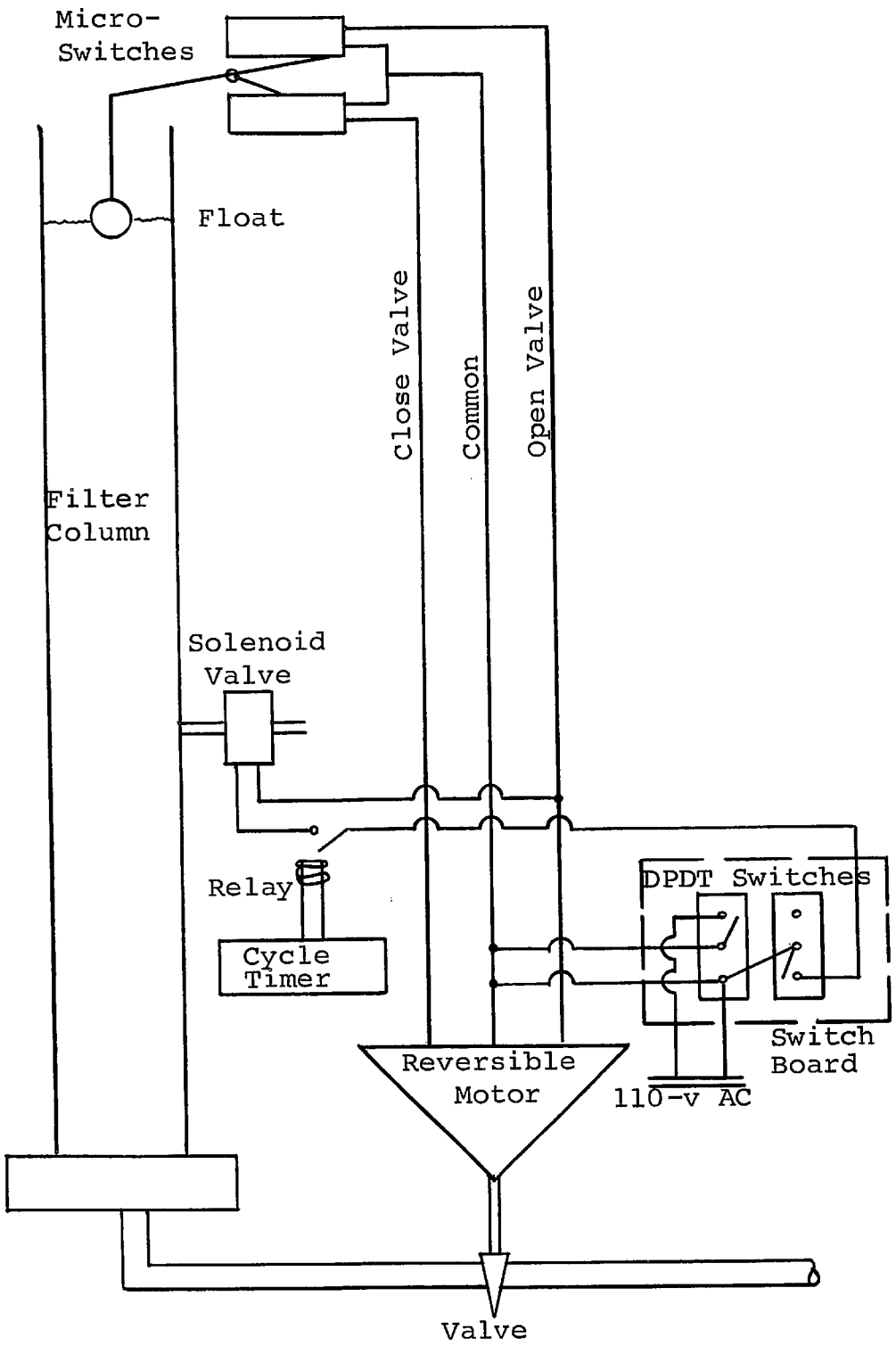


Figure 2-4. Schematic Diagram of Electrical Circuit for the Filter Flow-Controlling Mechanism

timer-activated relay was to open the 110-v solenoid line at periodic intervals. This action was found necessary because a residual voltage in the solenoid line after its operation prevented the motor from working properly.

The effluent needle valves and motors, for reasons of safety and convenience, were not placed directly beneath the filters but rather were mounted together on a wooden box which was placed on one side of the filter assembly. Polyethylene tubing was employed to carry water from the filters to their respective needle valves. The valves were mounted in a vertical position with 1-rpm Hearst reversible motors being located directly above them. Connection between motor and valve was made by means of a slotted steel shaft, one end of the shaft being fastened to the motor stem with a set screw, the other end being fitted over the valve stem and coupled with a pin. With this arrangement care had to be taken to avoid complete opening or closing of the valve in order to prevent stripping of the gears in the motor driving-mechanism.

The water-level and flow-rate control mechanisms operated in a completely satisfactory manner throughout the course of the experiments. It handled with equal facility runs in which there was rapid head loss build-up and runs in which the head loss increase was negligible.

CHAPTER 3

SAND FILTRATION THEORY

Flow Through Porous Media

In studying rapid sand filtration it is useful to have a basic understanding of the laws of fluid flow through porous media. The earliest formulation of laminar flow through granular material is that of Darcy (1856), which states that the head loss (H) through the bed is directly proportional to the bed depth (L) and to the rate of flow (v):

$$H = \frac{1}{K} v L$$

where K is the coefficient of permeability.

The refinement of this equation, i.e., the problem of relating the permeability coefficient to the properties of the fluid and the porous medium, has been the subject of numerous investigations. All of these have been based on the assumption that a porous medium is equivalent to a series of channels, or, in other words, that the streamline flow of water through sand is governed by essentially the same factors as the streamline flow of water through pipes.

The simplest models which have been constructed are those which picture the sand bed as consisting of capillaries.

These models aim at correlating the permeability with either an "average" pore size or with the pore size distribution curve. Unfortunately, views on the nature and size of the equivalent capillaries have differed considerably. The simplest capillaric model is one representing a porous medium by a bundle of straight parallel capillaries of uniform diameter d, and is expressed in the familiar equation of Hagen-Poiseuille:

$$H = \frac{128\,\mu}{d^4}\, v\, L$$

where μ is the fluid viscosity.

For various reasons none of the capillaric models, simple or complex, yielded a satisfactory explanation of the nature of the proportionality relationship in Darcy's law. As a result, more sophisticated models began to appear in the literature. These were also based upon the assumption that a porous medium is equivalent to a series of pipes, but the pipes were considered to be more elaborate than in the capillaric models. These theories all made use of the fundamental observation that the permeability, in absolute units, has the dimension of an area or of a length squared. They argued, therefore, that a length should be characteristic of the permeability of a porous medium, and they termed such a length "hydraulic radius". The most common measure of a hydraulic radius was taken as the ratio of pore volume to

surface area of the sand (109).

Starting with the Darcy-Weisbach equation for flow through pipes,

$$H = f \frac{L}{d} \frac{v^2}{2g}$$

where d is the pipe diameter and f the friction factor, two different investigators (18,35) by introducing the concept of hydraulic radius, independently arrived at the same flow expression:

$$H = f \frac{\mu L v}{\rho g} \frac{S^2}{d^2} \frac{(1 - p)^2}{p^3}$$

in which S is a shape factor--with a value of 6 for spheres, p is the bed porosity and ρ is the fluid mass density. Fair and Hatch (35) determined the value of S for sands of varying degrees of sharpness. Several investigators have evaluated f (14,18,35,89). This relationship, which is referred to interchangeably as the Carman-Kozeny or Fair-Hatch equation is today the most widely accepted description of the effects of the geometrical properties of a porous medium on its permeability.

Several other relationships have been developed which merit mention. Hazen (51) and Hulbert and Feban (61) each developed equations from experimental observations, and Rose (105) derived a relationship through dimensional analysis and empirical evaluation of constants.

It is clear from this brief discussion that even a description of the comparatively simple case of flow of clear water through uniform beds is complex and open to variable interprepation. When particulate matter is added to the water the problem of describing the head loss build-up in terms of the media and suspension characteristics becomes much more complicated. Nevertheless it has been attempted and some of the models will be discussed later in this chapter; first, the mechanisms and factors influencing filtration will be examined.

Mechanisms of Particle Removal in Porous Media

General

Many mechanisms have been suggested to explain the removal of small particles from water within a filter bed composed of relatively coarse material. These may be outlined as follows:

(1) Mechanisms governing particle transport to the media surface

  (a) gravitational sedimentation

  (b) Brownian movement

  (c) inertial impaction

  (d) chance contact (direct interception)

(2) Mechanisms governing particle attachment at the media surface

  (a) electrokinetic effects

(b) van der Waals forces

(c) specific chemical effects

(d) straining

In the following discussion, a more detailed consideration will be given of those mechanisms which are of greatest interest in this research.

Gravitational Sedimentation

That the void spaces in a rapid sand filter act as miniature settling basins was one of the first theories to explain the movement of particles from flow stream lines to the surface of sand grains. Hazen (52) in 1904 postulated that this mechanism can be expected to operate on particles as small as 0.3 μ in diameter. Based on Hazen's arguments, Fair and Geyer (37) set forth a convincing argument to show that a rapid sand filter should be able to remove, by settling, particles which are 1/20 of the diameter of particles removed in a settling basin of equal surface loading. Stanley (117), among others, has also expressed agreement with the arguments of Fair and Geyer.

In his mathematical developments of filtration theory, Ives (67,69) assumes that gravity is the principal force acting on particles of suspended matter in the flow within the filter. Hall (47) has postulated a theory for sedimentation removal in which gravitational sedimentation would

predominate as the sand size increases or the flow rate decreases. Similarly, gravitational sedimentation has been proposed as a primary removal mechanism in air filtration by Chen (19) and Humphrey and Gaden (62), and as a contributory removal mechanism in water filtration by Grace (45).

On the other hand, several other investigators have concluded that sedimentation is not an important mechanism for removing suspended particles from the flow streamlines. Heertjes and Lerk (55) found that iron hydroxide flocs with with a diameter of 10 microns have a sedimentation velocity of only about 8×10^{-4} m/hr. Stein (120) ruled out sedimentation on the basis of microscopic observations of a small simulated filter which showed that floc particles appeared to adhere mostly at points where the flow path was constricted and did not seem to have any preference for horizontal surfaces. Similarly, Ives, in more recent papers, seems to have altered his original concept that gravitational forces are of major importance. He states (70) that "it is difficult to explain the removal of small watery flocs of low effective density (1.005 g/cc) by any gravitational hypothesis", and in a later paper (74) that gravity was not a significant force in filtration studies using polyvinyl chloride particles of mean diameter 1.3 microns and density 1.4 g/cc.

Current thinking would seem to reject gravity as being a significant force in water filtration. This need not be the case in air filtration, however, where the difference in density between the particle and the fluid is much greater.

Brownian Movement

The significance of Brownian movement as a means of forcing particles from the flow lines and into contact with a solid surface has been discussed by several workers (19,28, 45,54,70,77,97,117). All agree, based on calculation and direct microscopic observation, that Brownian Forces are insignificant for particles greater than about 2 microns in diameter. However, Johnstone and Roberts (77) and Heertjes (54) suggest that this is probably the most important contact mechanism for particles in the colloidal size range.

A direct result of Brownian movement, diffusion, is the tendency for molecules and colloidal particles to migrate from a region of high concentration to a region of low concentration. Starkey et al. (119) appear to have been the first investigators to propose that diffusional forces operate on the particles of a disperse phase so as to displace them from the streamlines on which they initially move to other streamlines where the velocity (and concentration) gradient is lower. This concept received considerable support from Hunter and Alexander (63) who viewed the sand bed as consisting of regions

where the liquid flow approximates that in a capillary, and regions where the liquid flow is essentially zero. They reasoned, therefore, that when a clay suspension is passed through such a porous medium, the clay particles would diffuse across the streamlines into the regions of low flow due to the concentration gradient initially present. Both Starkey and Hunter and Alexander also postulated that colloidal migration from regions of high shear to regions of low shear can take place even against an adverse concentration gradient.

Recently, Edwards and Monke (33) reported that diffusional forces operated as the major transport mechanism in the removal of clay particles from their sand columns.

While diffusional forces can be demonstrated to be operative, no investigation thus far has presented solid evidence to suggest that they are of significant magnitude in the rapid sand filtration process. In any case, they would be limited to particles less than about 2 microns in diameter.

Inertial Impaction

The tendency of the particles in a suspension to continue in a straight-line path when the streamlines of the fluid bend to pass around a sand grain can cause particles with sufficient momentum to impinge on an adjacent grain. The force of inertia is dependent upon the viscosity and flow rate of the fluid, the size and density of the suspended

particle, and the diameter of the sand grain. A consideration of these factors has led to a virtual elimination of inertial impaction as a contact mechanism in water filtration by several investigators (28,55,70,97,117).

Chance Contact (Direct Interception)

Particles which have no inertia can be considered as massless and will therefore follow the fluid streamlines. If such particles have a finite diameter d, they will touch a sand grain when their center approaches within a distance d/2 of the grain surface. When this occurs it is variously termed chance contact or direct interception. According to Stein (120), this type of contact is brought about principally by the convergence of streamlines at contractions in the pore channels and in the vicinity of curved surfaces of the grains. This concept has received support from Craft (28) and Camp (17). Grace (45) has suggested that for particles 0.5 micron to 20 microns in diameter interception predominates over sedimentation, Brownian movement, and inertial impingement as a contact mechanism, and that interception increases in relative importance as the liquid viscosity increases.

At least two quantitative expressions have been developed relating the probability of removal by chance contact to measureable parameters of the fluid and bed (19,120). Both of these relationships involve solely the diameter of the

suspended particle and that of the collector. Humphrey and Gaden (62) report, however, that direct interception is also a function of Reynolds number.

Available evidence appears to support chance contact as a significant mechanism for promoting particle-sand contact in rapid sand filtration.

Electrokinetic Effects

General. Electrokinetic effects arise in filtration owing to the fact that all solid particles assume an electrostatic charge when placed in contact with an aqueous phase. The origin and sign of the charge and the distance over which it is effective vary, depending upon the surface chemistry of the substance and the composition of the water.

As Hauser (49) has pointed out, a suspension should not be represented as an aggregate of statically charged spheres. Rather, the charge on each particle should be viewed as being compensated by a double layer of counter ions from the solution so that the system as a whole is uncharged. The current concept of the double layer, evolved from the work of Helmholtz, Perrin, Chapman, Gouy and Stern, is depicted schematically in Figure 3-1.

When a suspended particle approaches the surface of a sand grain, the diffuse ion atmospheres of the two double layers begin to interact. If the double layers are of

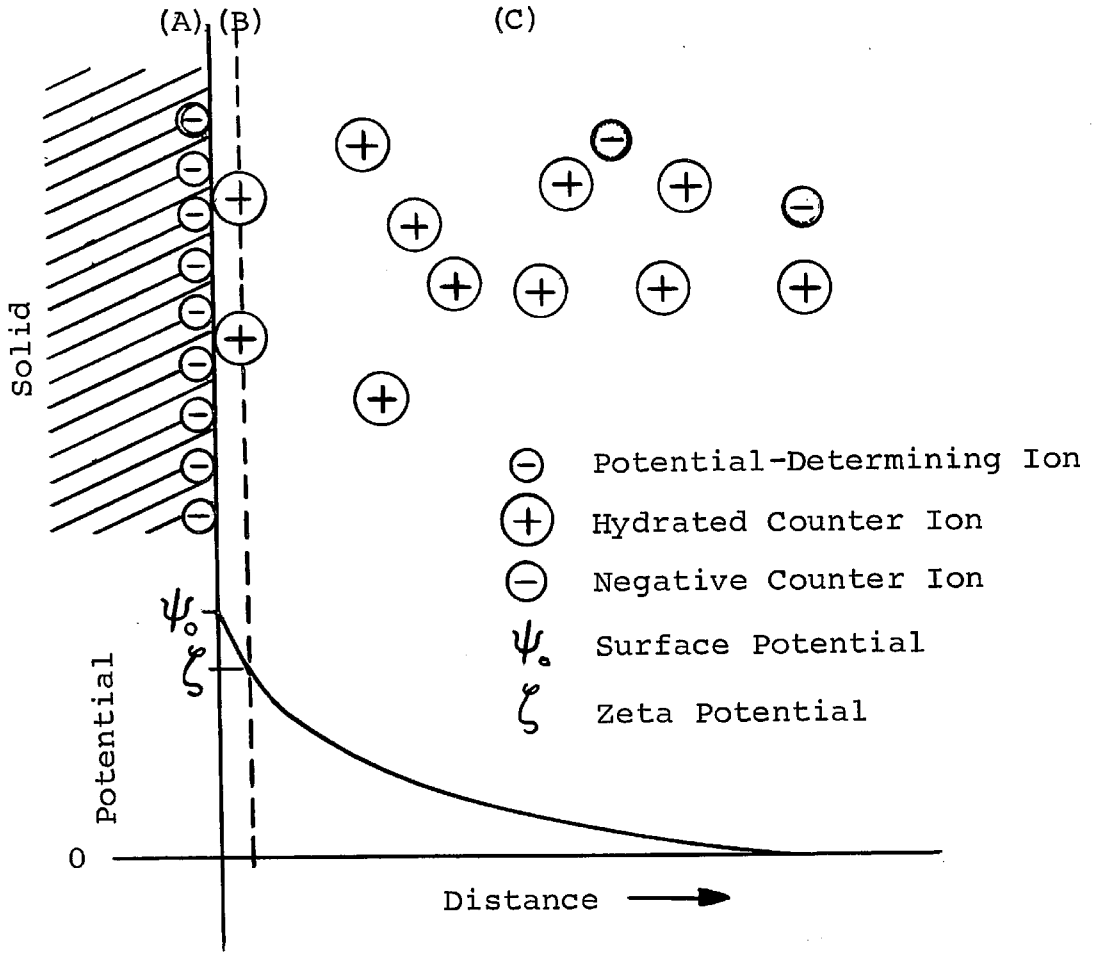


Figure 3-1. Schematic Representation of the Structure of the Double Layer and Potential Distribution in the Double Layer in Electrolyte Solutions; (A) Potential-determining ions which may be regarded as part of the solid lattice; (B) Fixed layer of counter ions in the Stern plane, a few Angstrom units in thickness; (C) Diffuse layer of counter ions.

opposite sign, this interaction will generate an attractive potential energy which, if of sufficient magnitude, will cause the particle to be pulled from the streamlines and become attached to the grain surface. In this respect, electrokinetic effects may be considered to contribute to particle transport as well as particle attachment, although there is considerable doubt that the transport function is significant based upon the work of Ives and Gregory (72). The distances over which electrical effects are significant are quite small in relation to the dimensions of the pore space in a sand filter. If, on the other hand, the double layers are of similar sign, the interaction will result in the formation of a repulsive potential energy which will act to prevent attachment of the particle on the media surface. Whether the interactions produce attractive or repulsive forces is determined largely by the pH and chemical composition of the fluid, as will be discussed later in the chapter.

For a long time, the retention of particles within a sand filter was thought to be strictly a mechanical sieving process. In the first half of the twentieth century several workers suggested that electrokinetic effects might be important, but none determined the nature or magnitude of these effects. In 1946, Ruth (106) concluded that electro-

kinetic phenomena play a dominant role in the success or failure of the filtration process. He based his conclusion on the observation "that particles so much smaller than the openings of a filter septum manage to become entangled in such a way as to block it early in the initial stages of filtration".

Flocculent Suspensions. In 1955 Stanley (117) reasoned that positively charged iron floc particles in suspension would be most readily removed in a filter so long as the surface of the filter medium remained negatively charged. He argued, however, that the sand grains become coated very rapidly, producing a charge essentially the same as that on the floc particles themselves. Under these conditions, he felt that the particles would have the best chance of adhering to a coated sand grain if the electrostatic repelling forces were at a minimum. His experimental work seemed to varify this, but no measurements of particle surface characteristics were made nor was floc size controlled precisely.

In 1961 Cleasby and Baumann (21) concluded that electrokinetic forces were primarily responsible for removal of hydrous ferric oxide particles. Their conclusion was based mainly on the observation that suspensions of small ferric-floc particles (1-20 microns) were more filterable (that is,

produced less bed penetration) than those containing larger particles (20-100 microns). However, the possibility that this effect might also have been produced by a shearing of the larger, more fragile flocs into much smaller particles within the filter was not investigated. Moreover, no measurements of particle surface properties were made.

Recently, O'Melia and Crapps (97) conducted investigations of the flow of ferric-floc particles through sand columns. Electrophoresis measurements were used to correlate the mobility of floc particles in various suspensions to the filtering characteristics of these suspensions. Sulfates, chlorides, and phosphates as well as three different pH values were used to alter the surface characteristics of the floc particles. A good qualitative correlation was obtained which showed that there is a trend towards more difficult filtration as the electrophoretic mobility of the applied floc particles becomes increasingly negative. The authors interpreted this result as indicating that there is an electrostatic interaction between the surfaces of the filter medium and the suspended floc particles; the alternative interpretation that there is an interaction between the suspended floc particles themselves (in accordance with Stanley's theory) was rejected. No flocculation tests were performed to substantiate this rejection.

A more recent paper by O'Melia (98) suggests that he may have modified his original position that floc-sand electrostatic interactions control the removal process. He states in this later publication that experimental evaluations of zeta potential are not sufficiently accurate upon which to base a double layer theory--indeed, that they can, at best, afford only a very rough measure of electrostatic action. He further implies that colloid chemical forces other than those of electrostatic origin may control floc attachment.

Several other workers have also concluded that electrostatic interactions between floc particles and sand surfaces are unimportant in filtration (108,111,115). Segall and Okun (111), for example, studied the relative importance of sand and anthracite media and found that the differences are attributable to dissimilarities in grain size and porosity of the two materials rather than the materials themselves. Similarly, Sanford and Gates (108) found that filter sands coated with a surfactant did not affect removal of aluminum floc. They concluded that sand surfaces do not play a major role in the removal of floc by rapid sand filters.

All of the investigations mentioned utilized comparatively large iron flocs (equivalent diameter greater than one micron). Heertjes and Lerk (54) studied the sand filtration of both small colloidal ferric hydroxide particles

(40 millimicrons diameter) and larger well-flocculated particles (0.1-10 microns diameter). It was concluded that the positively charged colloidal particles are removed by sorptive action between the particles and the filter material, and that this sorption is electrostatic in nature. Streaming and zeta potential measurements were used as supportive evidence, as well as the fact that the sorption could be described by an equation identicle to the Freundlich isotherm. However, it should be pointed out that many phenomena, apart from adsorption, can be described by a Freundlich isotherm. On the other hand, it was concluded that the particles of a well-flocculated suspension have such a low zeta potential that electrokinetic effects can be neglected, and that London-van der Waals attractive forces remain as the only possible interaction by which the suspended particles can be caught in the filter bed. This view is also the one expressed by Mackrle and Mackrle (86).

Discrete Suspensions. It is apparent that no concensus has been reached regarding electrokinetic effects in the filtration of iron floc. By contrast, several investigations of electrical effects in the filtration of non-flocculent materials within the last five years have demonstrated some uniformity of opinion. For the most part, these studies have utilized clay suspensions from which the settleable particles

have been removed. As a result, the remaining particles have generally been smaller than iron flocs, a significant percentage being in the sub-micron range.

Hunter and Alexander (63) conducted investigations of the flow of kaolinite suspensions through silica sand columns. It was found in one experiment that when the zeta potential of the sand was increased from -48 mv to +5 mv with 0.0001 M hexadecyltrimethylammonium ions, the deposition of negatively charged kaolinite in the sand was substantially increased. Presumably, this effect was the result of electrostatic interaction.

Smith (115) investigated the filtering properties of bentonite, considering only particles greater than 2 microns in diameter, which was the lower limit of his measuring technique. Streaming potential measurements on the clean sand bed, with Baltimore tap water as the fluid, indicated a positive zeta potential at the sand-liquid interface. The relatively soft Baltimore water contained only small quantities of multivalent cations, suggesting that the author's procedure or equipment was in error. Nevertheless, when the sand surface was made more negative by the addition of lithium ferrocyanide, poorer removals of the negatively charged bentonite particles resulted. The author concluded that the removal mechanism is primarily electrostatic in nature.

The flow of clay suspensions through slow sand filters has been studied by Jorden (78) and by Edwards and Monke (33). Jorden postulated the presence of a positively-charged bacterial film on the sand to explain the improved filtration noted when the clay particles were made more negative by adding sodium hexametaphosphate. Edwards and Monke confirmed the presence of a similar positively-charged bacterial film in their experiments with streaming potential measurements, but did not find a correlation between filter performance and relative charges of filter media and suspended particles. It should be mentioned, however, that there appear to be certain inconsistencies in their work. For example, they found that the zeta potential of bentonite clay particles became more positive as the pH of the clay sol was increased from 5.1 to 8.4, and stated that the cause of this effect was the higher electrolyte concentrations obtaining in the sol as the pH was increased. Edwards and Monke concluded that electrokinetic forces are but one possible explanation for the retention of clay colloids by a silica sand filter.

Marshall and Kitchener (87) investigated the deposition of negatively charged carbon particles (0.45 micron average diameter) from dilute aqueous suspensions onto glass and other surfaces of different character. Small discs composed of the various surfaces were rotated in the carbon suspen-

sion at a speed of 200 rpm. It was found that deposition was greatest when particles and solids had zeta potentials of opposite sign, and deposition was reduced by increased zeta potentials of like sign. The authors attributed the major forces causing adhesion or non-adhesion to London-van der Waals forces and electrical double layer interactions.

Oulman et al. (100) have demonstrated through streaming potential measurements that the surface charge of diatomaceous earth can be reversed from negative to positive values by coating with alum or cationic polyelectrolytes. It was found that diatomite filters coated with such materials provided increased removal of negatively charged colloids. Polyelectrolytes have also been used with success in rapid sand filtration (25,41).

The inaccuracy of zeta potential measurements notwithstanding, there is strong evidence to suggest that electrokinetic phenomena are very significant in the rapid sand filtration of discrete suspensions of clays and other particles in the colloidal size range. Information on electrokinetic effects in the filtration of flocculent materials, however, is clearly contradictory. Furthermore, there is little or no information of electrokinetic phenomena in the filtration of comparatively large discrete particles such as algae.

van der Waals Forces

These are molecular attractive forces between particles which can overcome the repelling forces of electrokinetic interactions and cause coagulation of particles of like charge. They have been discussed in detail in Kruyt (80). Mackrle and Mackrle (86) have shown by calculation that these forces are almost independent of the nature of the surface involved. They could, thus, account for the removal of negatively charged particles on negatively charged filter media.

While most workers agree that these forces can be significant in particle attachment at the sand surface, it is not yet clear whether they are of sufficient magnitude to control particle transport from the flow streamlines. Available evidence seems to indicate that they are not. Between two atoms, van der Waals forces vary inversely as the seventh power of their distance of separation (123); since these forces are additive, large particles composed of many atoms attract each other with a force that is inversely proportional to the cube of the separation distance. Because of the rapid decrease of effect as distance increases, Ives (70) concluded that a particle must be virtually touching a grain before molecular forces become operative. It is known, however, that the range of London-van der Waals

forces between colloidal particles is of the order of the particle radius (123).

Because of the practical difficulties in evaluating van der Waals cohesive forces--an estimate of the Hamaker constant in aqueous systems is involved--few quantitative studies of the importance of these forces have been made. The Hamaker constant depends upon the nature (particularly the number of atoms per milliliter and the polarizability) of the material in question; its value for particles in air has been established by direct measurement, but the exact modification required if the attractive forces are transmitted through water is not known. Mackrle and Mackrle (86) have developed a mathematical model based on van der Waals attractive forces and hydrodynamic effects, but these authors considered electrokinetic forces to be insignificant. Ives and Gregory (72) have developed a mathematical model considering both electrostatic and van der Waals effects, but several objections to their work have also been raised (98).

Specific Chemical Effects

It has been known for some time--but stated in explicit terms only recently (98)--that electrostatic interactions are but one of several types of colloid-chemical reactions which can occur at the water-filter interface. As evidence, a simple coulombic attraction model cannot account for the

observed charge reversal of filter media by coatings of certain multi-valent cations and polyelectrolytes; the Gouy-Chapman model for the double layer does not permit an attraction of counter-ions in excess of the original surface charge. Similarly, several investigators of particle attachment have observed adhesion patterns which cannot be explained by electrostatic attraction or any physical mechanism. Such phenomena have usually been attributed to the all-inclusive term "adsorption", or have not been defined at all.

Stein (120), for example, found that nearly every iron-floc stock suspension made for his filtration studies had its own peculiar characteristics, and that only slight differences in the final pH often affected the adhering ability of the floc and the resistance of the floc sheath to shear.

Filmer and Corey (38) studied the filtration of radioactively-labeled albumin molecules which were used to simulate viruses. Straining was ruled out and it was concluded that albumin retention was due to an adsorption mechanism, the exact nature of which was not understood. On the other hand, Clark and Chang (20) attributed the relative ineffectiveness of sand filters in removing viruses to "the inherently poor adsorption properties of the sand".

Edwards and Monke (33) proposed that "adsorption" is

one of the possible mechanisms operating in the removal of clay colloids in a silica sand column.

Several workers (83,90,91) have observed the adsorption of anionic polymers on negative surfaces. Michaels and Morelos (91) suggested three possible mechanisms to explain this behavior; (1) ion-interchange, (2) hydrogen bonding, and (3) the formation of coordinative bonds and linkages. O'Melia and Stumm (98) have proposed that these concepts should also be applied to particle attachment in water filtration.

The work of Harris and Satanek (48) appears to lend support to the preceding arguments. These workers investigated the adsorption of algal protein on various substances, including glass, quartz, porcelain, steel, stainless steel, aluminum, polyethylene, nylon and teflon. It was concluded that adsorption probably occurred via an "ion-exchange" mechanism with most of the substrates, although no information was presented on the nature of this process. Other workers (e.g., 122,123) have also postulated that algae are capable of behaving much like ion-exchange resins. It is well recognized that alginic acid occurs as an insoluble salt in algae and that it exists as a mixed salt with calcium and magnesium as the main cations (123). These calcium and magnesium ions presumably can exchange with other cations

outside of the cell by diffusion through the algal membrane. However, it is difficult to visualize how this property of algae could account for their removal in a sand filter.

Numerous investigators (7,24-26,53,57,60,79,82,92,95, 112,117) have observed the relationship between the stability, or state of flocculation, of a suspension, and its filterability. Indeed, filtration tests have been proposed to supplant jar tests as a means of determining optimum coagulant dosages (26,78,82). Unfortunately, some workers feel that conditions which are optimum for filtration are the same as those which are optimum for flocculation (24,53,117), while others do not (27,97,112). Nevertheless, these observations tend to suggest that some of the mechanisms purported to be operating in coagulation and flocculation, e.g., chemical bridging, may also be important in filtration.

There can be no doubt that specific chemical effects in water filtration have not received adequate study. Sufficient evidence of their importance has been collected to justify future work in this area.

Straining

This mechanism may be considered in two parts: (1) surface straining and (2) interstitial straining. That particles too large to flow through the openings of the filter medium will be strained out at, or near, the surface is obvious and

undisputed. That particles small enough to flow through the filter openings can be strained out in the small interstitial crevices where two grains touch is much-disputed and open to question.

Baylis (6) in 1937 was one of the first to postulate that the coagulated material which passes beneath the surface of the bed is filtered largely by lodgement of the coagulated particles in the wedge-shaped parts of the void where two grains of the material touch. His concept received support from Eliassen (34) in 1940 who found that the size of flocs taken from the filter at various sampling points decreased with filter depth. Likewise, Hall (47) in 1955 postulated a model based on interstitial straining of the type described by Baylis, and verified it with previously published data on the filtration of iron floc (10-25 microns diameter). Grace (45) and Agrawal (2) have also supported direct sieving at pore constrictions as a means of particle removal.

On the other hand, several other investigators (28,54, 115,117) have minimized the importance of straining as a removal mechanism. They point to the small sizes of most suspended particles in relation to pore diameters, and to the dependence of removal on the composition of the particle, irrespective of size. Heertjes and Lerk (54) state that

suspended particles must be at least one-fifth of the mean filter-pore diameter for straining to be appreciable.

Suspended particle growth produced by flocculation within filter pores has been proposed as an adjunct to straining by some investigators (37,115). This would explain the high removal efficiency observed for small flocculent particles in contrast to the low removals noted for non-flocculent particles of even larger size. However, a consideration of the flocculation process led Stanley (117) and others (97) to the conclusion that this mechanism is insignificant in rapid sand filters. Stanley found that, while the mean velocity gradient in a rapid sand filter is optimum for promoting contact of particles, the detention time of particles in the filter is far too short to promote growth to the extent necessary for straining.

The calculations presented by Stanley to illustrate the insignificance of flocculation in rapid sand filtration are very convincing. However, the idea that the filter acts as a "super" coagulator is still prevalent today (e.g.,115). The experimental difficulty of isolating the flocculation mechanism from all other influences is, perhaps, the reason for the continuing controversy. More work is needed in this area. Similarly, the impossibility of measuring suspended sizes accurately has, in the past, hindered efforts to prove

or disprove the interstitial straining theory. The use of the Coulter counter in this research should help to clarify this situation.

Effects of Filter-Sand Properties on Particle Removal

General

The relative importance of each of the removal mechanisms which have been discussed is determined largely by filter operational procedures and by various properties of the filter sand and fluid suspension. Hence, a knowledge of these factors is essential for control of the filtration process. The operational procedures and fluid suspension properties which affect particle removal will be considered in following sections; the filter sand properties which affect filtration are listed and discussed below.

(1) sand size

(2) sand shape

(3) packing arrangement of the sand grains

(4) bed porosity

(5) bed depth

(6) surface properties of the sand grains

Sand Size

In general it can be said that sand beds composed of smaller grains are more effective for filtration and, conse-

quently, that they clog faster. This result is presumably due to the dependence of the straining (47) and direct interception (19,62) mechanisms on the sand size. It is also possible that particle removal by chemical and electrostatic effects would be increased by smaller sand sizes by virtue of the increased surface area produced.

Numerous workers have attempted to develop an empirical relationship between filtration parameters and sand size (5,47,59,73,117). The results are remarkable only in their disagreement. In evaluating some of these relationships, Ives and Sholji (73) found that various workers had reported that filter efficiency varies with $d^{-1.0}$ to $d^{-3.0}$. There are at least two possible explanations for the lack of agreement: (1) grain size is itself a nebulous term as the grains are irregularly shaped; (2) the effects of all physical and chemical parameters on the filtration process have not been known and therefore have not been controlled adequately.

Sand Shape

Hudson (59) has pointed out that rounded sand grains produce clearer water than angular sand grains of the same equivalent diameter. The reason given is that round sand grains yield a lower bed porosity upon backwashing and settling than do angular grains. On the other hand, Ives (69) has stated that, at the same porosity, more angular media

gives improved filtrates. No explanation was given, but it is known that the surface area of angular media is greater than that of round media, other factors being equal.

Packing Arrangement of the Sand Grains

A change in packing arrangement manifests itself through a change in the bed porosity, which is discussed below. Any further discussion concerning mode of packing would be unfruitful since it is not a design or operational variable which can be controlled in filtration practice.

Bed Porosity

Using hand placement methods, porosities of beds of spheres have been obtained which vary from 0.259 to 0.875. In practice, however, bed porosities are determined by the backwashing and settling of the sand and, as a result, can be controlled only through choice of grain angularity, size, and density. For round sand particles, porosity is relatively independent of grain size and values of about 43 per cent are usually obtained; angular grains produce porosities of 48-55 per cent which are dependent upon the size (and size distribution) of the grains (59).

In spite of the limited control of bed porosities which can be exerted in filtration practice, this factor has received a great deal of attention. In general it can be stated that lower porosities produce higher initial head

losses and clearer filtrates, while higher porosities yield longer filter runs, owing to the greater floc storage capacity, and increased penetration (44,59). Grace (45) has reported that collection by direct sieving at pore constrictions becomes increasingly important as porosity decreases. Empirical equations relating porosity to length of filter run have been contradictory (5,56).

Bed Depth

Stanley (117) has stated that in order to assure a satisfactory quality of effluent, the sand bed must be deeper than the depth of penetration at the end of the run. Ives agrees and concludes (69) that deeper beds produce clearer filtrates. Camp (16), however, has argued that depth of penetration is a meaningless concept since some suspended matter always penetrates a filter. Still, the concept of depth of penetration continues to find meaning in current filtration literature (97). It must be concluded that all of these workers' statements present valid interpretations of the importance of bed depth under certain circumstances.

Surface Properties of the Sand Grains

As discussed previously, whether or not the sand surface is important in filtration appears to be dependent upon the nature of the particles being filtered. That is, flocculent materials have been found, for the most part, to have no

preference for any particular surface (54,86,108,111,115), while discrete particles seem to prefer a surface having an electric charge opposite in sign to their own (63,78,100,115). However, there are notable exceptions to both of these general rules (21,97,98).

Where the importance of sand surface in filtration has been cited, electrostatic effects have most often been invoked to explain the phenemenon. Hydrogen bonding and ion-exchange reactions between the grain and the particle surfaces have also received some attention. In order to gain a clearer understanding of these phenomena it is instructive to consider the surface chemistry of quartz sand.

Quartz is a crystalline form of silica, the crystal lattice containing silicon atoms each surrounded and attached to four oxygen atoms. Upon crushing, --Si--O--Si-- bonds are broken and a polar surface is created in the manner depicted in Figure 3-2. In aqueous media H^+ ions react with the negative oxygen sites and OH^- ions react with the positive silicon sites; the surface charge originates from the dissociation of this surface silicic acid (42). The pK_a of this dissociation is not known but the first dissociation constant of silicic acid is $pK_a = 9.8$ suggesting that in the pH range 2 to 8 the Si-OH group is dominant, with the number of $Si-O^-$ groups increasing with pH (85).

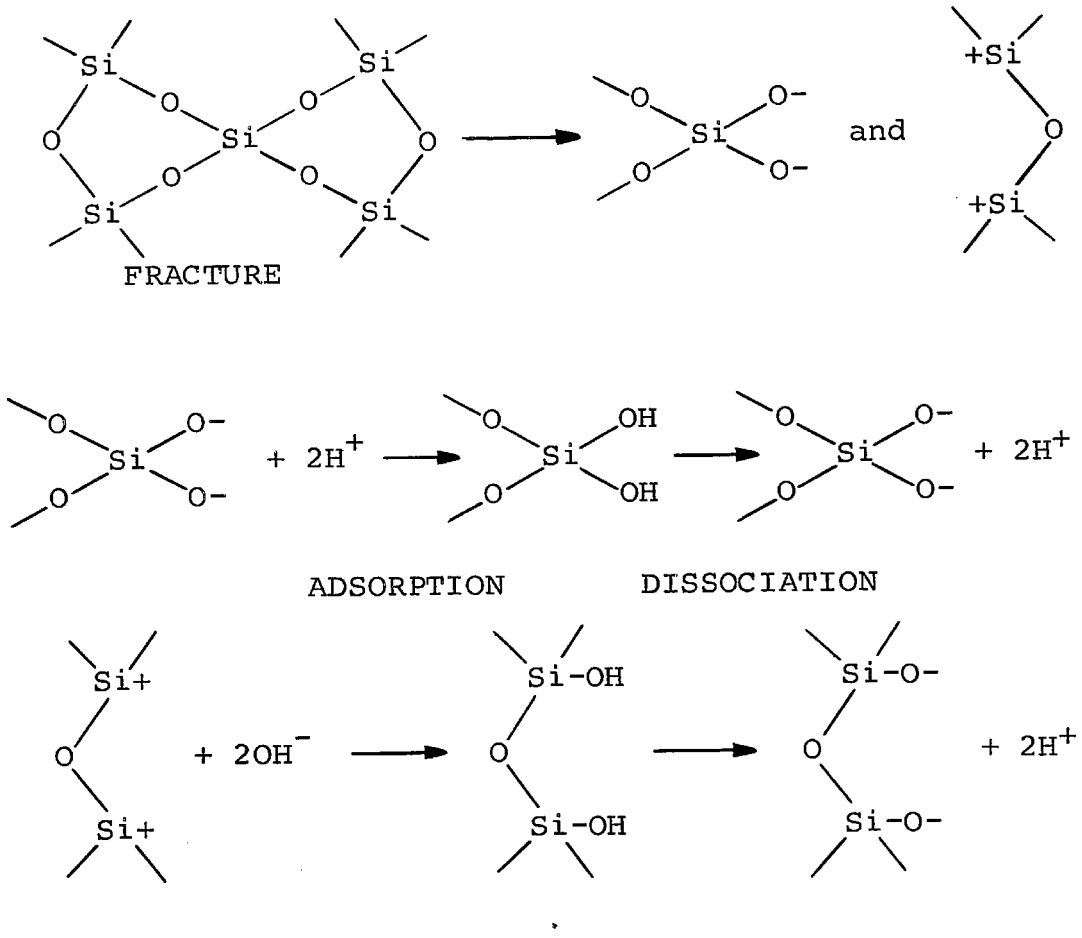


Figure 3-2. Mechanism for the Origin of the Electrical Charge at the Quartz Surface in Aqueous Solutions [After Gaudin and Fuerstenau (42)]

When there is no dissociation of the surface silicic acid, the surface of quartz particles will be uncharged. The neutral or isoelectric point has been determined experimentally by a number of workers with varying results as shown in Table 4 below. The discrepancies are probably due largely

TABLE 4

The Isoelectric Point of Quartz Particles as Determined by Several Investigators

SOURCE	ISOELECTRIC POINT
O'Melia and Crapps (97)	1.3
Gauden and Fuerstenau (42)	3.7
Mackenzie (85)	2.0-2.3
Parreira and Schulman (102)	2.0
Parks (101)	2.2
Iler (64)	4.0-5.0

to differences in ionic content of the fluid phase used by each worker. Abramson et al. point out that the "real" isoelectric point can be measured only in the absence of all ions other than hydrogen, hydroxyl, and those which are components of the solid. (1).

Since the charge at the quartz surface is determined by the concentration of hydrogen and hydroxyl ions in solution (i.e., H^+ and OH^- are potential determining ions), the pH of the solution will affect markedly the sorption of

electrolytes, and perhaps charged particulate matter, at the quartz-solution interface. This fact has been the basis of several electrokinetic theories of filtration. In addition, other ions have been used to alter the sand zeta potential for filtration purposes. These include both indifferent and potential-determining ions. The former reduce the value of the zeta potential by compression of the double layer without changing its sign, as, for example, sodium ions. The latter are specifically attracted to the surface by chemical forces in addition to electrostatic forces and may reverse the sign of the zeta potential. Examples of this type are Fe^{3+} and Al^{3+} ions and polyelectrolytes (42).

Effects of Fluid Suspension Properties on Particle Removal

General

The fluid suspension properties which affect filtration are listed below and then discussed individually.

(1) suspended particle size

(2) suspended particle shape

(3) suspended particle density

(4) suspended particle concentration

(5) fluid temperature

(6) chemical character of the suspended particles

(7) pH and chemical composition of the fluid

Suspended Particle Size

The earlier discussion of sand filtration mechanisms indicated that nearly all of these are affected in some manner by suspended particle size. Nevertheless, the effect appears to be small in comparison to other variables. This is evidenced by the widely different filtering properties of various suspensions having particles of similar size. It has already been mentioned, for example, that ferric-flocs filtered by Eliassen (34) were removed to a much greater extent than larger algal particles filtered by O'Melia (95).

On the other hand, the effect of particle size on filtration for a given material has not been adequately investigated. Based on the work of Friedlander (39), O'Melia and Stumm (98) calculated that the efficiency with which a suspended particle contacts a sand grain during filtration is dependent upon the size of the particle, a minimum occurring at about 3 microns. These authors concluded that very small particles, destabilized to permit attachment within the filter, might be removed from suspension as efficiently as larger aggregates. If this were true, it could have a marked effect on pretreatment practice.

Suspended Particle Shape

Apparently, no systematic study of suspended particle shape on filtration has been made. It can be deduced, how-

ever, that if surface effects are important more angular particles should be removed to a greater extent than spherical ones, owing to the greater surface-to-volume ratio. Unfortunately, other factors, such as particle orientation and maximum dimension, complicate matters. In any case, the shape of suspended material in a filter influent cannot be controlled, rendering any knowledge in this area purely academic.

Suspended Particle Density

Suspended particle density exerts its effects on filtration primarily through the gravitational sedimentation, inertial impaction and Brownian movement mechanisms. Since all of these were shown previously to be of minimal influence in the rapid sand filtration of water, it must be concluded that particle density is also relatively unimportant. This conclusion is substantiated by observations that flocculent materials of density 1.005 g/cc are much more filterable than algal cells of about the same density and diatomaceous earth particles which are considerable denser than either of these.

Suspended Particle Concentration

The effects of suspended particle concentration on filtration should be discussed separately for flocculent and non-flocculent materials. The reason is that filtration of the two types of materials is usually described by totally

different parameters: penetration and removal efficiency, respectively. In addition, the character and size of flocculent particles may change with increasing concentration, whereas with non-flocculent particles only the number of particles changes.

Stanley (117) investigated the effect of influent concentration on the filtration of ferric-floc particles and found that penetration increased significantly with increasing concentration for the same total iron passed into the filter. He noted that this was contradictory to the work of Geyer and Machis (43) who found that the influent concentration of aluminum had no effect upon bed penetration of alum floc when the results were based on total aluminum applied. Stanley, however, employed a wider range of influent coagulant concentration and, additionally, floc "age" was apparently not controlled in either study.

Davis and Borchardt (30) studied the filtration of a mixture of flocculent (iron floc) and non-flocculent (algae) particles. They found that for a given concentration of coagulant the per cent of organisms removed increased in a curvilinear manner with a decrease in the concentration of organisms in the filter influent.

Ghosh (44) along with Borchardt and O'Melia (11) have found relationships between filtration efficiency and influent

concentration of uncoagulated particles. However, Ghosh found that the percentage of material deposited did not vary considerably with initial turbidity, while Borchardt and O'Melia noted significantly higher removal percentages when the influent concentration was lowered. Both of the observations were based on constant filtration time as opposed to constant applied material.

Fluid Temperature

Traditionally temperature was thought to be of importance in filtration because of its effect on density and viscosity. This viewpoint accounted for the poor filtration observed at low temperatures since many of the removal mechanisms which were prevalent, e.g., gravitational settling and pore flocculation, happened to be adversely affected by cold water. This opinion may still be valid today, but it has also become appreciated that the difficulty of filtration at low temperatures is greater than would be predicted by viscosity changes in the fluid alone (27,118). Conley (27) found that "there is considerable evidence that the adhesive force (in filtration) is affected by temperature changes". Stanley (118) and O'Melia and Stumm (98) agree that temperature may also influence the character of suspended particles, perhaps by affecting the rate at which chemical "aging" takes place in dispersions of a metal coagulant.

Chemical Characteristics of the Suspended Particles

The significance of the chemical characteristics of suspended particles in filtration has been amply demonstrated. The most notable characteristic seems to be whether the particles are flocculent or non-flocculent in nature. However, within each of these two major groups important differences in chemical character may occur which, of themselves, affect filtration. These include primarily surface charge, although the specific chemistry of the surface may also be significant. The various investigations describing the effects of these factors on filtration have been discussed earlier in this chapter and will not be repeated here. Also, the surface chemistry of the particles used in this research will be considered separately in the chapters dealing with their filtration.

pH and Chemical Composition of the Fluid

The pH and, to a lesser extent, the ionic content of the fluid are of prime importance in determining, among other things, the zeta potential of both the sand filter media and the suspended particles. O'Melia and Crapps (97) have thus concluded that rapid sand filtration can be chemically controlled and that optimum utilization of filter bed capacity could be achieved by adding chemicals which would improve or impair adsorption.

Mechanisms involving electrokinetic and specific chemical interactions must be invoked to explain the influence of pH and other ions on filtration. Hydrogen and hydroxyl ions, for example, are potential determining ions for sand and for many of the suspended particles found in filter influents. Thus if the sand grain and the suspended particles have different isoelectric points, as is usually the case, the level of pH will determine whether electrostatic attractive or electrostatic repulsive forces exist. Similarly, the concentration of other ions in the water will influence the zeta potential of sand and other particles. In general, these ions are surface-inactive indifferent ions and not potential determining ions; increasing concentrations, therefore, act only to compress the double layer and reduce the charge which was present. If sufficient ions of this type are present, however, the charge can be completely eliminated.

The increasing use of polyelectrolytes in water treatment has introduced into filter influents ions of a different type. These are capable of reversing the charge on particles and also of sorbing onto particles having a charge of like sign. Hence their action cannot be characterized by the double layer theory, but must be explained by chemical forces.

Effects of Operational Procedures on Particle Removal

Rate of Fluid Flow

Increasing rates of fluid flow have two important effects on the filtration process; (1) they increase the head loss through the bed and (2) they cause deeper penetration of suspended matter in the bed. The relationship describing the first effect is a linear one and is given by the law of Darcy. This law holds only for laminar flow, but Cleasby and Baumann (22) have determined that such flow is maintained even in a dirty bed. On the other hand, a relationship relating filtration rate to depth of penetration (hence, length of filter run) has not been well defined. Various workers (5,84,117) have attempted a correlation by empirical equations but, in general these hold only for the system from which they were developed. A consideration of the variables involved leads to the conclusion that no unique relationship can exist.

As a result of the complicated influence of flow rate on penetration, filter designers for a long time conservatively adhered to a standard rate of 2 gpm/sq ft. When it became evident that higher rates could be used on some waters with greater efficiency, these gradually came into use. Stanley (117) and Hudson (58) also advocated the use of declining rate filtration. This involves the application

of a high rate initially when the bed is clean, with a gradual decrease in rate as the bed becomes clogged.

Cleasby and Baumann (22) have suggested that floc strength is the key to higher filtration rates. They found that acceptable water is not assured at 2 gpm/sq ft, or even at lower rates, unless the internal strength of floc particles is adequate to resist the hydraulic shear forces tending to wash the particles down into (and out of) the filter.

Backwash Procedures

Recently Johnson and Cleasby (76) conducted studies on the effect of filter backwashing on subsequent filtrate quality and compared their results to earlier investigations. The early studies generally found that a 50 per cent bed expansion was optimal for washing and that a better wash produced a better filter effluent. By contrast, Johnson and Cleasby found that the optimum backwash rate for their experiments produced only 16-18 per cent expansion of the sand bed, and that the terminal washwater turbidity after a backwash is not a valid indicator of the effectiveness of the filter wash.

Wall Effect

Of importance in very small laboratory filters is the effect of the wall which retains the porous medium. Carman (18) has shown that particles adjacent to the wall pack more

loosely than those in the bed proper. This effect of higher porosity at the wall increases as the ratio of particle diameter to diameter of container increases. It is generally agreed (14,126) that the effect is significant when the particle diameter is greater than 10 per cent of the container diameter.

Filtration Models

During the past three decades numerous investigators have formulated models of the filtration process. O'Melia and Stumm (98) have found it useful to classify these as either physical or chemical, and this distinction will also be used here.

Physical models attempt to describe filtration parameters such as head loss increase, depth of penetration, or length of run in terms of physical characteristics of the filter bed and fluid suspension, and the flow rate. The most noteworthy of these are the works of K. J. Ives (67-69, 71). Ives started with two rather simple differential equations formulated by Iwasaki (75) in 1937, extended the mathematics, and then successfully reproduced experimental curves obtained in the laboratory. Unfortunately, Cleasby and Fox (23) could not varify the same relationships in their own laboratory and concluded that, in any case, they were too

difficult to use for practical design and operation. Conversely, most other mathematical formulations describing the effects of physical variables on the filtration process (e.g., 36,84,117) have been too simple to be flexible enough to apply in practice. There is, therefore, no physical theory at the present time--either simple or complex--which is adequate for practical use.

In retrospect, it can be stated that any filtration model based upon purely physical variables was destined for failure at its conception. It has been demonstrated, for example, that particle attachment to the grain surface is primarily a chemical process; hence chemical factors must be taken into account in filtration models.

In recent years some investigators have undertaken studies of the effects of chemical parameters on the filtration process. Noteable among these are the works of O'Melia et al. (97,98). In general, chemical theories have not advanced to the mathematical state of refinement of the older physical theories. Nevertheless, many are already subject to some severe criticism. The criticism is usually expressed in terms of the workers lack of examination of all of the several possible chemical interactions, or his failure to control all of the physical filtration variables.

Up to the present time all filtration models have proven

to be less than satisfactory. Undoubtedly, much more work needs to be addressed to the determination of basic parameters which can affect the process before successful mathematical models can be developed. Filter design continues to be based on trial and error procedures.

CHAPTER 4

THE FILTRATION OF IRON(III) DISPERSIONS

General

Experimental Objectives

The overall objective of these filtration runs was to evaluate the significance of various mechanisms contributing to the attachment of flocculent particles to the media of a rapid sand filter. As discussed in Chapter 3 there is considerable divergence of opinion in this area, even among the foremost workers in the field. This confusion exists despite the fact that there would appear to be only four basic attachment mechanisms which would deserve serious consideration, namely, electrokinetic forces, chemical forces, van der Waal forces, and straining. Undoubtedly, a major cause of this confusion is the complicating influence of one or more of the particle transport mechanisms on each of the particle attachment mechanisms, rendering the latter difficult to isolate in laboratory experiments. In addition, particle removal mechanisms may be affected by some sixteen physical and chemical variables (discussed in Chapter 3) which therefore must also be controlled in studies of mechanisms.

Another possible reason for the continuing controversy is the fact that questionable ideas and theories are often perpetuated in the literature without ever being thoroughly evaluated and the relavent facts publicized by others. It was felt that this latter possibility could provide an important basis for accomplishing, in part, the previously stated overall objective. Consequently, while the primary aim of the studies presented here was to elucidate removal mechanisms for flocculent particles, some emphasis has been directed toward examining and reinterpreting, if necessary, some of the important and widely circulated works which were thought to be especially deserving of additional scrutiny.

Aqueous Chemistry of Iron(III)

In order to understand and interpret the various phenomena associated with the filtration of ferric-floc suspensions, it is necessary to have a basic knowledge of the aqueous chemistry of iron(III). The following discussion is aimed specifically at those areas of the chemistry which are pertinent to this research.

Hydrolysis Equilibria. When a salt of iron(III) is added to water a number of ferric iron species are formed, depending upon the concentration added and the pH of the solution. If these factors are such that the solution is undersaturated with respect to ferric hydroxide, soluble monomeric, dimeric,

and perhaps polymeric hydroxo-ferric complexes are formed, as well as the free aquo-ferric ion. In conventional water treatment processes, however, Fe(III) is added in sufficient quantities to exceed the solubility limit of ferric hydroxide. Under this condition a series of hydrolytic and polymerization reactions occur which eventually lead to the formation of a hydrous metal oxide precipitate (121). Along the way, charged colloidal hydroxo polymers are also formed which have been shown to be effective in colloid destabilization (99). In slightly acid solutions, these colloidal polymers are formed from cationic ferric hydroxo complexes and hence are positively charged. On the other hand, under alkaline conditions, the polymerization of anionic hydroxo ferrates leads to the formation of negatively charged colloids. The isoelectric point of the precipitated iron hydrolysis products has been variously reported as pH 6.7 (85) and pH 7.4-8.4 (101).

It is important to point out that the reactions described above can occur with complex forming anions other than the OH^- ion. When present, these ions may compete with OH^- ions for the coordinative sites; since less OH^- ions would then have to enter into the lattice to produce an electrically neutral precipitate, the pH of optimum coagulation will frequently be lowered (108). This effect is very pronounced with phosphates (126) and silicates (125,127), but several

other anions can also produce significant effects (88).

Coagulation* Behavior. For a long time the effectiveness of iron(III) as a coagulant was thought to be due to its valence of +3. This idea was perpetuated by the widespread acceptance of the Schultze-Hardy rule which states that a trivalent ion is 700-1000 times as effective as a monovalent ion in destabilizing a colloid of opposite charge. Thus, coagulation with ferric iron was thought to be a physical process, controlled by double layer compression. In recent years, however, various workers (88,113,114,121) have concluded that chemical properties of iron(III) are also significant in coagulation, for the following reasons:

(1) Optimum coagulation conditions almost never correspond to those producing zero mobility of the floc particles, as is required by a coulombic model.

(2) Iron(III) and aluminum(III) are both much more effective in neutralizing oppositely charged colloids than is predicted by their charge alone, and they are capable of reversing the charge of some colloids.

(3) Iron(III) and aluminum(III) do not produce equivalent results in the coagulation process.

(4) Systems have been observed (111) in which there

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* It should be mentioned that coagulation has been differentiated from flocculation by La Mer (81). However, for reasons of simplicity, both terms are used interchangeably in this work to denote particle aggregation.

were two pH values at which the mobility was zero, but only one pH value of optimum coagulation.

Aging Phenomena. If the reactions of iron(III) in water are allowed to proceed to their conclusion (an occurrence which does not take place in normal water treatment practice), the crystalline metallic oxide, e.g., Fe_2O_3, is ultimately formed. The aging process which leads to the formation of this species does occur during water treatment and is characterized by a progressive increasing of the density and inertness of the hydrous precipitate (98,121). As a result, aged iron solutions exhibit different coagulation (and filtration) behavior than fresh solutions (29,98,99). The rate at which these solutions age increases with temperature and pH and is also a function of applied metal ion concentration, type and concentration of anions, and perhaps the velocity gradient (98,121). The recent work of Schenk and Weber (110) indicates that dissolved monomeric silica, which is present in natural waters in concentrations ranging up to 120 mg/l, has a significant retardation effect on the aging reactions of iron(III).

Experimental Results and Discussion

Initial Studies

Although many investigators of filtration have expressed

some degree of difficulty in reproducing filter runs, none have published any quantitative information on the problem. Stanley (117) has presented some head loss curves (Figure 5 in his work) which show a lack of reproducibility but he did not pursue the matter. Initial studies conducted in this investigation were designed primarily to test for reproducibility of head loss versus iron applied curves, both within a given run and also between runs. Since these curves invariably plotted as straight lines, their slopes (dH/dC) were used as a basis for comparison. A secondary objective of these runs was to determine the effect of influent iron concentration on the value and reproducibility of dH/dC. It will be remembered that Stanley (117) has presented contradictory evidence on this point. Moreover, from a laboratory-experimental viewpoint, it would be desirable to be able to shorten filter runs by increasing the influent concentration.

A series of filtration runs was conducted in which all of the physical parameters were maintained as constant as practicable. Controls which were established included: (1) use of the same batch of sand throughout the experiments, (2) acid-washing of the sand prior to each run with dilute HCl, (3) employment of constant flow rates (2 gpm/sq ft) and constant overall bed porosities (40.0 per cent), and

(4) use of fresh iron suspensions, these being formed at the top of the filter from a mixture of the stock solutions (which were undersaturated with respect to ferric hydroxide) and the feed water. The feed water contained sufficient buffer capacity so that a pH of 7.0 ± 0.2 was maintained. No artificial mixing was provided at the top of the filters to disperse the coagulant, except where noted.

In two of the runs the same influent Fe(III) concentration was used in all of the filters in order to test for reproducibility within the run. The results of these runs, expressed in terms of the slopes of the head loss versus iron applied curves, are presented in Table 5 below. In

TABLE 5

The Slopes of Head Loss Versus
Iron Applied Curves (dH/dC) for Runs A-5 and A-6

Run	Filter Number	Influent Fe(III) Dose (mg/l)	$dH/dC \left[\frac{ft}{mg/sq\ in}\right]$
A-5	1	2.1	0.061
	2	2.0	0.055
	3	2.1	0.103
A-6	1	2.9	0.070
	2	2.9	0.070
	3	2.9	0.065

three additional runs, suspensions containing Fe(III) concentrations ranging from about 1 to 4.5 mg/l were filtered. The data from these, as well as the previous runs, are plotted in the lower portion of Figure 4-1. In all cases it can be seen that good duplication was obtained at the higher iron concentrations, and less satisfactory duplication was obtained at the lower values. A straight line fitted through the data by the method of least squares was found to have a negative slope, although statistical analysis showed that the slope was not significantly negative at a 95 per cent confidence level. This indicates that, within the statistical limits of confidence, bed-clogging may be considered similar at all influent iron concentrations for the same total iron applied for beds of 40 per cent porosity.

Effects of Porosity. The sand bed porosity employed in these runs was somewhat sensitive to the procedures of preparation and to vibrations occurring during the runs. This was evidenced by an observed lack of stability of the beds. It was found, for example, that the initial head loss readings (through the clean beds) exhibited considerable spread and did not agree well with the value calculated from the Carman-Kozeny equation (see page 33). As a result, it was decided to try other porosities to determine if this factor would have a significant effect upon filter reproducibility and

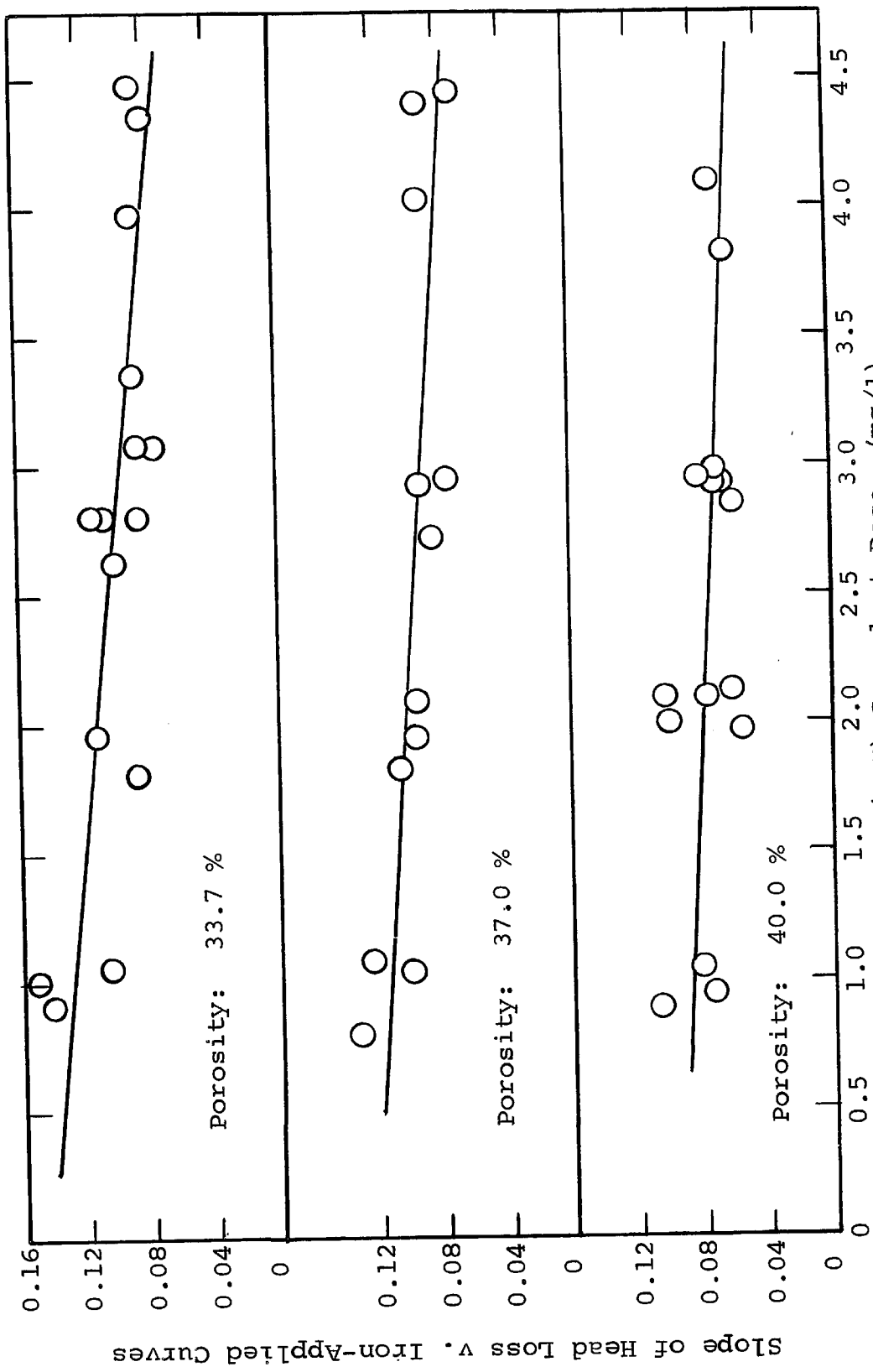


Figure 4-1. Slopes of Head Loss Versus Iron-Applied Curves as a Function of Influent Coagulant Dose and Sand Bed Porosity (Flow Rate=2 gpm/sq ft; Sand Size=0.503 mm; pH=7)

performance. Two additional methods of media placement were tried which yielded porosities of 37.0 and 33.7 per cent, as described in Chapter 2. As shown in Table 6 below, the use of these porosities resulted in beds which were hydraulically more reproducible and which displayed initial head losses that were in closer conformity to the Carman-Kozeny equation.

TABLE 6

Comparison of Observed Head Losses Developed in Clean Beds With Those Calculated by the Carman-Kozeny Equation

Bed Porosity	Head Loss Through Clean Bed - ft		Standard Deviation of Observed Head Loss Value
	Observed (average)	Calculated	
40.0	1.05	1.22	0.19
37.0	1.80	1.70	0.15
33.7	2.65	2.50	0.18

Note: Carman-Kozeny Equation,

$$H = f \frac{L}{g} \frac{\mu}{\rho} v \frac{S^2}{d^2} \frac{(1 - p)^2}{p^3}$$

where $f = 5$, $L = 24.5$ in, $g = 32.2$ ft/sec^2, $d = 0.503$ mm $\mu/\rho = 1.22(10^{-5})$ sq ft/sec, $v = 2$ gpm/sq ft, $S = 6$ (spheres)

The results of filter runs conducted at these porosities are also given in Figure 4-1. It can be seen that, again,

the data generated lines having slightly negative slopes and was somewhat more reproducible at the higher applied iron concentrations. In addition, the lines appear to be displaced upward on the ordinate with decreasing porosity. However, plotting the same experimental data with an expanded ordinate as in Figure 4-2, reveals not only a considerable spread of the data but a large degree of overlapping of data among the three porosities. This suggested the possibility that there was, in fact, no significant effect due to sand bed porosity on the slopes of the observed head loss v. iron applied curves. Because of the questionable significance of porosity in these runs, the data for porosities of 37.0 and 40.0 per cent were analyzed statistically by a student t test. It was found that the effects on dH/dC due to porosity were indeed significant at the 5 per cent level. The calculations for this analysis are presented in Appendix IV.

A further elucidation of the effects of sand bed porosity upon filter performance may be obtained by examining the penetration of floc into beds of different void-volume. Figure 4-3 presents such information for the same runs as are depicted in Figures 4-1 and 4-2. For the sake of clarity, only the data for the two extreme values of porosity which were studied is given. The results show that, for the same amount of applied iron, sand beds of 40 per cent porosity exhibited

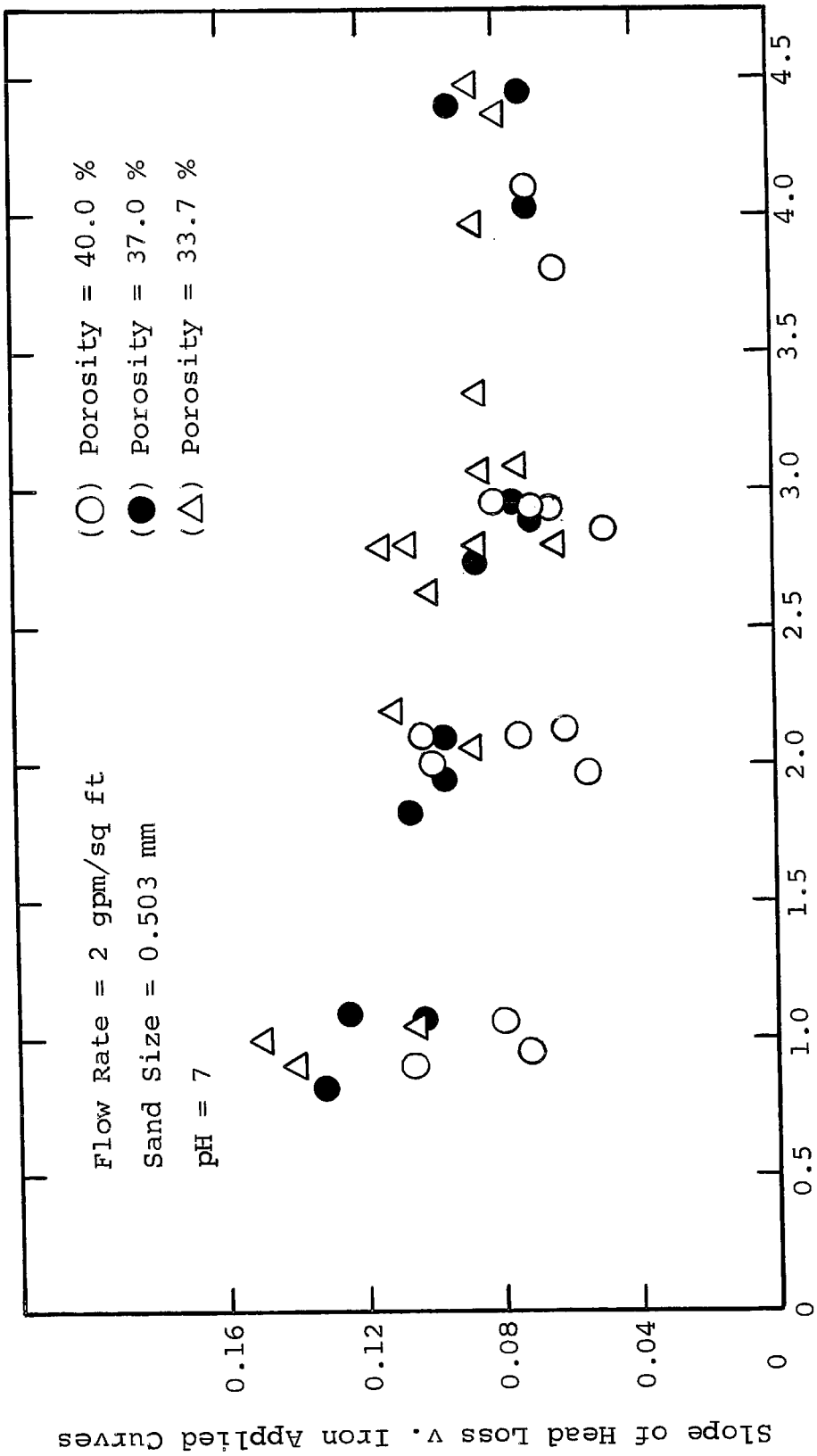


Figure 4-2. Slopes of Head Loss Versus Iron Applied Curves as a Function of Influent Coagulant Dose and Sand Bed Porosity

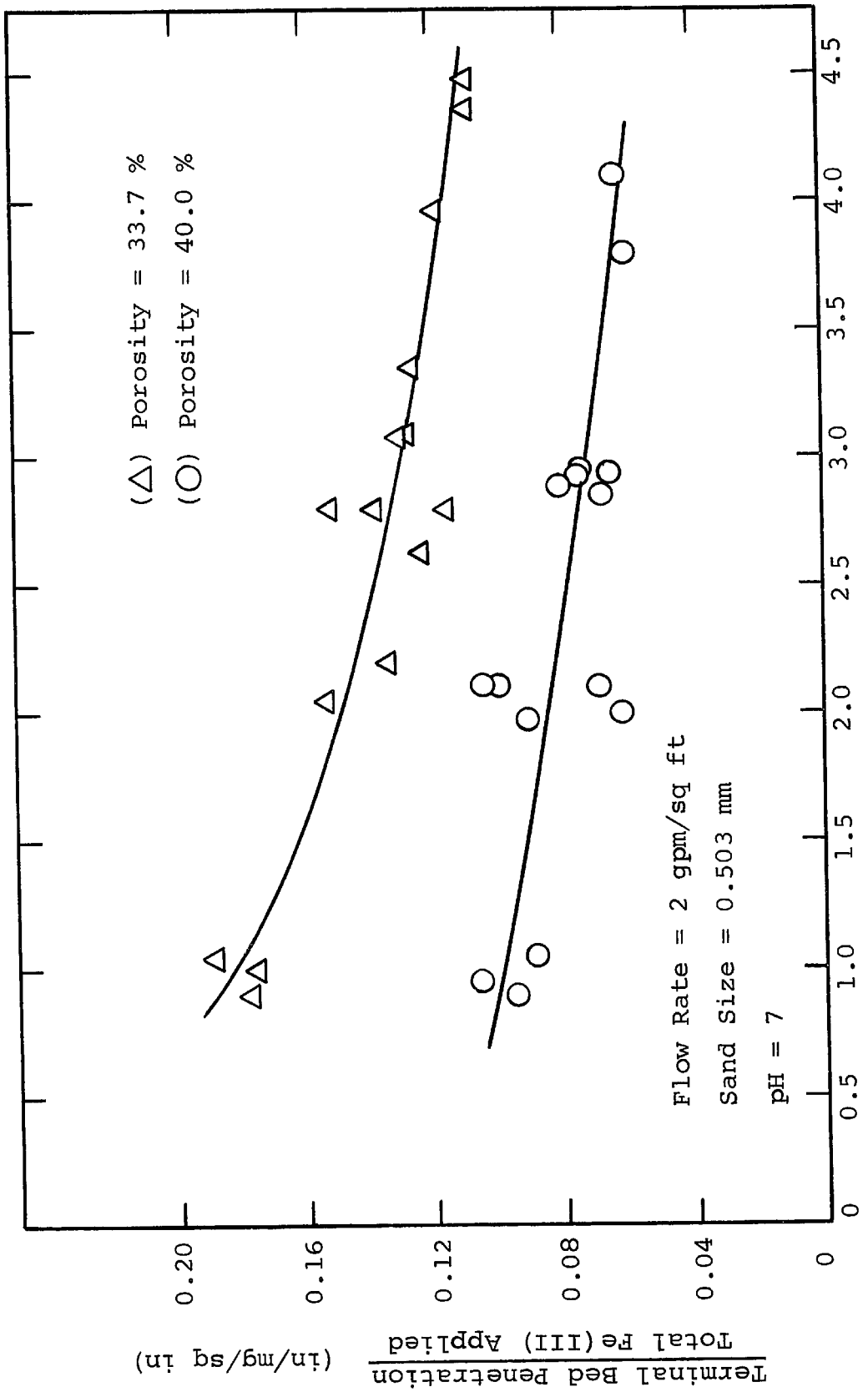


Figure 4-3. Penetration of Iron Floc into Sand Beds as a Function of Influent Coagulant Dose and Bed Porosity

less iron-penetration than did filters of 33.7 per cent porosity. Since the latter beds have more surface area per unit depth and would also be more effective in straining, these results suggest that iron removal was not accomplished strictly through a surface interaction between the sand and floc, as has been postulated by some workers, or through a straining mechanism. Rather, the data indicate that the pore volume available for deposition of floc may have controlled the removal process, i.e., that filter pores fill to capacity more rapidly in the beds of lower porosity and the resultant increasing pore-velocities produce more shear and hence greater penetration of floc.

Additional evidence that the penetration of small ferric-flocs into sand filters increases with decreasing porosity is illustrated in Figure 4-4. The curves were developed by determining the amount of iron which was deposited in successive layers of the filters, this being possible through the use of removable plastic cores (1 inch I.D.) which were placed in each of the filter columns prior to preparation of the sand bed. At the end of the run the cores were removed, cut into one-inch sections, and the iron content of the sand in each section analyzed. This same method has been used with success previously (14). Figure 4-4 shows that for the same amount of applied iron, a sand bed of 33.7 per cent

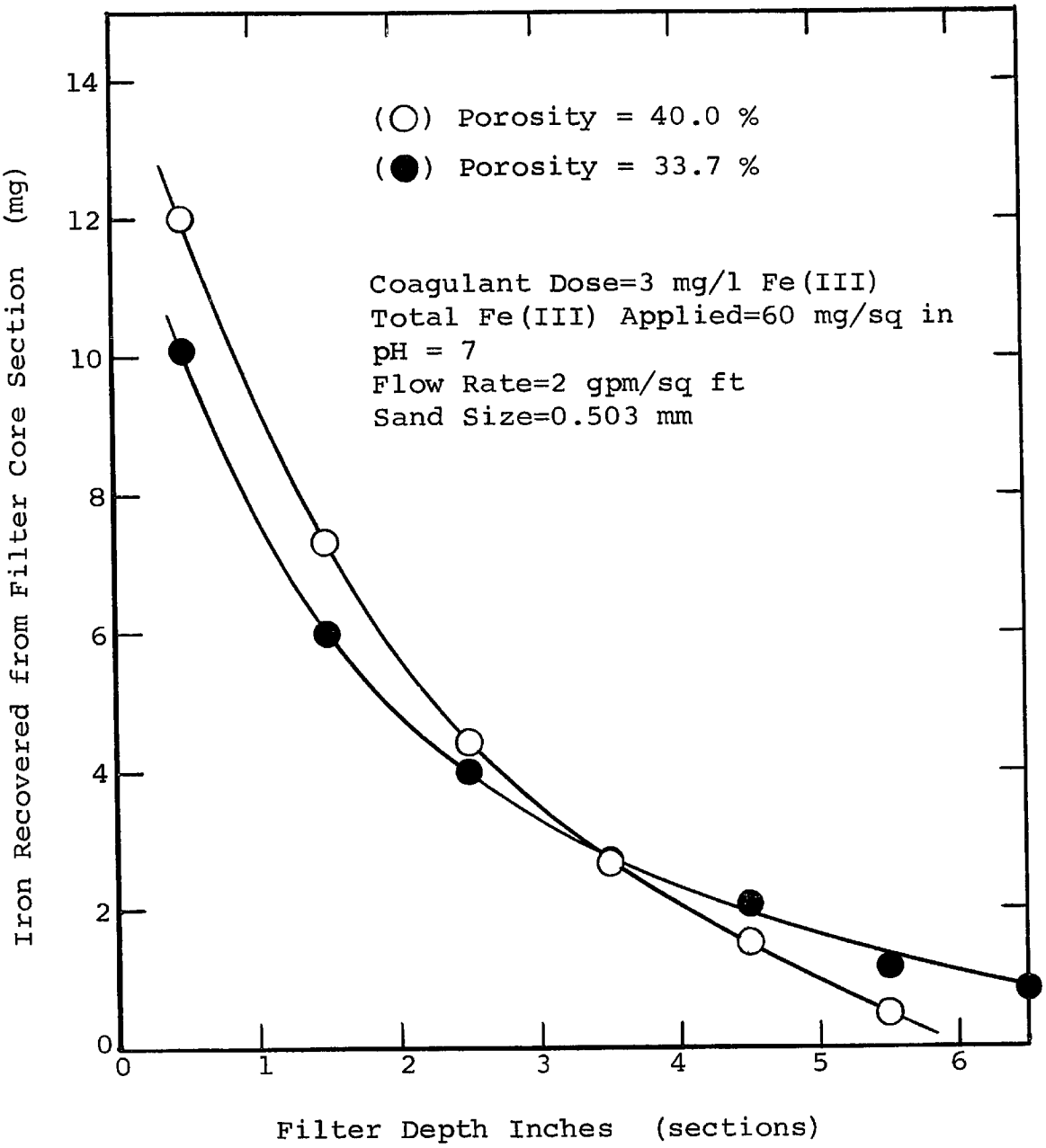


Figure 4-4. Pattern of Penetration of Iron Floc into Filter Beds of Different Initial Porosity - (Runs A-6 and B-4)

porosity retains less coagulant in each of the upper three inch sections of the bed than does a bed of 40 per cent porosity, and, of necessity, retains more coagulant thereafter.

Based upon the results of each of the preceding studies, the following conclusions are drawn:

(1) Head loss curves are more reproducible at higher influent iron(III) concentrations, within the concentration range studied.

(2) Results from similar filters within a given run may show as much disagreement as results from similar filters in different runs, i.e., variations in the tap water quality are not sufficient to affect reproducibility between runs.

(3) The three methods of sand bed preparation produce approximately equivalent results in terms of reproducibility of head loss versus iron applied curves but beds of 37.0 and 33.7 per cent porosity are more stable than those with 40.0 per cent porosity.

(4) The rate of increase of head loss in sand beds and the penetration per unit of applied iron both appear to decrease as the initial porosity of the bed is increased. It is concluded that the floc storage volume within a filter and the velocity of flow in the filter pores are more important than the surface area of the media in the filtration

of a flocculable dispersion.

A further consideration of the effect--or lack of effect--of the influent coagulant dose upon head loss buildup and bed penetration is not considered. An explanation of this phenomenon presumably involves a knowledge of the effects of solution concentration on the size and density of the individual floc particles which are formed from the solution, as well as a knowledge of the floc compaction which progressively takes place within the filter during a run. One further aspect of these studies does deserve mention, however. The added experience of carrying out these runs as a preliminary step unquestionably resulted in refinements of procedure and other intangible improvements. It is felt that these acted collectively to produce increasingly reproducible runs.

Effects of Floc Size

One of the more widely cited arguments in favor of electrokinetic effects in the filtration of flocculent particles has been the work in 1961 of Cleasby and Baumann (21). These investigators observed that suspensions of small ferric-floc particles (1-20 microns) produced less bed penetration than those containing larger particles (20-100 microns), an observation directly opposite to that obtained six years earlier by Stanley (117). Unfortunately, the literature is virtually devoid of other studies which have investigated the effects

of floc size on the filtration process.

In order to further delineate this parameter and to help clarify the previous disagreement, a filtration experiment was conducted in which as many physical and chemical variables were held constant as could be, except for the floc size. Initially it was attempted to investigate several different floc sizes in order to obtain definitive evidence on the effects of this parameter. However, it was found that floc sizes could neither be controlled nor reproduced with any degree of precision. Consequently, only two floc sizes were studied. The experiment was carried out by running two filters in parallel, each receiving the same feed water and identical concentrations of iron from the same stock solution. At the top of one of the filter columns, however, the water surface was agitated to promote flocculation of the coagulant, while in the other filter column the coagulant was allowed to mix naturally after addition to the top of the filter. As a result, the better flocculation which was promoted in the "mixed" filter column resulted in the production of substantially larger floc particles. Microscopic observations revealed that these particles were about 10 to 50 microns in diameter. In contrast, those in the unmixed column were not visible under the microscope.

Agitation of the water surface was accomplished through

the use of an air diffuser placed 6 inches below the water surface. The zone of turbulence was confined to the volume of water above the diffuser. In order to insure that the dissolved oxygen content of the water was not a factor in these experiments, the influent to the "unmixed" filter was also aerated, this being done prior to introduction of the coagulant. In addition, jar tests conducted separately revealed that mixing of an iron(III) dispersion with diffused air did not produce results which were distinguishable from those obtained when a motor-driven propellar was the mixing device.

The results of the filter run are presented in Figure 4-5. The filter which received the larger floc particles is seen to have clogged at a faster rate and produced less bed penetration than the one receiving the smaller, poorly flocculated particles. Similar information can be derived from Figure 4-6, in which the distribution of head loss within the filter at the end of the run is plotted. Based on the limitations of reproducibility experienced in the initial studies, the differences observed are significant. Nevertheless, the experiment was repeated and duplicated.

In so far as they may be compared, these observations agree in a qualitative way with those of Stanley, but are not in agreement with the work of Cleasby and Baumann. They

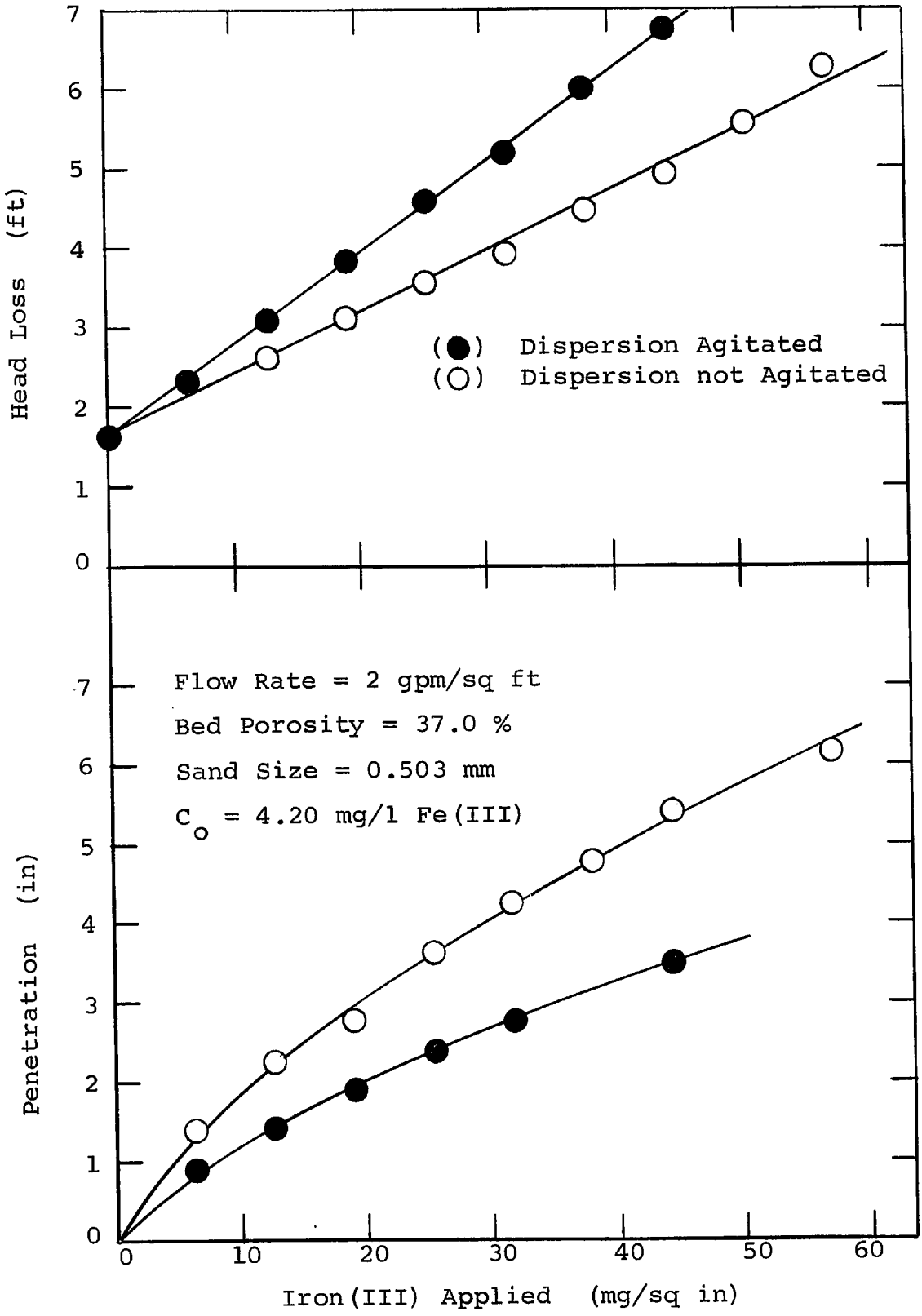


Figure 4-5. The Effect of Filter-Influent Agitation on the Filtration of Fresh Iron Floc Dispersions at pH=7 - (Run I-1)

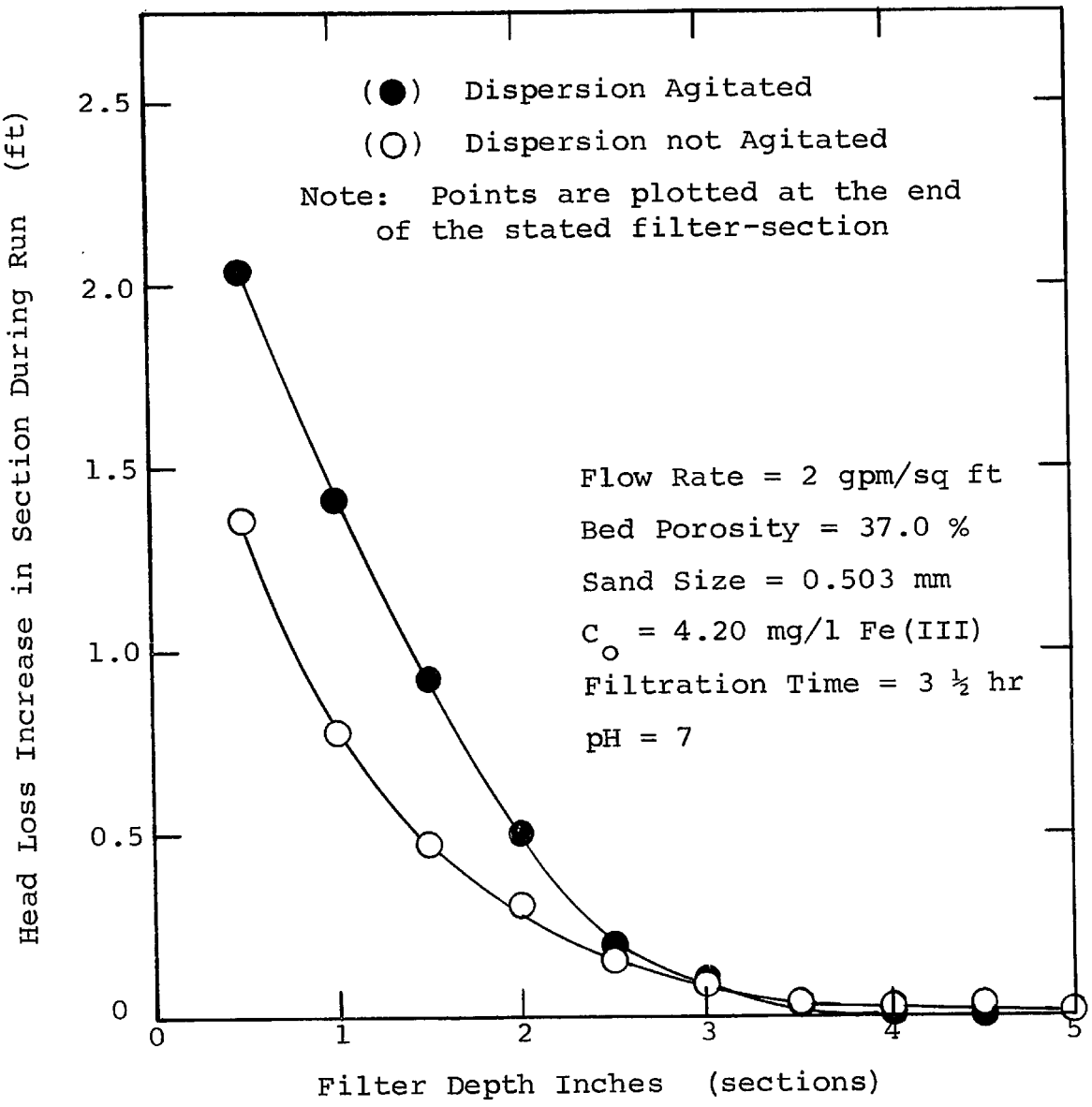


Figure 4-6. The Effect of Filter-Influent Agitation on the Distribution of Head Loss Increase - (Run I-1)

therefore tend to cast doubt on a major premise used by the latter workers to support an electrokinetic theory of floc removal. It seems reasonable to suggest that the comparatively deep penetration observed by Cleasby and Baumann for large ferric-flocs (20-100 microns) might be explained by shearing of the particles into smaller ones within the filter bed. From this point of view, the resistance of a floc particle to shear may be more important than its actual size as it approaches the filter. It should also be mentioned that Cleasby and Baumann did not control floc age in their experiments. It will be demonstrated in the following section that the chemical age of floc particles has an important effect upon their filterability. On the other hand, the group of data presented here is not, by itself, sufficient to disprove electrokinetic effects, or to support or disprove any other particle attachment mechanism. The possibility exists, for example, that the attachment mechanism is the same for both small and large floc particles and that a transport mechanism such as direct interception controls the removal process. These data do suffice, however, to demonstrate the general importance of floc size in filtration, and to illustrate the significance of the physical treatment afforded a dispersion prior to filtration.

Effects of Floc Age and Solution pH

The aging phenomena of iron solutions was discussed briefly at the beginning of this chapter. In essence, it was stated that floc character changes markedly with age and that aged solutions exhibit different coagulation and filtration behavior than fresh solutions. Since floc age also represents a parameter which can be controlled by pre-treatment practice, further investigations of its effects on the filtration process have been studied.

Only two previous investigations of the effects of floc age on filtration efficiency are known. Davis (29) conducted studies in which coagulant was added to a filter influent both as a pre-formed floc and in solution-form. It was found that the pre-formed floc, i.e., the aged floc, produced much lower filtration removal efficiencies of the algal cells in the influent. Similarly, O'Melia and Stumm (98) have also observed pronounced effects of the filtration process due to floc age. These workers undertook their studies primarily from a mechanistic standpoint, filtering fresh and aged iron(III) suspensions at different values of pH and then interpreting the differences observed as evidence of the importance of chemical factors in the attachment step in filtration.

The studies conducted in this research were aimed at increasing the knowledge of the effects of floc age and pH on the filtration process in general, and at expanding the

work of O'Melia and Stumm in particular. These workers have provided an excellent contribution from a theoretical point of view, but the equipment and procedures which they utilized were so far-removed from current practice that the general applicability of their results may be questioned. For example, the laboratory filter used were 10 in. long, 1 in. in diameter, packed at a porosity of 40 percent with 4 mm glass beads, and operated at a flow rate of 0.25 gpm/sq ft. Moreover, the use of media with a diameter of 4 mm in a 1 in. diameter column results in significant wall effects, according to the literature cited earlier in Chapter 3. By comparison, the studies reported here employed a 37 percent bed porosity and conventional parameters such as a sand size of 0.52 mm, a bed depth of 24-1/2 in., and a flow rate of 2 gpm/sq ft.

Filtration runs were made in which ferric-floc suspen- were filtered under different conditions of pH and "age". Figures 4-7 to 4-9 depict the relationships observed between both head loss and bed penetration and the total amount of ferric iron applied to the sand beds during the runs. Fresh ferric-flocs were prepared continuously at the top of the filters, with mixing provided, as in the previous experiment; aged suspensions were prepared 4 hours prior to the start of the runs in stock concentrations (approximately 0.002 M Fe^{3+}) at the desired pH and were added to the top of the filters

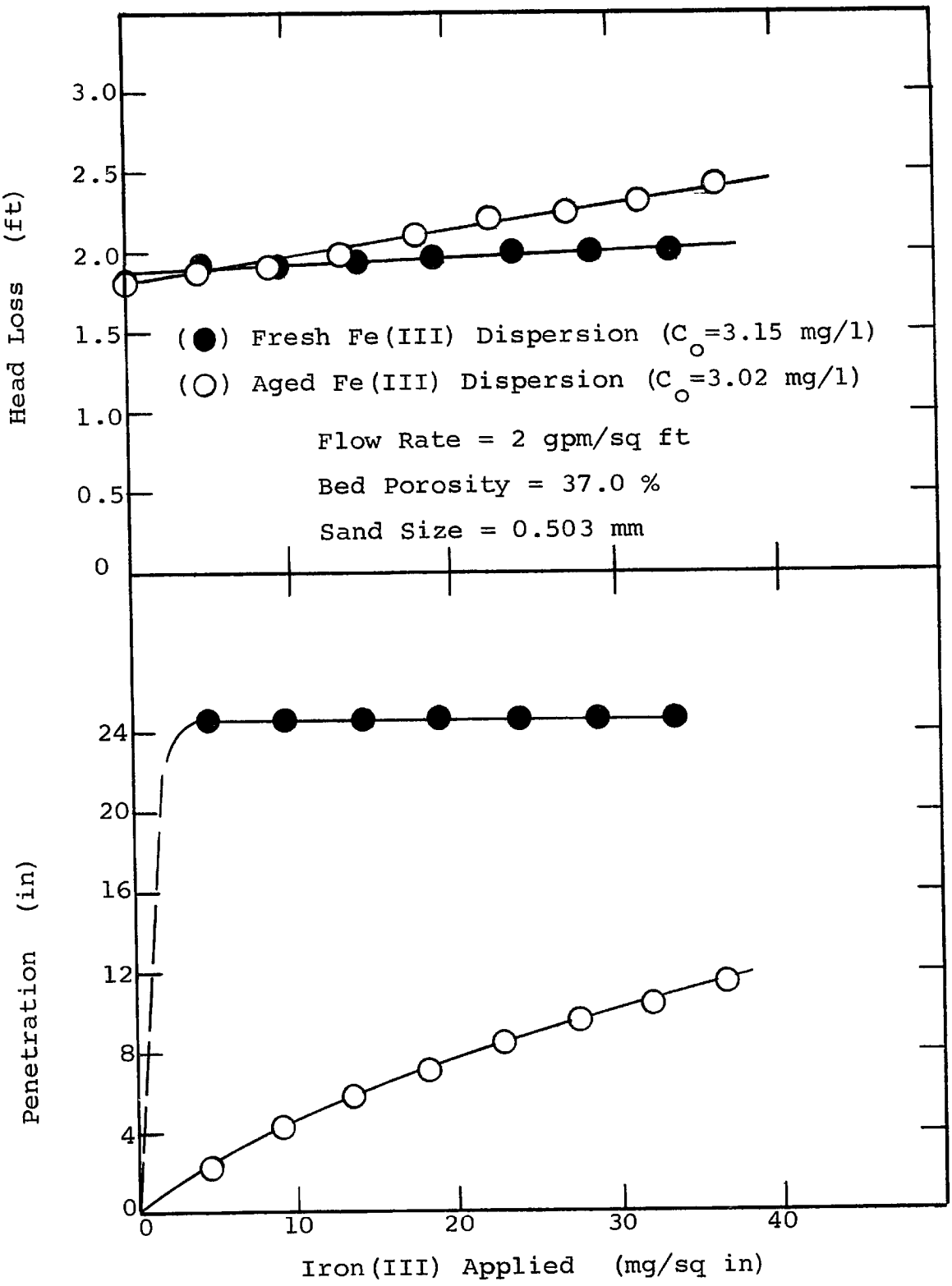


Figure 4-7. Filtration of Fresh and Aged Iron Floc Dispersions at pH=5.0 - (Runs M-2 and M-3)

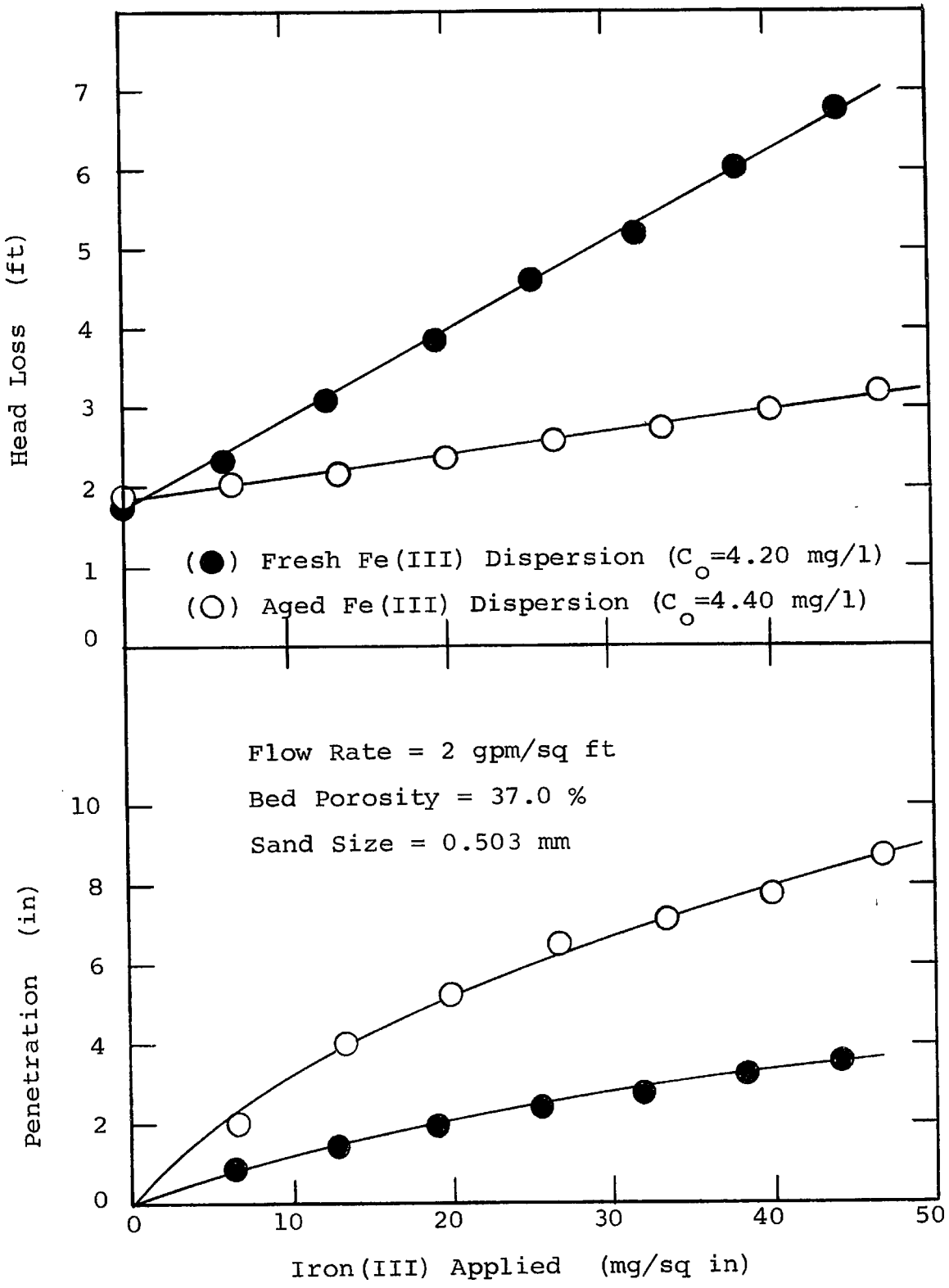


Figure 4-8. Filtration of Fresh and Aged Iron Floc Dispersions at pH=7.2 - (Run M-3)

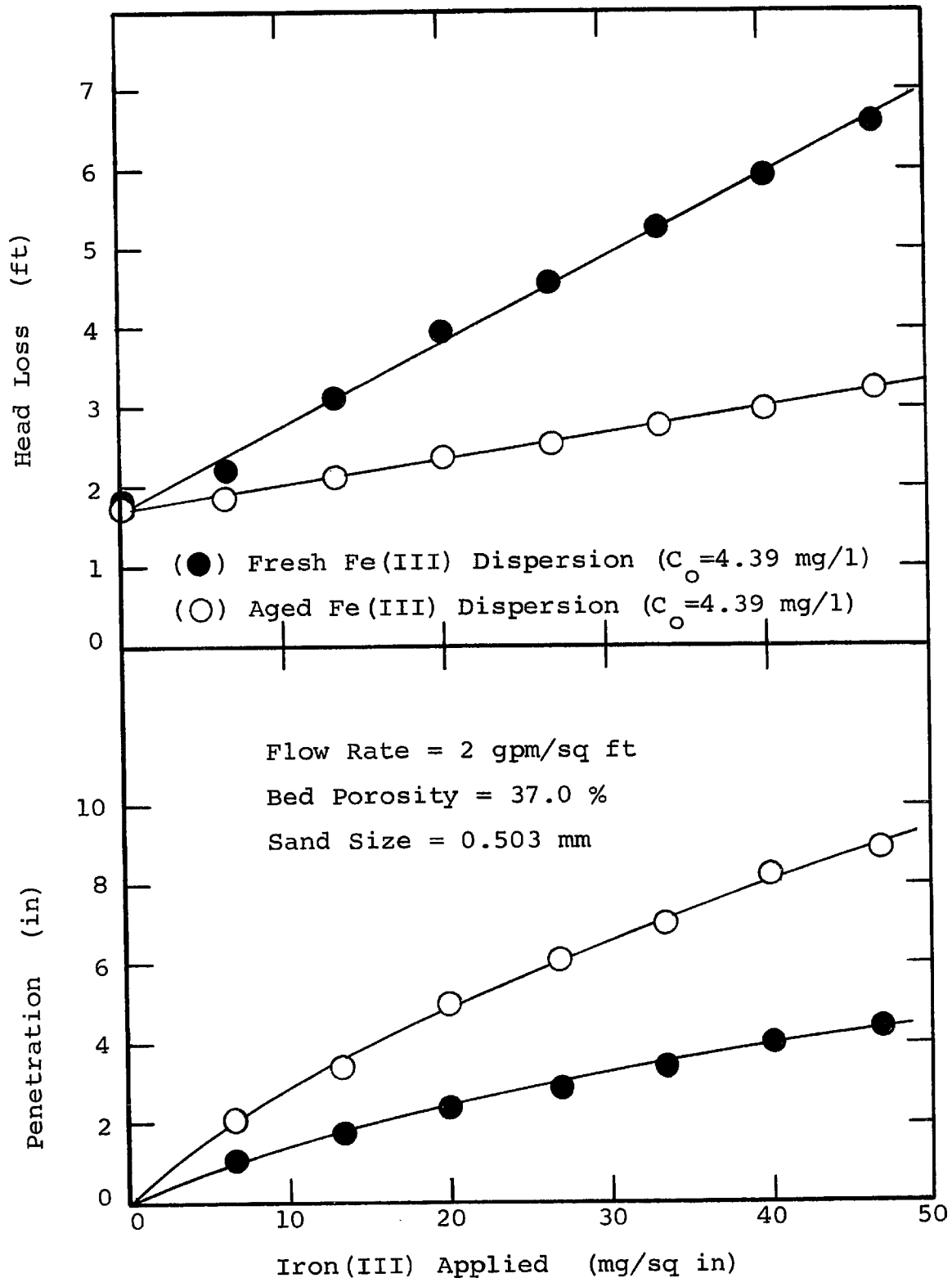


Figure 4-9. Filtration of Fresh and Aged Iron Floc Dispersions at pH=9.5 - (Run M-1)

without additional mixing. This procedure resulted in the application of flocs to the filters which were of similar size, the exception being runs at pH 5 in which the flocs in both the fresh and aged dispersions were much smaller than the flocs formed at higher pH values. Agitating the fresh dispersions at the top of the filter column may have increased their rate of aging somewhat but this was probably a minor factor.

The data presented in Figures 4-7 to 4-9 indicate that aging slightly improves the poor filtration observed at pH 5, and greatly retards filtration at pH values of 7.2 and 9.5. These results were also reproduced in duplicate runs. By plotting the data another way, as in Figures 4-10 and 4-11, the effects of pH can also be observed. For example, iron(III) removal is seen to be uniformly good at pH 7.2 and pH 9.5, but severely inhibited at pH 5. In addition, these data indicate that the influence of pH is much more pronounced in the filtration of fresh iron solutions than in the filtration of aged iron solutions. This is to be expected based upon iron(III) hydrolysis equilibria, described previously.

In contrast to these results, O'Melia and Stumm found that aging does not affect filtration at pH 5, slightly impairs filtration at pH 7, and greatly improves it at pH 9.5. In addition, they observed poor filtration of fresh suspensions

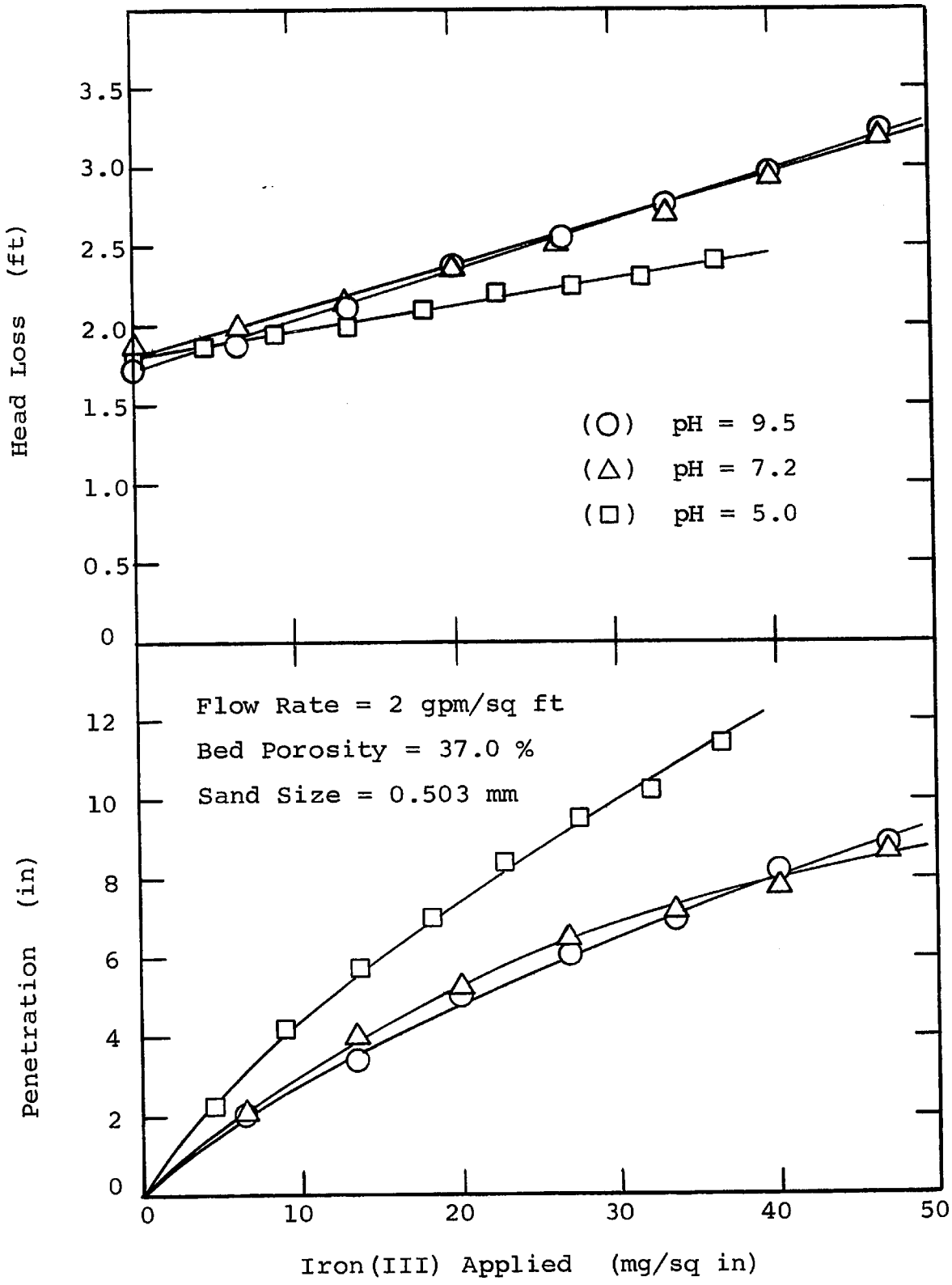


Figure 4-10. Filtration of Aged Iron Floc Dispersions at Three pH Values

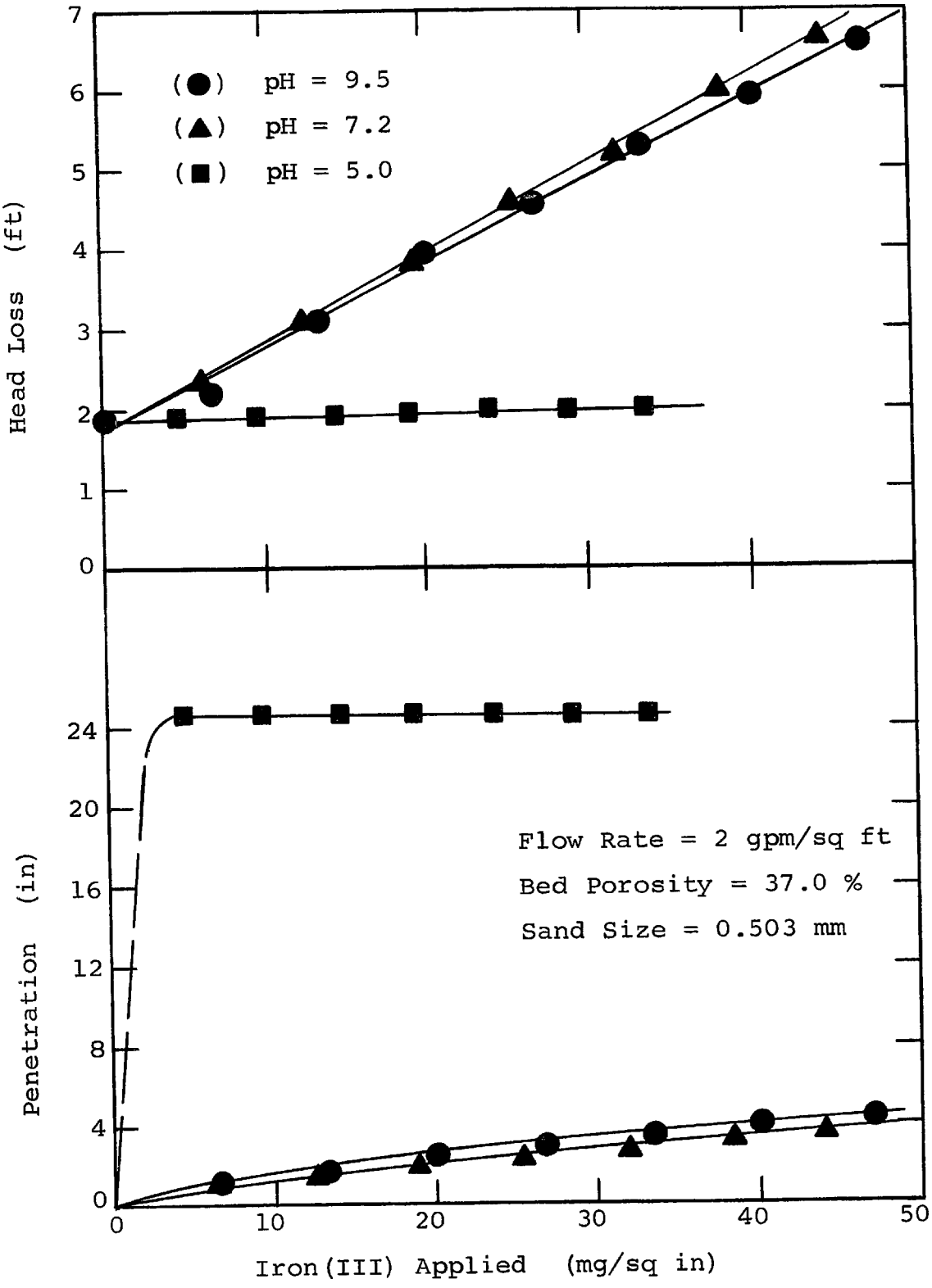


Figure 4-11. Filtration of Fresh Iron Floc Dispersions at Three pH values

at pH 9.5. Although both the present and the previous investigations demonstrate significant effects of aging and pH on the filtration of iron(III) suspensions, the nature and magnitude of the effects observed are quite different. The dissimilarities are most marked at pH 9.5, where the present study finds that filtration efficiency is lowered by aging, while the previous study indicates that the opposite is true.

The previously mentioned differences in materials and methods of the two studies would account for some of the observed discrepancies. However, three additional factors may be of more importance. First, the investigations reported here did not control ionic strength. It was not felt necessary to do so in view of the appreciable ionic strength already present in the tap water and of complementary studies made by O'Melia and Stumm in which wide variations of ionic strength effected only very minor changes in the filtration of iron(III) dispersions. Second, the earlier investigations utilized distilled water with $NaClO_4$ added for ionic strength, presumably so that known influences of sulfate and other anions on the filtration process would not mask the aging effects. The investigations reported here, on the other hand, purposely used tap water so that the effects of these ions would be included in the overall result. Finally, the method of preparation of the aged iron(III) suspensions filtered in

this research was different than the method used by O'Melia and Stumm. The latter workers both prepared and aged their dispersions at iron(III) concentrations of about 10^{-4} M. In the studies reported here, dispersions were prepared and aged at concentrations of about 0.002 M and then diluted to a concentration of about 0.7×10^{-4} M for application to the filters. Since the aging reactions were stated earlier to proceed at a faster rate in solutions of higher concentration, this procedure undoubtedly resulted in the application of flocs to the filters which were, in effect, somewhat older than 4 hours.

To conclude the studies on effects of aging, a filtration run was conducted to determine whether a minor variation in floc age is sufficient to produce significant effects. Two filters were run which received iron(III) dispersions differing in age by only about 20 minutes. This was accomplished by adding iron stock solution to the influents of the two filters at different distances above the sand bed. In one filter, for example, the coagulant solution was added 8 inches above the sand bed, while in the other it was added about 6 feet above the bed. In both cases, the floc particles were not microscopically visible as they approached the top of their respective filter beds. The results, presented in Figure 4-12 indicate that the first 20 minutes of aging have

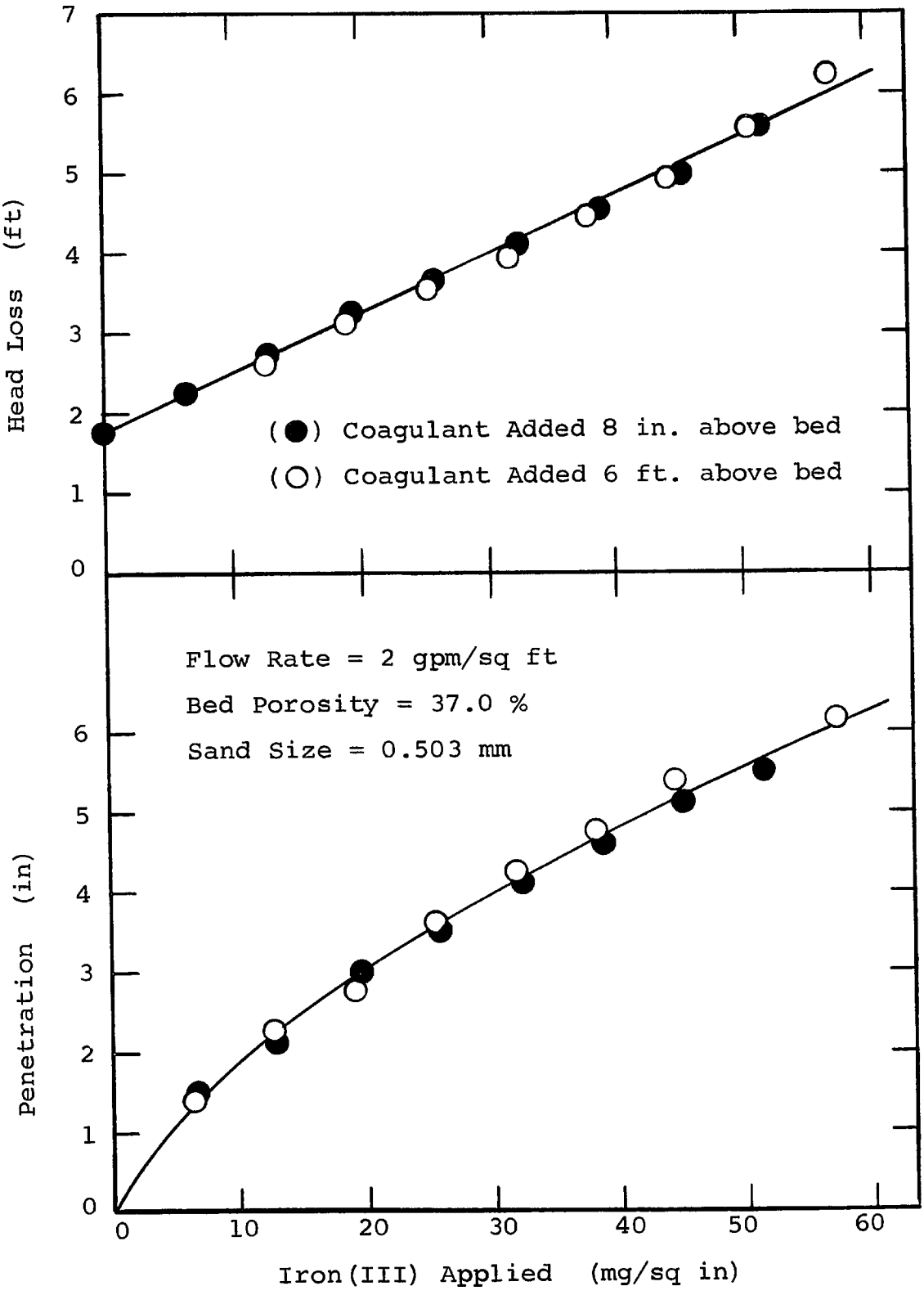


Figure 4-12. Effects of the Location of Iron(III) Coagulant Addition Upon Filtration Performance at pH=7.2 - (Runs I-1 and I-3)

virtually no effect on the filtration of iron(III) dispersions for the concentration employed.

A consideration of the preceding discussion of past and present research on aging and pH effects suggests that these factors are, indeed, significant variables in the filtration process. Unfortunately, the specific filtration effects of aging at a given pH, and of pH at a given age, have been demonstrated by a comparison of this investigation to previous ones to be dependent upon other physical and chemical parameters of the system. It appears possible that this dependency may involve complex synergistic and competitive, as well as direct, interactions among the various parameters. As a result, highly idealized filtration experiments such as the ones conducted by O'Melia and Stumm and perhaps even more practical ones like those reported here, are not necessarily representative of practical situations and may produce misleading results. Nonetheless, basic studies are still valuable as an initial step for outlining parameters deserving of additional study, and for understanding mechanisms of filtration.

Flocculation Studies

Jar tests were conducted on various selected dispersions to determine if the flocculation characteristics of these dispersions could be correlated with their filtration proper-

ties. This method is similar to recent studies in which filtration tests were used to predict flocculation efficiency (79,112). It was postulated that if a relationship between flocculation and filtration was found to exist, it would provide strong evidence for the importance of floc-to-floc interactions within a filter in addition to floc-sand reactions. There has been some tendency in recent filtration literature to make no distinction of this kind, despite the fact that operating conditions favorable to the first type of interaction might be entirely different from those for the latter if electrokinetic or chemical effects are important. In addition, such a relationship between flocculation and filtration would further suggest that some of the same mechanisms contributing to particle agglomeration in the flocculation process may also be operating to control particle attachment in the filtration process.

The dispersions chosen for study were those used in the filtration experiments of O'Melia and Crapps (97). These dispersions could be closely duplicated because of the utilization of deionized water by these workers. The four suspensions tested all had iron(III) concentrations of 4 ppm; in three of the dispersions additional inorganic ions were added in the form of 25 ppm of chloride, sulfate, or phosphate ions, in order to produce variations in the mobilities of the floc particles.

The use of the aforementioned dispersions provided an opportunity not only to further elucidate particle attachment mechanisms within the filter, but at the same time to examine the validity of the electrokinetic theory of floc removal proposed by O'Melia and Crapps. This theory was based upon correlations of observed floc and silica mobilities with the filtering properties of the flocculent dispersions. It will be recalled that some aspects of this theory have already been rather severely criticized by O'Melia himself in a recent paper (86). He suggested, for instance, that mobility measurements are not sufficiently accurate to support an electrokinetic theory, and he postulated that chemical effects, other than those of electrokinetic origin, may be responsible for floc removal (98). Nevertheless, it was felt that there were additional avenues of criticism, particularly with regard to floc size, that would be amenable to study by means of jar tests.

The results of the flocculation tests, expressed as percent of iron remaining in the supernatant after mixing and settling, are presented in Table 7, along with some corresponding filtration observations selected from the work of O'Melia and Crapps. No attempts at quantitative correlations of the flocculation test results and the observed filtration parameters were made, for obvious reasons.

TABLE 7

Comparison of Electrophoresis Measurements and Flocculation Tests as Indicators of Floc Filterability for Four Aqueous Systems at Three pH Values

pH	Anion	Residual Iron Concentration (%)	Relative Floc Size	Floc Mobility $\left[\frac{\mu/sec}{v/cm}\right]$	Slope of Head Loss Curve (ft/mg Fe^{3+}) $x10^{-2}$	Slope of Bed Pent'r Curve (in/mg Fe^{3+}) $x10^{-2}$
5.0	Demin. Water	100	Not Visible	+1.95	0.94	0.43
	Chloride	100	Not Visible	+2.23	1.14	0.50
	Sulfate	80	Medium-Small	+0.52	0.44	0.76
	Phosphate	90+	Small	-1.28	0.07	1.13
7.0	Demin. Water	31	Medium	-0.71	0.84	0.50
	Chloride	25	Medium-Large	-0.64	1.37	0.75
	Sulfate	27	Large	-0.77	0.58	0.89
	Phosphate	100	Pinpoint	-1.85	0.10	2.53
9.5	Demin. Water	45	Medium	-1.72	0.07	1.33
	Chloride	42	Medium	-1.03	0.14	1.40
	Sulfate	39	Medium	-1.55	0.16	1.12
	Phosphate	100	Small	-2.16	0.06	3.00

Notes:

(1) Residual iron concentration is the percentage of the original Fe(III) concentration remaining in suspension after mixing and settling (see page 22).

(2) The values in the last three columns were obtained from the data of O'Melia and Crapps (97); slopes were computed from the first and last points of the curves.

However, considering only the relative magnitudes of the numbers, it is seen that at pH values of 7.0 and 9.5 qualitative correlations between jar tests and filtration properties are reasonably good, despite the fact that the mixing conditions produced in the jars were probably quite different than those prevalent in the filtration experiments. At pH 7.0, particularly, the jar test correlations appear even more suitable than the correlations obtained by O'Melia and Crapps between floc mobility and the observed filtration parameters. For example, comparatively good filtration was obtained at pH 7.0 where the floc mobilities are negative. While this good filtration is consistent with the good flocculation noted at this pH value, it can not be reconciled by an electrokinetic removal mechanism based on floc-sand interactions as there would be a mutual repulsion between the floc particles and the sand grains. On the other hand, at pH 5.0 the results are more easily interpreted as an electrokinetic interaction between the floc and sand surfaces as there is no relationship between the jar test results and the observed filtration parameters. It is seen, for instance, that the dispersions which produced no flocculation at all were also the ones most filterable, i.e., the ones that produced the least bed penetration and highest head loss per unit of applied iron. A closer inspection of

Table 7 reveals, however, that floc size was an important variable in the flocculation studies and presumably also in the filtration runs. The two suspensions which filtered best at pH 5 actually contained particles which were in the colloidal size range, while the other two dispersions which filtered poorly contained much larger particles.

The preceding observations and discussion tend to suggest that positively-charged colloidal ferric hydroxide particles do not flocculate well and are removed in filtration via an electrokinetic adsorption process between the particle and the sand grain, while negatively charged floc units, by virtue of their greater flocculability, adhere to each other within the filter, as well as to the filter medium itself. The recent work of Heertjes and Lerk (54) also appears to support this concept. These workers found that positively charged colloidal ferric hydroxide particles are removed by electrostatic sorptive action between the particles and the filter material, and well-flocculated particles (with zero or a slightly negative charge) are removed by a different mechanism. This interpretation of the removal process could, then, account for the anomalous behavior at pH 5.0.

In order to provide additional evidence on the importance of floc-to-floc interactions for large particles within

the filter, a filtration run was conducted in which one of the filters contained sand that was precoated with iron to alter its surface. A second filter was operated in the usual fashion for comparsion purposes. The sand was precoated by repeatedly passing a 10^{-2} M iron(III) solution (at pH 3.5) through the filter. This procedure produced a yellowish stain on the sand which did not diminish after filtering clean water through the bed for three hours prior to the run, and which did not have any significant effect on the initial head loss through the bed. An analysis of the iron content on the surface of sand which had undergone similar treatment revealed 29.2 mg of adsorbed Fe(III) per gram of sand, compared to 2.7 mg/g for the control sand.

The results of the filtration run are depicted in Figure 4-13. It is observed that the precoat had virtually no effect on the observed head loss and bed penetration patterns. Thus it appears that the surface properties of the sand were insignificant, and that the main function of the sand in the filtration of suspensions of ferric flocs which are capable of flocculation, i.e., not highly positively charged, is merely to provide a solid matrix having interfaces upon which the floc particles can deposit. It cannot be stated at this time whether a floc particle in the flow becomes attached to one previously removed, or whether it flocculates

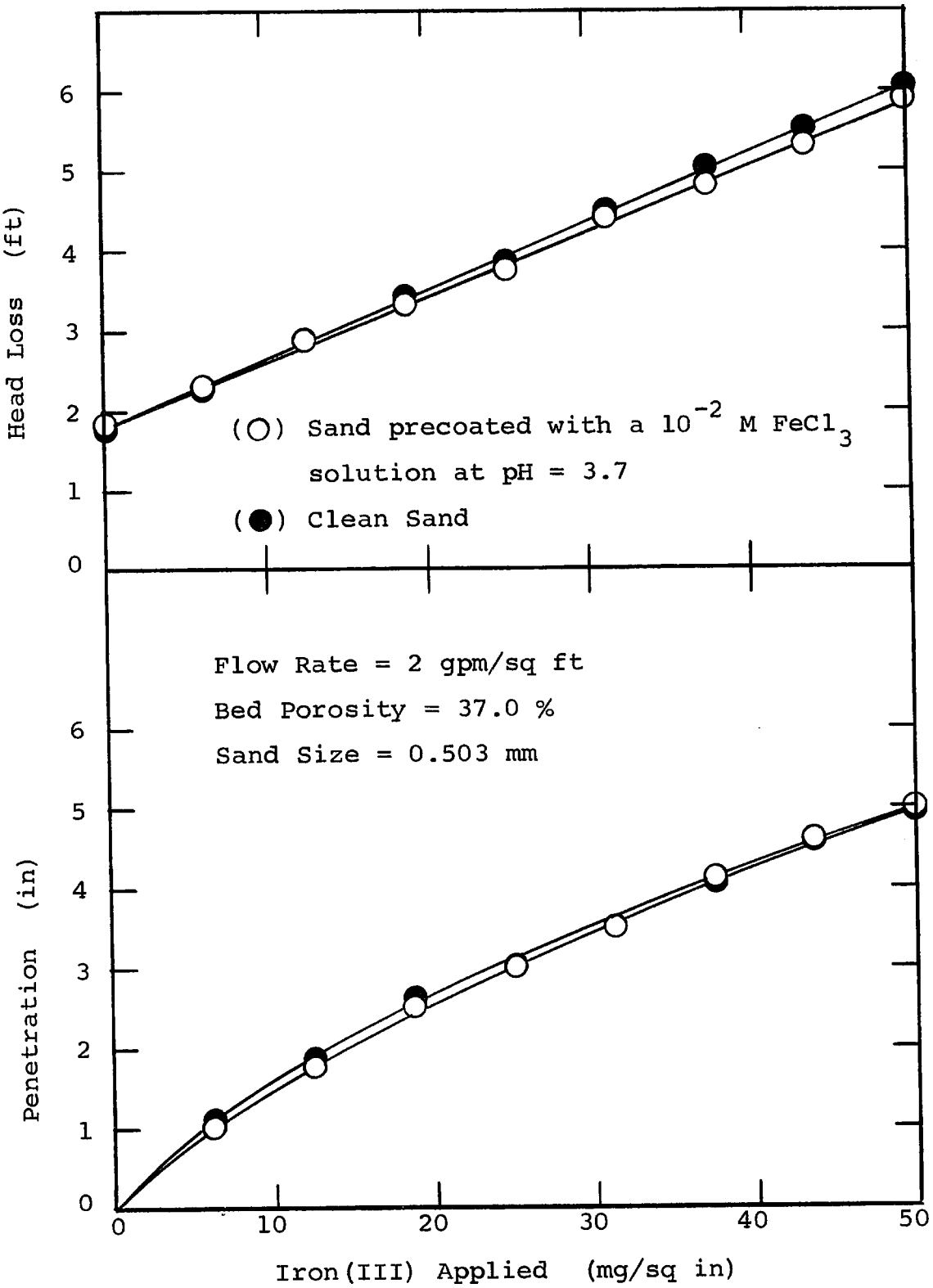


Figure 4-13. Filtration of Fresh Iron Floc Dispersions Through Fe(III)-Coated Sand and Clean Sand at pH=7.1 - (Run I-4)

with other particles in the pore space and then is removed by straining action in the interstices. The latter view is apparently the one expressed by Smith (115). In either case, however, the flocculation properties of the dispersion would control its removal in a sand bed.

Phosphate Studies

Regardless of which mechanism controls the filtration process, the results of the experiments of O'Melia and Crapps, discussed in the preceding section, appear to demonstrate that the filtration process may be chemically controlled by the addition of certain ions to the water. Indeed, this was one of the conclusions reached by these authors. Of the ions which were tested, phosphate was particularly effective in reducing the rate of head loss buildup and in increasing the rate of bed penetration. Phosphate ions were also observed to have a large effect on the size of floc particles in the flocculation studies conducted in this research. Presumably, phosphate exerts its effect because of the complex it forms with iron(III). Thus, it might well be anticipated that silica should also show a pronounced effect on the filtration behavior of iron(III) dispersions. Unfortunately, since all of the studies mentioned employed deionized water, the dispersions were of a very low ionic strength such as is not found in practice. In order to examine the effects of phos-

phate in a more realistic system, a filtration run was conducted utilizing tap water. More specifically, the purpose of the filter run was to determine the concentration of phosphate necessary to produce a significant effect on the filtration of an iron(III)-tap water dispersion.

A filtration run was conducted with two identical filters operated in parallel, the exception being that one filter received added phosphate at a concentration of 150 mg/l. This particular concentration was selected by running a series of jar tests on dispersions having an iron(III) concentration of 4 mg/l and phosphate concentrations ranging from zero to 200 mg/l in increments of 25 mg/l. It was found that up to a concentration of 150 mg/l there was no discernable effect of phosphate ions on the flocculation process, but at this concentration the size and settling characteristics of the floc particles were affected. In view of the relationship found earlier between flocculation and filtration, it was reasoned that this concentration would also affect the filtration process.

The outcome of the filter run is illustrated in Figure 4-14. The influent suspension which contained added phosphate is seen to have resulted in a lower rate of head loss build-up and a more uniform distribution of the head loss within the filter. However, even though the 150 mg/l phos-

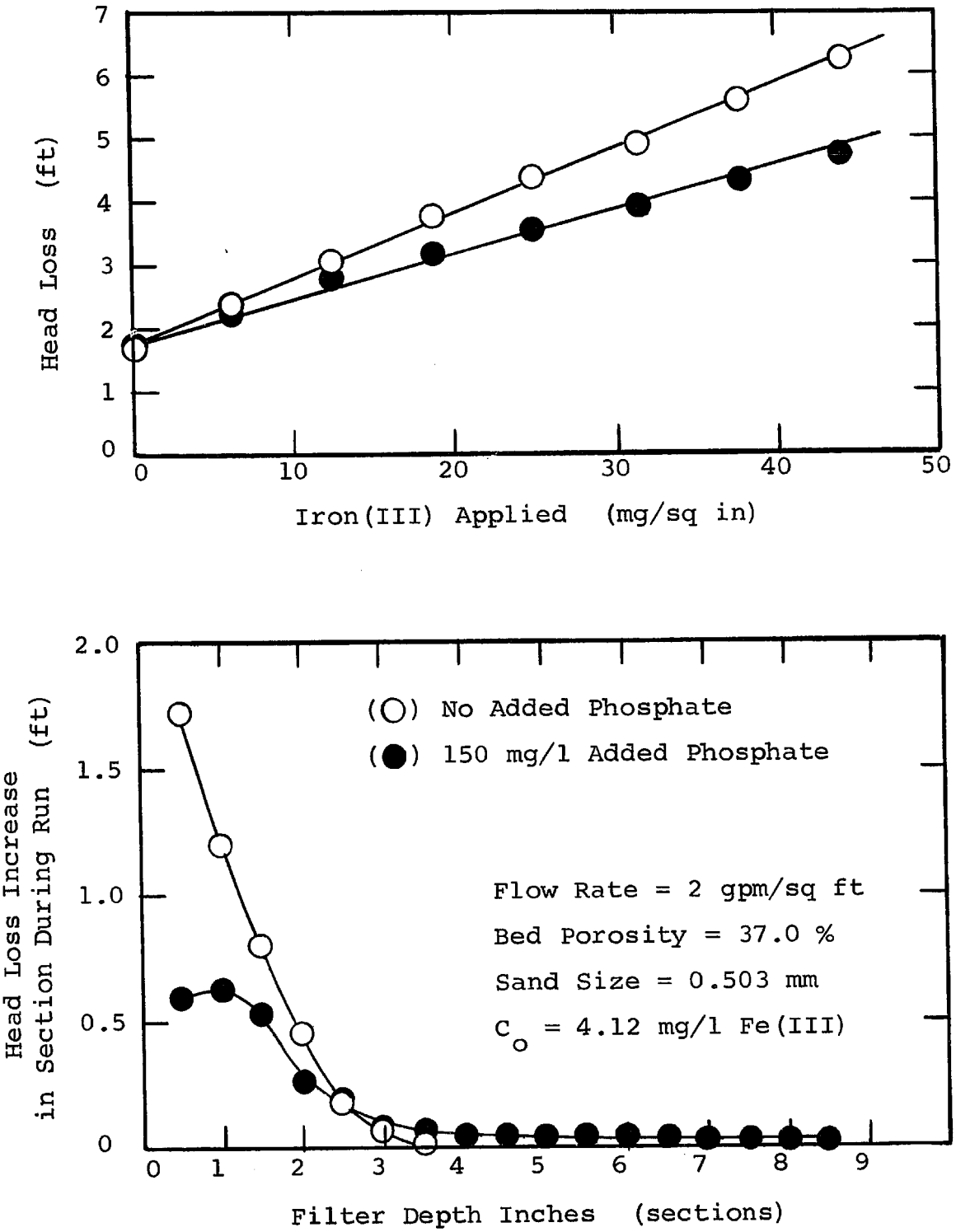


Figure 4-14. The Effect of Phosphate on the Filtration of Iron Floc Dispersions at pH=7 - (Run M-5)

phate concentration used was six times that employed by O'Melia and Crapps, the effects observed here are not nearly as great as those reported by these workers. Since the physical parameters used in the experiments of O'Melia and Crapps and in this research were nearly identical, the results may be directly compared in terms of the differences in chemical parameters of the systems. This work domonstrates, then, that much higher doses of chemicals may be necessary to control the filtration process when tap water, rather than deionized water, is the suspending medium. These experiments establish further that laboratory investigations conducted using deionized water may not be representative of many practical systems.

General Discussion

Data obtained in the laboratory experiments indicate that the filtration properties of iron(III) dispersions may be largely determined by the flocculability of these dispersions. Such parameters as aging time, pH, ionic strength, and phosphate ion concentration, which have a demonstrable effect on the flocculation process, have also been shown to affect filtration. Additionally, some correlations have been obtained between the flocculation properties of dispersions and their subsequent filterability.

An exception to the foregoing may occur in the filtra-

tion of positively charged colloidal ferric-flocs. Particles of this type were reported by O'Melia and Crapps (97) to filter well, yet were observed in this research to flocculate poorly. An electrostatic mechanism based upon floc-sand interactions may therefore by operative in the filtration process under certain conditions. It should be mentioned, however, that iron(III) dispersions at pH 5 did not filter well in the present studies. While no particle surface properties were measured, it seems plausible that these particles would be positively charged.

The optimum pH range for the filtration of both fresh and aged iron(III) dispersions has been observed in these studies to occur from pH 7 to pH 9.5. This is somewhat broader than ranges reported in earlier works, but differences in ionic strengths and types and concentrations of complex-forming ligands in the waters may account for the apparent disagreement. Such factors are known to affect the chemical characteristics of the floc particles, and they have also been shown in this research to control the size of flocs which are produced. Workers purporting the demonstrate the importance of chemical factors in the filtration process should therefore be certain that their observations are not actually due to differences in floc size and density, these being physical manifestations of the changes in chemical

parameters.

One further observation not previously reported seems pertinent to mention. When sand beds containing deposited iron were backwashed in these studies, large pieces of flocculated matter were invariably observed in the effluent wash water. These agglomerations had to have originated within the filter bed during filtration, supplying additional evidence as to the importance of interparticle bridging in the filtration process.

CHAPTER 5

THE FILTRATION OF ALGAL SUSPENSIONS

General

Experimental Objectives

The penetration of algae through rapid sand filters, both in the laboratory and in the field, is a well-documented occurrence (29). Since these organisms can be similar in size and density to floc particles, and the latter are removed nearly completely in a sand filter, the penetration of algae must apparently be explained through a consideration of their surface characteristics. The objectives of this research have been to elucidate the precise roles of the surface properties of both algae and sand in the filtration process, and thereby to suggest the mechanism(s) by which algae are removed in a rapid sand filter. Such parameters as organism size and sand bed porosity have also been studied in order to shed additional light on the removal process. Since algae are representative of a wider class of non-flocculent particulate matter, the results should be of general applicability.

Surface Characteristics of Algae

In contrast to the availability of information on the

aqueous chemistry of iron and the mobilities of ferric-floc particles, very little work has been undertaken in the determination of the surface characteristics of algae. Virtually all of the available literature on algae deals with the physiology and biochemistry of these organisms rather than their surface properties.

Ives (65,66) appears to have been the only worker to undertake an extensive study of the electrophoretic mobility of algal particles. Over the pH range investigated (approximately pH 2.5 to pH 11.5) the algae were found to remain electronegative, although a minimum charge which was nearly zero occurred at about pH 7-8. No interpretation of this rather unusual pH-mobility curve was given. Ives also found that cultured algae and natural algae exhibit the same charge characteristics when they are suspended in waters of identical chemical environment.

Some additional information on the surface characteristics of algae can be obtained by examining the composition of the cell wall. Northcote et al. (94) have conducted such an examination with a species of Chlorella. They found the wall to consist of two distinct phases: an organized microfibrillar structure which is embedded in a continuous matrix. An analysis of the cell wall showed an approximate concentration of protein, 27%; lipid, 9.2%; α-cellulose, 15.4%; hemi-

cellulose, 31.0%; glucosamine, 3.3%; and ash, 5.2% (containing iron and calcium). The relatively high concentrations of protein and cellulose observed suggests that these materials may control the surface properties of algae.

The electrophoretic behavior of proteins is well-defined. Their charge is known to arise from the ionization of surface groups, these being primarily -COOH and $-NH_2$. The colloidal protein ion thus carries a negative charge at high pH (owing to ionization of $-COOH \longrightarrow -COO^-$), and a positive one at low pH values (arising from $-NH_2 \longrightarrow -NH_3^+$). The isoelectric point, at which the charge contributions from the acidic and basic groups are equal and opposite, occurs around pH 4, although it may be shifted to lower values if certain anions are present.

Abramson et al. (1) have reported on studies of the surface characteristics of cellulose by microelectrophoresis. The pH-mobility curve for purified cellulose was stated to exhibit an isoelectric point at pH 2.5. Since cellulose is a compound held to be free of ionizable groups, its negative charge at higher pH values presumably results from preferential adsorption of OH^- ions (3).

If algal particles do exhibit mobilities similar to those observed for the major constituents of their cell wall then they would be expected to have an isoelectric point in the

acid pH region with an increasingly negative charge at higher pH values. The results of electrophoretic studies of algae performed in this research are presented later in this chapter.

Experimental Results and Discussion

Effects of pH

Jar Tests. The pH dependence of algal flocculation has been determined by running jar tests over a pH range of 2 to 11, in accordance with procedures given earlier. These were undertaken prior to mobility and filtration studies to determine if widely varying pH values have any effect on the physical characteristics of algal suspensions. A 5-day culture of Chlorella, diluted with tap water to an organism concentration of about 90,000 particles/ml, was the suspension employed. It was found that for all values of pH tested below 10, the algae remained in a dispersed state throughout the experiment and subsequent to it. Furthermore, size distributions run on the various suspensions with the Coulter counter were virtually identical. In short, no differences of any nature could be discerned over this pH range in any of the suspensions tested.

Above pH values of about 10.5 an entirely different situation existed. At these high values of pH, the algal particles flocculated irreversibly, apparently through a

mechanism involving lysis of the cells. The large flocs produced settled well and were similar in appearance to large ferric-flocs.

Electrophoretic Mobility Studies. The effect of solution pH on the electrophoretic mobility of algae and particles of sand have also been studied. The results are depicted in Figures 5-1 and 5-2 (see pages 18-21 for additional information).

For the algae, mobilities were negative throughout the pH range studied, although they decreased in magnitude as the pH was lowered. While an isoelectric point was not observed, it appears from extrapolation of the data that one would occur near pH 1. The general shape of the pH-mobility curve agrees quite well with that predicted by the theory, suggesting that the mobility of algae is in fact controlled by the protein and/or cellulose of the cell wall. The failure to observe an isoelectric point at pH values as low as 2.0 might be accounted for by the presence of chlorides (about 65 mg/l) and other anions in the Ann Arbor tap water. No measurements could be made above pH 10 because of the precipitation-flocculation effect described earlier. It should be mentioned that the results reported here disagree quite substantially with those reported by Ives (65,66).

An observation of Figure 5-2 reveals that the mobility

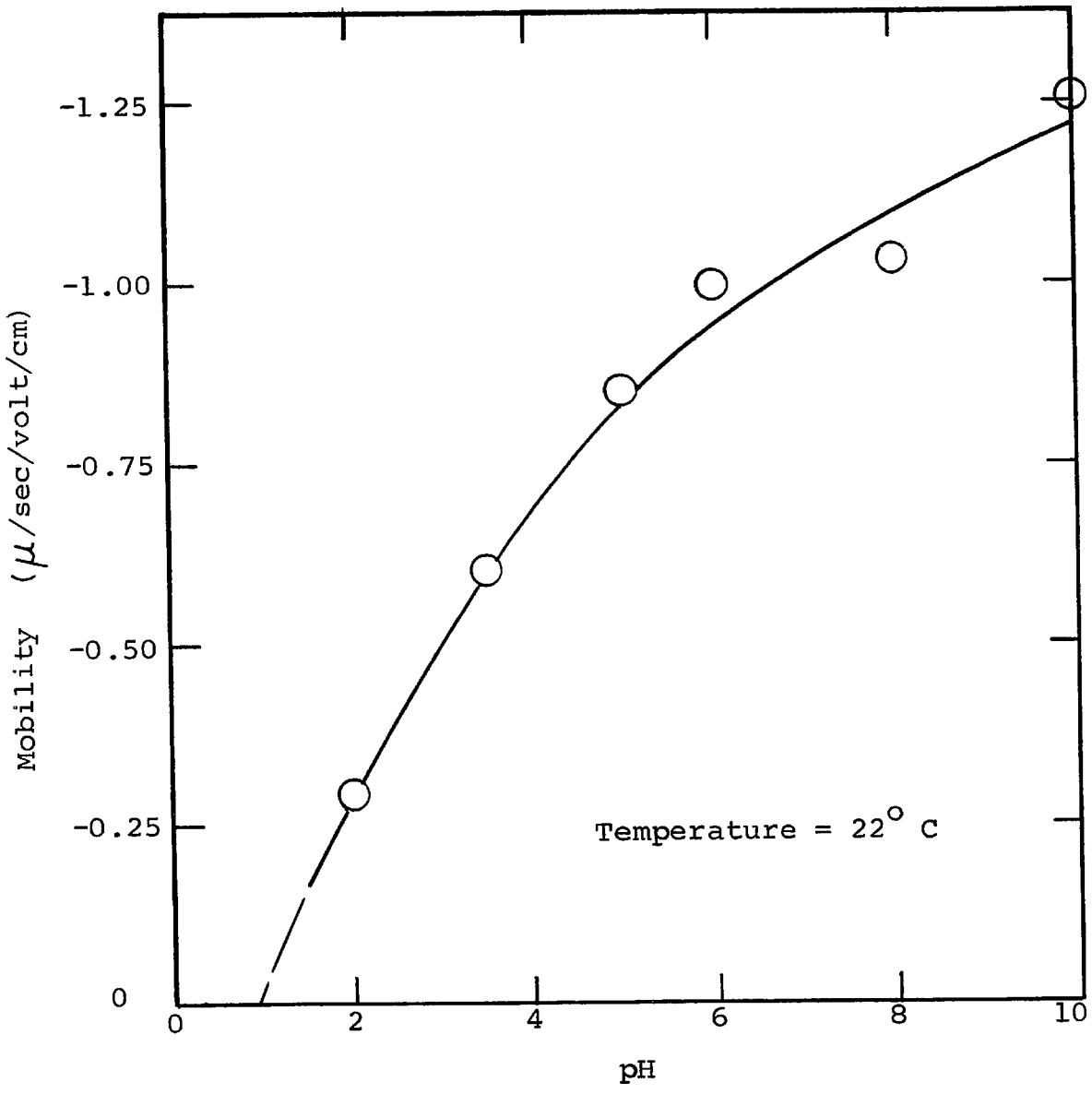


Figure 5-1. The Effect of pH on the Electrophoretic Mobility of Chlorella Suspended in Ann Arbor Tap Water

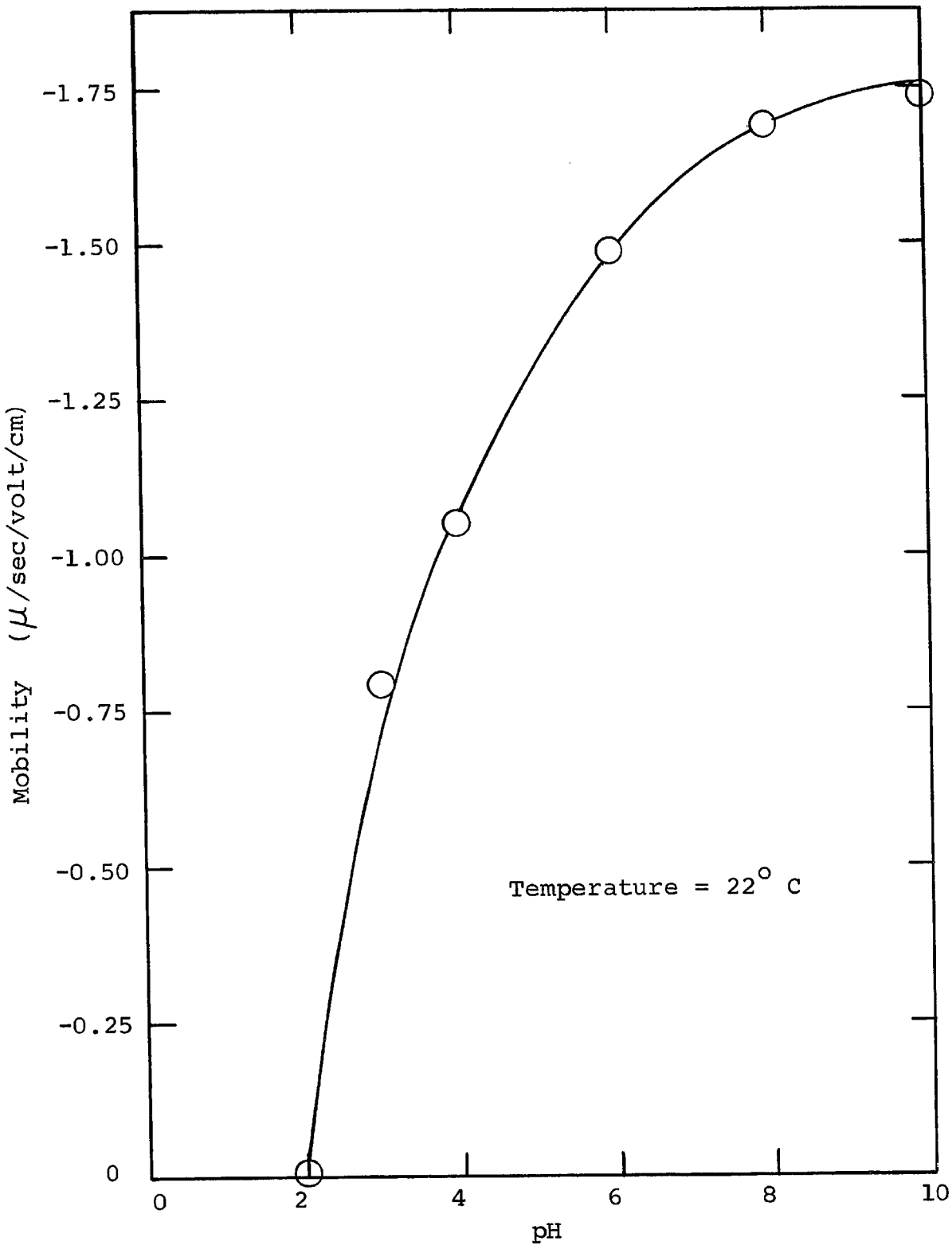


Figure 5-2. The Effect of pH on the Electrophoretic Mobility of Particles of Sand Suspended in Ann Arbor Tap Water

of sand grains exhibited a somewhat greater pH dependency than did the algal mobility. Nevertheless, the curves are quite similar. The mobility of the sand particles decreased toward zero with decreasing pH and reached a value of zero at pH 2.0. This isoelectric point is within the range observed by other workers (see Table 4).

The procedures adopted in these investigations were such that the mobilities obtained for both the sand and algal particles would be representative of those obtaining in subsequent filtration runs. That is, tap water was used as the aqueous media and pH adjustments were made in the same manner as was to be used in the filtration studies. It should be mentioned, however, that the mobility data presented in Figures 5-1 and 5-2 should not be taken as quantitatively precise. There are certain errors inherent in the measuring process and it is possible, if not probable, that algal mobility varies somewhat from culture to culture because of slight differences in the physical and chemical environment.

Filtration Studies. Filtration runs have been conducted employing variations in the electrophoretic mobility--and consequently the zeta potential--of the algae applied to the sand beds. Within a given run all other factors were maintained at constant levels, including sand size (0.711 mm), flow rate (2 gpm/sq ft), bed depth (24½ in), and

porosity (30.6%)*. In each of the three runs made, a different influent organism concentration was used.

Figures 5-3 to 5-5 depict the relationship observed between removal efficiency and the total number of algae applied. The ordinate (percent removal) is computed from numerical cell counts in the influent and effluent streams, while the abscissa (number of particles applied) is the product of the flow rate multiplied by the filtration time and the applied algae concentration. It is obvious from an inspection of the data that considerable differences in filtration characteristics of algae occurred in these runs. Since pH was the only parameter varied, it is to this factor that the observed differences in filtration are attributed. Moreover, having demonstrated previously that the physical characteristics of algae are unaffected by pH over the range investigated, the differences are further ascribed to attendant changes in the mobility of algal cells with pH.

A closer examination of the filtration characteristics shown in Figures 5-3 to 5-5 indicates that removal efficiencies were best in runs operated at pH 2-3. All runs in this pH range produced removal efficiencies in excess of 90 percent,

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* The 0.711 mm sand used in these runs produced somewhat lower bed porosities than the 0.503 mm sand employed in the earlier experiments when each was packed in the dry state; nonetheless, each size yielded a porosity which was highly reproducible.

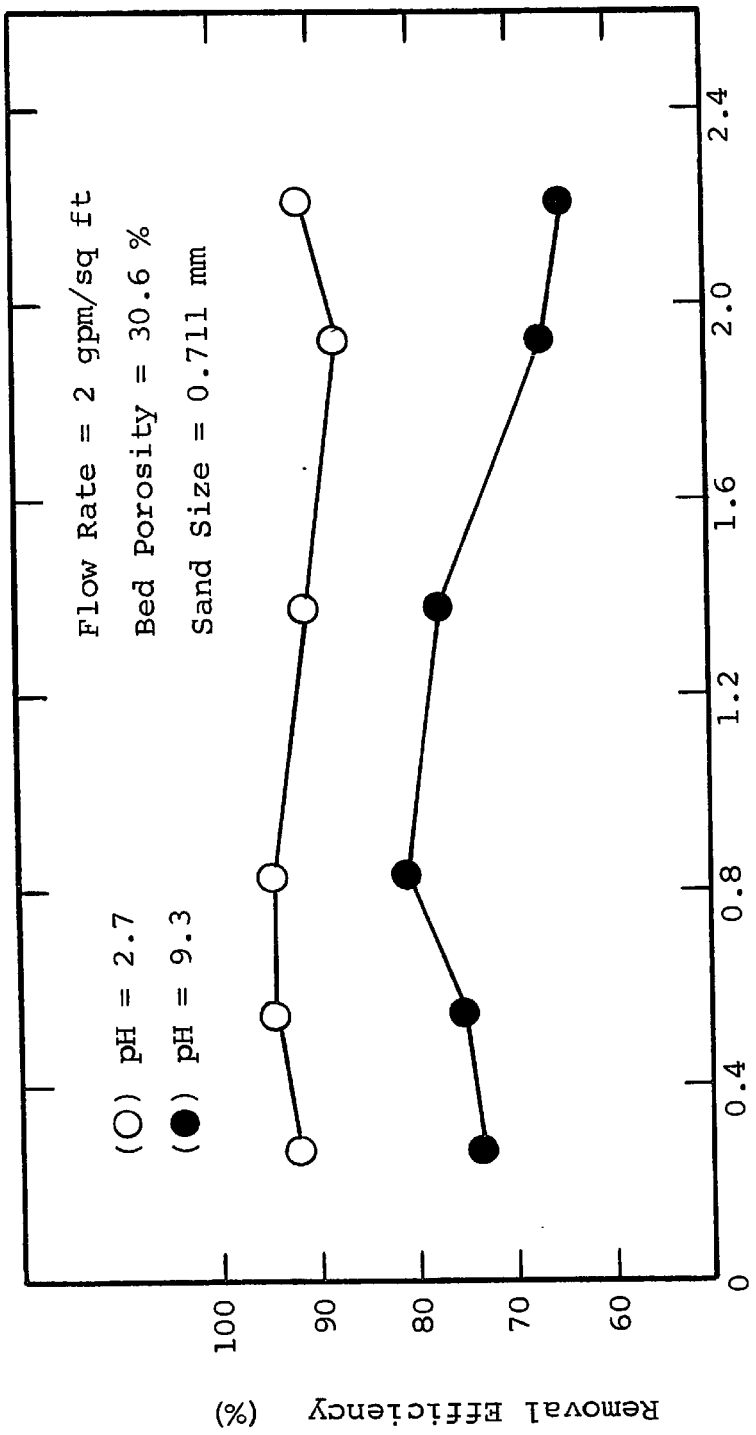


Figure 5-3. The Effect of pH on the Filtration of a Suspension of Scenedesmus (Applied Organism Concentration=8900 cells/ml; Run D-4)

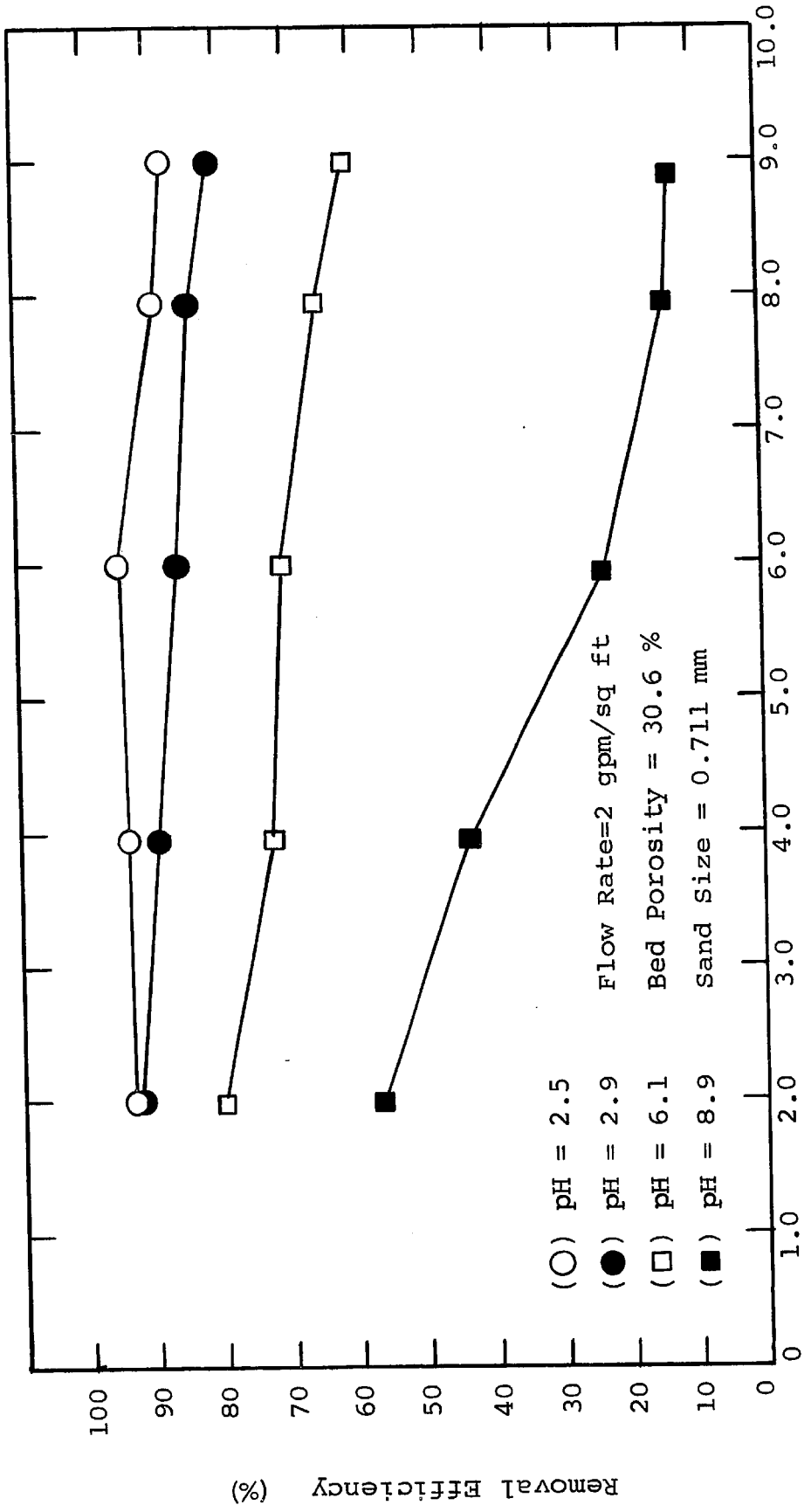


Figure 5-4. The Effect of pH on the Filtration of a Suspension of Scenedesmus (Applied Organism Concentration=31,900 cells/ml; Run D-5)

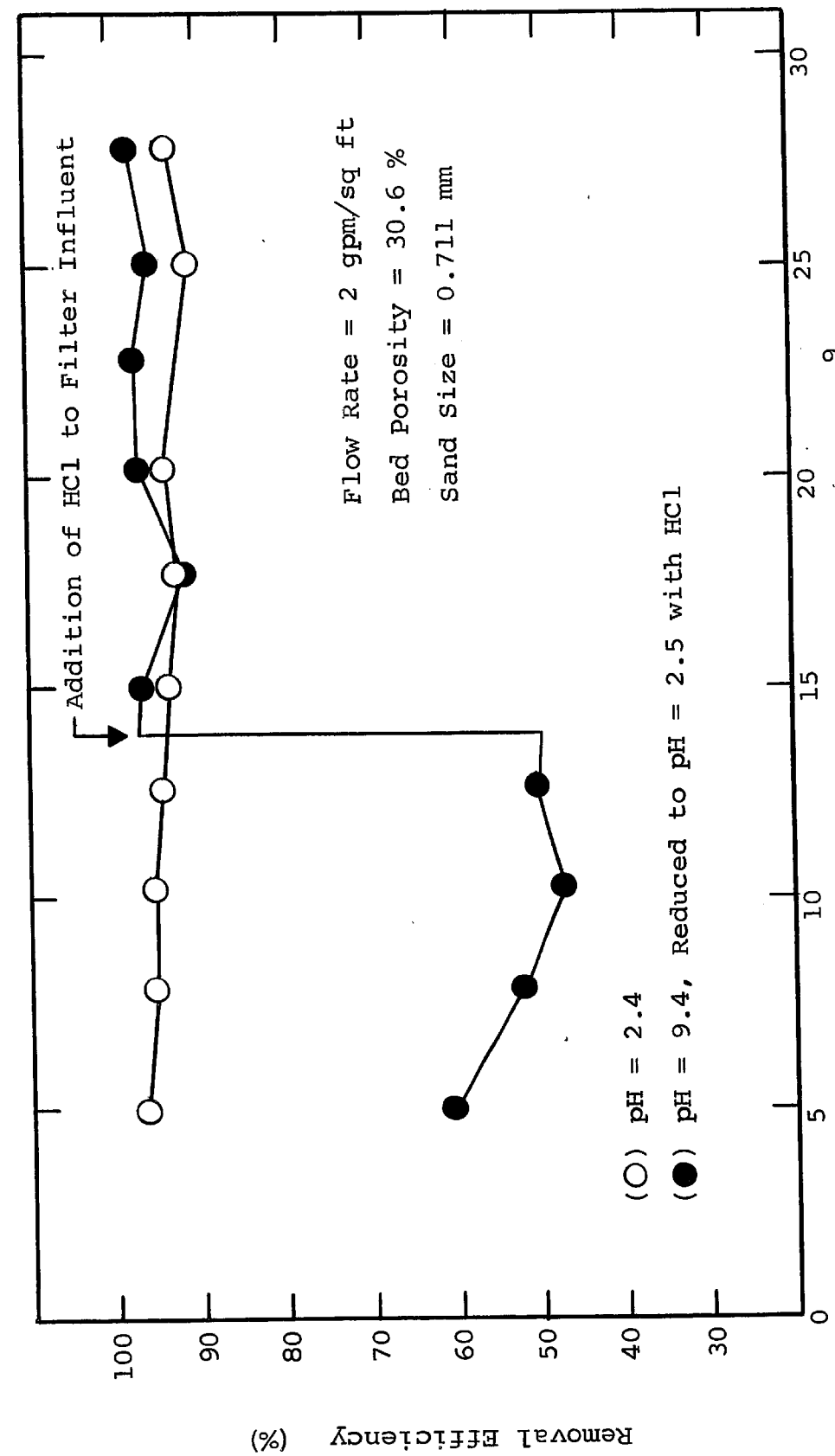


Figure 5-5. The Effect of pH on the Filtration of a Suspension of Chlorella (Applied Organism Concentration=81,600 cells/ml; Run F-1)

independent of the influent concentration. Figure 5-4 indicates that as the pH is successively raised there is a concomitant reduction in removal effeciency. The effect of pH is also shown in dramatic fashion in Figure 5-5. Hydrochloric acid was added to the influent stream of one of the filters in sufficient quantity to lower the pH from 9.4 to 2.5. An immediate increase in removal efficiency of over 40 percent (to above 90 percent) resulted.

Despite the nearly complete removals of algae obtained at low pH values, head loss buildup was negligible in every case. Examination of the filter beds at the end of the runs indicated that, while the major concentration of organisms occurred in the top inch or two of the sand, significant numbers of algae were deposited at lower depths in the bed. When the beds were backwashed, algae from all depths were removed and appeared to be in a dispersed state. Since the jar tests conducted earlier also showed that algae do not flocculate at low pH values, the preceding observations suggest that algal removal in filtration occurs via an organism-sand interaction.

Analysis of the effects of pH indicates that filtration was best in those runs operated at pH values near the isoelectric points of the sand and algae. At higher pH levels removals progressively worsened. This latter effect is

attributed to the electrostatic repulsion existing between the sand and the algae as a result of the interaction of the two negatively charged double layers. In the isoelectric region, van der Waals, and perhaps specific chemical, attractive forces predominate and these probably were responsible for the increased removals in this pH range. Because of the uncertainty in establishing precise isoelectric points it is also possible that some coulombic attraction existed at the lower pH levels.

Particle Size Studies

Although removal efficiencies of algae during filtration were shown above to be greatly reduced at higher pH values, presumably due to electrostatic repulsion forces, some removal of organisms was always obtained. This retention must necessarily be explained by an attachment mechanism independent of electrostatic forces. Ives and Gregory (72) have proposed an alternative mechanism such as interstitial straining for cases where removal cannot be attributed to surface forces. This explanation would seem to be valid for the present studies were it not for the apparently incongruous observation that removal efficiencies continually decreased with time in runs at high pH. Still, this observation does not completely rule out straining. Studies have therefore been made to determine, specifically, whether interstitial

straining is a factor in the filtration of algae, and, more generally, whether algal particle size is an important parameter in the filtration process.

Most of the filtration experiments in these studies ran for more than twelve hours. As a result, size distributions of the influent algal suspensions were made at various times during several runs to determine whether these distributions changed due to organism growth in the 700 gallon storage tank. Figure 5-6 gives the results of one such set of size distributions which were taken during the longest run. For all practical purposes, the influent size distributions are seen to have remained virtually constant over a 24 hour period. The cells ranged from below 3 to about 9 microns in diameter and approximately 50 per cent of the total were 3 to 5 microns.

In Figure 5-6, as well as in subsequent illustrations which deal with particle size, it should be mentioned that the data is plotted in the middle of the size range for which the cell counts were made. Some additional error has also been introduced into the abscissa values by computing the diameter of the particles counted on the basis of their being spheres; this assumption is true in the case of Chlorella but not for Scenedesmus.

Figures 5-7 to 5-9 present the results of particle size

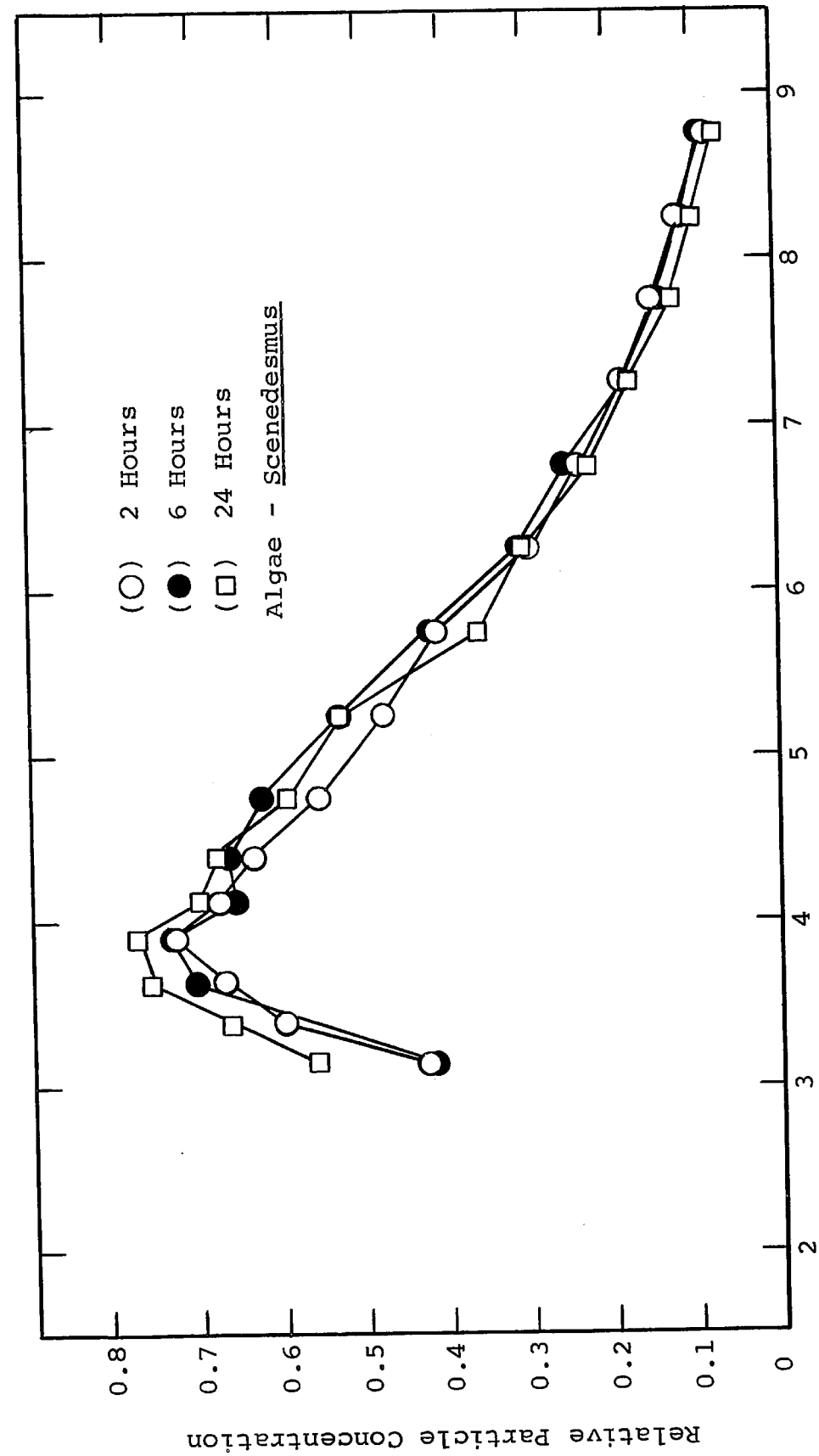


Figure 5-6. Particle Size Distributions of the Filter Influent at Different Times During Run D-6

studies for three representative runs. These figures show the efficiency with which algae of various size groupings within a suspension were removed during several typical filtration runs. Ordinate values are computed from the size distributions of the filter influent and effluent streams, as follows:

$$\text{Removal Efficiency} = 1 - \frac{\text{Algal count in effl. in given size range}}{\text{Algal count in infl. in given size range}} 100.$$

Along with these removal efficiency v. particle diameter curves, the size distributions of the influent have been given so that the relative number of organisms upon which the former curves are based can be observed.

The data from these figures show that for high pH values, particularly, removal of an algal cell from a given suspension is markedly dependent upon its size. However, also at the higher pH values there seems to be a relationship between the removal efficiency observed for a given particle diameter and the relative number of particles of the same diameter in the influent. In Figure 5-7, for example, the removal efficiency v. particle diameter curve for pH 8.9 is almost the mirror image of the influent size distribution curve. This latter observation suggests that the relative number of particles of a given size in the influent is a more important factor than the size itself in determining removal efficiency. Other filter runs, not included here, would

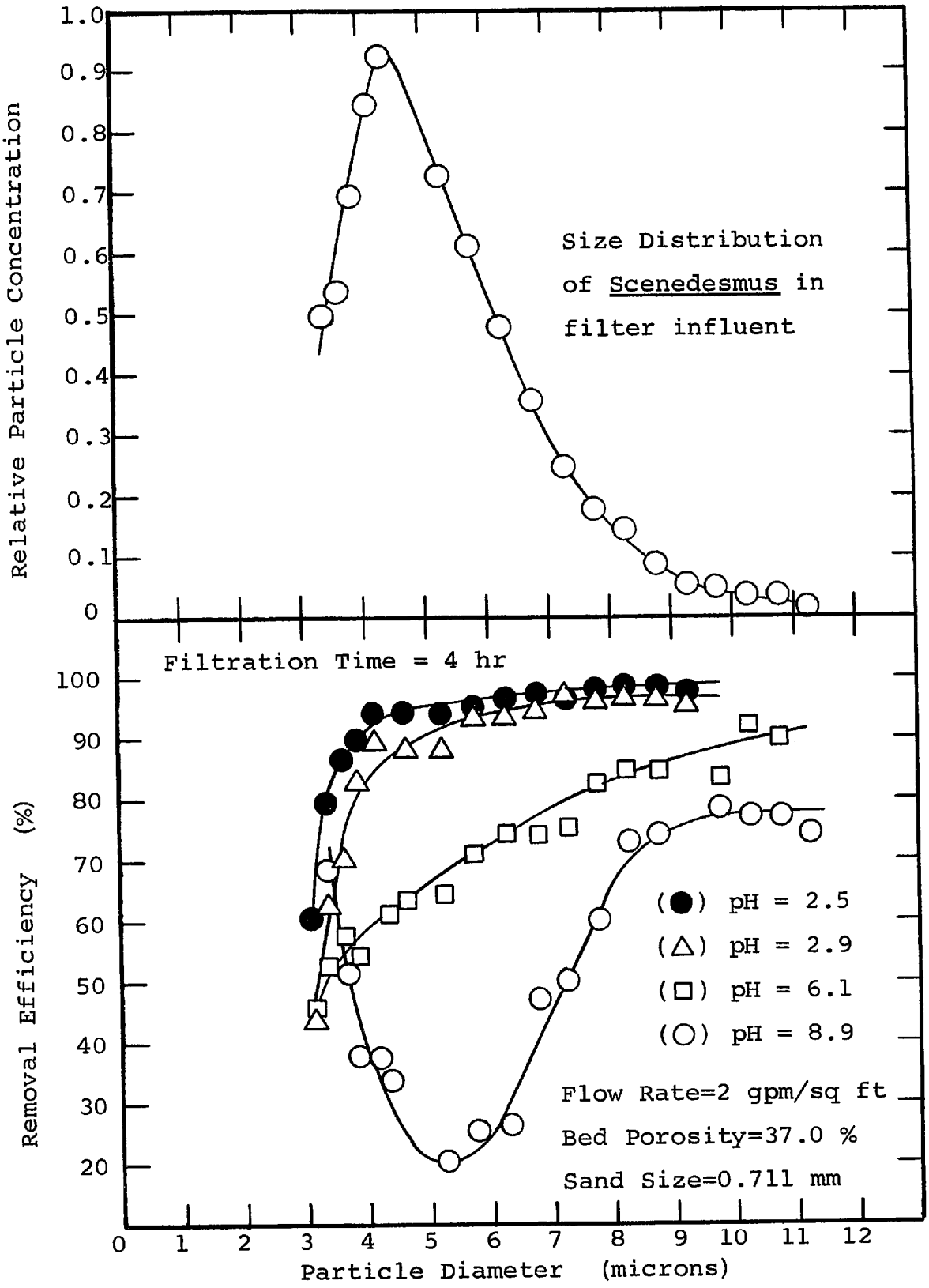


Figure 5-7. Filter Removal Efficiency as a Function of the Size of Organisms in the Filter Influent for Different Values of pH - (Run D-5)

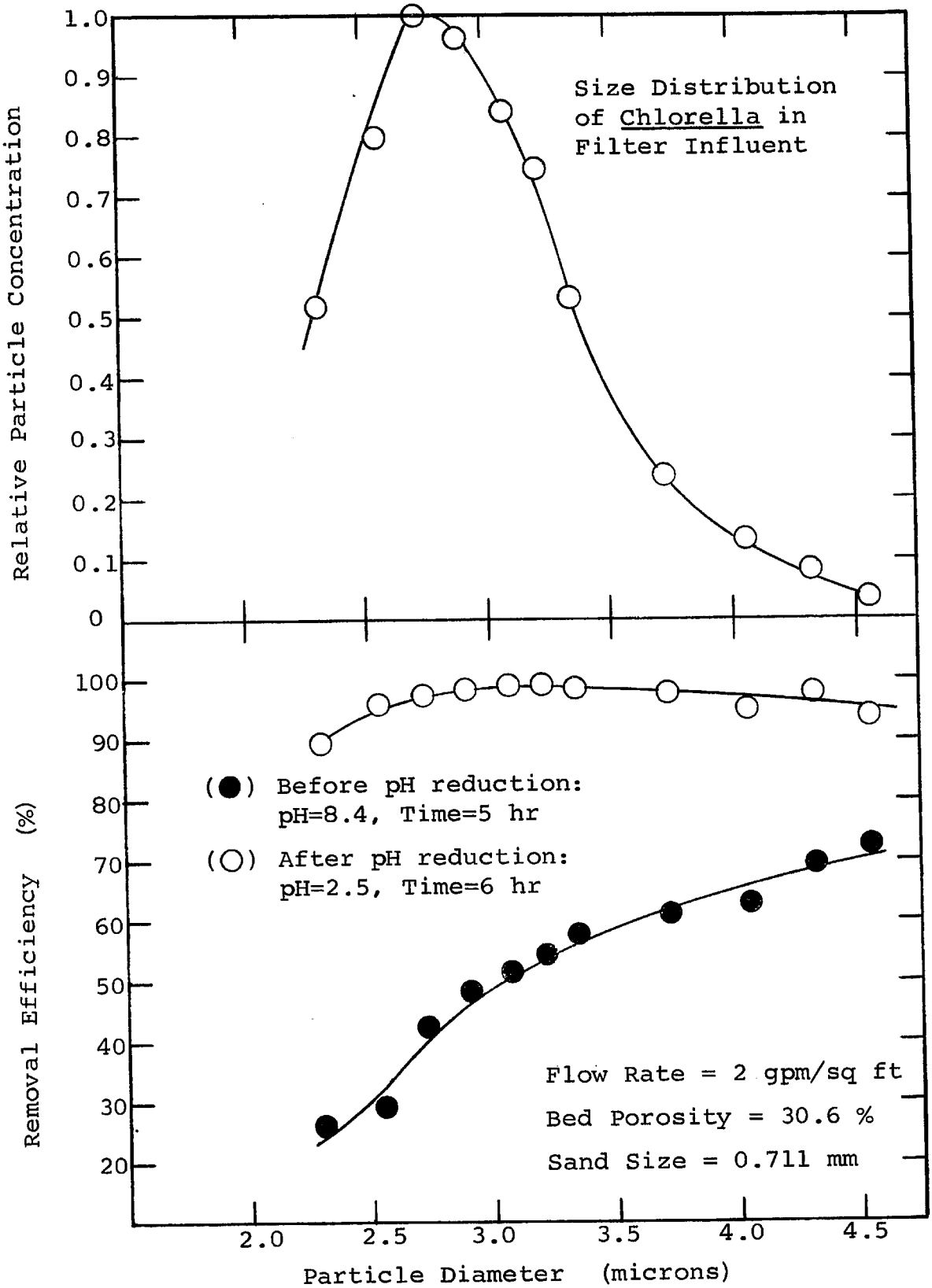


Figure 5-8. Filter Removal Efficiency as a Function of the Size of Organisms in the Filter Influent Before and After a pH Adjustment - (Run F-1)

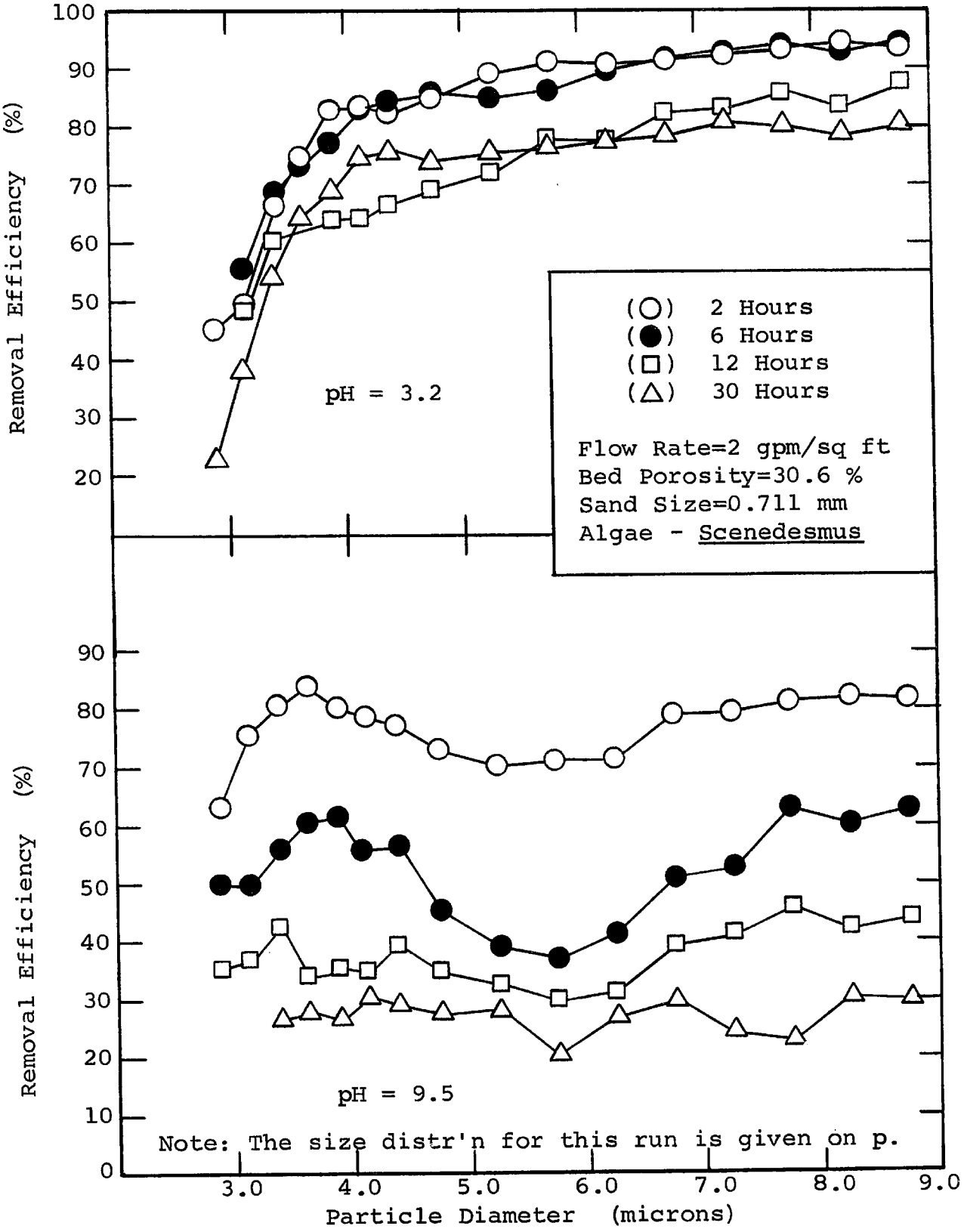


Figure 5-9. Filter Removal Efficiency Versus Particle Diameter for Several Filtration Times and pH Values of 3.2 and 9.5 - (Run D-6)

support this generalization but, unfortunately, it does not seem to be entirely valid for Figure 5-8, in which for pH 9.4 removals continually increased with particle size. These data suggest a straining mechanism, but it should be noted that Chlorella was the organism filtered and the whole size range covered is only about 2 to 4.5 microns.

For low pH values removal efficiency is seen to be high and relatively independent of algal size, except for sizes close to 3 microns where removal efficiencies drop. Since instrument noise prevented counting of particles below 2 microns, and sometimes was a problem in counting particles in the 2-3 micron range, it may account for some of this behavior.

Figure 5-9 illustrates how the removal efficiency v. particle size curve changes with time for both low and high pH. It can be observed that the curves are displaced with time to lower efficiencies in nearly parallel fashion, indicating that all particle sizes were affected uniformly by the passage of time during the filtration run. Thus, as the upper pores in the sand bed become partially filled, preferential removal of larger particles, indicative of a straining mechanism, still does not occur.

The results of the preceding research indicate that filtration is much more significantly affected by the pH of

the system than by the suspended particle size, within the ranges of these variables investigated. Interstitial straining has been all but ruled out as a removal mechanism for the algae which were used. However, two additional figures which deal with the question of interstitial straining are presented and discussed below.

Figure 5-10 gives the influent and effluent size distributions for run F-1, the same run as is depicted in Figure 5-8. It can be seen that the distributions are nearly identical. Similarly, Figure 5-11 presents the results of size distributions conducted on an algal suspension washed from the top one-half inch of a sand bed at the end of the run, and on the influent suspension to this filter. Again, the distributions are almost exactly the same. In these size determinations care was taken to avoid agitating the samples so that any agglomerations, if they existed, would not be broken-up. It is felt that Figures 5-10 and 5-11 provide confirmatory evidence that interstitial straining is not a mechanism of removal for particles of the size that were used in this research.

Effects of Ionic Strength

According to the double layer model, discussed in Chapter 3, an increase in the ionic strength of a solution should produce a reduction or elimination of repulsive energy barriers between similarly charged particles in the solution.

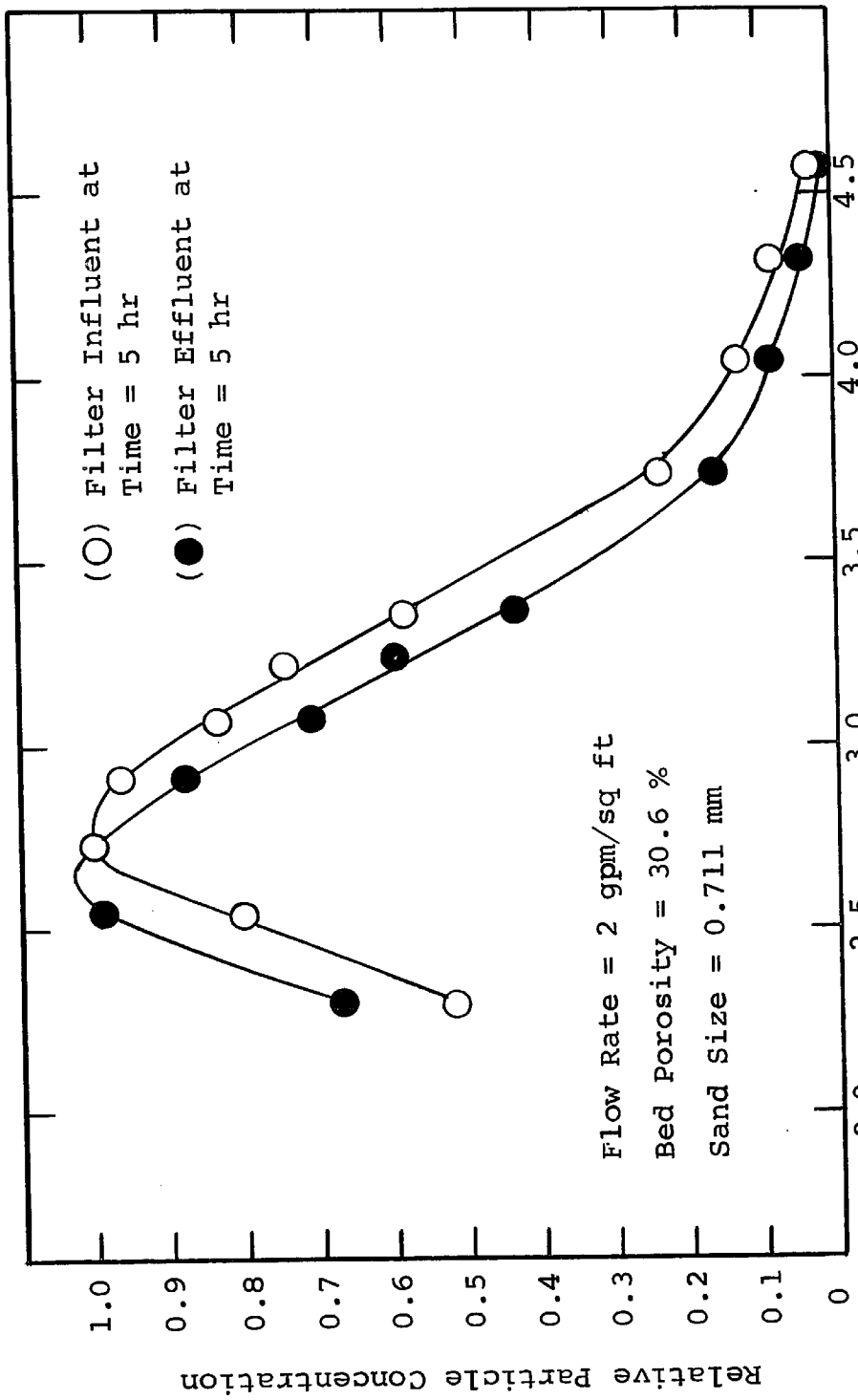


Figure 5-10. Size Distributions of Chlorella in a Suspension of pH=9.4 Before and After Filtration - (Run F-1)

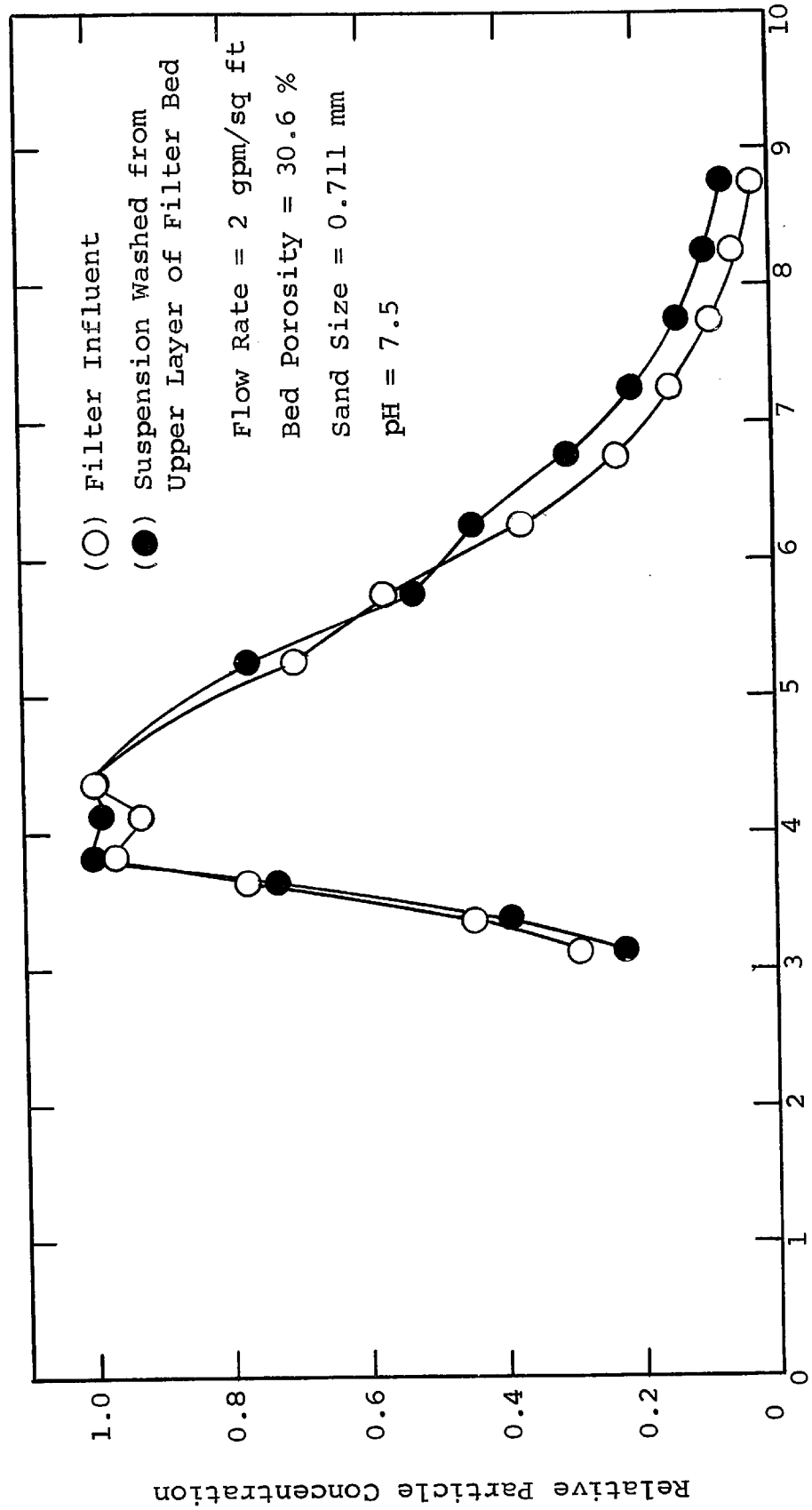


Figure 5-11. Comparison of the Size Distributions of Algal Cells Retained in the Upper Layer of a Filter Bed and Cells in the Filter Influent

The mechanism of this action, where neutral salts are concerned, is compression of the diffuse layer surrounding each particle. This theory predicts, then, that sand filtration of algae should improve with increasing ionic strength.

Investigations were made of the effects of ionic strength on the filtration of Scenedesmus suspensions. Ionic strength was varied from ca. 2.5×10^{-3} (tap water) to 1×10^{-1} using $NaClO_4$. Data presented in Figure 5-12 show that variation in ionic strength over this range did not affect removal of algae at pH 7.4.

The apparent failure of the double layer model in this study was thought at first to repudiate its applicability for filtration of algal suspensions. However, a subsequent measurement of the electrophoretic mobility of algal cells suspended in a solution of pH 7.4 and ionic strength 1×10^{-1} revealed that the algae were still negatively charged. Furthermore, an ionic strength of 1×10^{-1} is not too different in magnitude from those ionic strengths prevailing in earlier filtration investigations involving low pH. If the hydrogen ion is a potential-determining ion for algae, the addition in near eqi-molar concentrations of an indifferent electrolyte such as sodium perchlorate would not be expected to produce significant changes in the filtration process. It is concluded that much higher concentrations

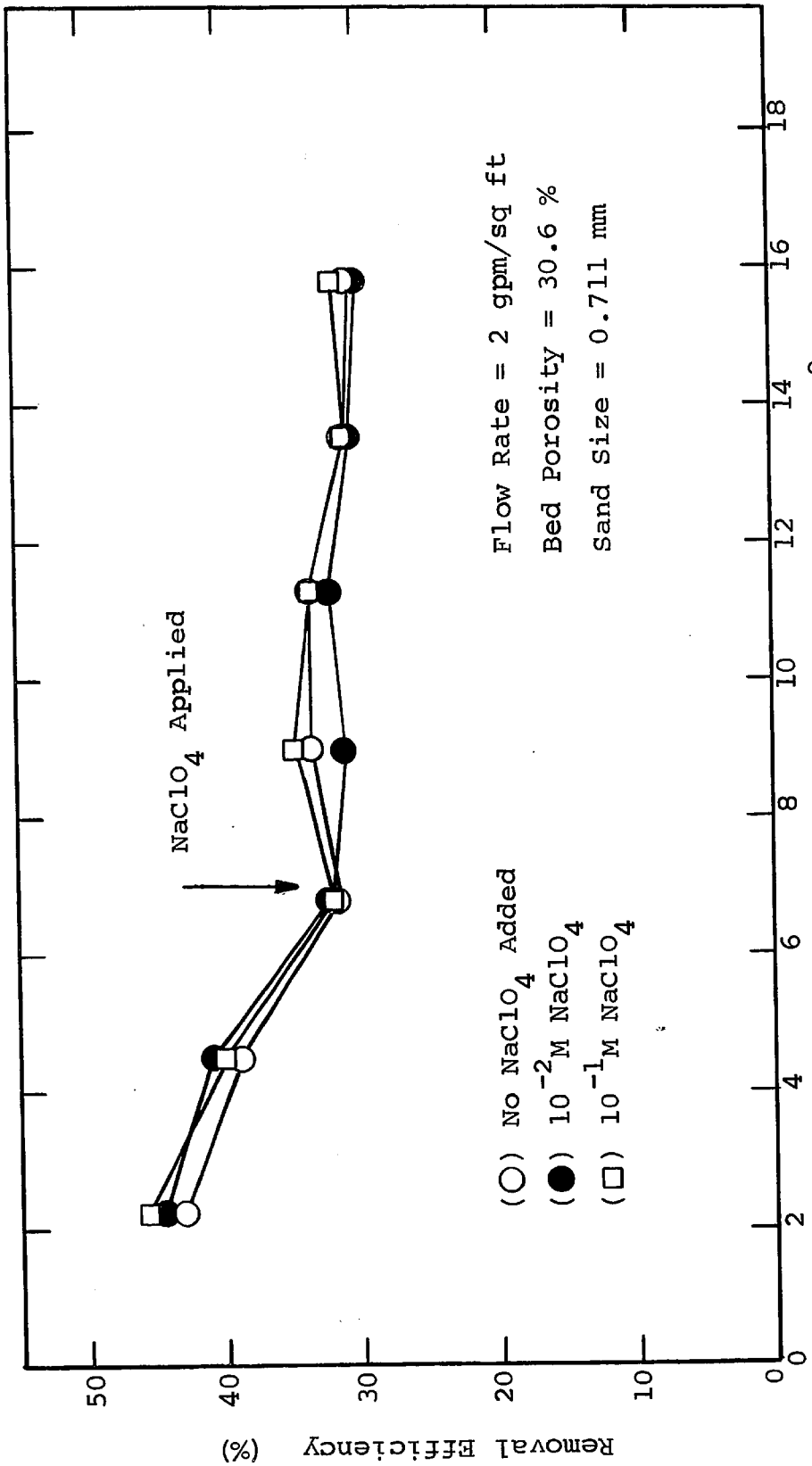


Figure 5-12. The Effect of Ionic Strength on the Filtration of a Suspension of Scenedesmus at pH=7.4
(Applied Organism Concentration=72,300 cells/ml; Run G-3)

of salt are necessary to induce a significant filtration effect; these were not tried because of their probable adverse effect on the algal cell.

Effects of Sand Coatings

In order to provide further evidence on the importance of electrokinetic effects in the filtration of algae, runs were made employing sands coated with iron(III) or thorium(IV). Previous works which have investigated the adsorption of these ions on sand surfaces have found that they are capable of reversing the charge on sand particles.

Mackenzie (85) measured the adsorption of ferric iron on quartz over a range of pH and Fe(III) concentrations by means of electrophoresis. The test results show positive values of zeta potential at pH values above 2 and a maximum positive quartz charge in the pH range 4-6. It was concluded that complex ferric ions containing hydroxide groups are more strongly adsorbed to the quartz surface than the simple Fe^{3+}. The adsorption mechanism was postulated to be related to hydrogen bonding between the OH groups at the quartz surface and the OH groups of the complex ferric ion.

Dulin and Elton (31) and Wood and Robinson (125) have observed the zeta potential of silica in contact with solutions of various cations, including thorium. These workers found that thorium ions produced positive potentials at all

concentrations greater than about 10^{-6} M. The pH of the solutions was not given.

In this research sand beds were coated with either thorium or iron solutions of concentration 10^{-2} M and pH 3.7, in accordance with the method described in Chapter 4. Control filters of uncoated sand were operated in parallel in each run. The results of three filter runs, conducted at different algal concentrations and pH are displayed in Figures 5-13 to 5-15.

The data presented in Figures 5-13 and 5-14 show that for high pH values, coatings of Fe(III) and Th(IV) are not effective as a means of increasing removals of algae for either low or high organism concentrations. This result is interpreted as an indication of the ineffectiveness of the filter coatings in changing the zeta potential of the sand to positive values at the high values of pH used. It is known, for example, that the zero points of charge for the hydrous oxides of iron and thorium occur at a neutral or slightly alkaline pH. This interpretation is supported by the observations given in Figure 5-15 for pH 5.3. At this lower pH both iron and thorium successfully promoted increased removals of algae, with thorium being slightly more effective than iron. A check of the electrophoretic mobility of sand particles coated with iron and thorium showed that these

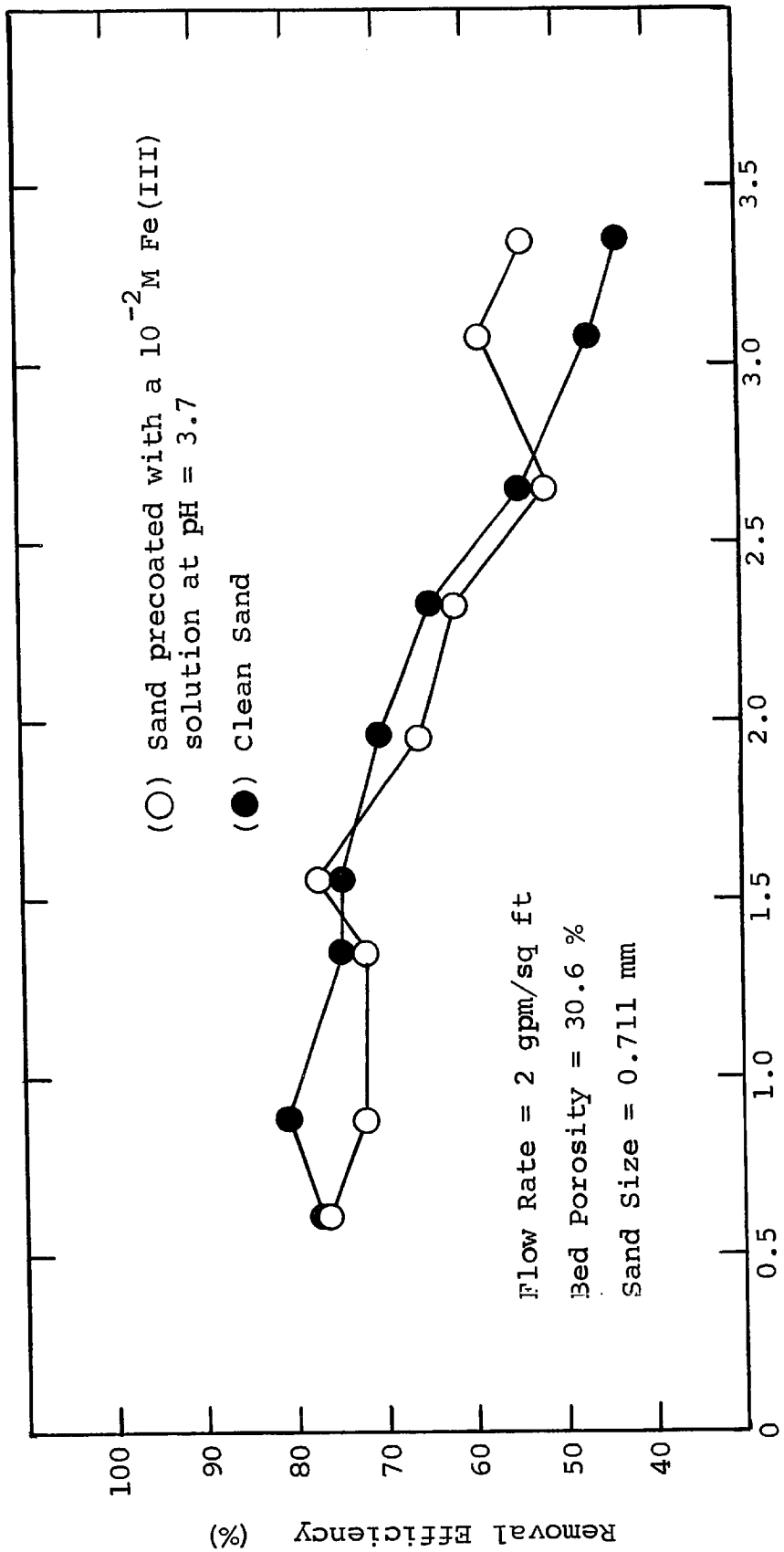


Figure 5-13. Filtration of a Suspension of Chlorella Through Iron(III)-Coated Sand and Clean Sand at pH=8.3 (Applied Organism Concentration=6130 cells/ml; Run E-1)

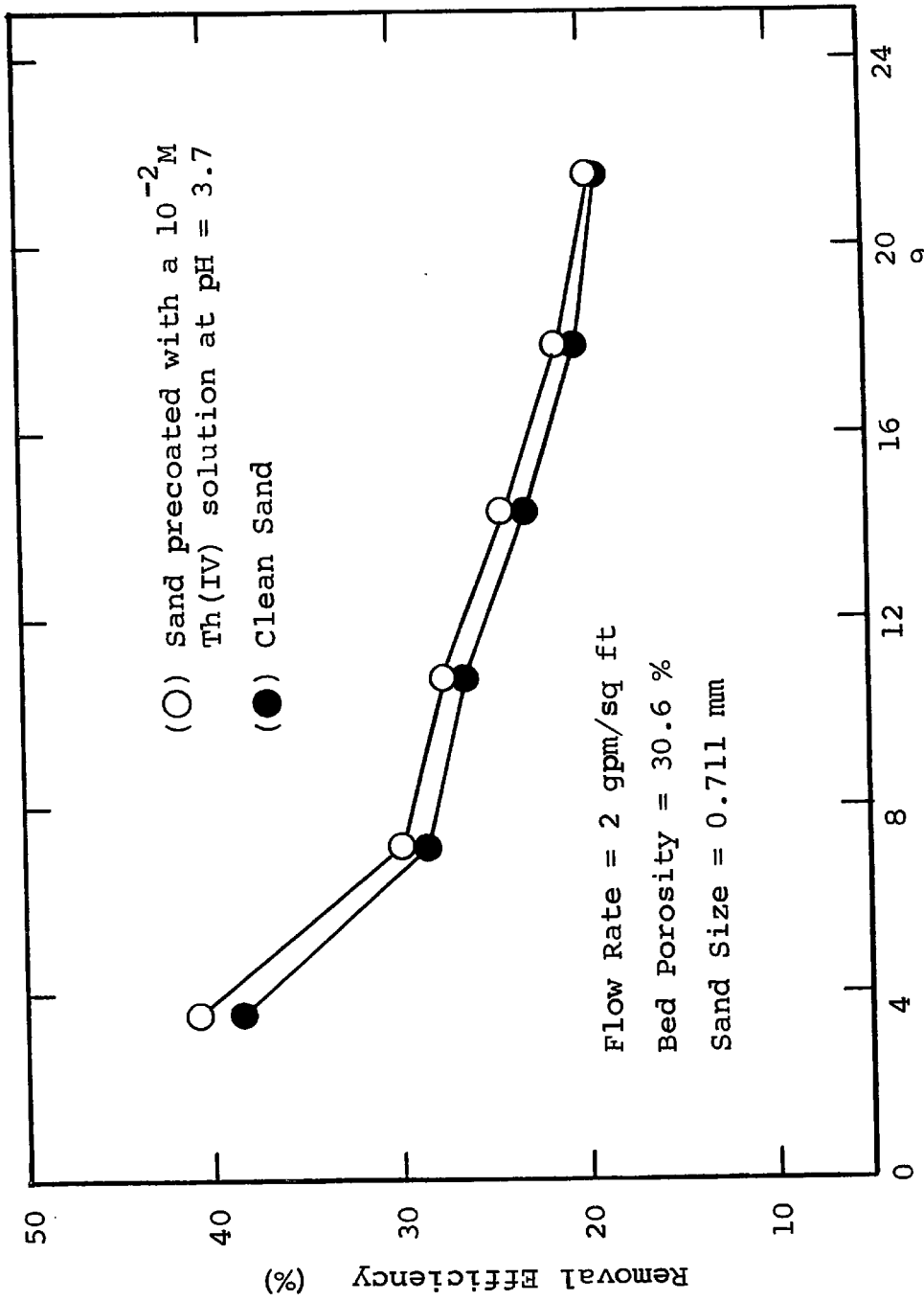


Figure 5-14. Filtration of a Suspension of Scenedesmus Through Thorium(IV)-Coated Sand and Clean Sand at pH=9.7 (Applied Organism Concentration=114,000 cells/ml; Run F-2)

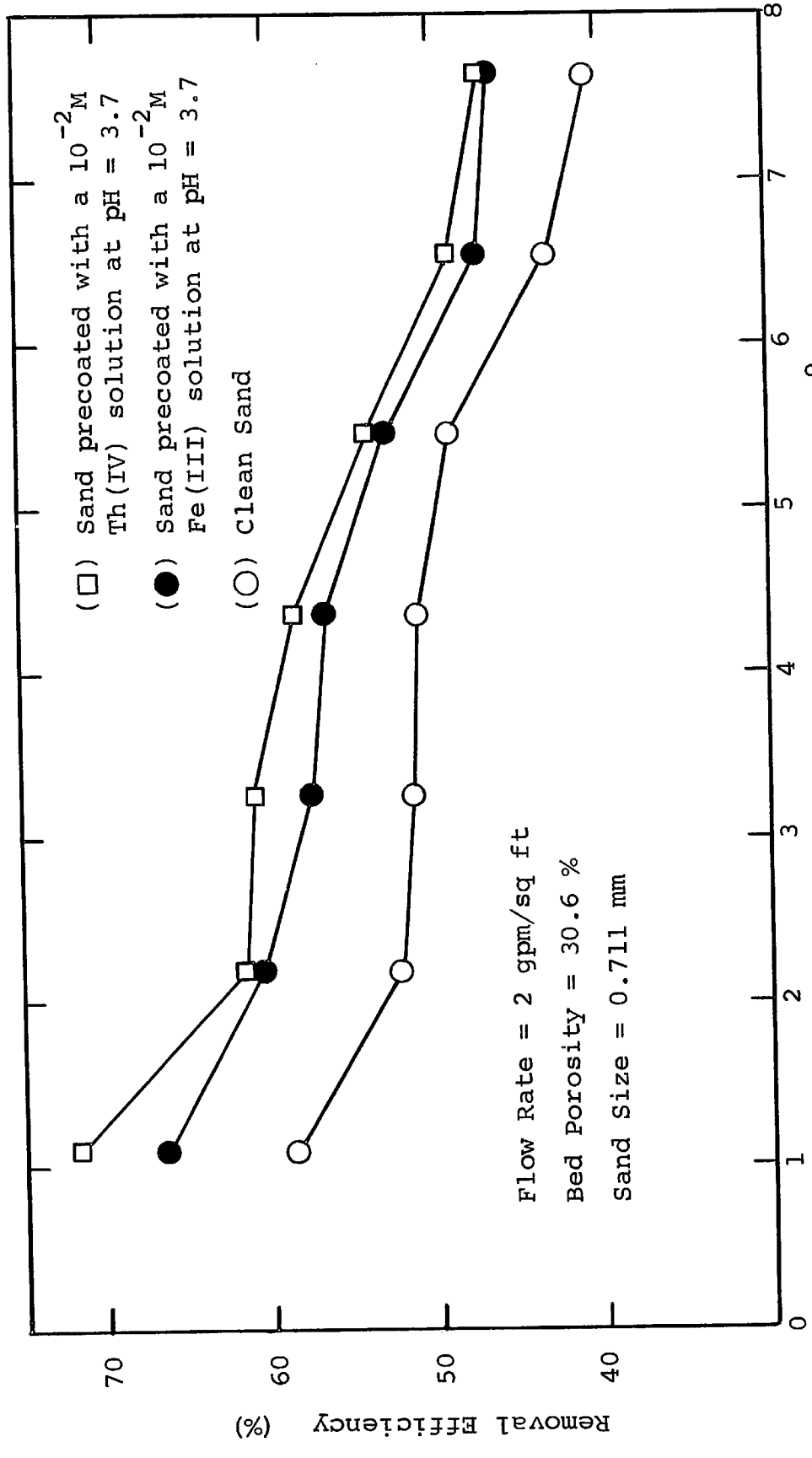


Figure 5-15. Filtration of a Suspension of Scenedesmus Through Iron(III)-Coated Sand, Thorium(IV)-Coated Sand and Clean Sand at pH=5.3 (Applied Organism Concentration=34,900 cells/ml; Run F-3)

complex metal-ion coatings raised the isoelectric point of the sand to the range 4.5 to 5.5, which would account for the observed filter performance. The mobility measurements were carried out on fines which had been washed from the sand as it was received from the manufacturer. The fines were coated with either iron or thorium in solutions of 10^{-2} M and pH 3.7, removed from the solution by millipore filtration, washed with tap water and then re-suspended in tap water for measurement. The pH was adjusted with dilute HCl, as in the filtration experiments.

Effects of Sand Bed Porosity

Although the effects of bed porosity on the filtration process have received a great deal of attention, most of the previous works have dealt with flocculent materials. In general, shorter filter runs and decreased floc penetration have been observed to be characteristic of lower porosities, these effects being attributed to a smaller floc storage capacity and more favorable sieving action at pore constrictions in beds of low porosity (43,45,59). This research has shown, however, that storage capacity and interstitial straining are of negligible import in the filtration of algal suspensions. Consequently a filtration run was undertaken to determine whether bed porosity has, in fact, any effect on the removal efficiency of algal cells.

Four filters were employed, each having a different bed porosity. The lowest porosity used, 30.6 percent, was obtained by the dry sand packing method described previously. The remaining beds were packed by backwashing different (but known) amounts of sand in the filter and then compacting the beds to the same overall depth. Straining was assumed to be a negligible removal mechanism in all of the filters in this study. This assumption was supported by the fact that straining would necessarily have to be most prevalent in the bed having the lowest porosity, and this porosity happened to be the one used in previous experiments to eliminate this mechanism.

Figure 5-16 depicts the results of the filter run. There was little difference in removal efficiency among the two intermediate levels of porosity employed, but otherwise a clear differentiation can be observed. Between the extreme values, particularly, a spread in removal efficiency averaging 10 to 14 percent was obtained. Perhaps not coincidentally, a filter bed having a porosity of 30.6 percent contains approximately 14 percent more surface area per unit depth than a bed with 39.4 percent voids, assuming spherical media of the size used. Thus, these results do not seem inconsistent with an algal removal mechanism based upon a surface reaction between the organism and the sand grain.

Filtration of Flocculated Algae

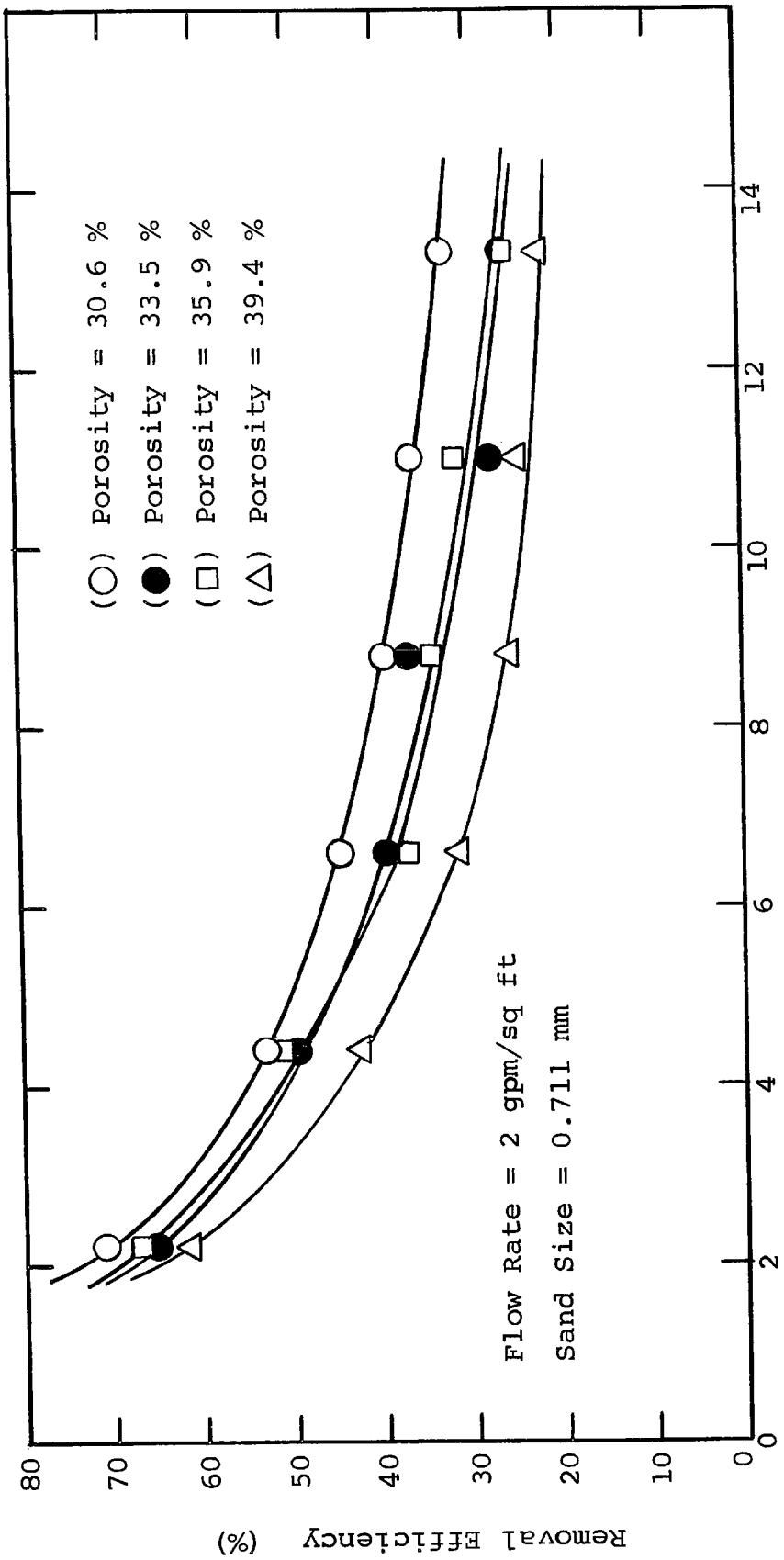


Figure 5-16. The Effect of Sand Bed Porosity on the Filtration of a Suspension of Scenedesmus at pH=7.6 (Applied Organism Concentration=35,550 cells/ml; Run G-1)

High removal effeciencies of algae have been obtained in this research at low pH but it appears that for neutral or alkaline waters the addition of a chemical coagulant or coagulant aid to the filter influent offers the most feasible means of improving removal efficiencies. It has already been mentioned that Davis (29) has conducted investigations of the filtration of algal suspensions flocculated with ferric chloride. Unfortunately, his results show that, while coagulant addition improves the filtration of algae, removal efficiencies of less than 70 percent were generally obtained with figures below 30 percent being not uncommon. However, some of Davis' observations, to be discussed further in the next section, suggest that much better removals could have been realized had greater coagulant doses been used. He limited ferric chloride additions to less than about 2.5 mg/l Fe^{3+} as it was found that a proportional increase in organisms removed did not accompany an increase in the amount of coagulant applied and because larger doses caused short filter runs. In order to complement and extend Davis' work by providing data for higher coagulant doses, a filter run was undertaken employing the optimum Fe(III) dose for the algal suspension to be filtered. Previous results of this research predict that this concentration should produce high removal efficiencies.

A jar test was run to determine the optimum coagulant

dose for a Scenedesmus suspension at pH 7.0. The outcome, illustrated in Figure 5-17, shows that a concentration of Fe(III) in the range of 10 to 12 mg/l produced optimum flocculation. A filter run was then conducted in which the optimum coagulant dose was fed to a suspension of Scenedesmus of similar concentration and pH used in the jar study. In all, three filters were used. One acted as a control and received no added coagulant; the other two received optimal iron(III) doses at the filter tops, one also receiving additional agitation to promote flocculation.

The results of the filter run are presented in Figure 5-18. Where coagulant was added, similar removal efficiencies in excess of 90 per cent were achieved. However, the rate of head loss increase in the filter receiving the mixed suspension was substantially higher, resulting in a significantly shorter run. This observation is similar to an earlier one involving the filtration of ferric flocs alone. The quite uniform percentage removal of algae with time established in this run does not agree with the pattern of organism removal reported by Davis (29). He found that the per cent removal started at a very low value, increased rapidly during the first part of filtration, and then increased more slowly with time until a constant removal was established.

These data indicate that high removals of algae can be

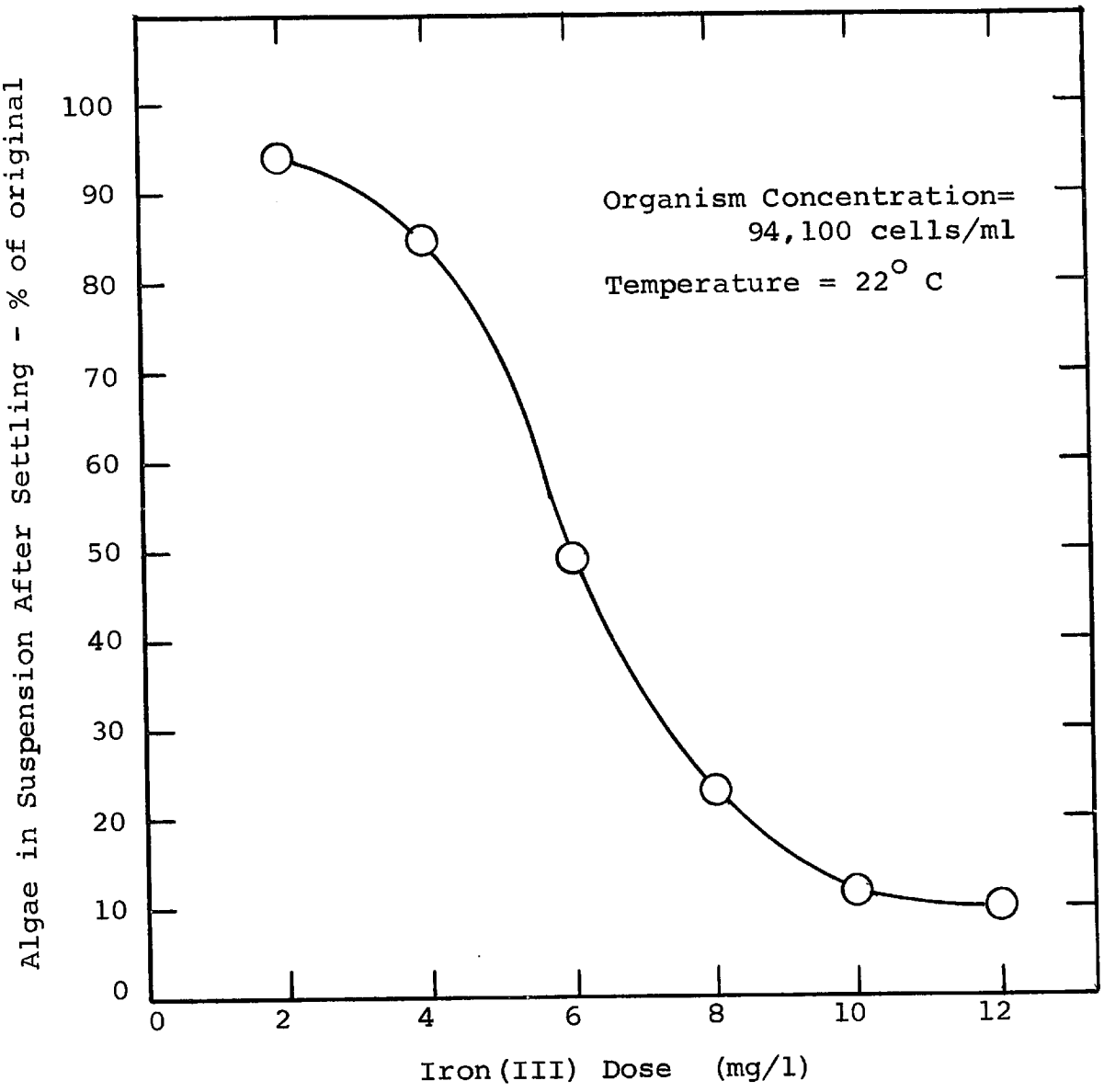


Figure 5-17. Flocculation Curve Developed From Jar Tests for a Suspension of Scenedesmus at pH=7.0

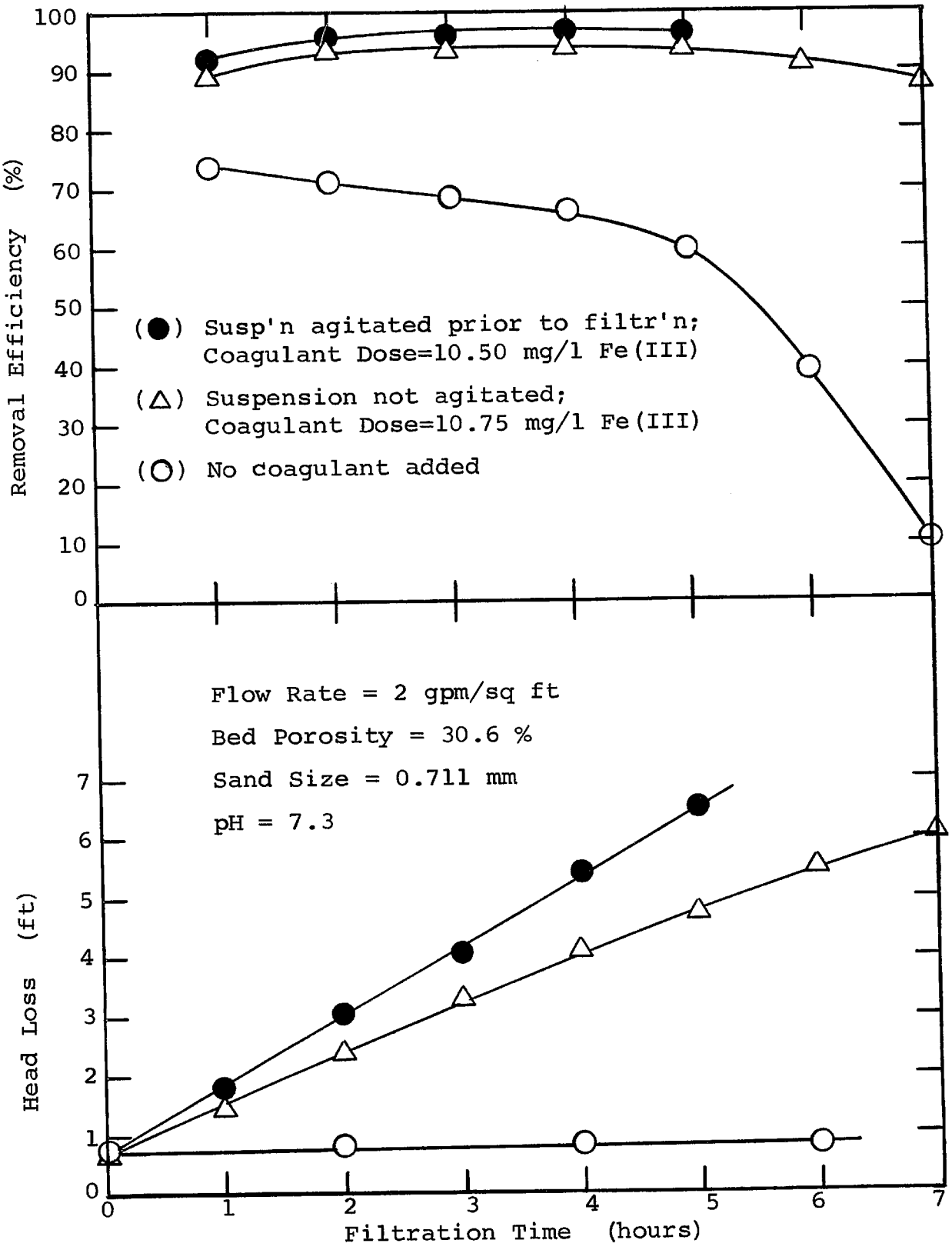


Figure 5-18. Organism Removal Efficiencies and Head Losses Developed During the Filtration of Suspensions of Scenedesmus in Different States of Flocculation (Applied Organism Concentration=70,200 cells/ml; Run G-5)

obtained in rapid sand filtration using coagulants, but at the expense of large chemical usage and concommitant short filter runs. Since the optimum coagulant dosage is undoubtedly dependent upon the concentration of organisms in the filter influent, better pretreatment would be an effective way of reducing coagulant addition at the filter while maintaining high removal efficiencies. Polyelectrolytes added to the filter influent might also provide a suitable alternative as a means of increasing removals of algae in the higher pH range without the disadvantage of short filter runs.

General Discussion

The results of this research demonstrate that the attachment mechanism for algae in sand filtration involves surface phenomena and can be chemically controlled. Precise size measurements on influent and effluent algal suspensions, as well as on cells extracted from the filter itself, have virtually eliminated interstitial straining as an important removal mechanism for the algae which were used.

Solution pH was determined to be a particularly effective parameter for controlling the removal process. Where the pH was lowered, rendering interaction energies between the diffuse layers of the sand and algal particles more favorable for adsorption of the two particles, removals significantly increased. Similarly, reducing the repulsive

energy between algae and sand by coating the latter particles with positively charged materials also increased removal efficiencies. Admittedly, these methods may not be directly applicable to practical situations, but they point out that modification of sand and particle surface properties is an effective means of increasing removal efficiencies with minimal head loss.

Flocculation measurements of algal suspensions, performed at widely varying values of pH, have helped establish that removal of an individual organism is accomplished by an interaction between it and the surface of the filter media. This is in direct contrast to the relationship between flocculation and filtration which was observed for ferric-flocs, showing that the removal of these particles involves interparticle sorptive forces.

Despite the electrostatic repulsion which exists between sand and algae at high pH, some removal of organisms was always obtained in runs conducted in the alkaline range. This removal has not been explained and represents a field for future study. One explanation which may be worthy of investigation is ion-exchange; several workers (32,48,93) have recently found that algal cells behave much like ion exchange resins (see page 53). This mechanism might be capable of explaining the rapid decrease in the affinity of

a sand bed for algae during the initial part of a run, observed recently by Davis and Borchardt (30), in terms of the exchange capacity of the bed.

In the light of the findings of this research some further comments can be made on certain of the observations reported by Davis (29) in his algal-ferric-floc filtration studies, specifically the following:

(1) For a given dosage of coagulant there was an increase in per cent removal of organisms associated with a decrease in concentration of algae in the influent.

(2) Regardless of the concentration of algae in the influent, percentage removals of organisms increased for an increase in coagulant application.

Both of these observations are similar in that they point to the fact that all of the algal suspensions filtered by Davis received coagulant doses less than the optimum value. It has been shown in this research that an algal suspension of given concentration exerts a definite coagulant demand for best flocculation, and that satisfaction of this demand also results in efficient filtration of the suspension. Applying this result to Davis' observations, it can be suggested that if chemical is added in concentrations less than the optimum value, then a given dose will be more effective the lower the influent algal concentration. Similarly, for

a given concentration of algae, increasing coagulant doses would produce progressively higher removal efficiencies until the optimum dose was reached.

In order to provide efficient control over the rapid sand filtration of suspensions of algae and other particles it is essential that the mechanisms by which these particles are removed from suspension be known and understood. This work provides experimental evidence that the filtration of algae, and probably other discrete particulate matter in the micron-range, can be controlled by the hydrogen ion concentration of the liquid media and also by the chemical characteristics of the filter media surface. Algae have also been shown to be removed more efficiently through modification of the pH of the water than by high doses of chemical coagulant, and with negligible head loss build-up.

CHAPTER 6

SUMMARY

The process of water filtration has been, and continues to be, one of the most widely used unit operations in the field of sanitary engineering. It is also among the most extensively investigated processes. Still, a fundamental understanding of the mechanisms of particle removal in a sand filter has been lacking. Improvements in operation have been made, to be sure, but for the most part these have resulted only from trial and error procedures. In view of the present disproportionately- high cost of rapid sand filters in comparison to other treatment units, it is becoming increasingly imperative that filters be designed rationally and operated under optimum conditions. To accomplish these objectives the basic mechanisms of particle removal must be known and understood.

Investigators of filtration have now established what the possible removal mechanisms are, and have categorized them into two groups: (1) particle transport mechanisms and (2) particle attachment mechanisms. In addition, many of the operational variables which control these mechanisms.

have been delineated. Unfortunately, however, there appear to be interrelationships between the various filtration mechanisms which are complicated by the numerous operational parameters. As a result, many former investigators have failed to isolate pertinent variables and have reached erroneous conclusions. On the other hand, some workers have undertaken studies of mechanisms under such idealized conditions that the general applicability of their results may be questioned. The objective of the current investigations, therefore, has been to study particle removal mechanisms under both controlled and realistic conditions. The studies have been restricted to particle attachment mechanisms.

This research has involved the filtration of both flocculent and non-flocculent (discrete) particles. Previous investigations have indicated that these two groups of materials exhibit markedly different filtration behavior. The difference has generally been attributed to electrokinetic effects since discrete particles usually carry a negative surface charge and flocculent particles a positive one. This explanation breaks down, however, when negatively charged flocculent particles are observed to filter well, as has indeed been the case. Under this condition, the filterability of flocculent dispersions is more easily explained in terms

of the flocculability of the dispersions. It was thought best, therefore, to study the filtration of flocculent and non-flocculent particles individually.

The Filtration of Iron(III) Dispersions

All of the runs involving the filtration of flocculent particles employed ferric chloride as the chemical coagulant and Ann Arbor tap water as the aqueous media. A hydraulic loading of 2 gpm/sq ft and a sand of 30/40 sieve fraction was utilized. Head loss readings and visual penetration data were the parameters used to evaluate filter performance.

Initially, experiments were performed using three different bed porosities (40.0, 37.0 and 33.7 per cent) and influent iron(III) concentrations ranging from about 1 to 4.5 mg/l to test for the effects of porosity and for reproducibility of runs. The linear head loss v. iron applied curves obtained were found to be more reproducible at the higher influent iron(III) concentrations, and approximately equally reproducible for all three methods of sand bed preparation, although beds of 40 per cent porosity were observed to be less stable than those of lower porosities. In addition, it was found that both the rate of increase of head loss in sand beds and the penetration per unit of applied iron appear to increase as the initial porosity of the bed is decreased.

A filter run conducted to determine the effects of floc size showed that the filters which received floc particles in the 10 to 50 micron size range clogged faster and exhibited less bed penetration than those which received floc particles in the sub-micron range. Floc size was varied through the physical agitation of the influent dispersion prior to filtration.

Aging of stock iron(III) dispersions for 4 hours prior to introducing them into the filter influents resulted in completely different filtration effects than those produced by fresh dispersions applied under similar conditions. Aging greatly retarded the good filtration observed for fresh dispersions at pH values of 7.2 and 9.5, but slightly improved the poor filtration observed at pH 5, presumably because of the slower hydrolysis reactions at low pH. The sizes of floc particles in both fresh and aged dispersions were comparable at pH values of 7.2 and 9.5, but were each much smaller at pH 5. These results generally do not agree with those reported by O'Melia and Stumm (98). The differences have been discussed in terms of the experimental equipment and procedures used by the previous workers.

Jar tests were conducted on various dispersions to determine if the flocculation characteristics of these dispersions could be correlated with their filtration properties. The

data of O'Melia and Crapps (97) was utilized in these experiments. For negatively charged floc particles, it was found that jar test results could be roughly correlated with filtration behavior. Positively charged floc particles, on the other hand, exhibited no such correlation as they displayed negligible flocculation yet filtered well. These results were interpreted as lending support to the importance of floc-to-floc interactions within the filter for negatively charged particles and a floc-sand electrostatic reaction for positively charged floc particles.

Further evidence that inter-particle surface reactions control the removal process for flocculable dispersions was obtained by conducting a filter run using sand of modified surface characteristics. A sand bed precoated with a 10^{-2} M iron(III) dispersion at pH 3.7 produced filtration effects nearly identical to an uncoated bed operated in parallel. The pH of the influent suspensions was 7.1.

In extending a portion of the filtration experiments of O'Melia and Crapps to a system using tap water (the previous workers employed deionized water) it was found that much more phosphate ion had to be added to a filter influent to produce a significant filtration effect. Moreover, the effect produced could be explained by the influence of phosphate on the flocculation of the iron(III) dispersion used;

the aforementioned investigators, in contrast, interpreted their results as being due to changes in floc mobility caused by phosphate ion. It was concluded that the use of deionized water in laboratory filtration experiments may yield results which are not indicative of many practical situations.

The Filtration of Algal Suspensions

Stock cultures of Chlorella and Scenedesmus added to tap water prior to filter runs provided the suspensions used in these studies. The organisms were counted and sized with a Model B Coulter counter. Sands of 20/30 sieve fraction packed to a porosity of 30.6 per cent by a special method were employed. As in previous runs, necessary chemicals were added at the top of the filter columns and a hydraulic loading of 2 gpm/sq ft was utilized.

Preliminary studies of the flocculation characteristics of algae showed that the organisms studied were completely resistant to agglomeration over the pH range 2 to 10. Concurrent cell-size experiments also indicated that this parameter was not affected over the same pH range. At approximately pH 10.5, however, the cells appeared to undergo plasmoptysis or a related phenomenon resulting in the production of large floc-like particles.

By means of microelectrophoresis it was found that both algae and sand possess a negative surface charge over most of the normal pH range when suspended in Ann Arbor tap water. However, the mobility of each type of particle decreased in magnitude with decreasing pH. No isoelectric point was observed for algae, although extrapolation of the data indicated that one would occur near pH 1. The isoelectric point for sand was found to be pH 2.0.

Removal percentages of algae during filtration were observed to be directly dependent upon the solution pH. Efficiencies greater than 90 per cent, quite uniform with time, were achieved in runs operated near the isoelectric points of the sand and algae, while progressively lower efficiencies resulted as the pH was increased. Runs at higher pH values were also characterized by removal efficiencies which were not uniform with time; removals usually began at a high level, decreased rapidly with time during the initial part of a run, and then approached a constant value. This removal pattern was the same as that observed previously by Davis (29). The poor filtration at high pH was attributed to coulombic repulsion forces between the algae and sand. The good removal efficiencies near the isoelectric points was ascribed to one or more of the following: van der Waals forces, specific chemical effects, and electro-

static attraction.

For Scenedesmus suspensions having particles in the size range 2 to 11 microns, removal efficiencies were relatively independent of particle size in runs operated at low pH. At higher pH values, removal efficiencies were dependent upon the particle size, but the dependency appeared to be due to the relative number of particles at a given size rather than to the size itself. These observations suggested that straining was not an important removal mechanism in the experiments. Size distributions performed on influent and effluent samples, and on a suspension washed from the top of a filter bed further indicated that neither direct nor interstitial straining was a mechanism of removal for the algae which were used.

A variation in ionic strength between the approximate values of 2.5×10^{-3} and 1×10^{-1} at pH 7.4 did not affect the filtration of a suspension of Scenedesmus, an apparent contradiction to the double layer repulsion theory postulated to be operating at higher pH values. However, a similar range in ionic strength also did not affect markedly the mobility of Scenedesmus cells. It was concluded that even higher concentrations of salt would be necessary to produce a significant filtration effect.

The effects of sand coatings have been studied using

thorium(IV) and iron(III). Beds precoated with 10^{-2} M solutions of these ions at pH 3.7 did not affect the filtration of algal suspensions in runs operated in the alkaline pH range, but significantly increased removal efficiencies in a run at pH 5.3. These results were in agreement with mobility studies of sand particles which showed that coatings of iron and thorium can render sand surfaces positively charged in suspensions having pH values up to 5.5.

Experiments conducted to determine the effects of sand bed porosity indicated that removal efficiencies increased with decreasing porosity. The increased removals obtained were shown to be remarkably similar to those that would be expected on the basis of the greater surface area per unit depth associated with lower porosities.

One experiment was conducted employing simultaneous filtration of algae and iron coagulant. It was found that the coagulant dose which was optimum for algal flocculation, according to jar tests, also produced high (and uniform) removal efficiencies in the filtration process, when the coagulant was added at the top of the filter column. Also discovered was the fact that the rate of head loss produced was rather markedly dependent upon the agitation afforded the influent suspension prior to filtration.

CHAPTER 7

CONCLUSIONS

Based upon the experimental results obtained in this research, the following conclusions have been reached:

The Filtration of Iron(III) Dispersions

(1) Filter runs employing high influent concentrations of iron floc are more reproducible than those utilizing lower concentrations, within the concentration range 1 to 4.5 mg/l of Fe(III).

(2) Reproducibility of filter runs is not materially affected by the porosity of the sand bed for porosities of 40.0, 37.0 and 33.7 per cent; however, beds of 40.0 percent porosity are not as stable as beds of 37.0 and 33.7 per cent porosity.

(3) Variations in the chemical composition of Ann Arbor tap water over the period of the experiments were not sufficient to affect reproducibility of filter runs.

(4) The rate of increase of head loss in sand beds and the penetration per unit of applied iron both appear to decrease as the initial porosity of the bed is increased.

It is concluded that the floc storage volume within a filter and the velocity of flow in the filter pores are more important than the surface area of the media in the filtration of a flocculable dispersion.

(5) Filters which receive fresh dispersions of floc particles in the 10 to 50 micron size range clog faster and exhibit less bed penetration than those receiving floc particles in the sub-micron range, for the same total iron applied.

(6) Dispersions of iron floc which are aged prior to filtration exhibit different filtration behavior than fresh dispersions; aging slightly improved the poor filtration observed for fresh dispersions at pH 5 and greatly retarded filtration at pH values of 7.2 and 9.5. These results are not in agreement with those of O'Melia and Stumm (98). It is concluded that the disparity is due to differences in the experimental equipment and procedures used in this and the previous research, the present work being more representative of current practice.

(7) Filtration behavior is the same when coagulant is added 8 inches above the sand bed as when it is applied 6 feet above the bed.

(8) Floc particles having a negative electrophoretic mobility, display flocculation properties which can be roughly

correlated with their filtration behavior. For dispersions of such particles, jar tests may serve as a useful procedure for predicting filter performance.

(9) There was no relationship observed between flocculation and filtration for positively charged floc particles. It is postulated that a removal mechanism based upon a sand-floc electrostatic interaction better explains the attachment of this type of particle in a sand filter.

(10) Floc size is markedly affected by the pH and the type and concentration of anions in the dispersion; phosphate ion and low pH are particularly effective in inhibiting floc growth. Filtration workers who purport to demonstrate the importance of chemical factors in the filtration process should therefore be cognizant of the fact that changes in chemical parameters can manifest themselves in physical ways.

(11) Modification of the surface of the grains in a sand bed by coating them with a 10^{-2} M solution of iron(III) at pH 3.7 does not affect the filtration behavior of a fresh floc dispersion at pH 7.1.

(12) Much higher concentrations of phosphate ion are required to produce a significant effect on the flocculation and the filtration of iron(III) dispersions when the aqueous media is deionized water than when it is Ann Arbor tap water.

It is concluded that the use of deionized water in laboratory filtration investigations--a common practice--may produce misleading results.

The Filtration of Algal Suspensions

(1) Suspensions of Chlorella and Scenedesmus do not exhibit any tendency to flocculate over the pH range 2 to 10. At approximately pH 10.5 the cell structure of the suspended organisms is destroyed and large floc-like particles are produced.

(2) The size distribution of cells of Chlorella and Scenedesmus is not affected by a change in pH of the algal suspension from 2 to 10.

(3) Cells of Chlorella suspended in Ann Arbor tap water possess a negative electrophoretic mobility which decreases toward zero with decreasing pH. This pH v. mobility relationship does not disagree with that expected on the basis of the relatively high protein and cellulose content of the algal cell-wall.

(4) Small particles of Ottawa sand suspended in Ann Arbor tap water have a negative electrophoretic mobility which decreases in magnitude with decreasing pH, reaching an isoelectric point at pH 2.0.

(5) Removal percentages of Chlorella and Scenedesmus

during filtration are directly dependent upon the pH of the influent algal suspension; nearly complete removals were achieved in runs operated near the isoelectric points of the sand and algae while progressively decreasing efficiencies were obtained as the pH was increased. The good removals at low pH are attributed to one or more of the following: van der Waals forces, specific chemical effects, and electrostatic attraction. The poor removals at higher pH values is in keeping with the previously demonstrated presence of coulombic repulsion forces between the sand and algae at high pH.

(6) At low pH, filter removal efficiencies of Chlorella and Scenedesmus are quite uniform with time and independent of the influent organism concentration, in agreement with a removal mechanism based upon algae-sand interactions.

(7) At neutral and high values of pH, filter removal efficiencies of Chlorella and Scenedesmus decrease with time, the rate of decrease appearing to depend upon the influent concentration of organisms. These results are the same as those reported by O'Melia (95) and Davis (29).

(8) Straining is not a mechanism of removal for the algae studied in this research based upon precise size measurments of particles in filter influents and effluents and on cells extracted from a filter bed.

(9) Runs at neutral pH employing variations in the ionic strength of the filter influent did not conform to the double layer model postulated to be operating. It is concluded that the ionic strengths utilized were not sufficiently high to compress the double layers of the sand and algae enough to be effective in the filtration process.

(10) Sand beds modified by precoating the grains with 10^{-2} M solutions iron(III) or thorium(IV) at pH 3.7 have no effect on the filtration of suspensions of Chlorella and Scenedesmus in runs operated in the alkaline pH range, but significantly increase removal efficiencies at pH 5.3. It was observed by mobility measurements that such coatings can reverse the surface charge of sand at lower pH values but not at higher ones.

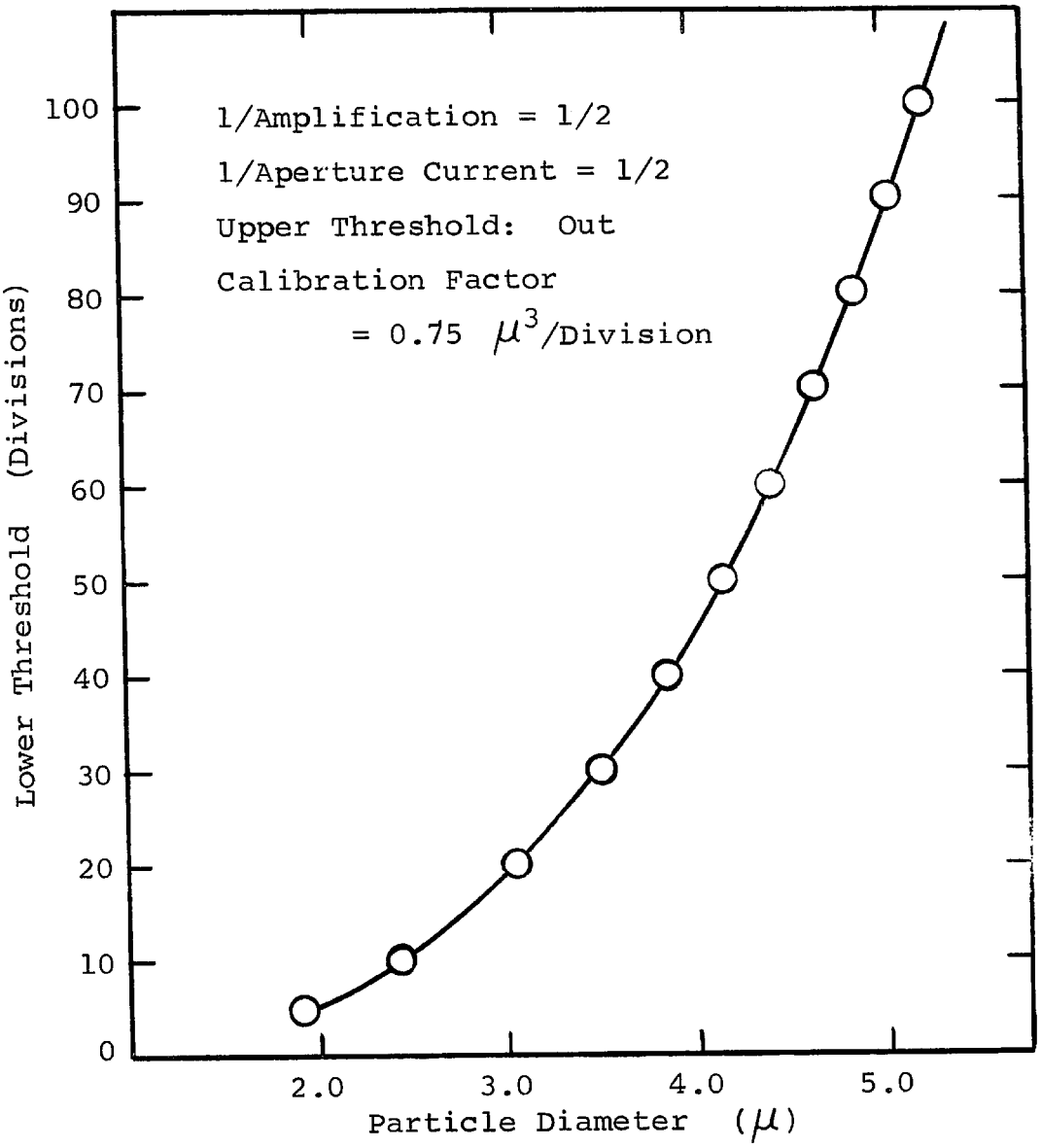
(11) Filter removal efficiencies of Chlorella and Scenedesmus increase with decreasing sand bed porosity; the increase is in keeping with the greater surface area per unit depth accompanying lower bed porosities.

(12) The coagulant dose which is optimum for flocculation of Scenedesmus, according to jar tests, also produces high removal efficiencies of this organism in the filtration process when coagulant is added at the top of the filter column; the rate of head loss increase produced is dependent upon the agitation afforded the influent sus-

pension.

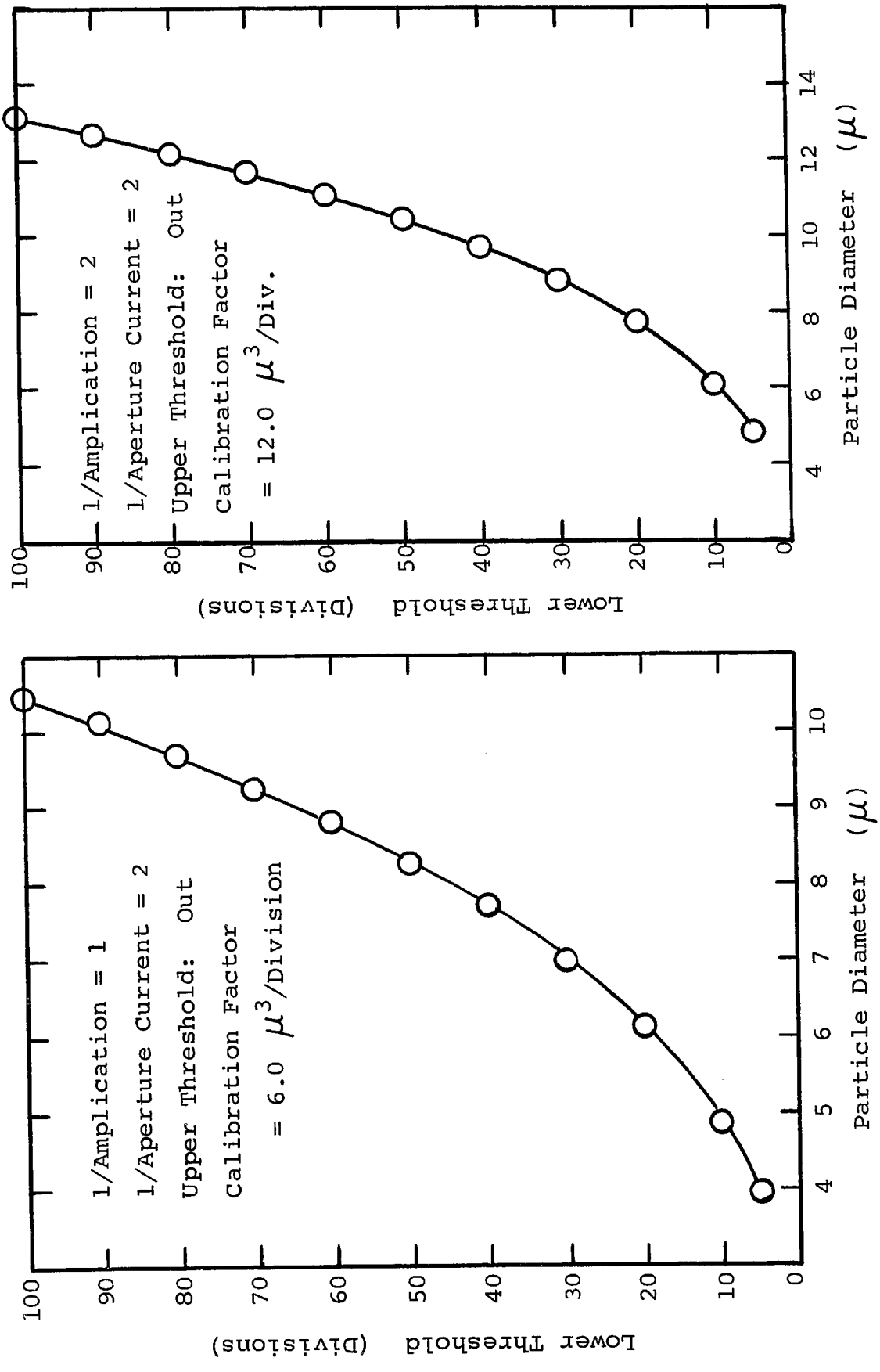
The results of this research have demonstrated, above all, the overriding importance of surface reactions in the sand filtration process. Accordingly, some of the reasons for the differences in filtration behavior of flocculent and non-flocculent particles have been crystallized. For flocculable dispersions particle-particle interactions appear to be dominant, while for discrete suspensions particle-sand interactions seem to prevail. Adjustment of surface properties has led to high removals of otherwise filter-penetrating algae, without the use of a chemical coagulant and therefore without appreciable head loss. It seems a logical next-step to consider the treatment of certain natural waters by filtration without prior flocculation--through suitable modification of particle surface properties with pH, polyelectrolytes, or other means. In this regard more work also needs to be addressed to the effects of influent particle size on the filtration process. It is quite conceivable in the light of this research that small particles, properly modified chemically, could be removed more efficiently than much larger particles.

APPENDIX I



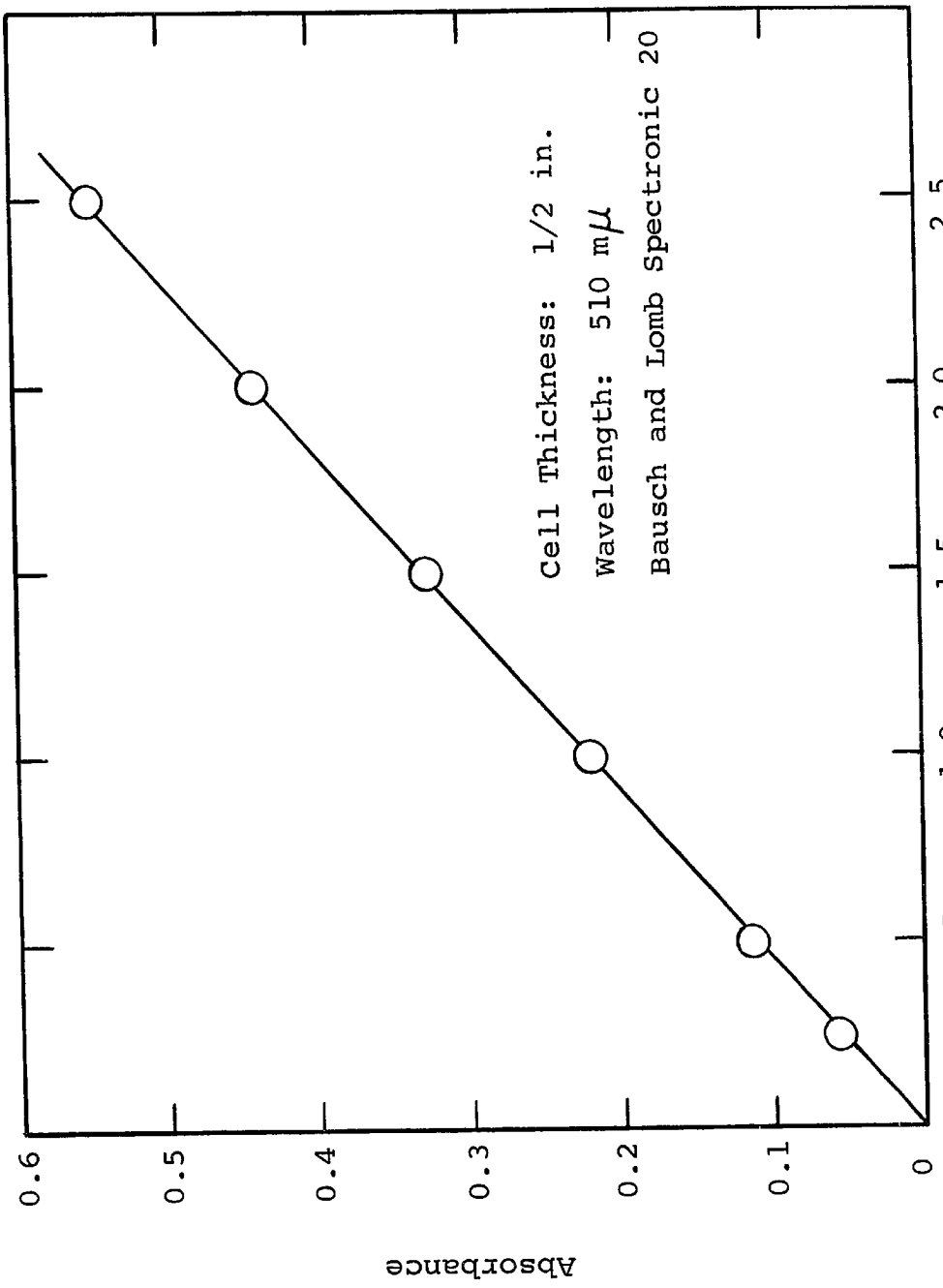
Appendix I. Size Calibration Curve for the Coulter Counter for Gain=4 Based on Pollen Grains and Human Blood Cells

APPENDIX II



Appendix II. Size Calibration Curves for Coulter Counter - Gains 1/2 and 1/4 Based on Pollen Grains and Human Blood Cells

APPENDIX III



Appendix III. Standard Calibration Curve for Iron(III) - Phenanthroline Method (115)

APPENDIX IV

Statistical Test of the Effects of Sand Bed Porosity on the Slopes of Head Loss v. Iron Applied Curves (dH/dC) for Coagulant Doses Ranging from 1 to 4 mg/l Fe(III) *

Null Hypothesis: Porosities of 40.0 and 37.0 per cent do not yield significantly different head loss v. iron applied curves for filter influent coagulant doses ranging from 1 to 4 mg/l Fe(III).

Fe(III) Coagulant Dose	Values of dH/dC**		Difference (x_i)
	Poros.=40.0%	Poros.=37.0%	
1	0.086	0.113	+0.027
2	0.079	0.104	+0.025
3	0.071	0.092	+0.021
4	0.064	0.080	+0.016

** Values obtained from Figure 4-1 using the lines fitted by least squares

$$\bar{x} = 1/4 \sum x_i = 1/4\,(0.089) = 0.02225$$

$$(4 - 1)\,s^2 = \sum (\bar{x} - x_i)^2 = (-0.00475)^2 + (-0.00275)^2 + (-0.00125)^2 + (-0.00625)^2$$

$$s^2 = 23.5833\ (10^{-6})$$

$$s = 4.853\ (10^{-3})$$

$$\frac{\bar{x}\sqrt{n}}{s} = \frac{0.02225\sqrt{4}}{0.004853} = 9.12$$

Using "t" tables, we find $t_{3;.025} = 3.18$

Since 9.12 > 3.18, the null hypothesis is rejected and it is concluded that the two porosities produce significantly

* See Guttman and Wilks (46), page 164.

APPENDIX IV (continued)

different head loss v. iron applied curves at the 5 % level. A similar set of calculations, not presented here, revealed that sand bed porosities of 33.7 and 37.0 per cent also yield significantly different head loss v. iron applied curves at the 5 % level.

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