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RICE UNIVERSITY

FORMATION AND MORPHOLOGY OF COLLOIDAL DEPOSITS
IN POROUS MEDIA

by

SRINIVAS VEERAPANENI

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IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
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APPROVED, THESIS COMMITTEE:

[Signatures]
Mark R. Wiesner, Chair
Associate Professor
Environmental Science and Engineering

Joseph B. Hughes, Assistant Professor
Environmental Science and Engineering

J. David Hellums, Hartsook Professor of
Chemical Engineering

[Signatures]
Raj Rajagopal, Professor
Chemical Engineering and Physics
University of Houston

Houston, Texas

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ABSTRACT

FORMATION AND MORPHOLOGY OF COLLOIDAL DEPOSITS
IN POROUS MEDIA

SRINIVAS VEE RAPANENI

The effects of physical parameters such as fluid velocity, particle size and influent particle concentration on the morphology of colloidal deposits, removal efficiency and head loss development in porous media are investigated. Monte Carlo (MC) simulations of colloid deposition on a one-dimensional permeable surface from a uniform flow field and on an impermeable one-dimensional surface in plane stagnation flow are performed. Simulation results indicate that (i) the morphology of the deposits formed in uniform flow field vary from open porous structure for small particles and low fluid velocities to compact structure with increase in particle size and fluid velocity and, (ii) the shape and structure of deposits formed in stagnation flow strongly depend on particle size and fluid velocity. At low velocities in stagnation flow, large particles form compact deposits while small particles form open porous structures. At high velocities, large particles form unstable pillar-like structure with fewer particles quickly building up the height of the deposit while smaller particles form fewer and more dense columns. Experimental observations of monodispersed latex particles filtered through a bed of spherical glass beads indicated that at high flow rates, influent particle concentration did not appear to have significant effect on the removal efficiency of the packed beds or on the head loss development as a function of retained particle mass. At low flow rates (< 0.1
cm/sec), most of the head loss was observed to occur in the top section of the bed. At high flow rates, the particle deposition was relatively more uniform along the depth of the bed. The fractal dimensions of the deposits was observed to vary from 1.6 to 2.4 with increasing fluid velocity from 0.002 to 0.4 cm/sec. A window of low fractal dimensions was observed at intermediate flow rates (0.04 - 0.15 cm/sec). It is hypothesized that in this flow regime, deposits may have attained pillar-like structures, similar to those observed in simulations. The fractal dimensions of such columnar structures are expected to be low.
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to her!
CHAPTER 1
INTRODUCTION

Research in the area of particle transport and deposition is of significance to a large number of problems that arise in natural and engineered systems. In natural systems, particles may be important vectors for the transport of materials in ground water. The transport of microorganisms in ground water is of importance in evaluating processes such as bioremediation of contaminated soils and for well head protection of drinking water supplies. The mobility of organic and inorganic compounds in ground water may be enhanced through sorption onto a mobile colloidal phase. Engineered processes such as sedimentation, sludge thickening, membrane filtration, packed bed filtration, packing of fine powders, and others involve the deposition of particles onto surfaces. The applications of these processes are widespread. In particular, packed bed filtration is a critical process in the treatment of potable water and is used as a polishing step in wastewater treatment. Industrial water treatment often includes the use of packed bed filters for the removal of precipitates, metal shavings, oil emulsions, and other materials.

Packed bed filters are employed to remove solids present in the waters, by the passage of the waters through granular media. The pores of the granular media are larger than the particles, to avoid the formation of a cake at the top layer of the bed. The particles are removed on the surface of the filter grains throughout the bed. The deposition of the particles on to filter grains can be thought of a two step process. The transport step, in which the particles are brought to the proximity of the deposition surface through a number of transport
mechanisms, and the adhesion step, the success of which determines if the particle is deposited. The deposited particles themselves become sites for subsequent particle deposition, thereby increasing the removal efficiency of the bed. Packed bed filtration can not reach a steady state, as the progressive deposition of particles on to the collecting surface continuously changes the flow field and hence the subsequent deposition of particles. In addition, the deposited particles undergo restructuring as they seek a position of minimum free energy. The morphology of the particle deposit may significantly influence the performance of a filter. For instance, the arrangement of the particles within a deposit can produce a shadowing effect in which some of deposition sites are blocked by upstream particles. The extent of this shadowing depends on the morphology of the deposit. Similarly, the morphology of the colloidal deposits affects the degree to which fluid flows around rather than through a deposit and therefore determines the degree to which deposited particle surface area is exposed to the fluid flow, and hence its contribution to the total drag force in the bed. To predict the behavior of porous media such as packed beds and aquifers in terms of the particle removal and head loss development over time, a better understanding of the relationship between deposit morphology and the physical-chemical processes that form deposits is critical.

The objectives of the present work are

1) to investigate the effect of physical parameters such as particle size, fluid velocity and influent particle concentration on the morphology of colloidal deposits in porous media,
2) to investigate the effect of deposit morphology on the removal efficiency and head loss development in porous media.
CHAPTER 2
LITERATURE REVIEW

Colloidal transport and deposition has been the subject of considerable research. In this chapter, a review of some of the work in this area is discussed. First, the forces acting on colloids suspended in fluids are discussed. A brief overview of the concepts of fractal geometry as applied to describe the morphology of colloidal aggregates and deposits is given. Finally, a review of the work concerning particle deposition in packed beds is given.

2.1 Particle Hydrodynamics

In many natural and engineered systems, we encounter fluids containing particles. Examples of natural systems include water bodies such as rivers, lakes and oceans, atmosphere, saturated soils and aquifers, rain drop formation, etc. In engineered systems such as, sedimentation (gravitational and centrifugation), filtration, fluidization, transport of slurries, etc., one invariably deals with particles suspended in fluids. In each of these processes, colloids may be subjected to different hydrodynamic fields. The net effect of these hydrodynamic fields defines the transport and the fate of colloidal particles in any system. Thus, the hydrodynamics of colloids is of great interest and has been the subject of extensive research.

The focus of this work is on the morphology of colloidal deposits in porous media. Thus, at the outset, a brief review of the several forces acting on colloidal
particles suspended in fluids, with relevance to water filtration and flow through porous media, is given.

The motion of a spherical particle in a flowing fluid can be derived, based on the laws of classical dynamics, from a force and torque balance on particles. It is common practice to ignore torque balance on small spherical particles, since their rotation is generally insignificant. However, when the hydrodynamic retardation effect is considered when estimating drag force on a particle close to a surface, particle motion is both translational and rotational and hence torques acting on the particle must be balanced. A force balance equation is obtained by balancing the particle inertia against the various forces acting on the suspended particle as follows:

\[ f_i = f_d + f_{pr} + f_{v\text{.mass}} + f_{\text{Basset}} + f^{\text{Re}l}_{\text{Lo}} + f_{DL} + f_{\text{lift}} + f_{\text{grav}} + f_{\text{Brownian}} + f_{\text{Magnus}} \]  

(2.1.1)

where:

- \( f_i \) = particle inertia;
- \( f_d \) = drag force imparted by the fluid on the particle;
- \( f_{pr} \) = force due to pressure gradient (also called Faxen's force); for an accelerating particle, the net hydrodynamic drag force exerted on the particle is the sum of Stoke's drag force and Faxen's force; Faxen's force is proportional to the Laplacian of the velocity field evaluated at the center of the particle;
- \( f_{v\text{.mass}} \) = virtual mass force accounts for the acceleration of the fluid along with an accelerating particle; it is usually considered as an added inertia of a sphere of mass equal to the half the mass of medium displaced; it is equal to zero for a non-accelerating particle;
\( f^{Re}_{LO} \) = London-van der Waals force arising from the instantaneous dipole moments generated by the temporary asymmetrical distribution of electrons around atomic nuclei;

\( f_{grav} \) = force due to gravitational attraction;

\( f_{DL} \) = Double layer force arising from the electrostatic interactions between charged particles;

\( f_{lift} \) = lift force experienced by the particle as a consequence of small inertial effects; for example, in a steady shear flow, particles tend to move such that the net force on the particle will be very nearly zero;

\( f_{Basset} \) = also known as viscous added mass force, accounts for the effect of deviation in the flow pattern from steady state; this is considered as a correction to the Stokes drag which is usually evaluated from the instantaneous velocity field, to include the effect of history of changes in a velocity field;

\( f_{Magnus} \) = force arising from the entrainment of the fluid surrounding a particle rotating in the presence of velocity gradients; fluid entrainment adds velocity to the side of the sphere where rotation and fluid velocity direction are the same, and conversely, retards the fluid velocity on the opposite side, causing the particle to move in the direction of higher velocity;

\( f_{Brownian} \) = Brownian force exerted on the particle as a result of the large number of fluid molecular collisions experienced by the particle.

The mathematical expression for these forces are listed in Table 2.1.
Table 2.1
Forces acting on a spherical particle suspended in a fluid

<table>
<thead>
<tr>
<th>Force</th>
<th>Mathematical Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inertial force</td>
<td>( f_i = \frac{4\pi}{3} a_p^3 \rho_p \frac{Du_p}{Dt} ) (2.1.2)</td>
</tr>
<tr>
<td>Drag force(^1)</td>
<td>( f_d = \frac{4\pi}{3} a_p^3 \rho_p F(u_f - u_p) ) (2.1.3)</td>
</tr>
<tr>
<td>Pressure gradient force (Faxen's Force)</td>
<td>( f_{pr} = -\frac{4\pi}{3} a_p^3 \nabla P ) (2.1.4)</td>
</tr>
<tr>
<td>Virtual mass force</td>
<td>( f_{v.mass} = \frac{1}{2} \frac{4\pi}{3} a_p \rho_f \frac{D}{Dt} \left[ (u_p - u_f) - u_p \cdot \nabla u_f \right] ) (2.1.5)</td>
</tr>
<tr>
<td>Basset force</td>
<td>( f_{Basset} = 6a_p^2 \sqrt{\pi \mu_f} \int_{-\infty}^{t} \frac{(d/d\tau)(u_f - u_p)}{\sqrt{t - \tau}} d\tau ) (2.1.6)</td>
</tr>
<tr>
<td>London-van der Waals force</td>
<td>( f_{LvdW} = -\frac{(2/3)(\eta/\rho_p)\alpha_{SP}}{\delta^+ (\delta^+ + 2)^2} ) n (2.1.7)</td>
</tr>
<tr>
<td>Double-layer force</td>
<td>( f_{DL} = \frac{\varepsilon a_p}{2(1-e^{-2\kappa \delta})} \left[ \frac{\zeta_p \zeta_c}{\zeta_p^2 + \zeta_c^2} - e^{-\kappa \delta} \right] n ) (2.1.8)</td>
</tr>
<tr>
<td>Lift force</td>
<td>( f_{lift} = C_L \varepsilon a_p^2 \sqrt{\rho_f \eta_f k} \hat{e}_k (u_f - u_p) ) (2.1.9)</td>
</tr>
<tr>
<td>Gravitational force</td>
<td>( f_{grav} = \frac{4}{3} \pi a_p^3 (\rho_p - \rho_f) g ) (2.1.10)</td>
</tr>
<tr>
<td>Brownian diffusion force</td>
<td>( f_{Brownian} = \frac{4\pi}{3} a_p^3 \frac{A(t)}{\eta_f} ) (2.1.11)</td>
</tr>
<tr>
<td>Magnus force</td>
<td>( f_{Magnus} = \pi a_p^3 \rho_f \omega (u_f - u_p)(1 + O(N_{Re})) ) (2.1.12)</td>
</tr>
</tbody>
</table>

\(^1\) In the vicinity of a surface, the drag on the particle must be corrected for hydrodynamic retardation (Goldman, Cox, and Brenner, 1967a; Goldman, Cox, and Brenner, 1967b; Goren and O'Neill, 1971; O'Neill, 1964; Tien, 1989).

The variables in Table 2.1 are defined as follows:
\( a_p \) = radius of the particle
\( A(t) \) = Brownian diffusion force
\( C_L \) = lift coefficient (=6.46)
\( \hat{e}_k \) = unit vector of \( k \)
\( F \) = time constant  
\( g \) = gravitational acceleration (vector)  
\( H \) = Hamaker constant  
\( k \) = rate of liquid shear (magnitude of velocity gradient)  
\( n \) = unit normal vector  
\( N_{Re} \) = Particle Reynolds number  
\( P \) = pressure  
\( t \) = time  
\( u_p \) = velocity of the particle (vector)  
\( u_f \) = velocity of the fluid (vector)  
\( \alpha_{sp} \) = retardation correction factor for the London-van der Waals force  
\( \delta \) = separation distance between particle and a surface  
\( \delta^+ \) = normalized separation distance between particle and a surface = \( \delta/\alpha_P \)  
\( \varepsilon \) = dielectric constant of fluid  
\( \kappa \) = Debye-Huckel reciprocal thickness of electric double layer  
\( \mu_f \) = kinematic viscosity of liquid  
\( \eta_f \) = dynamic viscosity of liquid  
\( \rho_p \) and \( \rho_f \) = density of the particle and fluid respectively  
\( \omega \) = angular velocity  
\( \zeta_p \) and \( \zeta_c \) = surface potentials of the particle and collector surface respectively

### 2.2 Concept of Fractal Dimension

The morphology of colloidal aggregates and deposits is geometrically complex and is difficult to characterize in terms of the concepts of Euclidean geometry. Aggregates and deposits have been typically described qualitatively (such as highly porous, tenuous, etc.) or in terms of porosity, strength, and size. In 1975 Mandelbrot (1975, 1977, and 1982) coined the term “fractal” to describe the non-integer dimensionality of complex geometrical properties of objects such as the shores of continents, the surface of clouds, or the branches of trees. Recently, the concepts of fractal geometry have been extended to describe the morphology of colloidal aggregates and deposits.
Fractal geometry allows the characterization of objects in terms of their self-similar (scale invariant) properties. An object is said to be self similar if parts of the object are similar to the whole after appropriate rescaling. A convenient way of measuring the property of scale invariance of an object is to measure some physical property of the object, such as length, volume, surface, or mass at different length scales. For example, consider the classic example of measuring the length of a coast line. The length of the coastline can be approximated by a set of line segments of length \( r_i \). For instance, \( N(r_1) \) segments of length \( r_1 \) might be needed to cover the entire coastline and if a segment of length \( r_2 \) (>\( r_1 \)) is used, \( N(r_2) \) (<\( N(r_1) \)) segments might be needed and so on. The smaller the length of segment, the higher the number of segments needed to cover the coastline. If the coastline were a straight line, \( N(r_i) \times r_i \) will always be equal to the length of the coastline for any length of the segment. In other words, it would satisfy the relation,

\[
N(r) \propto \frac{1}{r}
\]  

(2.2.1)

However, for complicated coastlines (which is generally the case), as \( r \) gets smaller, more tiny curves, which were missed for larger \( r \), will be noticed and the relation between \( N(r) \) and \( r \) will no longer be linear. In this case, the number of segments scale with the length of the segments to some power, \( D \), which may be non-integer as follows:

\[
N(r) \propto \frac{1}{r^D} = r^{-D}
\]  

(2.2.2)

where \( D \) is the fractal dimension of the curve. The fractal dimension in this example can be anywhere between 1 and 2.
For fractal objects such as aggregates, the fractal dimension can be calculated either by the box counting method or sandbox method. In the box counting method, the number of boxes of different sizes needed to cover the object are calculated. In sandbox method, the number of primary particles in an aggregate are counted within boxes of increasing size, centered on the same point. The fractal dimension can then be calculated from the relation,

\[ N(R) \sim R^D \]  \hspace{1cm} (2.2.3)

where \( N(R) \) is the number of boxes of size \( R \) needed to cover the fractal object in box counting method, and is equal to the number of particles belonging to the fractal and are within a box of size \( R \) in sandbox method. The equivalence of these two methods exists only when the object is an uniform fractal, i.e., no multifractal spectrum of their mass distribution occurs (Vicsek, 1989).

In physical objects of interest, there are always limits to the length scales over which the fractal (or scale invariant) properties of the objects are valid. For example, in the case of colloidal aggregates, the size of the primary particle defines the lower cutoff of the length scale, while the size of the aggregate itself will impose an upper limit on the length scales beyond which no fractal scaling can be observed. Thus, the relation \( N(R) \sim R^D \) holds only in the limit when \( R \) is less than the linear size of the aggregate and greater than the primary particle size. It should also be noted that fractal objects in physical processes are typically called random fractals; they exhibit self similarity only in a statistical sense and not in absolute sense. It is more appropriate to use the term scale invariant rather than self-similarity in describing random fractals (Vicsek, 1989).
Since random fractals exhibit fractal properties only in a statistical sense, an effective way of estimating their fractal dimension is through density-density or pair correlation function \( g(r) \) of the aggregate, expressed as,

\[
g(r) = \frac{1}{V} \sum_{r'} \rho(r + r') \rho(r')
\]

where \( V \) is the volume of the object, \( \rho \) is the local density.

The pair correlation function, \( g(r) \), is the expectation value of the event that two points separated by \( r \) belong to the same structure, i.e., it gives the probability of finding a particle at position \( r + r' \), if there is a particle at \( r' \). For an isotropic fractal, correlations are independent of direction, and hence the vector \( r \) can be replaced by the distance \( r \). For a fractal object, the pair correlation function exhibits a power law dependence on \( r \),

\[
g(r) \sim r^{-\alpha}
\]

The exponent \( \alpha \) can be related to the fractal dimension by the relation (Vicsek, 1989),

\[
D = d - \alpha
\]

where \( d \) is the embedding Euclidean dimension of the object. By using the pair correlation function to calculate \( D \), a better statistical result is obtained as one averages over many points within a single cluster.

2.2.1 Measurement of Fractal Dimension using Light Scattering

It is usually difficult to directly measure the scale-invariant properties of fractal objects as defined above. One has to rely on indirect measurements,
which can be either experimental (such as digital image processing, light scattering experiments, or direct measurement of physical properties), or computer simulations (where the actual growth process of the fractal object is simulated). Theoretical determination of fractal dimensionality based on renormalization group theory is usually limited to systems exhibiting second order phase transition, where a power law dependence of relevant physical quantities is observed. Among experimental techniques, light scattering experiments allow a powerful way of measuring the position correlations of particles, thereby providing means to characterize the internal structure of the aggregates. In this section, a brief review of the theory of light scattering from fractal aggregates and its relation to the fractal dimensionality of the object is given. It closely follows the analysis given by Schmidt (1989).

In static light scattering experiments, the structure of the aggregate leads to the interference of the scattered light waves. The angular dependence of the scattered light intensity is usually expressed as a function of the modulus of the scattering vector, \( q \), defined as,

\[ q = 4 \pi n \lambda^{-1} \sin(\theta/2) \]  

where \( \lambda \) is the wavelength of the incident beam, \( \theta \) is the scattering angle and \( n \) is the refractive index of the solvent.

The scattered intensity \( I(q) \) from a randomly oriented aggregate composed of \( N \) identical spherically symmetric scatterers of radius \( a \), averaged over all orientations of the aggregate, is given by (Kotlarchyk and Chen, 1983; Lin, Lindsay, Weitz et al., 1989; Martin and Hurd, 1987; Schmidt, 1989; Teixeira, 1988; Vicsek, 1989; and references therein),
\[ I(q) = Nl_0(qa)S(q) \quad (2.2.8) \]

where \( l_0(qa) \) is the scattered intensity from one scatterer. \( S(q) \), the structure factor, is the Fourier transform of the density-density correlation function, \( g(r) \), and is defined as,

\[ S(q) = 1 + 4\pi \frac{N}{V} \int_0^R r^2 g(r) \frac{\sin(qr)}{qr} \, dr \quad (2.2.9) \]

where \( V \) is the volume of the scattering sample, and \( R \) is largest value of the distance between the centers of any pair of scatterers. The density-density correlation function, \( g(r) \), gives the expected value of the event that two points separated by \( r \) belong to the same structure. Hence the quantity \( 4\pi(N/V)r^2 g(r)dr \) is equal to the probability, averaged over all orientations of the aggregate and over all scatterers in the aggregate, that the center of another scatterer is at a distance \( r \) from the center of one of the scatterers. For a scale invariant object, i.e. a fractal, the density correlations, \( g(r) \), exhibit power law dependence on \( r \), i.e., \( g(r) \sim r^{-\alpha} \) as per equation (2.2.5). For a mass fractal, \( \alpha = D - d \), where \( D \) is the fractal dimension and \( d \) is the embedding Euclidean dimension (Equations 2.5 & 2.6). Using a cut-off function \( f(r/R) \) to describe the structure of the aggregate when \( r \sim R \), we have,

\[ g(r) = G_0 f(r/R) r^{(D-3)} \quad (2.2.10) \]

where \( G_0 \) is a constant. The cut-off function \( f(r/R) \rightarrow 1 \) when \( r/R \ll 1 \) and \( f(r/R) \ll 1 \) when \( r/R > 1 \). For rigid spheres, and from the definition of the correlation function, it can be shown that,

\[ 4\pi \frac{N}{V} \int_0^a r^2 g(r) \, dr = 1 \quad (2.2.11) \]
For $R \gg a$, assuming $f(r/R)$ is equal to unity, from Equations 2.2.10 and 2.2.11, we can obtain,

$$G_0 = \frac{V}{4\pi N} \frac{D}{a^D} \quad (2.2.12)$$

Substituting Equation 2.2.12 in 2.2.10, we have the following expression for $g(r)$:

$$4\pi \frac{N}{V} r^2 g(r) = (D/a)(r/a)^{D-1} \text{ for } a \leq r \leq R \quad (2.2.13)$$

From Equations 2.2.9 and 2.2.13,

$$S(q) = \left( \frac{R}{a} \right)^D S_1(qR) + S_2(qa) \quad (2.2.14)$$

where,

$$S_1(qR) = D \int_{0}^{1} u^{D-1} f(u) \frac{\sin(qRu)}{qRu} \, du \quad (2.2.14a)$$

and,

$$S_2(qa) = D \int_{0}^{1} u^{D-1} \left( 1 - \frac{\sin(qau)}{qau} \right) \, du \quad (2.2.14b)$$

When $qR \gg 1$, the sine function in $S_1(qR)$ oscillates rapidly and the integrand is significant only in the neighborhood of $u = 0$ and hence $f(u)$ can be set equal to 1. When $qa \ll 1$, $S_2(qa) \to 0$. The limiting form of $S(q)$ for $qR \gg 1$ and $qa \ll 1$ is given by
\[ S(q) = D \Gamma(D-1) \frac{\sin[(D-1)\pi/2]}{(qa)^D} \]  \hspace{1cm} (2.2.15)

where \( \Gamma(D-1) \) is the gamma function.

Substituting Equation 2.2.15 in Equation 2.2.8, the following equation is obtained for scattering intensity

\[ I(q) = N l_0(qa) D \Gamma(D-1) \frac{\sin[(D-1)\pi/2]}{(qa)^D} \]  \hspace{1cm} \text{for } qR >> 1 \text{ and } qa << 1. \hspace{1cm} (2.2.16)

In this regime, \( l_0(qa) \) is close to a constant. Thus,

\[ I(q) \propto q^{-D} \]  \hspace{1cm} \text{for } qR >> 1 \text{ and } qa << 1 \hspace{1cm} (2.2.17)

Thus by measuring angular variation of scattered intensity, one can obtain the fractal dimension of the aggregate from Equation 2.2.17.

2.3 Morphology of Colloidal Aggregates

Several experimental observations of settling velocities of flocs demonstrated a power-law relationship between floc size and physical properties of floc such as mass, density and porosity (Cho, Colin, Sardin et al., 1993; Francois and Haute, 1985; Klimpel and Hogg, 1986; Li and Ganczarczyk, 1992; Li and Ganczarczyk, 1987; Tambo and Watanabe, 1979) suggesting that the flocs may be fractal in nature. Several numerical studies involving simulation of colloidal aggregation under different dominant transport mechanisms have indicated that the structure of an aggregate appears to depend on the dominant physical and chemical mechanisms that cause aggregation. The development of
diffusion limited aggregation (DLA) model by Witten and Sander (1981), in which particles are added one at a time to a growing cluster of particles leading to the formation of a fractal aggregate, stimulated interest in the area of aggregation models. Though a wide variety of aggregation models have been developed subsequent to the DLA model, most of them can be classified under three broad classes, diffusion-limited, ballistic, and reaction-limited aggregation models. In diffusion-limited aggregation models, the particles follow random trajectories, with $D_f = 2$ ($D_f$ is the fractal dimension of the particle trajectory), while in ballistic aggregation (BA) models, particles travel along linear (ballistic) trajectories with $D_f = 1$. In both of these models, the particles attach to the growing cluster at first contact. In reaction-limited aggregation (RLA) models, unlike DLA models, the particles explore several bonding configurations before binding to the aggregate. This might be interpreted as simulating the physical experimental conditions of aggregation processes when a small repulsive barrier exists between particles. In RLA models, the fractal dimension of the trajectory of the particle, $D_f$, may be considered to be zero. Further more, depending on the growth process, the aggregation models can be classified as either particle-cluster (P-C), cluster-cluster (C-C) aggregation or hierarchical models. In particle-cluster aggregation models, particles are added one at a time, to a growing aggregate. The aggregate starts from a “seed” or initial growth site, which may not be representative of particle aggregation processes encountered in liquid-solid separation. In cluster-cluster aggregation models, the simulation starts with an initial number of particles (which may be considered as single particle clusters). The particles may follow either random or ballistic trajectories and as they move through the fluid, they may come in contact with and stick to each other. Clusters formed this way continue to move and stick to each other, thus forming larger
clusters. The simulation is continued until a single large cluster consisting of all particles is formed or a mean cluster size has been reached. In hierarchical models, the simulation starts with $N_0 = 2^M$ particles, which are combined to form $N_0/2$ binary clusters, which in turn combine to form $2^{M-2}$ four-particle clusters, etc. The fractal dimensions of the aggregates formed by these different models are listed in Table 2.2. A detailed description of these aggregation models is given in Jullien and Botet (1987) and Meakin (1988a).

Table 2.2
Fractal dimensionality of aggregates obtained from different models
(Adapted from Meakin, (1988b))

<table>
<thead>
<tr>
<th>Dimensionality of space or Lattice</th>
<th>Particle-cluster</th>
<th>Polydisperse cluster-cluster</th>
<th>Hierarchical cluster-cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion Limited ($D_t = 2,3$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.71$^0$</td>
<td>1.45$^0$</td>
<td>1.44$^1$</td>
</tr>
<tr>
<td>3</td>
<td>2.50$^0$</td>
<td>1.80$^0$</td>
<td>1.78$^0$</td>
</tr>
<tr>
<td>Ballistic ($D_t = 1$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.0$^{0,1}$</td>
<td>1.55$^{0,*}$</td>
<td>1.51$^1$</td>
</tr>
<tr>
<td>3</td>
<td>3.0$^{0,1}$</td>
<td>1.95$^0$</td>
<td>1.89$^0$</td>
</tr>
<tr>
<td>Reaction Limited ($D_t = 0$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.0$^{1,+}$</td>
<td>1.61$^0$</td>
<td>1.54$^1$</td>
</tr>
<tr>
<td>3</td>
<td>3.0$^{1,+}$</td>
<td>2.09$^0$</td>
<td>1.99$^1$</td>
</tr>
</tbody>
</table>

$^0$ Off-lattice model
$^1$ Lattice model
$^*$ Unrealistic (constant) reaction kernel
$^+$ Theoretical model

$D_t$ is the fractal dimension of the trajectory of the particle

Several investigators have conducted controlled experiments to characterize the morphology of colloidal aggregates, formed under different
physical and chemical conditions, in terms of their fractal dimensionality. Lin et al. (Lin, Klein, Lindsay et al., 1990; Lin, Lindsay, Weitz et al., 1989) studied the structure of fractal colloidal aggregates formed in both diffusion- and reaction-limited regimes using both static and dynamic light scattering. Aggregation experiments were performed with three different colloids, viz., colloidal gold, silica and latex particles. The aggregation regime was controlled by adjusting the concentration of the aggregation initiator added to the colloidal suspension (for instance, pyridine was used for gold colloids, NaCl was used for silica particles, while HCl was used for polystyrene latex particles). At high concentrations of these agents in the respective colloidal suspension, aggregation was fast, and diffusion was the limiting factor in aggregation (DLCA). At lower concentrations of aggregating agents, the aggregation was reaction limited (RLCA). In the DLCA regime, the fractal dimensions of the aggregates as measured by static light scattering experiments were: for gold, $D=1.86$; for silica, $D=1.85$; and for polystyrene latex, $D=1.86$. In the RLCA regime, they reported the fractal dimension to be: for gold, $D=2.10$; for silica, $D=2.12$; and for polystyrene latex, $D=2.13$. Several others have reported similar fractal dimensions for aggregates formed under RLA conditions (Pusey and Rarity, 1987; Wiltzius, 1987). Wiltzius reported a fractal dimension of 2.08 for colloidal silica aggregates and Pusey and Rarity reported the same for polystyrene spheres. These values are consistent with the fractal dimensions of the simulated aggregates listed in the Table 2.2. These experiments confirm the universality of the aggregation regimes which was observed in numerical simulations. Axford and Herrington (1994) conducted aggregation experiments with sodium bentonite at varying pH. KCl was used to initiate aggregation, while HCl was used to adjust pH. Both static and dynamic light scattering experiments yielded a fractal dimension close to 3.0 for pH<4.3,
while for pH>4.3, a fractal dimension of 1.8 was observed. No other fractal dimension were observed, and the transition in the fractal dimensionality at pH=4.3 was sharp. Based on rheological studies, they confirmed that at low pH, sodium bentonite does form a tightly bound, band like structure, while at high pH, the structure of the aggregates is similar to a house-of-cards. These results again confirm that the aggregates belong to the universality classes listed in Table 2.2.

However, several other investigators have reported results of aggregation experiments under different physical and chemical conditions which yielded aggregates with fractal dimensionality which does not fit the universality classes as listed in Table 2.2. Zhou and Chu (1991) conducted NaCl induced aggregation experiments with latex particles. Aggregation experiments performed at 5 different NaCl concentrations (1.5, 0.75, 0.5, 0.4 and 0.3 mol/dm$^{-3}$) yielded aggregates with fractal dimensions $D=1.72$, 1.92, 2.05, 2.14, and 2.15 respectively. At high NaCl concentration, the fractal dimension of the aggregates does correspond to that of DLCA ($D=1.72$), while at low salt concentration, the fractal dimension is same as that expected for RLCA ($D=2.15$). For the intermediate NaCl concentrations, the fractal dimensions of the aggregates were observed to increase from 1.92 to 2.14. The authors attributed this to different degrees of cluster restructuring during aggregation. Carpineti, Giglio, Paganini et al. (1991) investigated the effect of polystyrene latex monomer concentration on the structure of aggregates formed by MgCl$_2$ induced aggregation. The experiments were performed under DLCA conditions. They reported that the fractal dimension of the aggregates decreased from 1.83 to 1.70 with a change in the initial monomer concentration from $1\times10^8$ to $1\times10^{10}$.
monomers/cm³, and reached a constant value of 1.60 for higher concentrations. They verified that multiple scattering was not the source of the discrepancy. They concluded that these aggregates do deviate from the universal picture, suggesting that the low values of $D$ at higher particle concentration might be caused by the fact that counter-ion screened spheres are polarizable. In another study, Zhu and Napper (1994) reported increase in fractal dimension of aggregates of polystyrene latex particles with increase in NaNO₃ concentration. The fractal dimension of the aggregates increased from 1.73 to 2.70, when the NaNO₃ concentration was increased from 0.8 to 1.38 M. They also observed an increase in fractal dimension of aggregates from 1.77 to 2.50, when the temperature was increased from 24 to 30°C, holding the NaNO₃ concentration constant at 0.845 M. They suggested that restructuring is the cause for the deviation of the fractal dimensions from the two relevant universality classes, viz., DLCA and RLCA.

Sonntag and Russel (1986) conducted aggregation experiments under DLA and various shearing conditions. They reported a fractal dimension of 1.6 for DLA regime based on dynamic light scattering measurements. For aggregates subjected to shear, they measured the fractal dimension by static light scattering. They reported a value of 2.2 for the fractal dimension of rehomogenized, but essentially unsheared flocs ($\mu \gamma \leq 10$ dynes/cm²) and 2.5 for higher shear rates ($100 \leq \mu \gamma \leq 200$ dynes/cm²). They attributed the increase in $D$ from 1.6 to 2.2 to the possibility of exchange of particles between flocs or rearrangement of the weaker segments caused by weak buoyancy-induced stresses. For flocs subjected to higher shear rates, they arrived at a fractal dimension of 2.48, based on the power law relationship between the floc mass
and size. Torres, Russel, and Schowalter (1991) conducted similar experiments, but investigated the structure of non-rearranging aggregates. The aggregates were formed either in DLA or shearing conditions. For both modes, they reported the fractal dimension to be the same and equal to 1.8, though the kinetics of aggregation were different. These studies again underscore the importance of aggregate rearrangement and the possibility of real flocs having a fractal dimensions other than the universal classes.

Fractal dimensions of the aggregates formed in various water treatment processes are listed in Table 2.3.
<table>
<thead>
<tr>
<th>Colloidal System</th>
<th>Fractal Dimension(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric hydroxide floc ((\text{Fe}_2\text{(SO}_4\text{)}_3))</td>
<td>2.61-2.85</td>
<td>Lagvankar and Gemmel (1968)</td>
</tr>
<tr>
<td>Alum</td>
<td>1.59-1.97</td>
<td>Tambo and Watanabe (1979)</td>
</tr>
<tr>
<td>Clay-iron flocs</td>
<td>1.92</td>
<td>Tambo and Watanabe (1979)</td>
</tr>
<tr>
<td>Ferric hydroxide floc ((\text{FeCl}_3))</td>
<td>2.3</td>
<td>Wiesner and Mazounie (1989)</td>
</tr>
<tr>
<td>Polyaluminum and silica</td>
<td>1.4-1.7</td>
<td>Axelos, Tchoubar, Bottero et al. (1985)</td>
</tr>
<tr>
<td>Polyesterene spheres ((\text{DLCA}))</td>
<td>1.7-1.85</td>
<td>Carpineti, Giglio, Paganini et al. (1991); Lin, Klein, Lindsay et al. (1990); Lin, Lindsay, Weitz et al. (1989); Zhou and Chu (1991)</td>
</tr>
<tr>
<td>Polystyrene spheres ((\text{RLCA}))</td>
<td>2.08-2.15</td>
<td>Lin, Klein, Lindsay et al. (1990); Lin, Lindsay, Weitz et al. (1989); Pusey and Rarit (1987); Wiltzius (1987); Zhou and Chu (1991)</td>
</tr>
<tr>
<td>alpha-FeOOH ((\text{DLA}))</td>
<td>1.6</td>
<td>(Hackley and Anderson, 1989)</td>
</tr>
<tr>
<td>alpha-FeOOH ((\text{RLA}))</td>
<td>2.0</td>
<td>Hackley and Anderson (1989)</td>
</tr>
<tr>
<td>Kaolin</td>
<td>1.31-1.42</td>
<td>Glasgow (1989)</td>
</tr>
<tr>
<td>Hematite</td>
<td>2.30-2.86</td>
<td>Amal, Raper, and Waite (1990)</td>
</tr>
<tr>
<td>Polystyrene spheres (shear-induced aggregation)</td>
<td>2.2-2.5</td>
<td>Sonntag and Russel (1986)</td>
</tr>
</tbody>
</table>
2.4 Morphology of Colloidal Deposits

Similar to aggregates, the morphology of colloidal deposits appears to be controlled by the dominant physical and chemical conditions under which the deposits are formed. Models describing colloidal deposition that draw on fractal geometry can be broadly classified as either diffusion-limited deposition or ballistic deposition. These modes of deposition are similar to the respective particle-cluster aggregation models (DLA and BA), the only difference being that deposition simulations start with a $d_s$ dimensional surface nucleation sites, instead of a single seed particle as in P-C aggregation simulations.

Meakin (1983b) reported results from diffusion-limited deposition simulations on fibers and surfaces. The simulations yielded deposits with very open, dendritic structures, which resembled a forest of tree-like structures. The morphology of the deposits may be characterized in several ways such as cluster-size distribution, interface exponents, density distribution, etc. (Meakin, 1984; Racz and Vicsek, 1983). In these simulations, a cluster is defined as a collection of particles connected to the same nucleation site through nearest neighbors. The clusters can be characterized in terms of several physical properties as described below.

The number of clusters of size $l$, $N(l)$, can be related to $l$ by the power law,

$$N(l) \sim l^{-\tau}$$  \hspace{1cm} (2.4.1a)

The density profile at a distance $r$ from the surface may be expressed as:

$$\rho(r) = r^{-\alpha_c}$$  \hspace{1cm} (2.4.1b)
The root-mean-square thickness of the deposit can be related to the total number of particles in the deposit, $N$, by the power law,

$$T \sim N^\epsilon$$ \hspace{1cm} (2.4.1c)

The average height of the deposit can also be related to the number of particles in the deposit by a power law relationship:

$$h \sim N^\phi$$ \hspace{1cm} (2.4.1d)

The density-density correlation function also depends on the distance $r$ according to the power-law relationship,

$$g(r) \sim r^{-\alpha}$$ \hspace{1cm} (2.4.1e)

where $d$ is the smallest Euclidean dimension of the space the deposit is embedded in.

The exponents in Equations 2.4.1a-e can be related to a fractal dimension describing the distribution of mass in the deposit as follows (Meakin, 1984; Racz and Vicsek, 1983):

$$D = \frac{d-1}{\tau-1}$$ \hspace{1cm} (2.4.2a)

$$D = d - \alpha_c$$ \hspace{1cm} (2.4.2b)

$$D = d - 1 + \frac{1}{\epsilon}$$ \hspace{1cm} (2.4.2c)

$$D = d - 1 + \frac{1}{\phi}$$ \hspace{1cm} (2.4.2d)

$$D = d - \alpha$$ \hspace{1cm} (2.4.2e)

The values of these parameters along with the calculated fractal dimensions for the diffusion limited deposition in 2- and 3-dimensions are listed in Table 2.4.
<table>
<thead>
<tr>
<th>Statistical Property</th>
<th>2-Dimension</th>
<th>3-Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exponent</td>
<td>$D$</td>
</tr>
<tr>
<td>$N(l) \sim l^{-\tau}$</td>
<td>1.55±0.05</td>
<td>1.8±0.17</td>
</tr>
<tr>
<td>$T \sim N^{\varepsilon}$</td>
<td>1.36±0.05</td>
<td>1.645±0.004</td>
</tr>
<tr>
<td>$T = A'N^{\varepsilon} + B'$</td>
<td>1.55±0.1</td>
<td>1.74±0.02</td>
</tr>
<tr>
<td>$T = A''N^{\varepsilon''}(1 + B''N^{-\gamma''})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho(r_s) \sim r_s^{-\alpha}$</td>
<td>1/3</td>
<td>1.66</td>
</tr>
<tr>
<td>$\bar{h} \sim N^{\phi}$</td>
<td>1.45±0.05</td>
<td>1.69±0.025</td>
</tr>
<tr>
<td>$g(r) \sim r^{-\alpha}$</td>
<td>0.38±0.02</td>
<td>1.62±0.02</td>
</tr>
</tbody>
</table>

* not reported.

Meakin, Kertesz, and Vicsek (1988) studied the effect of fluctuations in diffusion limited deposition models by using a 2-dimensional noise-reduced diffusion-limited deposition model. In this model, the incoming particle is not added to the deposit immediately after it hits a growth site, but only after the growth site had already been contacted $m$ times. The general appearance of a noise reduced diffusion-limited deposits is similar to that without noise reduction. The deposit is characterized by tree-like clusters. However, with increase in noise reduction, the stems of the clusters become more straight and with further reduction in noise, clusters become more needle-like with smaller width and a decreased sidebranching rate. The distribution of the particle density in the direction perpendicular to the substrate can be related to the height in a power law form, $\rho(h) \sim h^{-\alpha}$, where $\alpha$ can be related to the fractal dimension by $D = d - \alpha$. Based on this exponent, Meakin, Kertesz and Vicsek calculated the
fractal dimensions of the deposit for different values of \( m \) as: 1.725 for \( m=1 \) (typical diffusion-limited deposition in 2-dimensional Euclidean space), \( D=1.66 \) for \( m=5 \), \( D=1.64 \) for \( m=30 \). To study the scaling between mass of a cluster and its linear sizes, they calculated the dependence of mean tree height, \( H \), and width, \( W \), on the number of particles, \( s \), in a tree using the relations \( H \sim s^{\nu_\parallel} \) and \( W \sim s^{\nu_\perp} \). The simulation results indicated that the exponents have a weak dependence on \( m \) and the typical value for \( \nu_\parallel=0.65 \) and for \( \nu_\perp=0.56 \). Based on the expression for the case of directed lattice animals and DLA clusters, the fractal dimension can be calculated as \( D_{\text{eff}} = 1 + \frac{1 - \nu_\parallel}{\nu_\perp} \). Based on this, Meakin, Kertesz and Vicsek calculated the fractal dimension of these aggregates to be 1.63. However, since the trees scale differently, the authors conclude that the clusters are not self-similar but are self-affine fractals.

The other common deposition mode simulated is the ballistic deposition, first developed by Vold (1959) to study the sediment volume of moist spheres in hydrocarbon solvents. In these models, particles follow linear trajectories and stick to the deposit or substrate one at a time. Later studies (Ball and Witten, 1984; Bensimon, Shraiman, and Liang, 1984; Meakin, 1985), based on large scale computer simulations and theoretical arguments, showed that the fractal dimensionalities of ballistic aggregates are equal to their Euclidean dimensionality. This indicates that the internal structure of ballistic aggregates is uniform, except at short-length scales. However, the thickness of the active zone, defined as the sites capable of further growth, appear to have a power-law dependence on the width \( (l) \) and the height \( (\bar{h}) \) of the deposit (Family and Vicsek, 1985):
$$\xi^2 = \frac{1}{f} \sum_{i=1}^{f} (h_i - \bar{h})^2$$  \hspace{1cm} (2.4.3)

$$\xi \sim l^\alpha f(\bar{h}/l^\gamma)$$  \hspace{1cm} (2.4.4)

where the scaling function $f(x)$ is constant for large $x$ and $f(x) \sim x^\nu$ ($\nu = \alpha/\gamma$) for small $x$. That is, for small heights ($\bar{h} \ll l^\gamma$), $\xi \sim \bar{h}^\nu$, and for large heights, ($\bar{h} \gg l^\gamma$) $\xi \sim l^\alpha$. Based on the numerical simulations, Family and Vicsek found the values of the exponents to be $\alpha = 0.42 \pm 0.03$ and $\nu = 0.30 \pm 0.02$ for a two dimensional deposit. Meakin, Ramanlal, Sander et al. (1986) reported results from more extensive simulations and concluded that the values of the exponents to be $\alpha = 1/2$ and $\nu = 1/3$ for 2-dimensional deposits and $\alpha = 1/3$ and $\nu = 1/4$ for 3-dimensional deposits.

Jullien and Meakin (1987) reported results from several three-dimensional off-lattice models for deposition with several degrees of restructuring. The first degree of restructuring involved the particle following a path of steepest descent on the surface until it is either in contact with a second particle or is vertically below the initially contacted particle in the deposit. In the second stage of restructuring, if it is already in contact with a second particle from first stage restructuring, the particle continues to move downward until it either contacts a third particle or reaches the minimum height in contact with both clusters. In the third stage, the particle continues to move along the path of steepest descent until it reaches a local minimum on the surface. These degrees of restructuring yielded deposits of increasing density (0.1465±0.0003 for no restructuring and 0.3790±0.0003, 0.5231±0.0005, and 0.5815±0.0002 for the three degrees of restructuring respectively). The values of the exponent $\nu$ differed significantly
from the values reported for the lattice models discussed above. In fact, the calculated \( v \) for the deposits formed after different degrees of restructuring are so low that the authors suggested the possibility of a logarithmic dependence of \( z \) on \( \bar{h} \) or even a constant for large \( \bar{h} \). The authors attributed the discrepancy between these results and the lattice model results to the smaller scale of the simulations. However, the average density of the deposit with highest degree of restructuring compared well with experimental values. Tassopoulos and Rosner (1992) also performed similar studies and calculated the densities of the deposits formed after different restructuring stages and found them to be same as those reported by Jullien and Meakin (1987). They also calculated the mean coordination number distribution for the different modes of ballistic deposition (1.99±0.73 for no restructuring and 3.99±1.19 for one rolling event, 5.99±1.33 for two rolling events, 5.99±1.08 for three rolling events and 6.00±0.98 for minimum potential criterion).

Kim and Rajagopalan (1991) studied the ballistic deposition of particles with adhesive interactions with other deposited particles. They defined a parameter, \( s \), which represents the "sticking probability". The limit of \( s = 1 \) represents the typical ballistic aggregation models where particles stick to the deposit on first contact (no restructuring) and the limit of \( s = 0 \) represents reaction-limited deposition, i.e., complete restructuring. Intermediate values of \( s \) indicate different degrees of restructuring. Their results indicated that local sticking rules have a noticeable effect on the long-range structure of packings and deposits. With an increase in \( s \), the number of pores in the deposit increases and with further increase in \( s \), the pores become larger and elongated. The local density correlations decrease monotonically in the direction parallel to
substrate with increase in $s$, while in the direction normal to the substrate, the
correlation first decreases and then increases again and finally reaches an
asymptotic value. The packing density also decreased from a value of 0.82 for
$s = 0$ to 0.365 at $s = 1$.

In the ballistic models discussed above, the particles move along
trajectories normal to the substrate. However, the angle of incidence of the
particles, $\alpha$, can be varied, with respect to the normal to substrate, from 0
(normal to the substrate) to $\pi/2$ (parallel to the substrate). For instance, in
processes such as vapor deposition during the manufacture of crystalline or
amorphous thin films, particles are deposited at an angle to the normal. Such
processes lead to deposits with columnar morphology. Based on experimental
observations and computer simulations, it has been reported that the angle of
growth ($\beta$) is always less than the angle of incidence of the particles ($\alpha$) (Leamy,
Gilmer, and Dirks, 1980; and references therein). Some investigators (for
example, Dirks and Leamy, 1977; Leamy and Dirks, 1978; and references
therein) have reported an empirical relationship between $\beta$ and $\alpha$ ("tangent
rule"),

$$\tan(\beta) = \frac{1}{2} \tan(\alpha)$$

(2.4.5)

However, based on 2- and 3-dimensional ballistic models, Meakin, Ramanlal,
Sander et al. (1986) showed that the tangent rule is not quantitatively accurate.
They report a relation given by:

$$\beta = \alpha - C$$

(2.4.6)

where $C$ has a value of about $16^\circ$. 
2.5 Theory of Packed Bed Filtration

Packed bed filtration is a solid-liquid separation process, commonly employed to remove small concentrations of particles from a fluid. As the suspension flows through the packed bed, some of the particles, through a number of possible transport and attachment mechanisms, become associated with the immobile solid phase, which includes the filter grains and previously deposited particles. As particles are removed, the geometry and the structure of the medium and the surface characteristics of the filter grains change over time, influencing subsequent particle deposition and fluid flow. As the pores in the filter bed become clogged, interstitial velocity and shearing stresses increase, resulting in the reentrainment of the deposited particles which may re-deposit further down in the bed. The complexity of the problem accounts for the empirical approach adopted in the design of filtration systems in engineering practice. However, during the past two decades, progress has been made towards understanding the mechanisms of particle removal; particularly for the case of monodisperse suspensions and in clean beds. The transient behavior of a filter bed is still poorly understood. Literature in this area is extensive. An excellent review of the previous efforts can be found in Tien's book (Tien, 1989). More recent work is listed in the references (Adamczyk, 1989; Amirtharajah, 1993; Boller and Kavanaugh, 1995; Burganos, Paraskeva, and Payatakes, 1992; Burganos, paraskeva, and Payatakes, 1993; Choo and Tien, 1995a; Choo and Tien, 1995b; Darby, Attanasio, and Lawler, 1992; Darby and Lawler, 1990; Elimelech, 1991; Elimelech, 1992; Elimelech, 1994; Elimelech and O'Melia, 1990a; Elimelech and O'Melia, 1990b; Gimbel, Mulder, and Sontheimer, 1991;
Ginn, Amirtharajah, and Karr, 1992; Imdakm and Sahimi, 1991; Jung and Tien, 1993; Litton and Olson, 1993; Moran, Moran, Cushing et al., 1993a; Moran, Moran, Cushing et al., 1993b; Mulder and Gimbel, 1991; Ojha and Graham, 1994; Olson and Litton, 1992; Ramarao and Tien, 1989; Ramarao, Tien, and Mohan, 1994; Salles, Thovert, and Adler, 1993; Schmitz and Houi, 1991; Schwartz, Wilkinson, Bolsterli et al., 1993; Song and Elimelech, 1992; Song and Elimelech, 1993a; Song and Elimelech, 1993b; Song, Johnson, and Elimelech, 1994; Stenkamp and Benjamin, 1994; Tobiason, 1989; Tobiason, Johnson, Westerhoff et al., 1993; Vaidyanathan, 1992; Vaidyanathan and Tien, 1988; Vaidyanathan and Tien, 1989; Vaidyanathan and Tien, 1991; Veerapaneni and Wiesner, 1993; Vitthal and Sharma, 1992; Wiesner and Veerapaneni, 1991; Wiesner and Veerapaneni, 1994). Only a brief review of some of the previous studies relevant to the proposed work is given here.

2.5.1 Phenomenological Description of Deep Bed Filtration

Deep bed filtration involves a fluid stream containing suspended particles flowing with a superficial velocity \( u_s \) through a filter of radius \( R \) packed with granules of size \( d_g \). The particle conservation equation can be expressed in cylindrical polar coordinates as (Tien, 1989),

\[
 u_z \frac{\partial c}{\partial z} + u_r \frac{\partial c}{\partial r} + \frac{\partial (\varepsilon c)}{\partial t} + N - E_z \frac{\partial^2 c}{\partial z^2} - E_r \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) = 0 \tag{2.5.1}
\]

where \( c \) is the particle concentration in the fluid, \( u_z \) and \( u_r \) are fluid velocity components in \( z \) and \( r \) directions, \( E_z \) and \( E_r \) are axial and radial dispersion coefficients, \( \varepsilon \) is filter porosity at time \( t \), \( N \) is the filtration rate and \( t \) is time since
the suspension has been flowing. We can define a new time \( \theta \), the time for the suspension to reach a depth \( z \) in the filter when it has been flowing for time \( t \), as,

\[
\theta = t - \int_0^z \frac{dz}{u_s/\varepsilon}.
\]  \(2.5.2\)

If the particle concentration, \( c \), is expressed on a volume basis, then the filtration rate \( N \), defined as the volume of particles collected per unit filter volume per unit time, can be expressed as,

\[
N = \frac{\partial \sigma}{\partial t} \tag{2.5.3}
\]

where \( \sigma \), the specific deposit, is the volume of the deposited particles per unit filter volume. The filter bed porosity \( \varepsilon \) can be related to the clean bed porosity, \( \varepsilon_0 \), and specific deposit as,

\[
\varepsilon = \varepsilon_0 - \frac{\sigma}{1 - \varepsilon_d} \tag{2.5.4}
\]

For beds with relatively large ratio of bed diameter to granular diameter, the radial component of the fluid velocity can be neglected and the axial velocity can be set equal to the superficial velocity, \( u_s \). Noting that the axial and radial dispersion effects are negligible, Equation 2.5.1 (after substituting Equation 2.5.3 for \( N \)) can be simplified to,

\[
u_s \frac{\partial c}{\partial z} + \frac{\partial (c\varepsilon)}{\partial t} + \frac{\partial \sigma}{\partial t} = 0 \tag{2.5.5}
\]

Introducing the actual travel time for the suspension, \( \theta \) (from Equation 2.5.2) and the expression for \( \varepsilon \) (Equation 2.5.4), we have,
\[ u_s \frac{\partial c}{\partial z} + \left(1 - \frac{c}{1 - \varepsilon_d}\right) \frac{\partial \sigma}{\partial \theta} = 0 \]  
(2.5.6)

Equation 2.5.6 can be further simplified by taking into account that usually \( c \ll 1 \); thus,

\[ u_s \frac{\partial c}{\partial z} + \frac{\partial \sigma}{\partial \theta} = 0. \]  
(2.5.7)

The initial and boundary conditions are:

\[ c = 0, \, \sigma = 0 \quad \text{for} \quad 0 \leq z \leq L, \, \theta \leq 0 \]  
(2.5.7a)

\[ c = c_0 \quad \text{at} \quad z = 0, \, \theta > 0 \]  
(2.5.7b)

where \( c_0 \) is the influent particle concentration, and \( L \) is the depth of the filter bed.

Iwasaki (1937) proposed a macroscopic mathematical description of the filtration process, based on experimental data. He observed that the particle concentration profile throughout the depth of the filter bed can be described by the logarithmic law, expressed as,

\[ \frac{\partial c}{\partial z} = -\lambda c \]  
(2.5.8)

\[ \lambda = \lambda_0 + aS \]  
(2.5.9)

where \( \lambda \) is called the "impediment modulus" or filter coefficient, \( \lambda_0 \) is the initial filter coefficient, \( c \) is the particle concentration, \( z \) is the depth of the bed, \( a \) is an empirical coefficient of the impediment modulus and indicates the effect of deposition on filter coefficient, and \( S \) is the concentration of suspended particles retained at depth \( z \) of the bed in a certain time. The filter coefficient, \( \lambda \), varies over time as pore spaces become clogged and retained particles act as
collectors. The extent of clogging is normally expressed in terms of specific deposit, $\sigma$ (Equation 2.5.3). Comparing Equation 2.5.7 with Equation 2.5.8, we obtain the following expression for deposition rate:

$$\frac{\partial \sigma}{\partial \theta} = \lambda u_s c$$  \hspace{1cm} (2.5.10)

Hence, the development of a predictive model for filtration process would require an understanding of the dependence of the initial filter coefficient, $\lambda_0$, on the physical-chemical characteristics of the system and the relation between the filter coefficient, $\lambda$, and the deposit characteristics. Several functional forms have been proposed for the filter coefficient that include, among other parameters, the effects of porosity of the filter bed, interstitial velocity of the influent fluid, grain size and specific deposit (good compilations of these models are given by Ives (1975) and Tien (1989)). These functional forms have several model fitting parameters, and one needs to calibrate them to a given system. Frequently, a model calibrated for certain conditions fails when applied to a different set of conditions.

Evaluation of filter coefficient, $\lambda$, thus requires a more fundamental understanding of the process of particle transport and deposit in porous beds. Evaluation of the filter coefficient requires knowledge of transport mechanisms that bring suspended particles to the proximity of filter grains, and subsequent attachment to the filter media as well as the effect of the retained particles on subsequent particle deposition. Considerable progress has been made towards describing the transport and deposition of particles onto surfaces of collecting elements in various flow fields based on first principles. The developments in recent years enable us to predict particle removal in "clean" filters and porous
media within reasonable accuracy. The word "clean" here means that there are not enough previously deposited particles within the porous medium to significantly affect subsequent particle removal. Similarly, expressions such as Kozeny-Carman equation (Kozeny, 1927; Carman, 1937) yield reasonably accurate predictions of the head loss through "clean" beds of granular media. However, in spite of several attempts, the dynamic behavior of filters is still poorly understood and our basis for predicting particle removal and head loss development as particle deposition proceeds over time remains largely empirical. In the next few sections, a review of the models commonly used to predict "clean" bed removals is given.

2.5.2 Model Representation of a Packed Bed Filter

Payatakes, Tien, and Turian (1973) suggested that a homogeneous filter bed may be assumed to consist of $N$ unit bed elements (UBE) of length $l$ (known as periodicity; $N = L/l$, where $L$ is the depth of the bed) connected in series. Each UBE is composed of a number of geometrically similar unit cells which may or may not be of the same size. For a bed consisting of filter grains of uniform size, the unit collectors in each UBE may be assumed to be identical in size. In such a case, the particle collection efficiency of a UBE ($\eta_{ube}$) is same as that of a unit collector. The length of periodicity, $l$, can be related to the grain diameter and porosity of the bed as follows:

$$l = \left[ \frac{\pi}{6(1-\varepsilon)} \right]^{1/3} \langle d_g \rangle$$

(2.5.11)

where $\langle d_g \rangle$ is the average filter grain diameter and $\varepsilon$ is the porosity of the bed.
The collection efficiency of a unit collector, $\eta$, is defined as the ratio of the number of particles retained on a unit collector to the number of particles flowing past the collector per unit time. Assuming that the filter coefficient, $\lambda$, is constant within a UBE (which is a reasonable assumption, since the thickness of the UBE is quite small), the efficiency of a unit collector, $\eta$, and filter coefficient are found to be related as follows (Tien, 1989):

$$\lambda = \frac{1}{\eta} \ln \left( \frac{1}{1-\eta} \right)$$  \hspace{1cm} (2.5.12)

Since $\eta$ is often very low, the above expression can be approximated by:

$$\lambda = \frac{\eta}{I}$$  \hspace{1cm} (2.5.13)

Thus, modeling the performance of a packed bed filter requires the estimation of single collector efficiency, $\eta$, which is discussed in the next two sections.

2.5.3 Flow Field Representation in an Unit Bed Element

The first step in simulating the behavior of a filter is to specify a flow field within a unit bed element. Models for porous media have often been used to specify the flow within a UBE. These models can be broadly classified as external flow models and internal flow models. In external flow models, the flow field around the solid media (collectors) is considered, while for internal flow models, the fluid is considered to move through pores within the media. Happel's sphere-in-cell free surface model (Happel, 1958), Kuwabara's model (Kuwabara, 1959), Brinkman's model (Brinkman, 1947) (external flow models), and
constricted tube model (Payatakes, Tien, and Turian, 1973) (internal flow model) are the most commonly used models to represent flow through granular bed and are discussed briefly below.

a) Happel’s Sphere-in-Cell Model (Happel, 1958):

In Happel’s sphere-in-cell model, spherical collectors in the filter bed are represented by two concentric spheres. The inner sphere of radius $a_c$, corresponding to the solid collector, is surrounded by an imaginary outer fluid sphere of radius $b$ with a free surface. The fluid envelope contains the same amount of fluid as the relative volume of the fluid to particle (collector) volume in the entire bed (i.e., $a_c/b = (1 - \varepsilon)^3$). The velocity external to the spherical collector is obtained under the condition that the fluid is stationary as the solid sphere moves upward with a given velocity, $U$. The flow around the solid core is obtained by solving the creeping flow equations with the boundary conditions that radial velocity, $U_r$, at the outer surface of the liquid shell is zero, the tangential stress at the outer surface is zero, and that radial and tangential components of velocity ($U_r$ and $U_\theta$) vanish on the surface of the sphere. Mathematically, the stream function, $\psi$, of the flow and the boundary conditions are represented as:

\begin{equation}
E^4 \psi = 0
\end{equation}

\begin{equation}
E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right)
\end{equation}

\begin{equation}
U_r = U_\theta = 0; \quad r = a_c
\end{equation}

\begin{equation}
U_r = 0; \quad r = b
\end{equation}

\begin{equation}
\frac{1}{r} \frac{\partial U_r}{\partial \theta} + r \frac{\partial}{\partial r} \left( \frac{U_\theta}{r} \right) = 0; \quad r = b
\end{equation}
It is assumed that the fluid is incompressible, fluid velocity is slow enough that the inertial terms of the equations of fluid motion can be ignored and that the flow is axisymmetric. Under these conditions, the stream function for the region in the fluid envelope is given as follows:

$$\psi = A \left( \frac{K_1}{r} + K_2 r^* + K_3 r^{*2} + K_4 r^{*4} \right) \sin^2 \theta$$  \hspace{1cm} (2.5.15)

where

$$A = \frac{u_s}{2} a_c^2$$  \hspace{1cm} (2.5.15a)

$$r^* = \frac{r}{a_c}$$  \hspace{1cm} (2.5.15b)

$u_s$ is the superficial fluid velocity and $K_1$, $K_2$, $K_3$, and $K_4$ are functions of porosity of the bed ($\varepsilon$), defined as,

$$K_1 = \frac{1}{w}, \quad K_2 = -\frac{3+2p^5}{w}, \quad K_3 = \frac{2+3p^5}{w} \quad \text{and} \quad K_4 = -\frac{p^5}{w},$$

where $w = 2 - 3p + 3p^5 - 2p^6$ and $p = \frac{a_c}{b} = (1 - \varepsilon)^{1/3}$.  \hspace{1cm} (2.5.15c)

The head loss across a bed of depth $l$ is given by,

$$-\frac{\Delta P}{l} = \left( \frac{3+2p^5}{3-(9/2)p+(9/2)p^5-3p^6} \right) \frac{18\mu (1-\varepsilon)}{(d_g)^2} u_s.$$  \hspace{1cm} (2.5.16)

where $\mu$ is the viscosity of the fluid and $\langle d_g \rangle$ is the diameter of the filter grain.

\textbf{b) Kuwabara's Model} (Kuwabara, 1959):

Kuwabara's model is identical to Happel's model except for the boundary condition at the surface of the fluid shell. Instead of assuming zero tangential stress as in Happel's model (Equation 2.5.14d), Kuwabara assumed that the vorticity vanishes at the outer surface:
\[ \omega = \frac{\partial U_\theta}{\partial r} + \frac{U_\theta}{r} - \frac{1}{r} \frac{\partial U_r}{\partial \theta} = 0; \; r = b \]  
(2.5.17)

Hence, Kuwabara model differs from Happel's model only in the coefficients, 
\((K_{1-4})\), of the stream function, which are given below.

\[ K_1 = \frac{\left(\frac{1}{2} - \frac{p^3}{5}\right)}{K}; \; K_2 = -\frac{3}{2} \frac{1}{K}; \; K_3 = \frac{\left(\frac{1}{2} + \frac{p^3}{2}\right)}{K}; \; K_4 = -\frac{3}{10} \frac{p^3}{K}; \]

\[ K = (1-p)^3 \left(1 + \frac{6}{5} p + \frac{3}{5} p^2 + \frac{1}{5} p^3\right). \]  
(2.5.18)

The other variables are as defined in Equation 2.5.15.

The head loss is given by,

\[ \frac{-\Delta P}{l} = \frac{18(1-\epsilon)\mu}{\left(\frac{d_g}{2}\right)^2} u_s A(p) \]  
(2.5.19)

where

\[ A(p) = \left(1 + \frac{51}{50} p + \frac{3}{5} p^2 - \frac{7}{25} p^3 + \frac{2}{5} p^4 + \frac{12}{25} p^6 + \frac{6}{25} p^7 + \frac{2}{25} p^8\right) \]

\[ \times (1-p)^{-3} \left(1 + \frac{6}{5} p + \frac{3}{5} p^2 + \frac{1}{5} p^3\right)^{-2}. \]  
(2.5.20)

c) Brinkman's Model (Brinkman, 1947):

Brinkman's model considers collectors to be imbedded in a porous mass.

The flow around the collector is described by a combination of Navier-Stokes equation (without the inertial term) and Darcy's equation. Mathematically, this can be expressed as:

\[ \nabla P = -\frac{\mu}{k} u + \mu \nabla^2 u \]  
(2.5.21)
where \( \nabla \) and \( \nabla^2 \) are the gradient and Laplacian operators, respectively, \( \mathbf{u} \) is the fluid velocity vector, \( \mu \) is the viscosity of the fluid, and \( k \) is the permeability of the bed. The boundary conditions are velocity vanishing at the surface of the collector and approaching uniform value at a large distance away from the collector. The resulting stream function is given by,

\[
\psi = \left( \frac{\psi_\infty}{r^3} \right) \left[ \left( r^2 - 1 \right) + \left( 3/p^2 \right) \left[ (1 + pr^*) \exp(p - pr^*) - (1 + p) \right] \right]
\]

(2.5.22)

where,

\[
\psi_\infty = (\sqrt{2})u_s a_c^2 r^2 \sin^2 \theta \quad \text{as} \quad r^* = r/a_c \to \infty
\]

and \[ p = \frac{9 + 3 \left[ (8/(1-\varepsilon)) - 3 \right]^{\frac{1}{2}}}{\left( 4/(1-\varepsilon) \right) - 6} \]

(2.5.22a)

The head loss according to Brinkman's model is given by,

\[
-\frac{\Delta P}{l} = \frac{18(1-\varepsilon)\mu}{\left( d_g \right)^2} u_s A(m_1)
\]

(2.5.23)

where \( A(m_1) = 1 + m_1 + \frac{m_1^2}{3} \) and \( m_1 = \left( \frac{1}{k} \right)^{\frac{1}{2}} a_c \)

(2.5.23a)

Brinkman's model does not specify the extent of void space next to the filter grain, and hence presents some disadvantages in describing filter clogging.

d) Constricted Tube Model (Payatakes, Tien, and Turian, 1973):

Payatakes, Tien, and Turian proposed a model for granular porous media, assuming that each unit cell resembles a segment of constricted tube with dimensions which are random variables. The geometry and size distribution of the constricted tubes are determined from simple experimental measurements. The flow field within the tubes is axisymmetrical and two dimensional, first
convergent and then divergent. Several investigators have proposed solutions for laminar flow field in a constricted tube with different tube geometries (Chow and Soda, 1972; Payatakes and Neira, 1977; Payatakes, Tien, and Turian, 1973; Venkatesan and Rajagopalan, 1980). Because of the complexity of the geometry, only approximate expressions for fluid velocity vector can be obtained, based on numerical methods. However, owing to its geometry, constricted tube model is capable of predicting pore blockage, and is a more appropriate model to study the behavior of a clogged filter.

2.5.4 Models for Estimating Unit Collector Efficiency

Once the flow field is computed, the trajectory of a particle moving with the fluid around a grain of filter media can be computed by solving the particle motion equations, which are the mathematical expressions of the dynamic equilibrium of the suspended particle under the action of the fluid flow and various forces. Of the forces listed in Table 2.1, the forces of importance in hydrosol filtration are gravitational force ($f_{\text{Grav}}$), drag forces and torques ($f_D, t_D$), London-van der Waals force ($f_{\text{LO}}$), double-layer force ($f_{DL}$) and the Brownian diffusion force ($f_{\text{Brownian}}$). The dynamic equilibrium of a particle under these forces and torques can be expressed as,

$$f_{\text{grav}} + f_D + f_{\text{LO}} + f_{DL} = 0$$  \hspace{1cm} (2.5.24a)

$$t_{\text{grav}} + t_D + t_{\text{LO}} + t_{DL} = 0$$  \hspace{1cm} (2.5.24b)

All the forces included in the above expression for the determination of particle trajectory are deterministic. It should be noted that the stochastic force due to Brownian diffusion ($f_{\text{Brownian}}$), which is important for particles of diameter less
than approximately 1 μm, is not included in the above expressions. If included in the force balance, the stochastic nature of the Brownian diffusion force makes it difficult to obtain an unique trajectory of the particle, although one can obtain the trajectory of the particle in a probabilistic sense. In a strict sense, any analysis based on the above expression is valid only for larger particles for which the Brownian diffusion force is negligible. Solution of the trajectory equation, with the inclusion of Brownian diffusive force is discussed later.

Since it is computationally impossible to compute the trajectories of all the particles, the concept of a “limiting trajectory” is employed. The limiting particle trajectory is defined as that trajectory which demarcates the particle trajectories that are intercepted by the collector and those that escape the collector. The efficiency of a single collector in retaining a particle can be calculated by the ratio of the number of particle trajectories that are intercepted by the collector to the fluid trajectories that flow towards a collector. From the limiting trajectory analysis, one obtains the efficiency of the unit collector in retaining large particles for which Brownian diffusion is negligible. For very small diffusive particles, the deposition mechanism is treated as a mass-transfer process. The usual approach has been to calculate the efficiency of the unit collector in retaining diffusive particles by solving the convective-diffusive equation and calculating the retention efficiency for larger particles from trajectory analysis (which takes into account the deterministic forces) separately. The sum of these two deposition rates calculated independently approximates the overall deposition very closely (Rajagopalan and Tien, 1979).
a) Model of Rajagopalan and Tien (Rajagopalan and Tien, 1976)

Rajagopalan and Tien performed trajectory analysis on a unit collector, based on the Happel's Sphere-in-Cell flow model. Based on the results of numerical solution, Rajagopalan and Tien presented the following closed form expression for the collection efficiency of a "clean" single collector, $\eta_0$, in terms of the dimensionless groups that characterize the physical and chemical conditions of the filtration system:

$$\eta_0 = 4A_s^{1/3}N_{Pe}^{-2/3} + A_sN_{Lo}^{1/8}N_R^{15/8} + 3.38 \times 10^{-3} A_sN_G^{12}N_R^{-0.4}$$  \hspace{1cm} (2.5.25)

for $N_R \leq 0.18$ and $N_{Lo} > 0$.

where,

$$A_s = \frac{2(1 - p^5)}{w} \text{ (p and w are as defined in Equation 2.5.15c)}$$  \hspace{1cm} (2.5.25a)

$$N_{Pe} = \frac{u_s d_c}{D_{BM}}$$  \hspace{1cm} (2.5.25b)

$$D_{BM} = \frac{kT}{3\pi \mu d_p} \text{ (k is Boltzmann constant and T is absolute temperature)}$$  \hspace{1cm} (2.5.25c)

$$N_{Lo} = \frac{H}{9\pi \mu a_p^2 u_s} \text{ (H is Hamaker constant)}$$  \hspace{1cm} (2.5.25d)

$$N_R = \frac{d_p}{d_c}$$  \hspace{1cm} (2.5.25e)

and

$$N_G = \frac{2(\rho_p - \rho)a_p^2 g}{9\mu u_s}$$  \hspace{1cm} (2.5.25f)

$p_p$ and $\rho$ are densities of particle and liquid respectively.

The first term accounts for collection efficiency based on Brownian diffusion alone and is obtained from the analysis of Cookson (Cookson, 1970). Cookson
calculated particle transfer and deposition rates based on the results of (Pfeffer and Happel, 1964).

b) Yoshimura's Model (Yoshimura, Ueda, Mori et al., 1980):

Yoshimura, Ueda, Mori et al. developed a similar expression, using Kuwabara's model to represent flow in the filter bed. Yoshimura's model considers the retardation effect of the London-van der Waals force, in addition to all the parameters considered in Rajagopalan and Tien (1976) model. The closed form expression for clean unit collector efficiency, \( \eta_o \), proposed by Yoshimura and others is as follows:

\[
\eta_o = \frac{2}{3} K_w (1-\varepsilon)^{2/3} \left[ 2.26MK_w^{-m}N_R^{2(1-m)}N_{Lo}^{m} + 2.26WK_w^{-n}N_R^{2(1-n)}N_G^{n} \right]
\]

\[+4.9(4/3)^{2/3}(K_wN_{Pe})^{-2/3} \]  

(2.5.26)

for \( N_G < 0.5 \) and \( N_R < 5 \times 10^{-2} \),

where,

\[
K_w = \frac{5(1-p^3)}{5-9p+5p^3-p^6} \quad \text{(2.5.26a)}
\]

\[
N_{Rtd} = \frac{2\pi a_p}{\lambda_e} ; \lambda_e \text{ is the wavelength of the electron oscillation.} \quad \text{(2.5.26b)}
\]

\( M \) and \( m \) are related to the retardation group by the following relations,

\[
M = 5.71 \times 10^{-1} \quad m = 0.11 \quad N_{Lo}N_R^{-2}K_w^{-1} \leq 10^{-1} \quad \text{(2.5.26c)}
\]

\[
M = 1.79N_{Rtd}^{-0.18} \quad m = 0.3N_{Rtd}^{-0.16} \quad 10^{-4} < N_{Lo}N_R^{-2}K_w^{-1} \leq 10^{-1} \quad \text{(2.5.26d)}
\]

\[
M = 1.87N_{Rtd}^{-0.17} \quad m = 0.25N_{Rtd}^{-0.07} \quad 10^{-1} \leq N_{Lo}N_R^{-2}K_w^{-1} \leq 10^{2} \quad \text{(2.5.26e)}
\]

\[
M = 1.56N_{Rtd}^{-0.2} \quad m = 0.29N_{Rtd}^{-0.03} \quad 10^{2} \leq N_{Lo}N_R^{-2}K_w^{-1} \quad \text{(2.5.26f)}
\]
\(W\) and \(n\) are empirical functions of the London group, aspect ratio and porosity as defined below:

\[
W = 0.23 \left( N_L N_R^{-2} K_w^{-1} \right)^{0.06} \quad (2.5.26g)
\]
\[
n = 1.16 \left( N_L N_R^{-2} K_w^{-1} \right)^{-0.009} \quad (2.5.26h)
\]

c) Model of Payatakes et al. (Payatakes, Tien, and Turian, 1974):

Payatakes, Tien, and Turian reported results of trajectory analysis using a constricted tube flow model. The unit bed element is assumed to consist of large number of grains and half pores simultaneously. The dimensions and size distribution of unit cells in each UBE can be determined from experimental measurements. Based on the limiting capture trajectory analysis, the collection efficiency of each unit element is calculated and then used to compute the efficiency of the entire UBE. However, owing to the complexity of the problem, no closed form solution could be found and use of this model requires considerable computational effort.

2.5.5 Clean Bed Removal in Packed Bed Filters

The removal efficiency of a clean collector as calculated from either of the Equations 2.5.25 and 2.5.26, can be related to the removal efficiency of a clean filter bed of depth \(l\) through mass balance considerations as follows:

\[
\frac{C}{C_0} = \exp\left( -3(1 - \varepsilon) \alpha \eta \frac{l}{d_c} \right) \quad (2.5.27)
\]
In the above equation, $\alpha$ is an empirical collision efficiency factor, which describes the fraction of collisions that result in attachment of the particle to the collector. $\alpha$, commonly referred to as collision factor or sticking coefficient, is usually treated as an adjustable parameter to fit model predictions with experimental observations. Under favorable chemical conditions, $\alpha$ approaches unity.

The single collector efficiency, $\eta_o$, can be related to the initial filter coefficient, $\lambda_o$, as follows. Integrating Equation 2.5.8 over length $l$ yields,

$$\frac{C}{C_o} = \exp(-\lambda_o l)$$

Comparing Equation 2.5.28 with Equation 2.5.27, the following expression for the filter coefficient can be obtained.

$$\lambda_o = \frac{3(1-\varepsilon)\alpha \eta_o}{2d_c}$$

Experimentally, one can obtain the value of initial filter coefficient, $\lambda_o$, from Equation 2.5.28 by measuring the influent and effluent concentrations of the particles during the initial stages of filtration. The single collector efficiency along with stickiness factor ($\alpha \eta_o$) can then be determined from Equation 2.5.29. However, it should be noted that since $\eta_o$ is proportional to $C_o/C$, small errors in the determination of the concentrations results in significant uncertainty in the determination of $\eta_o$. This uncertainty increases as the ratio of $C/C_o$ decreases. For instance, a 1% error in concentration measurement when $C/C_o = 80\%$ may lead to 20% uncertainty in estimating $\eta_o$ (Tien, 1989).
2.5.6 Stochastic Trajectory Analysis

The trajectory analysis (Equation 2.5.24) discussed above does not include Brownian diffusive force. Since all the forces considered in Equation 2.5.24 are deterministic, it can be integrated to obtain a unique solution for the trajectory of the particle. However, for small particles, Brownian diffusion is a significant transport mechanism. The Brownian motion of a particle is caused by the fluctuations in the collisions with molecules of the surrounding fluid. Under normal conditions, a Brownian particle in a liquid suffers about $10^{21}$ collisions per second (Chandrasekhar, 1943). If each collision is thought to cause a kink in the trajectory of the particle, it is impossible to find the exact trajectory of the particle. The inclusion of stochastic Brownian force term in Equation 2.5.24 (which is then called Langevin equation), makes the solution non-unique. One can only hope to find a solution in the probabilistic sense. The Langevin equation is given by,

$$\frac{du_p}{dt} = f_d + f_e + A(t) \quad (2.5.30)$$

where,

- $u_p$ is the particle velocity vector,
- $f_d = \beta(u_f - u_p)$ is the drag force vector (per unit mass of particle),
- $\beta$ is the drag coefficient per unit mass $= 6\pi\mu a_p/m_p$,
- $m_p$ is the mass of the particle,
- $a_p$ is the radius of the particle,
- $f_e$ is the external force per unit mass such as gravity, etc., and
- $A(t)$ is the Brownian acceleration.
To solve Equation 2.5.30, several assumptions are made regarding \( \mathbf{A}(t) \). First it is assumed that \( \mathbf{A}(t) \) is independent of \( u_p \) and second that \( \mathbf{A}(t) \) varies extremely rapidly compared to the variations of \( u_p \). The second assumption implies that there exist two non-overlapping time scales, one is a fast scale (on the order of frequency of collisions) and the other a much slower time scale (on the order of \( 1/\beta \)) which represents the time needed for the adjustment of fluid velocity responding to changes in its momentum. The random acceleration, \( \mathbf{A}(t) \), is represented as a Gaussian white noise process, i.e., it has a mean of zero and its auto-correlation is an impulse function.

\[
\langle \mathbf{A}(t) \rangle = 0 \quad (2.5.31a)
\]

\[
\langle \mathbf{A}(t) \mathbf{A}(t + \tau) \rangle = K \delta(t - \tau) \quad (2.5.31b)
\]

Assuming that the fluid velocity vector is constant over a short time interval \( \Delta t \), Equation 2.5.30 can be integrated incrementally with the initial condition \( u_p = u_{p0} \) at \( t = 0 \) to yield (for example, Gupta and Peters, 1985; Kanaoka, Emi, and Tanthapanichakoon, 1983; Ramarao and Tien, 1991),

\[
u_p = u_{p0} e^{-\beta t} + u_r \left( 1 - e^{-\beta t} \right) + \frac{f_e}{\beta} \left( 1 - e^{-\beta t} \right) + R_v(t) \quad (2.5.32a)
\]

where \( R_v(t) = \int_0^t e^{\beta(\xi - t)} \mathbf{A}(\xi) \, d\xi \). 

\[
(2.5.32b)
\]

The displacement vector can be obtained by substituting \( dt/dt \) for \( u_p \) in the above equation and integrating with the initial condition \( \mathbf{r} = \mathbf{r}_0 \) at \( t = 0 \).

\[
\mathbf{r} = \mathbf{r}_0 + \frac{u_{p0}}{\beta} \left( 1 - e^{-\beta t} \right) + \left( u_r + \frac{f_e}{\beta} \right) \left[ t + \frac{1}{\beta} (e^{-\beta t} - 1) \right] + R_r(t) \quad (2.5.33a)
\]

\[
R_r(t) = \int_0^t e^{-\beta \eta} \left[ \int_0^\eta e^{\beta \xi} \mathbf{A}(\xi) \, d\xi \right] \, d\eta \quad (2.5.33b)
\]
The two integrals involving stochastic kernels (Equation 2.5.32b & 2.5.33b) are random deviates with bivariate Gaussian distribution (Chandrasekhar, 1943). The components of \( R_v(t) \) and \( R_r(t) \) can be calculated as follows:

\[
\begin{bmatrix}
  R_{v_i} \\
  R_{r_i}
\end{bmatrix} =
\begin{bmatrix}
  \sigma_{v_i} & 0 \\
  \sigma_{v_r}/\sigma_{v_i} & \left( \sigma_{r_i}^2 - \sigma_{v_i}^2 / \sigma_{v_r}^2 \right)^{\gamma/2}
\end{bmatrix}
\begin{bmatrix}
  n_i \\
  m_i
\end{bmatrix}
\]  

(2.5.34)

where,

\[
\begin{align*}
\sigma_{v_i}^2 &= \frac{q}{\beta} \left[ 1 - e^{-2\beta t} \right] \\
\sigma_{r_i}^2 &= \frac{q}{\beta^3} \left[ 2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t} \right] \\
\sigma_{v_r} &= \frac{q}{\beta^2} \left[ 1 - e^{-\beta t} \right]^2 \\
q &= \frac{\beta kT}{m_p}
\end{align*}
\]  

(2.5.34a - 2.5.34d)

and \( n_i \) and \( m_i \) are two normally distributed numbers.

### 2.5.7 Head Loss in Packed Beds

For a clean bed, the pressure drop across the filter is given by Kozeny-Carman expression (Kozeny, 1927; Carman, 1937),

\[
\frac{-\Delta P}{L} = \frac{180}{d_c^2} \frac{\mu u_s}{\epsilon^3} \frac{(1-\epsilon)^2}{\epsilon}
\]  

(2.5.35)

where \( \Delta P \) is the necessary pressure drop to maintain a superficial velocity of \( u_s \) over a filter depth of \( L \). This expression was derived assuming that flow is incompressible and laminar, that filter media are uniform spheres, and that the pressure drop results entirely from the form-drag loss as fluid moves around the
media. If the filter media grains are not spherical, \( d_c \) can be related to the surface area, \( A_c \), and volume of the particle, \( V_c \), as follows:

\[
d_c = \frac{6V_c}{A_c}
\]  

(2.5.36)

Substituting Equation 2.5.36 into Equation 2.5.35, and converting expressing pressure drop as head loss, \( \Delta H \), we obtain,

\[
-\frac{\Delta H}{L} = \frac{K}{\rho_l g} \left( \frac{u_s}{\varepsilon} \right)^2 \left( \frac{A_c}{V_c} \right)^2 \]  

(2.5.37)

where \( K \) is an empirical constant with a value of about 5 for flow in the laminar region, \( \varepsilon \) is the porosity of the filter bed.

O'Melia and Ali (1978) modified Equation 2.5.37 to account for increase in head loss due to the additional surface of the deposited particles. For a filter bed of depth \( L \) consisting of \( N_c \) filter grains and \( N_p \) retained particles, the head loss is given by (neglecting the change in bed porosity),

\[
-\frac{\Delta H}{L} = \frac{36}{d_c^2} \frac{K}{\rho_l g} \left( \frac{u_s}{\varepsilon} \right)^2 \left[ 1+ \beta' \frac{N_p}{N_c} \left( \frac{d_p}{d_c} \right) \right]^2 \]  

(2.5.38)

Here \( \beta' \) is an empirical coefficient that represents the fraction of retained particles that are exposed to the flowing fluid and contribute to the additional surface area. The change in porosity can be accounted for by relating the porosity of the entire bed to the porosity of the deposit and specific deposit of the particles using Equation 2.5.4.
Several authors have suggested different variations of Equation 2.5.38. Without exception, all of them have adjustable parameters, that need to be tuned to describe head loss for filtration systems under different conditions.

2.6 Morphology of Colloidal Deposits in Packed Beds

The structure of filter deposits is likely to be complex. A good qualitative and quantitative understanding of the deposit morphology is essential to describe the dynamic behavior of the packed bed filters. In this section, previous studies involving characterization of colloidal deposits in packed beds are reviewed. Although considerable amount of work was done to model the filter ripening process, only few studies have been reported in the literature to characterize the deposits in the packed beds. Because of the similarities between aerosol and hydrosol filtration (a significant difference being that inertial impaction is important in aerosol filtration, but is negligible in hydrosol filtration), and owing to the few studies reported on the morphology of hydrosol deposits, previous work reported on the morphology of aerosol deposits is also reviewed.

2.6.1 Morphology of Aerosol Deposits in Granular Media:

Payatakes and Tien (1976) proposed a model to describe deposition of aerosols in fibrous media as a dendritic type growth. Their model considers differential growth of dendritic deposits on a collector surface, assumed to be flat, on the basis of the relative size of the collector to the suspended particles, and the space above the surface is divided into layers, parallel to the collector
surface. The growth of the dendritic structure is obtained by computing the particles deposited in each layer. There is a limit to the number of particles that can be deposited on a given particle in a layer. The deposition in any layer, \( k \), is proportional to the number of available deposition sites offered by the particles in the previous layer \( k - 1 \). However, this model assumes that a dendrite once formed, is rigid and it does not distinguish between particles in the same layer; all the particles in a layer are assumed to behave identically. It was also assumed that the particles colliding with the upper half of a dendrite particle become members of the immediately higher layer, whereas particles that might collide with the lower half were accounted for as colliding with the upper half of a particle in the immediately lower layer. This assumption made no allowances for collisions with particles in a given layer that would lead to retention in the same layer. Payatakes and Tien considered the possibility that the dendrites are distributed over the surface of the collector and that dendrites grow at different rates. In a subsequent study, Payatakes (1977) revised this model to allow collisions of a particle to lead retention in the same layer. Furthermore, radial as well as angular contributions to deposition are considered. Payatakes reported model predictions for the expected configuration and rate of growth of a single dendrite as a function of angular position on the fiber and of time. He applied the model to describe the transient behavior of a fibrous filter in which deposition occurred only by interception. His results indicated that dendrite growth depends strongly on the angular position on the fiber. Dendritic growth is vigorous at around \( 2\pi/3 \) and decreases as \( \theta \) approaches \( \pi/2 \) or \( \pi \). He also observed a minimum growth rate at the forward stagnation point \( \theta = \pi \), where very lean dendrites are formed. In a later work, Payatakes and Gradon (1980a) extended the model to include inertial impaction, in addition to interception, as a deposition
mechanism. The results were qualitatively similar to those when only interception was considered. While deposition by interception alone led to particle capture over \( \pi/2 \leq \theta \leq 3\pi/2 \), inclusion of inertial impaction reduced this region to \( \hat{\theta} \leq \theta \leq 2\pi \hat{\theta} \) (\( \hat{\theta} \) is larger than \( \pi/2 \)), depending on several non-dimensional numbers which characterize the physical parameters such as particle size relative to fiber, velocity, etc. When the dominant transport mechanism was Brownian motion (Payatakes and Gradon, 1980b), dendrites were observed to form over the entire surface, though the largest dendrites were found on the upstream part of the fiber, in the range \( (\sim 135\pm15^\circ) \), and its symmetric strip \( (225\pm15^\circ) \). The dendritic growth on a smaller fiber was observed to be faster than on that of a larger fiber, leading to the conclusion that larger interception parameter values lead to more pronounced dendritic deposition. The dendrites formed under convective Brownian motion are less slender and elongated than those formed by inertial impaction and/or interception.

Tien, Wang, and Barot (1977) and Wang, Beizaie, and Tien (1977) proposed a 2-dimensional model that simulates aerosol deposition on a single collector, based on a consideration of particle size and the spatial distribution of the particles. The size of a particle plays an important role in its deposition, via the interception mechanism. Once deposited, the size of a particle is also important in determining the "shadow" area on the collector surface where other particles are blocked from deposition sites. This causes a non-uniform deposition on the collector surface. Particles that would otherwise be deposited in the shadow region attach themselves to the particle that creates the shadow, resulting in a dendritic growth. Since the locations of the individual particles at any instant do not follow any regular pattern, an imaginary control surface from
which particles are released is defined upflow of the collector. The particles are assumed to originate singularly and at random positions at this surface. Thus the phenomenon of particle deposition can be considered in terms of the singular and randomness of the approaching particles and the effect of the shadow areas created by the deposited particles. Beizaie, Wang, and Tien (1981) extended these modeling concepts to three dimensions and found qualitatively good agreement with experimental data. Their simulation results indicated that deposition process consists of three stages. During first stage, particle deposition occurs primarily on the clean collector. During second stage, deposition occurs both on collector surface and on previously deposited particles, though more deposition occurs on previously deposited particles. Deposition during this stage is characterized by dendritic growth. During the third stage, further particle deposition essentially occurs on deposited particles. During this stage, the individual dendrites become less distinctive and join together to form particle aggregates, similar to flocs in flocculation process. Later, Beizaie (1991) modeled deposition on to three identical, parallel and equally spaced circular cylinders with their axes perpendicular to the fluid velocity. Qualitative agreement with experimental results was reported in terms of collection efficiency of the fibers and drag. Pendse and Tien (1982) proposed a simulation model for the deposition of aerosols in granular media, based on the general principles suggested by Tien, Wang, and Barot (1977) and Wang, Beizaie, and Tien (1977), but using a constricted tube model to characterize the granular media. The simulation results confirmed the three-stage deposition theory of Beizaie, Wang, and Tien (1981). The model predictions of collector efficiency as a function of mass deposited agree qualitatively with experimental results, though it under predicted the experimental values.
In a more generalized model, Jung and Tien (1993) modeled aerosol deposition in granular media using a modified Happel model to characterize the structure of the granular media. In their study, they followed the trajectories of particles in a unit bed element (Happel’s cell) and recorded the locations of particle deposits. To speed up the simulations, the Happel’s cell was discretized along the \( \theta \) and \( \phi \) directions and the particle trajectories were estimated by interpolation. They also considered the effect of particle bounce off. Impacting articles were assumed to bounce-off if the inclement particle velocity exceeded a capture-limit velocity, determined from the adhesion energy. Simulations over-predicted increasing collection efficiency with increased specific deposit when the possibility of bounce-off was not accounted for in the model. When bounce-off was included in the model in the form a capture probability, good agreement was observed for capture probabilities between 0.14 and 0.23, depending on the experimental conditions. They discussed the deposit morphology in terms of size distribution and location of particle clusters. The clusters were observed to be bigger and fewer for experiments with high Stokes’ numbers \( N_{St} = \rho_p d_p^2 V / (9 \mu d_g) \), while a small aspect ratio, \( N_R = d_p / d_g \), resulted in a large number of smaller dendrites. At high Stokes’ numbers, most of the particle deposition took place in the neighborhood of the stagnation point, as expected. In an earlier study, based on experimental results from granular media filtration of aerosols, Jung and Tien (1991), arrived at the following empirical relations for head loss development when specific deposit was \( 10^{-3} \):

\[
F_2 = \frac{(\partial p/\partial z)}{(\partial p/\partial z)_0} = 1 + \beta_1 \sigma^{\beta_2} \tag{2.6.1a}
\]
\[
[F_2 - 1]_{\sigma=10^{-3}} = 0.3484 N_{St}^{1.199} N_R^{0.8568} 
\]
\[
\beta_1 = [F_2 - 1]_{\sigma=10^{-3}} 10^3 \beta_2 
\]
\[
\beta_2 = 3.5134 N_{St}^{-0.0925} N_R^{0.2748} 
\]

These correlations are valid for the following ranges of the \( N_R \) and \( N_{St} \):

\[
1.7 \times 10^{-3} \leq N_{St} \leq 3.8 \times 10^{-2} \\
1.72 \times 10^{-3} \leq N_R \leq 8 \times 10^{-3}
\]

Ushiki and Tien (1984) made \textit{in situ} observations of aerosol deposition on a two-dimensional model filter consisting of rows of cylindrical rods arranged in a centered hexagonal pattern. They reported that most of the initial retention was on the second row of collectors, immediately below the top layer. The deposits occurred in piles and the initial collection was found to be greater than theoretical estimation. The authors suggested that the flow field in the filter could be that of a two-dimensional jet and conceded that further work is needed to ascertain the extent to which this type of flow prevails in the actual filters. They noted that the extent of reentrainment became significant only after substantial deposition occurred. As reentrainment occurred, they observed the deposit geometry to change from pillar- to pile- or "Christmas tree-like". Yoshida and Tien (1985) constructed a two-dimensional model filter consisting of rows of cylindrical rods and observed the deposition of aerosols (aluminum oxide) over time. The rods were arranged in three patterns, viz., centered hexagonal, square and random order and experiments were performed at two different velocities. They observed that most of the deposition took place within the first three or four rows of collectors. On a collector, deposition was confined primarily in the neighborhood near the front stagnation point of the collector. In filters with randomly arranged
rods, significant deposition occurred on rods which had comparatively large pore constrictions above them. From the micrographs of the deposition process, they calculated the specific deposit $\sigma$, defined as volume of deposited particles per unit volume of bed, over time. They fitted an empirical expression relating the measured pressure drop to the specific deposit and reported that the data from all experiments, despite different rods arrangement and flow velocities, fitted well for the correlation,

$$\frac{(\Delta P - \Delta P_0)}{\Delta P_0} = 24.73\sigma^{1.247}$$

(2.6.2)

2.6.2 Morphology of Hydrosol Deposits in Granular Media:

Stein (1940) reported results from filtration of ferric flocs onto a two-dimensional filter bed composed of rods. His observations showed that during initial stages of filtration and at low filtration rate (2 cm/min), the flocs attach themselves to grains like "whiskers", forming a smooth layer on the upper half of the cylinder. At higher flow rates, the attached flocs exhibit a slow creeping or kneading action against the walls, with deposition spreading almost all around the circumference of the cylinders. As the thickness of the sheaths increased, the velocity and shearing forces also increased. The high shear intensity at the walls caused a continuous scouring, with the deposits forming almost parallel walls. The filter rods looked like an assemblage of hexagonal rods, with the deposits forming an encompassing hexagon over their circular cross-section. Ison and Ives (1969) conducted microscopic observations of kaolinite particle deposition in a filter bed of ballotini and reported that deposition occurs primarily on the upstream side of the filter grains.
Maroudas and Eisenklam (1964) built a model filter consisting of a two-dimensional network of interconnecting channels (3000 μm minimum opening) of a regular staggered-square pattern. They filtered polystyrene particles of either spherical (390 μm) or angular shape (125-1100 μm). They noted that no deposition occurred if the fluid velocity was above a critical value, which was found to be dependent of particle size and shape. At flow rates less than the critical value, particle deposition occurred in one of the two modes, either by gradual constriction of flow paths (constricting mode) or by rapid blocking of flow paths (blocking mode). Deposition by constricting mode was dominant when the particle size was less then 1/3 channel size for spherical particles and 1/10 for angular particles. At any level, the deposits grew and gradually constricted the channels, until the velocity reached the critical value, after which no further deposition occurred at that level. Eventually, the bed became non-retaining. The blocking mode was observed for angular particles of sizes 1/8 to 1/3 the channel size. In this mode, the deposition was observed to be uneven and its distribution varied over time. In some channels, deposits grew rapidly and soon became completely blocked, while other channels remained free and velocity in them gradually increased. At any time, they reported that the smallest number of free flowpaths was observed to be at the top of the bed and at any level, the number of free flowpaths was observed to decrease with time. Deposition in the blocking mode resulted in either complete blocking of the pores throughout the bed, thereby initiating cake buildup at the top, or the bed became non-retaining, i.e., the velocity was above critical in all the remaining open flowpaths. Visual observations indicated that in some experiments, only a fraction of the pore volume was filled with particles even at complete blockage, indicating that only a
few strategic junctions need be blocked to decrease the flow through the network. For experiments which ended in a non-retention stage, they reported that at low flow rates, only a few highly tortuous free flowpaths remained, while more free flowpaths were observed at high flow rates. Also, at high flow rates, deposits in the blocked flowpaths were found only at junctions. They also reported observations on liquid flow pattern from a tracer study. They noted that if a free flow-path was very tortuous while the entrance to an empty channel was blocked by a highly permeable deposit, a significant amount of liquid flowed through the latter. This caused a low flow rate through the tortuous free path, causing more deposition and ultimately leading to its blockage. They also reported that flow through deposits of small particles was very low, while flow through coarse deposits was often comparable to flow through free but tortuous paths.

Pendse, Tien, Rajagopalan et al. (1978) have developed a technique based on dispersion of tracers in clogged filter beds to study the nature of deposit morphology. In their model, the changes in dispersion coefficients, grain diameter, interstitial velocity, and cross-sectional area were calculated from the increase in pressure drop and assumed deposit morphology as filtration progresses. They calculated changes in the dispersion coefficient for the porous medium and estimated the travel time of the peak of the tracer through the clogged filter bed. The estimates were compared with results from the dispersion measurements. Results of experimental data showed good agreement with the theoretical prediction, when the deposit morphology was assumed to be controlled by the second stage, viz., "blocking mode", resulting from the complete blockage of some constrictions.
Payatakes, Park, and Petrie (1981) made direct observations of pore-clogging phenomena, in the presence of polyelectrolytes. Several experiments were conducted at varying chemical conditions. In all cases, it was noticed that the top layer of the filter bed behaved differently from the lower layers. Initially, in accordance with the trajectory calculations, the grains of the top layer accumulated deposits in the form of "snowcaps". However, when the shear stresses on these deposits overcame the adhesive forces of the deposit, these clusters are reentrained, moving down the filter and potentially re-depositing at new sites. Payatakes, Park and Petrie classified the filter clogging behavior into three categories based on the colloid stability. In the first category, the feed hydrosol is weakly unstable (sufficiently destabilized to allow extensive deposition) and consists mostly of singlets, with a few doublets and triplets. The main deposition pattern was found to be clogging of the narrow throats, leading to the formation of "pendant-" and "pouch-shaped" deposits. In the second category, the feed hydrosol was very unstable and extensive agglomeration occurred in the feed. Deposits resembled jagged quasi-conical pillars on top of grains, clogged the throats and eventually evolved into rough pendants. In the third category, the feed hydrosol was first destabilized, then re-stabilized by reversing the zeta potential of the particles. Large agglomerates, which had positive net charge were present in the feed, while the grains were still negatively charged. The deposits were those of large particle-clusters all around the grain. However they kept some distance from their neighbors, thereby giving a "checkboard" appearance. Most of the deposition was on the forward half of the grain.
Tien, Turian, and Pendse (1979) proposed a model based on the theoretical calculation proposed by Rajagopalan and Tien (1976) for the filter coefficient. A combination of spherical and constricted tube configurations was used to characterize the packed bed. The spherical configuration was used to estimate the rate of deposition, while the constricted tube configuration was used to characterize the effect of deposition. The deposition process was considered by them to be a two stage process. In the first stage, the deposition was mainly due to the adhesion of the particles to the collectors (filter grains). This results in an increase in the effective grain dimension, thereby, decreasing porosity. This stage continues until the specific deposit $\sigma$ reaches a transition value. In the second stage, the blockage of the pore constrictions occurs. This continues until the head loss is too high for the filter to be operable. The collector diameter at the end of the first stage (called the transition period) is assumed to remain unchanged throughout the second stage. However, the number of the open constrictions decreases during the second stage, resulting in an increase in the interstitial velocity. The change in the interstitial velocity is inversely proportional to the change in the number of open constrictions. The decrease in the number of open constrictions can be related to the specific deposit, $\sigma$, as shown by Tien, Turian and Pendse (1979).

The pressure drop during the first stage can be computed from the Kozeny-Carman equation, since the pressure drop is a function of the surface area of the grain and porosity of the bed and the change in both these parameters can be computed. During the second stage, the interstitial velocity changes as some of the pore constrictions become blocked. However, the pressure drop is proportional to the interstitial velocity. The ratio of the pressure
gradient during the second stage to the pressure gradient at the end of the first stage can be related to the specific deposit at the beginning of the second stage ($\sigma_{trans}$), porosity of the deposit and filter bed, and the number of constrictions in a clean bed (Tien, Turian , and Pendse, 1979). Based on previous experimental work, Tien and coworkers suggested some values for the three parameters that appear in this model, viz., porosity of the deposit, (0.7), specific deposit at the end of first stage, $\sigma_{trans}$, (0.05), and $\beta$ (1-10), where $\beta$ is a correction factor to take into account the possibility that the actual deposit causing blockage is in excess of the minimum required amount. However, since $\sigma_{trans}$ and $\beta$ cannot be determined a priori, this model is limited as a predictive tool. Tien, Turian and Pendse compared the predictions of this model with experimental results. While the predictions for concentration profile were in qualitative agreement, predictions for the head loss data were less satisfactory. The authors contend that their model can be used to provide an order of magnitude estimate on a truly predictive basis.

Chiang and Tien (1985) considered two limiting cases for particle deposition. In the first case, the collector geometry was continuously altered by the deposition of the particles. In this work, Chiang and Tien used a constricted tube model to characterize the packed bed. The tube radius was assumed to decrease as deposition proceeds. They solved the required moving boundary value problem numerically. The second case was based on the work of Tien, Wang , and Barot (1977) and Wang, Beizaie , and Tien (1977). In this case, the possibility of the particle deposits taking on a configuration different from a smooth-coating deposition was considered. The effect of deposited particle aggregates on the filter performance was considered, rather than the individual
deposited particles. The adhesion probability concept was incorporated in the model, to account for the fact that not all contacts made by the particle lead to removal. However, agreement with experimental results was very poor. Chiang and Tien suggested that the two limiting situations should be combined according to an empirical rule. They also proposed, based on experimental results, that the change in collector efficiency is only dependent on $\sigma$ and $N_r$ and suggested a way of obtaining a specific functional form for the above relation. Comparison of the resultant correlation with experimental data (obtained from filtering lycopodium and ragweed through a bed of glass beads) gave satisfactory agreement. However, they also observed that more than one correlation may be available for assessing the change in hydrosol collection efficiency resulting from deposition.

Mackie, Horner, and Jarvis (1987) proposed a model that considers both the microscopic and macroscopic effect of deposition on a grain, i.e., the model considers both the action of a single deposited particle as a collector and the effect of deposit on the flow field around a grain, including the increase in the interstitial velocity. They assumed that during the initial stages of ripening, the deposit is dendritic in nature and that owing to the high viscous forces in hydrosol filtration, they are only one particle in length, in the sense that each deposited particle contributes to further deposition. The average effect of these particles on the collection efficiency of the unit collector is computed using a simple probability model. During the later stages of filter run, after a significant number of particles have been deposited, the model considers both dendritic and smooth coatings for the deposit. Microscopically, the outermost deposited particles are viewed as individual collectors which contribute towards increase in collection
efficiency. Macroscopically, deposition results in an increase of the effective size of the grain and alters its shape and thereby the flow around it. The stream function for flow around a collector with a layer of deposit is computed by assuming porosity of the deposit and a deformed shape for the collector. The effect of shear forces with an increase in interstitial velocity was also considered, based on the hypothesis that there exists a critical velocity for each particle size, such that no adhesion of these particles occurs at the locations on the grain where the tangential velocity of the fluid is greater than or equal to the critical velocity. The critical velocity was found empirically, assuming that the shear force needed to dislodge a particle would be equal to London force. Deposition was assumed to be controlled by interception and sedimentation. Brownian motion and hydrodynamic retardation effect were not considered. The model showed good qualitative agreement with experimental results. However, as Mackie, Horner and Jarvis contend, the model does not account for the blocking of the pores and hence is not reliable in the later stages of the filtration. A reasonably good agreement between model predictions and experimental data from early stages of filtration was observed.

Hunt, Hwang, and McDowell-Boyer (1993) conducted a series of pilot plant filtration experiments to study particle accumulation and increasing hydraulic gradients within packed beds. A kaolin suspension (30 mg/L), destabilized with alum, was filtered through a sand bed. Two narrowly sized sands (0.54 mm and 1.29 mm) were used as filter media and experiments were conducted at three flow rates (0.145 cm/sec and 0.279 cm/sec in fine sand bed; 0.145 cm/sec, 0.279 cm/sec and 0.554 cm/sec in coarse sand bed). They observed that the top few centimeters of the bed removed particles very
efficiently for some time, beyond which no further removal was observed in the top layers, while the hydraulic gradient in these sections continued to increase for the entire filtration duration. The specific deposit in the top layers increased with time initially and reached a constant value at about the same time when no further removal occurred within these layers. The specific deposit in their experiments exhibited an interesting depth profile. In the fine sand filter beds, the specific deposit in any layer was higher than the layers beneath it for up to 120 minutes. After about 90 minutes, the specific deposit in the top 0.63 cm of the bed reached a constant value, which remained the highest compared to any other section of the bed for the rest of the run. However, after about 150 minutes, a depth dependent maxima of specific deposit was observed at a depth of 8.3 cm. Despite this uneven distribution of specific deposit at different depths, the hydraulic gradient in any section of the bed was always higher than the layers beneath it, during the entire duration of the filtration. In coarse sand filters, the depth profile of the specific deposit during the first 90 minutes of filtration behaved the same way as in fine sand filters. During the later stages, the depth profile of specific deposit also exhibited a maxima at about 8.9 cm depth. However, unlike fine sand filters, the specific deposit in the top sections attained a constant value which was lower than the maxima. The hydraulic gradient, however, followed the same trend as in fine sand filters, with upper layers experiencing a higher gradient compared to the lower layers during the entire filtration run.

Hunt, Hwang and McDowell-Boyer also observed that in all the experiments, the normalized head loss expressed as \((p - p_o)/p_o\) followed a \(\sigma^{2/3}\) dependency over the range of \(0.1 < \sigma < 4 \text{ g/L}\) for fine sand filter and over
the range $0.1 < \sigma < 10$ g/L for the coarse medium. The authors evaluated several models to describe the experimental data and reported that a qualitative agreement between the model and the data was observed only when the deposits were assumed to have a decreasing porosity with increasing thickness of the deposit.

Boller and Kavanaugh (1995) proposed a model to predict head loss development in a filter bed, based on particulate size and density, filtration rate and media grain size. Their model was based on the postulate that the deposits in a filter bed are analogous to the flocs formed through particle aggregation. They hypothesized that, just as in aggregates, the relative density of a deposit decreases as the number of particles captured at a deposit site increases. Based on this hypothesis, they proposed the following expressions for calculating the head loss gradient as a function of specific deposit and initial bed porosity:

$$\frac{l}{l_0} = \left(1 + p \frac{\sigma_v}{\varepsilon_0}\right)^x \left(1 - \frac{\sigma_v}{\varepsilon_0}\right)^y$$ \hspace{1cm} (2.6.3)

where $p$, $x$ and $y$ are empirical constants. $\sigma_v$ is the deposit volume of the aggregated particulates per unit filter volume. $\sigma_v$ includes the particle volume as well as the occluded water. Experimentally, one can measure the mass or volume of the particles deposited per unit filter volume ($\sigma_m$ and $\sigma_{v,p}$ respectively) by mass balance. Boller and Kavanaugh calculated $\sigma_v$ from $\sigma_{v,p}$ using the following expressions,

$$\frac{\sigma_{v,p}}{\sigma_v} = \frac{\rho_d - \rho_w}{\rho_s - \rho_w} = \frac{1}{a} N^{(1-b)}$$ \hspace{1cm} (2.6.4)

where,
\[ \rho_d \] = average density of the deposit

\[ \rho_s \] = density of primary particle

\[ \rho_w \] = density of water

\[ N = \text{number of particles in a deposit} \]
\[ N = \left( \frac{\sigma_y}{\eta g V_p a} \right)^{1/b} \]

\[ n_g = \text{number of media grains per unit filter volume} \]
\[ n_g = \frac{6(1-\varepsilon_o)}{d_g^3} \]

\[ V_p \] is the volume of primary particle.

\[ a, b = \text{empirical constants} \]

\[ \varepsilon_o = \text{clean bed porosity} \]

\[ d_g = \text{diameter of the filter grain} \]

This model can be fitted to the experimental data using \( b \) as the fitting parameter. They obtained a good fit with the experimental data of (Darby and Lawler, 1990) when the \( b \) values were in the range 1.05-1.11. The relative densities of the deposits, as calculated by Boller and Kavanaugh (based on their model fit) for deposits of different particles were as follows: \( \sim 0.68 \) for 6.5 \( \mu \)m latex, \( \sim 0.55 \) for 2.1 \( \mu \)m latex, \( \sim 0.35 - 0.4 \) for TiO\(_2\), \( \sim 0.2 \) for kaolin, \( \sim 0.1 \) for ferric hydroxides.

Arshad, Rahman, and Rahman (1993) and Husein, Rahman, and Rahman (1992) conducted experiments to measure head loss development in a microcapillary, by recirculating bentonite suspension. Experiments were performed with two capillaries of diameters 34.37 \( \mu \)m and 100 \( \mu \)m. They observed that at constant velocity, increased particle concentration resulted in increased pressure drop. At constant particle concentration, an increase in velocity resulted in an
increase in pressure drop. For experiments with a smaller capillary, a sudden increase in pressure drop at a high concentration (1000 ppm) and low velocity (0.0017 m/s) occurred at 225 hours, while for the same concentration but at higher velocity (0.0033 m/s), plugging occurred at 100 hours. They suggested that at high flow rates, increase shear caused aggregation of the particles; flocs thus formed clogged the capillary. Also at high concentrations, the probability of particles coming in to contact with each other is increased, causing aggregation and eventually plugging of the capillary. Based on experiments with larger micro-capillary (particle concentration = 1000 ppm), they identified two distinct deposition characteristics. At low velocities ($V < 1.4 \times 10^{-3}$ m/s) an equilibrium condition is reached with head loss remaining constant with time. At and above a critical velocity of $1.4 \times 10^{-3}$ m/s, the pressure drop first increased linearly and then sharply over time. They attempted to predict head loss based on trajectory analysis for particle deposition and found only qualitative agreement with experimental data.

2.6.3 Structure of Simulated Deposits

Several investigators have performed Monte-Carlo simulations of the colloidal deposition processes to study the structure of deposits formed between the two limiting cases (diffusion-limited and ballistic deposition). In this section, a brief review of this work is given.

Houi and Lenormand (1984, 1986) studied the properties of deposits formed under the combined effect of ballistic displacement (i.e., drag by the fluid flow) and diffusive (Brownian) motion through computer simulations. These
mechanisms are superposed, such that the resultant particle movement can be described in terms of a Peclet number (defined as the ratio between convective and diffusive displacement). The substrate was composed of a row of equidistant cylinders. Particle deposition on previously retained particles was deemed stable only when the angle between the line of centers of the particles and the direction of flow (sticking angle) satisfied a set of (rather arbitrary) sticking rules. The fractal dimensions of the deposits remained constant at 1.80 for Peclet numbers below $10^{-3}$ and gradually increases to a value of 2 for Peclet numbers greater than $10^{-1}$. For ballistic-dominated deposition, their simulations indicated that the density of the deposit increased with stricter adhesion rules (lower probability of adhesion), though the fractal dimension of the deposit remained unchanged. They conclude that the capture mechanism has no influence on the heterogeneity of the particle agglomeration (i.e., on fractal dimension), though the porosity and permeability of the deposit is sensitive to the sticking angle.

Tassopoulos, O'Brien, and Rosner (1989) developed a discrete stochastic model to simulate particulate deposition processes. Particle motion was determined by the superposition of a deterministic force acting towards the surface of the collector and a random (Brownian) force. They characterized the resulting deposit microstructure in terms of porosity, pore size/area distribution and surface area and their evolution over time. The effect of particle polydispersivity, spatial orientation for non-spherical particles, and mean-free path on the deposit structure was also studied. The particle movement was characterized by a Peclet number, defined as the ratio of a characteristic time for diffusion to a characteristic time for convection. Their results indicated that the
mean height of the deposit is independent of the $N_{Pe}$ for $N_{Pe} > 10$. After a
transition zone in the region $2 < N_{Pe} < 10$, the mean deposit height exhibits a
power-law dependence for $N_{Pe} < 2$ given by $\bar{h} \sim N_{Pe}^{-0.267 \pm 0.04}$ for 2-dimensions
and $\bar{h} \sim N_{Pe}^{-0.475 \pm 0.05}$ for 3-dimensions. Likewise, the active zone width shows a
strong power-law dependence for $N_{Pe} < 2$ given by $\xi \sim N_{Pe}^{-0.523 \pm 0.05}$ for 2-
dimensions and $\xi \sim N_{Pe}^{-0.756 \pm 0.04}$ for 3-dimensions. They also expressed the
dependence of the pore number on pore size for a deposit as
$N_L(\text{pore size}) = (\text{pore size})^k$ and found that $k$ varies (for deposits in 2-
dimensions) from $k = -2.72 \pm 0.05$ for $N_{Pe} = \infty$ to $k = -3.54 \pm 0.06$ for
$N_{Pe} = 0.4$. For $N_{Pe} < 0.4$, the deposits were very open with small number of
pores, requiring larger scale simulations to obtain statistically significant results.

Schmitz and Houi (1991) and Schmitz, Wandelt, Houi et al. (1993)
performed Monte-Carlo simulations to study the morphology of deposits formed
by non-Brownian spherical colloids on a membrane surface (a flat surface with
rectangular pores) in crossflow microfiltration. They defined a set of empirical
rules that govern the motion and adhesion of particles. The particles were
released randomly, one at a time, from a line normal to the membrane at an
incidence angle (measured from the membrane surface), which was a measure
of the ratio of the radial suction flow to the tangential shear flow near the
membrane surface. After being released, the particle followed a linear trajectory
(defined by the incidence angle) until it made a contact either with the membrane
surface or with previously deposited particles. Based on some empirical rules,
the particle either deposits on first contact or moves further to find another
location that satisfies a given set of adhesion rules. Deposition was declared
successful if the line joining the centers of the suspended and deposited particles
is inside the sector defined by a sticking angle. If not, the particle rolls either left or right on the particle it made contact with and either attains a vertical downward movement or reattains its original incident trajectory, based on another parameter called "number of reentrainments". Their simulations indicated that the deposits formed at low adhesion angles (flow entrainment is more prevalent) lead to very compact structures compared to those formed at high adhesion angles (attractive forces are more prevalent). They also observed that when a higher number of reentrainment steps are allowed, more compact deposits were formed. The porosity of the deposits formed under different adhesion angles attained the same asymptotic value after three steps of reentrainment. They also reported that all the deposits formed from particles which followed their motion and adhesion rules were statistically homogeneous (i.e., had similar fractal dimensions). They calibrated their model with experimental observations and suggested approximate ranges of various model parameters for different physical parameters.

Giona and Patierno (1993) reported results from Monte Carlo simulations of particle deposits and characterized their bulk, surface and topological properties in terms of two parameters, Peclet number and occupation probability, $f_m$. The Peclet number is related to the diffusive and ballistic motion in a way similar to that of Tassopoulos (1989). The occupation probability $f_m$ represents the ratio of the concentration of suspended particles to the maximum possible concentration in suspension. A value of 0 for $f_m$ would indicate that at any given time, only one particle is in motion and the next particle is released only after the deposition of the previously launched particle. As with previous studies, increases in the Peclet number resulted in more compact deposits. At low Peclet
numbers, the density of the deposit was sensitive to $f_m$. Higher values of $f_m$ resulted in higher densities, with the fractal dimension approaching the Euclidean dimension. For low $N_{Pe}$ and $f_m=0$, the fractal dimension of the deposit was found to be 1.70. However, for high values of $N_{Pe}$, the influence of $f_m$ was negligible, and aggregates attain a density of 0.8 irrespective of $N_{Pe}$. They observed that the deposits are highly porous for $N_{Pe} > 0$, and the pore-size distribution $n_p(A)$ is related to the pore area $A$ (number of empty sites forming a pore) through the power law,

$$n_p(A) \sim A^{\gamma_p} \quad (2.6.5)$$

Deposits formed with $N_{Pe} > 0$ and $f_m$ ranging between 0 and 1, $\gamma_p$ was in the range of 1.4-1.6, and was found to be independent of $N_{Pe}$ and $f_m$. They also reported that the length of the surface of the deposit ($L(\epsilon)$) scaled with the diameter $\epsilon$ of the yardstick covering it as:

$$L(\epsilon) = \Lambda_o \epsilon^{1-D_\sigma} \quad (2.6.6)$$

where $D_\sigma$ is the fractal dimension of the surface. The fractal dimension of the surface was found to be 1.35±0.08 for all values of $N_{Pe}$ and $f_m$. However, the maximal external length $\Lambda_o$ (corresponds to the length measured with a yardstick of one lattice site) scaled with $N_{Pe}$ as $\Lambda_o \sim N_{Pe}^{-\eta}$ for $N_{Pe} < 10$. The exponent $\eta$ depends on $f_m$ for low values of $f_m$ and tends to zero for high values of $f_m$. They also observed that $\Lambda_o$ is linearly related to height of the deposit ($\Lambda_o \sim h$) for low $f_m$, while a power law behavior, ($\Lambda_o \sim h^v$), is observed with increasing $f_m$, with $v = 1$ for $f_m = 0$ and $v = 0$ for $f_m = 1$. 
CHAPTER 3
MATERIALS AND EXPERIMENTAL METHODS

In this chapter, a detailed description of experimental materials and methods employed to study the morphology of colloidal deposits in porous beds formed under different physical conditions is given. The experimental design was chosen to closely approximate the assumptions commonly made in modeling filtration processes. Near-spherical and uniform porous media composed of glass beads was employed to filter spherical monodispersed latex particles under favorable chemical conditions. A steady and nearly pulse-free flow was provided. The influent and effluent concentrations as well as the head loss across the bed were monitored. The fractal dimension of the deposits formed in the bed were measured using static light scattering measurements.

3.1 Materials

3.1.1 Filter Media

Near-spherical glass beads of sizes between 40 to 50 U.S. Standard Sieves were used as filter media. Glass beads were obtained from the Potters Industries Inc., Hasbrouck Heights, New Jersey. Characteristics of these glass beads as reported by the manufacturer are listed in Table 3.1. Beads received from the manufacturer were sieved through U.S. Sieves 40 (425 μm sieve opening) and 50 (297 μm sieve opening) and those retained on U.S. Standard Sieve 50 were used in the experiments.
Table 3.1
Characteristics of Glass Beads

Typical Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.5</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.51-1.52</td>
</tr>
<tr>
<td>Coefficient of Friction (static)</td>
<td>0.9-1.0</td>
</tr>
<tr>
<td>% mass within mesh sizes 40-50</td>
<td>90</td>
</tr>
</tbody>
</table>

Chemical Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>72.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.4</td>
</tr>
<tr>
<td>CaO</td>
<td>9.8</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13.7</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Electrical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant 1 Kc</td>
<td>7.6</td>
</tr>
<tr>
<td>D.C. Volume Resistivity (Ohm-Cm) 25°C</td>
<td>6.5 × 10¹²</td>
</tr>
<tr>
<td>Loss Tangent 1 KC</td>
<td>2.0%</td>
</tr>
<tr>
<td>100 kC</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

The glass beads were cleaned using the following procedure outlined by Tobiason (1987):

1. A volume of 500-750 cm³ of beads were placed in a two-liter pyrex beaker and rinsed with de-ionized (D.I.) water about 5-7 times until turbidity of supernatant was found to be constant.

2. The beads were then sonicated using an ultrasonicator (model 8890, Cole Parmer Instrument Co., Chicago, IL) for about 10 minutes in 0.01 M NaOH solution and then rinsed with D.I. water 12 times.
3. Step 2 was repeated with 1 M HNO₃ solution.

4. Step 2 and step 3 were repeated again until the turbidity of the supernatant was very low.

5. Beads were dried overnight at 70 to 80 °C and then stored in sealed 500 cm³ nalgene bottles.

   The size distribution of the cleaned glass beads was determined gravimetrically using an automated sediment analysis system (Rice University Automated Sediment Analyzer (RUASA), Anderson and Kurtz, 1979). A sample is introduced into a large settling tube fitted with a weight sensing transducer at the bottom. The size and settling velocity distributions of the particles are obtained by summing the weight (output as voltage from the transducer) acquired during designated time intervals, which correspond to 0.25 φ grain size classes derived from Gibb’s formula (Gibbs, Matthews, and Link, 1971). The gravimetrical analysis reveals the glass beads to be relatively uniform in size with a mean diameter (volume weighted) of 358±38 μm and a dominant mode of 366 μm (Figure 3.1).
3.1.2 Suspended Particles

Suspensions of monodisperse latex particles were used in these experiments. A detailed description of the preparation of these particles is given by (Bangs, 1987). The latex particles smaller than 4 μm used in these experiments were produced by emulsion polymerization, while particles larger than 4 μm were produced by suspension polymerization. In emulsion polymerization, micelles of a surfactant such as sodium dodecyl sulfate are
initially formed and are swollen by addition of a monomeric hydrocarbon such as styrene. Addition of a water-soluble polymerization initiator, such as potassium persulfate and heating results in sulfate ion free-radicals. Each of these radical ions reacts with a styrene molecule forming a new sulfate ion/styrene free-radical, which in turn reacts with another styrene molecule, etc. resulting in oligomers or short polymer chains of styrene with a sulfate ion on one end. Each sulfate ion free-radical will initiate a polystyrene chain and polymerization will continue until all the unreacted styrene is scavenged or the free-radical reacts with another free-radical. Upon completion of this polymerization step, each polymer chain will have a sulfate ion on both ends and the chains will occupy the space formerly occupied by monomer in the swollen micelles. This one-step polymerization is used for particles smaller than 0.4 μm particles. For larger particles, more monomer and initiator are added to perform a second or "build-up" polymerization. Some particles are produced by using several different co-monomers such as acrylic acid (carboxylate-modified latex) and acrylamide (amide modified latex) with styrene. These monomers are more hydrophilic than styrene. In suspension polymerization process, which is used to produce particles of size 4 to 90 μm, a colloidal suspending agent such as colloidal silica is used in place of surfactant. By vigorously agitating the monomer or co-monomer mixture in water with colloidal agent, the monomer droplets can be coated with negatively charged colloidal particles, which stabilizes the droplets during and after polymerization. Continued agitation results in smaller particles, which require more colloidal particles to stabilize. In the absence of adequate colloidal material, the drops coalesce until a the exposed oil/water interface matches the available colloidal material. Finally, an oil-soluble polymerization initiator such as benzol peroxide is added to complete the process. Latex
particles used in this work were obtained from Seradyn inc., Indianapolis, IN.

Characteristics of the latex particles used in this work are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>0.038</th>
<th>0.069</th>
<th>0.044</th>
<th>0.09</th>
<th>0.944</th>
<th>7.6</th>
<th>10.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Deviation (μm)</td>
<td>0.0075</td>
<td>0.0035</td>
<td>0.003</td>
<td>0.0086</td>
<td>0.013</td>
<td>n/a</td>
<td>0.0908</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Refractive Index @589 nm</td>
<td>1.5905</td>
<td>1.5905</td>
<td>1.5905</td>
<td>1.5905</td>
<td>1.5905</td>
<td>1.5808 @ 589 nm</td>
<td>1.5808 @ 589 nm</td>
</tr>
<tr>
<td>Monomer</td>
<td>CML</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>PS</td>
<td>PS/DVB (2%)</td>
<td>S/DVB (2%)</td>
</tr>
<tr>
<td>Surface Groups</td>
<td>sulfate and carboxylate</td>
<td>sulfate</td>
<td>sulfate</td>
<td>sulfate</td>
<td>sulfate</td>
<td>colloidal silica</td>
<td>colloidal silica</td>
</tr>
</tbody>
</table>

CML = Carboxylate modified latex
S = Styrene
PS = Polystyrene
DVB = divinylbenzene
EP = Emulsion polymerization
SP = Suspension polymerization

### 3.1.3 Feed Solution

The glass beads (which make up the filter media) and the latex particles are negatively charged. To facilitate deposition of latex particles on to the glass beads, the latex particles need to be destabilized. Calcium nitrate was selected
as the destabilizing agent for several reasons. Addition of calcium nitrate increases the ionic strength of the solution which results in the double-layer compression of the latex particles. In addition to double-layer compression, it has been reported in the literature that calcium ions interact in some manner with the latex surface to further destabilize the particles. In Figure 3.2, the effects of the concentration of the $\text{Ca(NO}_3\text{)}_2$ on the zeta potential of the 0.944 $\mu$m latex particles at constant ionic strength is shown. The ionic strength has been adjusted using $\text{NaNO}_3$. These results indicate that $\text{Ca}^{2+}$ interacts with latex particles in some specific manner, thereby enhancing the destabilization of the latex particles. Tobiason and O'Melia (1988) discussed the possible mechanisms. They suggest that the mechanism could be a specific chemical interaction of $\text{Ca}^{2+}$ with the sulfate groups on the latex surface, or that $\text{Ca}^{2+}$ is electrostatically attracted in a fixed, or Stern layer of ions adjacent to the surface. They also report that calcium is more effective at reducing zeta potential as the pH is increased from 5 to 7. However, they postulate that the specific interaction is very weak and hence the possibility of restabilization or a positive zeta potential is not possible even at $\text{Ca}^{2+}$ concentration of 0.1 M. All the experiments were performed using 0.1 M calcium nitrate as the destabilizing agent. To obtain a pH in the range of 6.6 - 7.0, $5 \times 10^{-5}$ M $\text{NaHCO}_3$ was added to the feed solution.
Figure 3.2: Effect of Calcium on the zeta potential of 0.944 μm particles

3.1.4 Experimental Set Up

A constant and nearly pulse-free flow through the filter bed was provided by a magnetic-drive gear pump (Ismatic variable speed pump drive: Catalog number 07617-70; micropump pump heads: N-07002-25 and N-07002-27; Cole Parmer Instrument Co., Chicago, IL). The drive with various combinations of pump heads is capable of providing a flow of 1 to 4000 cm³/min. A 13 L Pyrex glass jar was used as a supply tank. The feed solution in the tank was mixed using a magnetic stirrer and a teflon coated stir bar. A rotometer was used to monitor
flow rate (Cole Parmer Instrument Co., Chicago, IL; Catalog number N-03226-10). A syringe pump (Harward Apparatus, Inc., South Natick, MA 01760; Catalog number 55-2222) was used to inject the latex particles into the main flow just above the column. The tube from the syringe pump was inserted into the main flow just above the column, in such a way that the latex particles were injected against the main flow, thereby providing a good mixing. In addition, turbulence was created by using an in-line turbulence promoter just above the injection point of the latex particles. A schematic of the experimental set up is illustrated in Figure 3.3. A cylindrical plexiglass column was used as the deposition column. The diameter of the column was selected to ensure that the ratio of the column diameter to the media grain diameter is greater than 50 to minimize wall effects. The column was fabricated from a 2.5 cm inside diameter cast plexiglass tube at an on-campus machine shop. A schematic of the column used in the experiments is shown in Figure 3.4. The ratio of the column diameter to the average media grain diameter is ~70.
Figure 3.3: Schematic of Experimental Set Up
3.2 Experimental Methods

3.2.1 Particle Concentration Measurement

Submicron Particle Concentration Measurement:

The influent and effluent concentrations of submicron latex particles were measured using Hitachi U-2000 Double-Beam UV/Vis spectrophotometer. The instrument has a wavelength range of 190 to 1100 nm, with an accuracy of ±0.4
nm and ±0.2 nm wavelength setting reproducibility. Light source is provided by deuterium lamp and tungsten iodide lamp. Photometric accuracy and reproducibility are within ±0.002 Abs. In Figure 3.5, the spectrum of absorbance of three sub-micron latex particles as a function of wavelength is shown.

![Absorbance of UV/visible light by submicron latex particles at different wavelengths](image)

**Figure 3.5:** Absorbance of UV/visible light by submicron latex particles at different wavelengths

All the three particles exhibit a steep decline in absorbance with wavelength in the range of 190 - 240 nm. At around 250 nm, the absorbance is not very sensitive to the wavelength. A wavelength of 262 nm was selected to measure the absorbance of the latex particles. The absorbance of the latex
particles at this wavelength is assumed to be linearly related to the concentration. In Figure 3.6, the absorbance of 69 nm particles at 262 nm wavelength for different concentrations is shown. A good linear relationship is evident.

![Graph showing linear relationship between Latex (69 nm) Concentration and Absorbance at 262 nm. The equation y = 1.0107 + 38.942x with R^2 = 0.991 is shown.]

Figure 3.6: UV light (@262 nm wavelength) absorbance by 69 nm particles at different concentrations

**Supramicron Particle Concentration Measurement:**

The number and size of particles larger than approximately 0.5 μm were measured using an electronic sensing zone (ESZ) type particle counter (Coulter Multisizer, Coulter Electronics Limited, Luton, England). A suspension of
particles in an electrically conductive liquid is forced to flow through a small aperture. On either side of the aperture, there are immersed electrodes to which a constant potential is applied. As a particle passes through the aperture, it changes the resistance between the electrodes producing a voltage pulse of short duration with a magnitude proportional to particle size. Pulses are electronically scaled and counted. The voltage pulses are amplified and fed to a threshold circuit having an adjustable threshold level. If this level is reached or exceeded by a pulse, the pulse is counted. By taking a series of counts at selected threshold levels, data is directly obtained for plotting cumulated frequency (larger than stated size) versus particle size. Integration of all or part of the resultant curve provides a measure of the particle count of the suspension. The pulse height and instrument response are proportional to particle volume and to fluid resistivity. The particle resistivity has very little effect on the response until it is quite close to the resistivity of the fluid. However, the principle does not permit significant discernment of particle shape and results are expressed in spherical equivalents. There is also the probability of multiple passages (of doublets, triplets, etc.). Hence particle concentrations should be such that the probability of such "coincident error" is less than 10%. Accuracy of this method is limited to particles having diameters between 2% and 50% of the orifice diameter. For this reason measurements using several orifices may be necessary to determine the particle size distribution of suspensions containing particles that differ considerably in size.

A 19 µm aperture and a 2% NaCl electrolyte solution (by weight) were used for particle measurements in this work. To obtain a particle-free solution, the NaCl solution was filtered in a closed loop through a 0.22 µm membrane.
3.2.2 Head Loss Measurement

Pressure was continuously monitored through three sampling ports. Two ports were located just above and below the bed while one was located at 0.5 cm below the top surface of the bed. Pressure transducers (IC Sensors, Milpitas, California; model 104-005G) were attached to each port using a tube adapter and a male pipe connector. A teflon screen was inserted between the male pipe connector and tube adapter to prevent flow of glass beads into the pressure transducer.

The pressure transducers have a silicon sensing element, which is an integrated circuit silicon chip with a micromachined diaphragm. Four piezo-resistive strain gage resistors are incorporated into the diaphragm to form a fully active wheatstone bridge. The silicon diaphragm deflects upon application of pressure which results in an electrical output that is proportional to the input pressure. Temperature compensation is provided over the range of 0-50 °C. The accuracy (including linearity, hysteresis and repeatability) is 0.25% of full span. A constant excitation voltage was supplied to the transducers. The transducers give an output signal of 1-6 V in linear relation to the applied pressure.

The analog signal from the transducers was converted to a digital signal using MacPacq hardware (Biopac Systems, Goleta, CA 93117). A software package, PacqManager (Biopac Systems, Goleta, CA 93117) was used to record all data on to a Macintosh SE computer (Apple Computer Inc.). The MacPacq
can sample at rates between 2 samples/hr and 10,000 samples/sec. Data from multiple channels can be acquired simultaneously.

A schematic of the pressure monitoring system is shown in Figure 3.3. To calibrate the transducers, the transducers were connected to an outlet at the bottom of the long column and the output voltage was measured over varying head of water. A plot of the measured voltage against applied pressure is shown in Figure 3.7. The output signal was found to be linearly related to the applied pressure.

![Graph showing linear relationship between water pressure and pressure transducer output](image)

**Figure 3.7: Calibration of pressure transducer**

\[ y = 1.2188 + 0.99069x \quad R^2 = 1.000 \]

Excitation Voltage = 20 V
Zero Voltage Offset = 0.216 V
3.2.3 Measurement of Fractal Dimension of Deposits

Static light scattering experiments were performed to measure the fractal dimensions of the deposits. A Malvern 4700c system comprising of a variable angle light scattering spectrometer (PCS100) interfaced to a K7032 computer correlator was used. The goniometer of the PCS100 allows the photomultiplier detector to be set to any scattering angle between 10 and 150 degrees with respect to the incident laser beam within an accuracy of 0.01 degree. The light source is provided by a vertically polarized (i.e., perpendicular to the scattering plane) Helium-Neon laser (wavelength = 632.8 nm) of 30 mW (Siemens Model LGK7626S) operating in a single mode (TEM $\infty$). The laser beam passes through a focusing lens bringing it to a "waist of focus" at the center of rotation of the goniometer system. The sample is placed in a PCS10 Burchard cells at the center of the goniometer, immersed in a vat of clean water that serves to couple the thermostat system to the sample. The temperature in the vat is maintained at the value set by the user within an accuracy of 0.1 degree. The Stepping Motor Control of the goniometer allows measurement of scattered light intensity over a range of angles at fixed intervals. At each angle the intensity is recorded for the length of time specified by the user and translated via the optical normalization (which corrects for the changing in viewing volume in the cell as a function of angle) required to a relative intensity value.

The alignment of the instrument was verified by measuring the intensity of light scattered by Toulene at different angles. The scattered light intensity, normalized by the average value is plotted as a function of angle in Figure 3.8.
As expected from Rayleigh scatterers, the deviation was < 1% for most of the range.

![Figure 3.8: Light scattered by Toulene at different angles](image)

Before introducing the sample cuvette, the vat was filled with DI water using a syringe fitted with a 0.22 μm syringe filter. The sample cuvette was then introduced into the vat and intensity of the scattered light was measured at different angles. For deposits composed of 44 nm and 69 nm particles, scattered intensity was measured over an angular range of 10° to 150°, while for 90 nm
particles, the angular range was limited to 10° to 110° to satisfy the limitation of qa << 1.

A simple diffusion limited aggregation experiment was performed to verify the ability to measure fractal dimensions. A dilute suspension (50 cm$^3$) of 0.069 µm particles was prepared in a beaker. A 50 ml solution of 0.2 M Ca(NO$_3$)$_2$·4H$_2$O was prepared in another beaker. The two solutions were then mixed in a 250 cm$^3$ Erlenmeyer flask. The mixture in the flask was then gently swirled for approximately 10 seconds, at a rate of about 1 rotation per second. The solution was then poured into the sampling cuvette. The cuvette was then placed in the PCS and light scattering at different angles was measured at regular intervals. Within few minutes, the slope of log(I) vs. log(q) curve reached a constant value. The scattered light intensity was then measured five times at several angles subsequently. In Figure 3.9, the average value of the logarithm of the scattered light intensity at different log(q) values is plotted, along with the standard deviations. The fitted line shows a linear regression of the data. The slope indicates that the fractal dimension of the deposits to be 1.67±0.02. This value is close to the value reported in the literature for diffusion limited aggregates.
Figure 3.9: Double logarithmic plot of intensity (in arbitrary units) against scattering vector, $q$

3.2.4 Typical Experimental Procedure

Deionized water from a Milli-Q water system was used in all the experiments. The Milli-Q water system (CDO F01205; Millipore Corporation, Bedford, MA 01730) consists of a carbon column, two ion exchange columns, one organex column and a 0.22 μm membrane filter. Milli-Q water used in these experiments was degassed by boiling and then cooling in a closed container overnight.
Based on the estimated porosity and the depth of bed needed, the required mass of glass beads needed was weighed. The glass beads were then soaked in feed solution overnight. Just before the beginning of the experiment, the glass beads were rinsed several times with the feed solution. The column was filled to half its height with feed water and the bottom of the column was filled with 6 mm diameter glass beads up to the lower pressure port. The same number of the 6 mm diameter glass beads were used in all the experiments. A Spectra/Mesh screen of Teflon (Cole-Parmer Instrument Company, Chicago, IL 60648) of pore size 297 μm and thickness of 410 μm was used to separate the large support glass beads (6 mm) from the smaller filter media. The small glass beads were dropped into the column using a funnel and spoon and the column was constantly tapped to ensure proper packing.

Measurements of head loss versus flow rate through the glass beads were obtained using particle-free water. Pressure transducer readings were taken over varying flow rates and compared with predictions based on the Kozeny-Carman model (Equations 2.5.35 and 2.5.37) for head loss through the porous bed. A typical plot of these data and calculations are shown in Figure 3.10.
Figure 3.10: Head loss across the packed bed as function of flow rate

Experimental results agreed well with predictions from the Kozeny-Carman equation using a value of 5 for the empirical constant $K$. Conformity to the Kozeny-Carman equation was used as a check on the preparation of the filter column before each experiment.

Two syringes (Monoject®, polypropylene, 140 ml) were thoroughly cleaned with soap and rinsed with DI water. They were then loaded with the latex solution and a small stir bar was placed inside the syringes for stirring the latex suspension during the course of the experiment. The syringes were
mounted on the syringe pump and the pump was set to the flow rate required for a desired latex concentration in the main flow. Feed to the filter was directed away from the column using a 3-way valve and the syringe pump was switched on. After about 10 minutes, several samples were taken and the influent particle concentration was measured to verify that the desired concentration of particles in the feed was obtained. The data acquisition system for monitoring pressure was then initiated and the flow was redirected to the filter column. Effluent samples were collected at appropriate intervals and the particle concentrations were measured. The frequency of sampling varied with the flow rate of the experiment. With few exceptions, samples were analyzed within a couple of minutes of collection.

At the end of the experiment, the feed pump and the syringe pump were turned off and the effluent valve on the filter column was closed. The flexible tube connecting the pressure transducers to the sampling ports was clamped and the pressure transducers were disconnected. The influent tube was then disconnected from the filter column and the top of the column was then removed by unscrewing the six screws. The solution in the head space contains some particles, which may aggregate to form small clusters. This solution was gently removed using a syringe. A protein solution of 12 g/l concentration was then gently added to the column along the walls of the column using a syringe fitted with a series of filters (1.2 μm, 0.8 μm, 0.45 μm and 0.22 μm in pore size). After filling up the head space, the effluent valve was opened and as the protein solution dripped out of the column under gravity, more was added at the top. After passing approximately 100 cm$^3$ of the protein solution through the column, the effluent valve was closed for one hour. At the end of one hour, the same
procedure was repeated with 10% solution of formaldehyde. After soaking the media and deposits with formaldehyde for one hour. A solution of similar chemistry was made in a beaker and the column was gently tilted into the beaker until the filter media gently slid into the beaker. Before attempting this, it is made sure that the head space in the column is filled with the solution and the while tilting the column into the beaker, care is taken to ensure that the packed column is always in contact with the solution. In most cases, the packed bed moved as a solid body, and as it settled into the beaker, it split up, with the glass beads settling to the bottom of the beaker and the deposits broke loose and were suspended in the solution. The deposits were then transferred into the Burchard cell and the light scattering experiments were performed. For light scattering experiments, relatively small volumes of sample is sufficient. For almost all the experiments, light scattering measurements were performed on at least 5 samples from each experiment and static light measurements on each sample were performed at least 5 times. During the earlier experiment, it was observed that during light scattering measurements, settling of the deposits was significant. The light scattering instrument available had a goniometer equipped with a stepping motor control. Scattered light was measured over a range of 15° to 150° angle at fixed intervals. By the time the goniometer could traverse this range, significant settling of the deposits was observed. To circumvent this problem, it was decided to use a solution of higher density as the suspending medium for the deposit. Hence, for later experiments the procedure was modified as follows. After soaking the deposit with formaldehyde for one hour, the same procedure as was done with protein and formaldehyde solutions was repeated with a 32.2% by weight glycerol solution. This concentration of glycerol
solution was found, by trial and error, to be ideal to avoid any significant settling during light scattering measurements.
CHAPTER 4
NUMERICAL SIMULATIONS

In this chapter, results from particle deposition simulations are presented. Results from Monte-Carlo simulations (lattice model) of colloid deposition on one-dimensional permeable surface in uniform flow field are presented in section 4.1. Results from simulations of particle deposition in plane stagnation flow onto an impermeable surface are presented in section 4.2.

4.1 Morphology of Colloidal Deposits on an Infinitely Permeable Membrane

In this section, Monte Carlo simulations of colloid deposition on a one-dimensional permeable surface from a uniform flow field are presented and discussed. The relationship between mechanisms of particle transport and deposit morphology is explored. The effects of particle size, fluid velocity, and particle density on the fractal dimension of colloidal deposits are described in terms of a Peclet number relating fluid drag, gravity settling, and Brownian motion.

4.1.1 Deposition Algorithm

Monte Carlo simulations of colloid deposition on a one-dimensional permeable surface from a uniform flow field were performed. The deposition algorithm used in this work shares many features of lattice models reported by previous investigators to describe deposition from a monodispersed
suspension (Meakin, 1983b; Meakin, Ramanlal, Sander et al., 1986b; Racz and Vicsek, 1983). The simulation lattice and several other features of the model are shown in Figure 4.1.1. A square lattice was employed. The substrate is assumed to be an infinitely permeable surface and is defined by a line of growth sites (i.e., a row of occupied sites). In the Monte Carlo simulations, particles are released, one at a time, from random lattice sites on a "release line", which is set 10 units above the original substrate line or the highest deposited particle, whichever is higher. Once released, the particle is allowed to move in any of eight directions corresponding to the lattice sites nearest to the particle (Figure 4.1.1)
Figure 4.1.1: Schematic representation of particle deposition as described in simulations

In this work, the probability of particle motion in any given direction is calculated from physical-chemical parameters of the system such as fluid velocity and particle size, as explained later in this section. A particle is considered to be deposited if, in moving from one lattice site to another, there is a single contact between lattice corners or a single side of the depositing particle and occupied lattice site. Occupied lattice sites may include the original growth sites or a previously deposited particle. A sticking probability of one is used in all the simulations, i.e., if the particle is in the immediate vicinity of one of the original growth sites, or a previously deposited particle, it is fixed at that position and a new particle is released. If a particle strays outside the
simulation grid, in a direction parallel to the substrate, it is reflected back into the simulation grid. If a particle migrates too far from the substrate (beyond the "kill line", which is set 110 units above the release line), it is discarded from the simulation and a new particle is released. This procedure is repeated until the desired number of particles has been deposited. Restructuring of the deposit is not considered in these simulations.

The simulation grid is normalized to the size of the smallest particle. Hence, in deposition experiments involving monodisperse suspensions, each particle, being one grid-length in diameter, occupies an area centered at a grid point. For polydisperse suspensions, the smallest particle occupies one grid lattice and larger particles occupy an $n \times n$ lattice surface area, where $n$ is the ratio of the larger particle’s diameter to that of the smallest particle in the simulation. The movement of the larger particles in a polydisperse experiment is tracked by the movement of the lower left corner of the $n \times n$ grid the particle occupies. If particles of different sizes are being deposited, the probability that a new particle to be released is of a given size is calculated from the relative concentrations of particles in a specified suspension.

Particle movement on the simulation lattice has been related quantitatively to physical-chemical characteristics of the system, including particle size, particle density, temperature, fluid viscosity and the velocity of the flow field. However, forces such as hydrodynamic retardation, London-van der Waals and double layer interactions are not considered. For the purpose of calculating particle transport, particles are assumed to be spherical and thus are depicted as such in Figure 4.1.1. The probability of a particle moving in a
given direction is calculated by superimposing the effects of fluid drag, Brownian motion and gravity. Gravity and fluid drag (in a downward uniform flow field) are assumed to act orthogonally to the deposition surface (Figure 4.1.1). Therefore, deviations in particle trajectory from a downward vertical direction are due to Brownian motion alone. A dimensionless Peclet-like quantity, $N_{Pe}$, describing the ratio of ballistic movement (gravity and fluid velocity) to diffusive movement can be used to characterize the probability that a particle moves in any given direction:

$$N_{Pe} = \left( v_g + v_f \right)/v_d \quad (4.1.1)$$

where,

$$v_g = \left( \frac{1}{48} \right) a_p^2 g \left( \rho_p - \rho_f \right)/\mu \quad \text{(Settling velocity)} \quad (4.1.1a)$$

$$v_d = \left( kT \right)/\left( 3\pi \mu a_p^2 \right) \quad \text{(Diffusive velocity)} \quad (4.1.1b)$$

$v_f$ = fluid velocity
$d_p$ = diameter of the particle of equivalent projected surface area as the $n \times n$ grid points the particle occupies
$g$ = acceleration due to gravity
$\rho_p, \rho_f$ = density of particle and fluid respectively
$k$ = Boltzmann constant
$T$ = temperature
$\mu$ = fluid viscosity

At any given time step in a simulation, the probabilities of a particle moving in any one of the 8 directions on the lattice must sum to 1. The probability of a particle moving vertically downward, $P(1)$ and the probability of moving in any one of the remaining directions, can therefore be expressed as:
\[
P(1) = \frac{1 + N_{Pe}}{8 + N_{Pe}} \quad (4.1.2a)
\]
\[
P(i) = \frac{1}{8 + N_{Pe}} \quad i = 2, 3, \ldots, 8. \quad (4.1.2b)
\]

The physical parameters used in these simulations are listed in Table 4.1. For very small particles, particle motion is dominated by Brownian diffusion, while for large particles, fluid drag and gravity result in a more ballistic trajectory towards the collector surface. The numerical experiments reported in this paper span a continuum from the diffusion-limited deposition models for small particles to the ballistic-deposition models for larger particles. The deposits were grown on a substrate of length 4000 units. The number of deposited particles in the simulations varied from \(5 \times 10^4\) to \(1.5 \times 10^5\), the criterion being that the deposit height should be at least 130 units. All the deposition experiments reported in this work were simulated on a CONVEX C240 supercomputer. Approximately 262 minutes of CPU time were required to simulate the deposition of 50000 particles of 0.001 \(\mu\)m on a substrate of length 4000 units.

<table>
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<th>Parameter</th>
<th>Value</th>
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<tbody>
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<td>Density of particles, (\rho_p)</td>
<td>1.05 g/cm(^3)</td>
</tr>
<tr>
<td>Density of the fluid, (\rho_f)</td>
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</tr>
<tr>
<td>Viscosity of the fluid, (\mu)</td>
<td>(8.949 \times 10^{-3}) g/cm–sec</td>
</tr>
<tr>
<td>Temperature, (T)</td>
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</tr>
<tr>
<td>Fluid velocity, (v_f)</td>
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</tr>
</tbody>
</table>
4.1.2 Calculation of the Fractal Dimension of Simulated Deposits

The morphology of colloidal deposits may be poorly defined within the scope of Euclidean geometry. However, after a sufficient number of particles has been deposited, it may be possible to describe these structures in terms of a non-integer or fractal dimension, $D$, which is equal to or less than the Euclidean dimension, $d$, of the space in which the structure is embedded (Mandelbrot, 1975).

The fractal dimensions of deposits grown by applying the algorithm described here can be calculated from the upper surface properties. The upper surface of a deposit is defined as the surface an observer would see when looking straight down at the deposit, i.e., the contour of the highest occupied lattices along the length of the substrate. It is observed that the mean surface height, $\bar{h}$, and $N$, the number of particles deposited, are related in a limit of $N$ tending to be infinity, by,

$$\bar{h} \sim N^\phi$$  \hspace{1cm} (4.1.3)

The fractal dimension is obtained by the relation: $D = d - 1 + 1/\phi$ (Meakin, 1984b), where $d$ is the smallest Euclidean dimension of the space the fractal is embedded in. A fractal dimension of 2 would indicate a Euclidean object with isotropic density, while values less than 2 would indicate the fractal nature of the object. In Figure 4.1.2, dependence of $\ln(\bar{h})$ on $\ln(N)$ for a deposit of 0.001 $\mu$m particles, under the physical conditions listed in Table 4.1, is shown. It is
observed that, after a sufficient number of particles has been deposited, the slope of this plot, $\phi = 1.393$, does not depend on the number of particles deposited. Hence, this value of $\phi$ can be assumed to remain unchanged in the limit of $N \to \infty$. For this value of $\phi$, the fractal dimension of the deposit of 0.001 $\mu$m particles, $D$, was calculated to be 1.72. The nonlinear relation between $\ln(h)$ and $\ln(N)$ during the initial stages of deposition is due to the influence of the boundary (substrate), at low heights of deposits.

![Graph showing the relationship between ln(h) and ln(N)](image)

Figure 4.1.2: Dependence of average height of the deposit on the number of particles deposited

4.1.3 Effect of Particle Size on Deposit Morphology

Deposit patterns of particles of three different sizes are shown in Figure 4.1.3a-d. The fluid velocity in these simulations was 0.135 cm/sec. (Although particles in these deposits appear to overlap, this is due to the latent influence of the scaling of the axes employed in the plots.) There is no more than a single
contact between any two adjacent particles in the deposit. It is observed that for small particles (0.001 μm; Figure 4.1.3a), the deposit looks like a forest of trees, with very open dendritic structures. The interface, defined by the contour of the top surface, is poorly defined. In such deposits, it is also observed that the tips of the tallest trees capture the incoming particles more effectively, and that the smaller trees quickly become inaccessible to the incoming particles and stop growing, despite their very open structure. The clusters, defined as collections of particles connected to the same nucleation site through nearest neighbors, are spaced far apart, with little lateral support. Such deposits are expected to be unstable in real systems. For example, deposits in packed bed filtration with relatively few "roots" on the collector surface may be more prone to break off and travel down through the filter bed. The fractal dimension of the deposit in Figure 4.1.3a was calculated to be 1.72. A value of 1.69 has been reported in literature for a deposit of completely Brownian particles (Meakin, 1984b).

The deposit of 0.01 μm particles (Figure 4.1.3b) appears to be more compact than the deposit of 0.001 μm, indicating that the clusters had a more uniform growth rate. Unlike the deposit of 0.001 μm particles, clusters in the deposit of 0.01 μm particles tend to be more interlinked, resulting in a relatively more stable deposit. The interface is also better defined than that of the 0.001 μm particle deposit. The fractal dimension of the deposit of 0.01 μm particles was calculated to be 1.84.

Deposits of larger particles (0.1 μm and 1.0 μm; Figures 4.1.3c & d) are more uniformly dense and the deposit interface is better defined, in comparison with deposits of smaller particles. The transport of larger particles is more
ballistic in nature, owing to the effects of gravity and fluid drag. The fractal
dimensions of these deposits were found to be 1.90 for 0.1 \( \mu m \) particles and
1.91 for 1.0 \( \mu m \) particles.
Figures 4.1.3a, b, c, d
Simulated deposits of monodisperse suspensions of particle sizes 0.001-, 0.01-, 0.1-, and 1- μm.
\( d_p = 0.001 \mu m \)

\( d_p = 0.01 \mu m \)
(c) \( d_p = 0.1 \mu m \)

(d) \( d_p = 1.0 \mu m \)
Calculations of particle density, $\rho(h)$, can be used to further quantify deposit morphology. In 2-dimensional dimensions, the density function is calculated as:

$$\rho(h) = \frac{1}{L} \sum_x \rho(h,x)$$  \hspace{1cm} (4.1.4)

where $\rho(h,x) = 1$, if the lattice height at $(h,x)$ is occupied by a particle and $\rho(h,x) = 0$ otherwise. The summation is over the length of the substrate, $L$. In Figure 4.1.4, $\rho(h)$ is plotted as a function of $h$ for deposits of three different particle sizes. The density of deposits of small particles (0.001 $\mu$m), for which transport is dominated by Brownian diffusion, is observed to decrease continually with height, owing to the open, dendritic structure. These deposits are characterized by a poorly defined interface. For ballistic deposits of larger particles (0.1 $\mu$m and 1.0 $\mu$m), whose transport is dominated by fluid drag and/or gravity, deposit density remains near a plateau value throughout most of the deposit depth, after an initial rapid decline. Density drops rapidly at the deposit interface.
Figure 4.1.4: Dependence of lateral density of the deposit on the height of deposit for various particles
The variation of the root-mean-square deviation (RMSD) of the upper surface height of the deposits with respect to the number of particles deposited or the mean height of the deposit can be used to quantify the irregularity of the deposit interface. The RMSD of the upper surface height was related to the number of particles deposited, \( N \), and mean height, \( \bar{h} \), as follows:

\[
\left\{ \frac{1}{L} \sum_{i=1}^{L} (h_i - \bar{h})^2 \right\}^{1/2} = N^\omega \quad \text{for large } N
\]

\[
\left\{ \frac{1}{L} \sum_{i=1}^{L} (h_i - \bar{h})^2 \right\}^{1/2} = \bar{h}^\psi \quad \text{for large } \bar{h}
\]

where \( h_i \) is the position of the highest particle above the \( i \)th lattice on the original substrate.

In Figure 4.1.5, the slopes of \( \ln\left(\left(\frac{(\bar{h} - \bar{h})^2}{L}\right)^{1/2}\right) \) vs \( \ln(N) \) and \( \ln(\bar{h}) \) are plotted for deposits of different particle sizes. A higher value of \( \omega \) or \( \psi \) indicates that irregularities in the upper surface in a deposit continue to increase with the growth of the deposit, leading to a more open structure. As the deposition of small particles progresses, the RMSD of the upper surface height increases more rapidly than that of the larger particles. This increasingly uneven growth of clusters, during the deposition of diffusive particles, results in a forest-like deposit, with trees (clusters) of varying sizes and a poorly defined interface. However, for particles in the size range of 0.001 \( \mu \)m - 0.05 \( \mu \)m, the irregularities in the deposit surface decrease significantly with an increase in particle size. For particles larger than 0.05 \( \mu \)m, irregularities on the surface of
the deposit are relatively small and are independent of the extent of deposit formation. These conditions correspond to a well defined interface of deposit growth.

![Graph](image)

Figure 4.1.5: Dependence of the exponents $\omega$ and $\psi$ (Equations 4.1.5a & b) on particle diameter ($v_f = 0.135$ cm/sec)

The fractal dimensions of deposits formed from monodisperse suspensions are plotted as a function of particle diameter in Figure 4.1.6. For a fluid velocity of 0.135 cm/sec, fractal dimension is observed to increase significantly with particle size in the range of 0.001 $\mu$m and 0.1 $\mu$m. The fractal dimensions of deposits produced by particles larger than 0.1 $\mu$m are similar, with values near 1.9. Transport of the smaller particles is dominated by Brownian motion while for larger particles, fluid drag and gravity tend to have greater influence on particle transport. For particles larger than about 0.1 $\mu$m, fluid drag and gravity dominate transport and trajectories become ballistic. The theoretical limit of the mass fractal dimension for ballistic deposition is 2. The
assumption of no deposit restructuring and the nature of deposition on the lattice constrain the maximum fractal dimension to values slightly below 2. The crossover in the fractal dimension value from the diffusion limited deposition (DLD) value of 1.7 to the ballistic deposition (BD) value of 2.0 can be related to a similar crossover in the fractal dimension of the respective trajectories of the particles.

The fractal dimensions of the particle trajectories are calculated by approximating the length of the trajectory of a particle, $L(\epsilon)$, using line segments of varying size ($\epsilon$). The slope of the plot $\ln[L(\epsilon)]$ versus $\ln(\epsilon)$ yields the fractal dimension of the trajectory. The fractal dimensions of the trajectories of the particles of different diameters are plotted in Figure 4.1.6, along with the fractal dimensions of the deposits formed from these particles. The fractal dimension of the trajectory of a diffusive particle (0.001 $\mu$m particle in this work), after an infinite number of steps, is expected to be 2.0. However, a value slightly less than 2 was obtained in this work, owing to the finite number of steps ($\sim$90000) considered in approximating the trajectory of the diffusive particle and also because of an imposed flow field. It is observed that there is a good correlation between the crossover of fractal dimensions of the deposits and that of particle trajectories with increasing particle size. While the crossover for the fractal dimension of particle trajectories is from a value of 2 for diffusive particle to a value of 1 for a ballistic particle, the crossover for the deposits made up of these particles is from 1.7 for DLD to an asymptotic value of 2 for BD. Such "crossover" behavior has been reported by other investigators for diffusion-limited aggregation, with particle drift (Meakin, 1983).
The crossover of the fractal dimensions of several deposits arising from monodisperse suspensions from a DLD limit of 1.7 to that of a BD limit of 2.0, can be related to a similar crossover in the fractal dimension within a deposit at different length scales. To observe this crossover phenomena within a deposit, the sandbox method of calculating fractal dimension is used. In this method, the number of particles, $N(L)$, within boxes of increasing linear size ($L$), centered at the same point within a deposit, are counted. The slope of the curve $\ln[N(L)]$ versus $\ln(L)$ gives the fractal dimension. By repeating the above procedure over different positions of centers and averaging, we can obtain an accurate fractal dimension. If there is a crossover in the fractal dimension within a deposit at different length scales, the slope of the curve $\ln[N(L)]$ versus $\ln(L)$ for a given deposit would vary for different values of $L$. To study the deviation of the fractal dimension of the deposit from a value of interest, $D_g$, the quantity
\(N(L)\) can be normalized with \(L^{D_g}\). If the true fractal dimension of the deposit is close to \(D_g\) at any length scale, the curve, \(\ln\left[N(L)/L^{D_g}\right]\) versus \(\ln(L)\) should be flat. In Figure 4.1.7, plots of \(\ln\left[N(L)/L^{D_g}\right]\) versus \(\ln(L)\) are shown for four different deposits. It is observed that for a deposit consisting of 0.001 \(\mu\)m particles, the curve remains flat for \(D_g = 1.7\), while for a deposit of 1.0 \(\mu\)m particles, the curve is flat for \(D_g = 2\), indicating that the true fractal dimensions of these deposits are closer to the theoretical limits of 1.7 (DLD) and 2.0 (BD) respectively at all length scales. The crossover in the fractal dimensions between these two limiting cases can be observed in the plots referring to deposits made up of particles 0.005 \(\mu\)m and 0.01 \(\mu\)m. For the deposit consisting of 0.005 \(\mu\)m particles, the curve \(\ln\left[N(L)/L^{D_g}\right]\) versus \(\ln(L)\) is flat for \(D_g = 1.7\) at short length scales, while at larger length scales, it is flat for \(D_g = 2.0\). At short length scales, the deposit of 0.005 \(\mu\)m particles corresponds to one of diffusion limited deposition, while at larger length scales, the deposit morphology reflects the ballistic nature of the large scale motion. A similar trend is observed for the deposit consisting of 0.01 \(\mu\)m. However, for the deposit of 0.01 \(\mu\)m particles, diffusion dominates over shorter length scales and ballistic domination is evident over a broader range, when compared with the deposit of 0.005 \(\mu\)m particles. This suggests that with increasing particle size, and hence Peclet number, there is a gradual crossover from diffusion limited deposition to ballistic deposition. This crossover within a deposit is not evident when fractal dimension is calculated according to Equation 4.1.3. This is because Equation 4.1.3 averages mass correlation at different length scales in a direction parallel to the substrate and takes into account only those correlations in a direction parallel to that of growth. The fractal dimension calculated by Equation 4.1.3 is
useful in back calculating several average properties of the deposit including its average height, porosity, and permeability. These quantities define the boundary conditions experienced by the bulk flow and hence, the components of large-scale ballistic particle motion in subsequent deposition.

Figure 4.1.7: Deviation of fractal dimensions of deposits at different length scales from the two limiting cases of deposition (diffusion limited and ballistic deposits)
The particle size range (0.001 μm - 0.1 μm) over which the crossover from DLD to BD occurs results in a significant change in the fractal dimension of the deposits consisting of these particles. Applications involving colloid deposition in the Brownian regime (<0.1 μm), where fractal dimension changes significantly, include the formation of ceramic membranes by a sol-gel procedure, cake formation during membrane filtration and the formation of colloidal deposits in aquifers. In the first case, colloid size may be an important control variable in fabricating membranes of specific permeability and surface roughness.

The assumptions of geometry and fluid flow used in these simulations differ markedly from those in a packed bed filter or a ground water aquifer. For example, in packed bed filters fluid flow is largely tangential to the collector surface. Shadowing of deposition surfaces may result in a more open, dendritic deposit characterized by a lower fractal dimension. However, factors that are not included in the simulations presented here, such as rolling events, stability and restructuring, may mitigate shadowing. As stated earlier, in this work, even physically unstable configurations were declared as successful deposits. By restricting the criterion for particle deposition to more stable configurations (for example, particles must be exactly above a previously deposited particle) a fractal dimension closer to 2 is possible for ballistic deposition. In light of these considerations, we hypothesize that particle aggregates typical of water and waste water treatment applications after coagulation ($d_p > 0.1 \mu m$) form compact deposits in packed bed filters.
4.1.4 Effect of Fluid Velocity on Deposit Morphology

In a fixed fluid flow, particle size determines if trajectories are more Brownian or ballistic. For a fixed particle size, changes in fluid velocity also affect particle trajectories and the resultant deposit morphology. The effect of fluid velocity on the morphology of 0.01 μm, 0.1 μm and 1.0 μm particle deposits is shown in Figure 4.1.8, where, fractal dimension is plotted as a function of fluid velocity. These deposits consist of 50000 particles, grown on a substrate of length of 3000. Owing to the smaller scale of the simulation, these values differ slightly from those listed in Table 4.2 for similar physical conditions. It is observed that the fractal dimensions of the deposits increase considerably with fluid velocity. At lower fluid velocities, particle movement is dominated by diffusion, leading to a smaller fractal dimension. At higher fluid velocities, the particle trajectories are more ballistic in nature, owing to the dominance of fluid drag and gravity on particle movement, resulting in a higher fractal dimension. For velocities less than 10^{-3} cm/sec, as might be typical of particle deposition to the sediments of surface waters or the velocity of a ground water, the morphology of a deposit of 0.01 μm particles converges to the diffusion-dominated limit (D → 1.7). However, in this range of fluid velocity, there are significant changes in the morphology of the deposits of larger particles (0.1 μm and 1.0 μm) as a function of fluid velocity. The fractal dimensions of deposits calculated from simulations of these larger particles increase from approximately 1.7 to nearly 1.9 as fluid velocity increases from 10^{-5} to 10^{-3} cm/s. For velocities typical of slow sand filtration and ultrafiltration (10^{-3} - 5×10^{-2} cm/sec), the deposits of 0.01 μm or 0.1 μm particles are sensitive to the fluid velocity. For velocities higher than 10^{-3} cm/sec, the morphology of
deposits composed of 1.0 μm particles converges to one of ballistic-limited growth \((D \rightarrow 2)\). As stated previously, simulation results converge to a value slightly less than 2 due to constraints imposed by the assumption of particle movement on a lattice. Velocities higher than \(5 \times 10^{-2}\) cm/sec, as might be typical of micro-filtration (~0.1 cm/sec) and packed bed filtration (0.1 - 0.3 cm/sec), have a negligible effect on the morphology of deposits composed of 0.1 μm and 1.0 μm particles. Fairly compact deposits of these particles can be expected for this range of fluid velocity. The fractal dimension of the deposit of 0.01 μm particles continues to increase with fluid velocity over a wide range of fluid velocity, and converges to the ballistic-dominated limit for velocities higher than 3 cm/sec.

![Graph showing the effect of fluid velocity on the fractal dimension of deposits of different particle sizes](image)

**Figure 4.1.8:** Effect of fluid velocity on the fractal dimension of the deposits of 0.01-, 0.1-, and 1.0- μm particles

These simulation results can be summarized by expressing the fractal dimension of the deposit as a function of the Peclet number characterizing
particle transport. A fit of the fractal dimension calculated for the simulated deposits to the Peclet number yielded the following result (Figure 4.1.9):

\[
D = \begin{cases} 
  \sim 1.7 & \log(N_{Pe}) < -1.7 \\
  1.8130 + 0.0873 \text{erf}(\log(N_{Pe})) & -1.7 \leq \log(N_{Pe}) \leq 3.0 \\
  \rightarrow 2 & \log(N_{Pe}) > 3.0 
\end{cases} \tag{4.1.6}
\]

where the theoretical limit of 2 for ballistic deposition has been substituted for the asymptote of approximately 1.9 observed in the simulations.

![Graph showing the relationship between Fractal Dimension (D) and erf(log(N_{Pe}))](image)

**Figure 4.1.9: Fractal Dimension as a function of Peclet number**

### 4.1.5 Deposition from Binary Suspensions:

The deposit pattern of a polydisperse suspension consisting of 40000 particles of 0.001 µm diameter and 500 particles of 0.01 µm in diameter is shown in Figure 4.1.10a. Even though the mass ratio of large particles to small particles is 12.55, the deposition pattern more closely resembles that of the
small particles. Shadow regions caused by the 0.01 μm particles may contribute to the open, dendritic, structure of the deposit. The fractal dimension of this deposit was calculated to be 1.74, which is similar to the fractal dimension calculated for a deposit consisting of only 0.001 μm particles \( (D=1.72) \). A deposit of 40000 particles, 0.01 μm in diameter, and 500 particles, 0.1 μm in diameter is shown in Figure 4.1.10b. Owing to the greater effect of gravity and fluid drag on the transport of these particles, the deposit is more dense than a deposit consisting of 0.001 μm and 0.01 μm particles. However, the shadow effect of the larger particles results in a deposit that is less compact than deposits produced by either the 0.01 μm or the 0.1 μm particles individually. A fractal dimension of 1.82 was calculated for this deposit, which is lower than that for the deposits formed from either of these particles alone \( (D=1.84 \text{ for } 0.01 \mu m \text{ and } D=1.90 \text{ for } 0.1 \mu m) \). A similar trend was observed in the case of a deposit consisting of 0.1 μm and 1.0 μm particles (Figure 4.1.10c). The fractal dimension of this deposit was calculated to be 1.84, while those of deposits consisting of 0.1 μm alone and 1.0 μm alone were 1.90 and 1.91 respectively.
Figures 4.1.10a,b, & c

Simulated deposits of (a) 0.001- and 0.01- µm particles, (b) 0.01- and 0.1- µm particles and (c) 0.1- and 1.0-µm
\( d_p = 0.001 \mu m \)
\( \& 0.01 \mu m \)
\( \frac{m_{lg}}{m_{sml}} = 12.55 \)
\[
d_p = 0.01 \mu m \\
& 0.1 \mu m \\
\frac{m_{10}}{m_{sm}} = 12.55
\]
\[ d_p = 0.1 \mu m \]
\[ & \text{and} \ 1.0 \mu m \]
\[ m_{\text{LGP}} / m_{\text{SMI}} = 12.55 \]
Fractal dimensions for these deposits and for those formed from suspensions of different relative concentrations are reported in Table 4.2. It is observed that the fractal dimensions of the polydisperse deposits consisting of Brownian particles are closer to those of deposits consisting of the smaller particles alone. The fractal dimensions of deposits consisting of a polydisperse suspension of ballistic particles are considerably less than those of the individual deposits of these ballistic particles alone due to the creation of shadow regions. This shadowing effect is more evident in the deposit patterns for the suspension of 0.1 μm and 1.0 μm particles. Transport of these particles is ballistic in a uniform velocity field of 0.135 cm/sec.
Table 4.2  
Fractal dimensions of deposits of polydisperse suspensions

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<th>Fractal dimension $D$</th>
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$m_{lrq} = \text{total mass of large particles deposited}$

$m_{sml} = \text{total mass of small particles deposited}$

Length of substrate = 4000 units

$v_f = 0.135 \text{ cm/sec}$
4.1.6 Summary

Monte Carlo simulations in 2-dimensions were performed to simulate deposition of colloids onto a one-dimensional surface of infinite permeability. Particle migration was defined to be a function of particle diffusivity, fluid drag, and gravity. A uniform flow field was assumed. Under these assumptions, simulations indicate that the structure of a colloidal deposit is strongly dependent on the size of the colloids and the fluid velocity. Small particles (~0.001 μm) produced open dendritic structures, while larger particles (≥ 0.1 μm) were found to form compact deposits. For a fluid velocity of 0.135 cm/sec and a sticking probability of one, the fractal dimension of deposits of particles larger than 0.1 μm converges to a value slightly less than the theoretical limit of 2 due to limitations imposed by the simulation lattice. For particle sizes in the range of 0.001 μm to 0.1 μm, fractal dimension was observed to increase significantly with an increase in particle size. These results indicate that in deposition processes involving small colloids, such as the formation of cakes in membrane filtration, colloid size may be an important factor in determining deposit morphology, and hence membrane permeation. The geometry and flow field assumed in these simulations differ greatly from that applicable to collectors in packed bed filtration. However, we speculate that in processes involving the deposition of larger colloids or colloidal aggregates, such as in packed bed filtration, deposits may be expected to be fairly compact.

At higher flow rates, more compact deposits can be expected, while deposits formed at lower fluid velocities should be more porous. For flow rates typical of ground water (< 10^{-3} cm/sec), deposits of larger particles (0.1 μm to
1.0 μm) appear to be sensitive to fluid velocity, while deposits composed of 0.01 μm particles converge to a diffusion-limited morphology ($D \to 1.7$). The trajectories of 0.1 μm and 1.0 μm particles are largely ballistic at fluid velocities greater than $10^{-3}$ cm/sec, resulting in a fractal dimension closer to that of ballistic-limited deposition ($D \to 2$). The morphology of the deposit of 0.01 μm particles appears to be sensitive to the changes in fluid velocity over a wide range ($10^{-3} - 3$ cm/sec), beyond which, it converges to that of a ballistic-limited deposition.

It is possible to summarize these results in functional form; expressing fractal dimension as a function of a Peclet number which describes the relative importance of ballistic and diffusive transport in the deposition process. For small $N_{Pe}$, ($\leq 10^{-17}$; small particles and low fluid velocities) deposit morphology converges to one of diffusion-limited growth ($D \to 1.7$). For large values of $N_{Pe}$ ($> 10^3$; large particles, higher fluid velocities) the deposit morphology converges to the theoretical limit of ballistic growth ($D \to 2$). For the intermediate values of $N_{Pe}$, the deposit morphology is sensitive to the changes in fluid velocity and particle size. The fractal dimension of these deposits can be calculated from Equation 4.1.7, if the Peclet number is known.

For the relative concentrations considered in this work, the deposit morphology of polydisperse suspensions containing at least one particle class whose trajectory is dominated by diffusion appears to be controlled by the more diffusive particles. Deposits composed of ballistic particles of two significantly different sizes have fractal dimensions that are smaller than the fractal dimensions of homogeneous deposits composed of either of the particles.
alone. This observation is attributed to a shadowing effect produced by the larger of the two particles. In actuality, rearrangement of particles within the deposit as they seek a position of minimum free energy is likely to reduce the effects of shadowing.
4.2 Colloidal Deposits in Stagnation Flow

In this section, the structure of the colloidal deposits formed in 2-dimensional (planar) stagnation flow is presented. The results from these simulations can be applied to the formation of deposits in porous media. The porous medium is usually modeled as either an assemblage of spherical collectors (external flow models) or as a network of pores (internal flow models) (see section 2.5.3). In external flow models, the flow field around the sphere is considered (Figure 4.2.1) and the deposition of particles around the front stagnation point of the sphere is similar to the simulations reported here. In network model, the porous medium is assumed to be represented by a network of interconnected pores with the pores intersecting at points called nodes (Figure 4.2.1). The flow field in each pore is modeled as laminar flow and it is assumed that the nodes have no volume and is considered to be a site of mixing. However, in reality, the nodes may well act as good collecting surfaces as shown in Figure 4.2.1.
The planar stagnation flow is represented in Figure 4.2.2. The flow arrives along the y-axis and impinges on the flat plane at y=0 (the deposition plane) and leaves in both directions. At heights close to the deposition plane viscous flow dominates, beyond which the flow may be considered to be ideal (i.e., potential).
The velocity profile is given as (Schlichting, 1979):

For ideal flow:
\[ u_x = \alpha x \]  \hspace{1cm} (4.2.1a)
\[ u_y = -\alpha y \]  \hspace{1cm} (4.2.1b)

For viscous flow:
\[ u_x = xf'(y) \]  \hspace{1cm} (4.2.2a)
\[ u_y = -f(y) \]  \hspace{1cm} (4.2.2b)

where
\[ f(y) = \sqrt{\alpha v} \phi(\eta) \]
\[ \eta = \frac{\sqrt{\alpha v} y}{v} \]

\( v \) is the kinematic viscosity of the fluid and \( \phi(\eta) \) is the solution of the non-linear differential equation:
\[ \phi''' + \phi'' - \phi' + 1 = 0 \]  \hspace{1cm} (4.2.3)

subject to the boundary conditions:
\[ \phi(0) = \phi'(0) = 0 \text{ and } \phi'(\infty) = 1. \]
Once the fluid velocity profile is calculated, the individual trajectories of the particles can be calculated by solving the Langevin equation (Equation 2.5.30) as described in section 2.5.6. The simulation of deposition is similar to that used by others (Gupta and Peters, 1985; Ramarao and Tien, 1991; Ramarao and Tien, 1989; Ramarao, Tien, and Mohan, 1994). Particles are released at random positions in the $x$-direction at a height $H$ from the collector surface. The initial velocity of the particles was set equal to the fluid velocity at the release height. The trajectory of the particle was then calculated by successive use of Equations 2.5.32 and 2.5.33. The forces acting on the particle were limited to drag force, gravitational force and Brownian diffusion force. The time interval $\Delta t$ was chosen such that the particle moved at most one diameter during each integration step. This small time step in the integration levied a heavy toll on the computational time required to deposit significant number of particles. Such a small time step was necessary to ensure that the particles, during their movement in time step $\Delta t$, would not miss any needle like dendrites formed by the previously deposited particles. After each step, the distance of the particle from (i) previously deposited particles, (ii) collector surface and (iii) boundaries of the domain was calculated. The particle trajectory was calculated until the particle either deposited or escaped. A particle is said to be deposited if it came in contact with a previously deposited particle or the collector surface, upon which the particle position was recorded and a new particle was released. If the particle strays outside the imaginary flow boundaries (Figure 4.2.2), it was discarded from the simulations and a new particle was released. In reality, there is a free exchange of particles between the domain under consideration and the neighboring domains across the
imaginary boundaries depicted in Figure 4.2.2. In other words, no concentration gradient exists at the boundary. This can be incorporated in the model by reflecting the particles that were impacting the boundary into the simulation domain. However, in several trial simulations it was found that negligible fraction of particles thus reflected deposited later on. To save computational time, any particle leaving the boundary was terminated and a new particle was released. If the particle strayed beyond a predetermined number of steps (~10^5), the trajectory calculations for that particle were terminated and a new particle was released (In trial simulations, it was observed that few particles took many steps (2 to 3 orders of magnitude more than the average number of steps taken by the rest of the particles) before either depositing or escaping, thus slowing down the simulation considerably). The simulations were performed on Paragon L38, an Intel® supercomputer (Intel Corporation, Santa Clara, CA), operated by Caltech on behalf of the Concurrent Supercomputing Consortium (CSCC). Paragon L38 consists of an ensemble of 512 nodes connected by a high-speed internal network. Each node has a peak speed of 75 Milops. Simulations were performed using 100 nodes. At the beginning of the simulation, 100 particles were released and each particle was tracked by a node. Once the particle was deposited, other nodes were informed of the position of the newly deposited particle and the node would release a new particle and track its movement. The deposition algorithm is shown in Figure 4.2.3. The limitations of these simulations are that the possibility of restructuring was not included and the flow field was assumed to be unaffected by the growing deposit. Owing to the intense cpu time required, simulations were performed on two particle sizes, 5 and 1 μm. Attempts at simulating deposition of 0.1 μm particles were unsuccessful, as these particles required
prohibitively large cpu time to grow deposits of even a few particle diameters height.

**Figure 4.2.3:** Schematic of the simulation algorithm for particle deposition in stagnation flow
In Figure 4.2.4, deposits of 5 μm particles formed at four different fluid velocities are shown. At the lowest fluid velocity simulated (0.001 cm/sec), the fluid velocity components \( u_x \) and \( u_y \) are low in the whole domain and the fluid exerts minimal drag on the particle. The trajectory of the particle is dominated by gravity and the resulting deposit structure is similar to the ballistic deposits obtained in lattice simulations presented in the previous section. At a higher fluid velocity of 0.01 cm/sec, the fluid velocities are still low at regions close to the collector surface, but considerably higher at large heights. This results in a deposit which is broad at low heights; as the height of the deposit grows into regions of higher velocities, the fluid drag on the particles causes the particles move with the fluid away from the collector. This results in deposition of fewer particles and the deposit becomes narrow as it grows. At still higher velocities (0.1 and 1.0 cm/sec), the deposit becomes more narrow at greater heights.

In Figure 4.2.5, the deposits of 1 μm particles formed at four different fluid velocities are shown. The deposits of 1 μm particles at low fluid velocities (0.001 cm/sec and 0.01 cm/sec) differ markedly from those formed by 5 μm particles at the same velocities. Owing to the smaller size of 1 μm particles, even at these low velocities, gravitational force on these particles is not as significant as it was in the case of 5 μm particles. The fluid drag and Brownian force dominate the motion of these particles. Hence at low velocities, the deposits of 1 μm particles look like the diffusion limited deposits discussed in previous section. At higher velocities (0.1 and 1.0 cm/sec), the deposits attain columnar structure. It is surprising to see two distinct columns develop on either side of stagnation point, both tilting towards each other. This trend is evident
even at 0.01 cm/sec. At 0.01 cm/sec, the outward "trees" seem to be growing faster than the interior structures and were tilting towards each other. At higher velocities, the growth of the interior columns is stunted. At a fluid velocity of 1.0 cm/sec, no significant growth of deposit was observed around stagnation point.
Figure 4.2.4: 5 μm particle deposits in plane stagnation flow at four different fluid velocities
Figure 4.2.5: 1 μm particle deposits in plane stagnation flow at four different fluid velocities
The total number of 5 μm particles as a function of deposit height from the surface of the collector are plotted in Figure 4.2.6. As expected from the structure of the deposits shown in Figure 4.2.4, the at low fluid velocities, more particles are deposited within a given height. At higher fluid velocities, fewer particles form long narrow pillars. To compare the average density of the deposits as a function of the height of the deposit, the area of all the particles within a given height was divided by the total area of the domain of the deposit (i.e., width of the base of the deposit x height of the deposit). The average density thus calculated was plotted as function of the height of the deposit in Figure 4.2.7. The average densities of the deposits are high at regions close to the surface of the collector and quickly fall down to an asymptotic value after the deposit reaches a height of approximately 15 particle diameters. The average density of the deposit formed at 0.001 cm/sec fluid velocity remained constant at about 0.3 with increasing height of the deposit. Such behavior is characteristic of deposits formed from particles with ballistic trajectories. At a fluid velocity of 0.01 cm/sec, the average density of the deposit is high at low heights of the deposit, where gravity dominates the motion of the particles. The density of the deposit at low heights is even higher than the deposit formed at a fluid velocity of 0.001 cm/sec. This is attributed to the two small columns formed at a fluid velocity of 0.01 cm/sec on either side of the deposit at low deposit heights. Such ancillary growths were absent at 0.001 cm/sec, probably due to the shadowing of the bulk of the deposit. Once the deposit reached a height of 60 particle diameters, the two small columns on either side of the main deposit structure remained unchanged in height and even the bulk deposit structure tapers with height, causing a decrease the average density of the deposit. The tapering is more evident at higher flow rates and the average density of the
deposits is much lower (approximately 0.1) in the deposits formed at 0.1 and 1.0 cm/sec.

Similar analysis for the 1 μm - particle deposits gave different results. The number of particles in the deposits within a given height appear to vary slightly with fluid velocity (Figure 4.2.8). Even the slight trend that was observed was in contrast to the trend observed with 5 μm particles. Deposits formed at lower velocities had slightly fewer particles within a given height compared to those formed at higher velocities. Correspondingly, the average density of the deposit is slightly lower for deposits formed at low fluid velocities (Figure 4.2.9). The average density of all the deposits declined steeply with the height of the deposit up to 20 particle diameters, after a gradual decline was observed. From the actual structure of these deposits shown in Figure 4.2.5 and from the variation in the number of particles (or average density of the deposit, Figures 4.2.8 and 4.2.9), it appears that with increasing fluid velocity, the deposit becomes more narrow and at the same time more dense.
Figure 4.2.6: Total number of 1 μm particles as a function of deposit height at four different fluid velocities

Figure 4.2.7: Average density of 5.0 μm particle deposits as a function of deposit height at four different fluid velocities
Figure 4.2.8: Total number of 1 \(\mu m\) particles as a function of deposit height at four different fluid velocities

Figure 4.2.9: Average density of 1.0 \(\mu m\) particle deposits as a function of deposit height at four different fluid velocities

The results from these simulations can be compared with the results of the visual observations of particle deposition made by Payatakes, Park, and
Petrie (1981). Payatakes et al. made direct observations of deposition of latex particles (2.02 μm in diameter) on cylindrical rods arranged in a centered hexagonal pattern. They classified their experiments into three categories, based on the feed hydrosol and classified the deposition behavior as follows:

(i) feed hydrosol weakly unstable and virtually unagglomerated: depositional pattern is clogging of narrow throats, leading to the formation of pendant- and pouch-shaped deposits.

(ii) feed hydrosol very unstable and extensively agglomerated: deposits resemble jagged conical pillars on top of grains and eventually evolve into rough pendants.

(iii) feed hydrosol has first been destabilized and then has acquired a substantial opposite zeta potential and contains numerous large agglomerates: deposits accumulate with a checkered pattern all around each grain, but mostly on the forward half.

In all cases, the behavior of the top layer grains was different than the grains in the lower layers. The grains in the top layers of the filter bed accumulated deposits in the form of "snowcaps". The grains in the top layer have stagnation flow near their forward stagnation point and the deposit structure would be similar to the simulated shapes shown in Figures 4.2.4 and 5. As the shear stresses on these deposits increased, the parts of the "snowcaps" became reentrained and redeposited further down in the bed.

Deposits of the pillar-like shape shown in Figure 4.2.5c were observed in the lower layers of the grains when the feed hydrosol was unstable and
contained flocs of 5-10 particles. The growing pillars eventually blocked the throats above them.
CHAPTER 5
EXPERIMENTAL RESULTS

Experiments involving filtration of suspended latex particles through porous beds of glass beads were conducted under controlled physical and chemical conditions. Results from these experiments are presented and discussed in this chapter.

5.1 Physical and Chemical Conditions of Filtration Experiments

Filtration experiments were conducted under varying physical conditions such as particle size, depth of the porous bed, and flow rate. The physical and chemical conditions of these experiments are listed in Tables 5.1 to 5.4. Experiments are listed in separate tables, based on bed depth and suspended particle size. Table 5.1 lists the physical and chemical conditions of experiments conducted using a 13.5 cm deep bed. The remaining experiments were performed with a bed depth of 2 cm (Tables 5.2 - 5.4). These experiments differed with respect to the size of particles in the influent suspension (0.069-, 0.09-, 0.044- μm diameter particles in Tables 5.2, 5.3 and 5.4 respectively). The porosity of the bed in all the experiments was determined to be 0.4 based on measurements made on a typical bed. In all the experiments, 0.1 M Ca(NO₃)₂·4H₂O was used as the destabilizing agent to achieve favorable chemical conditions for deposition. The electrophoretic mobility and zeta potential values for the influent suspensions are also included in Tables 5.1 - 5.4. All the values were close to zero indicating that the influent latex particles
were destabilized. A solution of $5 \times 10^{-5}$ M NaHCO$_3$ was also used to buffer the feed. The pH of the influent suspensions in most of the experiments was between 6.5 and 7.0. The temperature was not constant in all the experiments and varied from 21 to 24 °C. The air conditioning in the laboratory was prone to frequent failures, causing variations in the ambient temperatures of the laboratory.
Table 5.1
List of filtration experiments in 13.5 cm deep beds
Bed depth ($L$) = 13.5 cm, Filter grain diameter ($d_C$) = 365 μm

<table>
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<th>Expt. No.</th>
<th>$d_p$ (μm)</th>
<th>$C_o$ (mg/L)</th>
<th>$u_s$ (cm/s)</th>
<th>$\zeta_p$ (mV)</th>
<th>$u_e$ (μm/s /V/cm)</th>
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a the zeta potential and mobility are too low to measure
b could not measure because of low concentrations of particles
Table 5.2
List of filtration experiments in 2 cm deep beds
Bed Depth \((L) = 2 \text{ cm}\), Suspended particle diameter \((d_p) = 0.069 \mu \text{m}\), Filter grain diameter \((d_c) = 358 \mu \text{m}\)

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<th>Expt. No.</th>
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<th>(u_s) (cm/s)</th>
<th>(\zeta_p) (mV)</th>
<th>(u_e) ((\mu \text{m/s}) /V/cm)</th>
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List of filtration experiments in 2 cm deep beds
Bed Depth ($L$) = 2 cm, Suspended particle diameter ($d_p$) = 0.09 µm, Filter grain diameter ($d_c$) = 358 µm
Table 5.4
List of filtration experiments in 2 cm deep beds
Bed Depth \((L) = 2\) cm, Suspended particle diameter \((d_p) = 0.044\) \(\mu\)m, Filter grain diameter \((d_c) = 358\) \(\mu\)m

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5.2 Clean Bed Removals in Filtration Experiments

As a particle suspension flows through a filter bed, particles deviate from the fluid streamlines and are transported to the surface of the filter grains through various mechanisms such as Brownian diffusion and gravity. Even if the particles follow fluid streamlines, they may come in contact with the filter grains through interception. The fraction of suspended particles retained by a porous bed during the initial stages of filtration is usually referred to as "clean bed removal". During the initial stages of filtration, there is an insignificant amount of deposited particles, and suspended particles are deposited primarily upon "clean" filter grains. The clean bed removal can be calculated from the effluent concentration after one pore volume of influent suspension has passed through the packed bed. However, the time required for this initial flush of the filter bed is dependent on the depth of the bed, superficial velocity, media size and porosity. Also, since particles are much larger than the ions in solution, the break through of the particles occurs earlier than the breakthrough of the solute.
ions. A practical way of estimating the clean bed removal is to measure the effluent concentration at frequent intervals during the initial stages of filtration and choosing the highest measured concentration. The clean bed removal, $R$, can then be calculated from the influent, $C_0$, and effluent concentration, $C$, of the particles as follows:

$$R = 1 - \frac{C}{C_0}$$  \hfill (5.2.1)

The clean bed removal of particles under the conditions listed in Tables 5.1 through 5.4 are shown in Figures 5.2.1 through 5.2.8 as a function of two parameters, particle size ($d_p$) and superficial velocity ($u_s$). The scatter in the data might be due to several reasons. First, accurate measurement of the ratio $C/C_0$ depends on the accuracy with which $C$ and $C_0$ are measured. For experiments run at low concentrations, both $C$ and $C_0$ are low and are difficult to measure accurately. Similarly, in filtration experiments characterized by high particle removals, the effluent concentration is very low. The theoretical predictions of clean bed removals based on the Rajagopalan and Tien model (Equations 2.5.25 and 2.5.27) are also included for comparison. Theoretical predictions for three values of the "adhesion factor ($\alpha$)" are shown. It should be noted that the correlating expression for single collector efficiency, $\eta$, (Equation 2.5.25) was obtained from trajectory analysis as a best fit expression for a wide range of values of the dimensionless numbers that appear in Equation 2.5.25. Trajectory analysis for any specific physical and chemical conditions of a filtration system gives slightly different $\eta$ values (Tobiason, 1987; Vaidyanathan, 1986). In this work, Equation 2.5.25 was used without any modification.
The removals of particles of different sizes through a 13.5 cm "clean" bed at a filtration rate of ~ 0.134 cm/sec are shown in Figure 5.2.1. The clean bed removals varied as a function of particle size. Minimum removal was observed for particles about 1 μm in diameter. Removal of particles smaller than 1 μm is greater due to Brownian diffusion, while particles larger than 1 μm are transported by gravity. Large particles are also deposited when their trajectories are intercepted by the collector. Particles at about 1 μm in diameter fall in the range where transport by Brownian diffusion, gravity and deposition due to interception are at a minimum. The experimental observations seem to fit the model predictions for alpha values in the range 0.73 - 0.22. A similar trend of clean bed removal dependence on particle size was observed at two other velocities, ~ 0.031 and ~ 0.246 cm/s (Figures 5.2.2 and 5.2.3).

![Figure 5.2.1: Clean bed removals of different particles at \( u_s \sim 0.134 \text{ cm/sec.} \)](image-url)
Figure 5.2.2: Clean bed removals of different particles at $u_s = 3.08 \times 10^{-2}$ cm/sec

Figure 5.2.3: Clean bed removals of different particles at $u_s = 0.2464$ cm/sec

The clean bed removal is highly dependent on the superficial velocity. At higher filtration velocities, increased fluid drag causes the particles to follow fluid stream lines, thus suppressing other transport mechanisms such as
Brownian diffusion and gravity. Thus, with increase in superficial velocity, the clean bed removal decreases. In Figures 5.2.4 and 5.2.5, the clean bed removals of 0.944 - and 0.069 - µm particles through \(\sim13.4\) cm deep beds is shown as a function of superficial fluid velocity. The clean bed removals of 0.044 - 0.069 - 0.09 - µm particles through 2 cm deep beds at different superficial velocities is shown in Figures 5.2.6 through 5.2.8. In all these experiments, the removal efficiency of a clean bed decreased with increase in superficial velocity.

![Figure 5.2.4: Clean bed removals of 0.069 µm particles filtered at different superficial velocities through a 13.37 cm deep filter bed.](image-url)
Figure 5.2.5: Clean bed removals of 0.944 μm particles filtered at different superficial velocities through a 13.3 cm deep filter bed.

Figure 5.2.6: Clean bed removals of 0.044 μm particles filtered at different superficial velocities through a 2 cm deep filter bed.
Figure 5.2.7: Clean bed removals of 0.069 μm particles filtered at different superficial velocities through a 2 cm deep filter bed.

Figure 5.2.8: Clean bed removals of 0.09 μm particles filtered at different superficial velocities through a 2 cm deep filter bed.
5.3 Typical Effluent Concentration Profile and Head Loss Development During A Filtration Experiment

As filtration progresses, particles retained in a porous medium may themselves act as collectors thereby improving the overall efficiency of the bed in subsequently removing particles over time. This improvement in particle removal is referred to as "ripening" of the filter bed. The effluent concentration profile of 0.069 μm particles over time (normalized with influent concentration) and head loss across the bed during a typical filtration experiment are shown in Figures 5.3.1a & b. The increase in the overall particle removal efficiency of the bed over time is reflected in the exponential decrease in effluent concentration (Figure 5.3.1a). During the ripening stage, the pressure drop across the bed also increases (Figure 5.3.1b). As retained particles fill in the void spaces in the bed, thereby partially clogging the bed, the fluid exerts more drag force on the newly retained particle surfaces and head loss increases. The effluent concentration profiles and the evolution of head loss over time for all the experiments listed in Tables 5.1 - 5.4 are shown in Appendix A.
Figure 5.3.1a: Effluent concentration profile over time in a typical filtration experiment

Figure 5.3.1b: Head loss profile over time in a typical filtration experiment

The relative efficiency of the filter bed in removing particles can be expressed as,
\[
\frac{R}{R_0} = \frac{1 - \frac{C}{C_0}}{\left[1 - \frac{C}{C_0}\right]_{\text{clean bed}}}
\] (5.3.1)

Once the filter bed attains 100% efficiency in retaining particles (i.e., \( C = 0 \) or \( R = 1 \)), \( R/R_0 \) attains its maximum value, given by \( R/R_0|_{\text{max}} = 1/R_0 \).

One premise of this research is that the increase in the removal efficiency and head loss across the filter bed over time (\( R/R_0 \) and \( h/h_0 \)) is intimately related to the manner in which particle mass is distributed both locally and with depth through the porous medium. The particle mass retained in the bed at different time intervals can be calculated from mass balance over the filter depth, from the measured effluent particle concentration profiles over time (influent particle concentration was constant over time in all the experiments). The extent of deposition is usually expressed in terms of the specific deposit, \( \sigma \), defined as the volume of particles deposited per unit volume of porous medium. To obtain a better understanding of the increase in removal efficiency and head loss due to particle deposition in a filter bed, these two parameters are plotted as a function of deposited particle mass as well as specific deposit in Figures 5.3.2a & b.
Figure 5.3.2a: Increase in removal efficiency of a filter bed as a function of retained particle mass and specific deposit, $\sigma$.

Figure 5.3.2b: Increase in head loss in a filter bed as a function of retained particle mass and specific deposit, $\sigma$. 
The bed removal efficiency, as expected, increased with retained particle mass. For the conditions listed in the Figure 5.3.2a, $R/R_0$ appears to follow an inverse power-law relationship with particle mass retained. The increase in $R/R_0$ with particle mass deposited also depends on other parameters such as influent particle concentration and superficial velocity as discussed in the next section. Thus, different values for each of these parameters should produce a different relationship for $R/R_0$ versus particle mass deposited. The head loss evolution is slightly different than that of bed removal efficiency. The profile of normalized head loss ($h/h_0$) increase as a function of particle mass shown in Figure 5.3.2b was typical and was observed in almost all the experiments. The increase in head loss tends to be negligible for small amounts of deposited particle mass. During early stages of particle deposition, the small amounts of deposited particles probably formed a uniform coating on the surface of the filter grains. However, as more particle mass is deposited, a rapid increase in head loss may occur. During this stage, the deposits on filter grains grow significantly. This could be due to the formation of dendrites by the deposited particles on the collector surface and/or due to the exceedence of a threshold of pores blocked by the growing deposits (Payatakes, Park, and Petrie, 1981).

5.4 Effect of Influent Concentration on Filter Ripening and Head Loss Development

At higher concentrations, more particles are predicted to be retained by a clean filter bed per unit time. This in turn leads to a higher rate of particle removal by retained particles and rapid decline in $(C/C_0)$ such as that illustrated in Figure 5.3.1a. Thus faster ripening over time should occur when
the influent suspensions have higher concentrations of particles. The head loss increases correspondingly, exhibiting higher head loss at higher influent concentrations at any time. Comparing the effluent concentration profile and head loss over time from experiments with different influent concentrations would not in itself give any more information than experiments at a single concentration. It is more appropriate to compare the filter efficiency and head loss increase as a function of retained particle mass. If the influent particle concentration has no effect on the performance of the bed (in terms of deposit morphology and the effect of retained particle mass on further removal of particles and head loss development), the filter efficiency and head loss increase in experiments with different influent concentrations, when plotted as a function of retained particle mass, should remain unchanged. Any significant differences would mean that the influent particle concentration might be influencing the performance of the bed by changing the deposit morphology or the relative distribution of the retained particle mass within the bed. First, results from three replicate experiments are presented to estimate the degree of reproducibility and the extent of scatter in experimental results. Next, results from a series of sets of experiments are presented. In each set of experiments, all the physical and chemical parameters are constant and the only variable is the influent concentration. The superficial velocities in some experiments varied slightly.

The particle removal efficiency of the bed and head loss across the bed as a function of retained particle mass (as well as specific deposit) in three replicate experiments are shown in Figures 5.4.1a & b. The removal efficiencies of the filter beds, as well as the head loss across the beds increased
with particle mass deposited. This is expected, since increase in retained particle mass in the bed would mean more surface area available for further deposition. Also, more surface area would also mean more drag loss experienced by the fluid flow, resulting in higher head loss. The scatter in the data is small, suggesting reasonable reproducibility. However, it should be noted that the initial removal efficiencies of the bed (the first points of the three curves in Figure 5.4.1a) varied considerably. The possible explanation for the scatter in the clean bed removal efficiency was discussed previously in Sections 2.5.5 and 5.2.

Figure 5.4.1a: Removal efficiency of the bed as a function of retained particle mass in three replicate experiments
Figure 5.4.1b: Head loss increase as a function of retained particle mass in three replicate experiments

The particle removal efficiency of the bed and head loss increase as a function of retained particle mass for two experiments at different influent concentrations but similar superficial velocities (~0.2 cm/s) are shown in Figures 5.4.2a & b.
Figure 5.4.2a: Removal efficiency of the filter bed as a function of retained particle mass at two different influent particle concentrations and $u_s = 0.2$ cm/sec.
The removal efficiency of the bed and head loss showed only a slight increase despite a three fold increase in influent concentration. For a given retained particle mass, the increase in head loss is within the experimental error. At this superficial velocity, the influent particle concentration does not seem to have significant effect on the head loss and only a slight effect on the effluent profile.

At a superficial velocity of ~0.14 cm/s, the removal efficiency of the bed improved slightly when the influent concentration was increased from 4.14 mg/l to 8.23 mg/l, which is about a two fold increase. However, a significant increase was observed with a four fold increase in influent concentration (Figure 5.4.3a).
Though head loss development as a function of retained mass showed a similar trend (Figure 5.4.3b), the increase is not as significant as was observed in the case of removal efficiency of the bed.

![Graph showing specific deposit (σ) vs. cumulative particle mass deposited (mg)](image)

Figure 5.4.3a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s = 0.14$ cm/sec.
Figure 5.4.3b: Increase in head loss as a function of retained particle mass at different influent particle concentrations and $u_s = 0.14 \text{ cm/sec}$.

At a superficial velocity of $\sim 0.1 \text{ cm/s}$, neither the removal efficiency nor the increase in head loss in the bed, for any amount of retained particle mass, showed any dependence on influent particle concentration (Figures 5.4.4a & b).
Figure 5.4.4a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s = 0.1$ cm/sec.

Figure 5.4.4b: Increase in head loss as a function of retained particle mass at different influent particle concentrations and $u_s = 0.1$ cm/sec.
For the experiments conducted at a superficial velocity of ~0.05 cm/s, though the removal efficiency of the bed differed significantly with influent particle concentration, the head loss as a function of retained particle mass was very similar at different influent concentrations (Figures 5.4.5a & b). However, it should be noted that the influent concentrations varied by only ~30%, while in previous experiments, the variation was as much as 3 to 4 times. The effluent concentration profile for experiment 98 was not shown for the following reason. An on-line spectrophotometer was used to measure the effluent concentration in experiment 98. However, it was realized that the spectrophotometer gave erroneous results, because of particles clogging the sample cell in the spectrophotometer. Since experiment 97 was conducted under conditions very similar to those of experiment 98, the effluent fraction data in experiment 97 (i.e., $C/C_0$) was used, along with $C_0$ of experiment 98 in estimating the cumulative mass retained in experiment 98 for the purpose of plotting the head loss data for experiment 98 (Figure 5.4.5b). The head loss evolution as a function of retained mass in both the experiments was observed to be very similar (Figure 5.4.5b). This implies that the effluent concentration profiles in both the experiments might have been similar.
Figure 5.4.5a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s \sim 0.05$ cm/sec.
Figure 5.4.5b: Increase in head loss as a function of retained particle mass at different influent particle concentrations and $u_s \sim 0.05$ cm/sec. (Cumulative particle mass deposited is estimated for experiment 98. See text.)

At lower velocities, ($\sim 0.03$ cm/s and $\sim 0.02$ cm/s; Figures 5.4.6a & b and 5.4.7a & b), the increase in head loss with retained particle mass depended on the influent particle concentration. At $\sim 0.03$ cm/s, the removal efficiency of the bed, as well as the increase in head loss, is higher at $C_0 = 16.3$ mg/l compared to those when $C_0 = 3.3$ mg/l. At $u_s = 0.02$ cm/sec, the removal efficiency did not change significantly when the influent concentration was changed from 2.4 mg/l to 4.1 mg/l, though the head loss was significantly higher for higher influent concentration during later stages of the filtration. Similar results were observed when the superficial velocity was $\sim 0.0065$ cm/s (Figure 5.4.8a & b).
Figure 5.4.6a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s = 0.03 \text{ cm/sec}$.

Figure 5.4.6b: Increase in head loss as a function of retained particle mass at different influent particle concentrations and $u_s \sim 0.03 \text{ cm/sec}$.
Figure 5.4.7a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s = 0.02$ cm/sec.

Figure 5.4.7b: Increase in head loss as a function of retained particle mass at different influent particle concentrations and $u_s \sim 0.02$ cm/sec.
Figure 5.4.8a: Removal efficiency of the filter bed as a function of retained particle mass at different influent particle concentrations and $u_s = 0.0065$ cm/sec.
In general, the influent particle concentration does not seem to have significant effect on the performance of the bed (in terms of removal efficiency and head loss development as a function of retained mass) at higher velocities. At lower velocities, the effect of influent concentration on head loss evolution as a function of retained particle mass is not clear. For instance, at a flow rate of 0.03 cm/sec, the rate of increase of head loss with retained particle mass is same at two different influent concentration. At a flow rate of 0.02 cm/sec, higher influent concentration caused greater head loss for the same mass deposited. At a flow rate of 0.0065 cm/sec, the trend again reversed, with higher head loss occurring when the influent concentration was higher. At low velocities, the efficiency of the bed in removing particles is very high (for instance, see Figures 5.2.4 to 8). Most of the particles may be retained by the
top layers of the bed, there by constricting or even blocking most of the pores in
the top sections of the bed, with few particles reaching the bottom layers. At
higher influent concentrations, this might be occurring at a faster rate, leaving
the bottom layers almost unused. Thus, in experiments with high influent
concentrations and low velocities, most of the mass might be retained in the top
narrow layers, while the distribution may be more broad for experiments run
with lower influent concentrations and high velocities. Under these conditions,
there is also a possibility of particles coagulating in the tubing and in the open
head space above the bed. Even though no visible signs of significant
flocculation were observed, the particles might have formed dimers or trimers,
which might influence the performance of the filter bed. At higher velocities, the
penetration of the particles into the bed is high and the influent particle
concentration does not have a significant effect on the performance of the bed,
in terms of removal efficiency and head loss development as a function of
retained particle mass.

5.5 Effect of Superficial Velocity on Head Loss Development
Across Filter Bed

At a given superficial velocity, the head loss across the filter bed
increases over time during the course of a filtration experiment, as more
particles are retained by the bed. The deposited particles partially clog the
pores within the bed and exert more drag loss on the fluid. The morphology of
the particle deposits and their distribution along the depth of the bed may
depend on the superficial velocity. At low velocities particle transport may have
a relatively larger diffusive component and more porous deposits may result. In
addition, more deposits may be formed in the top sections of the bed. At higher velocities, particle trajectories are more ballistic and the deposits formed are likely to be more compact. Also, particles penetrate deeper into the bed and lead to a more homogeneous distribution of the deposits along the depth of the bed. To better isolate the effect of morphology of the deposit on head loss development from the effect of deposit distribution along the depth of the bed, experiments were run on shallow beds of 2 cm depth. Even for this shallow depth, at very low superficial velocities, it was observed that the top 0.3 cm bed retained significantly more particles than the rest of the bed. This was evident when a distinct white band (the latex particles are milky white in color) was observed at the top of the bed. At higher velocities, no such distinct white bands were visible and the whole bed had a light whitish color (though a slight gradation along the depth of the bed was evident), suggesting that the deposits may be more uniformly distributed with depth. The concentration of the effluent was measured only at the bottom of the bed, which was 2 cm deep. The head loss was measured over the entire depth of the bed, as well as at one intermediate depth (at 0.6 cm depth from upstream end of the bed in some experiments, and at 1.2 cm depth in other experiments). First, the head loss per unit depth in the top and bottom sections of the bed are compared with the average head loss (per unit depth) of the entire bed at different superficial velocities as a function of total particle mass retained by the bed. Next, the head loss across the whole bed as a function of total retained particle mass is compared for different superficial velocities.
a) 0.069 μm particles

Experiments conducted at superficial velocities less than 0.017 cm/sec showed no increase in head loss in the bottom sections of the beds and hence results from those experiments (experiments 68 and 92) are not shown. In Figure 5.5.1, the head loss per unit depth (normalized by the initial head loss per unit depth) in the top and bottom sections of the bed as well as head loss across the whole bed is shown as a function of total particle mass retained by the entire bed at a superficial velocity of 0.01664 cm/sec (experiment 70). The head loss across the whole bed is represented by closed circles. The head loss in the top section of the bed is depicted with open triangles and that in the bottom section of the bed is represented by inverted open triangles. If the deposits are uniformly distributed along the depth of the bed, the three curves would coincide. At a flow rate of 0.01664 cm/sec, most of the head loss occurred in the top 0.6 cm of the bed, and negligible head loss occurred in the bottom 1.4 cm of the bed. It should be noted that most the head loss might have occurred over a depth smaller than 0.6 cm, but the head loss was measured only at depth of 0.6 cm. Similar trends were observed for superficial velocities up to 0.1 cm/sec (Figures 5.5.2 through 5.5.5).
Figure 5.5.1: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.01664$ cm/sec)

Figure 5.5.2: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.0353$ cm/sec)
Figure 5.5.3: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.04993$ cm/sec)
Figure 5.5.4: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.06956$ cm/sec)

Figure 5.5.5: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.1062$ cm/sec)
At superficial velocities above 0.1 cm/sec, the bottom layer registered significant head loss. For a superficial velocity of 0.135 cm/sec and influent concentration of 4.14 mg/l, the average head loss (i.e., head loss per unit depth) in the bottom 1.4 cm of the bed was slightly less than the average head loss over the entire bed (Figure 5.5.6). However, the upper 0.6 cm section of the bed still dominated with higher head loss per unit depth compared to the average across the whole depth of the bed and the bottom section of the bed. At about the same superficial velocity, but twice the influent particle concentration (8.234 mg/l), the contribution from the top section of the bed increased, while that of the bottom layer decreased (Figure 5.5.7). At a still higher concentration of 16.15 mg/l (Figure 5.5.8) and slightly higher superficial velocity, the head loss profile in different sections of the bed showed an interesting trend. While the upper 0.6 cm of the bed registered higher average head loss throughout the run, the head loss leveled off after a specific deposit of 0.0045 (~ 45 mg of retained particle mass) was formed. At that stage, a steeper increase in head loss was observed in the lower section of the bed. This suggests two possibilities. One possibility is that the upper section of the bed might have reached a non-retentive stage. No further particle collection would have occurred in the upper section of the bed and further deposition occurred primarily in the lower section of the bed. A second possibility is that even though deposition of particles continued in the upper section of the bed, the increased shear stresses in the bed might be constantly scouring the deposits and carrying the fragments to the lower section of the bed. It should be mentioned that no breakthrough was observed in this experiment (Figure 5.4.3a) suggesting near-complete removal of influent particles, or the scoured deposits from the upper section of the bed, by the
upper and lower sections. This behavior of the head loss profile in the upper section was not observed in the other two experiments (experiments 62 and 66; Figures 5.5.6 and 5.5.7) run at the same superficial velocities but at lower influent concentrations. This could be due to the comparatively low cumulative mass loading in the other two experiments and the resultant retained particle mass. (The experiments were run for comparable lengths of time; however owing to the significant differences in influent concentrations, the total retained particle mass varied considerably). Similarly, low retained particle masses resulted in lower head losses in these experiments (experiments 62 and 66) compared with the head loss produced in experiment 64. If scouring of deposits was the cause of constant head loss in the upper section of the bed in experiment 64, then the shear stresses in experiments 62 and 66 might not have been high enough to cause comparable head losses in these two experiments.

![Graph showing cumulative particle mass retained vs specific deposit]

*Figure 5.5.6: Head loss in different sections of the bed as a function of total retained particle mass (\( u_s = 0.1351 \, \text{cm/sec}; \, C_0 = 4.14 \, \text{mg/l} \))
Figure 5.5.7: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.1371 \text{ cm/sec}; C_o = 8.234 \text{ mg/l}$)

Figure 5.5.8: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.1385 \text{ cm/sec}; C_o = 16.15 \text{ mg/l}$)
A similar trend was observed at a superficial velocity of $\approx 0.17$ cm/sec (Figure 5.5.9). The head loss in the top section of the bed was higher than that in the lower section and maintained a plateau for specific deposits greater than 0.005 (corresponding to retained particle mass greater than 55 mg).

![Cumulative Particle Mass Retained (mg)](image)

**Figure 5.5.9:** Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.1688$ cm/sec)

At still higher superficial velocities (0.2 to 0.51 cm/sec), the contribution to head loss from the lower section of the bed increased considerably (Figures 5.5.10-5.5.16). The head loss in the top section of the bed still dominated the head loss across the bed. During the course of these experiments, the head loss in the top section increased with specific deposit and did not reach a plateau. These experiments were not run long enough for the bed to reach
complete (100%) removal efficiency (i.e., effluent concentrations were not zero at the end of these experiments). Owing to the higher superficial velocities, the particle penetration into the bed was higher. Also, the removal efficiency of the bed is lower at higher superficial velocities. For these reasons, the deposits should be more uniformly distributed along the depth of the bed at higher velocities and the upper section of the bed may not have reached its maximum retention capacity. No section of the bed had reached the non-retentive stage and hence the plateau in head loss that was observed in experiments at lower velocities was absent in these experiments.

Figure 5.5.10: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.2044$ cm/sec)
Figure 5.5.11: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.223$ cm/sec)

Figure 5.5.12: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.233$ cm/sec)
Figure 5.5.13: Head loss in different sections of the bed as a function of total retained particle mass \( (u_s = 0.2558 \text{ cm/sec}) \)

Figure 5.5.14: Head loss in different sections of the bed as a function of total retained particle mass \( (u_s = 0.3115 \text{ cm/sec}) \)
Figure 5.5.15: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.3328$ cm/sec)

Figure 5.5.16: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.5112$ cm/sec)
b) 0.09 and 0.044 μm particles

The trend observed in experiments with 0.09 μm particles was same as that observed in the case of 0.069 μm particles. For superficial velocities less than 0.03 cm/sec, no increase in head loss was observed in the lower section (bottom 1.4 cm) of the bed during the course of filtration. Even at superficial velocities of 0.034 and 0.1 cm/sec, the head loss in the bottom section of the bed was negligible (Figures 5.5.17 & 18). At a superficial velocity of 0.1705 cm/sec, the head loss in the lower section of the bed was significant, though the head loss per unit depth in the upper 0.6 cm of the bed was higher than average head loss (per unit depth) over the entire depth (Figure 5.5.19) suggesting non-uniform distribution of the deposited particle mass along the depth of the bed. Similar results were observed in experiments run with 0.044 μm particles (Figures 5.5.20 & 21). At $u_s = 0.033$ cm/sec, negligible increase in head loss across the bed was observed. However, at $u_s = 0.32$ cm/sec, the increase in head loss in the bottom 0.8 cm of the bed was significant, though the head loss across the top 1.2 cm of the bed dominated.
Figure 5.5.17: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.03378$ cm/sec)

Figure 5.5.18: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.09985$ cm/sec)
Figure 5.5.19: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.1705$ cm/sec)

Figure 5.5.20: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.03328$ cm/sec)
Figure 5.5.21: Head loss in different sections of the bed as a function of total retained particle mass ($u_s = 0.3162 \text{ cm/sec}$)

In the following discussion, head loss over the entire bed depth (2 cm) as a function of total particle mass retained at different superficial velocities is compared. First, results from experiments conducted with 0.069 $\mu$m particles are presented (Figure 5.5.22). For clarity, the results are plotted on a semi-log axes. For the same particle mass deposited, higher head loss was observed at lower superficial velocities. Steep increases in head loss were observed at very low superficial velocities ($u_s < 0.07 \text{ cm/s}$). At higher superficial velocities, the increase in head loss was more gradual as particle mass deposited. Similar trends were observed during the filtration of 0.09 $\mu$m and 0.044 $\mu$m particles (Figures 5.5.23 & 24).
The typical head loss across the whole bed depth as a function of specific deposit (or retained particle mass) shown in Figures 5.5.22 through 5.5.24 (or Figures 5.4.1b through 5.2.8b, where data are plotted on linear axes) indicated that the head loss can be related to the specific deposit through the following expression

\[
\frac{h}{h_o} = \beta_1 \sigma^\beta_2 + 1
\]  

(5.5.1)

Figure 5.5.22: Head loss increase as a function of specific deposit during filtration of 0.069 \( \mu \)m particles at different superficial velocities
Figure 5.5.23: Head loss increase as a function of specific deposit during filtration of 0.09 \( \mu \text{m} \) particles at different superficial velocities.

Figure 5.5.24: Head loss increase as a function of specific deposit during filtration of 0.044 \( \mu \text{m} \) particles at different superficial velocities.
In Figure 5.5.25, Equation 5.5.1 was fitted to typical $h/h_o$ versus $\sigma$ data. The experimental data fitted the expression well for $\beta_1 = 1.9185 \pm 0.01984$ and $\beta_2 = 1.8885 \times 10^6$. Within the range of specific deposit for which Equation 5.5.1 has been fitted, the head loss evolution can be assumed to be characterized by the parameters $\beta_1$ and $\beta_2$. The parameters $\beta_1$ and $\beta_2$ can be calculated for all experiments run at different superficial velocities by fitting the $h/h_o$ vs. $\sigma$ data of these experiments to Equation 5.5.1.

![Graph showing the relationship between $h/h_o$ and specific deposit $\sigma$.](image)

**Figure 5.5.25:** Typical $h/h_o = \beta_1 \sigma^{\beta_2} + 1$ fit

First, to study the effect of influent concentration ($C_o$) on $\beta_1$ and $\beta_2$, these parameters are plotted as a function of influent concentration for different superficial velocities in Figure 5.5.26.
Figure 5.5.26: Effect on influent concentration on $\beta_1$ at different superficial velocities

Figure 5.5.27: Effect on influent concentration on $\beta_2$ at different superficial velocities

There appears to be a slight dependence of $\beta_1$ and $\beta_2$ on influent concentration. However, given the experimental scatter and based on the
actual head loss data (Figures 5.4.1b-8b), the effect of influent concentration on these two parameters, if any, can be neglected.

In Figures 5.5.28 & 29, the values of parameters $\beta_1$ and $\beta_2$ obtained by fitting Equation 5.5.1 to the head loss data obtained from experiments conducted with 0.069 $\mu$m particles are shown. The replicate experiments at same superficial velocity but different influent concentrations are also shown.

![Figure 5.5.28: Effect of superficial velocity on $\beta_1$ during filtration of 0.069 $\mu$m particles](image)

$d_p=0.069 \mu$m;
$L=2 \text{ cm}; d_c=358 \mu$m;
Figure 5.5.29: Effect of superficial velocity on $\beta_2$ during filtration of 0.069 μm particles

The parameter $\beta_1$ is observed to decrease with increasing superficial velocity. At low superficial velocities, the $\beta_1$ decreases rapidly with increasing superficial velocity, while at higher velocities the decrease is more gradual. $\beta_2$ also shows a similar trend, though not as consistent. At very low superficial velocities (< 0.02 cm/sec), $\beta_2$ does not show a strong dependence on superficial velocity. However, at higher superficial velocities, $\beta_2$ decreased with increasing superficial velocity. At velocities greater than 0.2 cm/sec, $\beta_2$ exhibits a weak dependence on superficial velocity. It should be noted that at some superficial velocities, multiple points are plotted. These are results from experiments conducted at about same flow rate but with different influent concentrations. The scatter in the values of $\beta_1$ and $\beta_2$ at any given superficial velocity includes experimental scatter as well as effect of influent particle concentration, if any. From the discussion concerning Figures 5.4.1 - 8 (Section 5.4), it may be assumed that the effect of influent particle concentration on $\beta_1$ and $\beta_2$ is
negligible and that the scatter in the data results solely from experimental error and can be averaged to give clarity to the graphs. In Figures 5.5.30 & 5.5.31, the values of $\beta_1$ and $\beta_2$, averaged over different experiments conducted at same superficial velocities, are plotted.

Figure 5.5.30: Effect of $u_s$ on $\beta_1$ during filtration of 0.069 $\mu$m particles (values of $\beta_1$ obtained from experiments conducted at same $u_s$ are averaged)

Figure 5.5.31: Effect of $u_s$ on $\beta_2$ during filtration of 0.069 $\mu$m particles (values of $\beta_2$ obtained from experiments conducted at same $u_s$ are averaged)
In these averaged plots, the parameters $\beta_1$ and $\beta_2$ retain the general trend observed in Figures 5.5.28 & 29. The decrease in the values of these two parameters with $u_s$ seems to be more asymptotic at higher superficial velocities. In the region of $u_s = 0.15-0.4$ cm/s, $\beta_2$ appears to be constant, except for a steep decline at a velocity of 0.51 cm/sec. Though a similar drop was observed in $\beta_1$, it appears that $\beta_1$ decreases with $u_s$ throughout the range of $u_s$ studied.

The values of $\beta_1$ and $\beta_2$ calculated for the $h/h_0$ vs. $\sigma$ data from experiments conducted with 0.09 and 0.044 $\mu$m particles conducted at different superficial velocities are shown in Figures 5.5.32 - 35. For both particle sizes, $\beta_1$ decreased with increasing superficial velocity. For the 0.09 $\mu$m particles, $\beta_2$ decreased as superficial velocity increased to 0.1 cm/s, after which it appears to level off. For the 0.044 $\mu$m particles, few data are available to see any trend for $\beta_2$. However, the increase in $\beta_2$ observed at 0.4 cm/s is different from the trend observed in the case of 0.069 $\mu$m and 0.09 $\mu$m particles.
Figure 5.5.32: Effect of superficial velocity on $\beta_1$ during filtration of 0.09 $\mu$m particles

Figure 5.5.33: Effect of superficial velocity on $\beta_2$ during filtration of 0.09 $\mu$m particles
Figure 5.5.34: Effect of superficial velocity on $\beta_1$ during filtration of 0.044 $\mu$m particles

Figure 5.5.35: Effect of superficial velocity on $\beta_2$ during filtration of 0.044 $\mu$m particles

It should be noted that $\beta_1$ and $\beta_2$ show a consistent trend (both decrease with superficial velocity) despite the non-uniform distribution of the deposit along the depth of the bed at different superficial velocities. Even for
experiments where the head loss in the top section of the bed leveled off, the
two parameters did not deviate from the general trend. It appears that the
morphology of the deposits formed at any depth in the bed is similar and that
these deposits cause similar drag loss per unit mass of the particles deposited.
The effect of a non-uniform distribution of the deposits with depth on the
parameters $\beta_1$ and $\beta_2$ can be illustrated by head loss evolution data as a
function of the specific deposit at a superficial velocity of 0.04993 cm/sec
(Experiment 98; See Figure 5.5.3). In this experiment almost no head loss was
observed in the lower section of the bed (i.e., bottom 0.8 cm). It is reasonable to
assume that most of the particle mass was retained in the top 1.2 cm of bed and
may be even at shorter depths. However, since head loss was not measured at
depths less than 1.2 cm, let us assume that all the particle mass removed by the
bed is retained in the top 1.2 cm of the bed. The specific deposit in the top
section ($\sigma_{1.2\text{cm}}$), can then be calculated by dividing the volume of the total
number of particles retained by the bed with the volume of the upper section
(top 1.2 cm). In Figure 5.5.36, head loss in the top section of the bed is plotted
against the specific deposit (calculated based on particle retention in the top 1.2
cm of the bed only). For comparison, head loss across the whole bed is also
plotted against specific deposit, assuming that the deposit is uniformly
distributed over the full depth of the bed. The data are fitted to equation 5.5.1
and the values of the parameters $\beta_1$ and $\beta_2$ are calculated. $\beta_1$ increased
considerably (about 38%) when the total particle mass removed was assumed
to be retained in the top 1.2 cm of the bed. In actuality, the particle mass might
have been retained over a smaller bed depth, yielding still higher value for $\beta_1$.
However, $\beta_2$ appears to be independent of the deposit distribution along the
depth. It remained around 1.8, irrespective of the distribution of the deposit. It
appears that even if the deposit distribution along the depth of the bed is taken into consideration, the variation of $\beta_2$ as a function of superficial velocity as shown in Figures 5.5.29, 5.5.31, 5.5.33 and 5.5.35 may remain unchanged. It appears that $\beta_2$ is characteristic of the structure of the deposit itself. This is consistent with the asymptotic behavior of head loss observed at higher specific deposits. On the other hand, consideration of deposit distribution along the depth of the bed may result in higher values for $\beta_1$, than those shown in Figures 5.5.28, 5.5.30, 5.5.32 and 5.5.34. However, $\beta_1$ may still decrease with increasing superficial velocity, if it is assumed that more uniform deposition over depth occurs with increasing superficial velocities. It is not clear whether $\beta_1$ depends only on the deposit distribution or if it depends on the structure of the deposit also.

Figure 5.5.36: Effect of deposit distribution along the depth of the filter bed on the parameters $\beta_1$ and $\beta_2$
Based on these results, it may be concluded head loss increases in porous media are a function of the deposit distribution along the depth of the bed as well as the morphology of the deposits. Both vary with superficial velocities. At higher velocities, the deposit distribution in the bed is more uniform, resulting in lower head losses per unit particle mass deposited. Morphology of the particle deposits also depends on the superficial velocity. At low fluid velocities, the trajectories of the particles are likely to be more diffusive resulting in more porous deposits. At higher fluid velocities, particle trajectories are more ballistic in nature and the deposits formed from such particles are more compact. Hence, for the same mass deposited, deposits formed at lower fluid velocities occupy more pore space in the filter bed, causing the fluid to experience more drag losses, thereby resulting in higher head losses. The morphology of the deposits can be characterized in terms of fractal dimensions and will be discussed in the next section.

5.6 Fractal Dimensions of Deposits of 0.069, 0.09 and 0.044 μm Particles Filtered Through 2 cm Deep Beds

The fractal dimensions of the deposits formed during filtration of 0.069-, 0.09- and 0.044-μm particles through 2 cm deep beds were measured using a light scattering method. This method has been described in Chapter 3 (Section 3.2.3) and is not discussed here. The purpose of these measurements was to characterize the morphology of the deposits formed at different superficial velocities in terms of their fractal dimensionality. However, the procedure suffered from several limitations which could not be completely resolved. They are discussed below.
1. The light scattering measurements were performed on the deposits at the end of an experiment. The "stage" at which the experiment ended could not be determined. For instance, some experiments may have ended before significant restructuring/break-up of the deposits occurred during the course of the filtration and some after or during the restructuring process. These potential differences complicate comparison of fractal dimensions.

2. Since all the deposits in the filter bed were removed at one time (i.e., at the end of the experiment), the light scattering measurements reflect the scattering properties of all the deposits formed at different depths of the bed. This adds to the uncertainty as to the actual nature of the sample on which light scattering experiment was being performed. If there had been any restructuring and/or break-up of the deposits during the course of filtration, the measured fractal dimension on the sample yields an "averaged" fractal dimensions of all the deposits. There is also a possibility of the sample consisting of deposits composed of "stacked" fragments of sheared and re-captured deposits.

3. There is always a possibility of deposit break-up and/or rearrangement of the deposits during transfer from the bed to the sample cell. The chemical fixation of the deposits was thought to minimize break-up and rearrangement. This procedure of "chemical freezing" the deposits using protein and formaldehyde treatment as described in Section 3.2.3 was found to yield satisfactory results for trial aggregates formed in the Diffusion-Limited Aggregation regime. However, since deposit morphology was not measured in situ, deposit
restructuring during the removal of deposits from the filter column and transferring to the sample cell could not be entirely ruled out.

4. In earlier experiments, the deposits were found settling during the scattering intensity measurements. Settling introduced considerable noise to the light scattering signal. To slow down or even make the deposits neutrally buoyant, an appropriate concentration of glycerol was used as described in Section 3.2.3. Results obtained with and without glycerol are indicated as such in the discussion below.

Owing to all the factors listed above, considerable scatter in the experimental data was observed during the measurement of fractal dimensions of deposits formed during the filtration experiments. However, since no previous study involved measurement of fractal dimensions of the deposits in packed beds, results from this study, despite their limitations are hoped to give at least a qualitative view of the dependence of fractal dimensions of the deposits formed in filtration experiments under different physical conditions.

The fractal dimensions of the deposits formed during the filtration of 0.069 μm particles at several superficial velocities are shown in Figure 5.6.1. The solid circles represent the experiments in which deposit samples were suspended in glycerol (see Section 3.2.3) while the open circles represent the experiments where no glycerol was added to the sample. Although there is considerable scatter in the data (note the rather high error bars), three distinct regions can be identified. The fractal dimensions of the deposits seem to increase with increasing superficial velocity from 0.002 to 0.04 cm/s. In the
range of 0.04 to approximately 0.15 cm/s, the fractal dimensions of the deposits decreased, beyond which it increased with superficial velocity. The experiments in which glycerol was used yielded lower fractal dimensions at higher velocities compared with the results from the experiments in which no glycerol was used during sample preparation. At lower velocities, experiments with both methods of sample treatment yielded similar results. The cause of this effect is not clear. One possible reason could be that the time taken for glycerol to diffuse into aggregates at higher fractal dimensions may have been significantly higher than the time taken to penetrate aggregates at lower fractal dimensions (the bed with the deposits was soaked in glycerol for one hour in all the experiments in which glycerol was used during sample preparation).

![Fractal Dimension vs. $u_s$](image)

**Figure 5.6.1:** Fractal dimensions of the 0.069 μm particle deposits formed during filtration at different superficial velocities

The fractal dimensions of the 0.09 and 0.044 μm particles deposits formed during filtration experiments conducted at different superficial velocities
are shown in Figure 5.6.2. The fractal dimensions of the 0.044 μm particles increased from 1.79 to 2.2 with an increase in superficial velocity from 0.0066 to 0.0333 cm/sec. With a further increase in superficial velocity to 0.32 cm/s, the fractal dimension remained unchanged at about 2.2. The fractal dimensions of the deposits formed during filtration of 0.09 μm particles showed no particular trend. The fractal dimension of the deposits first decreased from approximately 2 to 1.55 with an increase in $u_s$ from 0.007 to 0.034 cm/s. With an increase in velocity to ~0.1 cm/sec, $D$ increased to 2.1212. With a further increase in $u_s$ to 0.17, the fractal dimension of the deposits decreased to ~1.24.

![Fractal Dimension Diagram](image)

*Figure 5.6.2: Fractal dimensions of the 0.044 and 0.090 μm particle deposits formed during filtration at different superficial velocities*

To compare the fractal dimensions of deposits of different particle sizes, Figures 5.6.1 & 2 are combined in Figure 5.6.3.
are shown in Figure 5.6.2. The fractal dimensions of the 0.044 μm particles increased from 1.79 to 2.2 with an increase in superficial velocity from 0.0066 to 0.0333 cm/sec. With a further increase in superficial velocity to 0.32 cm/s, the fractal dimension remained unchanged at about 2.2. The fractal dimensions of the deposits formed during filtration of 0.09 μm particles showed no particular trend. The fractal dimension of the deposits first decreased from approximately 2 to 1.55 with an increase in $u_s$ from 0.007 to 0.034 cm/s. With an increase in velocity to ∼0.1 cm/sec, $D$ increased to 2.1212. With a further increase in $u_s$ to 0.17, the fractal dimension of the deposits decreased to ∼1.24.

![Graph showing fractal dimensions](image)

Figure 5.6.2: Fractal dimensions of the 0.044 and 0.090 μm particle deposits formed during filtration at different superficial velocities

To compare the fractal dimensions of deposits of different particle sizes, Figures 5.6.1 & 2 are combined in Figure 5.6.3.
Figure 5.6.3: Fractal dimensions of the 0.044-, 0.069- and 0.09- μm particle deposits formed during filtration at different superficial velocities

The general trend of increase in fractal dimensions with superficial velocity in the range of 0.002 to 0.04 cm/sec is consistent with the decrease in specific head loss (head loss per unit particle mass deposited) with increasing superficial velocity. However, the low fractal dimensions observed in the range of 0.04 to approximately 0.15 cm/sec are not consistent with the head loss data discussed in the previous section. One possibility is that at these velocities, the deposits may attain pillar like structures as observed in simulations (section 4.2). However, as the deposits grow the local fluid shear stresses increase, tearing down parts of the deposit structures, which in turn redeposit further down the bed. When the deposits were removed from the bed for fractal dimension measurement, these columnar structures might be dominant, thus yielding low fractal dimensions. Though direct evidence of scouring of the deposits is not available, the head loss data in different sections of the bed presented in section 5.5 provides insight into that possibility. In Figures 5.5.8
and 5.5.9, the normalized head loss per unit bed depth in the top and bottom sections of the filter bed are shown. The head loss in top section of the bed reaches a plateau at a critical amount of specific deposit, while the head loss in the bottom section registers steeper increase in head loss at about the same specific deposit. The superficial velocities in these experiments were 0.14 and 0.17 cm/sec, which falls in the region where low fractal dimensions were observed (Figure 5.6.3). At higher superficial velocities (> 0.15 cm/sec) the fractal dimensions of the deposits increased, consistent with the head loss data reported in section 5.5.
CHAPTER 6
CONCLUSIONS

In this work, the effect of physical parameters such as fluid velocity and particle size on the morphology of the colloidal deposits in porous media were studied. Experimental work involved filtration of monodispersed latex particles through a bed of glass beads under different physical conditions such as particle size, influent particle concentration and flow rate. The effect of these parameters on the performance of the packed bed was evaluated in terms of changes in removal efficiency and head loss evolution as a function of particle mass retained. The fractal dimensions of the deposits formed under different physical conditions were measured using a light scattering method. Monte Carlo simulations of colloid deposition on one-dimensional surface of infinite permeability from a uniform flow field and on an impermeable one-dimensional surface in plane stagnation flow were performed. The dependence of the morphology of the simulated deposits on physical parameters such as particle size and fluid velocity was studied. In this chapter, the results of the experimental and numerical work are summarized, followed by engineering implications of the results and suggestions for future research.

6.1 Conclusions from numerical simulations

Monte Carlo simulations of colloid deposition on a one-dimensional permeable surface from a uniform flow field indicated that the morphology of the deposits strongly depended on particle size, fluid velocity, and particle density.
The effect of these parameters on the transport of particles to the collector surface by fluid drag, gravity settling, and Brownian motion are described in terms of a Peclet number, \( N_{Pe} \). For small values of \( N_{Pe} \) (small particles and low fluid velocities), the deposit morphology converges to one of diffusion-limited growth with a fractal dimension of 1.7. At large values of \( N_{Pe} \) (large particles and higher fluid velocities, deposit morphology was more compact and reaches the theoretical ballistic limit of \( D \to 2 \). For intermediate values of \( N_{Pe} \), the deposit morphology is sensitive to the changes in fluid velocity and particle size.

Deposition simulations in stagnation flow indicated that the shape and the structure of the deposit also strongly depend on the particle size and fluid velocity. At low velocities, large particles form compact deposits. At high velocities, the deposits of large particles form unstable pillars with fewer particles quickly building up the height of the deposit. As fluid velocity increases, the deposit becomes more narrow and increases in height. Small particles behave in a different manner. At low velocities, small particles form open porous structures. With an increase in velocity, almost the same mass of particles attains dense columnar structures similar to those formed with larger particles. These structures are likely to form on the top surface of the filter beds, where stagnation flow may be dominant at the forward stagnation point of the filter grains.
6.2 Conclusions from experimental work

The influent particle concentration does not seem to have significant effect on the removal efficiency of the packed beds or on the head loss development as a function of retained particle mass at high superficial velocities. However, even for instances when removal efficiency of the bed as a function of retained particle mass improved at quite high influent concentrations, the head loss profile remained unaffected. At lower velocities, the influent particle concentration seems to induce greater variability in removal efficiency and head loss development as a function of retained particle mass, though no clear trend could be observed.

The head loss development as a function of total particle mass retained at different superficial velocities varied with bed depth. At low superficial velocities (<0.1 cm/sec), the top section of the bed registered significant head loss while the bottom section of the bed showed no increase in head loss. At superficial velocities greater than 0.1 cm/sec, even though the bottom section of the bed registered considerable head loss, the top section of the bed still dominated, producing a higher head loss per unit depth compared with the average head loss per unit depth across the whole bed. For the influent concentrations used in this work, at superficial velocities around 0.15 cm/sec, the head loss in the top section of the bed reached a plateau at a specific deposit of approximately 0.004.

Flow rate appears to play an important role in head loss development by influencing the morphology of the deposits as well as the relative distribution of
the deposit along the depth of the bed. At high flow rates, a more uniform distribution of the deposit occurs, which results in low head loss per unit particle mass deposited. At low flow rates, the top layers of the filter bed retain most of the deposited mass, causing more head loss per unit particle mass deposited. Flow rate also influences head loss evolution by influencing the morphology of colloidal deposits. At low flow rates, more porous deposits are likely to form while at high flow rates, the deposits are more compact. For the same mass deposited, porous deposits extend more into the pore space of the bed and cause higher head losses.

The fractal dimensions of the deposits formed in the filter bed were observed to vary with the superficial velocity and qualitatively agreed with results obtained in simulations of particle deposition. The fractal dimensions of the deposits increased with increasing superficial velocity at the either end of the range of flow rates (0.002 to 0.04 cm/sec and 0.15 to 0.4 cm/sec) investigated. At intermediate flow rates (0.04 - 0.15 cm/sec) low fractal dimension were observed. Based on the simulations of particle deposition and head loss evolution in different sections of the bed, it is hypothesized that in this flow range, significant restructuring of the deposit occurred. At these intermediate flow rates, the deposits may have attained pillar-like structures as observed in the simulations. As the deposits grow, the local fluid shear stresses increase, tearing down parts of the deposit structure, which in turn re-deposit further down the bed. The fractal dimensions of such columnar deposits are expected to be low. At high fluid velocities, shear stresses prevent formation of columnar structures and a more compact, evenly distributed deposit is formed.
6.3 Engineering Significance

In processes involving particle transport through porous media, physical parameters such as particle size and flow rate may give an indication of the performance of the process in terms of pressure drop and particle retention.

It is well known that for low head loss development and better particle removal in packed bed filters, larger particles (or flocs) and higher flow rates should be preferred. However, in the context of this work, for a given particle size the improvement in head loss reduction (per unit particle mass deposited) with increase in flow rate appears to be marginal at higher flow rates. Based on raw water particle size distribution (PSD) and pilot scale studies, one can determine the optimum flow rate beyond which no significant reduction in head loss can be obtained with increase in flow rate. The operating flow rate (at or above the optimum flow rate obtained from the head loss considerations) can then be determined from the particle removal efficiency considerations. Such a strategy is applicable in water treatment processes involving direct filtration where there is little or no control over the influent particle size distribution.

Higher flow rates should also be preferred for better utilization of the complete depth of the filter bed. In this aspect, multi-media filters offer the advantage of higher removal efficiency at smaller flow rates as well as reduced head loss development, since the open porous deposits have enough void space to fill up before clogging up the filter.
The possibility of formation of unstable deposit structures at certain physical conditions should also be considered in the design of packed bed filters. This could be advantageous, as the reentrainment of the deposit structures from upstream sections of the bed would free those filter locations for new deposition. However, redeposition of these sheared deposit fragments in the lower sections of the bed is not certain and requires vigilant monitoring of the filtrate for break-through.

In some instances, it has been a practice to operate a filter at variable flow rate. During the initial stages of the filter run, the rate would be low to achieve better particle removal. Once acceptable filtrate quality is obtained, the flow rate is increased to the design flow rate. In such cases, careful consideration should be given regarding the duration of low flow rate operation. If the filter is operated for extended periods at low flow rates, highly open porous deposits may fill significant portion of the open pore space of the filter bed. If the deposits are stable (for instance when polymers are used for destabilizing the particles) subsequent removal at higher flow rates will occur on top of these open deposits, there by causing higher head losses. If sheared by the higher flow rates during the later stages of the filter run, the possibility of breakthrough exists.

In deposition processes involving small colloids, such as formation of cakes in membrane filtration, colloid size may be an important factor in determining deposit morphology, and hence membrane permeation. The compact deposits expected to form at high flow rates may cause significant reduction in membrane permeation. Colloid size may also be an important
control variable in other applications such as formation of ceramic membranes of specific permeability and surface roughness by a sol-gel procedure.

In ground water remediation processes such as pump and treat involving ground water reinjection, the primary objective is to avoid significant particle deposition. In such cases, higher flow rates will reduce the clogging of aquifer pores.

6.4 Suggestions for Future Research

Numerical Work:

The particle deposition simulations employed in this work are limited in terms of particle sizes, forces acting on the particle, flow field, collector geometry, and deposit restructuring. These simulations, while conceptually simple, require significant CPU time. There is considerable progress to be made in improving and extending these algorithms to simulate real processes involving particle deposition. The effort is worthwhile, since the stumbling block in modeling particle deposition processes is the lack of knowledge of deposit morphology. Good description of the deposit morphology is essential to estimate important parameters such as porosity and permeability of the deposit and also the stability of the deposit. The shape of the deposit is essential to better model the fluid-deposit interface, which influences pressure losses and subsequent particle retention. The morphology of the deposits controls process parameters such as permeation in membrane filtration, head loss development in packed bed filters.
Experimental Work:

To isolate the effect of morphology of the deposits formed at different flow rates on head loss evolution from the deposit distribution along the depth of the packed bed filter, controlled filtration experiments should be conducted on shallow beds. However, it is very difficult to conduct experiments at very shallow depths. Instead, at each flow rate, several experiments may be conducted at different filter depths. Alternatively, one can introduce sampling ports at different depths. However, such a set-up may introduce other uncertainties, by influencing the flow field in the bed and the deposit structure around the sample ports.

The effect of chemistry of the system on deposit morphology needs to be investigated. In filtration systems where the raw water is fed directly to the filter (membrane or packed bed) with little or no pretreatment, chemistry of the feed solution may influence the deposit morphology significantly.

Direct observation of deposit formation in situ through video-microscopy offers realistic view of undisturbed deposits. Image analysis of the deposits may be performed to characterize the deposits in terms of porosity. However, such experiments can be conducted for a porous medium of simple geometry. Alternatively, a better method of "freezing" the deposits (other than the "chemical freezing" reported in this work) in a typical filter bed should be developed.
The morphology of the deposits is sensitive to changes in particle size and flow rate at low values of these parameters, as encountered in ground water flow. More experimental work under such physical conditions is needed to better understand particle transport through ground water.
LIST OF REFERENCES


