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REMOVAL OF PARTICULATE MATTER ON COATED FILTER MEDIA

by

Donald Edward Burns

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ABBREVIATIONS

A	cross-sectional area of a filter cake, ft^2
Å	angstroms
°C	degrees centigrade
C_e	concentration of particulate matter in the filter effluent, mg/l
C_e'	turbidity of particulate matter in the filter effluent
C_e/C_i	ratio of effluent to influent particulate matter concentrations
C_i	concentration of particulate matter in the filter influent, mg/l
cm	centimeters
cps	cycles per second
°F	degrees Fahrenheit
ft	feet
gm	grams
gpm	gallons per minute
H	head loss across a filter cake, ft of water
I.D.	inside diameter
in.	inches
K	coefficient of permeability (independent of liquid viscosity) ft^2
K_o	coefficient of permeability at a filtration time of zero, ft^2
L	thickness, or depth, of a filter cake, ft
l	liters
m	meters
mg	milligrams
mg_a	milligrams of particulate matter applied to a filter cake (equals 1700 C_i Q t), mg

min	minutes
ml	millileters
mm	millimeters
mv	millivolts
N	normality, equivalents per liter
P	pressure drop across a filter cake, lb/ft^2
pH_e	effluent pH
pH_i	influent pH
Q	(dV/dt) flow rate, ft^3/sec
R_e	effluent resistivity, ohm-meters ($\Omega \cdot m$)
R_i	influent resistivity, ohm-meters ($\Omega \cdot m$)
sec	seconds
t	elapsed time of filtration, min
t_v	elapsed time of filtration to the end of adsorption, min
W	weight of filter media, lb

γ_c	in place bulk density of a clay filter cake, lb/ft^3
γ_d	in place bulk density of a diatomite filter cake, lb/ft^3
γ_w	bulk density of water, lb/ft^3
$\Delta\ mg_r$	weight of particulate matter retained in a filter cake in a time increment of Δt (equals 1700 $(C_e - C_i)\ Q\ \Delta t$), mg
ΔH	head loss increase in a time increment Δt, ft of water
Δt	an increment of time during a filter run, min
ϵ	filter cake porosity
ζ	zeta potential (see Figure 1), mv

μ	liquid viscosity, $lb \cdot sec/ft^2$
$\Sigma(\Delta H)$	sum of Δ H's from zero filtration time, feet of water
$\Sigma(\Delta mg_r)$	sum of Δmg_r's from zero filtration time, mg
Ψ	electrical potential (see Figure 1), mv
Ψ_δ	Stern potential (see Figure 1), mv
Ψ_o	surface (or volta) potential (see Figure 1), mv
Ω	electrical resistance, ohms
601	Purifloc 601, a cationic polyelectrolyte used in this study

INTRODUCTION

A variety of processes are employed to produce water of acceptable quality for industrial and domestic uses. The process which can be used in any given situation normally depends on the quality of the raw water supply and the quality of the water needed. For example, water used for domestic consumption must be biologically and chemically safe and palatable. This normally means that biological organisms, in the form of algae, bacteria, and viruses, and chemicals, such as iron, nitrates, phenols, and taste and/or color producing organics, and mineral particles such as clays must either be removed from the water or changed to an acceptable state.

Removal of suspended solids or particulate matter by filtration through porous filter media is a conventional water treatment process which has been used for several millenniums. In recent history the filtration process held a position of great importance in domestic water treatment. In current domestic water treatment practice, the filtration process has been relegated to the role of "polishing" water previously pretreated, for example, by chemical coagulation, flocculation, and gravity sedimentation. During the past few decades the filtration process has been subjected to a critical evaluation. The result has been a gradual change in design of filtration plants from the application of the "art of filtration" toward the application of the "science of filtration." The evolution is still incomplete but the rate of evolution in the past two decades has been very high.

Conceptually, the process of solids-liquid separation by filtration involves the retention by a filter media of particulate matter as a suspension is passed through the filter. Any particle that is larger than the pore openings through which the water passes will obviously be retained by the filter media. Particles which are one to two orders of magnitude smaller in size than the granular filter media are also effectively removed in many cases. In the practical application of water filtration, the particulate matter is often two or more orders of magnitude smaller in size than the granular filter media used. In order for these suspended particles to be retained in the filter bed, they must first be transported from some point in the liquid phase to the filter media surface. Particle transport to the surface of the filter media is basically a physical process. A particle near to or in contact with the filter media surface must then undergo a positive interaction with this surface if it is to be retained in the filter bed. Usually this interaction results in a decrease in the free energy of the system if it occurs spontaneously. Such an interaction is usually called adsorption.

There has been considerable dialogue in the technical literature concerning the specific forces involved in particulate matter-filter media surface interaction. Of special interest recently has been the theory of electric double layer interactions. However, it has been noted that:

> . . . to understand the complexity of phenomena that occur during . . . filtration . . ., not only must electrical phenomena be considered, but also the chemistry involved. Steric factors, conformation between surfaces . . ., van der Waals forces, hydrogen bonding, or even formation of chemical bonds should be taken into consideration as mutually interacting parameters. (5)

It is improbable that precise evaluation of these electrical, chemical, and physical parameters will ever be made for the diverse ill-defined systems encountered in practice. The filtration engineer can generally use only a qualitative evaluation of these parameters when evaluating filtration phenomena.

Any modification of the filter media surface-liquid interface which would enhance a positive particulate matter-filter media surface interaction should result in improved filtration removals of sub-micron size particulate matter. One such modification which has been attempted is to coat electronegative filter media surfaces with electropositive coating materials. This approach is not new having been employed before 1922 (11). In this case slow sand filters were "charged" with solutions of aluminum salts resulting in an adsorbed layer of aluminum hydrolysis species. Improvement in color removals were reported. In a more recent report, diatomite filter media was coated with aluminum hydrolysis species. Diatomite filter media so coated was found to remove substantially more color compounds, bacteria, and turbidity from a river water than did uncoated media (4). It has also been reported that electropositive coatings of cetyl trimethylammonium on granular silica filter media removes significantly more kaolinite clay particles from suspension than uncoated silica media (29).

Previous research by the author has shown that a commercially available cationic polyelectrolyte will coat diatomite filter media producing an electropositive zeta potential with no significant change in the permeability of the filter media (8). It has also been established that cationic polyelectrolytes are readily adsorbed on various clays (6, 54). In addition, this type of polymer has been shown to act as a coagulant, which presupposes adsorption, for certain types of waters (13).

Based on these scant observations, it would be reasonable to expect that electronegative filter media coated with a cationic polyelectrolyte would enhance electronegative particulate matter-filter media surface interaction. This study was undertaken, therefore, to evaluate the pattern of removal of different types of sub-micron suspended matter on filter media coated with a cationic polyelectrolyte.

The specific objective of this research was to demonstrate whether or not improved particulate removal could be observed. If improved removals were observed, the study was to be expanded to evaluate the effect of certain operational variables on the solids removal pattern.

BACKGROUND

To better understand the filtration process, pertinent literature was reviewed, and is discussed briefly in this chapter. The following discussion will be concerned with the principle variables affecting the filtration process, with removal mechanisms, and with previous coated filter media studies.

The process of filtration as applied to relatively dilute aqueous suspensions encountered in water treatment practice consists of passing the suspension through a fixed bed of porous filter media of such characteristics that the suspended matter is retained in the filter bed. Under certain conditions of filtration, a relatively impermeable cake of suspended material can be formed on and/or near the surface of a granular filter (12, 16). This phenomenon is classified as cake filtration and will not be considered in this discussion.

To the cursory observer, the filtration process may appear as a straightforward physical straining process. However, one who is concerned with a fundamental analysis of the process cannot help but be overwhelmed by the complexity of the physical, chemical, and electrical interactions involved. One can momentarily be impressed with researchers who have applied "powerful tools of modern scientific investigation" (33) and developed elegant mathematical models of the filtration process (19, 32, 42). However, when one considers the basic assumptions on which these theories are based, and the lack of consideration of pertinent variables, one is only impressed with the ambition of these researchers. It appears obvious that we are only on the first step of a long path leading to a full understanding of the filtration process.

Variables Affecting Filtration

The complexity of the process of filtration can best be grasped by considering a dimensional analysis of the process. To do this one must list the pertinent physical, chemical, and electrical parameters which may affect the removal of particulate matter. The filtration process involves three phases of matter:

1. the filter media, a solid phase;
2. the liquid phase in which the particulate matter is suspended; and
3. the particulate matter, a solid phase.

The effects that the filter media has on the filtration process are dependent on all of the following parameters and perhaps more:

1. the depth of the filter bed;
2. the volume of the filter bed;
3. the bulk density of the filter media in the filter bed (lb/ft^3) ;
4. the porosity, or void volume in the filter bed occupied by the liquid phase;
5. the chemical composition of the media as represented by:
    a. the mass density of the media,
    b. its mechanical strength or resistance to attrition,
    c. the chemical nature of the solid-liquid interface, and
    d. the conformation of the exposed surface; and
6. the size, shape or configuration, and the orientation

of the media particles in the filter bed.

The effects that the liquid phase has on the filtration process will depend on the following parameters and perhaps others:

1. the mass density of the liquid;
2. the absolute viscosity of the liquid;
3. the motion of the liquid phase relative to the filter media and relative to the particulate matter;
4. the concentration, type, and valence of the ionic species present in the liquid phase; and
5. the concentration and type of molecular species present in the liquid phase.

The liquid temperature and pressure will affect many of the parameters listed above.

The effects that the particulate matter has on the filtration process will depend on the following particulate matter parameters:

1. the concentration of particulate matter at all points in the system;
2. the size, shape or configuration, and the orientation of the suspended particles;
3. the rheology of the material as removed in the filter, including the particle surface area exposed per mass removed and the volume of deposit per mass removed; and
4. the chemical composition of the particulate matter as represented by:
    a. its mass density,
    b. the chemical nature of the solid-liquid interface,

and

c. the conformation of the exposed surface.

Not all of the listed parameters are entirely independent and the list is probably incomplete. However, it can be readily appreciated that the formulation of a mathematical model for the filtration process which would include all of the variables describing the parameters listed above, which have only five basic dimensions, would be a most ambitious task. In light of this observation, most researchers have been content to develop conceptual models of the filtration process.

Removal Mechanisms

By combining the conceptual and mathematical theories presented in the literature, it is possible to obtain a general understanding of the phenomena which can affect the removal of particulate matter in a fixed-bed porous filter.

When a suspension of particulate matter flows through a porous filter media, there are physical and hydrodynamic forces applied to the moving particles which will cause the particle to be transported from the bulk of the suspension to the vicinity of the filter media surface. When the particle finds itself near this surface, there are a variety of physical, chemical and electrical force systems which may or may not cause it to become attached to or retained by the filter media surface, or attached to or retained by previously deposited particulate matter. The generality of this model is still incomplete, since the attachment of the particulate matter to the filter media may be a reversible process. Indeed, some filtration theories have included such a reversible attachment, or a displacement of the attached material (43, 59).

Possible removal mechanisms

The following general presentation of phenomena affecting particulate matter removal is not concerned with the applicability of these phenomena to any specific filtration system. No distinction will be made between transport and attachment phenomena since most can affect both.

Straining Any particle which is larger than the pores in a filter media through which the liquid phase passes will be physically retained at or near the surface of the filter media. Extensive surface straining can result in cake formation. The original filter media then serves only to support the filter cake which then serves as its own filter media.

Interstitial straining is considered possible when a particle is confronted with a narrow passage in the filter pore existing near the point of contact(s) between filter grains (24). Obviously, the number of particles removed in this manner is directly related to the volume of flow which passes through these narrow interstitial passages. It would be reasonable to assume that irregularly shaped filter media grains provide a larger number and variety of shapes of contact points where interstitial straining could occur than would a more spherical grain of the same relative size.

In addition to possible interstitial straining, diatomite filter media particles, which are essentially microsieves, provide for a direct straining action through the filter media particle itself.

See Figures 33 and 34 in the Appendix.

Gravitational forces The force of gravity acts on the filter media grains, the particulate matter and the liquid phase at all times. Indeed, gravity forces are usually employed to hold the filter media in a fixed position.

The motion of a particle relative to its liquid environment can be predicted in part by evaluating the gravity, buoyant, and frictional drag forces acting on the particle. In the absence of other possible forces, a spherical particle will move in the direction of the gravity force vector if the mass density of the particle is greater than the mass density of the liquid. Hence, it is conceivable that a particle located above a given filter media grain, could settle, under the action of the gravity force, onto the upper exposure of the filter media grain. This type of removal has been observed (31). For very small, sub-colloidal, particles with densities near that of the liquid phase, the effect of gravity forces become vanishingly small.

Inertial forces In laminar flow a particle in suspension is considered to have a constant velocity vector unless acted upon by external forces. A particle flowing along a fluid streamline has an inertial force directed along a tangent to the streamline. If this tangent intercepts a filter media particle, then this inertial force will cause the particle to move toward the filter media particle. A suspension flowing through a granular porous filter media, usually under laminar flow conditions, is characterized by continually changing streamline direction due to the random orientation of the void spaces. This change in fluid streamline direction will result in a viscous drag force acting on the particle which tends to transport the particle along the same streamline. The inertial force will tend to force the particle along the tangent to the streamline. It is conceivable that this inertial force could ultimately cause the particle to come into contact with the filter media surface. However, in aqueous suspensions under laminar flow conditions, viscous drag forces and gravity forces are considered to be much more significant than inertial forces (24).

The concept of converging streamlines at constrictions in the filter media voids causing particles to contact the filter media surface involves gravity and inertial forces acting along similar vectors (downflow filtration) which intercept the filter media grains.

Brownian movement and particle diffusion Particles and macromolecules in an aqueous medium are continually being randomly bombarded by molecules of water. This results in the phenomenon of Brownian movement. The random motion resulting from such collisions produces a random translation of particles. The mean translation, in a plane surface, of a spherical particle can be predicted by Einstein's quantitative theory of Brownian movement (55). For a one-micron spherical particle in water at 25°C, this translation would be 0.3 micron in one second.

A granular porous filter is generally conceived as consisting of an array of void volumes interconnected by constrictions. Depending on the configuration and orientation of the particles making up the filter media, this generalized picture can be extended and the presence of regions of little if any fluid motion postulated. This concept provides the basis for suggesting the possibility of particle diffusion causing particle transport from the flowing suspension to these regions of low fluid flow.

The time rate of mass flow for colloidal particles will be very small. For example, calculations using Fick's Law for diffusion (55) predicts that 8.8×10^{-10} mg of one micron diameter spheres will diffuse one mm in one second through an area of one mm^2 under a concentration gradient of 20 mg/l/mm, in water at 25°C.

As has been shown in the examples above, the rate of mass transfer over a significant distance by diffusion is extremely small and one could hardly expect this phenomenon to account for bulk particle transfer as has been done (47). However, when considering diffusion across a distance of less than one micron the phenomenon can be significant. Indeed, aerosol filtration efficiencies for the removal of particles less than one micron in diameter correlate very well with a diffusion parameter. A positive correlation has also been found between the removal efficiency, by rapid sand filters, of polyvinylchloride microspheres about 1.3 microns in diameter and a diffusion parameter (31).

Van der Waals forces Van der Waals forces are a universal attractive force between atoms. These forces arise from interacting, fixed and induced, atomic dipoles and fundamental dispersion forces (39). The magnitude of the attractive energy between atoms (force times distance of separation) is inversely proportional to the sixth power of the separation distance. For interaction between particles, which are aggregates of atoms, the attractive energy is found by integration over all interacting atomic pairs. Typical equations for interaction energies are presented in the literature (34, 39). Attraction energy between a spherical particle and a flat plate, a system considered applicable in a filtration system, is directly proportional to the sphere radius and inversely proportional to the separation distance. A comprehensive discussion of attractive van der Waals forces in rapid sand filtration has recently been presented (34). Van der Waals interaction energies were found to be significant for separation distances of less than a few hundred angstrom units (34, 39).

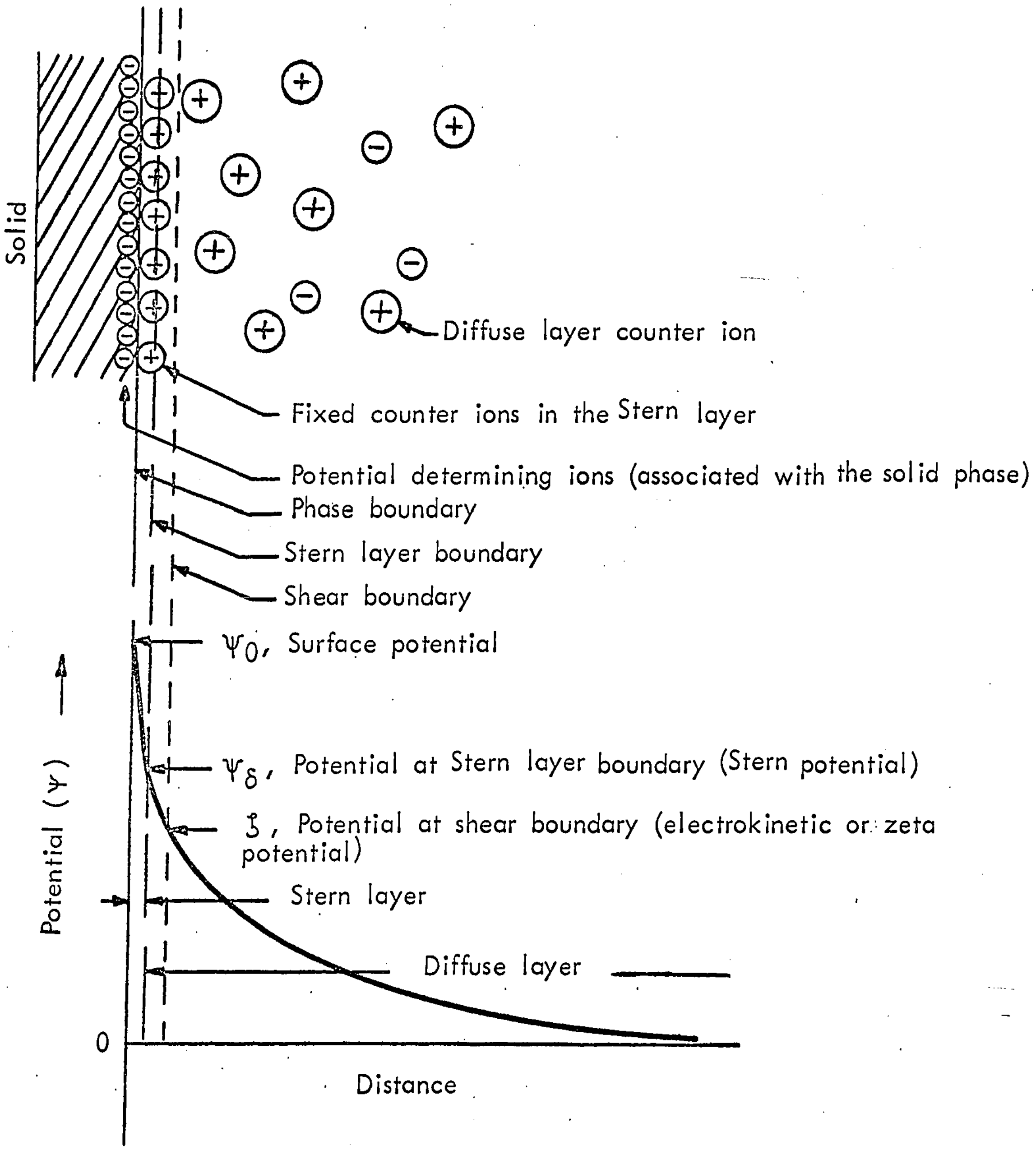
Electrical forces between surfaces The electrical properties at the solid-liquid interface are dependent on the origin of the solid surface and the physical-chemical properties of the solid and liquid phases. Solid particles encountered in water treatment originate from three general sources:

1. degradation of larger particles,
2. biological agents, and
3. condensation of small particles forming larger particles.

In water the surfaces of these solids exhibit a surface charge which may arise from specific adsorption of potential determining ions, dissociation of ionic species, internal atomic defects in the solid phase, or possibly other causes. This surface charge is counter-balanced by oppositely charged ions in the liquid adjacent to the solid-liquid interface. The distribution of ions in the region adjacent to the solid-liquid interface is different from that in the bulk of the solution and is described by electrical double layer theory.

Figure 1 is a diagrammatic picture of the electrical double layer based on Stern's modification of the Gouy-Chapman model (39). A layer of fixed, nearly immobile ions adjacent to the negatively charged surface reduces the surface potential, Ψ_0, to the Stern potential, Ψ_δ. Outside this fixed layer, called the Stern layer, is a diffuse layer of ions,

Figure 1. A diagrammatic picture of the structure of the electrical double layer and the variation of electrical potential in this layer, according to the theory of Stern


Solid
Diffuse layer counter ion
Fixed counter ions in the Stern layer
Potential determining ions (associated with the solid phase)
Phase boundary
Stern layer boundary
Shear boundary
Ψ_0, Surface potential
Ψ_δ, Potential at Stern layer boundary (Stern potential)
ζ, Potential at shear boundary (electrokinetic or zeta potential)
Stern layer
Diffuse layer
Potential (Ψ)
0
Distance

the concentration of which are assumed to be described by a Boltzman distribution. In the diffuse layer there is an excess of positive ions, such that the total charge in the diffuse layer equals the total surface charge minus the total charge in the Stern layer.

When two charged surfaces are brought together so that their diffuse layers overlap, an electrical force between the two surfaces will exist. For surfaces with similar Ψ_δ's, a repulsive force will exist. For surfaces with opposite Ψ_δ's, an attractive force will exist. The magnitude of the repulsive or attractive force is related to the magnitudes of their respective values of Ψ_δ and the distance of separation of the surfaces. In order for particulate matter to become attached to a filter media surface of like charge, the individual particles must be transported to the filter media surface with sufficient energy to overcome the repulsive electrical force and come within the range of the forces causing attachment, i.e., van der Waals or chemical forces. Of course, when the two interacting surfaces are oppositely charged, a particle approaching the filter media surface experiences no electrical force barrier.

In practice, the electrokinetic (or zeta) potential, ζ, is measured and is used in place of Ψ_δ to compute electrical forces. Electrokinetic potentials are measured in systems where the diffuse layer outside the viscous shear boundary and the charged surface are caused to move relative to one another (39). The mathematics of the electrical double layer and equations for computing the electrical forces resulting from interacting diffuse layers are presented elsewhere (39).

In a recent study of electrical and van der Waals forces in water filtration systems, it was concluded that, in natural waters with moderate amounts of dissolved salts, the range of these force systems are less than about 0.02 micron (34). That electrical forces in colloidal and filtration systems can be of paramount significance is hardly questionable. However, the evaluation of electro-chemical phenomena on the basis of electrical theories is highly questionable.

Chemical forces The exact nature of these forces as they might affect removal of particulate matter by filtration are not known. However, the literature indicates that they must be considered (5, 14, 40). It can be speculated that coulombic forces, as in ion exchange, hydrogen bonding, and surface tension forces could be significant.

Rheology of deposited material This is not proposed as a filter removal mechanism per se, but comments concerning its possible importance in water filtration have appeared in the literature (24, 33, 43, 59). It can be viewed as a boundary condition for the removal of certain types of particles which would not adhere to previously deposited material if the shearing force, due to the viscous flow of water, is larger than the forces causing adhesion.

In one study, deposition of iron floc on circular rods, transverse to the direction of flow, was observed with a microscope. The deposited material exhibited a sort of plastic flow with some breaking away of the deposited material (59). Obviously, the rheological properties of this deposit were significant.

In using recently presented filtration equations, it is necessary to compute the volume of material removed in the filter pores in order to evaluate some of the important filtration parameters (32). Another integral part of this theory assumes that an observed initial improvement in removal efficiency near the start of a filter run results from a linear increase in surface area with increase in the volume of material deposited. However, experimental results indicate that this initial removal is a function of flow rate, in addition to, or conceivably to the exclusion of, area per volume of deposited material (32).

Hydrodynamic considerations   Hydrodynamic phenomena are not at all independent of other mechanisms already discussed, e.g., sedimentation, inertia, and particle diffusion phenomena. At normal water filtration rates, interstitial flow is considered as laminar based on an overall response to d'Arcy's Law; however, the complex flow paths through granular filter media may lead to secondary laminar flow conditions. It has been reported that filtration efficiency, for filtration of kaolinite suspensions through rapid sand filter media, can be correlated with the hydrodynamic parameter, Reynolds Number (31).

The size, shape or configuration, and orientation of individual filter grains in a granular filter bed are some sort of random distribution and a precise mathematical description of the geometry of voids in a filter bed has not been developed. There have been attempts to obtain a visual picture for idealized flow systems (27, 59). These studies were made for laminar flow around cylindrical rods using a two-dimensional flow system. Though no mathematical models for these flow systems were developed, the physical picture they provide can be of value when conceiving removal patterns in porous media filters.

Observations from the literature

There is much filtration data in literature. Unfortunately, there is little opportunity for direct comparison of results. Almost every report describes a different filtration system employing a variety of analytical techniques for monitoring the process.

The following discussion of results reported in the literature will be grouped on the basis of the type of particulate matter being removed. In nearly all cases cited, granular fixed-bed pilot or bench-scale filters were employed.

Mineral particles Two reports on the removal of Fuller's earth from tap water suspensions by uniform-sized sand filters have been reported. In the first, results were typical of those obtained with rapid sand filters. That is to say, good effluent quality was obtained, the upper portion of the filter produced most of the removal early in the filter run and the burden of removal moved down the filter depth with time (41). The results indicate a high degree of transport and/or retention for the system used. In the second study, it was observed that removal didn't occur preferentially in the upper portion of the filter early or late in the filter run (23). In the first study interstitial concentrations at various depths were determined, whereas in the second study only effluent concentration was determined. In the second study an unsuccessful attempt was made to correlate the change in void volume based on head loss build up data with the amount of material removed as determined by concentration measurements (23). It was reported that the degree of compaction of the deposited Fuller's earth within the pores was probably a changing function. It was also observed that sand filter media produced better removals than glass ballotini media, all other variables being constant (23).

Mechanical filtering (mechanical straining) was proposed as the removal mechanism in a study of the sealing of a granular carborundum filter by bentonite clay suspensions (16). Sealing was observed when suspensions of clay particles with a diameter less than 2 microns were filtered through columns of "medium sharp" carborundum whose particle size was either 0.08 mm or 0.16 in diameter. No sealing occurred using carborundum media with a diameter of either 0.385 or 0.775 mm.

The shape of filter grains was considered significant since filters with 63-micron diameter carborundum grains were completely sealed by the bentonite sols yet spherical glass beads of this size were not sealed. Filters containing spherical glass beads with particle diameters of less than or equal to 36 microns were sealed by the bentonite sols (16).

In another study, kaolinite sols (1.14 gm/1 and 0.2 - 1.2 micron equivalent settling diameters) were passed through columns of silica (0.29 - 0.21 mm[1] and 0.42 - 0.29 mm sieve sizes) and pertinent data observed (29). It was postulated that clay particles diffused across streamlines into "dead spaces," or regions of low shear, due to the concentration gradient present initially, until an equilibrium deposit occurred. In addition to the above diffusion transport, interstitial straining and sedimentation were considered to be significant, or implicit in the assumed removal model. Surface charge reversal of the silica media, by adsorbed cetyl trimethylammonium ions, produced a significant increase

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[1] For example, passing a 0.29 mm sieve and retained on a 0.21 mm sieve.

in kaolinite removals as compared to those obtained using uncoated silica. The change in permeability per mass of clay removed was greater for removal on the coated silica than it was on the uncoated silica (29).

A more recent study adds support to gravity, and possibly diffusion, removal of kaolinite particles. In this study kaolinite suspensions (2.5 - 10 micron diameter) were filtered through columns of spherical glass beads (0.42 - 0.50 mm diameter) (31). The kaolinite was observed to be removed only on the upper faces of the filter media during both downflow and upflow filtration. The upflow study is significant since for this system, inertial forces would not have been additive to gravity forces.

Another investigator studied the removal of a 6-micron diameter bentonite clay by a pilot rapid sand filter (0.42 - 0.84 mm filter grains) (56). Based on electrokinetic and particle size analysis, it was concluded that the clay was removed by adsorption and, thus, it followed that electrokinetic phenomena associated with the sand surface must be involved. It was stated that a decrease in the positive zeta potential of the sand filter media surface

> . . . caused an increase in the electrostatic force barrier of the sand surface, which, in turn, increased the energy hump that the clay particles had to overcome in order to move within the range of the van der Waals forces and, ultimately, be adsorbed onto the sand surface. (56)

Recalling the previous discussion about electrical forces between surfaces starting on page 13, it appears that the author did not understand electric double layer interaction theory.

Interstitial straining and sedimentation have been proposed as the removal mechanisms involved in the removal of $CaCO_3$ particles from a softening pretreatment process by a pilot rapid sand filter (12). In another study using $CaCO_3$ and ferric floc particles, the filtration results were found to correlate with a mathematical model derived on the basis of van der Waals and hydraulic shear forces. However, little significance can be attached to a model based on only two of the possible force systems affecting removal patterns since it was not conclusively established that these two force systems were controlling. (42)

It is apparent from the studies cited that the removal of clay particles by granular filter media might result from a variety of removal mechanisms. Indeed, all of the previously discussed mechanisms have been suggested or implied as being applicable.

Flocculent materials This classification of particulate matter has received much attention from filtration researchers, undoubtedly due to the fact that in practice, rapid sand filtration usually follows a coagulation-flocculation-sedimentation process. Iron floc formed from flocculation of ferric iron hydrolysis species has been the particulate material most often used.

Visual observation of the removal of ferric floc in a simulated filter has resulted in the conclusion that these floc are removed by "chance contact." (59) Chance contact was described as resulting from the convergence of streamlines at constrictions within the filter pores. The floc particles were observed to exhibit a varied affinity for the artificial media used and for previously deposited floc particles. The floc attached to the media appeared to exhibit a slow creaping or kneading action.

In a study using radioisotope-labeled iron floc, it was observed that floc removed from suspension did not become detached and redeposited deeper in the filter (58). This observation contradicted an earlier observation to the contrary (59). The radioisotope study also showed that the penetration of iron floc into the filter bed varied with solution pH and was a minimum at a pH of about 7, the pH which was considered to be near the isoelectric point of the iron floc. This observation was interpreted as indicating the significance of electrical forces in iron floc removals (58).

In another study "electrokinetic" forces have been considered as being predominantly responsible for the removal of hydrous ferric oxide particles (12). This deduced conclusion was based partially on the elimination of sedimentation (gravity forces) and interstitial straining as probable mechanisms.

It has been reported that E. coli and aluminum floc removal by rapid sand filtration was not affected by coating the normally polar, hydrophilic sand surface with a non-polar hydrophobic coating (57). It was concluded, therefore, that adsorptive forces between the floc and sand surfaces did not play a major role in the removal of the floc by the rapid sand filters.

An analysis of filtration data for iron floc removal by rapid sand filters resulted in the suggestion that " . . . the adhesive characteristics of the floc, or the sand, or both, are less at the lower depths" (9). It has also been observed that weak particles in adsorbed floc "sheaths" were torn off and replaced by stronger particles that adhered more firmly (59). Based on the computation of hydraulic shearing forces in a clean filter and the shearing forces necessary for cleaning the clogged filter (i.e., backwashing), it has been concluded that, if coulombic forces and molecular bonds (including van der Waals forces) are involved in adhesion of iron floc to the sand surface, the number of such bonds per cm^2 of filter media surface must be extremely small (10). It was noted that floc sheaths formed around the filter grains during a filter run had resisted shearing forces four times as great as those applied during backwashing. It was suggested that during filtration these floc sheaths

> . . . were resting on the grains with small adhesion to them, like a cap pulled tight on a man's head, and that the tensile strength of the floc was sufficient to resist the high shearing forces. (10)

It was also mentioned that:

> Because interfacial tension must be involved in binding the water within the hydrous oxide floc particles . . . it may also account for the adhesion of the floc to the grains. (10)

Along this same line of thought, another report indicates that "floc strength" is very important and, to a certain degree, affects the way in which a floc is removed (52).

Two studies have been reported where the chemical aspects of iron floc removal by granular filter media were investigated. One study involved varying the type of anion species present, at different pH's, and observing head loss and bed penetration during a filter run (46). Electrophoretic mobilities, which are related in a complex way to the electrokinetic, or zeta, potential, of the iron floc were also observed. It was reported that the surface properties (electrophoretic mobility was the only parameter evaluated) of ferric floc markedly affect their filter-ability and that these properties depend on the chemical composition of the aqueous phase. These authors went on to say:

> These chemical effects in the filtration process are considered to result from interactions between the surfaces of the filter medium and the suspended floc particles; this conclusion lends strong experimental support to adsorption as a predominant removal mechanism in rapid sand filters. (46)

Another very brief study on chemical aspects shows removal patterns to be dependent on the pH, age, concentration of sulfate ions, and ionic strength of the iron floc suspensions (47).

In an excellent discourse on surface forces in rapid sand filtration, an inverse relation was observed between the magnitude of the energy barrier between the suspended particles and the filter media surface (the sum of electrical double layer interaction energy and van der Waals interaction energy) and filtration efficiency (34). For large energy barriers resulting in poor filtration efficiencies, some solids removal occurred; hence, some mechanism other than electrical double layer interaction was causing removals. The data presented indicated that for natural waters containing moderate amounts of dissolved salts, the range of surface forces was less than about 0.02 - 0.03 micron. Therefore, it was concluded that such surface forces are not responsible for the bulk transport of particulate matter from the water to the media surface. This very important point has often been overlooked by researchers when they propose surface forces as a predominant removal mechanism (12, 42, 46, 56). It is conceivable however, that particle-media and/or particle-particle electrical double layer interactions are a rate determining factor for some systems and as such might be called the predominant removal mechanism.

The drastic difference in the filtration removal patterns of iron sol particles and iron floc particles has been reported (25). Iron flocs were shown to be readily filtered with the burden of removal progressing downward from the top toward the bottom of a filter bed. The floc was adsorbed on previously deposited floc, clogging the filter media pores and causing significant head losses to occur. Iron sols, on the other hand, presented a drastically different removal pattern. Their removal was explained as an adsorption process. The amount of iron sol removed was dependent on the amount of filter media surface area available and the head loss build up was insignificant (25).

Recent research has shown that the adsorption of iron sols on various materials is governed by interfacial electrical properties (37). No evidence of chemical or hydrogen bonding was found. Sol particles were reported to adsorb in incomplete monolayers due to the electrical double layer interactions of the adsorbing particles. The amount of sol particles which could be adsorbed on a given surface was shown to depend on the surface charge characteristics of the sol particles and on those of the surface of the adsorbent. However, the surface charge characteristics of the sol particles were found to be much more important than those of the adsorbent. It was further observed that a coagulating iron sol could be adsorbed in multilayers and that adsorption of these sol particles onto the surfaces studied was much faster than the adsorption of sol particles onto each other (i.e., coagulation). It was concluded, therefore, that the van der Waals attraction between the surface and sol particles was much greater than the van der Waals attraction between the sol particles. Theoretical computations of van der Waals interaction energy supported this conclusion (37).

Based on the literature reviewed, it appears that the removal of iron floc by rapid sand filters is largely controlled by the chemical, electrical, and physical (including rheological) properties of the floc particles rather than the electrical, chemical, and physical properties of the filter media surface. That is to say, particle-particle interactions are more significant than particle-filter media interactions. Of course, the particle surface-aqueous interfacial properties are dependent to a large degree on the chemical properties of the aqueous phase.

Other particulate matter Studies involving the removal of algae from water by rapid sand filters have been conducted by numerous investigators (17). Though some observations are made concerning the pattern of removal, there isn't enough information compiled to draw any meaningful conclusions concerning the predominant removal mechanisms involved.

The same observation applies to the removal of bacteria and viruses (52, 53). It is generally accepted that pretreatment removes most of these organisms.

Lag period At the start of a filter run, whether in a prototype or a pilot-model filter plant, the water in the pores of the filter media is usually clean water, free of the particulate matter to be removed. Of course, in research work a greater effort is made to insure a clean filter bed at the start of a run. When the filter run is started, the water being filtered begins to displace the clean water in the filter voids. In many cases the concentration of material in the filter effluent increases up to a maximum value significantly less than the influent concentration, and then gradually decreases to a minimum value. The time lapse to the maximum value is often found to agree with the theoretical detention time determined from the volume of clean water present in the filter voids and the flow rate. The time elapsed to observation of the minimum particulate concentration in the effluent has been called the "lag time." (41)

The improvement in effluent quality with increasing filtering time has been observed with a variety of suspended materials by numerous investigators (12, 31, 33, 35, 41, 53). Though the lag time phenomenon appears to be a general observation, it has never been critically analyzed or satisfactorily explained. An attempt has been made to predict this phenomenon mathematically based on the premise that it results from an increase in the filter media surface area because of the material being deposited (32). Unfortunately, filtration results have not supported this premise (35). Lag time observations have been used to lend indirect support to an "electrokinetic" removal mechanism (12).

Diatomite Filtration

Diatomite filtration is a fundamentally different process than fixed-bed granular filtration. It is, in a sense, a modification of cake filtration. Conceptually, it consists of filtering a suspension through diatomite, or diatomaceous earth, which is fine enough to be capable of mechanically straining the solids in suspension. Diatomite is fed continuously to the filter cake in amounts needed to prevent an impermeable surface mat of solids from building up. Diatomite used in this way is referred to as body feed. If too little body feed is fed, head loss will increase exponentially with increasing time of filtration.

There is an optimum concentration of body feed which will produce a linear head loss vs time curve. If body feed is fed in amounts greater than this optimum, the head loss build up remains linear but it increases at a lower rate.

In the design of diatomite filtration plants, pilot plant tests are first made using different grades (or sizes) of diatomite and the water to be treated. These tests are used to determine the grade, or particle size, necessary for removing the particular suspended solid involved and will provide an estimate of the amount of body feed necessary to obtain linear head loss build up curves. The use of this design procedure assumes that a grade of diatomite will be found which can remove the suspended solids by mechanical straining. This is possible if the suspended particles are larger in diameter than a few microns since the smaller grades of diatomite have an approximate mean particle size of less than 5 microns. However, there are reports of bacteria, turbidity, and color compounds passing through the finer grades as well as coarser grades of diatomite in quantity (4, 28, 51). This observation indicates a need to increase the effect of other possible mechanisms of removal, as previously discussed, in an effort to improve the removal of colloidal and subcolloidal particles by diatomite filtration.

Some properties of diatomite filter media are presented in the Appendix.

No less than six arbitrarily defined parameters have been used to indicate the permeability of diatomite and suspended solids-diatomite filter cakes (19). In all cases d'Arcy's Law, corrected for the viscosity of the flowing water, was considered as the fundamentally applicable equation. This equation can be stated as:

$$\frac{dV}{A\ dt} = \frac{K\ P}{\mu\ L} \tag{1}$$

where:

dV/dt = volumetric liquid flow rate, ft^3/sec

A = area of the filter cake, ft^2

μ = liquid viscosity, lb sec/ft^2

P = pressure drop across the filter cake, lb/ft^2

L = thickness, or depth, of the filter cake, ft

K = permeability coefficient independent of liquid viscosity, ft^2

In constant-rate filtration, dV/dt is constant and is normally designated as Q. The head loss, H, across the filter cake in feet of water is equal to P/γ_w, where γ_w is the bulk density of water in lb/ft^3. Using this conversion, rearrangement of Equation 1 gives:

$$K = \frac{Q\ L\ \mu}{H\gamma_w A} \tag{2}$$

If direct observation of filter cake depth, L, is not possible, the value of L may be obtained if the weight of the filter media, W, in lb, and its in-place bulk density is known.

Stating L in terms of the weight of filter media and its in-place bulk density, Equation 2 becomes:

$$K = \frac{Q\ W\ \mu}{H\gamma_w\gamma_d A^2} \tag{3}$$

Equations 2 and 3 were used to compute filter cake permeabilities in this study.

Coatings for Filter Media

Diatomite coated with coagulants have been reported to produce removal of bacteria, color, and turbidity significantly better than the removal obtained with like grades of uncoated diatomite (4). However, more recent studies indicate that the removals of bacterial suspensions by coated and uncoated diatomite are not significantly different (28). It was explained that the earlier filtration tests, in which bacteria removals were improved, the raw water had turbid material in addition to bacteria and the bacteria were probably associated with the turbidity which was removed more effectively by the coated media. In the latter tests, the suspensions of bacteria were prepared with a turbidity-free water and removals using coated diatomite were not significantly different than those with uncoated diatomite (28).

Mention has already been made of a study in which a porous granular silica media was rendered electropositive with a coating of cetyl trimethylammonium. It was observed in that study that the general features of the removal process were unchanged but that the amount of removal of kaolinite particles was substantially increased (29).

The report of an investigation aimed at evaluating the electrokinetic properties of diatomite filter media indicated that normally electronegative diatomite could be rendered electropositive by coating the diatomite with coagulants (aluminum and ferric iron salts in water) and with a cationic polyelectrolyte (49). An extension of the above work has produced useful information concerning the electrokinetic and permeability characteristics of diatomite filter media coated with various polyelectrolytes (8, 45). Some of the results of these studies were relevant to the design of and the analysis of the results of this study and will be referred to when applicable.

It has been proposed several times that electropositive coatings on diatomite filter media should be more effective in removing electronegative colloids from water than electronegative diatomite (8, 45, 49). This research was designed to establish the significance of these proposals.

OBJECTIVES AND APPROACH

Objectives

As previously stated this study was undertaken to evaluate the pattern of removal of different types of sub-micron particulate matter on filter media coated with a cationic polyelectrolyte. The specific objectives were basically two-fold: First, to demonstrate that coated filter media would remove effectively more particulate matter than uncoated filter media; second, to evaluate the removal patterns observed during the removal of sub-micron particulate matter by coated filter media in order to elucidate the predominant removal mechanisms. Of course, achievement of the first objective was a prerequisite to achievement of the second. To achieve the first objective, a filtration system had to be designed in which the interaction at the filter media surface between the particulate matter and the filter media surface would control both the solids removal capacity and the removal rate. This meant that bulk transport of the particulate matter to the filter media surface would have to be accomplished in both the coated and uncoated filter cakes so that it would not be a limiting factor in the solids removal. In addition, it was considered desirable to use a filter media with a large filter media surface area per unit volume of filter media. This would provide a large surface area for coating and should result in significant amounts of removal. The coating material to be used must effectively coat the filter media, must undergo a positive interaction with the particulate matter to be used, must not significantly alter the permeability of a filter cake, and if possible must be susceptible to variation of its electro-chemical properties. Finally, it was felt that several types of particulate matter should be used in order to at least partially establish the range of application for the coating material used. Anticipating that improved removals would be demonstrated for at least some particulate matters, it was decided to evaluate the removal patterns of materials removed effectively on the coated filter media. It was hoped that the predominant removal mechanisms could be elucidated by evaluating the effects on the removal patterns of several parameters which affect the electro-chemical properties of the coating material and of several parameters which affect the filtration system (e.g., amount and/or depth of media, flow rate).

Approach

The general approach used to accomplish the objectives in this study was:

1. to select filter media, coating material, and particulate matter with the desired properties;
2. to design a filtration system and develop a testing procedure which would provide for obtaining data necessary to evaluate filtration removal patterns; and
3. to design and conduct laboratory tests which would provide data that would demonstrate the effectiveness of coated filter media and would permit determination of the predominant removal patterns.

Choice of filter media and coating material

In order to prevent the bulk transport of sub-micron particles to the media surface from being a limiting factor in solids removal and to provide for a relatively large surface area per unit of volume of filter media, a very fine and irregularly shaped filter media was desired. It was also desirable that the electrical surface properties and the hydraulic characteristics of the filter media be known or easily determinable. Diatomite was the natural filter media choice for several reasons. The specific surface area of diatomite on a basis of square feet per cubic foot of the media is two to three orders of magnitude greater than conventional rapid sand filter media. A most important reason was that the small particle size, the very irregular particle shape (see Figures 31 and 32 in the Appendix), and the porous structure of the diatomite particles should provide for filter cakes in which bulk transport of sub-micron particulate matter could be readily accomplished. Another important reason for choosing to use diatomite filter media was that previous studies at Iowa State University had established some electrical, hydraulic, and coating characteristics of such media (8, 18, 45, 49). Some of the physical, electrical, and chemical properties of diatomite filter media resulting from these studies are presented in the Appendix.

The choice of a coating material, a commercially available cationic polyelectrolyte called Purifloc 601[1], was based on previous experience. Purifloc 601 (hereafter referred to simply as 601) contains 37 percent

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[1] A product of Dow Chemical Company, Midland, Michigan.

polyalkyl polyamine, 45 percent water, and 18 percent inorganic compounds. Previous studies with 601 have established that:

1. The zeta potential of a diatomite filter cake of C-545[1] can be varied from about -55 mv to about +50 mv by coating with from zero to about 1.0 mg 601/gm C-545 (8, 45). Zeta potentials were measured by streaming potential techniques using about 10^{-4} N KCl-distilled water solutions.
2. The zeta potential of C-545 coated with 1.0 mg 601/gm C-545 is dependent on solution pH. The zeta potential will vary from about +50 mv at a pH of about 6 to a negative value at pH levels above 7-8 (8, 45).
3. There is no significant difference in the permeability of a 601-coated and an uncoated C-545 filter cake (8). In addition, the permeability of 601-coated C-545 is not affected by changes in the electrolyte concentration of the solution being filtered as has been observed for other cationic polyelectrolytes (45).
4. The adsorption of 601 on C-545 appears to form in monolayers (45).
5. No special procedure is necessary for coating diatomite. Mixing of diatomite in an aqueous solution of 601 for a few minutes produces a coated media which can then be hydraulically deposited on a filter septum (8, 45).

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[1] A specific grade of diatomite manufactured by Johns-Manville Products Corporation, Manville, New Jersey.

Choice of particulate matter

It has been shown that a cationic polyelectrolyte will adsorb on a kaolinite-type clay (6). Coagulation-flocculation-sedimentation studies indicated that, because of particle-particle interactions, individual cationic polymers will adsorb on more than one clay particle in accordance with the "bridging model" proposed by La Mer (40). However, it was postulated that for very dilute suspensions a polymer could well adsorb completely on one particle (6). A high degree of affinity between the clay and polymer must have existed since adsorption was more than 85 percent completed in 30 seconds with the mixing conditions studied (6). Studies of the adsorption of a cationic polyelectrolyte on a bentonite clay indicated that the polymer was adsorbed between the basic layers in a particle of the montmorillonite, increasing the c-axis spacing of the clay (54). From the above observations, it would be expected that a particle of clay coming into contact with a cationic polyelectrolyte which had previously been adsorbed on the surface of a filter media particle could be removed from suspension by adsorption.

The removal of color colloids from water by coagulants is generally considered to result from electro-chemical interactions. Coagulation-flocculation-sedimentation studies using alum as a coagulant have been reported in which solutions of instant coffee were used as the source of color colloid (38). This study showed that the color of instant coffee was more difficult to remove from water by alum treatment than a variety of other synthetic and natural color compounds. Above a pH of about 5.5, this material appeared to have an electronegative surface charge (38).

Based on these scant observations from the literature, it was decided to evaluate the removal patterns observed when clay minerals and a coffee color compound were filtered through 601-coated diatomite filter cakes.

In the hope of being able to prepare reproducible suspensions of particulate matter, it was decided to work with somewhat pure materials. Three types of clays and an instant coffee material were selected for study. The clay minerals had been used in previous filtration studies (1, 16, 50, 51, 56). Some physical and chemical properties of these commercially available clays are presented in the Appendix.

Two of the clays were montmorillonite-type clays. These were Black Hills clay[1] and Panther Creek clay[2]. The former is a sodium montmorillonite and the latter is a calcium montmorillonite. The third clay used was Ball clay[3], described as a kaolinite-type clay. One of the reasons for choosing to use clay as a suspended solid was the fact that it exhibits little variation in electrophoretic mobility (an approximate measure of zeta potential) over a water pH range of 5.5 - 9.0 (6, 7, 50). This characteristic was desirable, since over the same range of pH the charge characteristics of 601 vary considerably. By varying solution pH, it was possible to produce gross changes in the electrical surface properties of 601-coated diatomite filter media without a similar gross change in the electrical surface properties of the clay particles.

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[1] A product of International Minerals & Chemical Corporation, Old Orchard Road, Skokie, Illinois.

[2] A product of American Colloid Co., 5100 Suffield Court, Skokie, Ill.

[3] A product of Old Hickory Clay Co., P. O. Box 271, Paducah, Kentucky.

A color compound, instant Folgers coffee, was used to provide removal patterns for a significantly different type of particulate matter.

Choice of filtration system

Since the research proposed was of an exploratory nature, it was felt that use of bench-scale apparatus employing small quantities of materials would be adequate to achieve the objectives of this study. A bench-scale filter was designed, fabricated and installed in a filtration system including such other appurtenances necessary to obtain data to evaluate filtration removal patterns.

As mentioned previously, in normal diatomite filtration practice body feed is fed continually during a filter run to maintain an incompressible filter cake. This process has the desirable feature of continually providing new filter media surface area on which the particulate matter might be adsorbed. Consideration was given to using a body feed system. However, in the process of designing a filtration apparatus for use in this study, it was recognized that a problem would exist in providing a uniform body feed at the small rates of flow which were to be used. It is generally considered that an upflow velocity of about 12 gpm/ft^2 (or 0.82 cm/sec) is needed to keep diatomite in a somewhat uniform suspension. This velocity is well above the normal 1 - 3 gpm/ft^2 filtration rates normally used. In a horizontal pipe the average velocity necessary to transport diatomite in a uniform suspension is much higher due to the variable velocities over the cross-sectional area of the pipe. These high velocity requirements and the changes in body feed media characteristics due to mechanical degradation of one of the grades of diatomite used in this research (see the Appendix), prompted the ultimate decision to use a fixed-bed filter of diatomite. It was felt that data collected with such a filter would permit a more direct comparison of the filtration results obtained with the results obtained using other media in fixed-bed filters.

The objectives of this study placed no restrictions on the filtration system to be employed. The choice of particulate matter, filter media, and filter design, however, did. It became apparent early in the study that a certain combination of influent particulate matter concentration, amount of filter media (depth), flow rate and grade of diatomite media would best demonstrate the effect of 601 coatings on particulate matter removal patterns. The most dramatic evidence of the effect of the coating on solids removal would exist when no solids removal is observed using uncoated media and 100 percent solids removal is observed using the same media coated with 601. Therefore, an attempt was made to design a filtration system which would provide dramatic evidence such as this and yet would economize the time and effort necessary to complete the study.

Evaluation of the filtration process

The fundamental data which had to be collected to evaluate the filtration process for the system used in this study included observation of the changes in particulate matter concentration and the head loss across the filter cake. Measurements of these parameters at any given time during a filter run will provide an indication of the removal efficiency (the fraction of applied material retained in the filter cake) and the hydraulic characteristics of the filter cake and removed material at the moment the observation was made. If regular periodic measurements are taken during the course of a filter run, the total amount of material removed and the changes in hydraulic characteristics resulting from the removal of material can be predicted. An arithmetic plot of the ratio of solids concentration in the effluent to the solids concentration in the influent (the fraction of material passing through the filter cake) versus time of filtration is referred to in this study as an effluent history curve. The shape of an effluent history curve can be used to predict the predominant removal mechanisms at work during the run (12, 25, 32). An arithmetic plot of head loss across a filter cake versus time of filtration, referred to as a head loss build up curve, can also be used to predict the predominant removal mechanisms (12, 25). In the interpretation of the results of this study, both effluent history and head loss build up curves were utilized in elucidating filtration removal patterns.

Of the multitude of variables which can affect the filtration process, and which are described in the background chapter of this thesis starting on page 5, only a few were evaluated in this study. The remaining variables were held constant insofar as possible.

The most significant variable in the present study was the amount of 601 coating material used to coat the diatomite filter media. It was anticipated that an improvement in removal of particulate matter on coated diatomite should result from adsorption of the suspended colloidal solids onto the 601 coating. Therefore, if such adsorption in fact occurred, increasing the amount of coating material present should increase the amount of particulate matter removed. Of course, since only a limited amount of filter media surface area existed in a given filter cake, there was a limit to the amount of coating material which was exposed at the filter media surface. Previous studies have indicated that 601 will adsorb on diatomite filter media in increasing amounts up to a maximum amount (8, 45). These observations were based on electrokinetic measurements of coated diatomite filter cakes. The electrokinetic, or zeta, potential of a diatomite filter cake changes uniformly from a negative value when no coating is present to a maximum positive value at some determinable level of coating (see Figure 37 in the Appendix). For increasing levels of coating beyond the level which produces the maximum positive zeta potential the zeta potential does not change significantly. It was assumed, and reasonably so, that the lowest level of coating, represented by the weight of coating material per weight of diatomite, at which the maximum zeta potential was observed corresponds to the maximum amount of coating material which could be adsorbed on the diatomite using the coating methods employed used in these studies (8, 45).

Varying the level of coating from zero to the maximum effective level will vary the apparent zeta potential of the partially coated diatomite filter media surface and should vary the removal capacity of a coated filter cake. It might also vary the rate of removal of particulate matter by increasing the number of adsorption sites. To evaluate these possible effects, filtration runs were conducted with various levels of 601 coatings on the filter media.

Since the active ingredient of 601 is a polyalkyl polyamine, the charge density of this material should be pH dependent. In acidic solution a large positive charge density should exist, and in alkaline solutions the charge density will be small. The zeta potential of diatomite filter cakes coated with 601 at the maximum level possible obtained with the methods used varies from a maximum positive value at a pH of about 6 to zero at a pH of about 7 - 7.5, and becomes increasingly negative for pH's increasing above 7.5 (45). See Figure 38 in the Appendix.

The positive charge density of a polyamine decreases as the solution pH increases from about 6. Therefore, if the adsorption removal capacity of a 601-coated diatomite filter cake is affected by the charge density of the adsorbed polyamine, then filtration runs conducted at various solution pH's should establish the magnitude of this effect.

In anticipation of observing adsorptive removals a series of filtration runs were planned in which only the depth of the coated filter cake, which for a constant filter cake cross-section amounts to varying the weight of filter media in the filter cake, would be varied. If adsorptive removals predominate in these runs, the amount of particulate matter removed should be proportional to the weight of filter media in the filter cake. If the amount of particulate matter removed is independent of filter cake depth, then some removal mechanism other than adsorption predominates.

LABORATORY APPARATUS AND PROCEDURES

Bench-Scale Filter and Appurtenances

The bench-scale filtration apparatus included a filter cell designed to contain the filter cake, a precoat pot used to coat the filter media with 601, a flow meter for controlling the suspension flow rate to the filter cake, a manometer system for measuring head loss across the filter cake, conductivity cells on both sides of the filter cell for measuring suspension conductivity, and a precoating pump and flow meter used to form the filter cake in the filter cell. The influent suspension jugs used to store the suspension of the particulate matter to be filtered were located about 12 feet above the filter cell. Gravity flow was provided through the system. A constant-temperature water bath was used for maintaining the influent suspension at a constant temperature. Figure 2 is a general schematic diagram of the apparatus used.

The following discussion includes a detailed description of the various components of the filtration system and the instruments used for measuring filtration parameters.

Filter cell

Figure 3 shows the construction details of the filter cell used. The design provided for the deposition of a layer or cake of diatomite on a horizontal filter septum. The significant features of the filter, which was made of clear plexiglass, were the inlet and outlet taps, the pressure taps on each side of the filter cake, the inlet flow diversion ball and two-piece construction incorporating a pressure seal between the two cell chambers. The flow to the filter inlet chamber was

Figure 2. Schematic flow diagram of the filtration apparatus used in this study

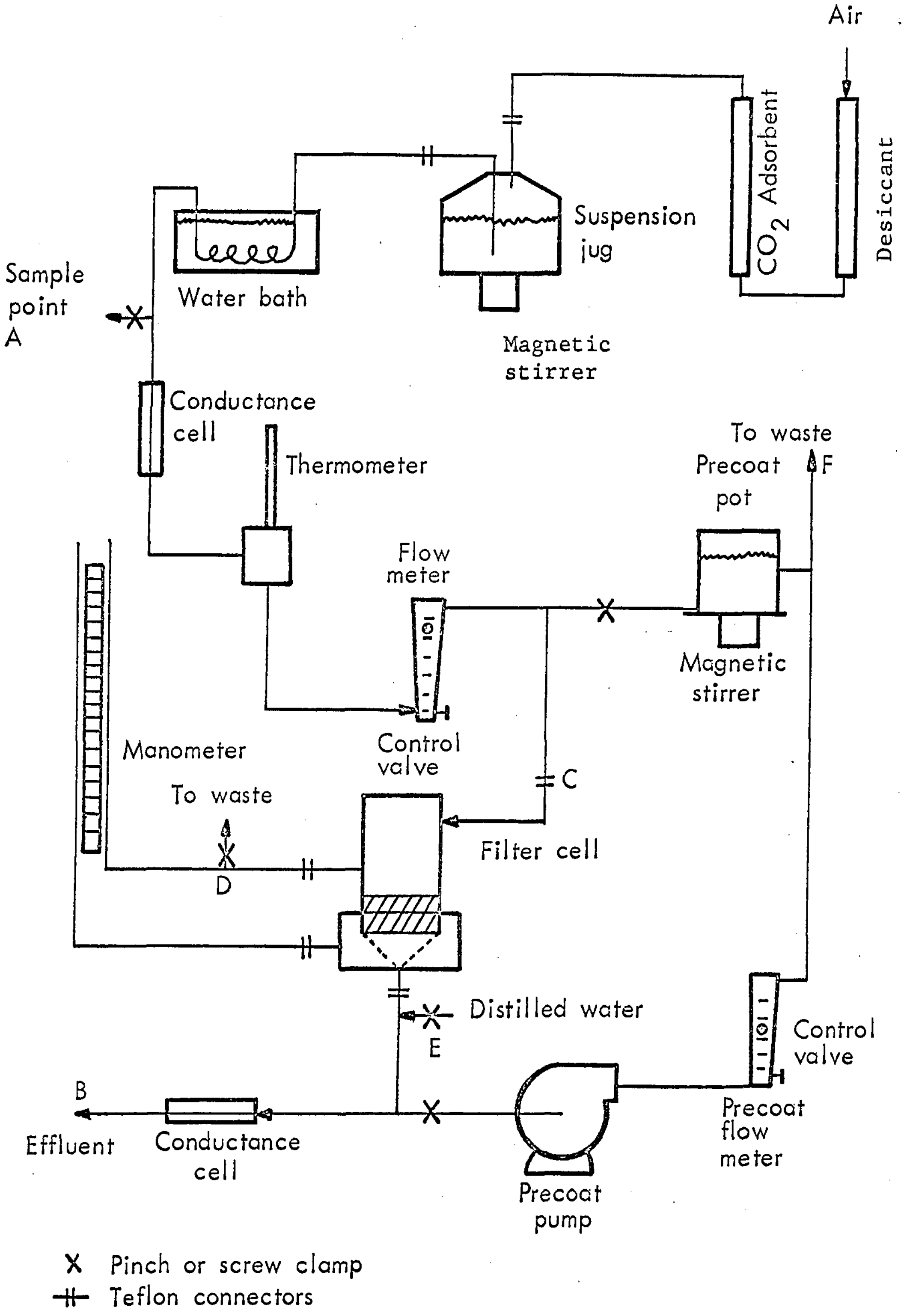
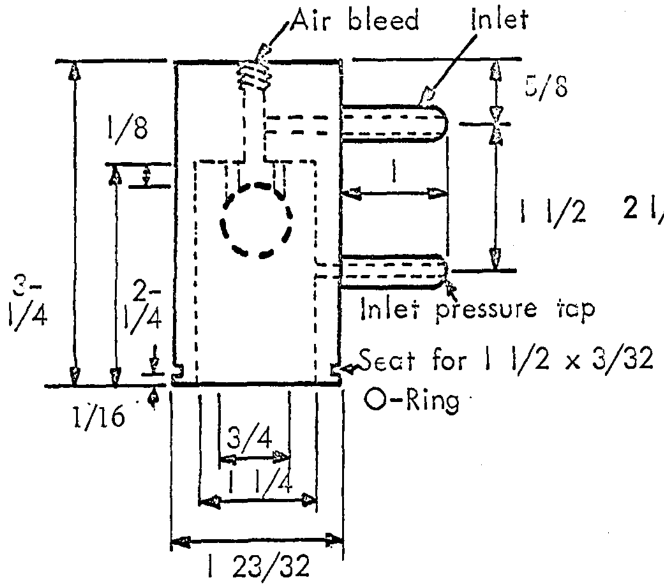
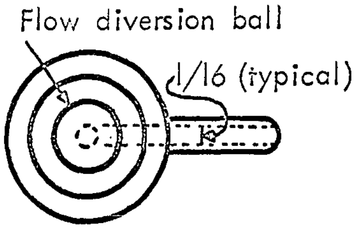

Air
Desiccant
CO_2 Adsorbent
Suspension jug
Magnetic stirrer
Water bath
Sample point A
Conductance cell
Thermometer
To waste
F
Precoat pot
Magnetic stirrer
Flow meter
Control valve
Manometer
To waste
D
C
Filter cell
Distilled water
E
B
Effluent
Conductance cell
Precoat pump
Control valve
Precoat flow meter
X Pinch or screw clamp
-||- Teflon connectors

Figure 3. Construction details of the plexiglass filter cell

Top Half

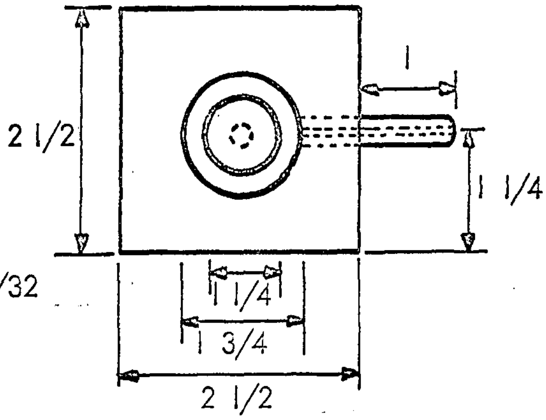


Side view

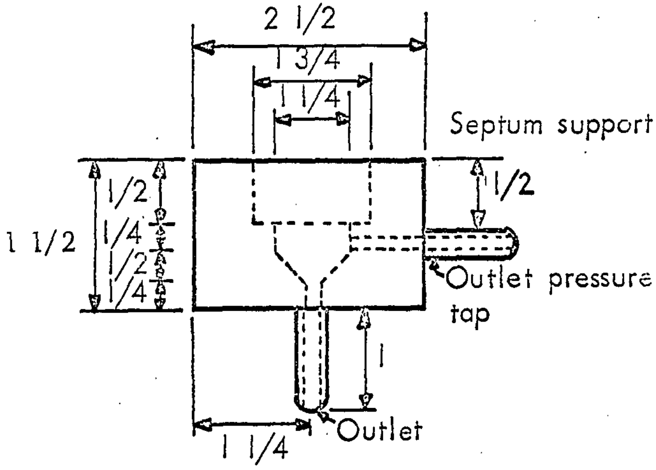


Bottom view

Bottom Half



Top view



Side view

All dimensions are in inches

1 inch

vertically downward and a flow diversion ball was employed to prevent gross short-circuiting of flow to the filter cake which might produce scouring of the filter cake already formed. There was no special reason for choosing a ball instead of a flat plate or other diversion device. A 100-mesh stainless steel wire screen was used as the septum to support the filter cake. It was held in place between the top and bottom parts of the filter cell. A screw-clamping device served to hold the two parts of the filter cell together during use. This clamping device was machined from aluminum stock. The pressure seal between the parts of the filter cell was provided by an O-Ring fitted into the outer circumference of the top part of the filter cell. An air bleed was provided on the top of the filter inlet chamber for releasing air entrapped in the filter cell during the precoating operation.

The two-piece construction and the quick-opening screw-clamping device made it relatively easy to remove the dewatered filter cake from the cell after a filter run was completed. Observation of the dewatered filter cake made it possible to measure the depth of filter cake and, most important of all, to observe any preferential removal of particulate matter at the surface of the filter cake. The 1 1/4 - inch I.D. of the filter cake chamber provided a filter cake surface area of 0.00852 ft^2.

Precoat pot

The precoat pot was used to mix the diatomite and 601 to form the cationic polyelectrolyte coating on the filter media prior to and during the process of forming the filter cake. This device was made of clear plexiglass tubing with a 3-inch I.D. and 4-inch length. The walls were 1/4 - inch thick. A 4 1/2 - inch by 4 1/2 - inch by 1/2 - inch plexiglass block was cemented with plexiglass solvent to one end. The outlet from precoat pot was tangent to the bottom whereas the inlet entered 3 inches from the bottom. The precoat pot was placed on a magnetic stirrer (Magnestir, Catalog No. 52617, Chicago Apparatus Company). A small magnetic stirring bar was placed in the precoat pot to keep the diatomite in suspension during both the 601 coating and the precoating operations.

Flow meter

The flow rate was observed and controlled using a rotameter (Brooks Instrument Company, Inc., Hatfield, Pa.). Two rotameter tubes were employed. The suspension flow was controlled with a tube of size R-215-D which had a maximum flow capacity of about 35 ml/min. Increased precision in observing the flow rate was obtained by using three separate 1/8 - inch diameter floats (pyrex glass, stainless steel, and carboloy) which were all contained in the rotameter tube at the same time. The precoating flow rate was controlled using a rotameter tube of size R-2-15-C which had a maximum capacity of about 340 ml/min using a 1/8 - inch diameter carboloy float.

Manometers

The head loss or pressure drop across the filter cake was measured using a manometer. A positive pressure of about 15 cm of water was maintained during all runs on the outlet side of the filter cake. When the head loss build up was not expected to exceed about 100 cm of water, an open end water manometer was employed. This manometer consisted of two 8-mm pyrex glass tubes connected to the filter cell pressure taps and held on either side of a white meter stick in a vertical position.

When head losses greater than 100 cm of water were anticipated, a differential manometer was connected to the filter cell pressure taps. This manometer contained a red colored fluid with a specific gravity of 2.94 at 20°C (Indicating Fluid No. 294, Part No. 2992, King Engineering Corporation, Ann Arbor, Michigan). The differential manometer used (50 inch Standard Cleanout Manometer, The Merian Instrument Company, Cleveland, Ohio) had a maximum capacity of 50 inches of red fluid, or 246 cm of water.

Constant temperature water bath

The temperature of the filter influent was held constant by use of a constant temperature water bath (Magni Whirl Utility Bath, Model No. MW 1152SSA-1, Blue M Electric Company, Blue Island, Illinois). This device had a 6-liter liquid reservoir which was maintained at any given temperature with a temperature variation of $\pm$ 0.05°C. A four-foot coil of 8-mm pyrex glass tubing through which the influent suspension passed was submerged in the water bath. Since room temperature varied as much as 6-8°C in a given working period, some adjustment of water bath temperature was necessary. After flow equilibrium was established, the temperature variation during a single filter run seldom exceeded a few tenths of a degree centigrade.

The influent temperature was measured in a special temperature block made from a piece of 1 3/4 - inch by 1 3/4 - inch by 2 1/2 - inch plexiglass with a 3/4 - inch diameter hole centered in the piece and running along the major dimension. Entering and leaving this 3/4 - inch chamber were taps similar to those on the filter cell. A 0-30°C thermometer graduated in 0.1°C was inserted in a rubber stopper and placed in the 3/4 - inch diameter hole with about 1 3/4 - inches of the mercury bulb and stem in the flowing liquid.

Conductivity cells and bridge

Influent and effluent resistivities were determined by passing the flow through influent and effluent conductivity cells (Models D02 and A01 respectively, Industrial Instruments, Inc., Cedar Grove, Essex County, New Jersey). The cells, located as shown in Figure 2, had cell constants, determined with standard solutions of KCl at 25.0°C, of about 0.198 and 0.101 cm^{-1}.

Resistances of the cells were measured using a manually-balanced AC Wheatstone bridge supplied with bridge current at 1000 cps from a vacuum tube oscillator (Model RC-16B2, Industrial Instruments, Inc., Cedar Grove, Essex County, New Jersey). Null point was visually observed using an electron ray "eye" tube null indicator.

Precoat pump

A small pump was employed during precoating. The pump had a shut-off head of 11.8 feet of water and a capacity of 5.0 gpm at one foot of water outlet pressure (Model 2E-38N, Little Giant Pump Company, Oklahoma City, Oklahoma).

Influent suspension jugs

Influent suspensions were prepared and stored in a 20-liter pyrex glass jug. The jug was supported on a magnetic stirrer (Magnestir, Catalog No. 52617, Chicago Apparatus Company). A magnetic bar was placed in the jug to provide for gentle mixing of the jug contents. The suspension withdrawn from a jug during the course of a filter run was replaced with air which had passed through a desiccant column (anhydrous $CaSO_4$) and a CO_2 adsorbent column (Ascarite, Arthur H. Thomas Company, Philadelphia, Penn.).

Miscellaneous

The filter cell and appurtenances were connected with 1/4 - inch I.D. Tygon tubing. Where tees were needed, 1/16 - inch I.D. Teflon tees were used. To facilitate removing the filter, manometers, influent suspension jugs and conductivity cells from the apparatus, 1/16 - inch I.D. Teflon connectors were utilized. Screw or pinch clamps were used to block the flow of liquid through any given line.

The various units in the filtration apparatus were located on shelves, laboratory benches, or were attached to a pegboard frame. A schematic flow diagram of the filtering system is presented in Figure 2. The influent suspension jugs were located about 12 feet above the filter cell.

Turbidimeter

Clay concentrations in the influent and effluent were determined indirectly using a bench-scale laboratory turbidimeter. The turbidimeter used was a nephelometric or light scattering device (Hach Laboratory Turbidimeter, Model 2100, Hach Chemical Company, Ames, Iowa). Light was passed upward through a flat bottomed, 30-ml, sample tube which contained a sample of the clay suspension. A constant portion of the light which struck the clay particles in suspension was scattered at a right angle to the incident light beam and received by a photo multiplier tube and converted into an electrical signal. The electrical signal was handled electronically so as to deflect a meter needle. This deflection was observed on a turbidity scale. The instrument was standardized before each observation with a turbid acrylic plastic rod furnished with the instrument.

The sample tube was handled from 30-50 times during a single filter run and sometimes as many as 120 times in a series of runs. Though the tube was well rinsed with distilled water, it was observed that after this prolonged handling some skin oils collected on the outside of the sample tube. The sample tube was cleaned, therefore, after each series of runs with a dilute mild detergent solution.

Spectrophotometer

When a colored coffee compound was being filtered, the concentration of this material was determined by photometric analysis. A spectrophotometer designed for transmittance and absorbance measurements in the 300-1000 millimicron spectral range was used (Model B, Beckman Instruments, Inc., Fullerton, California). To increase accuracy, two sets of absorption cells were used. Cells with a 1-cm light path were used with concentrated solutions and cells with a 5-cm light path were used with more dilute concentrations.

pH meter

Observations of pH were made using a standard pH meter with standard-sized glass and reference electrodes (Model 9600 Zeromatic Beckman Instruments, Inc., Fullerton, California). Manual temperature compensation adjustments were made. The electrodes were checked according to the manufacturer's recommendations and found to be satisfactory. The instrument was standardized prior to each filter run. The pH measurements were made using 70-90 ml of the sample held in 100 ml beakers.

Procedures

Clay suspensions

A gravity settling procedure was employed to prepare a fine fraction stock clay suspension. Sixty-eight grams of Black Hills clay or Ball clay, or 17 grams of Panther Creek clay were placed in 20-liter pyrex glass jugs containing 17 liters of distilled water. The mixture was then air-agitated for about 24 hours. The jugs were then stoppered and allowed to sit quiescently in the laboratory for several weeks. The exact period of settling varied for most runs and will be referred to when the test results from any series of runs are presented.

Prior to a filter run, about 6 1/2 inches (about 9 liters) of supernatant was siphoned from the settled suspensions and gently air-mixed for three minutes. The pH and turbidity of the mixed supernatant or stock clay suspension was observed and recorded. Two 200-ml samples of the stock clay suspension were saved for determination of the clay concentration by gravimetric analysis. When a specific turbidity was desired, portions of the stock clay suspensions were added to a tared 20-liter jug containing a known amount of distilled water. These suspensions were gently air-mixed for three minutes before observing turbidity. When the desired influent turbidity was obtained, a calibration curve was prepared for use with the Hach Model 2100 turbidimeter using 0, 20, 40, 60, 80, and 100 percent suspensions of the influent clay suspension diluted with distilled water. Linear calibration curves were obtained between the turbidity reading and the percent suspension, or clay concentration.

Coffee solutions

A solution of about 300 mg/l of instant coffee was passed through a 0.45 micron Millipore membrane filter and used to determine a spectral absorption curve for the coffee compound. There was less than 1 percent of light transmittance between a light wave length of 320 and 335 millimicrons. Above this wave length, the transmittance increased rapidly for small increases in wave length. A wave length of 325 millimicrons was used to determine a Beer's Law calibration curve for the colored coffee solutions. It was found that the natural logarithm of the percent transmittance was directly proportional to the coffee concentration.

During some preliminary tests with coffee solutions, it was observed that a biological growth appeared in the coffee solution after about 24 hours. To eliminate this undesirable contaminant, a stock solution of coffee was prepared and sterilized in an autoclave at about 14 $\mathrm{lb/in.}^2$ and 230°F for 25 minutes. In the preparation of the stock solution, about four grams of instant coffee were dissolved in four liters of distilled water. This solution was passed through #42 Whatman filter paper and then through an 0.8 micron Millipore membrane filter. After being autoclaved, this solution was stored on a laboratory shelf. No biological growth was observed after storage for four months. The concentration of this stock coffee solution (940 mg/l) was determined gravimetrically before and after this four-month period and no significant change in concentration was observed.

Filter operation

A set procedure was followed rigorously prior to starting a filter run. After the influent suspension had been prepared and placed in the flow system, the filter, tubing, and appurtenances from point A in Figure 2 forward were flushed with distilled water entering the system at point E. This procedure served as both a cleaning and an air-purging operation. About 200 ml of distilled water was then put into the precoat pot. The desired amount of 601 stock solution (about 1 gm/l) was then pipetted into the precoat pot and the pot contents were mixed with the magnetic stirrer. Then the diatomite to be coated with polyelectrolyte was added to the 601 solution during the mixing operation. When C-560[1] was used, a two-minute mixing period was employed to minimize degradation of the filter aid particles (see the Appendix). When Hyflo SuperCel[1] was used, a five minute mixing time was employed. This mixing step was used prior to precoating the filter regardless of whether or not 601 was present in the solution.

While the diatomite was being coated in the precoat pot, about 250 ml of influent suspension was flushed through all tubing and

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[1] Product of Johns-Manville Products Corp., Manville, New Jersey.

appurtenances up to the connector at point C. At the end of the mixing period the pump was turned on and the precoating operation was started. For one minute, flow was directed through a closed system consisting of the precoat pot-filter-pump-precoat flow meter-precoat pot-etc. Initially, some of the diatomite fines passed the 100 mesh septum and recycling brought these fines back to the precoat pot. After the one minute recycle period, the contents of the precoat pot were passed through the filter cell. The diatomite was retained by the filter septum and the suspension medium was wasted at point F. The walls of the precoat pot were then rinsed with distilled water. When only a few ml of liquid were left in the precoat pot, about 250 ml of distilled water were added to the precoat pot and flushed through the filter cake which had been deposited in the filter cell. This was done to wash any excess 601 from the filter inlet tubing and housing. The precoating and flushing was carried out at a flow rate of about 3.10 gpm/ft^2 (100 ml/min). Continuous observation of the precoat flow rate was necessary as some diatomite fines would become lodged in the needle valve and would have to be dislodged by gently tapping of this valve with a plastic rod. After precoating and flushing, the flow through the filter cake was stopped.

In the next step, the distilled water in the filter inlet housing and tubing was flushed out with the influent suspension. This was accomplished by wasting at point D. It was determined that a five minute flush at a flow rate of about 32 ml/min was adequate to build up the influent suspension concentration in the filter inlet housing to the level which existed in the influent suspension jug.

After these preliminary procedures were completed, filtration through the filter cake was commenced at the desired flow rate. The first 50 ml of effluent were wasted in order to eliminate diatomite fines which were, on occasion, observed in the first effluent sample. This bleed through of fines as flow was started up was evidently caused from relaxation of the filter cake when flow was stopped after precoating and the subsequent compaction of the filter cake during the start up of the filtration cycle. Flushing of the filter inlet housing and wasting of the first 50 ml of filtrate eliminated initial dilution effects.

During the filter run the only manipulations of the apparatus needed was an occasional adjustment of the flow rate and an infrequent adjustment of the thermostat switch on the constant-temperature water bath. Flow rate adjustment was necessary because there was a constant head loss across the entire system; hence, as the head loss through the filter cake increased the head loss through the control valve had to be decreased in order to maintain a constant flow rate. Each flow rate adjustment was in the range of zero to one percent the total flow rate.

Effluent samples used for making analyses of effluent turbidity and pH were collected and composited over short periods of time. Head loss and temperature were observed at the end of each compositing period. Intermittently during a run, influent and effluent resistances and the volumetric flow rate were observed.

The influent suspension turbidity or solution transmittance measured after a run were not significantly different than the turbidity or transmittance measured before the run. This observation indicated that the suspensions used were stable, at least during the filter run.

Particulate matter turbidity or transmittance and pH were measured for at least 3 to 4 samples of the influent suspension before and after each run.

Some uncertainty was incorporated in the effluent pH values observed because of the unbuffered suspensions used in this study. The maximum effluent compositing time was about ten minutes during which the CO_2 in the solution tended to reach equilibrium with the CO_2 in the atmosphere. An attempt was made to eliminate this uncertainty from the influent pH determinations by collecting 80-ml samples in about 3 to 4 seconds and observing pH readings after about 60 to 80 seconds of exposure to the atmosphere.

After the effluent turbidity data had indicated that the adsorptive removal capacity of the media had been exhausted (i.e., effluent turbidity approached influent turbidity), the filter run was terminated. Influent turbidity or transmittance and pH were then determined. The filter cell was then drained and removed from the apparatus. Air was sucked through the filter cake to dewater it. The depth of filter cake was determined by marking the side of the filter cell during the filter run, and by making a direct measurement of cake thickness after dismantling the filter cell and removing the dewatered filter cake.

The filter cell was then washed, rinsed and returned to the apparatus which was again flushed with distilled water. Another filter run could then be started. At least two, and in some cases six, filter runs were made with the same influent suspension. This was desirable since it would have reduced or possibly eliminated any effect on removal patterns which might result if tests in a series were made with influent suspensions prepared at different times.

In the test series in which suspension pH was changed between runs, the pH change was accomplished by adding a few drops of 0.83 N KOH or 1.2 N HCL to the gently mixing contents of the influent suspension jug.

Distilled water used in this study was prepared from softened Iowa State University tap water. The tap water was softened by an automatic zeolite water softener (Model PFA-7, Everpure, Inc., Oak Brook, Illinois). This water was then distilled in a Barnstead still (Barnstead Still and Sterilizer Company, Boston 31, Massachusetts). The distillate was stored in a stainless steel reservoir. The distilled water from this supply had a pH of about 5.7 and a resistivity of about 3000 ohm-meters or a conductivity of 3×10^{-6} mhos/cm.

PRESENTATION OF RESULTS

General Format

Table 1 is an example of how the data for a given filtration run were reported and analyzed. The observed or measured data are time of filtration (t), head loss (H), suspension temperature, influent and effluent resistivities (R_i and R_e), effluent pH (pH_e), and effluent turbidity measured in a sample composited over the time interval indicated (C_e'). Other data shown are the influent clay concentration (C_i), influent suspension pH (pH_i), flow rate (Q), weight of clean diatomite filter cake (W), and level of 601 coating. The reduced data presented in Table 1 are effluent clay concentration (C_e), the ratio of effluent to influent clay concentrations (C_e/C_i), the sum of incremental head loss increases $\Sigma(\Delta H)$, the incremental time rate of change of effluent clay concentration ($\Delta C_e/\Delta t$), milligrams of clay applied to the filter (mg_a), milligrams of clay retained in the filter during the time interval indicated (Δmg_r), and the accumulated milligrams of clay retained in the filter, or removed from the liquid $\Sigma(\Delta mg_r)$.

Values of mg_a were computed from the relationship, mg_a equals C_i Q t. Values of Δmg_r were computed from the relationship Δmg_r equals $(C_i - C_e)$ Q Δ t, where C_e is the effluent clay concentration of a sample composited over the time increment Δ t.

Values of filter cake permeability (K), computed from Equation 2 or 3, are not shown in Table 1. For a given filter run where Q, L, μ, γ_w, and A, as defined in Equation 2, were constant, the value of K determined using Equation 2 will be dependent on H only. To give an indication of the

Table 1. Example of recorded and reduced data for a Black Hills clay filter run
C_i = 156 mg/l, pH_i = 6.10, Q = 16.4 ml/min (0.508 gpm/ft^2)
4.00 gm Hyflo SuperCel with 2.00 mg 601/gm Hyflo SuperCel

Time t (min)	Head loss, H (in. of H_2O)	Temp (^oC)	Resistivity R_i	Ω·m R_e	pH_e	C'_e (turb)	C_e mg/l	$\frac{C_e}{C_i}$	Σ(Δ H)	$\frac{\Delta C_e}{\Delta t}$ (mg/l/min)	mg_a	Δ mg_r	Σ(Δ mg_r) (mg)
0	25.2	25.1	---	---					0	---	0		0
					<—6.58—>	.35	2	.01				5.05	
2	29.5	25.1	498	---					4.3	.5	5.12		5.05
						.30	1	.01				5.08	
4	34.4	25.2	---	---					9.1	1.5	10.2		10.1
						.40	4	.03				4.99	
6	37.2	25.2	---	---					12.0	14	15.4		15.1
					<—6.87—>	1.35	32	.20				4.07	
8	39.6	25.1	---	---					14.4	36	20.5		19.2
						3.80	104	.67				1.71	
10	41.5	--	---	---					16.3	15	25.6		20.9
						4.80	134	.86				.72	
12	43.0	25.1	---	---					17.8	3.5	30.7		21.6
					--	5.05	141	.90				.49	
14	44.5	25.1	---	---					19.2	.5	35.8		22.1
					--	5.10	142	.91				.46	
16	46.5	25.1	490	437					21.4	0	41.0		22.6
					6.72	5.10	142	.91				.92	
20	49.0	25.1	---	---					23.9	0	51.2		23.5
					6.69	5.05	141	.90				1.23	
25	52.8	25.1	---	---					27.4	0	64.0		24.7
					6.58	5.15	144	.92				.99	
30	56.3	25.1	---	---					31.0	0	76.7		25.7
					6.56	5.10	142	.91				.99	
35	59.8	25.1	490	443					34.5	0	89.5		26.7
					6.47	5.10	142	.91				.99	
40	62.7	25.1	---	---					37.5		102		27.7

effect of 601 coatings and the process of forming a filter cake on the permeability of the diatomite filter cakes, values of K will be given. The initial head loss at the start of the run (H at time zero) was used to compute K. This initial permeability will be represented by the symbol K_o.

The filtration results will be presented in the order that the different clay and coffee suspensions were studied. For each suspension, the results will be presented in sections which will describe the series of runs conducted to evaluate the effect of a pertinent variable on removal patterns. In the report of each series of runs the preparation of the influent suspensions will be discussed briefly and then the pertinent operational variables will be listed (e.g., level of coating, K_o, temperature, pH_i and pH_e, R_i and R_e, and C_i). The results of the series of runs will then be presented in three types of graphs - - effluent history curves, material removed versus material applied curves, and head loss increase versus material removed curves.

Effluent history curves will be presented as plots of C_e/C_i, a dimensionless term, versus the time of filtration at which the value of C_e was determined. For example, see Figure 4. Any point on a given curve represents the fraction of influent material passing the filter cake at the time indicated. As previously noted, effluent samples were composited over definite time intervals, Δt. Effluent history data could, therefore, be more realistically presented as a bar diagram. However, in the plotting system used, the value of C_e/C_i for a given time increment was plotted at the mid-point of this time increment and the points were connected by straight lines. This procedure will represent more closely the uniform change in C_e/C_i which would have been observed if the effluent concentration had been monitored continuously.

In any increment of time, Δ t, the amount of material removed by the filter cake (Δ mg_r) will be equal to (1 - C_e/C_i) C_i Q Δ t. The total amount of material removed up to a given time of filtration will be the sum of the incremental removals or $\Sigma(\Delta$ $mg_r)$. The total amount of material removed will be presented by plotting $\Sigma(\Delta$ $mg_r)$ versus the amount of material applied to the filter cake, mg_a. Recall that mg_a is equal to C_i Q t. Figure 5 shows typical plots derived from an analysis of the data in Figure 4. The value of $\Sigma(\Delta$ $mg_r)/mg_a$ for the coordinates describing any data point is the ratio of the total amount of material retained by the filter cake to the total amount of material applied to the filter cake. Obviously, a value of 1.00 indicates 100 percent removal of particulate matter.

When suspended solids are retained in a filter cake, the void volume in the filter cake is reduced and the constrictions in the filter media pores through which the liquid flows can be partially or completely blocked. For a constant flow rate, Q, this can result in increasing interstitial velocities which increases the energy required to maintain a constant Q. Under these conditions, the head loss build up across a filter cake which is removing suspended solids from suspension gives an indication of these increasing energy requirements. The relationship between the head loss build up and the amount of material removed will be shown by plotting the sum of incremental head loss increases $\Sigma(\Delta$ H) versus the sum of incremental amounts of material removed $\Sigma(\Delta$ $mg_r)$ which caused the head loss increase. Typical plots are shown in Figure 6.

Removal of Panther Creek Clay

Preliminary runs using Panther Creek clay suspensions, settled for 2-3 weeks, indicated that gross surface straining occurred when stock clay suspensions were filtered through C-560 filter cakes. The influent concentrations, C_i, of these influent clay suspensions used were in the range of 75-110 mg/l. The basis for concluding that surface straining occurred was the observation that exponential head loss build up curves (H vs t) resulted. The appearance of the dewatered filter cakes confirmed the existance of surface straining since the filter cakes were discolored in a thin layer at the surface. When the stock clay suspensions were diluted with distilled water to a clay concentration of about 20 mg/l, no gross surface straining was observed. Indeed, about 95 percent of the clay passed through 1/2-inch deep C-560 filter cakes when filtered at a filtration rate of 1 gpm/ft^2. Several series of runs were then made to evaluate the effect of pertinent variables, using a C_i of about 20 mg/l, a filtration rate of about 1 gpm/ft^2 (32.3 ml/min), and 3.50 gm C-560 filter cakes (15/32-inch deep cakes).

Effect of varying the level of 601 coating

A series of five runs was made using coated C-560 with coating levels of 0.00, 0.10, 0.20, 0.30, and 0.50 mg 601/gm C-560. One influent suspension was used in all five runs. It was prepared from a stock clay suspension (settled 53 days) having a Panther Creek clay concentration of 53.2 mg/l. The stock clay suspension was diluted with distilled water to provide an influent clay concentration, C_i, of 22.6 mg/l. A filtration rate of 1.00 gpm/ft^2 (32.3 ml/min) and filter cakes containing 3.50 gms of

C-560 (0.960 lb/ft^2) were used in this series. The average operational variables for the five runs were:

$\frac{\text{mg 601}}{\text{gm C-560}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. °C	pH_i	pH_e	R_i $\Omega \cdot m$	R_e $\Omega \cdot m$
0.50	1.07	22.6	25.0	5.9	6.1	2030	1960
0.30	1.25	22.6	25.4	6.0	6.1	2050	1980
0.20	1.25	22.6	25.0	6.0	6.1	2130	2060
0.10	1.04	22.6	24.8	6.1	6.1	2190	2120
0.00	1.25	22.6	24.8	6.1	6.1	2240	2170

The results of this series of runs are presented in Figures 4, 5, and 6. Figure 4 shows the effluent history curves for this series of runs. Coating C-560 filter cakes with increasing amounts of 601 significantly increased the amount of Panther Creek clay which was removed. The relationship between the total amount of clay removed and the total amount of clay applied is shown in Figure 5. This figure indicates more clearly that increasing the level of the 601 coating results in increasing the amount of the clay removed. Figure 6 shows the accumulated head loss increase resulting from the accumulated amounts of clay removed. The head loss increase per unit of clay removed is somewhat uniform until a certain amount of clay has been removed. Thereafter the rate of the head loss increase per unit of clay removed is significantly higher. This indicates that the manner in which the clay is removed in the filter cake before the discontinuity is different from the manner in which the clay is removed after the discontinuity. Comparison of data in Figures 5 and 6 indicates

Figure 4. Effluent history curves in a series of runs using Panther Creek clay where the level of coating was varied

W = 3.50 gm C-560

Q/A = 1.00 gpm/ft^2 (32.3 ml/min)

C_i = 22.6 mg/l

pH_i = 6.0

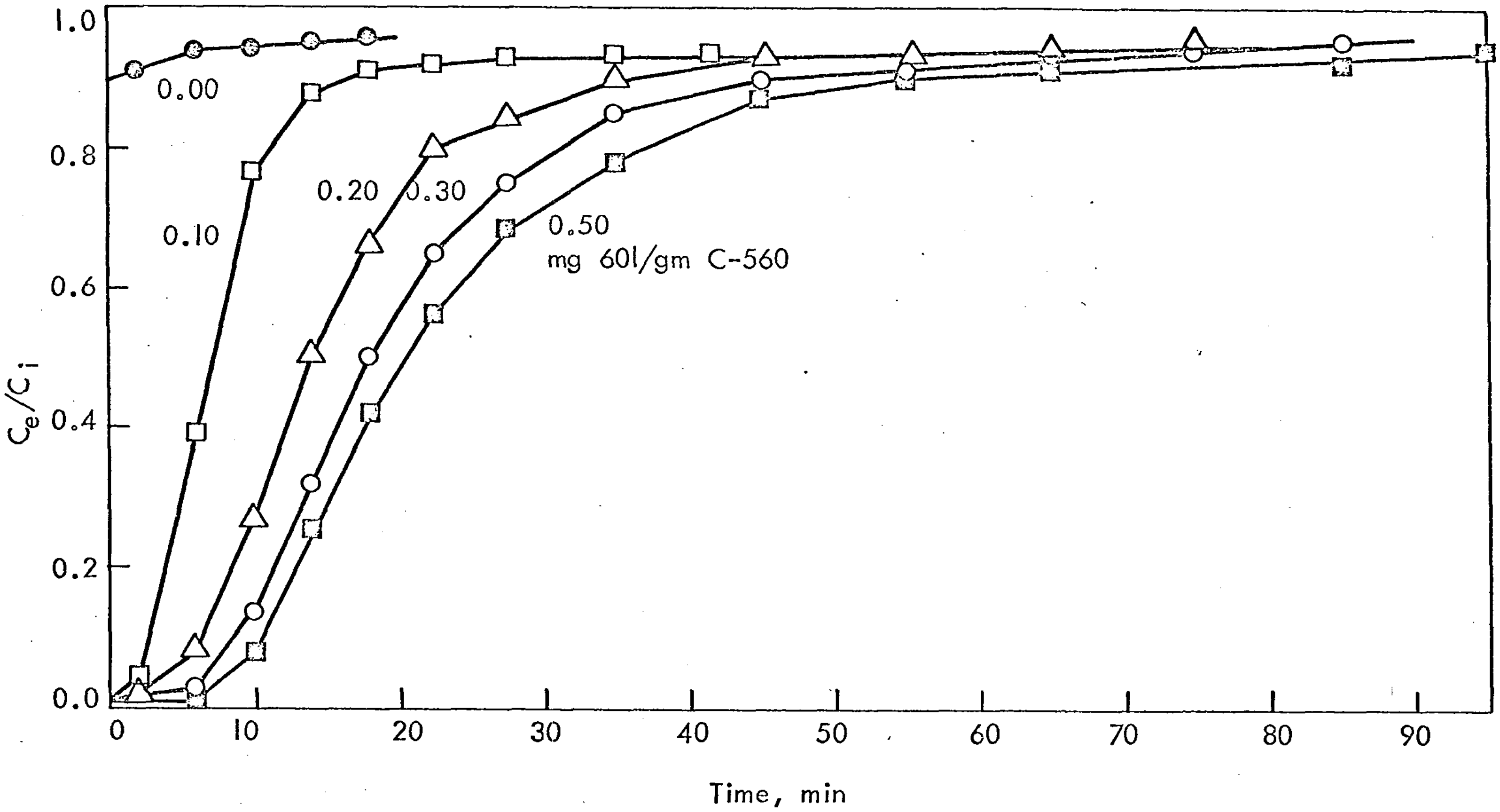

1.0
0.8
0.6
0.4
0.2
0.0
C_e/C_i
0
10
20
30
40
50
60
70
80
90
Time, min
0.00
0.10
0.20
0.30
0.50
mg 60l/gm C-560

Figure 5. Clay removed versus clay applied in a series of runs using Panther Creek clay where the level of 601 coating was varied (0.73 mg_a in one minute of filtration time)

W = 3.50 gm C-560

Q/A = 1.00 $\mathrm{gpm/ft}^2$ (32.3 ml/min)

C_i = 22.6 mg/1

pH_i = 6.0

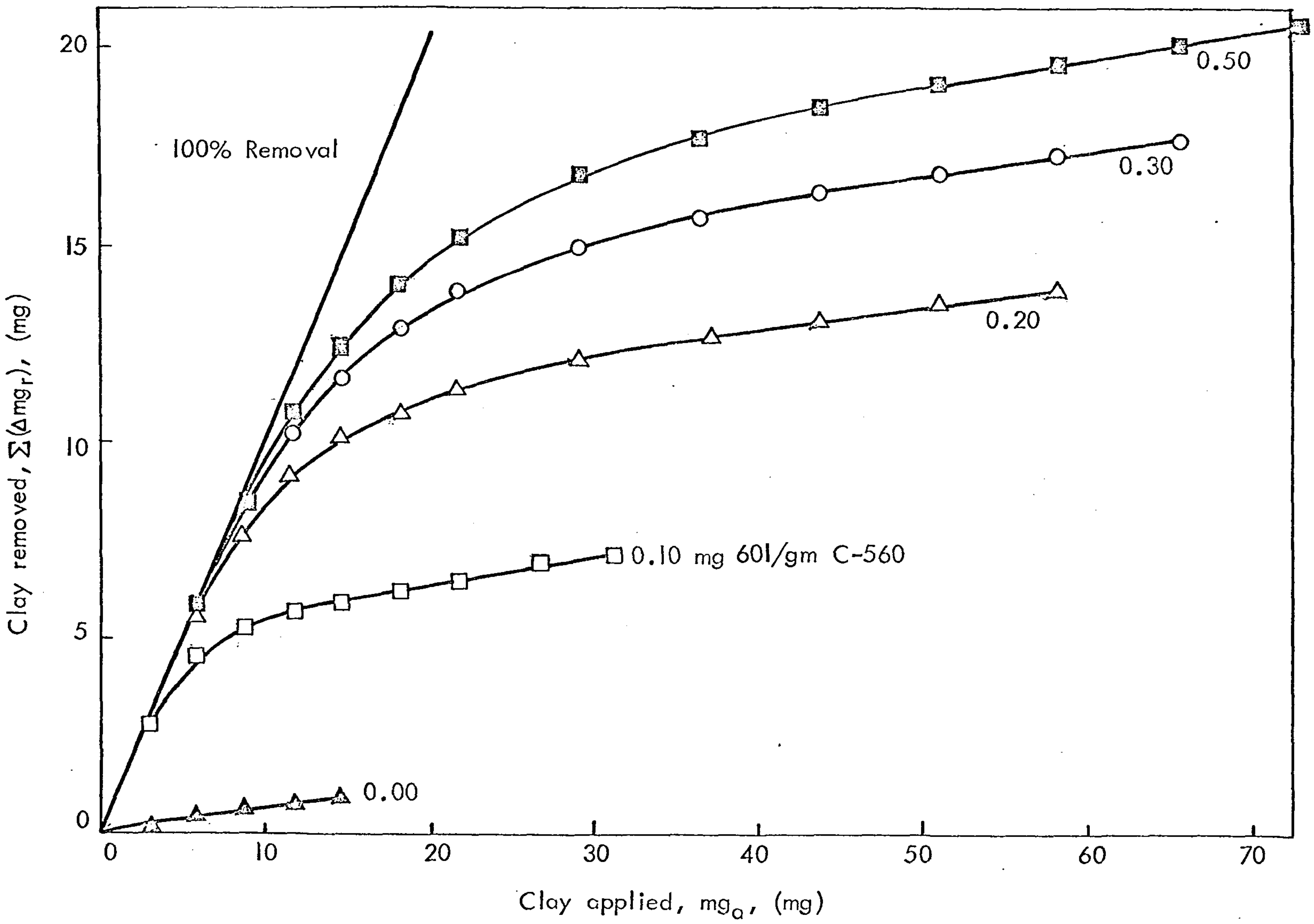

100% Removal
0.50
0.30
0.20
0.10 mg 601/gm C-560
0.00
Clay removed, $\Sigma(\Delta mg_r)$, (mg)
0
5
10
15
20
Clay applied, mg_a, (mg)
0
10
20
30
40
50
60
70

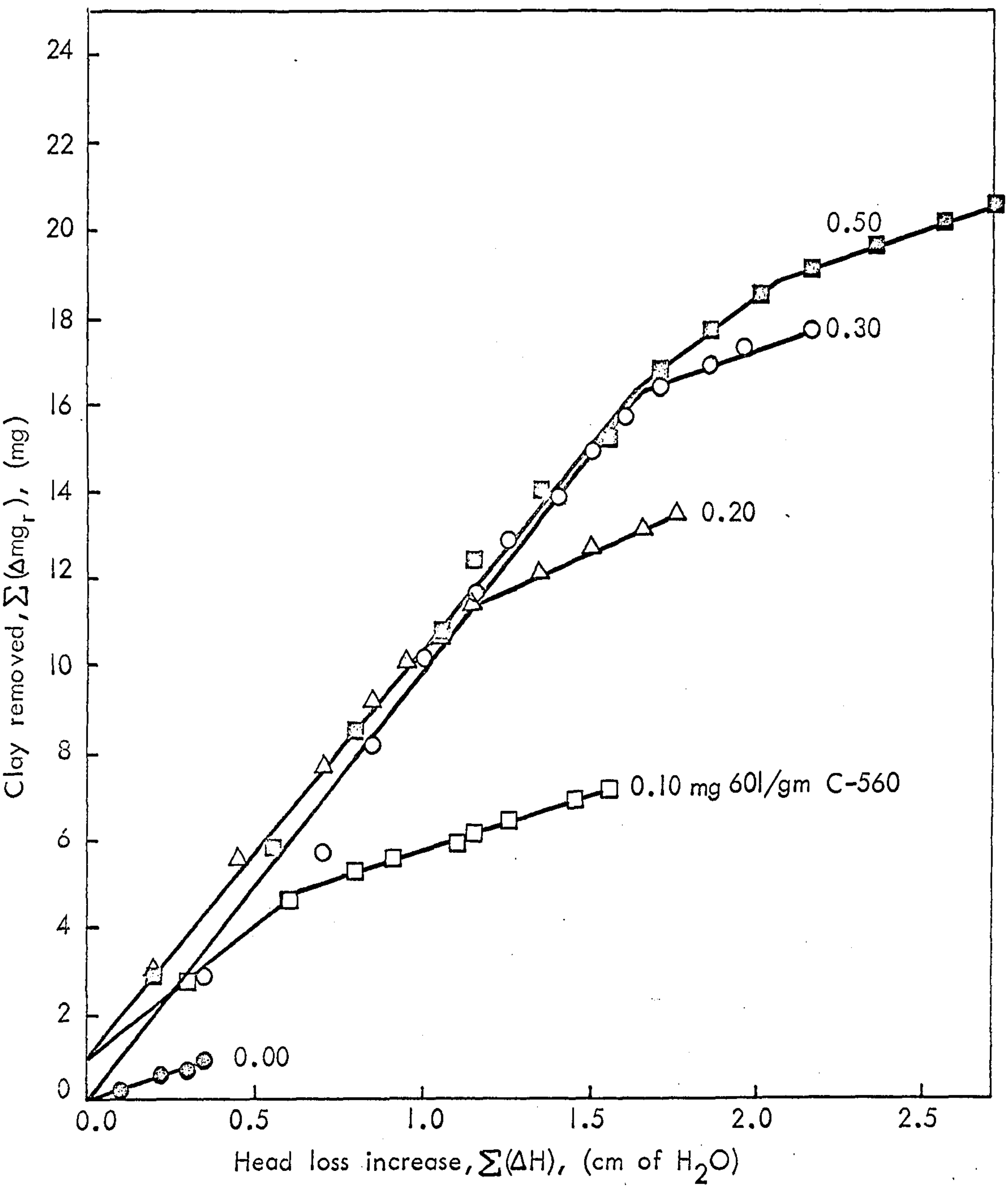
Figure 6. Head loss increase versus clay removed in a series of runs using Panther Creek clay where the level of coating was varied (corresponds to data shown also in Figures 4 and 5)

$W = 3.50$ gm C-560

$Q/A = 1.00$ gpm/ft^2 (32.3 ml/min)

$C_i = 22.6$ mg/l

$pH_i = 6.0$


Clay removed, $\sum(\Delta mg_r)$, (mg)
0
2
4
6
8
10
12
14
16
18
20
22
24
0.0
0.5
1.0
1.5
2.0
2.5
Head loss increase, $\sum(\Delta H)$, (cm of H_2O)
0.50
0.30
0.20
0.10 mg 601/gm C-560
0.00

that the amount of clay removed when the head loss increase per unit clay removed changes abruptly (Figure 6) corresponds approximately to the point where the change in clay removed per unit clay applied becomes constant (Figure 5). The significance of this observation will be developed in the next chapter of this thesis.

Effect of varying the suspension pH

A series of five runs was made with influent suspension pH values of 5.9, 6.5, 6.9, 7.9, and 9.2 to evaluate the effect of pH on the removal patterns of Panther Creek clay filtered through a coated C-560. A filtration rate of 0.99 gpm/ft^2 (31.8 ml/min) and filter cakes containing 3.50 gm of C-560 coated with 0.40 mg 601/gm C-560 were used in this series of runs. This level of coating was used because it provided significant clay removal at a pH of 6.0 (see Figure 5).

A stock clay suspension of Panther Creek clay (settled 53 days) which had a clay concentration of 44.6 mg/l was diluted with distilled water to provide an influent clay suspension of 22.9 mg/l and a pH of 5.9. The influent suspension pH was changed to the levels used in each run by adding a few drops of 0.83 N KOH to the influent suspension. No attempt was made to control the ionic strength of the influent suspensions which increased slightly as KOH was added. The average operational variables in the five runs are shown below.

As mentioned in the last chapter, the significance of effluent pH data is in doubt because of the exposure of the unbuffered effluent suspension samples to the atmosphere during the period the composite samples were collected.

Figure 7. Effluent history curves for a series of runs using Panther Creek clay where the influent suspension pH was varied

Level of coating = 0.40 mg 601/gm C-560

W = 3.50 gm C-560

Q/A = 0.99 gpm/ft^2 (31.8 ml/min)

C_i = 22.9 mg/1

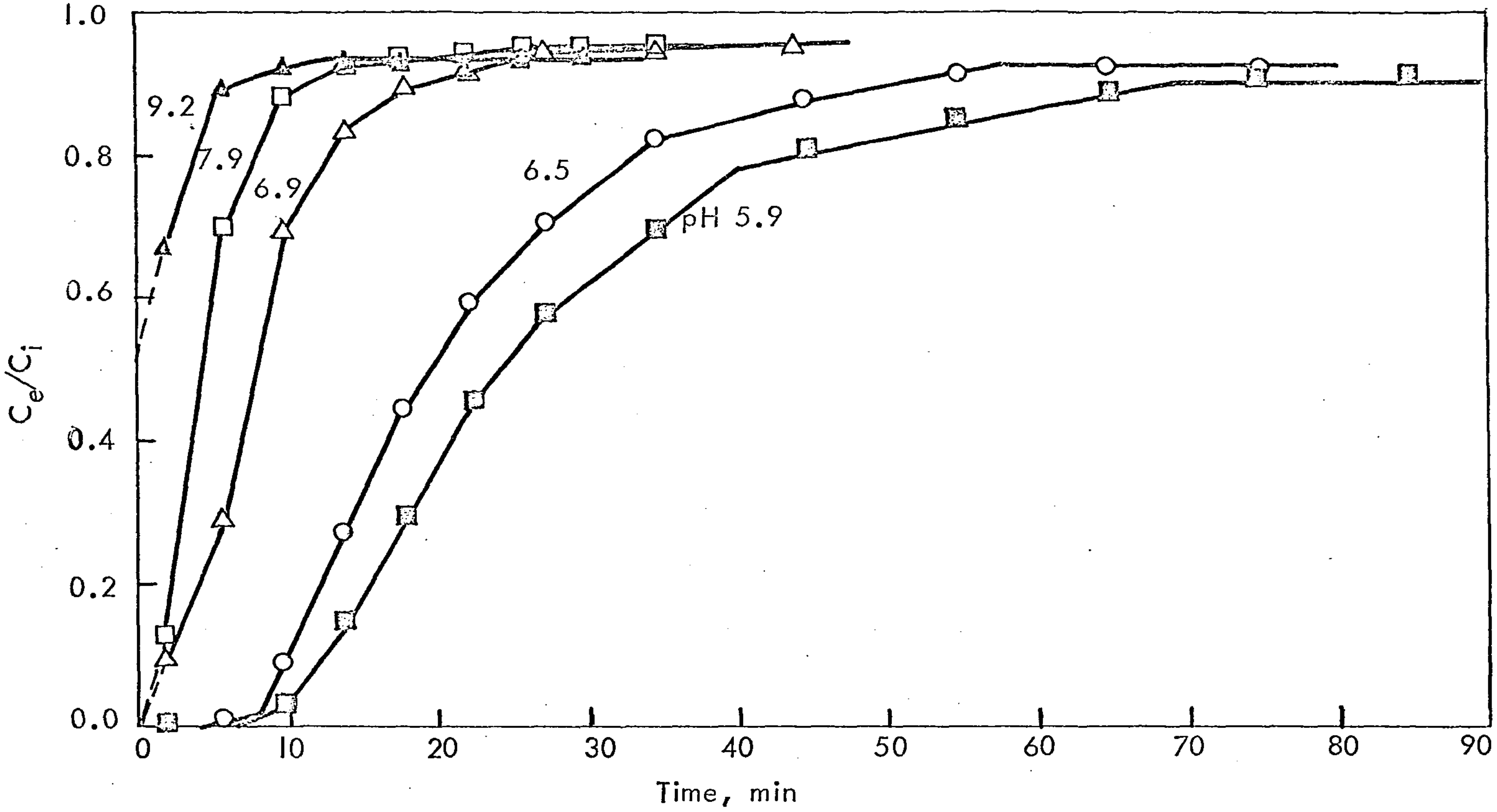

1.0
0.8
0.6
0.4
0.2
0.0
C_e/C_i
0
10
20
30
40
50
60
70
80
90
Time, min
9.2
7.9
6.9
6.5
pH 5.9

Figure 8. Clay removed versus clay applied in a series of runs using Panther Creek clay where the influent suspension pH was varied (0.73 mg_a in one minute of filtration time)

Level of coating = 0.40 mg 601/gm C-560

W = 3.50 gm C-560

Q/A = 0.99 gpm/ft^2 (31.8 ml/min)

C_i = 22.9 mg/1

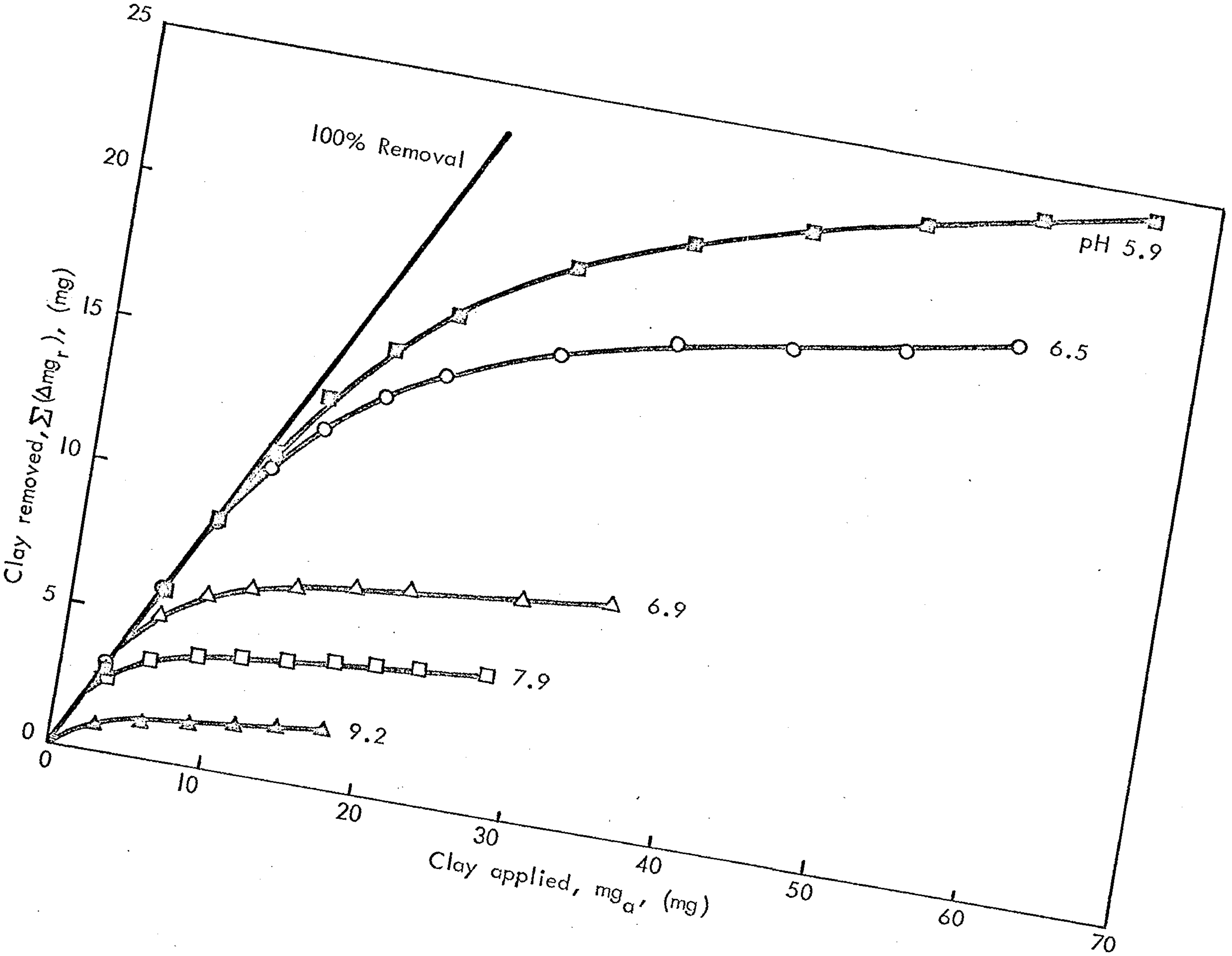

100% Removal
pH 5.9
6.5
6.9
7.9
9.2
Clay removed, $\Sigma(\Delta mg_r)$, (mg)
Clay applied, mg_a, (mg)
0
5
10
15
20
25
0
10
20
30
40
50
60
70

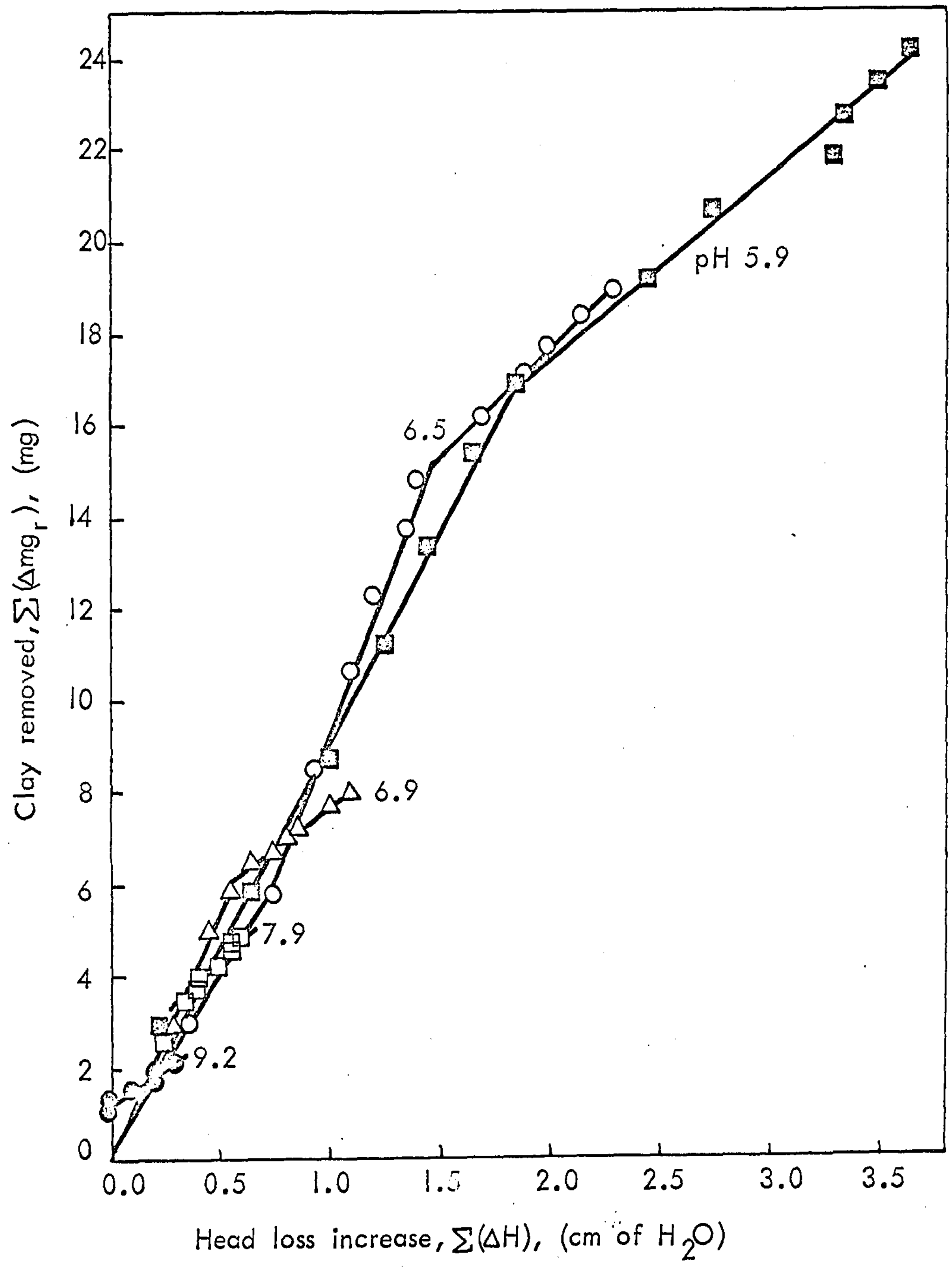
Figure 9. Head loss increase versus clay removed in a series of runs using Panther Creek clay where influent suspension pH was varied (corresponds to data shown also in Figures 7 and 8)

Level of coating = 0.40 mg 601/gm C-560

W = 3.50 gm C-560

Q/A = 0.99 gpm/ft^2 (31.8 ml/min)

C_i = 22.9 mg/1



Clay removed, $\sum(\Delta mg_r)$, (mg)
Head loss increase, $\sum(\Delta H)$, (cm of H_2O)
0
2
4
6
8
10
12
14
16
18
20
22
24
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
pH 5.9
6.5
6.9
7.9
9.2

$\frac{\text{mg 601}}{\text{gm C-560}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. °C	pH_i	pH_e	R_i $\Omega \cdot m$	R_e $\Omega \cdot m$
0.40	0.97	22.9	24.9	5.9	6.1	1760	1730
0.40	1.04	22.9	24.9	6.5	6.5	1590	1530
0.40	1.08	22.9	25.0	6.9	6.8	1370	1350
0.40	1.08	22.9	24.9	7.9	7.1	1120	1150
0.40	1.11	22.9	24.9	9.2	9.0	645	660

The results for this series of runs are presented in Figures 7, 8, and 9. Figure 7 demonstrates quite conclusively that the removal of Panther Creek clay is significantly affected by the suspension pH. Figure 8 indicates that in this series of runs the largest amount of removal was obtained with the lowest pH, and that the removals decreased with increased pH. The data in Figure 9 show an abrupt change in the head loss increase per unit of clay removed similar to that observed in Figure 6.

Effect of varying the depth of filter cake

Four runs were made in which suspensions of Panther Creek clay were filtered through four different depths of filter cake. The reason for conducting these runs was to establish whether or not the amount of Panther Creek clay removed by a coated C-560 filter cake was directly proportional to the amount of media present, i.e., the amount of filter media surface area. Filter cakes of 1.75, 3.50, 5.25, and 7.00 gm of C-560 coated with 0.35 mg 601/gm C-560 were used. The filtration rate in all four runs was 1.02 gpm/ft^2 (32.8 ml/min).

Two influent suspensions were used. The first was prepared from a stock Panther Creek clay suspension (settled 44 days) which had a clay concentration of 55.5 mg/l. An influent suspension was prepared by diluting the stock suspension with distilled water to provide a C_i of 19.6 mg/l. This influent suspension was filtered through filter cakes containing 1.75 and 7.00 gm of C-560. The second influent suspension was prepared from a stock clay suspension (settled 44 days) which had a clay concentration of 50.8 mg/l. The stock suspension was diluted with distilled water to provide a C_i of 22.6 mg/l. This suspension was filtered through filter cakes containing 3.50 and 5.25 gm of C-560. The average operational variables in the four runs in this series were:

W gm C-560	$\frac{\text{mg 601}}{\text{gm C-560}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. °C	pH_i	pH_e	R_i $\Omega \cdot m$
1.75	0.35	1.21	19.6	24.8	5.9	6.1	2210
7.00	0.35	1.25	19.6	25.1	6.0	6.2	2260
3.50	0.35	1.04	22.6	24.7	5.8	6.1	1870
5.25	0.35	1.25	22.6	25.0	6.0	6.1	1930

The results of this series of runs are presented in Figures 10, 11, and 12. Figures 10 and 11 clearly show that the amount of clay removed is positively correlated with the amount of filter media or depth of filter cake present. The shape of the effluent history curves in Figure 10 appears to depend to a minor degree on the depth of the filter cakes. The significance of this observation will be elucidated in the

Figure 10. Effluent history curves for a series of runs using Panther Creek clay where the amount (or depth) of filter cake was varied

Level of coating = 0.35 mg 601/gm C-560

Q/A = 1.02 gpm/ft^2 (32.8 ml/min)

C_i = 19.6 mg/1 (for 1.75 and 7.00 gm of C-560)

C_i = 22.6 mg/1 (for 3.50 and 5.25 gm of C-560)

pH_i = 5.8 - 6.0

Note: These runs were made using a compressed N_2 pressure system - - see text, page 89.

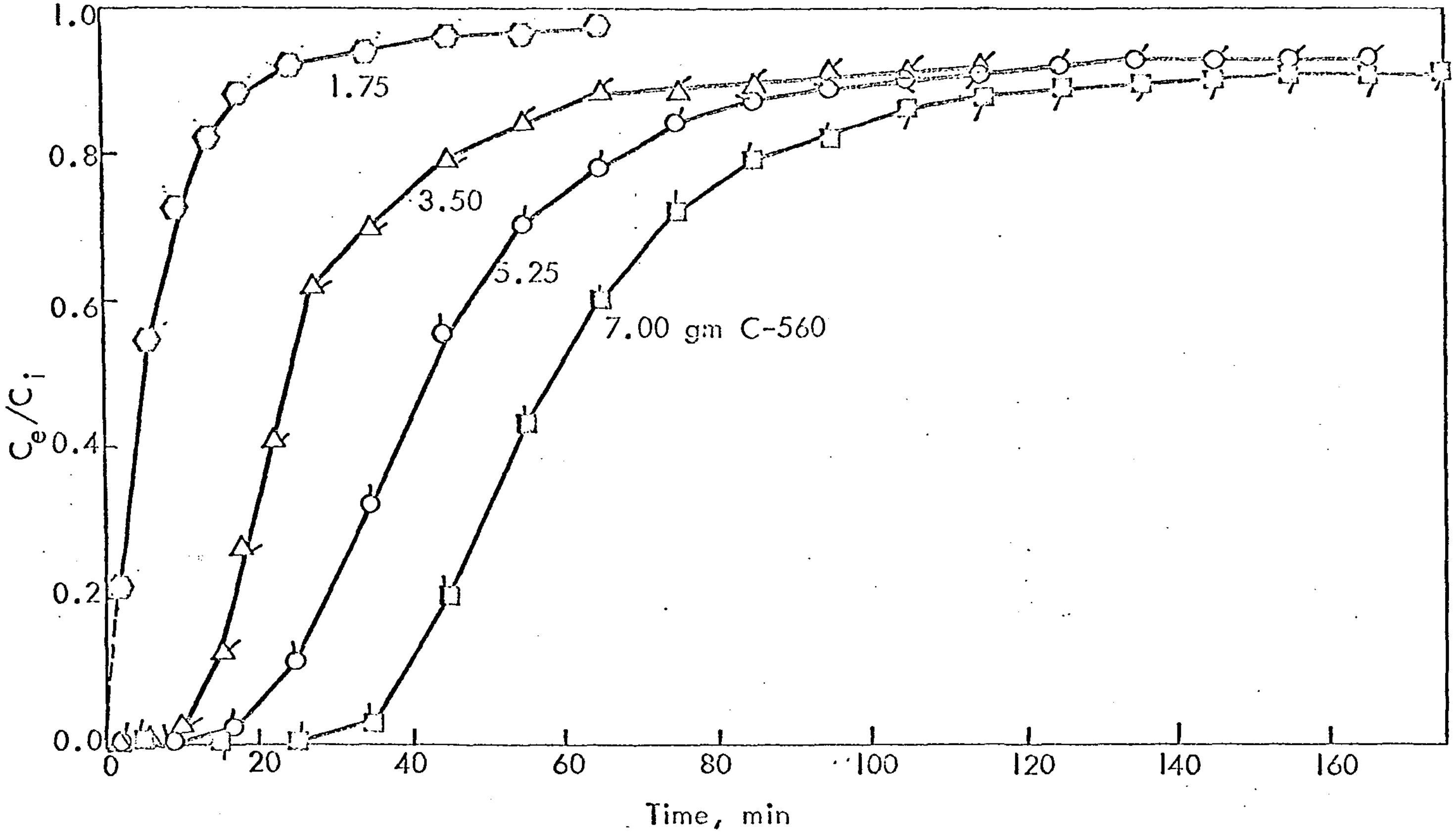

1.0
0.8
0.6
0.4
0.2
0.0
C_e/C_i
0
20
40
60
80
100
120
140
160
Time, min
1.75
3.50
5.25
7.00 gm C-560

Figure 11. Clay removed versus clay applied in a series of runs using Panther Creek clay where the amount (or depth) of filter cake was varied (0.73 mg_a in one minute filtration time, for 3.50 and 5.25 gm of C-560, and 0.64 mg_a in one minute of filtration time, for 1.75 and 7.00 gm C-560)

Level of coating = 0.35 mg 601/gm C-560

Q/A = 1.02 gpm/ft^2 (32.8 ml/min)

C_i = 19.6 mg/l (for 1.75 and 7.00 gm of C-560)

C_i = 22.6 mg/l (for 3.50 and 5.25 gm of C-560)

pH_i = 5.8 - 6.0

Note: These runs were made using a compressed N_2 pressure system - - see text, page 89.

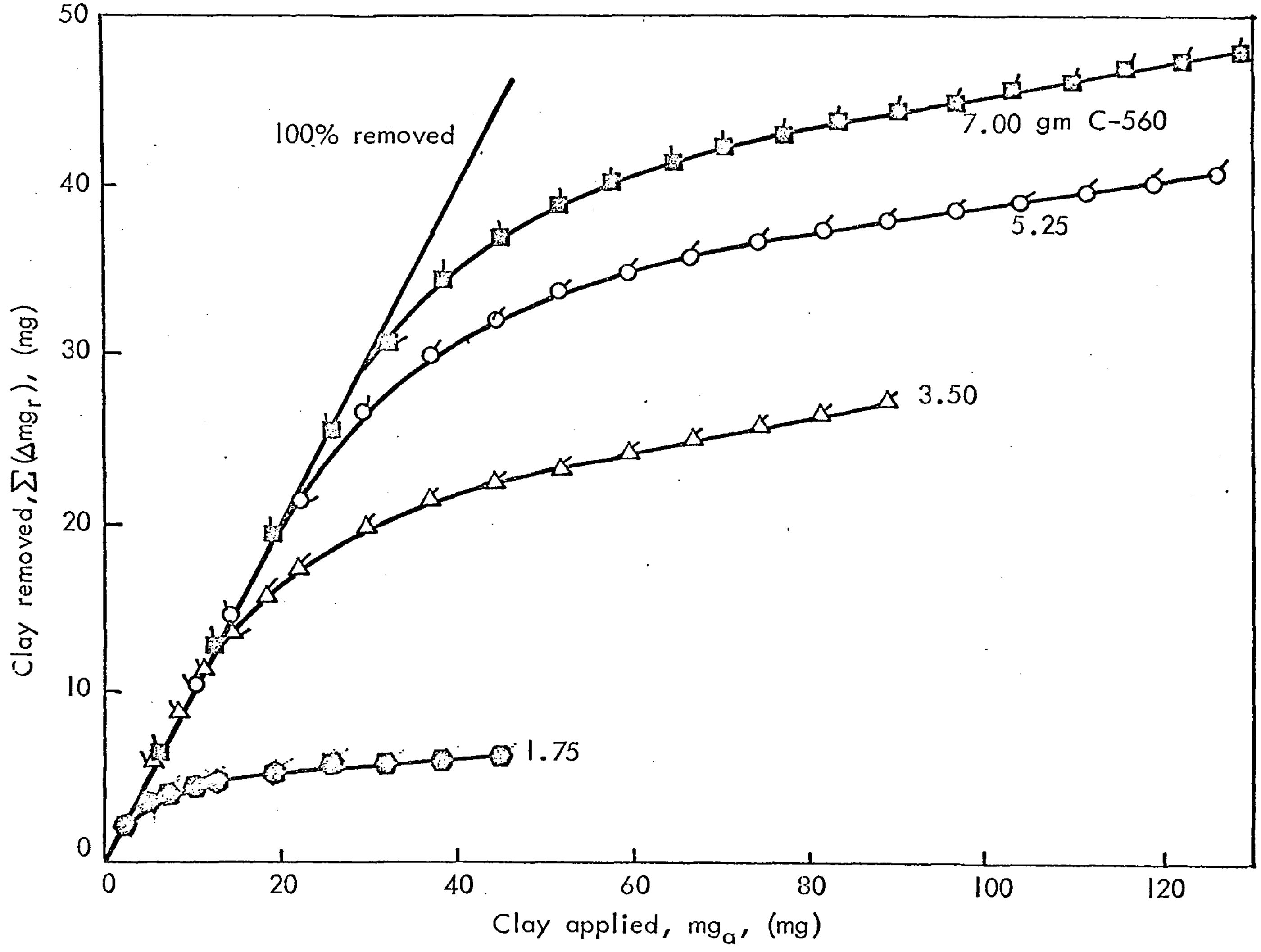

100% removed
7.00 gm C-560
5.25
3.50
1.75
Clay removed, $\sum(\Delta mg_r)$, (mg)
Clay applied, mg_a, (mg)
0
10
20
30
40
50
0
20
40
60
80
100
120

Figure 12. Head loss increase versus clay removed in a series of runs using Panther Creek clay where the amount (or depth) of filter cake was varied (corresponds to data shown also in Figures 10 and 11)

Level of coating = 0.35 mg 601/gm C-560

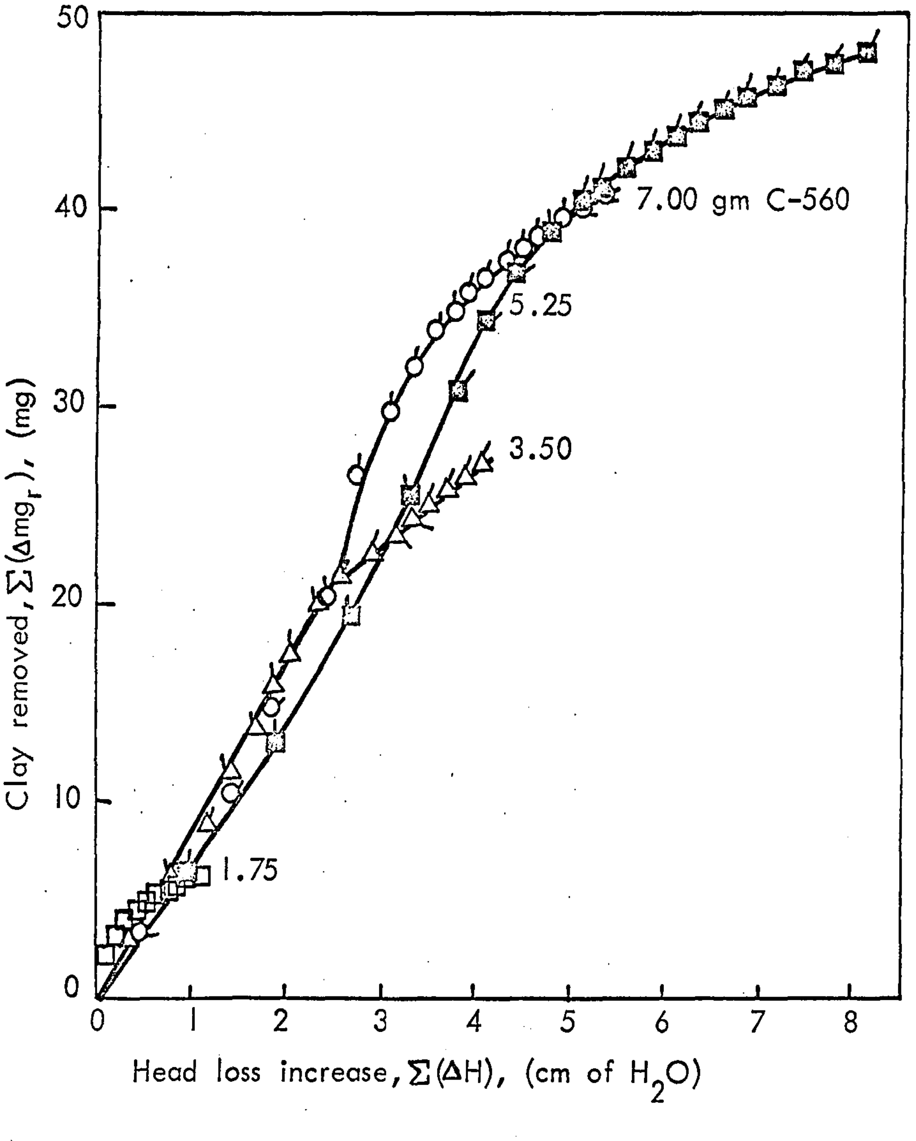
Q/A = 1.02 gpm/ft^2 (32.8 ml/min)

C_i = 19.6 mg/l (for 1.75 and 7.00 gm of C-560)

C_i = 22.6 mg/l (for 3.50 and 5.25 gm of C-560)

pH_i = 5.8 - 6.0

Note: These runs were made using a compressed N_2 pressure system - - see text, page 89.


Clay removed, $\Sigma(\Delta mg_r)$, (mg)
Head loss increase, $\Sigma(\Delta H)$, (cm of H_2O)
7.00 gm C-560
5.25
3.50
1.75
0
10
20
30
40
50
0
1
2
3
4
5
6
7
8

next chapter of this thesis. The shapes of the head loss increase versus clay removed curves in Figure 12 also appear to be different with different depths of the filter cake. However, the general observation can still be made that the head loss increase per unit of clay removed is significantly smaller early in the filter run than it is later in the run.

It should be noted that these four runs were conducted early in this study before operating techniques had been fully developed and standardized. In these runs, a compressed nitrogen gas pressure system was used to force the suspension through the filter cake. In all other filtration runs reported the gravity flow system described in the test procedures was used. Use of the compressed nitrogen gas pressure system was discontinued because after about two hours of a filtration run dissolved gas was observed coming out of solution in both the influent and effluent samples. In addition to making the measurement of turbidity of questionable value, solubility calculations indicated that significant gas binding could have occurred in the filter cake.

Other observations

Since Panther Creek clay was the first particulate matter for which removal patterns were investigated, a large quantity of data was compiled before an acceptable standard filtration procedure and operational technique could be evolved. Two observations will be recorded here; but because of differing procedures no comparisons should be made of these observations to other reported observations made using the standard test procedures.

A series of four runs was made to evalute the effect of filtration rate on the removal of Panther Creek clay by 601-coated C-560 filter cakes. Flow rates of 0.5, 1.0, 2.0, and 3.0 gpm/ft^2 were used. Pertinent average operating variables were as follows:

1. the filter cakes (about 1/2-inch deep) contained 3.4 gm of C-560,
2. the level of coating was 1.0 mg 601/gm C-560,
3. the suspension temperature was 25°C,
4. the influent clay concentration was 23 mg/l, prepared from a stock clay suspension (settled 16 days),
5. the influent suspension pH was 6.0, and
6. the influent suspension resistivity was 2700 Ω·m.

The results of this series of runs plotted to show clay removed versus clay applied, indicated that the total amount of clay removed was not significantly different for filtration rates from 0.5 to 3.0 gpm/ft^2.

The other observation of interest concerns the stability of the Panther Creek clay suspensions used. In one run, KCl was added to a 16 mg/l clay suspension in an attempt to evaluate the effect of solution ionic strength on the solids removal patterns. Complete removal of the clay resulted when this suspension was filtered at a rate of 1 gpm/ft^2 through a filter cake containing 3.4 gm of C-560 coated with 1 mg 601/gm C-560. Observation of an exponential head loss build up and visual observation of a clay layer on the surface of the dewatered filter cake indicated that removal had occurred by surface straining. A similar observation was made when 6 liters of a stock clay suspension (50 mg/l) was diluted with 10 liters of Iowa State University tap water and this suspension was filtered through an uncoated C-560 filter cake at 1 gpm/ft^2. These observations indicated that destabilized Panther Creek clay suspensions would not pass through C-560 filter cakes.

Removal of Black Hills Clay

Black Hills clay suspensions were prepared by mixing 68 grams of Black Hills clay in 17 liters of distilled water and settling for more than 50 days. The supernatant was used as a stock clay suspension and had a concentration of about 1.4 gm/l.

Filter cakes of Hyflo SuperCel were used to evaluate the removal patterns of Black Hills clay on coated filter cakes. The filtration system which was used in all Black Hills clay runs included use of filter cakes containing 4.00 gm of Hyflo SuperCel (1.03 lb/ft^2), which formed filter cakes 5/8-inch deep, and a filtration rate of 0.508 gpm/ft^2 (16.4 ml/min).

Effect of varying the level of 601 coating

A series of five runs was made with the same influent Black Hills clay suspension to evaluate the effect of the level of coating on the removal of Black Hills clay. The influent suspension used was prepared from a stock clay suspension (settled 59 days) which had a clay concentration of 1400 mg/l and a pH of 8.0. The stock clay suspension was diluted with distilled water to provide a clay concentration of 156 mg/l and a pH of 6.6. The suspension pH was then lowered to 6.0 by addition of a few drops of 1.2 N HCl. The average operational variables in this series of runs were:

$\frac{\text{mg 601}}{\text{gm Hyflo}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. °C	pH_i	pH_e	R_i Ω·m	R_e Ω·m
0.00	.144	156	25.1	6.0	6.5	495	436
2.00	.079	156	25.1	6.1	6.6	494	435
4.00	.076	156	25.1	6.1	6.7	495	435
1.00	.090	156	24.8	6.2	6.7	499	430
0.50	.103	156	24.8	6.2	6.7	498	430

The results of this series of runs are shown in Figures 13, 14, and 15. Figures 13 and 14 indicate very clearly that increasing the level of coating up to a level of about 1.70 mg 601/gm Hyflo SuperCel provided increased removal of Black Hills clay. The data for the run with a coating level of 1.70 mg 601/gm Hyflo SuperCel was collected in the next series of runs to be presented and was made under nearly identical test conditions.

The data in Figure 13 indicate that 100 percent of the clay passed through the uncoated filter cake. In fact, the effluent turbidity measurements observed were greater than those of the influent for the first ten minutes of the run. Visual observation of the effluent samples indicated that some diatomite fines were present. No fines were observed in the initial effluent samples collected during runs made using coated filter cakes.

Figure 15 shows the same abrupt change in the head loss increase per unit clay removed relationship observed using Panther Creek clay suspensions and coated C-560.

Figure 13. Effluent history curves for a series of runs using Black Hills clay where the level of coating was varied (data for the 1.70 mg 601/gm Hyflo SuperCel run were taken from Figure 16)

W = 4.00 gms Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 156 mg/1

pH_i = 6.0 - 6.2

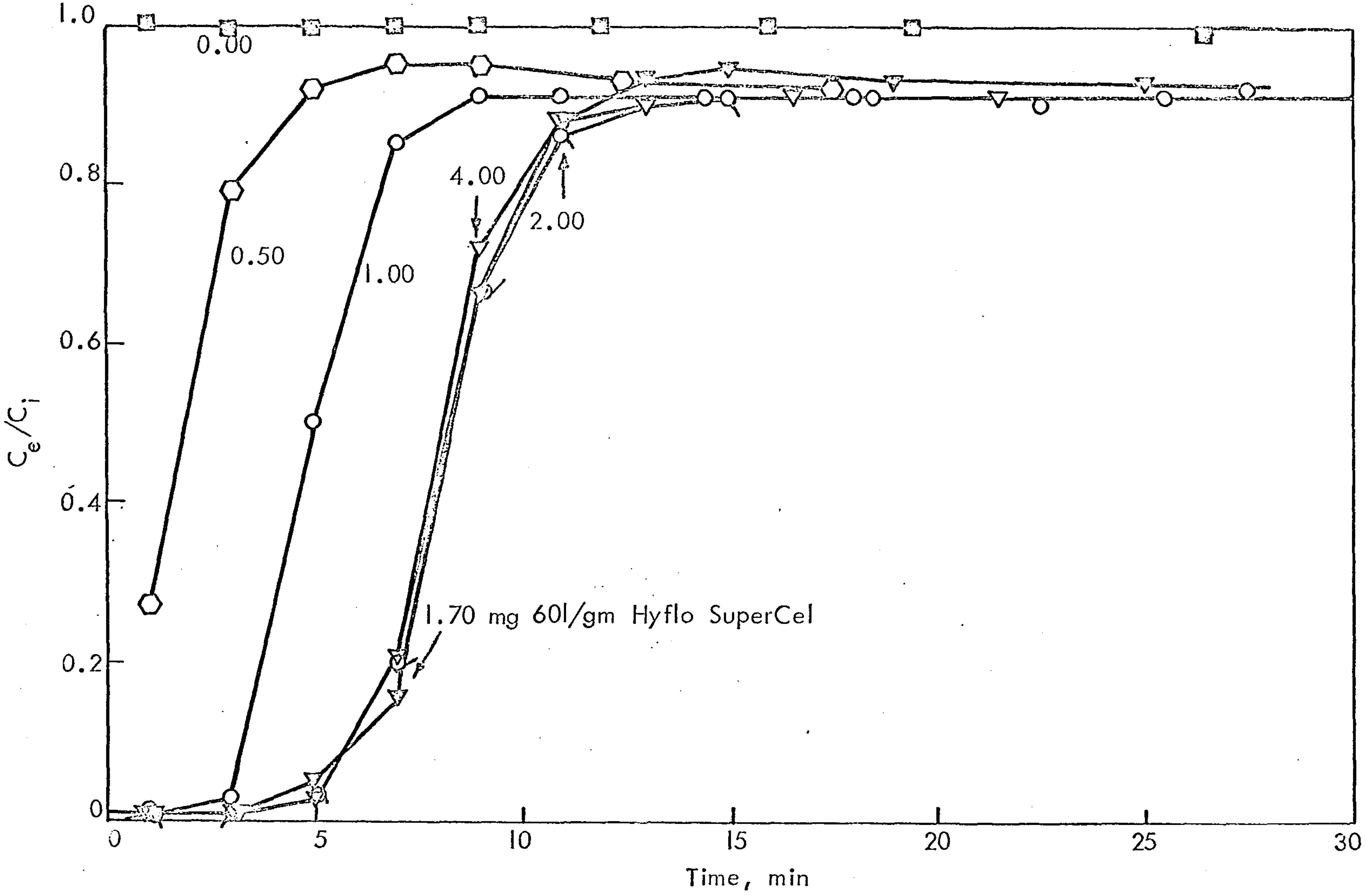

1.0
0.8
0.6
0.4
0.2
0
C_e/C_i
0
5
10
15
20
25
30
Time, min
0.00
0.50
1.00
4.00
2.00
1.70 mg 601/gm Hyflo SuperCel

Figure 14. Clay removed versus clay applied in a series of runs using Black Hills clay where the level of coating was varied; data for the 1.70 mg 601/gm Hyflo SuperCel run were taken from Figure 17 (2.56 mg_a in one minute of filtration time)

W = 4.00 gm Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 156 mg/1

pH_i = 6.0 - 6.2

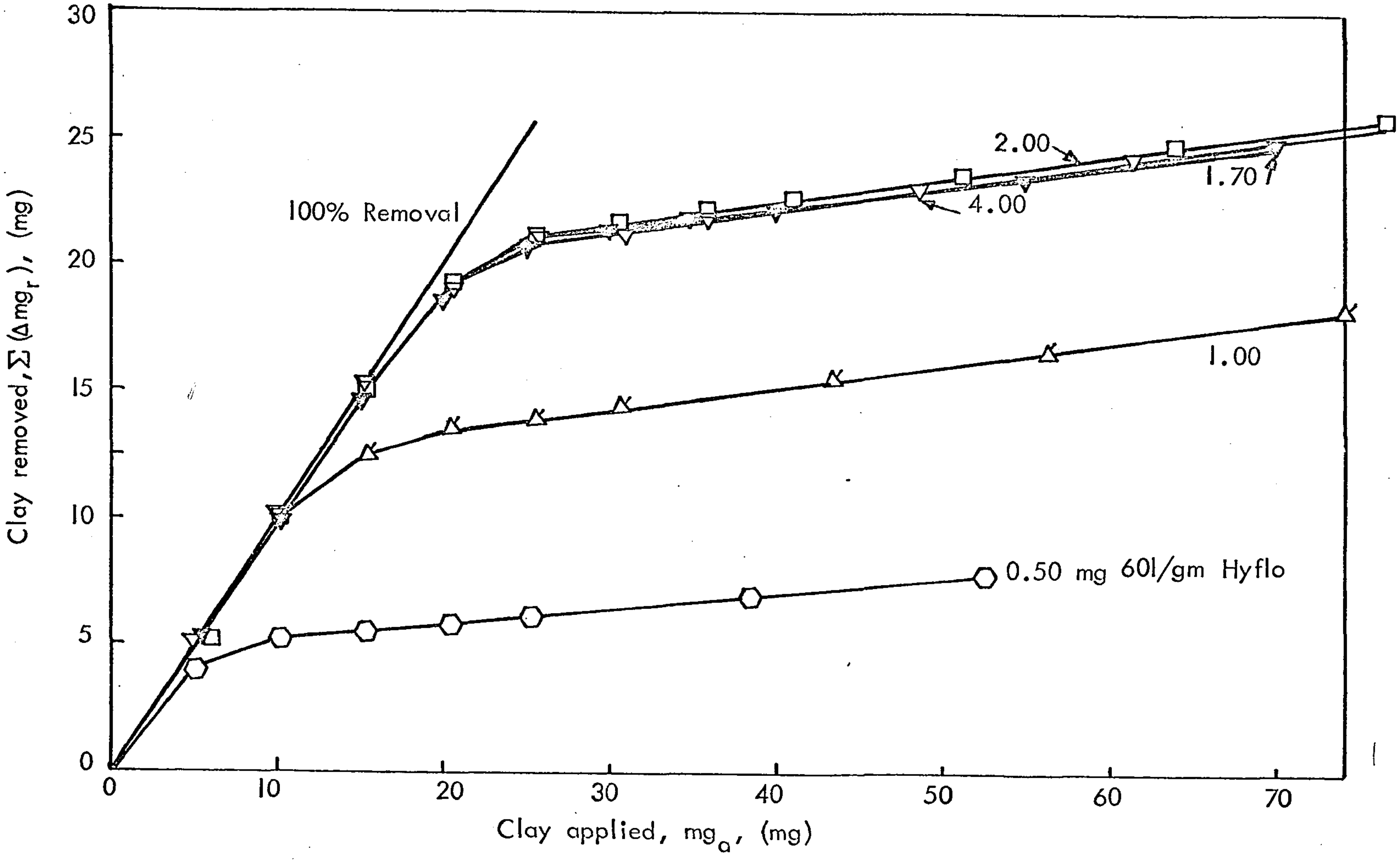

100% Removal
2.00
1.70
4.00
1.00
0.50 mg 601/gm Hyflo
Clay removed, $\Sigma(\Delta mg_r)$, (mg)
Clay applied, mg_a, (mg)
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70

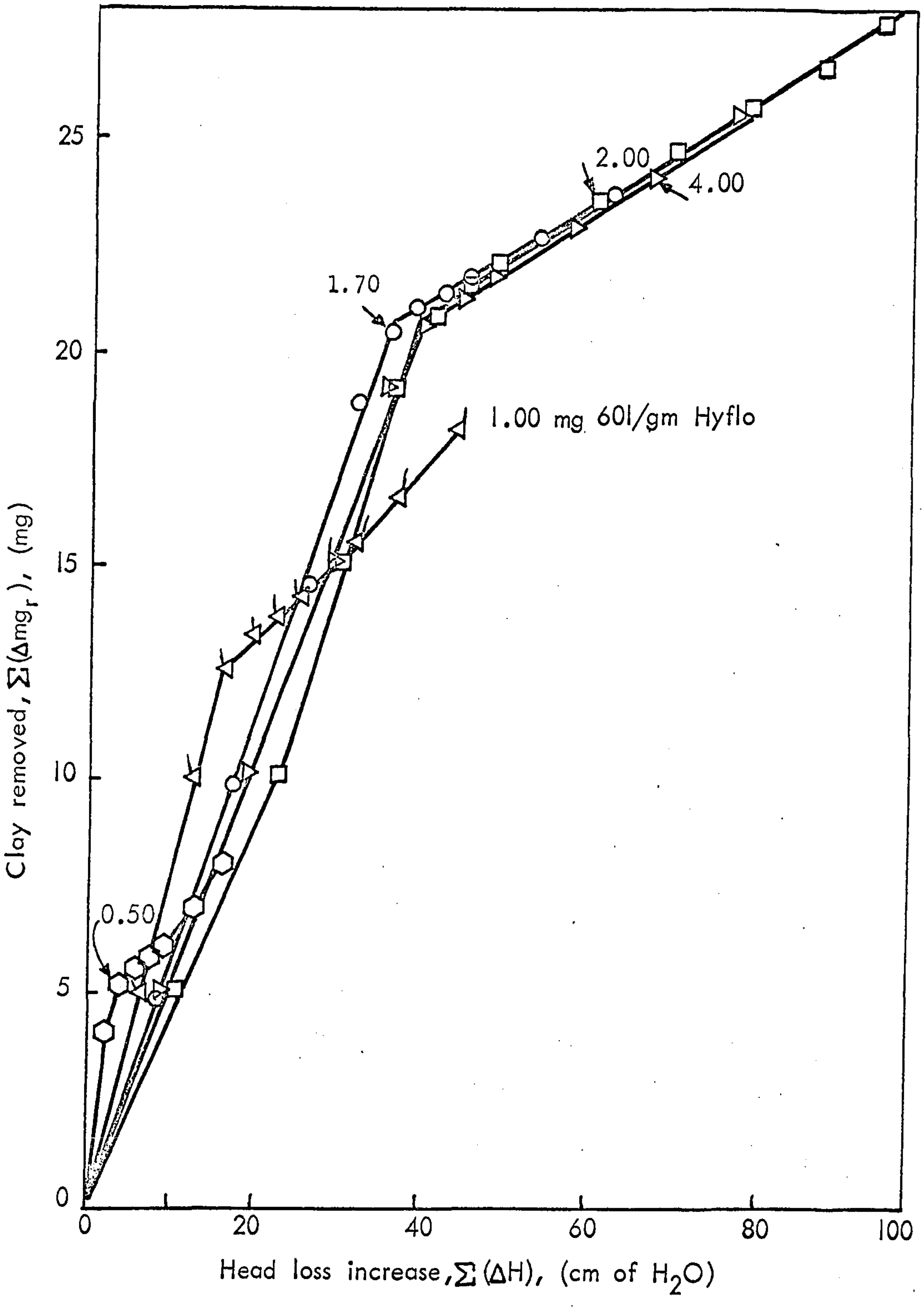
Figure 15. Head loss increase versus clay removed in a series of runs using Black Hills clay where the level of coating was varied; data for the 1.70 mg 601/gm Hyflo SuperCel run were taken from Figure 18 (corresponds to data shown also in Figures 13 and 14)

W = 4.00 gm Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 156 mg/1

pH_i = 6.0 - 6.2


Clay removed, $\sum(\Delta mg_r)$, (mg)
0
5
10
15
20
25
Head loss increase, $\sum(\Delta H)$, (cm of H_2O)
0
20
40
60
80
100
0.50
1.70
2.00
4.00
1.00 mg 601/gm Hyflo

Effect of varying the suspension pH

A series of five runs was conducted to evaluate the effect of the suspension pH on Black Hills clay removal by coated Hyflo SuperCel. The level of coating in these runs was 1.70 mg 601/gm Hyflo SuperCel. The influent suspensions for these runs was prepared from a stock clay suspension (settled 54 days) which had a clay concentration of 1,370 mg/l and a pH of 8.1. The stock clay suspension was diluted with distilled water to provide a clay concentration of 152 mg/l and a pH of 6.5. The suspension pH was changed between runs by adding a few drops of either 1.2 N HCl or 0.83 N KOH. No attempt was made to control the ionic strength of the suspension. The average operational variables in this series of runs were:

$\frac{\text{mg 601}}{\text{gm Hyflo}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. ^oC	pH_i	pH_e	R_i $\Omega\cdot m$	R_e $\Omega\cdot m$
1.70	0.086	152	25.5	6.6	7.0	532	460
1.70	0.083	152	25.2	6.0	6.6	474	406
1.70	0.082	152	25.0	6.9	7.2	355	328
1.70	0.118	152	24.8	8.2	7.8	302	---
1.70	0.102	152	24.8	8.8	7.8	276	270

As noted earlier, the effluent pH values recorded are of questionable accuracy. An additional complication was observed during the two runs at the higher solution pH levels. During the course of the filter run the influent suspension pH decreased about 0.3 pH unit. This evidently occurred because the clay was not in equilibrium with the aqueous medium at the beginning of the filter run.

Figure 16. Effluent history curves for a series of runs using Black Hills clay where the influent suspension pH was varied

Level of coating = 1.70 mg 601/gm Hyflo SuperCel

W = 4.00 gm Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 152 mg/1

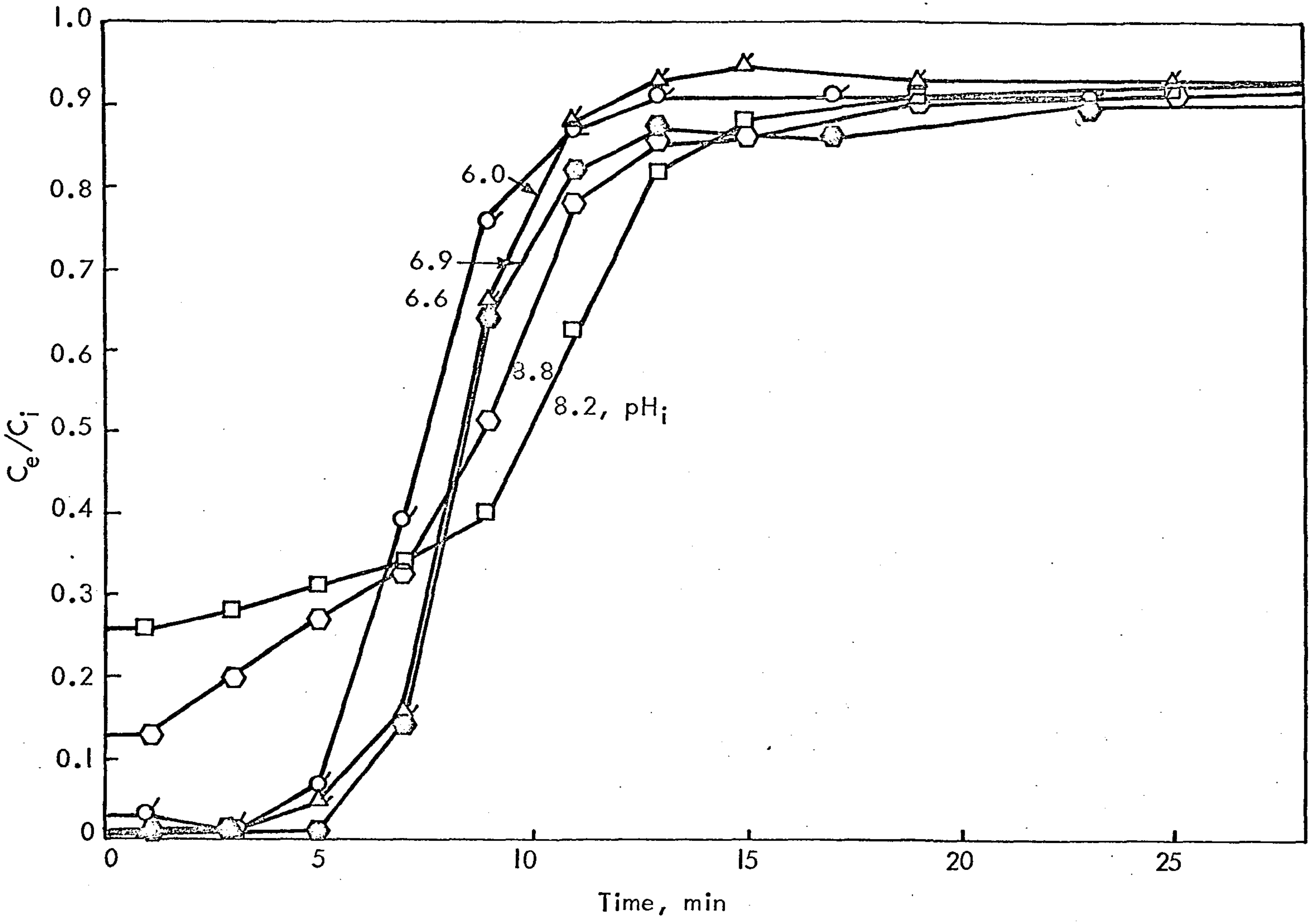

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C_e/C_i
0
5
10
15
20
25
Time, min
6.0
6.9
6.6
8.8
8.2, pH_i

Figure 17. Clay removed versus clay applied in a series of runs using Black Hills clay where influent suspension pH was varied (2.49 mg_a in one minute of filtration time)

Level of coating = 1.70 mg 601/gm Hyflo SuperCel

W = 4.00 gm Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 152 mg/1

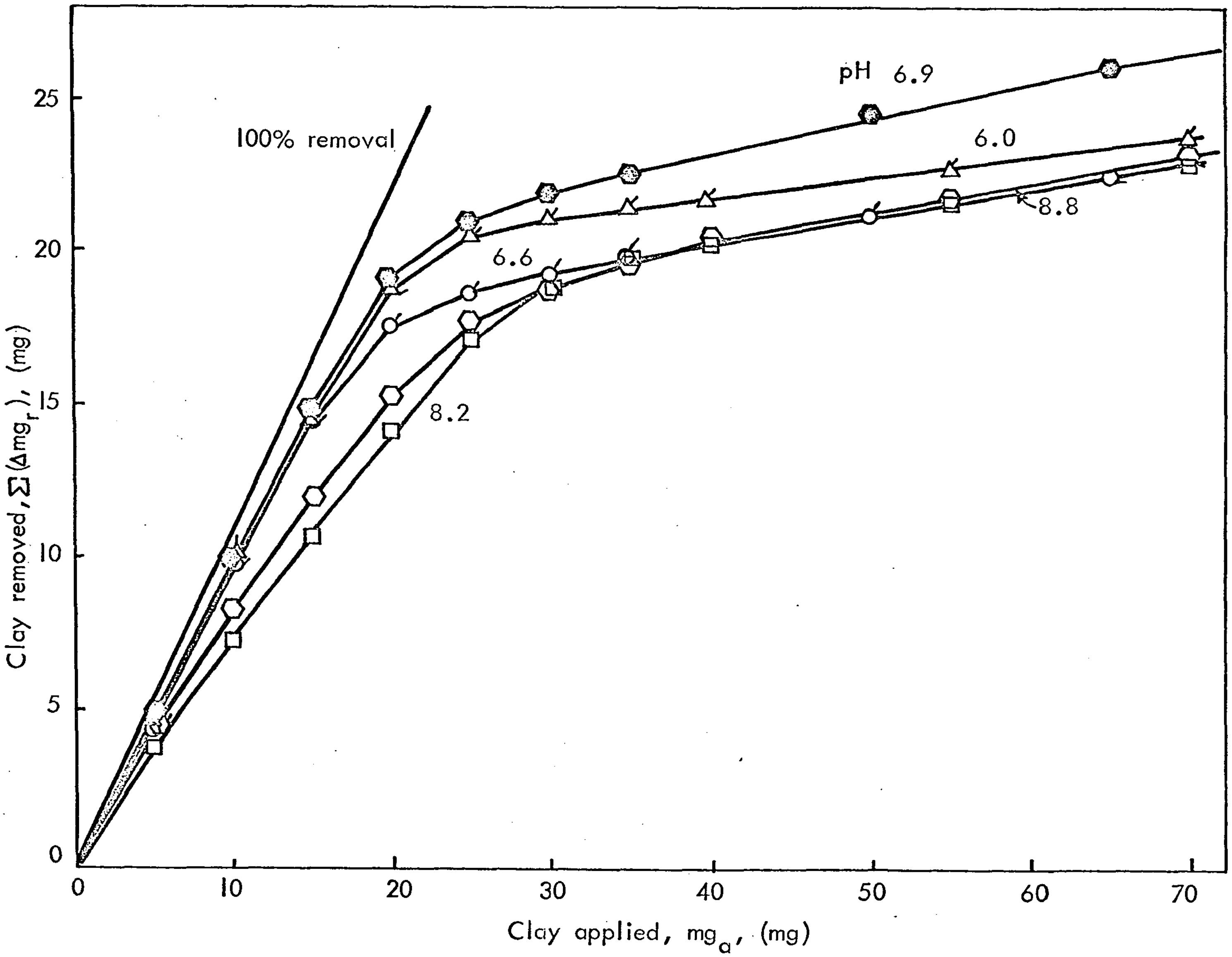

pH 6.9
6.0
100% removal
6.6
8.2
8.8
Clay removed, $\Sigma(\Delta mg_r)$, (mg)
0
5
10
15
20
25
0
10
20
30
40
50
60
70
Clay applied, mg_a, (mg)

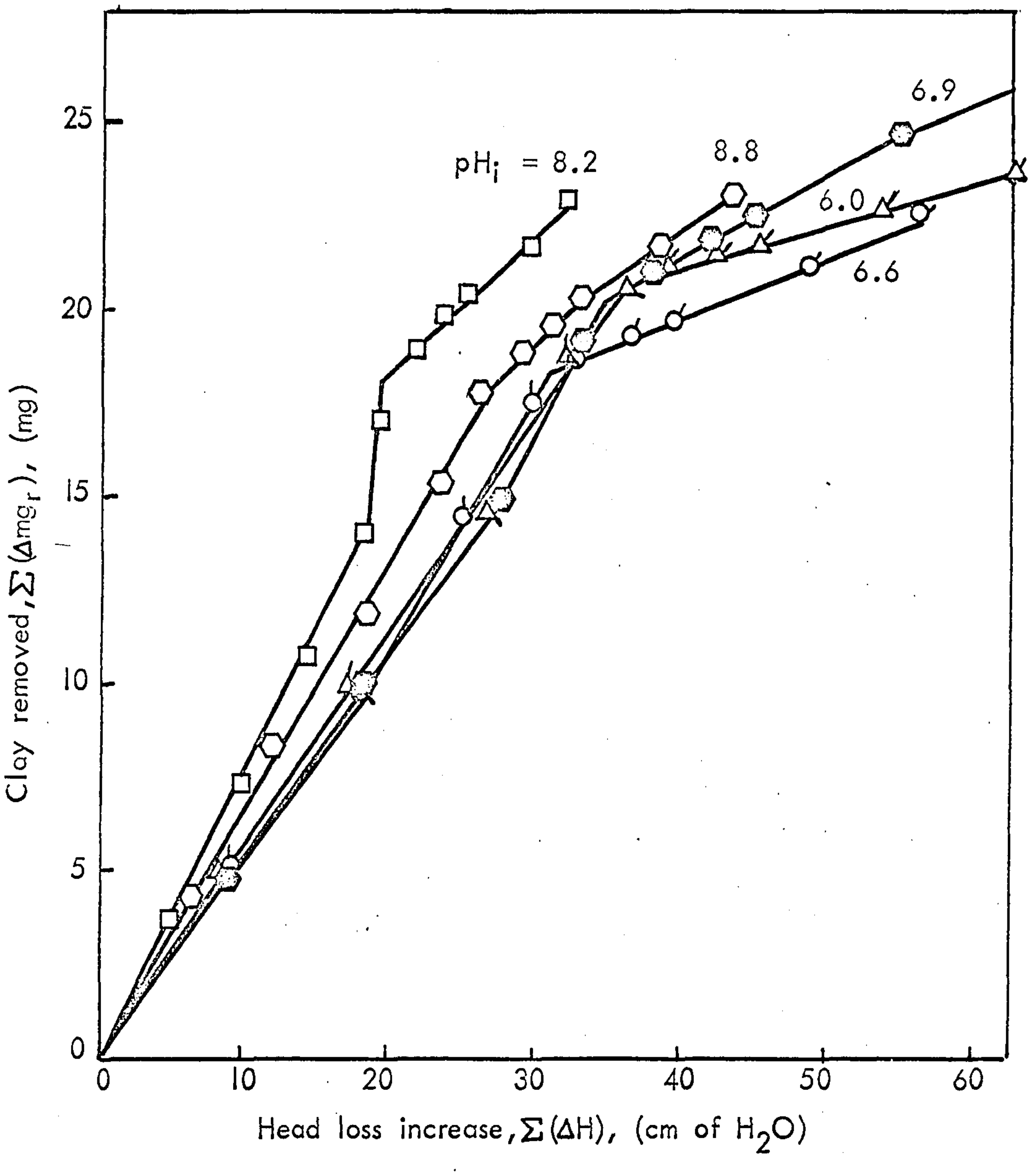
Figure 18. Head loss increase versus clay removed in a series of runs using Black Hills clay where the influent suspension pH was varied (corresponds to data shown also in Figures 16 and 17)

Level of coating = 1.70 mg 601/gm Hyflo SuperCel

W = 4.00 gm Hyflo SuperCel

Q/A = 0.508 gpm/ft^2 (16.4 ml/min)

C_i = 152 mg/1


pH$_i$ = 8.2
8.8
6.9
6.0
6.6
Clay removed, $\sum(\Delta mg_r)$, (mg)
Head loss increase, $\sum(\Delta H)$, (cm of H_2O)
0
5
10
15
20
25
0
10
20
30
40
50
60

The results of this series of runs are presented in Figures 16, 17, and 18. Figure 16 indicates that the pattern of removal was different at higher pH values than it was at lower values. Figure 17, however, indicates that the amount of clay removed did not differ greatly. Figure 18 shows the relationship between the head loss increase and the amount of Black Hills clay removed. The double discontinuity in the curve for the results of the run made with a solution pH of 8.2 seems inconsistent with the other curves.

Removal of Ball Clay

No system was developed which would give Ball clay removal patterns similar to those observed with the other clays. The Ball clay, as prepared, was removed by C-560 filter cakes in quantity by surface straining. Results of three runs will be presented to give a qualitative indication as to the effect of coating diatomite with 601 on the removal pattern with Ball clay.

A coarse fraction of C-560 was used. This fraction was prepared using the following procedure: Sixty grams of C-560 was placed in a one-liter graduated cylinder filled with distilled water. The contents were mixed by inverting the cylinder ten times. The suspension was allowed to settle 3 1/2 minutes at which time the supernatant was decanted to within about 1/2 inch of the sediment. The cylinder containing the sediment was then filled with distilled water and the same process repeated 49 more times. See the Appendix for particle size distribution curves of the coarse fraction and regular C-560.

One filtration run was conducted using uncoated diatomite and an influent suspension pH of 6.6. A second run was made using 601-coated media (0.41 mg 601/gm coarse C-560) and a suspension pH of 6.7. A third run was made using 601-coated media (0.41 mg 601/gm coarse C-560) and a suspension pH of about 8.4. In all three runs a filtration rate of 0.90 gpm/ft^2 (29.0 ml/min) and filter cakes containing 3.4 gm of coarse C-560 were used. The influent suspension used in all three runs was prepared from stock clay suspension (settled 13 days) which had a clay concentration of about 22 mg/l and a pH of 7.1. A sample of this stock suspension was diluted with distilled water to provide a clay concentration of about 11 mg/l and a pH of 6.6. The average operating variables during the three runs were:

$\frac{\text{mg 601}}{\text{gm coarse C-560}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. °C	pH_i	pH_e	R_i Ω·m	R_e Ω·m
0.00	2.85	11	25.0	6.6	6.7	669	651
0.41	2.85	11	25.0	6.7	6.8	669	657
0.41	2.85	11	25.0	8.4	7.8	438	441

The results of the three runs are presented in Figures 19 and 20. The results shown in Figure 19 demonstrate that at a suspension pH of 6.7, a coated filter cake will remove considerably more Ball clay than an uncoated filter cake. It is also apparent that the removal pattern observed using a coated filter cake is affected by the pH of the influent suspension. Removal of clay from the suspension at a pH of

Figure 19. Effluent history curves for a series of runs using Ball clay in which the level of coating and influent suspension pH were different

$W = 3.4$ gm coarse C-560

$Q/A = 0.90$ gpm/ft^2 (29.0 ml/min)

$C_i = 11$ mg/l

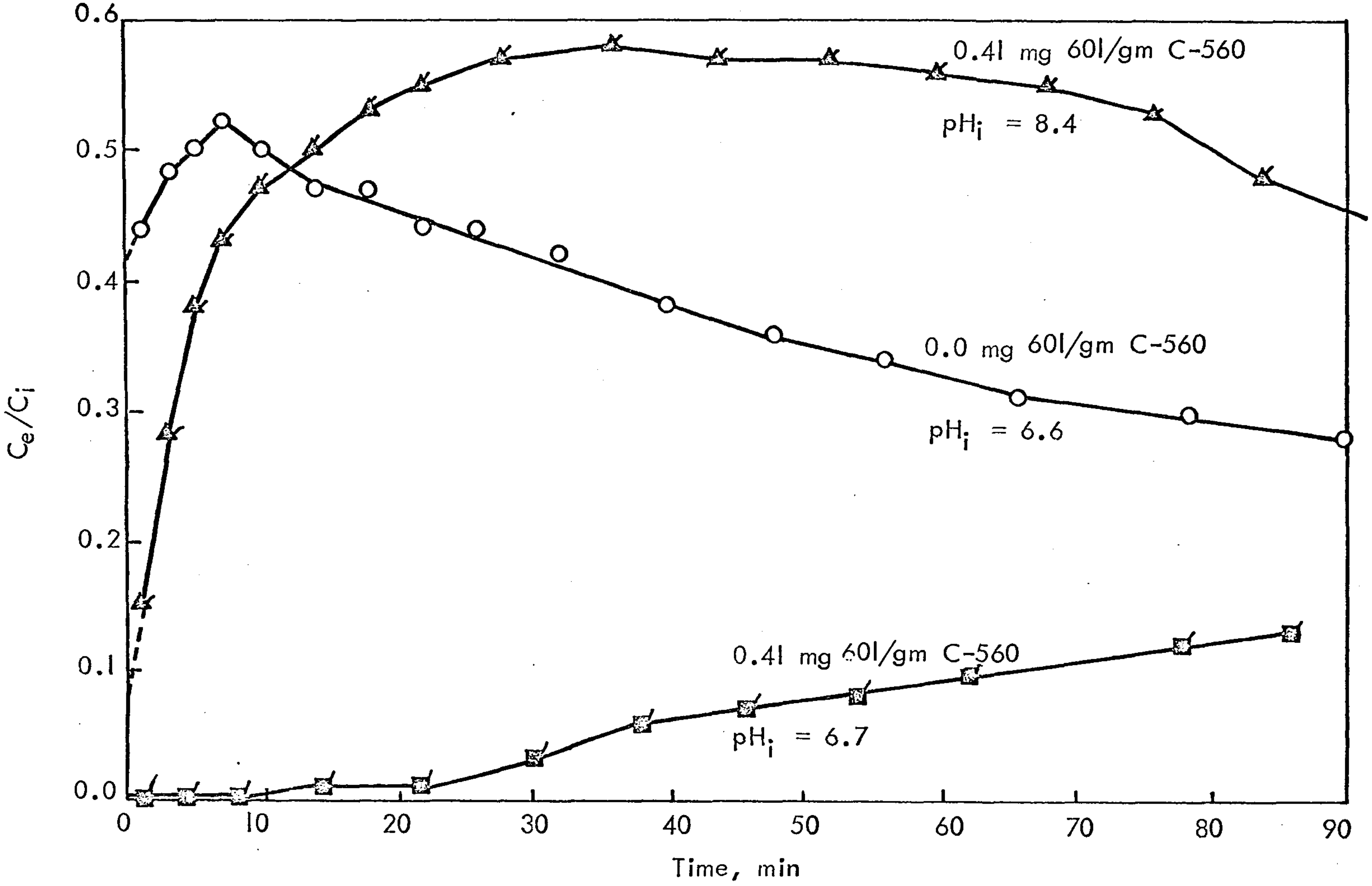
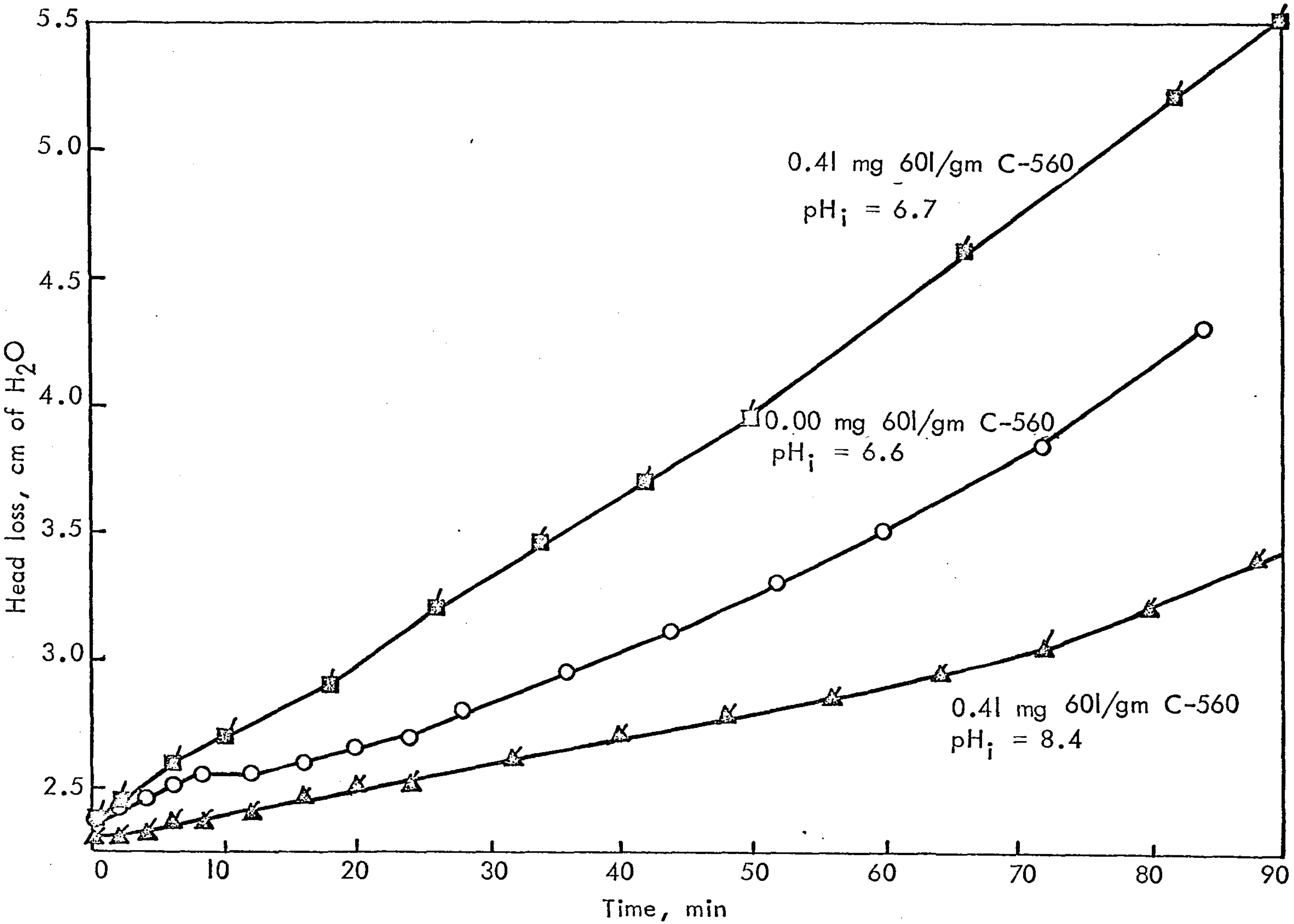

0.41 mg 601/gm C-560
pH$_i$ = 8.4
0.0 mg 601/gm C-560
pH$_i$ = 6.6
0.41 mg 601/gm C-560
pH$_i$ = 6.7
C_e/C_i
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
70
80
90
Time, min

Figure 20. Head loss build up curves in a series of runs using Ball clay where the level of coating and influent suspension pH levels were different (corresponds to data shown also in Figure 19)

W = 3.4 gm coarse C-560

Q/A = 0.90 gpm/ft^2 (29.0 ml/min)

C_i = 11 mg/1


0.41 mg 601/gm C-560
pH$_i$ = 6.7
0.00 mg 601/gm C-560
pH$_i$ = 6.6
0.41 mg 601/gm C-560
pH$_i$ = 8.4
Head loss, cm of H_2O
Time, min
5.5
5.0
4.5
4.0
3.5
3.0
2.5
0
10
20
30
40
50
60
70
80
90

about 8.4 was significantly less than the removal of clay from a suspension at a pH of 6.7. Figure 20 indicates, as would be expected, that the head loss build up is greater for the system which is removing the greater amount of material.

Visual observation of the dewatered filter cakes provided evidence of surface removal. After the dewatered cakes were air dried overnight, the coarse C-560 cake had crumbled except for a 1/16-inch surface layer which was cemented together by particles of the clay removed by surface straining.

Removal of Coffee Compounds

Preliminary filtration runs were made to establish a suitable filtration system for evaluating the removal of coffee colored compounds on diatomite filter cakes coated at increasing levels of coating. Based on the results obtained, a series of six runs was conducted using filter cakes containing 4.00 gm of Hyflo SuperCel and a filtration rate of 0.49 gpm/ft^2 (16.0 ml/min). An influent coffee solution was prepared with distilled water which had been filtered through a 0.22 micron Millipore filter. This insured the absence of extraneous particulate matter of any consequence and also provided some degassing of the distilled water which is normally supersaturated with CO_2. The required amount of a stock coffee solution was pipetted into the distilled water to provide a coffee concentration of 30.1 mg/l. The average operating variables during this series of runs are shown below (K_o was calculated using a value of H at a filtration time of 2 minutes).

$\frac{\text{mg 601}}{\text{gm Hyflo SuperCel}}$	$K_o \times 10^{10}$ ft^2	C_i mg/l	Temp. ^oC	pH_i	pH_e	R_i $\Omega \cdot m$	R_e $\Omega \cdot m$
0.00	.141	30.1	24.7	5.8	6.4	1200	1120
0.50	.141	30.1	25.1	5.8	6.4	1190	1150
1.00	.128	30.1	24.8	5.9	6.4	1210	1150
1.50	.120	30.1	24.9	5.9	6.5	1240	1180
2.00	.112	30.1	25.0	6.0	6.5	1260	1180
3.00	.166	30.1	25.1	6.0	6.5	1260	1180

The results of this series of runs are presented in Figures 21, 22, and 23. Figure 21 shows that effluent history curves for coffee removal are somewhat similar to those observed for clay removal except that a fraction of the coffee material, about 15 percent, was not removed with any level of filter media coating. Figure 22 indicates that increased levels of filter media coating up to 1.50 mg 601/gm Hyflo SuperCel results in increased removal of the coffee material. Figure 21 shows that the largest amount of coffee removal occurs in about the first 15 minutes of filtration. Figure 23 shows that between two and 15 minutes little head loss build up occurs. These observations indicate that the coffee is retained in the filter cake in a manner which does not restrict the flow of liquid.

The jump in head loss during the first two minutes in Figure 23 is difficult to explain. It cannot be correlated with the level of coating or the amount of coffee removed in this time interval. It was not observed in the Black Hills clay test series. The only difference between the two test series was the type of suspension being filtered.

Figure 21. Effluent history curves for a series of runs using coffee colored compounds where the level of coating was varied

$W = 4.00$ gm Hyflo SuperCel

$Q/A = 0.49$ gpm/ft^2 (16.0 ml/min)

$C_i = 30.1$ mg/l

$pH_i = 5.8 - 6.0$

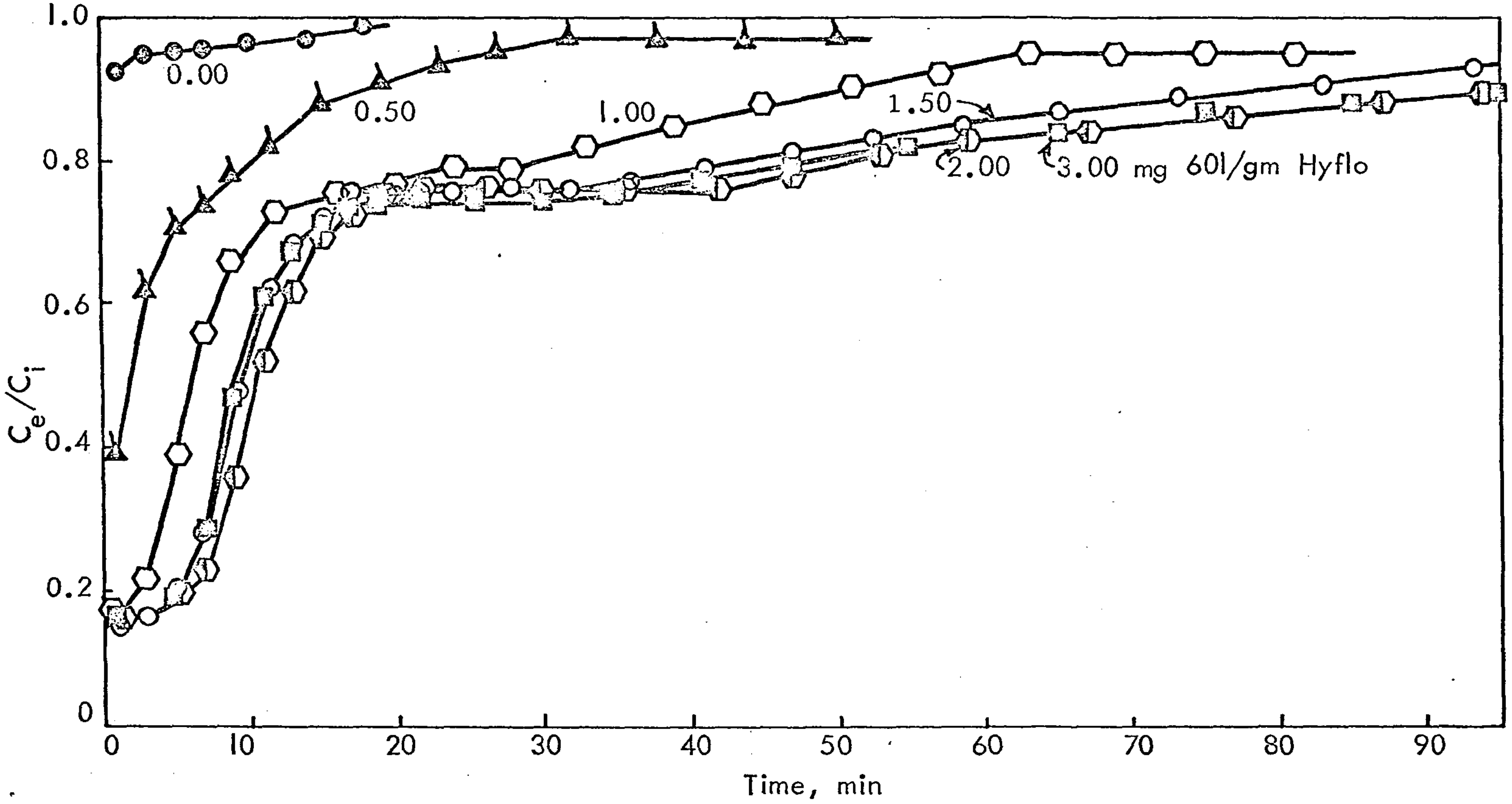

1.0
0.8
0.6
0.4
0.2
0
C_e/C_i
0
10
20
30
40
50
60
70
80
90
Time, min
0.00
0.50
1.00
1.50
2.00
3.00 mg 601/gm Hyflo

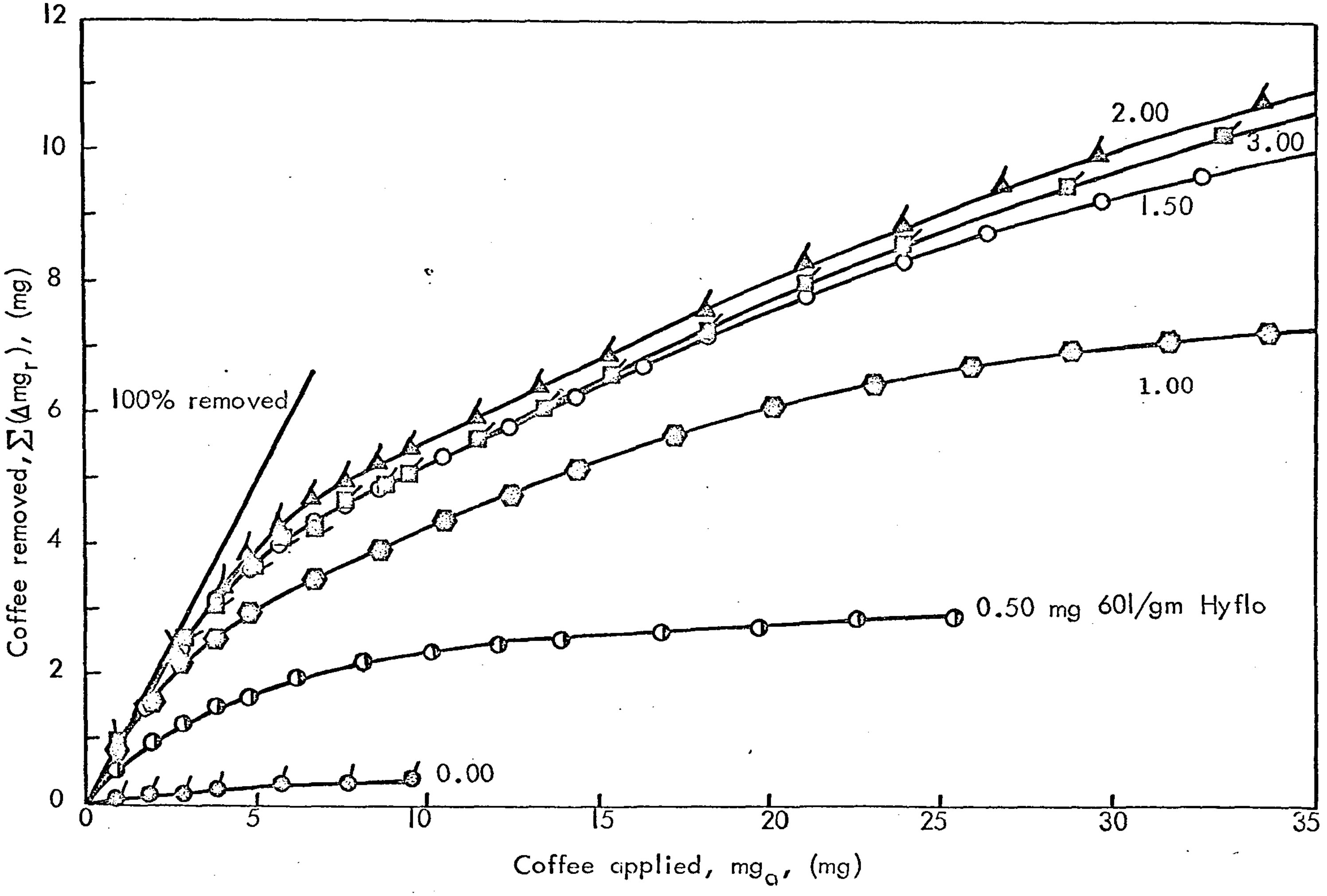
Figure 22. Coffee removed versus coffee applied in a series of runs using coffee colored compounds where the level of coating was varied (0.48 mg_a in one minute of filtration time)

W = 4.00 gm Hyflo SuperCel

Q/A = 0.49 gpm/ft^2 (16.0 ml/min)

C_i = 30.1 gm/l

pH_i = 5.8 - 6.0



12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
Coffee removed, $\sum(\Delta mg_r)$, (mg)
Coffee applied, mg_a, (mg)
100% removed
2.00
3.00
1.50
1.00
0.50 mg 601/gm Hyflo
0.00

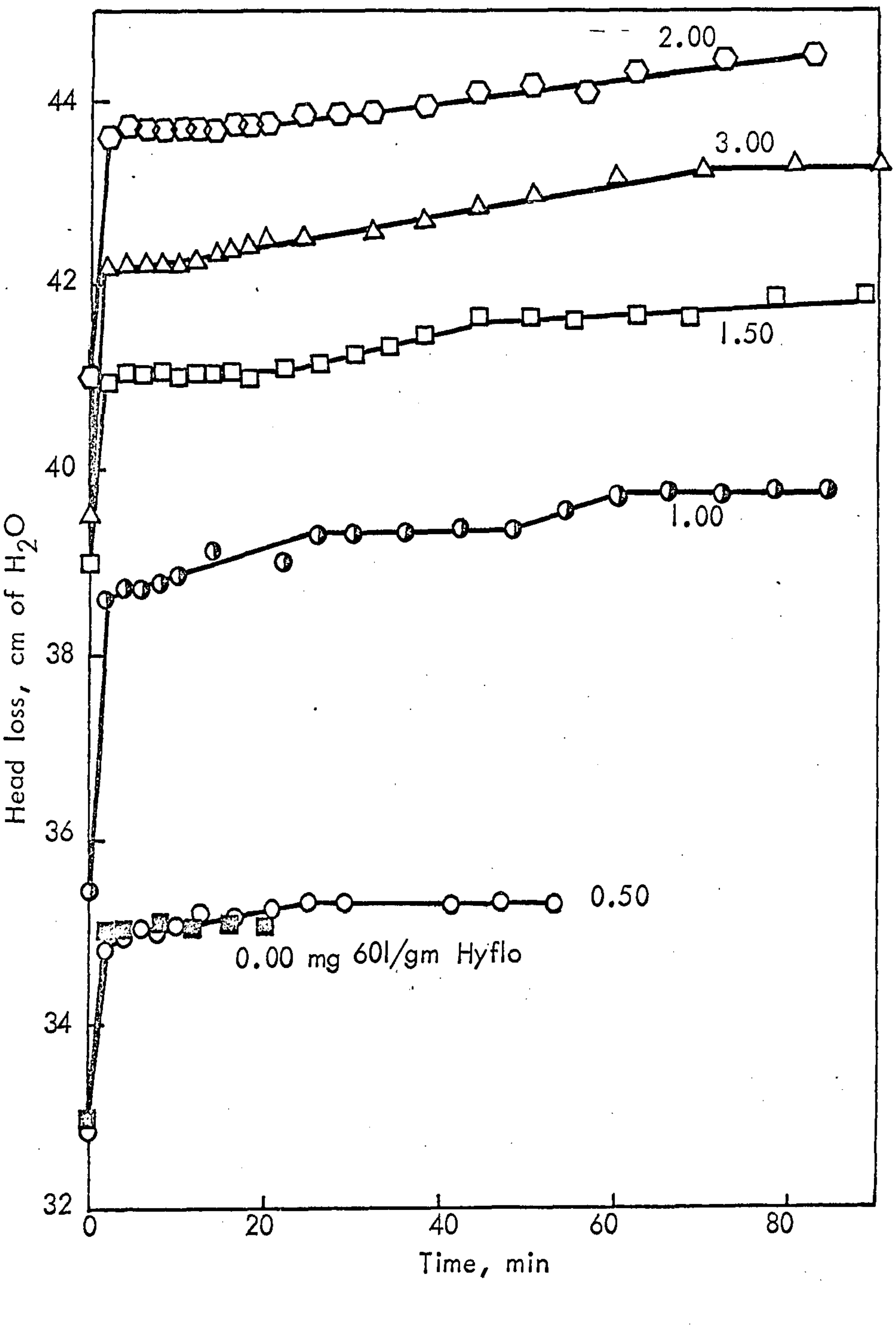
Figure 23. Head loss build up curves in a series of runs using coffee colored compounds where the level of coating was varied (corresponds to data shown also in Figures 21 and 22)

W = 4.00 gm Hyflo SuperCel

Q/A = 0.49 gpm/ft^2 (16.0 ml/min)

C_i = 30.1 mg/l

pH_i = 5.8 - 6.0


Head loss, cm of H_2O
Time, min
2.00
3.00
1.50
1.00
0.50
0.00 mg 601/gm Hyflo
32
34
36
38
40
42
44
0
20
40
60
80

INTERPRETATION OF RESULTS

Effluent History Curves

The effluent history curves developed for the removal of Panther Creek clay, Black Hills clay, and coffee colored compounds on 601-coated diatomite are shown in Figures 4, 7, 10, 13, 16, and 21. The shape of these effluent history curves is similar when significant removal of particulate matter is accomplished. Significant removal was obtained when the diatomite filter cakes were coated with 601, indicating the existence of a specific interaction between the particulate matter and coating material at the filter media surface. The effluent history curves presented are of the same general type that are observed with granular carbon adsorption columns, ion exchange columns, and during the filtration of iron sols through granular filter media (25, 26). Removal of macromolecules, ionic species, and iron sol particles in these systems results from a specific interaction between these species and the filter media phase. Therefore, those parameters which are used to describe and analyze the removal patterns by adsorption columns will be used to describe and analyze the removal patterns observed in this study.

Background information

As liquid containing the suspended solids to be removed enters a column containing the filter media, adsorption begins to occur. If the particulate matter is effectively transported to the filter media surface and has a large affinity for this surface, it will be completely removed from the liquid phase. The particle-free liquid will then continue through the filter bed and the effluent will contain no suspended particles. As the influent is fed continuously, the top layers of the filter bed are constantly exposed to particle laden liquid. Eventually, the top layers of the filter bed will have adsorbed as much particulate matter as possible. That is to say, the filter media's adsorption capacity will be used up or exhausted. If the suspended particles have an affinity for each other in addition to an affinity for the filter media surface, multilayer adsorption can occur. If the particles have no special affinity for one another, or are repelled by one another, then monolayer or incomplete monolayer adsorption will occur; wherein, some fraction of the available surface area will be covered by adsorbed particles. After the top layer of the filter bed has adsorbed as much particulate matter as possible, the influent suspension will pass through this layer essentially unchanged. The zone in which adsorption occurs is thus displaced further into the filter bed.

The adsorption zone is the depth of filter bed over which the adsorption process causes a change in interstitial particulate matter concentration from C_i to C_e. Ultimately, this zone reaches the bottom of the filter bed and particulate matter will then appear in the effluent. This first appearance of suspended solids in the effluent is defined as the beginning of breakthrough of the particulate matter. As influent is continually fed, the adsorption zone is displaced from the bottom of the filter bed and the solids concentration in the effluent goes from zero just before breakthrough to the same solids concentration as in the influent at the end of the breakthrough period. The shape of the effluent history curve describes the breakthrough and provides information concerning the manner in which particulate matter is adsorbed in the filter bed.

The adsorptive capacity of the filter bed is described as:

$$\int_{0}^{t_v} (1 - C_e/C_i)\, C_i\, Q\, dt\ , \qquad (4)$$

where, t_v is the time at which breakthrough is completed, i.e., when C_e becomes equal to C_i. From Equation 4 it is seen that the adsorption capacity of the filter bed is simply the summation of removals occurring over increments of time.

The shape of the breakthrough curve is dependent on three factors. These three factors are the equilibrium between adsorbed and unadsorbed particulate matter, the rate at which adsorption occurs, and operating conditions such as flow rate and depth of adsorption column (26). Equilibrium is favorable when there is a high degree of affinity between the filter media surface and the particulate matter. The larger the affinity, the smaller the zone where adsorption occurs and the sharper, or steeper the breakthrough curve, all other factors being constant. When a high degree of affinity exists, the shape of the breakthrough curve attains a steady-state shape and remains the same for increasing depths of the filter bed. Equilibrium is unfavorable when the particulate matter has a low degree of affinity for the filter media surface. Then the zone in which adsorption is taking place becomes larger as it moves through the filter bed (26). This results in a diffuse breakthrough curve, i.e., the time period during which C_e goes from zero to C_i is large.

The rate of adsorption and the filter operating conditions also affect the shape of the breakthrough curve. As a suspension flows through a filter bed, a given volume of liquid is in contact with a given layer of the filter bed for only a limited time. If the rate of adsorption is low and/or the interstitial velocity is high, local equilibrium will not be attained and the breakthrough curve will become more diffuse. Therefore, any measure taken which will increase the rate of adsorption or decrease the rate of motion of the adsorption zone through the filter bed will tend to cause the breakthrough curve to become steeper. The rate of adsorption is proportional to the rate at which particles come into contact with unoccupied adsorption sites and stay there. Hence, any measure taken which will increase the rate of particle transport to the filter media surface will result in a steeper breakthrough curve. In addition, any measure taken which would increase the number of adsorption sites in a given volume of filter bed should result in a steeper breakthrough curve. The rate of motion of the adsorption zone through the filter bed will be decreased by decreasing the flow rate, decreasing the influent concentration of particulate matter, or by increasing the number of adsorption sites per unit volume of filter bed.

The effect of filter bed depth on the shape of the breakthrough curve will depend on equilibrium conditions. If a favorable equilibrium exists, a steady-state breakthrough curve will be developed and will not change with increasing filter depths. However, if unfavorable equilibrium exists, the zone in which adsorption takes place will become larger as it passes through the filter bed and the breakthrough curve will become more diffuse with increasing depth.

Observations of effluent curves presented

The significant factor which differentiates the effluent curves presented in Figures 4, 7, 10, 13, and 16 from pure adsorption effluent curves is the observation that after breakthrough, removal of from 5 to 10 percent of the particulate matter was still observed. Though removals prior to and during breakthrough can be likened to adsorption phenomena, this residual removal cannot. The fact that a residual removal was observed indicated that removals were occurring by some mechanism in addition to adsorption.

By far the most significant observation to be made as the result of this study is the observation that filter cakes coated with 601 removed nearly 100 percent of the applied clays; whereas, uncoated filter cakes removed insignificant quantities of the same materials under similar test conditions. See Figures 4, 10, 13, and 19.

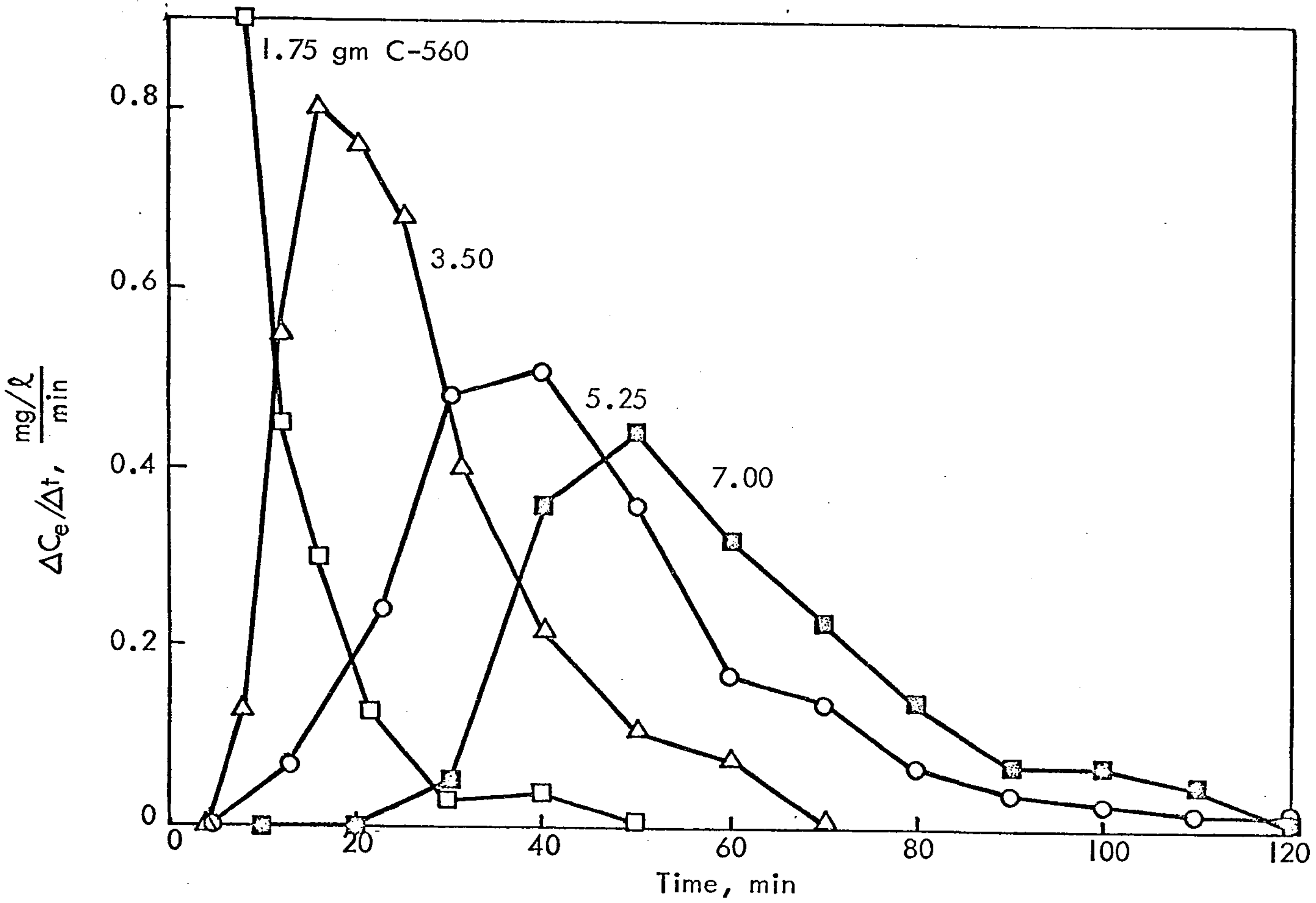
Figure 21 indicates that about 15 percent of the coffee compound was never removed by coated filter cakes. A rapid breakthrough of only about 60 percent of the influent concentration occurred, i.e., C_e/C_i went from 0.15 to about 0.75 very quickly. In the Panther Creek clay and Black Hills clay runs presented in Figures 4 and 13, breakthrough ended when 90 to 95 percent of the clay in the influent was passing through the filter cake, i.e., C_e/C_i went from about zero to 0.90 to 0.95 very quickly. For a pure adsorption column, breakthrough would end when 100 percent of the clay in the influent would pass through the filter, or C_e/C_i would go from zero to 1.0. It would appear from the observations and comments just made, and from the results shown in Figure 21, that the coffee material used in this study was a heterogeneous mixture of organic compounds which had a varying affinity for the 601 coating material used. Some of these compounds could be removed by adsorption; others could not.

The effluent history curves presented in Figure 4 for the removal of Panther Creek clay on 601-coated C-560 indicate that as the adsorptive capacity of the filter cake increases, the breakthrough curves become more diffuse. The most plausible explanation for this observation would be that unfavorable equilibrium existed between the Panther Creek clay in suspension and that adsorbed on the 601 coating present. Increasing levels of coatings, or increasing adsorptive capacities, should cause the zone of adsorption to pass through the filter cake at a slower rate, i.e., the breakthrough curve would be displaced to a larger filtration time in Figure 4. Unfavorable equilibrium causes the depth of the adsorption zone to become larger as it passes through a filter cake. Therefore, a slower rate of travel of the adsorption zone would result in a more diffuse breakthrough curve.

Figure 10 indicates that the shape of the breakthrough curve for Panther Creek clay adsorption on 601-coated C-560 is affected by the depth of the filter cake and/or the time of filtration. A more visual picture of this effect can be seen in Figure 24, which is a plot of the data in Figure 10 showing the change of the effluent clay concentration per unit time versus the time of filtration. A sample of the calculation procedure used in determining $\Delta C_e/\Delta t$ is presented in Table 1. Obviously, the curves in Figure 24 are simply an indication of the

Figure 24. The time rate of change in effluent concentration versus filtration time in a series of runs using Panther Creek clay where the depth of filter cake was varied (7.00 gm C-560 resulted in a 1 5/16 inch deep filter cake)

The data were derived from data presented in Figure 10. Refer to Figure 10 for the values of operational variables.


1.75 gm C-560
3.50
5.25
7.00
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
Time, min
$\Delta C_e/\Delta t$, $\frac{mg/\ell}{min}$

slope of the breakthrough curves in Figure 10 at increasing filtration times. Figure 24 indicates that, for increasing depths of filter cake, the breakthrough curve which describes the solids concentration variation in the adsorption zone as it passes from the bottom of the filter cake is more diffuse and that the maximum slope decreases. These observations support the previous contention that unfavorable equilibrium exists between the Panther Creek clay in suspension and that adsorbed on the 601-coated C-560 using the systems studied. Increasing the depth of the filter cake, all other factors being constant, decreases the rate of movement of the adsorption zone through the filter cake. Unfavorable equilibrium results in the depth of the adsorption zone becoming larger as it travels through the filter cake. Therefore, for increasing depths of filter cake the breakthrough curve becomes more diffuse.

Figure 24 also indicates that the trailing end of the breakthrough curve is more diffuse than the leading end. This is most likely due to a decreased rate of adsorption in the trailing end of the adsorption zone. In the trailing end of the adsorption zone, the suspended solids concentration is higher than in the leading end and the number of available adsorption sites is decreased. Increasing suspended solids concentrations tend to increase the adsorption rate by increasing the concentration gradient between the bulk suspension and the filter media surface. On the other hand, decreasing the number of available adsorption sites tends to decrease the rate of adsorption. Evidently the effect of decreasing adsorption sites outweighed the effect of increasing concentration gradients and the net result was a decrease in the rate of adsorption in the trailing end of the adsorption zone.

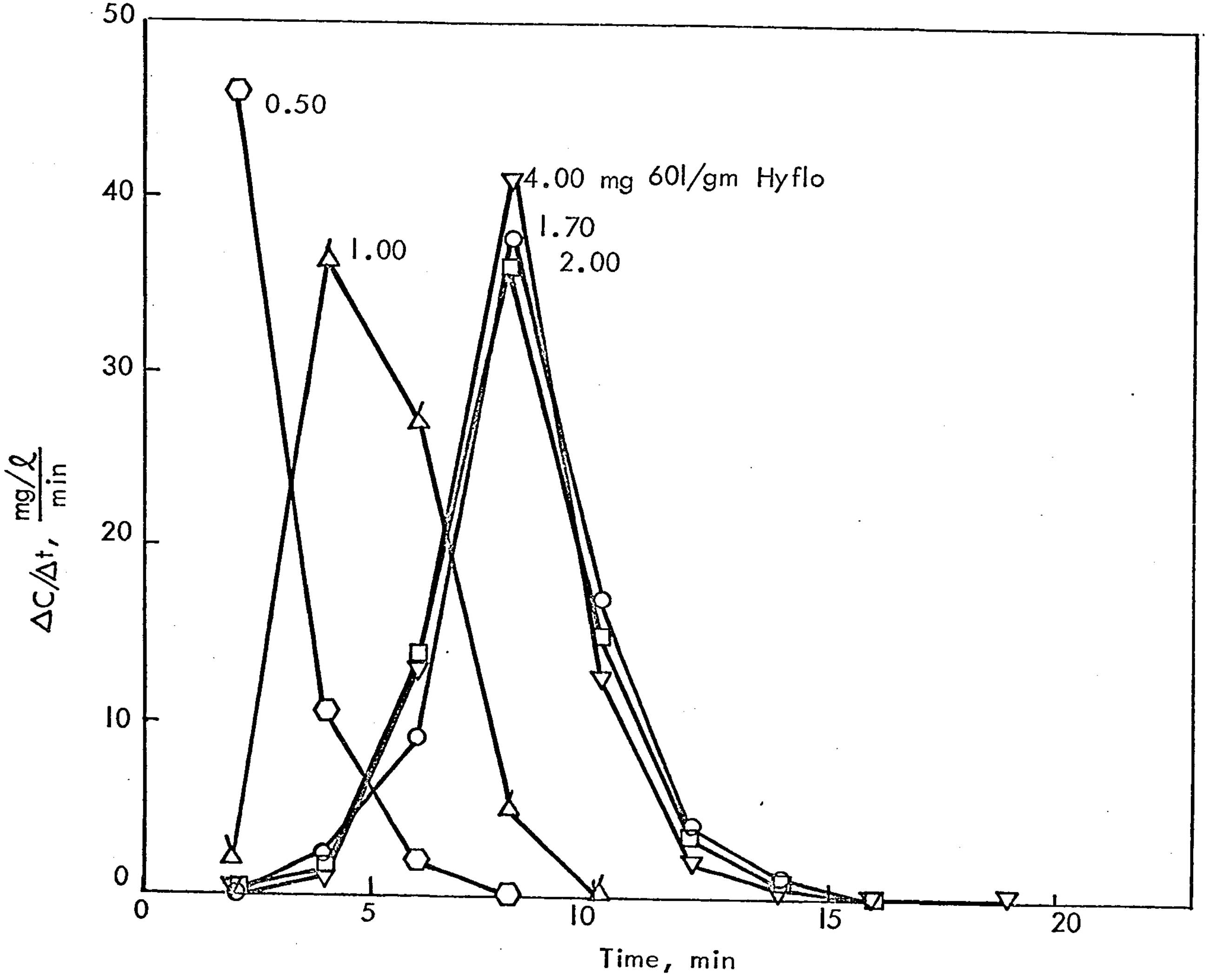
Figure 7 shows the removal of Panther Creek clay on 601-coated C-560 at different levels of suspension pH. An analysis of these breakthrough curves leads to the same conclusions that have just been made concerning the breakthrough curves shown in Figures 4 and 10. It appears that unfavorable equilibrium existed in the filtration system used to evaluate the removal patterns of Panther Creek clay by 601-coated C-560 and that some removal occurred by another mechanism in addition to removal of the clay by adsorption on the 601 coating.

The effluent history curves in Figure 13 are for the removal of Black Hills clay on Hyflo SuperCel at various levels of 601-coating. The shape of the breakthrough curves is not significantly affected by the adsorptive capacity of the filter cakes. This observation is more clearly confirmed in the results shown in Figure 25, which is a plot of the data in Figure 13 showing the time rate of change in the effluent clay concentration versus the filtration time.

The effluent history curves in Figure 16 are for the removal of Black Hills clay on 601-coated Hyflo SuperCel at various levels of suspension pH. At pH_i levels above 8.2, the shape of the breakthrough curve was significantly different than at pH_i levels below 6.9. However, the results shown in Figure 17 indicate that the clay removal capacity of 601-coated Hyflo SuperCel was not affected by the level of pH_i. Since all operational variables other than pH_i were held constant in this series of runs, the only plausible explanation for the more diffuse breakthrough curves at pH_i levels above 8.2 is that the higher pH's must have caused a decrease in the rate of adsorption of Black Hills clay on the 601 coatings. The suspected reason for the

Figure 25. The time rate of change in effluent concentration versus time in a series of runs using Black Hills clay where the level of coating was varied

The data are taken from Figure 13. Refer to Figure 13 for the value of operating variables.



50
40
30
20
10
0
0
5
10
15
20
Time, min
ΔC/Δt, mg/ℓ / min
0.50
1.00
4.00 mg 601/gm Hyflo
1.70
2.00

decreased rate of adsorption at pH_i levels above 8.2 will be presented in a later section where the effects of pH_i are interpreted.

Effect of Variables Studied on Adsorptive Removal Capacities

The results of the studies made were analyzed to provide a quantitative value of the adsorptive capacity and the effect of various parameters on the removal capacity of 601-coated diatomite filter cakes.

Determining removal capacities

Equation 4 cannot be used to calculate the adsorptive removal capacities using data from the effluent history curves presented in Figures 4, 7, 10, 13, 16, and 21. In Equation 4, t_v is defined as that time when C_e becomes equal to C_i. In the effluent history curves presented, the value of C_e did not approach C_i but some fraction of C_i (usually about 0.90 to 0.95). Therefore, t_v had to be redefined in order to analyze the data produced in this study.

After breakthrough, the effluent concentration, or C_e/C_i, became, or approached, a constant value. For example, in Figure 13 for the run at 2.00 mg 601/gm Hyflo SuperCel, C_e/C_i reached a value of 0.91 after 14 minutes of filtration and remained constant thereafter. This is shown in Figure 25 where $\Delta C_e/\Delta t$ became zero at about the same time. Using a value of 14 minutes for t_v and solving Equation 4 by graphical integration of the effluent history data (as in the example in Table 1) the milligrams of clay removed can be computed. Figures 5, 8, 11, 14, 17, and 22 in which $\Sigma(\Delta mg_r)$ is plotted versus mg_a can also be used to determine the amount of clay removed. In these figures, the curves approach a constant slope. Since mg_a equals a constant ($Q\ C_i$) times time (t), $\Delta\ mg_a/\Delta\ t$ also equals a constant. Since $\Delta\ mg_r/\Delta\ t$ becomes constant when C_e/C_i becomes constant (i.e., $\Delta\ mg_r$ equals $(1 - C_e/C_i)\ C_i\ Q\ \Delta\ t$), the change in $\Sigma(\Delta\ mg_r)$ per unit change in mg_a also becomes constant. It should be apparent that the level of mg_a at which the change in $\Sigma(\Delta\ mg_r)$ per unit change in mg_a becomes constant corresponds to a time of filtration at which C_e/C_i becomes constant or $\Delta\ C_e/\Delta\ t$ approaches zero. Adsorption removal capacities were determined by taking an average of the value of $\Sigma(\Delta\ mg_r)$ where the change in $\Sigma(\Delta\ mg_r)$ per unit change in mg_a become constant and the value of $\Sigma(\Delta\ mg_r)$ which corresponded to the time when $\Delta\ C_e/\Delta\ t$ approached zero. An example of the calculations is included in Table 1. Such an average value of $\Sigma(\Delta\ mg_r)$ will be referred to, as in Figure 26, as being derived from effluent history data.

The head loss increase versus clay removed relationships shown in Figures 6, 9, 12, 15, and 18 indicate that in nearly all cases (except Figure 12) that an abrupt change occurs in the head loss increase per unit of clay removed. This abrupt change seems to correspond to the end of adsorption removals. A critical analysis of the head loss data will be made in a later section of this chapter. It was assumed that the value of $\Sigma(\Delta\ mg_r)$ corresponding to the abrupt change in head loss increase per unit clay removed provided an independent method of determining adsorptive removal capacities. A value of $\Sigma(\Delta\ mg_r)$ derived in this way will be referred to as being derived from head loss data. Such a reference is included in Figure 26.

Filter cake solids removal capacity obtained by the methods just described include removals by any and all mechanisms occurring. It has been noted that some removal occurs even after the apparent adsorptive capacity of the coated filter cake has been exhausted. Since it would be difficult to determine the extent of removals from causes other than adsorption, prior to completion of effluent breakthrough, and since such a determination would not alter the observations to be made, no attempt was made to determine adsorptive removals independent of the small secondary removals taking place.

Effect of level of 601 coating on removal capacity

Curves were prepared to show the amount of particulate matter removed by diatomite filter cakes coated with different amounts of 601. The significant features of these data will be presented and discussed in the sections that follow.

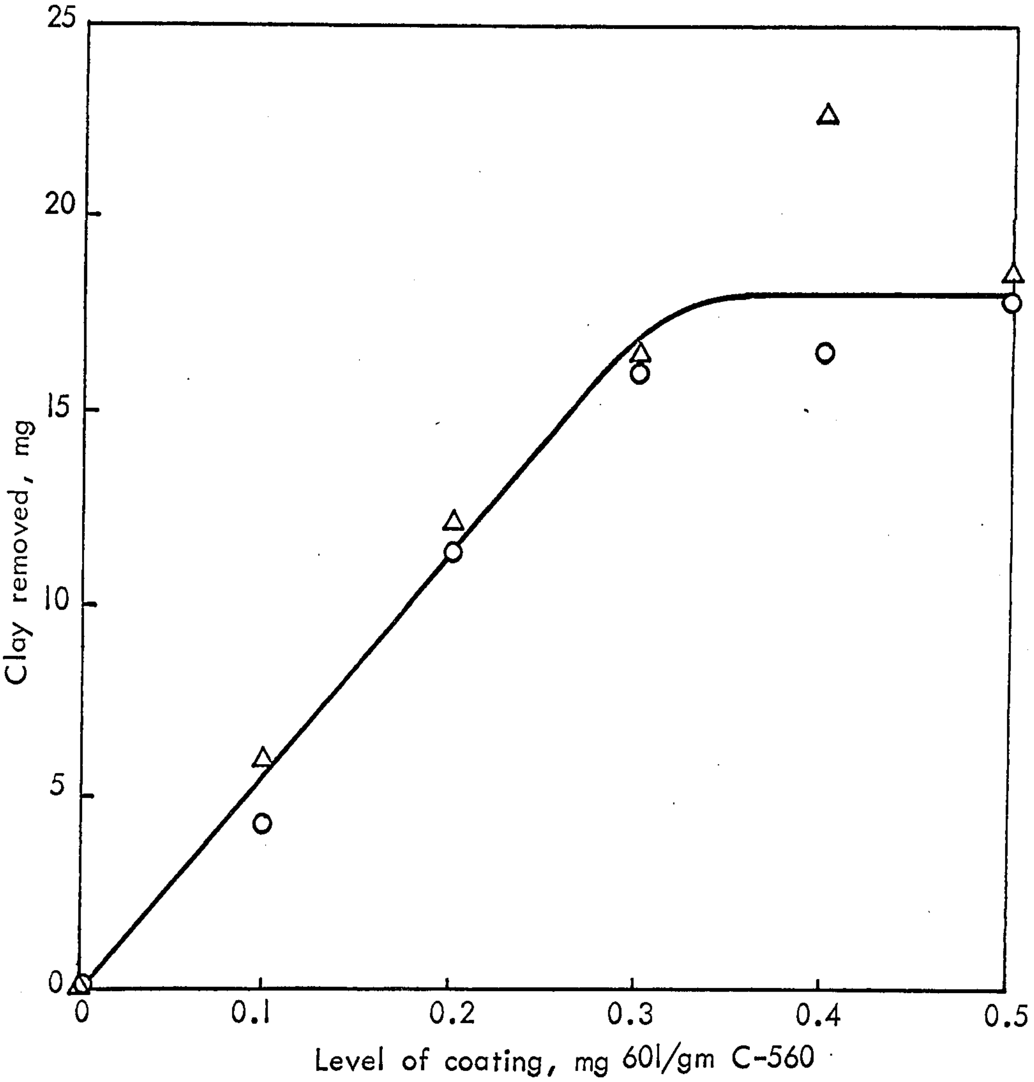
Panther Creek clay   Figure 26 shows the effect of the amount of 601 coating on the amount of Panther Creek clay removed by coated C-560 filter cakes. The data shown in Figure 26 were derived from the effluent history data in Figures 4 and 5 and the head loss data in Figure 6. The results obtained at a coating level of 0.40 mg 601/gm C-560 are from Figure 29, which will be presented later.

The data in Figure 26 show that the amount of Panther Creek clay removed is directly proportional to the level of coating up to a level of coating of about 0.3 mg 601/gm C-560. Below this level of coating, the slope of the straight line shown is 57 mg of clay removed per mg 601 per gm C-560. For the 3.50 gm filter cakes used, this amounts to 57/3.5 or 16 mg of Panther Creek clay removed per mg of 601 coating

Figure 26. Panther Creek clay removal by 3.50 gm C-560 filter cakes coated with various amounts of 601 (refer to Figure 4 for the values of operating variables)

◬ Values derived from effluent history data in Figures 4 and 5

⊙ Values derived from head loss data in Figure 6


25
20
15
10
5
0
Clay removed, mg
0
0.1
0.2
0.3
0.4
0.5
Level of coating, mg 601/gm C-560

present.

For levels of coating above about 0.35 to 0.40 mg 601/gm C-560, the amount of Panther Creek clay removed by the filter cake did not increase. It would appear that 0.35 to 0.40 mg 601 is the maximum amount which can be adsorbed on one gram of C-560 using the coating procedure followed in this study. This value agrees with the level of coating that produces the maximum change in the apparent zeta potential of 601-coated C-560. The effect of coating level on zeta potential is shown in Figure 37, presented in the Appendix. The results shown in Figures 26 and 37 indirectly indicate that for coating levels below 0.30 mg 601/gm C-560 the amount of Panther Creek clay removed can be positively correlated with the apparent zeta potential of the coated C-560 filter cakes. This observation raises the question of whether Panther Creek clay removal is dependent on electrical double layer interactions or on some other specific clay-polymer interaction. This question will arise again later and be discussed then.

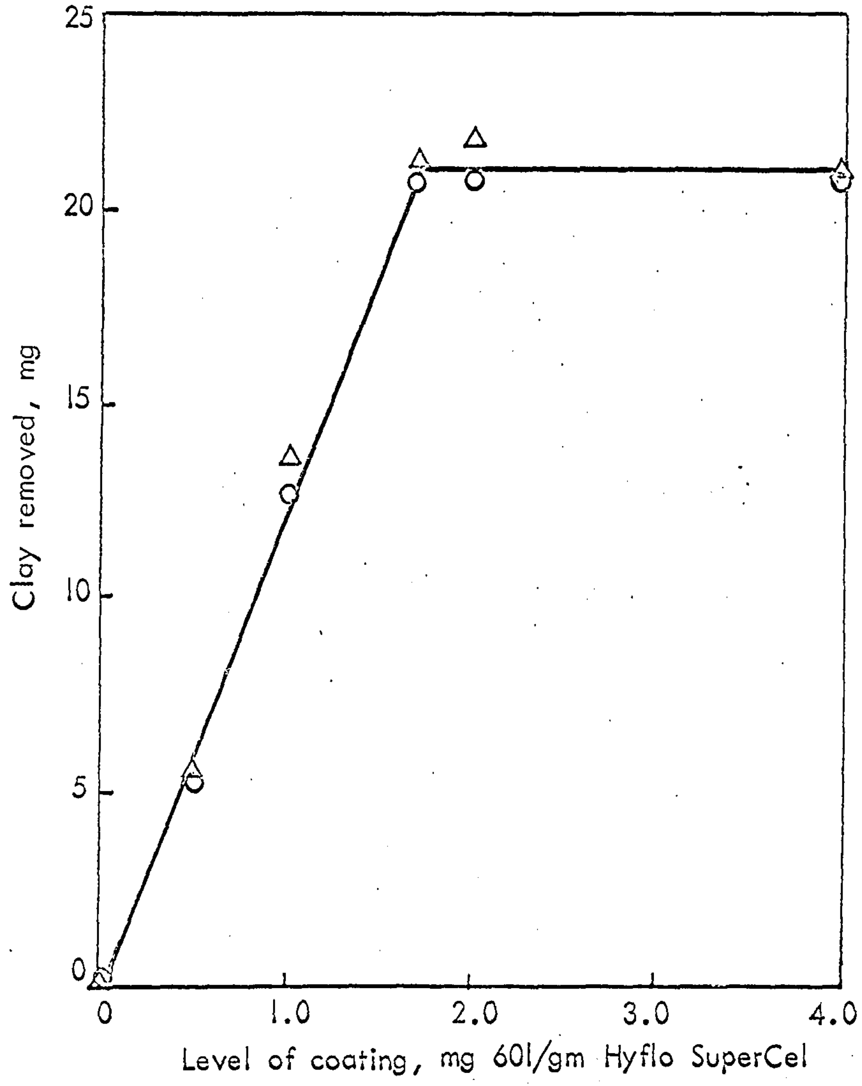
<u>Black Hills clay</u> Figure 27 shows the effect of the amount of 601 coating on the amount of Black Hills clay removed by coated Hyflo SuperCel. The data shown in Figure 27 were derived from the effluent history data in Figures 13 and 14 and the head loss data in Figure 15.

The data in Figure 27 show that the amount of Black Hills clay removed is directly proportional to the level of coating up to a level of about 1.7 mg 601/gm Hyflo SuperCel. Below this level of coating, the slope of the straight line shown is 12.3 mg of clay removed per mg 601 per gm of Hyflo SuperCel. For the 4.00 gm Hyflo SuperCel filter cakes used, this amounts to 12.3/4.00 or 3.1 mg of Black Hills clay

Figure 27. Black Hills clay removal by 4.00 gm Hyflo SuperCel filter cakes coated with various levels of 601 (refer to Figure 13 for the values of operating variables)

◬ Values derived from effluent history data in Figures 13 and 14

Θ Values derived from head loss data in Figure 15


Clay removed, mg
0
5
10
15
20
25
0
1.0
2.0
3.0
4.0
Level of coating, mg 601/gm Hyflo SuperCel

removed per mg of 601 coating present.

For levels of coating above 1.7 mg 601/gm Hyflo SuperCel, the amount of Black Hills clay removed by the coated Hyflo SuperCel does not increase. It would appear that 1.7 mg 601 is the maximum amount which can be adsorbed on one gram of Hyflo SuperCel using the coating procedure followed in this study.

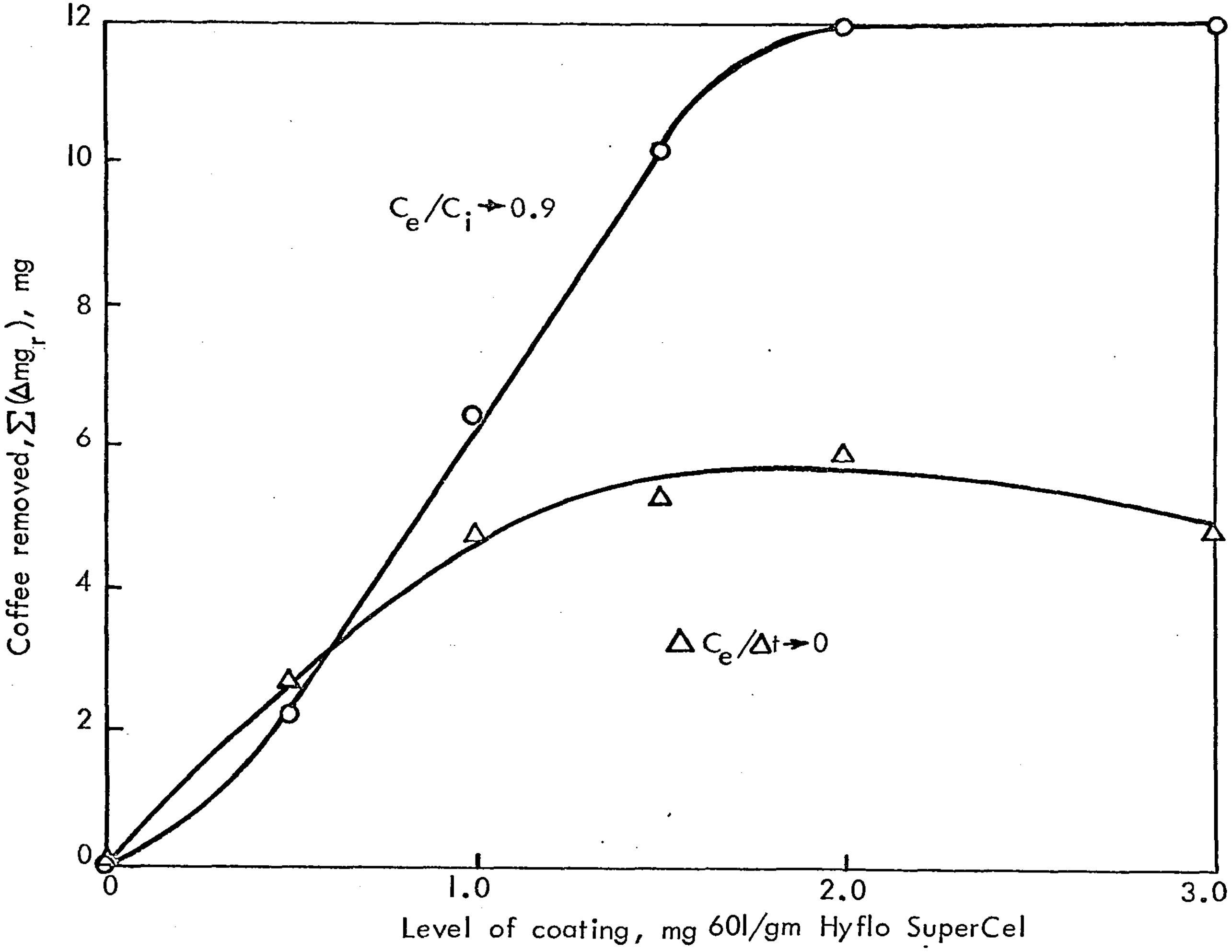
Ball clay Figure 19 indicates that a diatomite filter cake coated with 601 removed all of the Ball clay that passed through an uncoated filter cake provided that the pH was satisfactory and the removal capacity of the coating was not exceeded. The meager data available indicate that this clay readily adsorbs on the 601 coatings. However, the quantitative data needed to predict the weight of Ball clay removed per mg of 601 coating were not collected.

Coffee The criteria used to determine clay removal capacities by coated filter cakes are not applicable to the determination of coffee removal capacities. Figure 21 shows that the effluent history curves for coffee removal are not uniform. It is seen that for levels of coating above 1.00 mg 601/gm Hyflo SuperCel $\triangle C_e/\triangle t$ goes to zero, at a C_e/C_i of about 0.75 to 0.80, and then becomes a positive value again. Figure 23 shows that insignificant head loss build up occurred during the coffee removal runs and, hence, the head loss criteria used previously in calculating clay removal capacities cannot be applied for determining coffee removal capacities.

Figure 28 is an approximation of the amount of coffee removed by 4.00 gm filter cakes containing coated Hyflo SuperCel. The data presented in Figure 28 were derived from the data in Figure 21. The two

Figure 28. Coffee removal by 4.00 gm Hyflo SuperCel filter cakes coated with various levels of 601 (refer to Figure 21 for the values of operating variables)

◬ , ⊖ Values derived from effluent history data in Figures 21 and 22.


12
10
8
6
4
2
0
Coffee removed, $\sum(\Delta mg_r)$, mg
0
1.0
2.0
3.0
Level of coating, mg 601/gm Hyflo SuperCel
$C_e/C_i \rightarrow 0.9$
Δ $C_e/\Delta t \rightarrow 0$

curves describe coffee removals up to the point where C_e/C_i reaches 0.9 and the point where $\Delta C_e/\Delta t$ reaches zero for the first time. The upper curve indicates that about 1.7 mg of coffee was removed per mg of the 601 coating (10 mg of coffee removed/(4.0 gms of Hyflo SuperCel) (1.5 mg 601/gm Hyflo SuperCel) equals 1.7 mg coffee/mg 601). The lower curve indicates that about 1.2 mg of coffee was removed per mg of 601 (4.7 mg of coffee removed/(4.0 gms of Hyflo SuperCel) (1.0 mg 601/gm Hyflo SuperCel) equals 1.2 mg coffee/mg 601). The lower curve levels off at about 1.5 to 2.0 mg 601/gm Hyflo SuperCel which is about the same coating level at which Black Hills clay removal leveled off in Figure 27.

General comments It has just been shown that the amount of Panther Creek clay, Black Hills clay, and coffee material removed on 601-coated diatomite filter cakes was proportional to the amount of 601 coating present up to a certain level of coating. It was concluded that about 0.35 to 0.40 mg 601/gm C-560 and about 1.7 mg 601/gm Hyflo SuperCel were the maximum amounts of 601 that were adsorbed on the respective grades of diatomite. The maximum amount of 601 which can be adsorbed on diatomite filter media is limited by the surface area available and the chemical and physical properties of the 601 coating material. The method of coating was arbitrarily established for use in this study. A few basic calculations based on reasonable assumptions will show that the method of coating used was undoubtedly a relatively poor one.

The specific surface area of diatomite has been reported to be about 20 m^2/gm (48). The results in Figure 27 indicate that about 1.7 mg of 601 is the maximum amount which was adsorbed on one gm of Hyflo SuperCel. Since the polyalkyl polyamine in 601 represents only 37 percent of the total weight of 601, the amount of polymer actually adsorbed was only about 0.63 mg polymer per gm of Hyflo SuperCel. This would provide about 0.032 mg of polymer per m^2 of diatomite filter media surface area. If the density of the polymer is assumed to be about 1 gm/cm^3, the thickness of a monolayer covering all the available surface area would be about 0.32 Å. This, of course, is an impossible value, since the thickness is significantly less than the atomic diameters involved. If the polyalkyl polyamine were adsorbed as a fully extended linear molecule, the effective thickness of such a molecule could hardly be less than about 10 Å and would more likely be about 20 - 30 Å. If a thickness of 16 Å were assumed, the available surface area actually covered by polymer in the example above would be about 2 percent. No matter what the precise value may be, it is apparent that the coating procedure used in this study resulted in coating only a small percentage of the available diatomite surface area with polyalkyl polyamine.

Calculations can also be made to give an indication of the surface area covered by the Black Hills clay removed in the studies conducted. It has been reported that a unit cell of montmorillonite is 10 Å thick and has a surface of 5.15 Å by 8.9 Å and that there are 1.23×10^{-21} gm of mineral per unit cell (60). The data in Figure 27 indicate that 3.1 mg of Black Hills clay was removed per mg of 601 and that 1.7 mg 601/gm Hyflo SuperCel was the maximum level of coating possible.

Thus, the weight of Black Hills clay removed per gram of diatomite would be (3.1) (1.7) or 5.3 mg clay/gm Hyflo SuperCel. This weight of clay would result in 5.3×10^{-3} gm/1.23×10^{-21} gm/unit cell or 4.3×10^{18} unit cells of clay would be removed per gram of Hyflo SuperCel. Since the surface area per unit cell is (5.15) (8.9) or 46 $\mathring{A}^2$ or 46 x 10^{-20} m^2, 5.3 mg of clay unit cells will cover an area of (46 x 10^{-20} m^2/unit cell) (4.3 x 10^{18} unit cells) or 2.0 m^2/gm diatomite. Assuming as before, that diatomite has a surface area of about 20 m^2/gm, the percentage of the surface area covered by unit cells would be about 10 percent. It is apparent that, if Black Hills clay were removed as unit cells of the montmorillonite, the surface area covered would be in the same order of magnitude as the surface area covered by adsorbed 601, previously calculated to be about 2 percent. It is extremely unlikely that the Black Hills clay particles were unit cell sized and it is also unlikely that the exposed polyalkyl polyamine (601) coating was completely covered by adsorbed clay. The intricate structure of diatomite, as shown in Figures 31, 32, 33, and 34 in the Appendix, could result in less than 100 percent of the total surface area of a diatomite filter cake being available to polymer or clay which could adsorb. The significance of these computations is problematical, but they provide an indication of the order of magnitude of surface areas covered by both the polymer and the clay.

Effect of pH on removal capacities

The charge characteristics of a polyamine is pH dependent. As the solution pH is varied from about 5 to about 10 the number of charged amine groups decreases somewhat uniformly. If the adsorption capacity of the polymer is related to the charge character of the 601 coating material, the variable pH studies should indicate this relationship.

Panther Creek clay   Figure 7 shows that increasing the pH of the clay suspension reduces the amount of Panther Creek clay removed on 601-

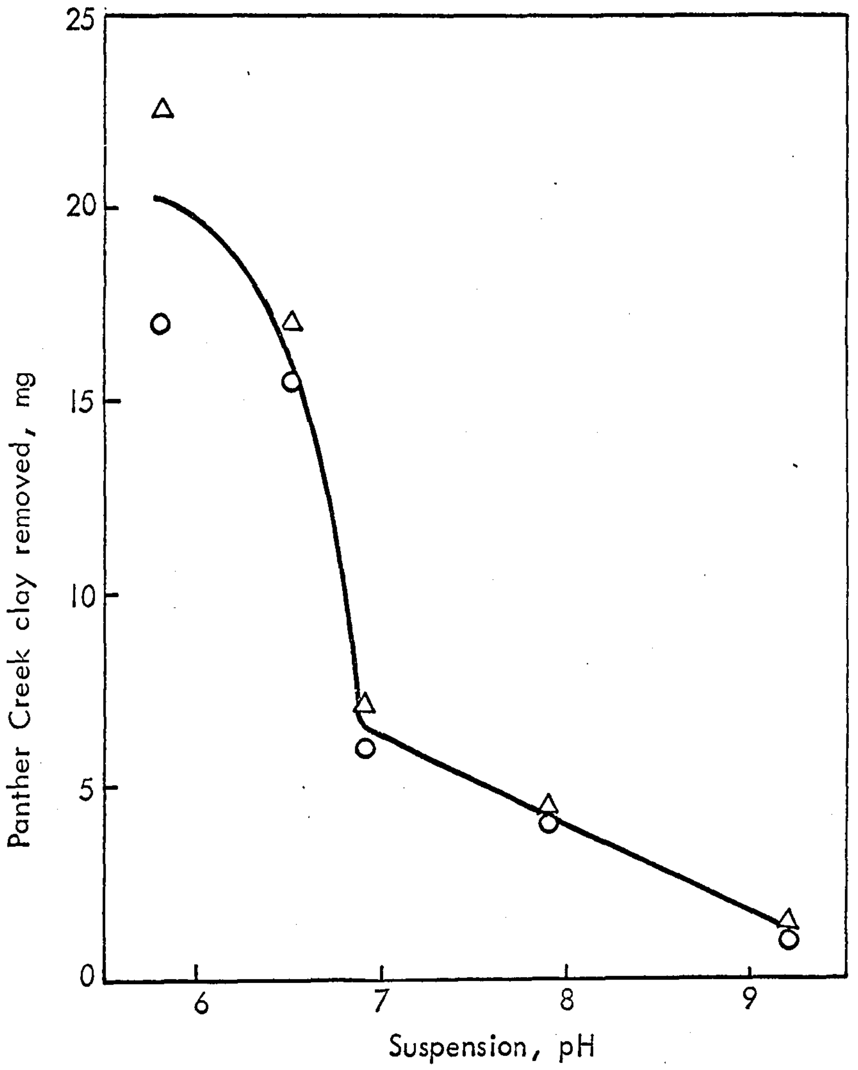
Figure 29. Effect of pH on Panther Creek clay removal by 3.50 gm C-560 filter cakes coated with 0.40 mg 601/gm C-560 (refer to Figure 7 for the values of operating variables)

◬ Values derived from effluent history data

in Figures 7 and 8

Θ Values derived from head loss data in

Figure 9


Panther Creek clay removed, mg
0
5
10
15
20
25
6
7
8
9
Suspension, pH

coated C-560. Figure 29 shows the effect of the suspension pH on the removal capacity of 3.50 gm of C-560 coated with 0.40 mg 601/gm C-560. The data presented in Figure 29 were derived from the effluent history data in Figures 7 and 8 and the head loss data in Figure 9.

Figure 29 indicates that for pH's below 6.9, a small decrease in pH results in a large increase in removal capacity. This observation correlates in a very crude manner with electrical double layer interaction theory. Figure 38 in the Appendix shows that with pH values below about 7, the apparent zeta potential of 601-coated diatomite is positive and increases with lower pH values. This should result in increasing the attractive electrical double layer interaction energy which in turn could increase the adsorption rate and/or capacity of the electronegative clay and electropositive 601-coated filter media system. Figure 29 also indicates that the removal of Panther Creek clay decreases as the suspension pH increases above 6.9. Figure 38 in the Appendix, demonstrates that the apparent zeta potential of 601-coated diatomite becomes increasingly negative as solution pH increases above about 7 to 8. This should result in increasing the electrical double layer energy barrier which could decrease the adsorption rate and/or capacity for the electronegative clay and electropositive 601-coated filter media system.

Black Hills clay The effect of suspension pH on the removal of Black Hills clay was different from its effect on the removal of Panther Creek clay. The data in Figures 17 and 18 indicate that the removal capacity of Black Hills clay by Hyflo SuperCel coated with 1.70 mg 601/gm Hyflo SuperCel was not grossly affected by the suspension pH. The data in Figures 17 and 18 indicate that the average removal capacity of the coated filter media was about 20 mg of Black Hills clay per 4.00 gm of Hyflo SuperCel coated with 1.70 mg 601/gm Hyflo SuperCel. This would be a removal of about 20/(4.00) (1.70) or 3 mg of Black Hills clay per mg of 601. Evidently the predominately uncharged polyamine at a pH of 8.8 can adsorb as much Black Hills clay as the predominately positively charged polyamine at a pH of 6.0.

Figure 16 indicates, however, that at pH values above 8.2 the rate of adsorption is less than at pH values below 6.9. The basis for this observation was developed in the first section of this chapter.

Of all the removal mechanisms discussed in the background chapter of this thesis, the only ones which should be significantly affected by solution pH would be the electrical double layer interaction and perhaps some specific chemical forces. However, it should be noted that the initial permeability, K_o, observed with coated Hyflo SuperCel filter cakes was about 25 percent higher in the higher pH runs than it was in the lower pH runs. Whether or not this difference in K_o resulted from some factor which would also have significantly affected the removal patterns is problematical.

There are at least two possible explanations for the observed difference in Black Hills clay removal rates at high and low pH values based on electrical double layer interactions. One deals with particle transport when attractive forces exist and the other deals with adsorption energy barriers when repulsive forces exist.

It is conceivable that the transport of clay particles is affected by electrical surface potentials. When electrical double layers of oppositely charged surfaces interact, the larger the Stern potentials (approximated by zeta potential) the larger will be the attractive electrical force between the two surfaces at any given separation of the surfaces. As the Stern potential of either or both surfaces decreases, the attractive electrical force decreases. When the Stern potentials are of the same sign, the electrical force causes repulsion when the electrical double layers interact.

At low pH values, when the apparent zeta potential of the 601-coated diatomite is a relatively large positive value, a significant electrical attractive force could exist between the electronegative clay and the electropositive coated diatomite surface when their electrical double layers interact. At increasing pH values above about 7 to 8, the apparent zeta potential of coated diatomite is increasingly negative and it would be expected that increasing repulsive electrical forces would exist. If the transport of clay particles by electrical double layer interaction were significant, a somewhat uniform decrease in adsorption rate would be expected over the pH range of 6 to about 7. This was not observed in the Black Hills clay removal data. Indeed, the effluent history curves for runs in which the pH is in this range are very similar, as evidenced by the data in Figure 16. In addition, there is no indication in Figure 7 that the rate of removal of Panther Creek clay increases as the pH is decreased from about 7. It would appear, therefore, that in this study electrical double layer interaction did not significantly affect the rate at which the clay particles were transported to the coated diatomite surface. This observation, of course, applies only to the systems analyzed. The lack of extensive data may well mean that no significance should be attached to this observation.

A second possible explanation for the difference in the rate of removal of Black Hills clay at high and low pH values indicated by the data in Figure 16 is based on the concept of an electrical energy barrier. At pH values below about 7, there should be no electrical repulsive force when electrical double layers of an electropositive coated diatomite and an electronegative clay particle interact. However, at pH values above about 7, there should be an electrical repulsive force acting when electrical double layers interact. As the pH increases above 7, the magnitude of the electrical repulsive force should increase for any given separation of surfaces. In order for a clay particle to be adsorbed on a 601-coated surface, it must approach this surface with sufficient energy to overcome the electrical energy barrier (electrical repulsive force times separation distance) and come close enough to the surface to be acted upon by the specific forces causing adsorption, i.e., van der Waals forces and/or chemical forces.

The different removal patterns indicated in Figure 16 could result from the absence or presence of such an electrical energy barrier. Below a pH of 6.9, where an electrical attractive force should exist between the 601 coating and the clay particles, removal patterns are not significantly different. Above a pH of 8.2, where an electrical energy barrier should exist, the removal pattern changes. The fact that removals do occur above a pH of 8.2 indicates that some of the clay particles do approach the surface with sufficient energy to overcome the electrical energy barrier and become adsorbed. A significant portion of the clay particles must not have sufficient energy to overcome the electrical energy barrier, since some of the Black Hills clay appears in the effluent from the very start of the filter runs.

Effect of filter cake depth on removal capacity

Figures 10 and 11 indicate that the amount of Panther Creek clay removed by coated C-560 can be increased by increasing the amount, or depth, of the filter cake. Figure 30 shows the amount of Panther Creek clay removed as a function of the amount, or depth, of the filter cake with 0.35 mg 601/gm C-560. The data in Figure 30 were derived from effluent history data in Figures 10 and 11 and head loss data in Figure 12.

The purpose of this series of runs was to demonstrate that the solids removal capacity of a filter cake could be correlated with the amount of surface area in the filter cake. The amount of surface area in a filter cake is directly proportional to the amount of filter media present. Figure 30 shows that the amount of Panther Creek clay removed by coated C-560 is approximately directly proportional to the amount of filter media present. Therefore, the desired relationship between removal capacity and filter media surface area was demonstrated. It is apparent that removals must have occurred over the full depth of the filter cakes.

Head Loss Data

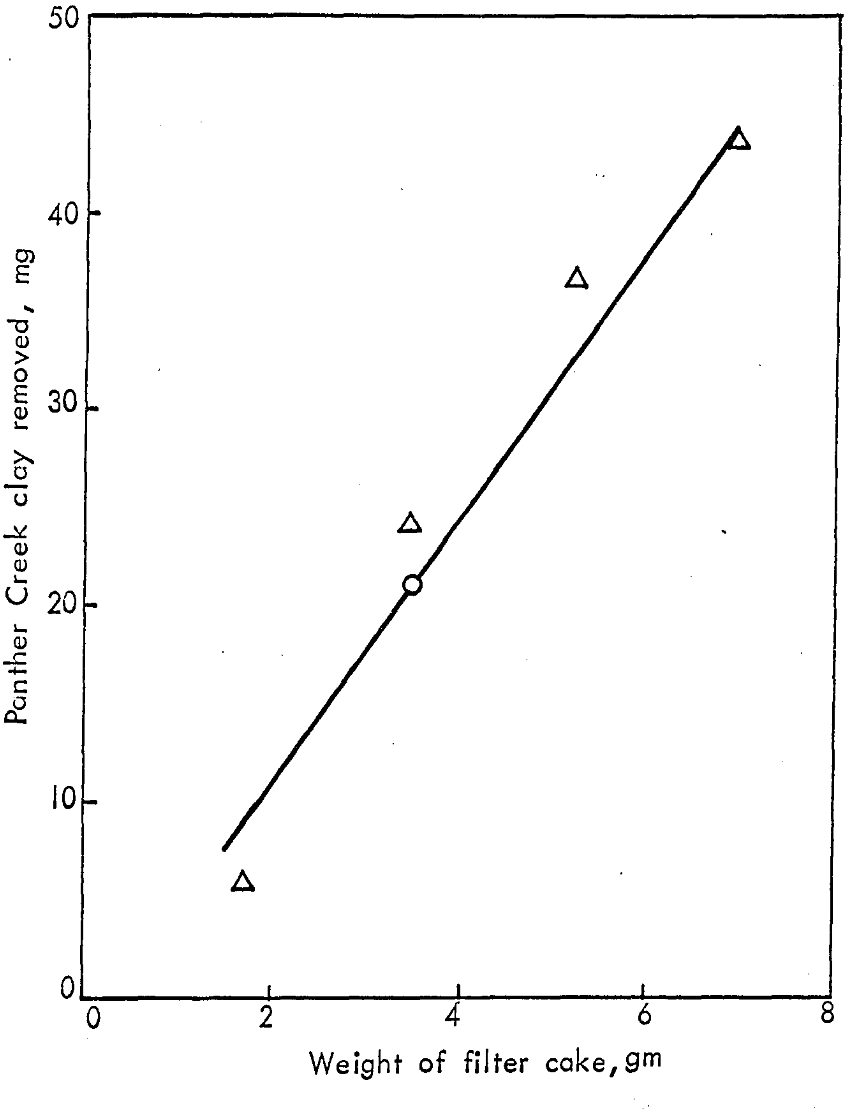
Figures 6, 9, 15, and 18 indicate that the removal of Panther Creek clay and Black Hills clay produced somewhat similar head loss responses. In general, the head loss increase per unit of clay removed was constant, but changed abruptly at a point which correlated

Figure 30. Effect of weight of filter cake coated with 0.35 mg 601/gm C-560 on Panther Creek clay removal (7.0 gm of C-560 produce about a 0.9 inch filter cake)

Refer to Figure 10 for the values of operational variables.

△ Values derived from effluent history data in Figures 10 and 11.

⊙ Values derived from head loss data in Figure 12.


Panther Creek clay removed, mg
0
10
20
30
40
50
0
2
4
6
8
Weight of filter cake, gm

well with the point where the adsorptive capacity of the filter media coating was exhausted. The values of clay removal derived from head loss data indicated by the symbol ⊙ in Figures 26, 27, 29, and 30 show this correlation. As a first approximation, it was expected that the head loss increase initially resulted from adsorptive removals and that after the adsorptive capacity was exhausted, the head loss increase resulted from removal of clay by some other removal mechanism. Computations to be made later show that this "first approximation" was not a sound one.

The head loss data for coffee removal shown in Figure 23 indicates that this material was removed by adsorption in a manner which resulted in very small increases in flow resistance.

Head loss response

When clay particles are retained in a diatomite filter cake, they occupy a finite volume and reduce the volume of void space which is available for transport of the liquid phase. Any increase in head loss across a filter cake which has retained particles is not necessarily, however, a direct consequence of the reduction in void volume available to the liquid. Instead, the head loss response is dependent on the manner in which the particles are removed. The orientation and location of the particles removed in the filter media voids and the rheological properties of the particles removed are important in determining head loss response. To begin to understand the manner in which particles may be removed, it is necessary to have a conceptual model of the pore structure of a porous filter cake.

Granular filter beds are generally conceived as consisting of separate void spaces interconnected by constrictions. In other descriptive terminology, the filter voids are conceived as some sort of random network of various sized conduits connected in a parallel and series arrangement. The same descriptions apply to diatomite filter cakes. As liquid flows through the void spaces in a porous filter cake under what are usually considered to be laminar flow conditions, the flow streamlines converge at constrictions, or small conduits, and diverge at larger void spaces, or large conduits. In regions of converging streamlines, the liquid velocity increases and the viscous shearing forces increase. In regions of diverging streamlines, liquid velocity decreases and the viscous shearing forces decrease. A unit volume of particulate matter removed in regions of high viscous shearing forces will produce a larger head loss increase than would the same amount of matter removed in regions of low shearing stress. If the particulate matter were removed in a uniform manner over the entire filter media surface area available, as would be expected in the case of monolayer adsorption, it is entirely reasonable to expect that the material removed in regions of high viscous shearing forces would make a larger contribution to the resulting head loss response that would the material removed in regions of low viscous shearing forces. Unfortunately, no methods are available to analyze the relative significance of particulate matter removal in low and high viscous force regions of the filter cake voids.

Some of the head loss and clay removal data collected in this study were analyzed by assuming a removal pattern and making theoretical computations of the expected head loss response or the change in the void geometry. Computed values were then compared with the observed values and, depending on the agreement of these two values, the assumed removal pattern was accepted or rejected.

Changes in filter cake porosity

The porosity of a filter cake is defined as the ratio of the void volume within a filter cake to the total volume of the filter cake. Porosity is designated herein by the symbol ϵ. Particulate matter that is retained in a filter cake decreases the porosity of the filter cake due to the volume of the voids actually occupied by the particulate matter. If the decrease in ϵ is large enough, a head loss response should result. A theoretical relationship between head loss and ϵ was developed and the head loss and removal data presented in Table 1 were analyzed to ascertain if the changes in ϵ observed could possibly have caused the head loss response observed.

Several formulas have been presented which predict that the head loss across a filter bed is inversely proportional to ϵ^4, all other factors being constant (20). This relationship implies that for a given filtration system, a change in head loss can be predicted from a change in ϵ by the relationship $H_1\epsilon_1^4 = H_2\epsilon_2^4$, where the subscripts 1 and 2 refer to different porosity conditions.

The porosity of a Hyflo SuperCel filter cake can be computed if its in-place bulk density, γ_d, and the specific gravity of the diatomite are known. The porosity, ϵ, is equal to one minus γ_d divided by specific gravity times the bulk density of water, γ_w. Values of γ_d and specific gravity for Hyflo SuperCel are given in the Appendix as about 21 lb/ft^3 and 2.30 respectively. The value of γ_w is 62.3 lb/ft^3 at 25°C. Therefore, ϵ equals $1 - 21/(2.30)(62.3)$ or 0.85. For the run in Table 1, the level of coating was 2.0 mg 601/gm Hyflo SuperCel. For the 4.00 gram filter cake used, the volume of the filter cake was (4.00 gm)/(454 gm/lb) (21 lb/ft^3) or 4.2×10^{-4} ft^3 or 12 cm^3. The void volume was (0.85) (12) or about 10 cm^3. Assuming that the density of the polyalkyl polyamine coating material was 1.0 gm/cm^3, the volume of polymer adsorbed was $(0.37)(2.00 \times 10^{-3})(4.00)/1.0$ or 0.0030 cm^3 (601 is 37 percent polymer). This volume of the coating material is insignificant compared to the 10 cm^3 void volume computed above. It can, therefore, be assumed that at the start of the filter run presented in Table 1, the filter cake porosity was 0.85. During the first 12 minutes of this filter run, 21.6 mg of Black Hills clay was removed and the head loss increased from 25.2 to 43.0 inches of water. If the Black Hills clay montmorillonite mineral particles were fully hydrated, their specific gravity would have been 1.85 (60). Therefore, 21.6 mg of clay would have occupied a volume of only $(21.6 \times 10^{-3})/(1.85)(1.00)$ or 0.0117 cm^3. This volume of clay removed is also relatively insignificant compared with the 10 cm^3 void volume in the filter cake. The change in ϵ was 0.012/12 or 0.001. The observed change in head loss from 25.2 to 43.0 inches of water could hardly be predicted from the computed change in porosity using the relationship $H_1\epsilon_1^4 = H_2\epsilon_2^4$. This observation indicates that the observed head loss increase per unit of Black Hills clay removed did not result from a uniform change in the filter cake void volume. This observation is contrary to what would be expected for adsorptive removals. Therefore, either the head loss-ϵ relationship isn't applicable to the system analyzed or the head loss increase observed resulted from some fraction of the clay being removed by some mechanism other than by uniform adsorption. It has been noted several times that in the clay removal studies some clay was removed by a mechanism other than adsorption. It is entirely possible that some small fraction of the clay was removed by a straining mechanism at constrictions between void spaces or at pores in the individual diatom skeletons. The head loss increase resulting from such a removal pattern could hardly be predicted by a uniform change in the filter cake void volume.

Straining of clay particles

It is possible that some clay was removed by straining at constrictions between void spaces and by the pores of the individual diatomite particles. This type of removal could have caused significant head loss development since the clay particles would have been removed at regions where high interstitial velocities existed. Clay particle removal at constrictions would have caused a further increase in interstitial velocity either at that constriction or some other constriction or both. Of course, increased interstitial velocities result in increased energy losses which are indicated by increased head losses, all other variables remaining constant.

The limiting condition for removal by straining would be complete plugging of all the constrictions. This would result in essentially clay cake filtration and the diatomite would have served only to support the clay cake. A montmorillonite type clay has been reported to plug completely the pores of a granular carborundum filter media which had particle diameters of 160 microns (16). It can be shown by the data in Table 1 that, if all the Black Hills clay removed had been strained at the surface of the diatomite filter cake, the head loss predicted from clay cake filtration data would be more than an order of magnitude greater than the head loss actually observed.

Rearrangement of Equation 3 for application to clay cake filtration gives:

$$\frac{H}{W} = \left[\frac{(Q/A)\ \mu}{A\ \gamma_W} \right] \left[\frac{1}{\gamma_c\ K} \right], \tag{5}$$

where the terms are in ft-lb-sec units as defined for Equation 3. The value of Q/A is given in Table 1 as 0.508 gpm/ft^2 which is equal to 0.508/(7.48) (60) or 1.13 x 10^{-3} ft/sec. Values of γ_w and μ at the suspension temperature found in standard tables are 62.3 lb/ft^3 and 1.8 x 10^{-5} lb sec/ft^2, respectively. The cross-sectional area of the 1 1/4 - inch diameter filter cake was 0.00852 ft^2. Substitution of these values in Equation 5 will give, for incremental increases in head loss and clay removed:

$$\frac{\Delta H}{\Delta W} = (3.83 \times 10^{-8}) \left(\frac{1}{\gamma_c\ K} \right) \tag{6}$$

Values of $1/\gamma_c K$ have recently been reported for Black Hills clay cake filtration (1). The value of $1/\gamma_c K$ was found to be dependent on the total pressure on the surface of the clay filter cake (1). The filtration system used in this study had a water pressure of about 0.50 ft on the effluent side of the filter cake. The observed head loss, shown in Table 1, increased from about 25 to 63 inches of water. Therefore, the total pressure on the surface of the filter cake increased from 31 to 69 inches of water. From Figure 19 in reference 1 the values of $1/\gamma_c K$ for 31 and 69 inches of water are about 6×10^{13} and 10×10^{13} ft/lb, respectively. If the lower value is substituted in Equation 6, the expected unit head loss increase per unit of Black Hills clay removed would be:

$$\begin{aligned}\frac{\Delta H}{\Delta W} &= 2.3 \times 10^{6} \text{ ft of water/lb of clay, or} \\ &= 61 \text{ inches of water/mg of clay.}\end{aligned}$$

Therefore, based on clay cake filtration data, if all the Black Hills clay were removed as a surface mat on the filter media surface during the filter run whose data are presented in Table 1, the head loss increase per unit mass of clay removed would be predicted as 61 inches of water/mg of clay removed.

A plot of the increase in head loss versus clay removed using the data in Table 1 is presented in Figure 15. The values of $\Delta H/\Delta W$ can be obtained from the slope of the straight line portions of the curves. In the run with a coating of 2.00 mg 601/gm Hyflo SuperCel, the approximate slope is about 0.8 inch of water/mg Black Hills clay removed before adsorptive capacity was exhausted. After the adsorption capacity had been exhausted, the slope indicates a head loss of about 3.3 inches of water/mg Black Hills clay removed.

Since $0.8 << 61$, it is obvious that the head loss build up during adsorptive removals did not occur from complete plugging of the filter media pores near the surface of the filter cake. After removal by adsorption was complete, the observed head loss response to clay removed was much less, $3.3 < 61$, than would be predicted for complete plugging of the pores. Of course, complete plugging of the filter media voids near the filter cake surface was not observed. The effluent data in Table 1 indicate that after the end of adsorptive removals, about 91 percent ($C_e/C_i = 0.91$) of the clay applied passed through the filter cake. Had complete plugging occurred, little if any clay would have been found in the effluent.

From this analysis of head loss data, it can be hypothesized that the head loss increases did not result from uniform adsorptive removals or from extensive straining near the filter cake surface. It would appear that the clay which caused the significant head loss increases was removed over some portion, or all, of the depth of the filter cake.

Clay removal in depth

The data shown in Figures 14 and 15 indicate that the rate of head loss increase per weight of Black Hills clay removed, $\triangle H/\triangle mg_r$, was inversely proportional to the depth over which adsorptive removals occurred. This is tantamount to saying that $\triangle H/\triangle mg_r$ was inversely proportional to the adsorptive capacity, or to the level of coating of the filter media. This is seen in Figure 15 where increasing levels of the 601 coating, up to 1.70 mg 601/gm Hyflo SuperCel, resulted in increasing values of $\triangle H/\triangle mg_r$. Another way of showing this is to consider the approximate depth over which the initial 5 mg of Black Hills clay was removed during runs with different levels of coating. For the run in which the coating level was 0.50 mg 601/gm Hyflo SuperCel, breakthrough was nearly completed when 5 mg of clay had been removed. This indicates that the entire depth of the filter cake had contributed what adsorptive removal capacity it had. Figure 14 indicates that breakthrough started when the curve departs from the 100 percent removal line and was completed when the slope of the curve became constant. For the run in which the coating level was 1.00 mg 601/gm Hyflo SuperCel, Figure 14 shows that when 5 mg of Black Hills clay had been applied, 5 mg of clay had been removed and breakthrough did not occur until 10 mg of clay had been applied to the filter. The start of breakthrough indicates that the adsorption zone is just starting to be displaced from the bottom of the filter cake. If the reasonable assumption is made that the adsorption zone passes through the filter cake at a constant rate, then when mg_a equals 5 mg the adsorption zone is in the upper half of the filter cake since it doesn't begin to be displaced from the bottom of the filter cake until mg_a equals 10 mg. Therefore, at the 1.00 mg 601/gm Hyflo SuperCel coating level, significant removal occurred in less than the upper one-half of the filter cake when 5 mg of clay had been removed. A similar analysis of the data from the 1.70 mg 601/gm Hyflo SuperCel run indicated that significant removals occurred in less than the upper one-third of the filter cake. Figure 15 indicates that $\Sigma(\Delta H)/\Sigma(\Delta mg_r)$ increases for increasing levels of coating, or as has just been developed, for removals over smaller depths of the filter cake.

The significance of this approximate correlation cannot be absolutely established. The variability in the increase in head loss versus clay removed data obtained in other series of runs is but one limiting factor. More important is the fact that clay removal which caused significant head loss increases could have occurred in a small layer near the surface of the filter cake in the three runs just analyzed. Since head loss was measured over the entire filter cake depth, it was impossible to determine whether significant head loss increases occurred in a layer near the surface of the filter cake or over the entire depth of the filter cake which was removing clay at any given time.

It is possible that the 601 coating had a catalytic effect in promoting some removal pattern other than uniform adsorption throughout the filter cake depth. Perhaps the 601 coating and later the adsorption of the clay on the 601 coating could have effectively plugged the small openings in the individual diatomite particles shown in the Appendix, Figures 33 and 34. This same process could also occur at the constrictions connecting the void spaces in the filter cake. This type of removal would predominate in the upper portion of the filter cake before breakthrough, since this is where significant removals were occurring, but could occur over the entire depth after breakthrough. The head loss build up resulting from this type of removal could not be predicted assuming a uniform removal over the entire filter media surface area.

DISCUSSION

The laboratory tests conducted during this study were limited and at least one serious error in judgement may have been involved in the design of the experiments. The coating procedure should have been evaluated more fully before use in this study. Even accepting these shortcomings, the results of the study are significant. A brief discussion of their significance will provide a basis for suggesting some possible practical applications for coated filter media in water filtration practice.

The significance of this study lies in the fact that adsorptive removals were observed and confirmed. It has been shown that cationic polyelectrolytes will adsorb from solution onto mineral clay particles and will also promote coagulation and flocculation of other particulate matter encountered in water treatment practice (6, 13, 54). This study has also demonstrated conclusively that a cationic polyelectrolyte can be adsorbed on the surface of filter media and can provide a positive interaction between the coated filter media and suspended particulate matter brought to the fixed polymer. This observation supports the contention of those who have conceived the filtration process as one of coagulation of particulate matter onto the filter media surface and/or onto previously deposited particulate matter. Of course, this generalization presupposes that other mechanisms exist to transport the particulate matter to the filter media surface and that there will be a positive interaction between the particulate matter and the coated filter media surface or the previously deposited material.

Bulk transport of the suspended particulate matter to the media surface is dependent on the geometry of the filter media and the forces acting on the suspended particles, such as hydrodynamic, gravitational, inertial, and molecular forces. In rapid sand filtration, bulk transport can be a limiting factor since filtration efficiencies have been correlated with parameters controlling bulk transport (31). The diatomite filtration process has been designed chiefly on the basis of mechanical straining, therefore, bulk transport is eliminated as a possible limiting factor. For the filtration system used in this study, bulk transport was not a limiting factor. However, the capacity for a positive interaction between the filter media surface and the particulate matter was a limiting factor. Based on this author's interpretation, the Black Hills clay runs, the results of which are presented in Figure 16, indicated that the rate-controlling factor under some filtration conditions was the presence of an electrical energy barrier at the filter media surface.

The interaction between the particulate matter and the filter media surface is dependent on the physio-chemical properties of the particulate matter, filter media, and the aqueous phase. Since this interaction is basically an interfacial phenomenon, the properties of this region are, of course, the most important to consider. It is the opinion of the author that this study demonstrates conclusively that significant advancements can be made in water treatment technology by improving the positive interaction between particulate matter and the filter media surface.

The efficiency of a filtration system employing filter media coatings, such as were used in this study, will depend on at least the following factors, presupposing efficient bulk transport:

1. the amount of filter media surface area available for interaction with the coating material and with the particulate matter being removed,
2. the amount of coating material which can be adsorbed on a unit of filter media surface area,
3. the capacity for a positive interaction between the coating and the particulate matter,
4. the feasibility of regenerating the adsorptive capacity of the coated filter media, and
5. the manner in which particulate matter is removed in the filter cake voids.

The amount of filter media surface area available to the coating material and to the particulate matter will depend on the size, shape or configuration, and the orientation of the filter media particles in a filter bed. The amount of 601 coating material that can be adsorbed is directly related to the particle size of diatomite, as shown in the Appendix. Figure 36 shows that the amount of coating material adsorbed per gram of diatomite is inversely proportional to the mean particle size of the diatomite, based on the Stoke's settling diameters. These data simply demonstrate the well known fact that for decreasing particle sizes the ratio of particle surface area to particle volume increases. The shape or configuration, and the orientation of filter media particles in a filter bed will affect the flow of liquid through the void spaces in the filter. This will affect both particle transport and the manner in which the particles are removed in a filter bed.

The amount of coating material which can be adsorbed on a unit of filter media surface area will depend on the electro-chemical properties of the coating material, and the electro-chemical properties of the filter media surface and the method of coating. Obviously, there must be a high degree of affinity between the filter media surface and the coating material. The interactions between the adsorbing species are also an important point to consider. It has been reported that the maximum amount of iron oxide sol particles which can be adsorbed on glass and other surfaces depends on the electro-chemical interactions of the adsorbing particles (37). Decreasing electro-chemical repulsive interactions between adsorbing particles resulted in increased surface coverage, and for systems where sols were coagulating slowly, multilayer adsorption was observed (37).

In this study, highly charged polymers (polyamine in a solution pH of about 5.8) were adsorbed on diatomite. The approximate amount of the available surface area actually coated was computed as about 2 percent. If a solution pH of about 7 to 9 were used during the coating operation, instead of about 5.8, the positive charge density of the polyamine would be greatly reduced. This should result in a significant decrease in the electrical repulsive forces between adsorbing polymers, and an increase in the diatomite surface area covered by the polymer should result. If there are no repelling forces between individual polymers, multilayer adsorption would most likely result. This would be inefficient and undesirable. Previous research has shown that multilayer adsorption of cationic polyelectrolytes on diatomite filter media can result in large decreases in filter cake permeability (45). There should be an optimum coating procedure whereby a maximum amount of surface area would be covered with monolayers of polymer with a minimum of undesirable side effects, such as decreased permeability. Of course, the real test to determine an optimum coating procedure would be to conduct filtration removal studies using various coating procedures where removal efficiency and operating economics could be evaluated.

The capacity for a positive interaction between the particulate matter and the coating material will depend on the interfacial properties of these materials. Since most colloidal materials encountered in water treatment practice have electronegative surface potentials, the natural choice for a coating material would be a cationic polyelectrolyte. The specific coating material used in this study, 601, was chosen because previous work had established that it could effectively coat diatomite without causing any decrease in permeability. The results of this study indicated that for the filtration systems studied, an unfavorable equilibrium existed between Panther Creek clay and the 601 coating, and some fraction of the coffee material used was not adsorbed on the 601 coating. These observations indicate that a high degree of affinity did not exist between these materials and the 601 coating, or possibly that particle transport to the coating material was not accomplished effectively.

An undesirable feature of the 601 coating material was that its filtration removal effectiveness was reduced at the high pH levels encountered with most natural waters. This study indicated that a polyamine is most effective in producing adsorptive removals at a pH of about 6. Of course, had a larger filter media surface area been effectively coated, efficient removals might have been obtained at pH values above 7.

A cationic functional group whose charge density would be less pH dependent than was the polyamine used in this study should be a more desirable coating material. For example, a polymer with a quaternized nitrogen functional group would have a charge density less dependent on solution pH than a polyamine.

Another important consideration in using filter media coatings would be the feasibility of regenerating the adsorptive capacity of the coated filter media. In diatomite filtration, the filter media is wasted after being used, and hence, a coating material whose adsorptive capacity was exhausted would be wasted. The cost of using a coating material would be an operating cost which would be directly proportional to the amount of diatomite used.

If coatings were used in fixed bed granular filters, consideration would need to be given to the removal of the adsorbed solids and/or coating material, after exhaustion of the adsorptive capacity of the coating. The most desirable system would be one in which the normal filter backwashing procedures would remove the adsorbed particles but not the coating material. If the coating material were removed, then between filter runs a new coating would have to be formed. An intolerable system would exist if the normal backwashing procedures would not remove either the adsorbed particles or the coating material.

Since the head loss response is dependent on the manner in which the particulate matter is removed in a filter cake, this parameter is of paramount importance. The interpretation of the results of this study suggest that the head loss response for uniform monolayer adsorptive removals was probably insignificant compared to removal by some other mechanism, i.e., straining.

The results of this research suggest two approaches which might be pursued to enhance particulate matter-filter media surface interactions. One approach would be to develop coating procedures and coating materials to be used with filter media presently used in practice. A second approach would be to develop synthetic filter media which could improve filter media surface-particulate matter interaction. Obviously, both are means to the same end.

Any meaningful pursuit of either of these approaches would be seriously handicapped by the current lack of knowledge concerning the precise manner in which particulate matter is removed in a filter bed. Though our knowledge is not precise, guide lines have been and are being formed. The laws and theories of physical chemistry as they apply to colloidal systems are being used to elucidate the electrochemical interactions involved in removal phenomena. The laws and theories of hydrodynamics are being used to elucidate mass transport phenomena. Continued application of these and other fundamentals will result in a more precise knowledge of removal patterns and eventually in a more economical and efficient filtration process.

The results of this study also suggest more immediate practical application of coated filter media. As noted earlier, the process of body feed diatomite filtration incorporates the desirable feature of continuous addition of new filter media surface to the filter cake.

The process is now designed on the basis of finding a grade of diatomite which will mechanically strain the particulate matter to be removed. By coating the diatomite, particulate matter which normally would not be strained might be removed by adsorption. The process might then be designed on the basis of mechanically straining large particles and adsorbing smaller particles, rather than reducing the particle size of the filter media to the point where it will strain out the smallest particles to be encountered. This should result in the use of coarser grades of diatomite for a given application and also in being able to apply the process to removal of small particles not strained by the finest grades of diatomite available.

Another possible application of coated filter media to diatomite filtration would involve using a coated precoat layer of a fine grade diatomite and a coated coarser grade of body feed. Presumably the coated coarser grade would remove large particles by mechanical straining and some adsorption and the coated precoat layer would remove by adsorption the smaller particles which would pass through the coarser grade.

Though the results of this study may suggest possible practical applications of coated filter media, extrapolation of the quantitative data compiled using 601 coatings to practical systems indicates that insignificant benefits would be gained.

From Figure 27, it is seen that 4.00 gm of Hyflo SuperCel coated with 1.70 mg 601/gm Hyflo SuperCel will remove 21 mg of Black Hills clay. This amounts to 0.0053 mg of clay removed per mg of Hyflo SuperCel. From Figure 26, it is seen that 3.50 gm of C-560 coated with

0.35 mg 601/gm C-560 will remove about 18 mg of Panther Creek clay. This amounts to 0.0052 mg of clay removed per mg of C-560. These values of removal, about 0.005 mg of clay/mg of diatomite, are one to two orders of magnitude less than are normally obtained by body feed diatomite filtration. It would be necessary, therefore, to improve adsorptive removals by at least one order of magnitude to make an adsorptive removal process economically competitive, based on removal efficiency. Improvement of coating procedures or coating materials should make such an improvement possible. An important point which should not be forgotten is that adsorptive removals would complement straining removals and a process designed on the basis of both types of removals should be vastly superior to one designed on either basis alone.

CONCLUSIONS

Based on the filtration results reported in this thesis, the following significant conclusions can be made.

1. Coating diatomite filter media with Purifloc 601, a polyalkyl polyamine, significantly increased the removal of Panther Creek clay, Black Hills clay, Ball clay, and certain coffee compounds when filtered through coated filter media. The increase in removal resulted from adsorption of these materials on the cationic polyelectrolyte coating.
2. The adsorptive removal capacity was directly related to the amount of 601 coating present. For Panther Creek clay, about 16 mg of clay were removed per mg of 601 coating present. For Black Hills clay, about 3 mg of clay were removed per mg of 601 coating present. For coffee, about 1 1/2 mg of coffee were removed per mg of 601 coating present.
3. The capacity for Panther Creek clay removal appeared to depend on the charge character of the polyamine coating material, whereas the capacity for Black Hills clay removal was not so dependent. The rate of removal of Black Hills clay on 601-coated diatomite appeared to be affected by the existence of an energy barrier resulting from electric double layer interaction. The rate of removal of Panther Creek clay appeared not to be so affected.

4. Head loss build up resulting from the removal of the clays on 601-coated diatomite did not result from uniform adsorptive removal over the filter media surface area. No significant head loss build up occurred for the adsorption of coffee on 601-coated Hyflo SuperCel filter cakes.

RECOMMENDATIONS

Based on the interpretation of results of this study and the conclusions drawn, it is recommended that:

1. Additional studies should be made to elucidate more fully the effect of filter media coatings on filtration removal patterns in which:
    - a. A filter media in addition to diatomite be used, specifically a fine grade of uniform sand which would significantly reduce the possibility of straining. Tests with such a media should be designed to permit evaluation of head loss build up resulting exclusively from adsorptive removals.
    - b. Different coating materials be used; perhaps a cationic polyelectrolyte whose functional group is a quaternized nitrogen rather than an amine. The charge character of a quaternized nitrogen group would not be as pH dependent as that of an amine.
    - c. Other types of particulate matter be used. Virus and bacteria would be significant suspended particles for use because of their significance to public health.
    - d. Operational techniques be developed to measure more accurately the amount of particulate matter removed by adsorption.

   e. Coating procedures be evaluated with the specific objective of increasing the amount of filter media surface area covered by the coating material.

2. Serious consideration should be given to developing synthetic filter media with surface properties which would improve particulate matter-filter media surface interaction.

3. Diatomite filtration studies with body feed should be conducted to evaluate the effect of using coated diatomite on removal efficiencies and operational economics.

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APPENDIX: PROPERTIES OF MATERIALS USED IN THIS STUDY

A brief presentation of some general and specific properties of some of the materials used in this research is included in this appendix. Those properties which were pertinent to the design of the laboratory experiments and to the interpretation of the test results are referred to in the text where needed. Other properties which are of general interest are included in this appendix to the thesis.

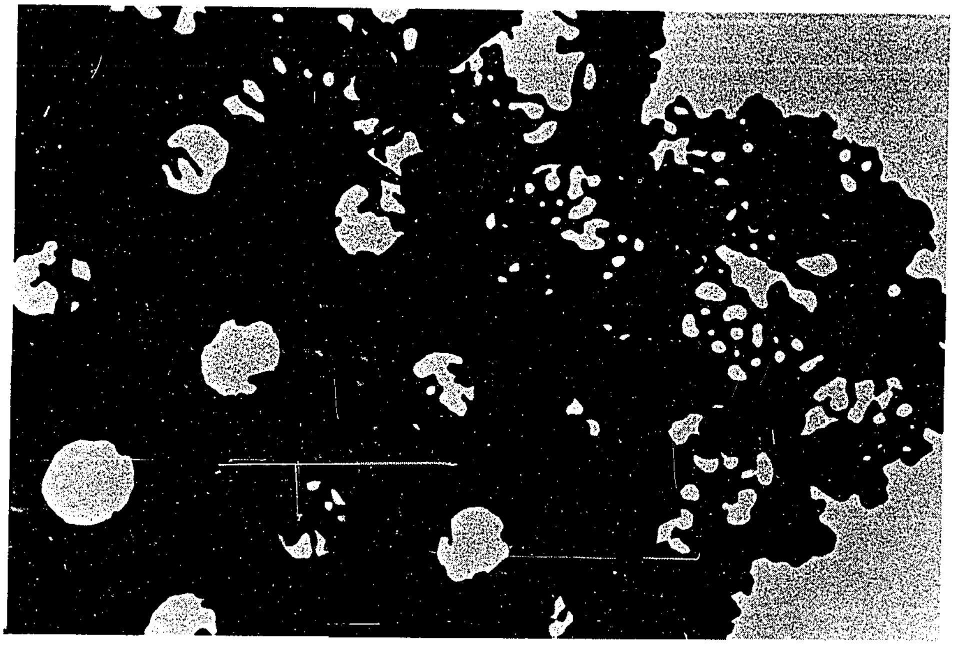
Diatomite

Diatomite is produced from diatomaceous earth, a mineral resulting from an accumulation of minute fossil shells of diatoms, which are a class of algae. Diatomite is largely amorphous silica (specific gravity equals 2.30 - 2.33) and is light in weight owing to the porous structure of the diatom's skeleton. A qualitative indication of the shape and configuration of some individual diatom fragments can be obtained from Figures 31, 32, 33, and 34. These are electron micrographs of the Hyflo SuperCel used in this study. Specimens were prepared by placing a drop of a Hyflo SuperCel-distilled water suspension on a carbon film supported by a copper mesh grid. When the water was evaporated, the particles adhered to the carbon film. The electron micrographs presented clearly indicate the porous structure of the diatoms and their potential high straining capacity. It can readily be appreciated that any attempt to describe the pore geometry of a diatomite filter cake mathematically would be an extremely ambitious endeavor.

A comprehensive array of photomicrographs of different species of (15) diatoms and grades of commercial diatomite can be found in the literature.

Figure 31. An electron micrograph of diatom fragments in the Hyflo SuperCel used in this study showing a variety of pore sizes (8600 X)

Figure 32. An electron micrograph of the Hyflo SuperCel used in this study showing irregular diatom fragments (18500 X)



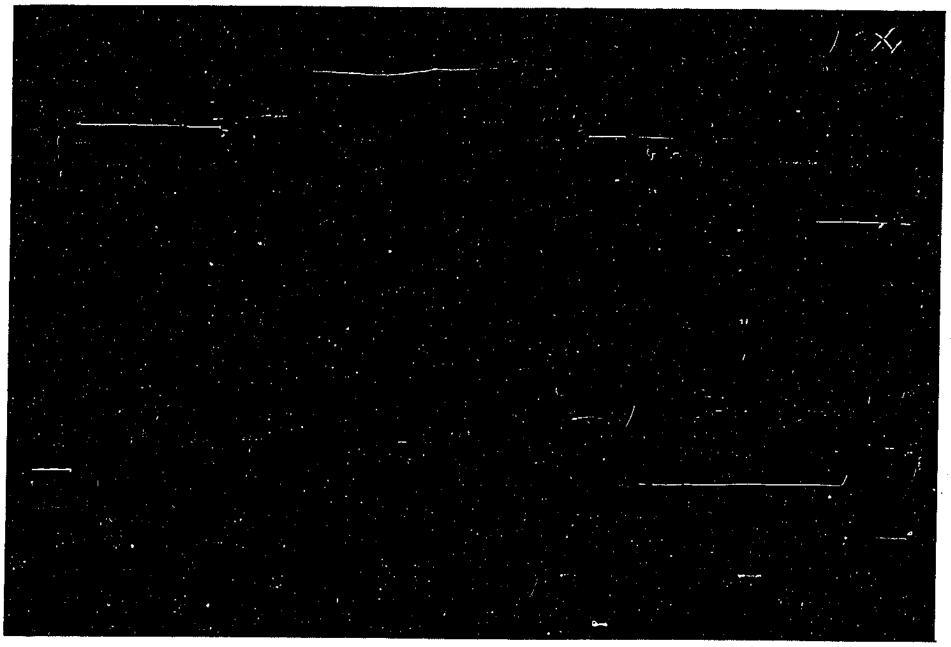
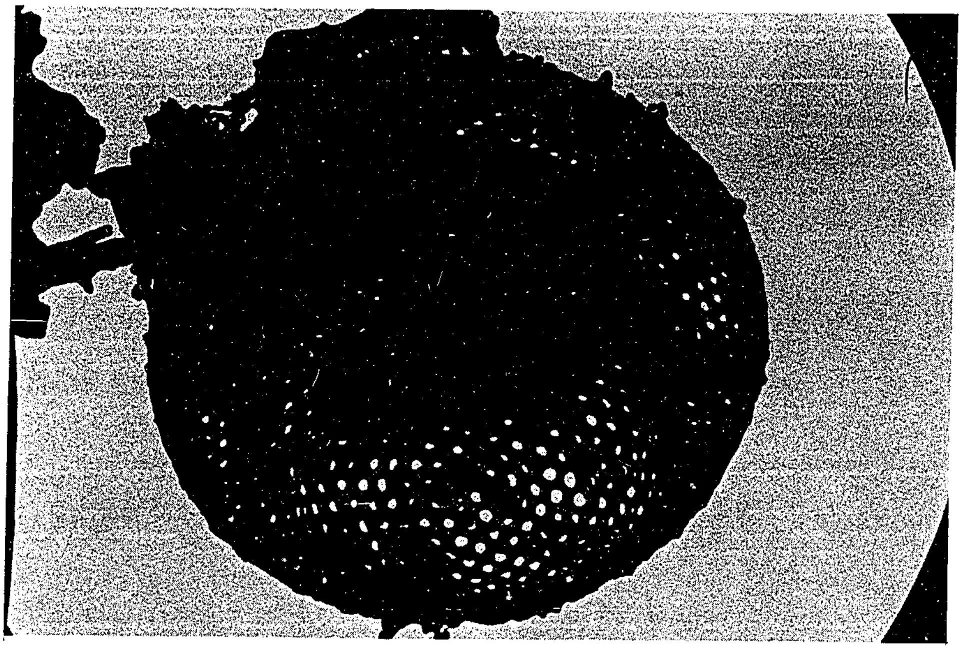


Figure 33. An electron micrograph of an individual diatom from the Hyflo SuperCel used in this study, which gives an indication of the straining potential of the media (4200 X)

Figure 34. An electron micrograph of the Hyflo SuperCel used in this study showing irregular diatom fragments (7800 X)



The production of diatomite

The grades of the diatomite used as filter media in this study were products of the Celite Division, Johns-Manville Products Corporation, Manville, New Jersey. The manufacturing process employed in producing these diatomite products is basically one of particle-size classification and flux calcining. The diatomaceous earth is obtained from open pit mines. It is milled, dried, and the dry diatomite is then flux calcined. The diatomite is transported through the various processing steps by moving hot gases.

The flux-calcining process amounts to passing the diatomite through a heated rotary kiln, 300 - 400°F feed and less than 2,200°F discharge temperatures, in the presence of fusible alkali salts (48). This flux-calcining affects the filtering properties of diatomite by changing the surface texture, reducing the surface area per unit volume of finished product, agglomerating fines, and converting clay mineral impurities to aluminum silicate slag (48). These slag particles are then largely removed in subsequent processing. Following calcining, the diatomite flows through air separators for removing any dense particles still present and then through air classifiers for particle size control.

A typical moisture-free chemical analysis of diatomite filter media is given below (36). Some other general properties are (36):

1. Hardness of 4.5 - 6.5, on the Mohr scale,
2. Refractive index of 1.40 - 1.45,
3. Specific surface area up to 20 - 25 m^2/gm, and
4. Specific gravity of 2.30 - 2.33 (flux-calcined grades).

Composition	Weight %
Loss on ignition	3.0
SiO_2	89.4
Al_2O_3	4.1
Fe_2O_3	1.5
$Ti\ O_2$	0.1
CaO	0.2
MgO	0.7
Na_2O (and K_2O)	0.8
Total	99.8

Approximate bulk densities, γ_d, of the diatomite filter medias used in this study were determined by measuring the depth of the filter cakes during filter runs. Knowing the weight of diatomite, the cross-sectional area and the depth of the filter cake bulk densities could be computed. For Hyflo SuperCel, γ_d was found to be about 21 lb/ft^3 and for C-560, γ_d was about 24 lb/ft^3. No difference in γ_d was found between the coated and uncoated filter cakes.

Particle size determinations

Particle size distribution curves were determined for the diatomite filter media used. A standard sedimentation method was used with two exceptions (3). No dispersing agent was used and the samples were prepared analogous to the procedure used in the filtration runs conducted in this study. This consisted of mixing 30 gm samples of the diatomite in about 500 ml of distilled water in one-liter beakers by a magnetic stirring device. Particle-size determinations were made for uncoated and 601-coated samples of Hyflo SuperCel, C-560, and a coarse fraction of C-560. Two determinations were made for each grade and level of coating. In addition, a sample of uncoated Hyflo was prepared using a standard air-dispersion technique (3).

The particle size distribution curves are presented in Figure 35. Curve A is for uncoated Hyflo SuperCel which was air-dispersed and curve B is for uncoated Hyflo SuperCel dispersed by the method described above. The size distributions are similar, but the air-dispersion results in slightly smaller particles. Curve B^1 is for Hyflo coated with 1.5 mg 601/gm Hyflo SuperCel. It is obvious that the 601 coating grossly affects the settling properties of the Hyflo. This effect is most likely due to coagulation-flocculation of the diatomite. This would cause particle agglomeration which evidently results in increased settling rates. It was observed that the sediment from the coated Hyflo SuperCel determinations was much more voluminous than was the uncoated sediment.

Curves C and C^1, in Figure 35, are for uncoated and coated C-560 (0.35 mg 601/gm C-560) used in the Panther Creek clay removal studies. The settling velocities for C-560 were much less affected by the presence of the 601 coating than were the settling velocities of the coated Hyflo SuperCel. However, the settling velocities of the coated media were still increased.

Curves D and D^1 in Figure 35 show the particle size distribution of the uncoated and coated (0.3 mg 601/gm C-560) coarse C-560 used in the Ball clay removal study. As was noted with C-560, the settling velocities of the media are slightly increased when coated.

Figure 35. Particle size distributions of uncoated and 601-coated grades of diatomite used in this study

Curve A, Hyflo SuperCel (standard air-dispersed technique)

Curve B, Hyflo SuperCel

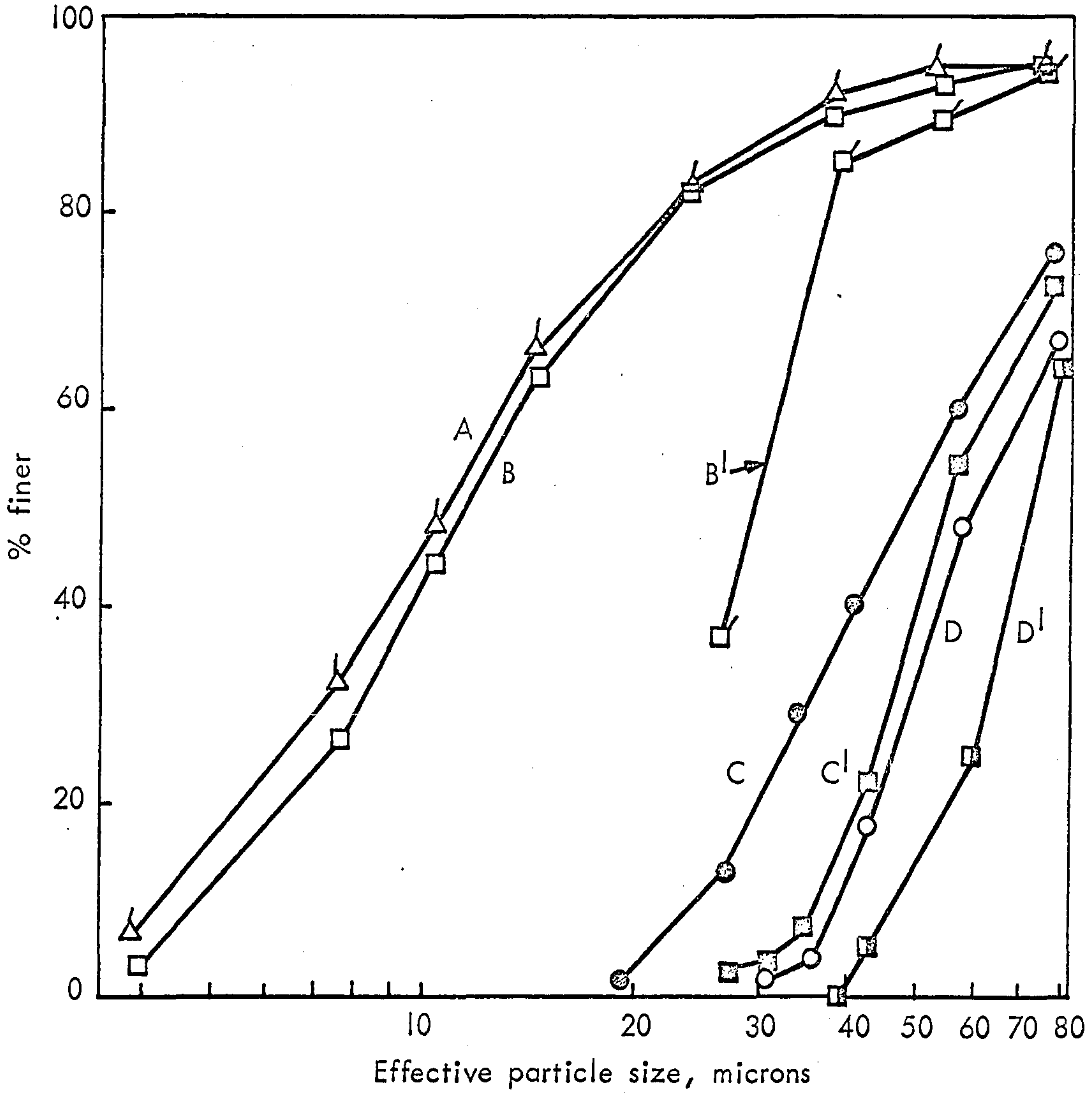
Curve B^1, Hyflo SuperCel coated with 1.5 mg 601/gm Hyflo SuperCel

Curve C, C-560

Curve C^1, C-560 coated with 0.35 mg/601 gm C-560

Curve D, Coarse C-560

Curve D^1, Coarse C-560 coated with 0.3 mg 601/gm coarse C-560


100
80
60
40
20
0
% finer
10
20
30
40
50
60
70
80
Effective particle size, microns
A
B
B'
C
C'
D
D'

In practice, the coating of the polyelectrolyte on the filter media should not significantly affect the size distribution of the filter media particles. It may be concluded, however, that the coating does affect the accuracy of the sedimentation analytical technique used in determining the media particle size, probably by coagulation of the smaller-sized particles.

The particle size distribution of diatomite filter media affects the permeability of diatomite filter cakes. The following is a list of the grades of diatomite produced by Johns-Manville Products Corporation, Manville, New Jersey; the list includes mean particle sizes (that particle size for which 50 percent of the particles are smaller than) and filter cake permeabilities (18):

Grade	Mean particle size (microns)	Permeability at 25°C, K, (10^{-10} ft^2)
C-560	50.0	1.3
C-545	21.0	0.49
C-535	16.2	0.36
C-503	12.8	0.17
Hyflo SuperCel	9.5	0.10
Standard SuperCel	6.4	----
FilterCel	4.0	----

The permeabilities in the above listing were computed from values of $1/K\gamma_w\gamma_d$ given in reference (18). Values of γ_d were assumed to be 21 lb/ft^3 except for C-560 for which γ_d was assumed to be 24 lb/ft^3. The values of K and the mean particle size listed for C-560 and Hyflo SuperCel agree well with the results of this study. In this study

K and the mean particle size for C-560 were found to be 1.25 x 10^{-10} ft^2 and 49 microns. The values of K and the mean particle size for Hyflo SuperCel were found to be 0.144 x 10^{-10} ft^2 and 11 microns.

Particle size and maximum coating level

The maximum amount of 601 coating which can be adsorbed on diatomite, using a given coating procedure, will depend on the available surface area of the diatomite. For particles with a uniform shape, i.e., spheres, rods, and flat cylinders, the surface area per unit volume of material equals a constant divided by a characteristic length, i.e., diameter, or length. The same relationship should also hold for diatomite particles. For instance, if the diatom shown in Figure 34 were broken in half, the ratio of surface area per volume of material would not change significantly. Whether or not this ratio would equal a constant divided by a characteristic length would depend on how the characteristic length were defined. The results of this and other studies indicate that the mean particle size, determined by sedimentation techniques, may be an appropriate definition of a characteristic length.

The data presented in Figures 26 and 27 indicated that the maximum amount of 601 which could be adsorbed on C-560 and Hyflo SuperCel was 0.35 - 0.40 mg 601/gm C-560 and 1.7 mg 601/gm Hyflo SuperCel, respectively. Figure 37, to be presented, shows that 0.35 - 0.40 mg 601/gm C-560 is the minimum level of coating which results in the maximum change in zeta potential. Figure 35 shows that the mean particle sizes of C-560 and Hyflo SuperCel were 49 and 11 microns.

The work of others has shown that 0.85 to 0.95 mg 601/gm C-545 was the minimum level of coating which resulted in the maximum change in zeta potential for 601-coated C-545, whose mean particle size was about 21 microns (8, 45). The data just presented are shown in tabular form below:

Grade of diatomite	Mean particle size (m.p.s.), (microns)	$\frac{1}{\text{m.p.s.}}$, (microns)$^{-1}$	Maximum level coating fully adsorbed (mg 601/gm diatomite)	
			from ζ determinations	from clay filtration studies
Hyflo SuperCel	11	0.091	- - - -	1.70
C-545	21	0.048	0.85-0.95	- - - -
C-560	49	0.020	0.35-0.40	0.35-0.40

Figure 36 shows the maximum weight of 601 which can be adsorbed on one gram of diatomite, for the coating procedure used in this study, versus the reciprocal mean particle size of the diatomite. It is reasonable to expect that the maximum coating density, amount of 601 per unit surface area, would be the same for each grade of diatomite. Therefore, the straight line relationship shown in Figure 36 indicates that the surface area per volume ratio of diatomite particles equals a constant divided by the mean particle size which was determined by sedimentation tests.

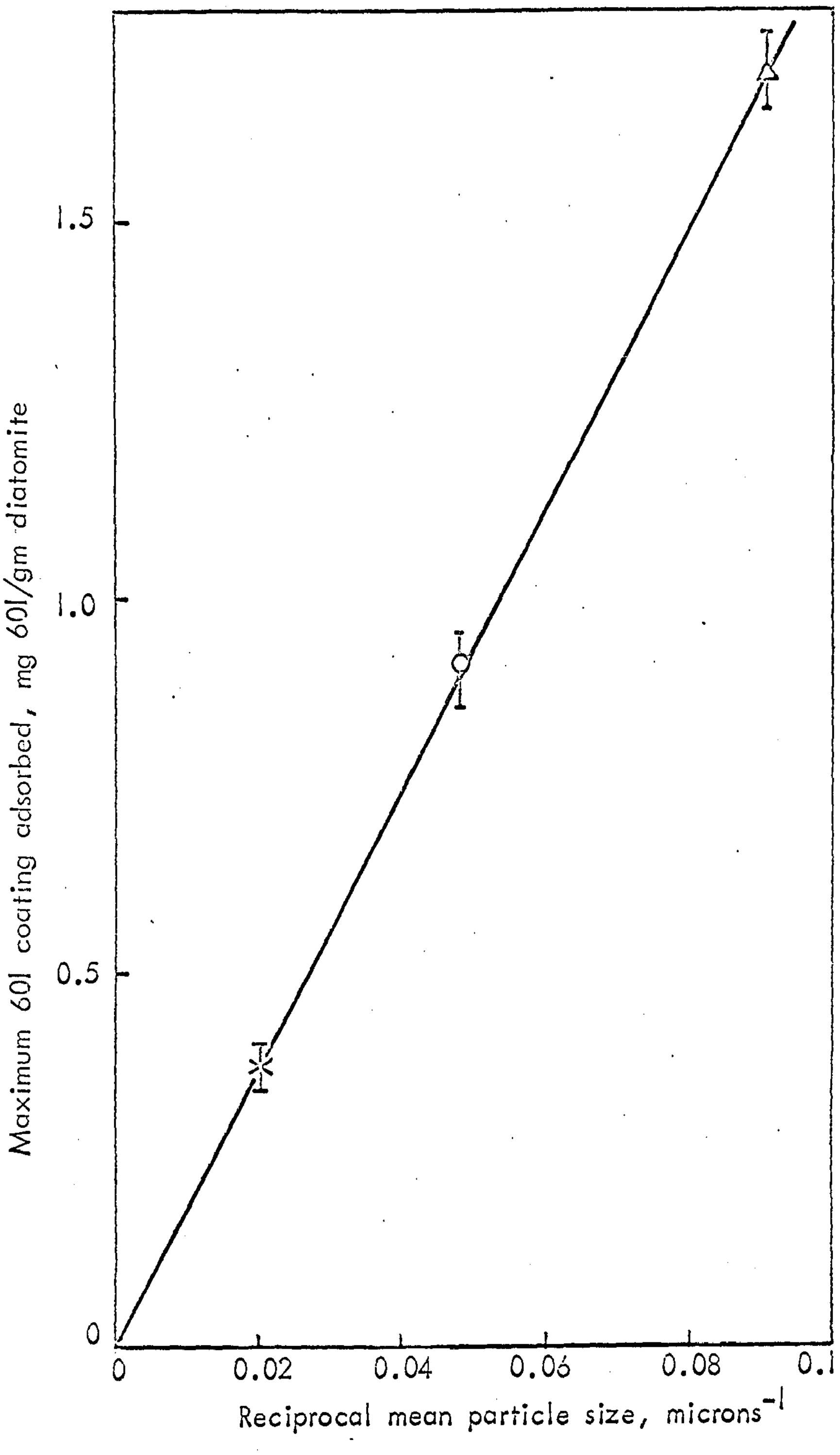
Figure 36. Maximum level of coating which can be completely adsorbed on diatomite filter media versus the reciprocal mean particle size of the diatomite

△ Hyflo SuperCel

⊖ C-545

X C-560

I indicates the scatter of the data


Maximum 601 coating adsorbed, mg 601/gm diatomite
1.5
1.0
0.5
0
0
0.02
0.04
0.06
0.08
0.1
Reciprocal mean particle size, microns^{-1}

Electrical properties of the diatomite surface

The electrical surface properties of flux-calcined diatomite results from the chemical composition of the raw material, diatomaceous earth, and are modified by the flux-calcining manufacturing process. Diatomite is about 89 percent amorphous silica (SiO_2) and about 5.6 percent aluminum and ferric iron oxides. Flux calcining with fusible alkali salts such as Na_2CO_3, NaOH, and/or NaCl results in some alkali cations combining with the silicate material. This fusion process causes localized "melting" of the diatomite surface. This localized "melting" and subsequent cooling causes some diatoms and fragments of diatoms to be fused together.

The electrical surface properties of diatomite would be expected to result basically from the predominate silica surface and be modified by the presence of aluminum, ferric iron, and fusible alkali cations. The electrical surface properties of quartz (SiO_2) particles have been described in the literature (22). The surface charge of the silica surface was considered to arise from the dissociation of H^+ ions from Si-OH surface groups. This is essentially the dissociation of silicic acid and, as would be expected, the degree of dissociation, or surface charge density, was found to be pH dependent (22). The electrokinetic, or zeta potential, of flux-calcined diatomite has also been shown to be pH dependent (45).

The effect of aluminum and ferric iron on the electrical surface properties of a silica surface would depend on how these chemicals are incorporated in the silica structure. If these cations are substituted for Si^{+4} in the lattice structure of silica, then the effect would be the addition of a constant negative surface potential. If these cations are associated at the surface of the silica in some manner that does not satisfy their +3 valence, then the effect would be to reduce the negative surface charge of the diatomite.

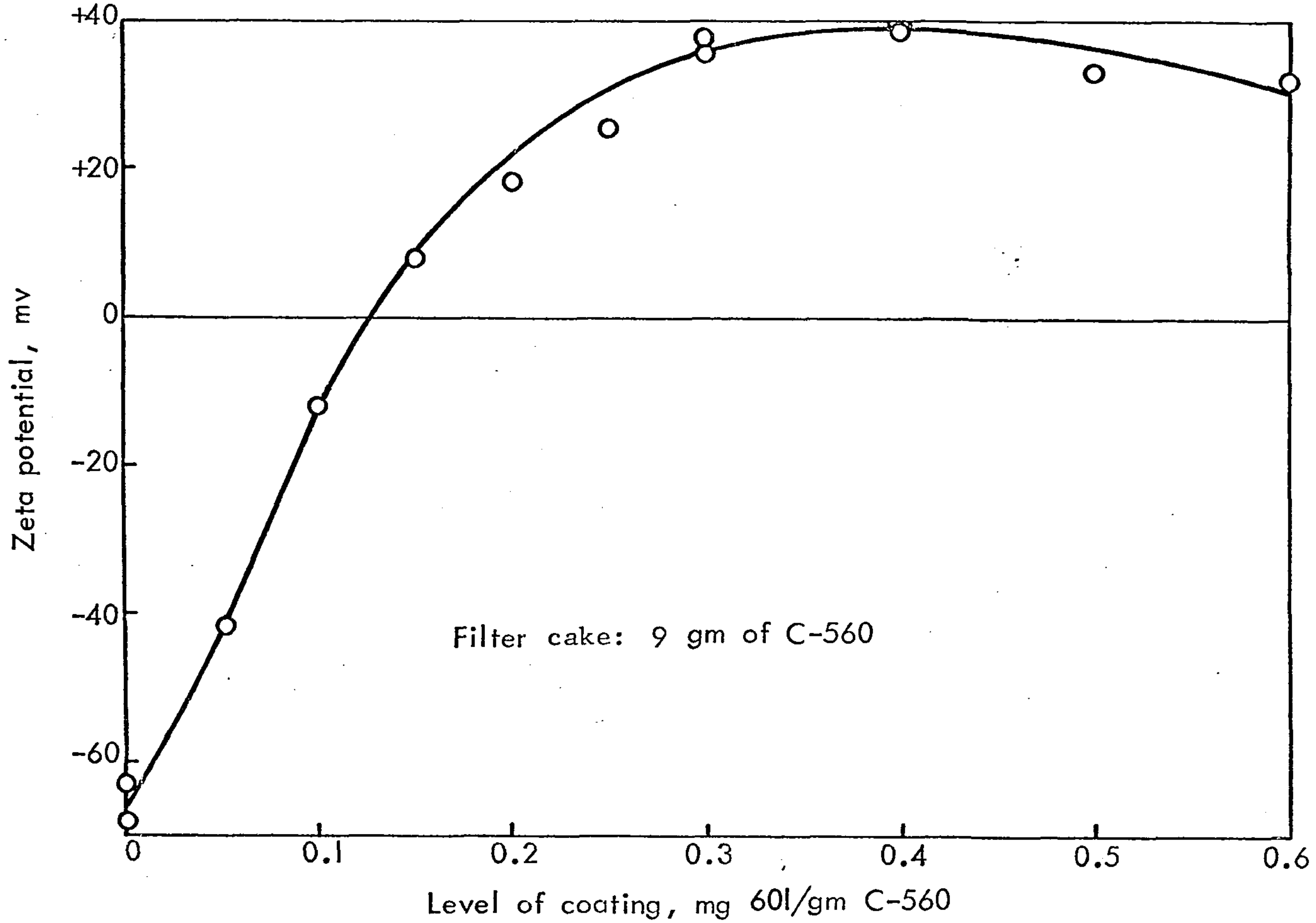
The effect of fusible cations on the surface charge of diatomite may be negligible. The reason for this would be based on the following observations. When flux-calcined diatomite is placed in water, the solution pH increases. It has been reported that sodium ions are released from the surface and go into solution (45). The increase in pH is obviously due to ion exchange of H^+ ions for Na^+ ions. If this exchange of H^+ ions for fusible cations is carried nearly to completion, then the effect of fusible cations on the surface charge of diatomite would be negligible.

It would seem reasonable to assume that the surface charge of flux-calcined diatomite basically results from the dissociation of H^+ ions from -OH surface groups.

601 coatings

Adsorption of a positively charged polyalkyl polyamine, the active ingredients of 601, on diatomite would presumably result from coulombic bonding and/or ion exchange, and perhaps be affected by van der Waals forces. The adsorption of increasing amounts of 601 on C-545 causes the zeta potential to decrease from a negative value and eventually become positive (45). Similar data were compiled for the adsorption of 601 on the C-560 used in this study and is presented in Figure 37. The apparatus and procedure used to collect these data are presented elsewhere (45).

Figure 37. Effect of level of coating on the zeta potential of 601-coated C-560 (5 x 10^{-4} N KCl solution with a pH of 6.0)

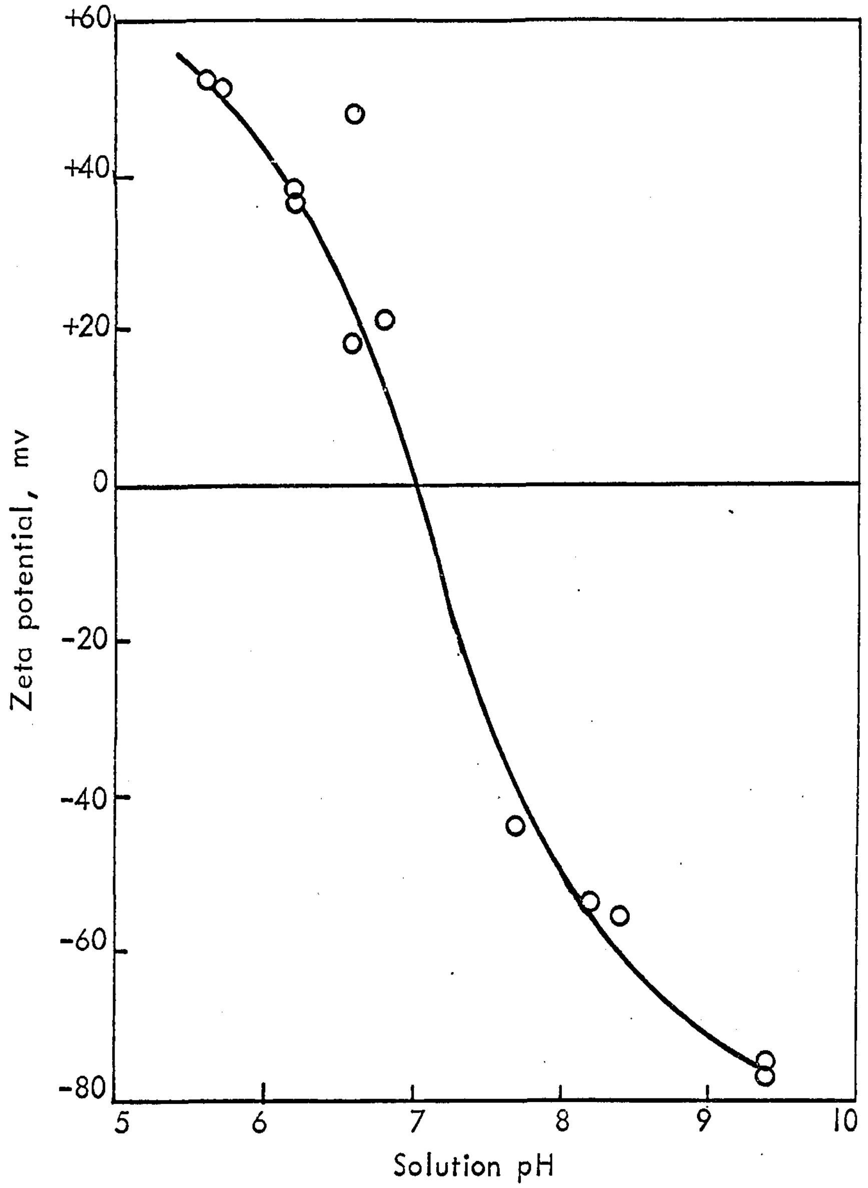

+40
+20
0
-20
-40
-60
Zeta potential, mv
0
0.1
0.2
0.3
0.4
0.5
0.6
Level of coating, mg 601/gm C-560
Filter cake: 9 gm of C-560

The apparatus used was a streaming potential device. A solution of 5×10^{-4} N KCl was passed through a 9-gram filter cake of C-560 (about 1/2-inch deep) and the pressure drop, streaming potential, solution conductivity, solution pH and solution temperature were measured. The mathematical equation relating zeta potential to these parameters has been presented elsewhere (39).

The value of zeta potential in Figure 37 is a sort of average of the uncoated diatomite surface and the coated diatomite surface. The coating method used in this study evidently resulted in only about 1 to 10 percent of the diatomite surface being coated. Because of this, the level of coating corresponding to zero zeta potential does not correspond to zero surface charge. Instead, it corresponds to the level of coating which results in no net convection current being produced by displacement of part of the diffuse layer of the electrical double layer.

The fact that only about 1 to 10 percent surface area coverage by polyalkyl polyamine (601) changes the zeta potential from about -66 mv to about +38 mv indicates that the charge density of the adsorbed polyalkyl polyamine is much greater than the charge density of the diatomite surface under test conditions. The effect of solution pH on the zeta potential of a filter cake of C-545 coated with 1.0 mg 601/gm C-545 is shown in Figure 38. The data shown in Figure 38 were collected in a separate study using a coating procedure identical to that used in this study (45). Figure 38 shows that the zeta potential of 601-coated C-545 decreases uniformly as the solution pH increases from 6.0. This would be expected since the positive charge density of a polyamine decreases uniformly as the solution pH increases from 6.0.

Figure 38. The effect of solution pH on the zeta potential of C-545 coated with 1.0 mg 601/gm C-545 (ionic strength equaled 4×10^{-4} moles/liter); data shown were taken from Figure 24 (45)


+60
+40
+20
0
-20
-40
-60
-80
Zeta potential, mv
5
6
7
8
9
10
Solution pH

Degradation of C-560 during coating operation

Prior to obtaining the data shown in Figure 37, a suitable method of coating the diatomite with 601 had to be established. Previous workers used procedures identical to those used in this study (8, 45). They used a magnetic stirrer to mix the 601 and the diatomite suspension for periods of 5 and 15 minutes. No problem of degradation was reported. In using the same method for coating C-560, a problem was encountered in this study. The permeability of a C-560 filter cake was found to decrease as the mixing time was increased. The mixing speed was just high enough to keep most of the C-560 particles suspended. For mixing periods from one to 19 minutes, filter cake permeability was found to decrease about 3 percent per minute of mixing time. It was assumed that the decrease in filter cake permeability was due to a mechanical degradation of the large fragile diatoms making up the C-560. To minimize such degradation, a two-minute mixing time was used in coating C-560 with 601.

Clay Minerals

The average moisture-free chemical analysis of the three clays used, as given by the manufacturers of these products, are listed below.

Panther Creek clay was described as consisting of 85 percent montmorillonite clay mineral (2). Black Hills clay is a western bentonite clay which also is predominantly montmorillonite clay mineral (2). The major difference between Panther Creek clay and Black Hills clay is the predominant exchangeable cation. For the former it is calcium and for the latter it is sodium. Panther Creek clay is described

Compound	Weight fraction in percent Black Hills clay (30)	Panther Creek (2)	Ball clay (44)
Silica, SiO_2	64.72	64.00	51.61
Alumina, Al_2O_3	20.82	17.10	33.38
Iron, Fe_2O_3 and FeO	3.44	4.70	0.94
Magnesia, MgO	2.38	3.80	trace
Lime, CaO	.49	1.50	0.05
Soda, Na_2O	2.92	0.20	0.08
Potash, K_2O	----	0.50	0.14
Other minor constituents	0.50	0.20	----
Chemically held water	5.20	8.00	----

as being non-suspending in water (2). In this study about 5 percent of a 1 gm/l distilled water suspension remained in suspension after 7 to 9 weeks of gravity settling. Black Hills clay, which is predominately sodium montmorillonite, is a swelling clay and can adsorb several layers of water molecules between its well-defined parallel layer of atoms (unit cells). In aqueous suspensions of Black Hills clay, the sodium ion can be replaced by H^+ ion. At low pH's, the clay is largely in the hydrogen form and at high pH's it would be largely in the sodium form. The suspensions prepared for use in this study had a clay concentration of 4 gm/l in distilled water. The pH of the distilled water was usually about 5.8 before addition of the clay. After mixing and gravity settling for about 50 days, the suspension pH was about 8. Evidently the clay had been partially converted to the hydrogen form.

A very thorough presentation of the colloidal properties of montmorillonites can be found elsewhere (60).

The wet particle size distributions of Ball clay and Panther Creek clay used in this study were reported as:

Size in microns	Weight fraction in percent Panther Creek (2)	 Ball clay (42)
> 5	30	11
$> 0.5, < 5$	35	42
< 0.5	35	47
< 0.1	--	16

No suitable method was found for determining the particle size of the clays. An attempt was made to use a Coulter Counter, but the high electrolyte concentrations used with this device caused coagulation of the clay suspensions.

Black Hills clay suspensions were found to pass an 0.80 micron Millipore filter but did not pass an 0.45 micron Millipore filter. Panther Creek clay suspensions would not pass an 0.80 micron Millipore filter.

An attempt was made to make electron micrographs of the Black Hills clay and Panther Creek clays. Specimens were prepared by evaporating a drop of clay suspension placed on a carbon film supported on a copper mesh grid. No meaningful micrographs of Black Hills clay were obtained. Figures 39 and 40 are electron micrographs of the Panther Creek clay. These figures are presented only to give a general indication of the clay particle size. Any correlation between the particles seen in Figures 39 and 40 and the particles being filtered in the filter runs conducted in this study is problematical. The particles shown are less than a micron in size.

Figure 39. Electron micrograph of Panther Creek clay from a mixed supernatant preparation used in this study (15700 X)

Figure 40. Electron micrograph of Panther Creek clay from a mixed supernatant preparation used in this study (23200 X)