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*Chapter 9*

## **COLLOID TRANSPORT AND RETENTION: RECENT ADVANCES IN COLLOIDS FILTRATION THEORY**

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### **ABSTRACT**

Colloid transport and retention in porous media is of great importance for a number of environmental and engineering applications. Tremendous efforts have been devoted to understanding the transport and fate of colloids in porous media. The purpose of this chapter is to overview the recent advances and the limitations in the colloid filtration theory, including the effects of non-DLVO interactions, surface blocking, surface charge heterogeneity (geochemical heterogeneity and particle population heterogeneity), physical heterogeneity (straining and non-Fickian transport) and the migration on colloid filtration processes. The current understanding of mechanisms, factors, and mathematical models are reviewed at four different scales: the interface scale, the collector scale, the pore scale, and the macroscopic scale. Remedies for the classical colloid filtration model in some limiting cases are recommended. Specifically, the straining, the surface charge heterogeneity, and the migration of deposited colloids are preferential factors for consideration under unfavorable attachment conditions. In heterogeneous porous media, the models accounting for the straining and the non-Fickian transport effects are desirable. Whether to incorporate the effects of straining and migration of deposited colloids can be examined based on the torque analysis at the pore scale. Both physical and chemical factors influencing these processes are emphasized in the chapter.

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## ABBREVIATIONS

CFT	Colloid filtration theory
ADE	Advection-dispersion equation
IFBL	Interaction-force-boundary-layer
DLVO	Derjaguin-Landau-Verwey-Overbeek theory
RT correlation	Rajagopalan and Tien's correlation
TE correlation	Tufenkji and Elimelech's correlation
RSPF	Radial stagnation point flow system
PDF	Probability density function
CTRW	Continuous time random walk

## 1. INTRODUCTION

Colloids are the particles dispersed in liquids (in most applications, water or water solutions) with the sizes in between dissolved macromolecules and suspended particles that resist rapid sedimentation. The typical size of colloid particles usually ranges from 10 nm to 10  $\mu\text{m}$  [1-3]. Colloids in nature include mineral fragments, microbes, and plant decay debris. The mineral fragments, such as silicate clay, are mainly derived from soil and formation rocks [4-7]. These particles can be released into or from soil, ground water and oil reservoirs via a variety of processes.

There is a considerable and ongoing effort aimed at understanding and predicting the transport, the deposition and the release of colloids in both synthetic (model) and natural porous media [8-13]. The fate and transport of colloids in porous media is of a great concern for the following reasons, among other: (i) The migration of colloids may facilitate the transport of low-solubility contaminants [14-21]; (ii) The spread of pathogenic microbes during waste water reclamation and aquifer recharge poses a risk to public health [22-31]; (iii) Deposition and migration of colloids cause permeability damage, which subsequently leads to injectivity decline and productivity decline [32-39]; (iv) Injection of the microbes producing surfactants may enhance oil recovery [40-42].

The fundamental filtration theory has been focused on the transport and fate of colloid at different scales: the interface scale, the collector (median grain) scale, and the pore scale. At the interface scale, the interfacial energy of a particle at the solid-water interface (SWI), the air-water interface (AWI), and the colloid-colloid interface can be quantified. Such a technique is used to predict attachment conditions and colloid stability [43-48]. At the collector scale, the flow field of water around a collector or an air bubble can be calculated. The probability of flowing particles being in contact with the collector can be quantified [49-52]. At the pore scale, the fate of colloids is studied in the presence of multiple grains and pores (grain-grain contacts) or solid-water-air triple points [53-55]. The favorable sites of attachment, straining and size exclusion can be identified in different pore geometries.

At the interface scale, the conditions for attachment and the colloid stability are primarily determined by the interaction energies [1, 38, 44]. The interactions can be classified into two main categories: the DLVO, and the non-DLVO interactions. In the classical DLVO theory, the total interaction energy is composed of electrostatic and van der Waals energies [43, 48,

56]. The available expressions for the electrostatic energy are derived from the Poisson-Boltzmann equation for surface-charged bodies of various geometries on the basis of the electrical double layer theory. The classical DLVO theory has been widely accepted as a powerful tool to predict attachment conditions and colloid stability. Nevertheless, it fails to describe biotic and abiotic colloidal behavior in some cases. The discrepancies are attributed to the so-called non-DLVO interactions. Such interactions may include hydrogen bonding, hydrophobic interaction, capillary forces, Lewis acid base interactions, and steric interactions [1, 3, 46, 57].

At the collector scale, the study of deposition rates takes into account the transport of particles from the bulk fluid to the collector surface and the capture via surface attachment. The approaches to simulating the colloid transport can be classified into two types, Lagrangian and Eulerian. The Lagrangian approach focuses on the motion of a single particle that is governed by Newton's second law. The particle trajectory in a flowing fluid is tracked [58-60]. The Eulerian approach accounts for evolution of the concentration or of the probability density of particles [61-63]. The Lagrangian approach has been extensively applied to describe the capture of non-Brownian particles, the trajectories of which are deterministic and can be solved analytically. The incorporation of Brownian motion into the Lagrangian approach, however, entails tedious and time-consuming step-by-step integration of the stochastic equation. Such an approach is essential for applications like industrial filtration, where the filter efficiency is determined by mesoscale particle behavior in a filter, which structure is presumably known [51, 64-67].

In contrast, the Eulerian approach is more attractive and widely applied for description of filtration in natural porous media and other media of stochastic structures, since it can describe more easily collective particle behavior and takes into account their Brownian motion. The implementation of Eulerian approach requires much less computational effort compared to the Lagrangian approach with Brownian motion, which may require multiscale treatment [68-70].

In the Eulerian approach, the motion of particles is characterized by the advection flux, the diffusive flux and the external-forced flux, caused by such forces as gravity, the DLVO forces, and the non-DLVO forces [1, 3, 13]. The convective-diffusion equation is usually solved in an ideal representation for the porous medium, such as Happel's sphere-in-cell model [71]. It assumes that identical sphere collectors enveloped in fluid shells are packed densely. The boundary conditions on the collector surface reflect the attachment conditions for the colloids. The most common boundary condition is the perfect-sink model which assumes the disappearance of particles at the collector surface, namely irreversible capture of particles on the surface [63, 72, 73]. Such a boundary condition completely neglects the accumulation and the release of immobilized particles. A more realistic boundary condition is the non-penetration model, which overcomes the above limitations [74-78].

At the pore scale, the convection-diffusion equation is also solved in between packed collectors or in the pores with different shapes. The study of colloid retention, in contrast to that at the collector scale, takes into account both straining and size exclusion at grain-grain contacts or constrictions. It is suited for examining different colloid capture mechanisms in a variety of pore geometries [79-82]. Such a technique can also be applied to study unsaturated systems, such as the retention at triple contact points (solid-water-air) [53, 83, 84].

The goal of the fundamental filtration theory at the interface, the collector and the pore scales is to arrive at an analytical deposition model which can predict the single collector

removal efficiency. It is a parameter reflecting the colloid removal efficiency by a single collector under known physical and chemical conditions [1, 13, 49]. Under favorable attachment conditions, the single collector removal efficiency can be approximated by the single collector contact efficiency since the physical contact can lead to direct chemical capture. Under unfavorable attachment conditions, the efficiency must be derived from the product of the single collector contact efficiency and the colloid collision efficiency [1, 45, 85, 86]. The colloid collision efficiency is a parameter reflecting the probability of effective collisions that overcome the energy barrier and lead to attachment.

There have been several theoretical approaches to expressing these efficiencies analytically. The Smoluchowski-Levich approximations [87, 88] and the interaction-force-boundary-layer (IFBL) approximations [89, 90] were used to calculate the single collector removal efficiency under favorable attachment and unfavorable attachment conditions, respectively. The Rajagopalan and Tien correlation equation was extensively used for calculating the single collector contact efficiency. Recently, Tufenkji and Elimelech [91] improved this correlation equation by considering the hydrodynamic and van der Waals effects on the deposition of particles by Brownian diffusion. Two types of collision efficiency were proposed to account for the attachment via the primary energy minimum (IFBL) [89, 90] and the attachment via the secondary energy minimum [92-94].

The derived deposition models (single collector removal efficiency) are commonly used to complete the system of equations for the mass balance of colloids at the macro-scale [1, 38, 95-97].

In this approach, the mass balance of suspended colloids is characterized by the advection- dispersion transport and the deposition while the release of retained colloids is neglected. The advection-dispersion equation (ADE) with a single sink term is also referred to as the classical filtration theory approach (CFT) or the perfect sink model [1, 13]. It can be solved either numerically or, in many cases, analytically [98-100]. The classical CFT, however, is derived under a number of over-simplified assumptions: (i) irreversible deposition, (ii) uniform flow field at the pore scale, (iii) uniform surface charges of colloids and porous media, (iv) straining or size exclusion is not considered. It should be noted that the classical CFT may be based on the classical DLVO theory for the description of interface interactions, but this is not always the case. The Non-DLVO interface interactions may also be incorporated into the classical CFT [1, 3, 13, 46, 47].

There is a growing body of studies suggesting that the classical CFT fails to fully describe a number of practically important processes or phenomena, such as filtration under unfavorable attachment conditions and filtration in stochastically (physically or geochemically) heterogeneous porous media [12, 101-105]. The discrepancies between the model predictions and experimental observations are as follows. Under unfavorable attachment conditions, the classical CFT and the DLVO theory predict the collision efficiencies several orders of magnitude smaller than those observed experimentally. Experimental collision efficiencies and critical deposition are insensitive to particle sizes [1, 86, 106-109]. Hyperexponential or non-monotonic deposition profiles are observed rather than the exponential deposition decay predicted by the classical CFT [101, 102, 110-113]. Long tails are observed in the breakthrough curves [111, 112]. In the porous media with irregular-shaped median grains, hyperexponential deposition is also often observed [79-81, 114, 115]. In heterogeneous porous media, both early arrival and delay of particles are observed in the breakthrough curves [10, 11, 104, 116-118].

Large research efforts were devoted to explaining the above observed discrepancies. Under unfavorable attachment conditions, underestimation of the collision efficiency, insensitivity to particle sizes, and hyperexponential deposition were mainly attributed to the deposition via the secondary energy minimum [92, 93, 101, 103, 119, 120] and heterogeneity of the surface charges [13, 73, 101-103, 110, 113].

Apart from the surface charge heterogeneity, the deposition hyperexponentiality has also been attributed to the effects of straining [79, 121, 122] and non-Fickian transport due to physical heterogeneity of porous media [104, 105, 123]. The non-Fickian transport was also claimed to be responsible for the early arrival and delay of particles [10, 11, 104, 105, 117, 124, 125]. The algebraic-decaying long tails in the breakthrough curves after the end of injection were either attributed to the migration of captured particles [80, 126-133] or to the physical non-equilibrium between the mobile and the immobile regions [134]. Rarely observed non-monotonic deposition profiles were either attributed to the migration of surface-attached particles via weak association or to the detachment of large aggregates [111, 135, 136].

The purpose of this chapter is to overview the recent advances in the colloid filtration theory. It reviews the new approaches that overcome the difficulties to incorporate surface charge heterogeneity, straining effects, non-Fickian transport, and migration of deposited particles. The current understanding of the mechanisms, factors, and mathematical models at different scales are reviewed. Remedies for reducing the discrepancies between model predictions and experimental observations are recommended.

## 2. TRADITIONAL THEORIES

This section reviews the traditional theories of colloid filtration, including the DLVO theory for surface interactions, the Eulerian approach for colloid transport and retention at the collector scale, and the macroscopic approach for modeling colloid filtration in porous media. These studies related to the three different scales have been the theoretical foundations of many further developments and consistency examinations for the colloid filtration theory.

### 2.1. DLVO Surface Interactions

The traditional theory for the colloid surface interactions is the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The interaction energy between the two surfaces is calculated as the sum of the electrical double-layer interaction and the van der Waals interaction energies:

$$\Phi_{total} = \Phi_{dl} + \Phi_{vdW}, \quad (1)$$

where  $\Phi_{total}$ ,  $\Phi_{dl}$  and  $\Phi_{vdW}$  are the total, the double-layer, and the van der Waals interaction energies, respectively. The expressions for the electrical double-layer interaction energy are available for varying geometries and different assumptions [1, 44]. These expressions were

derived on the basis of the Poisson equation for the charge density potential and the Boltzmann equation for the ion concentration dependency on the potential. The commonly applied expression for  $\Phi_{dl}$  is based on the sphere-sphere interactions [1]:

$$\Phi_{dl} = 64\pi \frac{a_1 a_2}{a_1 + a_2} \left( \frac{kT}{ze} \right) \tanh\left( \frac{ze\psi_1}{kT} \right) \tanh\left( \frac{ze\psi_2}{kT} \right) \exp(-\kappa h), \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $a$  is the colloid radius,  $z$  is the valence of the ions,  $e$  is the elementary charge,  $h$  is the separation distance between two surfaces, and the subscripts '1' and '2' represent the two surfaces. The Debye reciprocal length  $\kappa$  is calculated by:

$$\kappa = \sqrt{\frac{2e^2 N_A I}{\varepsilon \varepsilon_0 kT}} \quad (3)$$

where  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the vacuum permittivity, and  $I$  is the ionic strength. For the colloid-collector system, the radius of the collector is assumed to be far larger than that of the colloid particle, leading to  $a_1 a_2 / (a_1 + a_2) \approx a_1$ . The zeta potentials measured by electrophoresis are usually applied as substitutions for the surface potentials.

The classical approach to evaluate the van der Waals interaction between two bodies is derived by Hamaker [137] from the pairwise summation of all the relevant interaction energies. The expressions stemming from this approach can be split into the product of a purely geometric multiplier and of the so-called Hamaker constant. The total Hamaker constant of the different bodies is typically estimated by the geometrical mean value of the individual Hamaker constants [138]:

$$A_{12} = \sqrt{A_{11} A_{22}};$$

$$A_{123} = \left( \sqrt{A_{11}} - \sqrt{A_{33}} \right) \left( \sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad (4)$$

where  $A_{11}$  and  $A_{22}$  are the Hamaker constants for the two solid bodies,  $A_{33}$  is the Hamaker constant for the aqueous solution,  $A_{12}$   $A_{123}$  are the resulted mean Hamaker constants for a multi-body system. The approximate Hamaker constant for a material can be expressed in terms of the limiting refractive index and characteristic dispersion frequency [137]. The geometrical mean assumption is only valid if the dispersion frequencies of the particle and the medium are not very different. For sphere-sphere interactions,  $\Phi_{vdW}$  can be calculated by [56]:

$$\Phi_{vdW} = \frac{A_{123}}{6h} \frac{a_1 a_2}{a_1 + a_2} \left( 1 + \frac{14h}{\lambda} \right)^{-1} \quad (5)$$

where  $\lambda$  is the characteristic wave length, usually 100nm [56]. It should be noted that the van der Waals forces may be retarded, since electrodynamic interactions leading to dispersion forces are propagated at the finite speed of electromagnetic radiation. Retardation effects have been revealed experimentally by Israelachvili and his co-authors [139]. The last term on the right hand side of Equation (5) results from this retardation effect, which is implicitly included in the full Lifshitz treatment [140]. The van der Waals interaction is attractive in the systems of polystyrene-water-glass and polystyrene-water-quartz, while it is repulsive in the system of polystyrene-water-air [138]. The DLVO theory has been widely applied as a tool to explore the influence of the solution chemistry and the particle size on the attachment conditions. Figure 1 presents the comparison of colloid radii and ionic strengths for the polystyrene-quartz-water system. The DLVO calculations exhibit significant energy barrier to attachment via the primary energy minimum. Under such unfavorable conditions, the effect of colloid interactions is often expressed in terms of the collision efficiency, which is the ratio between the number of effective collisions leading to the attachment (via the primary energy minimum or the secondary energy minima) and the total number of collisions. In many cases, the attachment condition and colloid stability can be successfully predicted by such calculations as shown in Figure 1. For example, the larger the energy barriers are as in Figure 1, the more stable the colloidal system is. Nevertheless, the analytical expressions for interface interaction energies are based on the two strong assumptions: (i) the colloids and the collectors possess uniform and regular shapes; (ii) the surface charges of colloids and collectors are homogeneous.

## 2.2. Colloid Transport

At the interface scale, the attachment condition is primarily determined by the surface interaction energies between the collectors and the colloids in their close proximity. The deposition rate, however, is dependent on both the collector-colloid surface interactions and the rate with which the particles are transported toward the collector walls.

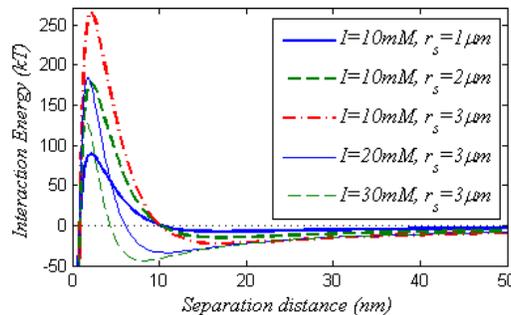


Figure 1. Particle size and ionic strength effects on the interaction energy, colloid surface potential is -77mV, collector surface potential is -35mV, polystyrene-quartz-water system.

There are two approaches for calculating the deposition rate on a stationary collector surface, the Lagrangian and the Eulerian approaches. As mentioned above, the Lagrangian approach tracks the trajectory of each single colloid governed by Newton's second law, leading to the Langevin-Itostochastic differential equations for the particles in the flow [141-143], while the Eulerian approach (the Fokker-Planck-Kolmogorov-Feller partial differential equation for the particle distribution) treats the particles as an ensemble [144-146]. Introduction of the Brownian motion into the Lagrangian approach leads to a series of step-by-step integration of the stochastic equation which requires intensive computation. In contrast, the Brownian motion can be easily taken into account by the diffusion term in the convective-diffusion equation within the Eulerian method. Extensive discussions on the two approaches are available in the literature [50, 63, 147, 148], while only the Eulerian method is discussed in detail here. The convective diffusion equation describing the concentration or the probability density of colloid particles is usually given by [13, 62, 63, 85]:

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = Q \quad (6)$$

where  $c$  is the particle concentration with regard to pore volume,  $Q$  is the source term, and  $\mathbf{J}$  is the flux which can be decomposed into the advection flux, the diffusive flux, and the external-forced flux:

$$\mathbf{J} = \mathbf{u}c - \mathbf{D}\nabla c + \frac{\mathbf{D} \cdot \mathbf{F}}{kT}c \quad (7)$$

here  $\mathbf{D}$  is the diffusion tensor,  $\mathbf{u}$  is the fluid velocity field which can be found by solving the Navier-Stokes equation in the corresponding geometry, and  $\mathbf{F}$  is the external force vector determined by the total colloid interaction energy:

$$\mathbf{F} = -\nabla\Phi_{total} \quad (8)$$

The non-DLVO forces can also contribute to Equation (8), if the non-DLVO interaction energies are added in Equation (1).

Equation (6) can be solved numerically and provides insight into the deposition rate when proper boundary conditions at the collector surface are given. Due to insufficient knowledge of the physical and chemical conditions at the surfaces, only simplified forms of the boundary conditions have been studied. Two types of the boundary conditions are commonly adopted: the perfect sink model and the non-penetration model.

The most commonly used boundary condition is the perfect sink model. This approach assumes the suspended concentration to be zero or constant convective flux at the surface or close proximity of a collector, corresponding to irreversible capture of colloid at the collector surface [74, 149-151]. Mathematically, the boundary condition can be expressed by:

$$c|_{h=\Delta} = 0, \text{ or } \left. \frac{\partial(uc)}{\partial h} \right|_{h=\Delta} = 0; \quad (9)$$

The first boundary condition and the second boundary condition in Equation (9) were shown to produce the same results by Song and Elimelech [73]. The second boundary condition is the constant convective flux condition, namely that the radial flux at the collector surface equals to that at the fluid shell (forward difference regime), and that the particles may flow through the collector surface and disappear.

The value of  $\Delta$  was assumed to be either zero or an arbitrary separation distance beyond the surface interaction energy barrier. Equation (9) and non-zero values of  $\Delta$  reflect the physics that after overcoming the energy barrier, the particle will effectively capture and that the convective flux will be zero. The particles at this point will “penetrate” in the collector body and “disappear” due to the external forces.

Based on the perfect sink assumption, many expressions for the deposition rate have been established, such as the Smoluchowski-Levich and the interaction force boundary layer (IFBL) approximations of the single collector removal efficiency. Nevertheless, one major disadvantage of this approach is the neglect of the accumulation of retained particles on the collector surface.

On the contrary, the next boundary condition, the non-penetration model, takes into account the deposition concentration at the collector surface [63, 74].

In the non-penetration model, flowing particles are prohibited to penetrate the collector surface or disappear. Mass balance is formulated for two particle populations, the mobile and the immobile species. Mathematically, the boundary condition takes the following form:

$$J_{\perp}|_{h=0} = 0; \quad (10)$$

$J_{\perp}$  is the total flux perpendicular to the collector surface. Equation (10) neglects the growth of the deposition thickness on the collector surface. The source term  $Q$  in Equation (6) may also be used to account the non-DLVO interactions.

### 2.3. Porous Medium Model

One of the simplest and widely applied porous medium models for colloid filtration is Happel’s sphere-in-cell representation [1, 13, 51, 71, 85, 152-154]. In Happel’s model, the packed bed is composed of identical spherical grains enveloped by fluid shells, as seen in Figure 2. The thickness of a fluid shell  $b$  is selected so that the overall porosity of the medium is maintained for each single collector:

$$b = r_c (1 - \phi)^{-\frac{1}{3}} \quad (11)$$

where  $r_c$  is the radius of the collector (median grain) and  $\phi$  is the overall medium porosity. The convection-diffusion equation can be solved numerically in Happel's porous medium model, with the flow field derived from the Navier-Stokes equation. Many theoretical studies were performed with other porous medium models, such as parallel capillaries, capillary networks, and fibers [106, 155-161]. These models were suited for the filtration in some specific natural and engineering processes, such as the fines in petroleum reservoirs, the industrial filtration with filter presses, and the membrane filtration. Generally, selection of a model depends on particular tasks of a researcher and his ideas about the structure of the porous medium under study. In this chapter we will refer to Happel's model as a specific example.

## 2.4. Single Collector Removal Efficiency

A useful concept for studying the deposition rates is the single collector removal efficiency, a dimensionless parameter as defined in Equation (12). This parameter is convenient to incorporate into the classical CFT of colloid transport and retention, which will be discussed later.

$$\eta = \frac{\text{rate of particle capture on a collector surface}}{\text{particle flux toward the projected area of the collector}} \quad (12)$$

The removal efficiency can be found from the numerical solution of the convective-diffusion equation or the trajectory equation in any given geometry of collectors. The main disadvantage of this approach is the lack of exact analytical solutions. Thus, an approximate expression for the efficiency is desirable.

Ruckenstein and Prieve [89] and Spielman and Friedlander [90] derived an approximate analytical solution for the deposition rate for Brownian particles under the condition of repulsive double-layer interactions.

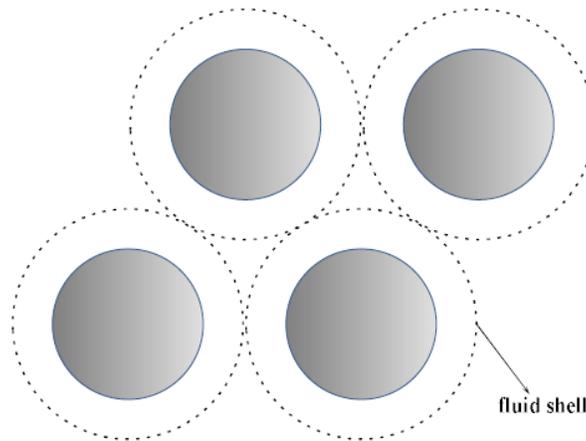


Figure 2. Happel's representation of granular porous media.

This approach, as the most classical theory for the removal efficiency under unfavorable attachment conditions, is often referred to as the interaction force boundary layer (IFBL) approximation. The interaction force boundary layer represents the transport in the close proximity of a surface, where the surface interactions dominate and the convective transport is negligible. The thickness of the layer is usually deemed to be in the same order of magnitude as the Debye length. The interaction forces are neglected outside this layer, where the convective transport dominates.

As derived in [89, 90], the single collector removal efficiency may be approximated by:

$$\eta = 4.04 A_s^{\frac{1}{3}} \left( \frac{D_\infty}{2r_c U} \right)^{\frac{2}{3}} \left( \frac{\beta}{1+\beta} \right) S(\beta) \quad (13)$$

$$\beta = \frac{\sqrt[3]{2}}{3} \Gamma\left(\frac{1}{3}\right) A_s^{-\frac{1}{3}} \left( \frac{D_\infty}{r_c U} \right)^{\frac{1}{3}} \left( \frac{k_F r_c}{D_\infty} \right) \quad (14)$$

where  $A_s$  is a porosity-dependent parameter of Happel's model ( $A_s \approx 38$  for porosity of 0.4),  $D_\infty$  is the bulk diffusion coefficient,  $U$  is the fluid approach velocity, and  $S(\beta)$  is a slowly varying function of  $\beta$  with tabulated numerical values [90].  $k_F$  is the pseudo-first-order rate constant given by [90, 162]:

$$k_F = D_\infty \left\{ \int_0^\infty \left[ f(h, r_s) \exp\left(\frac{\Phi_{total}}{kT}\right) - 1 \right] dh \right\}^{-1} \quad (15)$$

where  $f(h, r_s)$  is a hydrodynamic function which accounts for the reduced mobility of the colloids in close proximity of collectors. An approximation for this function is suggested by Dahneke [162]:

$$f(h, r_s) = 1 + \frac{r_s}{h} \quad (16)$$

It is worth mentioning that Equation (13) in the absence of all the parts depending on  $\beta$  is reduced to the Smoluchowski-Levich approximation for the single collector removal efficiency for Brownian particles under favorable attachment conditions. The efficiency reflects how fast the Brownian motion can bring particles to the collector surface. It is regarded as the single collector contact efficiency in the IFBL approximation:

$$\eta_0 = 4.04 A_s^{\frac{1}{3}} \left( \frac{D_\infty}{2r_c U} \right)^{\frac{2}{3}} \quad (17)$$

The parts depending on  $\beta$  in Equation (13) are responsible for the interactions between the hydrodynamic forces and the colloidal forces. They are usually referred to as the collision efficiency: the probability of the fact that a collision results in attachment. Here, in IFBL approximation, these terms reflect the effective collisions that overcome the repulsive double-layer force and drag the colloids into the primary energy minimum:

$$\alpha = \left( \frac{\beta}{1+\beta} \right) S(\beta) \quad (18)$$

Typical values of the collision efficiency vary from  $10^{-3}$  to 1 [1, 85, 86, 163-165]. A more general form of the single collector removal efficiency can be inferred by substituting Equations (17) and (18) into Equation (13). The single collector removal efficiency becomes the product of the single collector contact efficiency and the collision efficiency:

$$\eta = \eta_0 \alpha \quad (19)$$

The IFBL approximation takes into account only the colloid transport by Brownian motion to the collector surface for the single collector contact efficiency (see Equation (17)).

This assumption makes it impossible to apply the IFBL approximation to the capture of larger particles, where the effects of interception and gravity are not negligible. Limitations and further developments of the single collector contact efficiency will be discussed in the following sections.

## 2.5. Classical CFT Approach

The goal of introducing the single collector removal efficiency is to express the deposition rate explicitly, and to further apply this expression in the macroscopic approach for modeling colloid transport and retention. At the macroscopic scale, the transport and retention of colloid particles is usually described by an advection-dispersion equation (ADE) with a first-order kinetic sink term representing the deposition rate of colloid. Such an approach is also referred to as the classical colloid filtration theory (CFT) approach. For a simple 1-D problem, it is written as [1, 95]:

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - \frac{\rho_b}{\phi} \frac{\partial s}{\partial t} \quad (20)$$

where  $c$  is the bulk concentration of colloid with regard to pore volume,  $s$  is the deposited concentration with regard to unit mass of the porous medium,  $\rho_b$  is the bulk density of the dry porous medium,  $v$  and  $D$  are the particle velocity and dispersion coefficient. The accumulation of deposition is calculated by:

$$\frac{\rho_b}{\phi} \frac{\partial s}{\partial t} = k_d c \quad (21)$$

where  $k_d$  is usually referred to as the deposition rate constant, related to the filtration coefficient in a deep-bed filtration process:  $\lambda = k_d / v$ . The deposition rate constant is calculated on the basis of the single collector removal efficiency:

$$k_d = \left[ \frac{3(1-\phi)}{4} \frac{v}{r_c} \right] \eta \quad (22)$$

It can be seen from the above expression that the deposition rate constant is a parameter depending on the fluid velocity, while the filtration coefficient is not. The multiplier in square parentheses in Equation (22) represents the particle flux towards the projected area of a single collector. This multiplier may vary depending on the particular flow model on micro-level. For example, for the sphere-in-cell envelope (Happel) model of the porous space, multiplier  $(1-\phi)$  in Equation (22) should be replaced by  $(1-\phi)^{1/3}$  [1, 13, 166].

The analytical solutions to Equation (20) with various boundary conditions have been studied in the literature [98-100].

For the steady state flow problem (although with non-steady deposition), the temporal derivative in Equation (20) is zero. The analytical solutions for clean bed filtration in such cases can be expressed in terms of the logarithm of attenuation. Neglecting dispersion, the solutions are given by:

$$\ln \left[ \frac{c(x)}{c_0} \right] = -\lambda x \quad (23)$$

$$\ln \left( \frac{s(x,t) \rho_b / \phi}{c_0 k_d t} \right) = -\lambda x \quad (24)$$

Such solutions are commonly applied for examining the agreement between the experimental collision efficiency and the model predictions. The collision efficiency determined from a column experiment can be calculated by:

$$\alpha = -\frac{4}{3} \frac{r_c}{L(1-\phi)\eta_0} \ln \left( \frac{c_L}{c_0} \right) \quad (25)$$

where  $L$  is the column length, and  $c_L$  is the effluent concentration at  $x = L$ . It should be noted that an accurate determination of the collision efficiency from experiments is essentially dependent on the accuracy of the single collector constant efficiency.

More accurate expressions of the single collector constant efficiency will be discussed later.

## 2.6. Equilibrium and Non-Equilibrium Attachment

Beside the permanent deposition via the primary energy minimum, the Langmuir and Freundlich isotherms were applied to describe the equilibrium “adsorption” of colloids [132, 167-175]. Such theories have been widely applied to describe the equilibrium “adsorption” of multi-components in the flowing fluid, such as solutes, onto solid surfaces [99, 100, 176-179]. The simplest form of isotherm is the linear dependency  $s = K_{eq}c$ , where  $K_{eq}$  is the equilibrium attachment constant. The mass balance equation for the CFT taking into account the equilibrium “adsorption” can be rewritten as:

$$R \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad (26)$$

where  $R$  is the retardation factor calculated as  $R = 1 + \rho_b K_{eq} / \phi$ . It can be seen from the above equation that the equilibrium “adsorption” mechanism does not result in actual retention of colloid particles, but only slowing down the colloid transport. In more complex models, like the Langmuir model for adsorption, the retardation coefficient becomes dependent on the concentration (see more detailed discussion in Section 3.4). A more general model describes reversible attachment of the particles, with the possibility of detachment. This model is also referred to as the two-site non-equilibrium model [99, 100, 134]:

$$\left( 1 + f \frac{\rho_b K_{eq}}{\phi} \right) \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - k [(1-f) K_{eq} c - s] \quad (27)$$

$$\frac{\partial s}{\partial t} = k [(1-f) K_{eq} c - s] \quad (28)$$

where  $f$  is the fraction of surface sites for equilibrium attachment, and  $(1-f)$  is the fraction of those for non-equilibrium attachment;  $k$  is the kinetic constant for the non-equilibrium processes, or the release rate constant. In the absence of equilibrium sorption, the deposition rate constant is reduced into  $k_d = k K_{eq}$ .

## 3. LIMITATIONS AND EXTENSIONS OF THE CFT

The classical CFT has been widely applied to simulate colloid transport and retention in both the engineered and the natural porous media. The model predictions were tested with both laboratory and field data. The traditional approach seems to be successful only within certain limitations: under favorable attachment conditions, for small particles, whose transport can well be described as the Brownian motion, for physically and chemically homogeneous

porous media, for uniform particle populations, and under the absence of the developed collective behavior (like bridging etc.).

Large ongoing efforts aimed at understanding the transport and deposition of colloids in porous media are beyond these limitations. The deviations from the classical CFT were attributed to non-DLVO interactions, blocking of collector surfaces, unfavorable attachment conditions, chemical and physical heterogeneity of porous media, population heterogeneity of colloids, and migration of deposited colloids. In this section, the limitations and advances in the colloid filtration theory are discussed in detail.

### 3.1. Non-DLVO Interactions

The DLVO theory has been widely applied to predict colloid-collector interactions and colloidal stability for the last decades. Nevertheless, it failed to match the experimental observations in many cases [46, 180, 181]. The deviations, often referred to as the non-DLVO effects, were attributed to the following reasons: hydrogen bonding and hydrophobic effects, hydration pressure, non-charge transfer Lewis acid base interactions, and steric forces.

Most of the colloidal interactions in the nature take place under the presence of water molecules, which exhibit hydrogen bonding between each other. Hydrophobic colloids tend to aggregate in the aqueous phase. The water molecules are ordered around them [182-184]. The ordered water molecules can be regarded as hydration shells radially propagating and decaying from the particle surface.

Similar effects can be found on polar surfaces. It has been suggested in the literature that ordering of the water molecules results in “hydration pressure” or “structural forces”. The interactions of hydration shells contribute to the total interaction energy. It has been suggested by a number of authors [13, 57, 185-187] that non-DLVO interactions can be incorporated as additives to the right hand side of Equation (1). Many of these non-DLVO interactions are still incompletely understood.

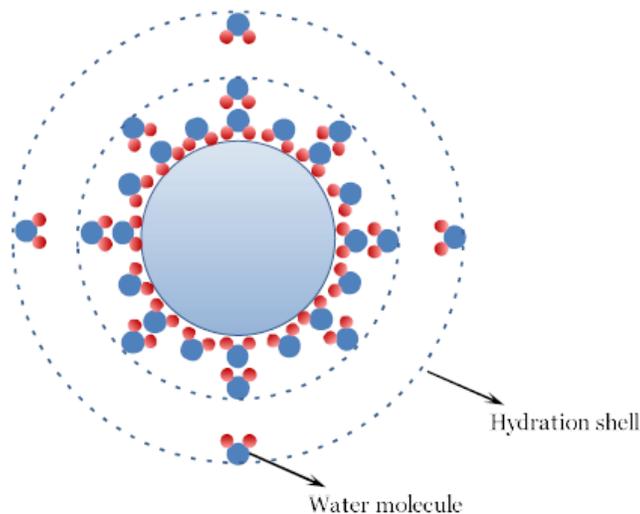


Figure 3. Illustration of hydration shells.

Only few empirical expressions for the non-DLVO interactions are available in the literature. Some of them are based on the assumption about the exponentially decaying hydration pressure [188, 189], while others are based on the short range Lewis acid base interactions [47, 57].

Additivity of the DLVO and non-DLVO interactions, assumed in the literature, may also be questioned. Further study is required to provide more insight to the extensions of DLVO theory.

### 3.2. Single Collector Contact Efficiency

In the IFBL and Smoluchowski-Levich approximations, calculation of the single collector contact efficiency takes into account only the Brownian motion, while other mechanisms of particle transport to the collector surfaces, such as interception and gravity of large non-Brownian particles, are neglected. Inaccurate calculation of the single collector contact efficiency leads directly to inaccurate determination of the collision efficiency from experiments (see Equation (25)).

Subsequently, examination of the consistency between the model predictions and the experimental observations is compromised. Hence, a more comprehensive model for the contact efficiency is desirable, to consider as many transport mechanisms as possible.

It has been suggested on empirical grounds [51, 89-91, 107] that the single collector contact efficiency may be calculated by summing individual contributions from the different transport mechanisms. The total efficiency can be expressed as the sum of the diffusion, the interception, and the gravity contributions to colloid transport toward the collector:

$$\eta_0 = \eta_D + \eta_I + \eta_G \quad (29)$$

where  $\eta_D$  is the contribution from diffusion,  $\eta_I$  is the contribution from interception, and  $\eta_G$  is the contribution from gravity.

The regression analysis of the rigorous numerical solution to the transport equation (either the stochastic differential or the convective diffusion equations) leads to semi-empirical expressions for the different efficiencies. Each contribution is expressed in terms of the power functions of some dimensionless numbers. The most commonly applied dimensionless numbers are listed in Table 1.

Apart from the IFBL or Smoluchowski-Levich approximations, there are two approaches for calculating the single collector contact efficiency, the RT correlation (after Rajagopalan and Tien [51] ) and the TE correlation (after Tufenkji and Elimelech [91] ). A summary of these expressions is useful for selecting the proper expressions for different conditions, as seen in Table 2.

The RT correlation was derived in [51] to account for gravity and the combined influence of van der Waals and the viscous interactions on the particle capture via interception. Neither of the RT and the IFBL correlations takes into account the effects of the van der Waals and the viscous interactions on the particle capture.

**Table 1. Dimensionless numbers for single collector contact efficiency**

Number	Definition	Physical interpretation
$N_R$	$r_s / r_c$	Aspect ratio
$N_{Pe}$	$2Ur_c / D_\infty$	Ratio of convection transport to diffusion transport
$N_{vdW}$	$A_{123} / kT$	Ratio of van der Waals interaction energy to thermal energy
$N_G$	$2(\rho_s - \rho)gr_s^2 / (9\mu U)$	Ratio of Stokes particle settling velocity to fluid approach velocity
$N_A$	$A_{123} / (12\pi\mu r_s^2 U)$	Combined influence of van der Waals and viscous interactions on particle capture via interception

**Table 2. Expressions of the contributions from diffusion, interception and gravity**

	$\eta_D$	$\eta_I$	$\eta_G$
IFBL approximation [89, 90]	$4.04A_s^{1/3}N_{Pe}^{-2/3}$	0	0
RT correlation [51]	$4.04A_s^{1/3}N_{Pe}^{-2/3}$	$1.04A_sN_A^{0.125}N_R^{1.875}$	$3.38 \times 10^{-3}A_sN_G^{1.2}N_R^{-0.4}$
TE correlation [91]	$2.4A_s^{1/3}N_{Pe}^{-0.715}N_R^{-0.081}N_{vdW}^{0.052}$	$0.55A_sN_A^{0.125}N_R^{1.675}$	$0.22N_G^{1.11}N_R^{-0.24}N_{vdW}^{0.053}$

Unlike the RT correlation, the TE correlation incorporates the effects of the van der Waals and the viscous interactions on the particle capture. The other distinction between the TE correlation and the RT correlation lies in the expression for the gravity contribution.

This contribution is independent of the medium porosity in the TE correlation (absence of  $A_s$ ), while this parameter is present in the RT correlation. Lastly, in the TE correlation, the effect of the van der Waals interactions is incorporated in all of the three transport mechanisms, namely the three expressions include either  $N_{vdW}$  or  $N_A$ . It has been shown by Tufenkji and Elimelech [91] that the TE correlation matches the numerical solution for the particle transport at the collector scale better than the RT correlation.

It is worth mentioning that the above expressions of the single collector contact efficiency are derived from the deposition rate normalized by the flux toward the projected area of a single collector. The expressions for the efficiency with regard to the projected area of the sphere-in-cell envelope (Happel's model) can also be found in the literature [1, 13, 166]. In such cases, a factor of  $(1-\phi)^{2/3}$  is introduced into the right hand side of (29).

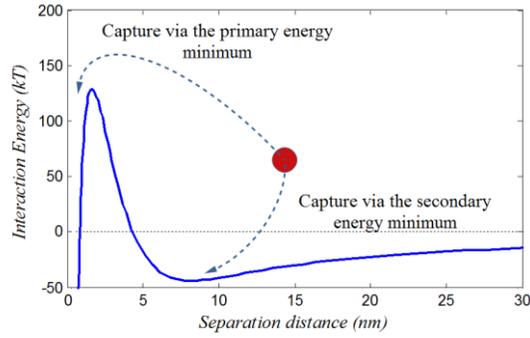


Figure 4. Particle capture via the primary and the secondary energy minima.

### 3.3. Collision Efficiency

The collision efficiency determined by Equation (18) only accounts for the effective collisions that overcome the repulsive double-layer force and drag the colloid particles into the primary energy minimum. It does not take into account the particles captured via the secondary energy minimum, as seen in Figure 4. This expression for the efficiency has been widely applied to predict the collision efficiency and to compare with experiments [1, 12, 45, 73, 85]. Despite the widespread use of the expression, a growing body of evidence suggests that the predicted collision efficiency is several orders of magnitude smaller than the experimentally observed one [85, 86, 106, 107, 190]. Several explanations were proposed to account for the reported derivations, including the heterogeneity of surface charges and the deposition via secondary energy minima [13, 73, 92, 93, 101-103, 110, 113, 119, 120].

A simple model for calculating the collision efficiency, which takes into account the deposition via the secondary energy minimum, was proposed by Hahn [92-94, 120]. In this model, the value of  $\alpha$  in Equation (18) is derived from the Maxwell distribution of kinetic energies:

$$\alpha = 1 - \int_{-\Phi_{2\min}}^{\infty} f(\Phi) d\Phi$$

$$f(\Phi) = 2 \sqrt{\frac{\Phi}{\pi(kT)^3}} \exp\left(-\frac{\Phi}{kT}\right) \quad (30)$$

where  $\Phi_{2\min}$  is the total interaction energy at the secondary energy minimum,  $f(\Phi)$  is the Maxwell distribution of interaction energies. The calculation of the collision efficiency accounts for the particles with insufficient energy to escape from the secondary energy well. The collision efficiency may be also expressed in terms of the particle velocity rather than the interaction energy. In such cases,  $\Phi$  in Equation (30) is substituted by  $0.5m_s v_s^2$  where  $m_s$  and  $v_s$  are the colloid mass and the colloid velocity in the close proximity of the collector.

The effects of deposition via the secondary energy minimum were demonstrated by the complimentary experiments in a packed bed filter and radial stagnation point flow (RSPF) system [119, 191-193]. In the RSPF system, the microorganisms (interpreted as “colloid particles”) captured via the secondary energy minimum are swept away by the radial flow component. The microorganisms captured via the primary energy minimum are left in the filter. There are mounting experimental evidences showing that the calculation of  $\alpha$  based on the deposition via the secondary energy minimum improves the accuracy of model predictions [92-94, 101, 103, 120]. The resulted collision efficiency from (30) is larger than that from (18), since Equation (30) takes into account for both the particles captured via the primary minimum and those via the second energy minimum.

### 3.4. Blocking Dynamics

In the classical CFT, the deposition of colloids is described as a kinetic process, reflecting the fact that for the most colloid particles, their attachment to the surface is irreversible [1, 12, 13, 186]. As a consequence, the kinetic equation of deposition (21) can also be written in terms of the fractional surface coverage  $\theta$ :

$$\frac{\partial \theta}{\partial t} = \pi r_s^2 k_d c \quad (31)$$

The accumulation of particles on the surface has its limits. In most cases, the rate of deposition declines as the retained particles block subsequent attachment. Due to the blocking effects, the kinetic equation of deposition rate is usually modified into:

$$\frac{\partial \theta}{\partial t} = \pi r_s^2 k_d c B(\theta) \quad (32)$$

where  $B(\theta)$  is the blocking function describing the probability of a particle contacting the unoccupied collector surface. It is a correction factor that accounts for the effects of blocking. The expressions of the blocking function may be of the two types: the Langmuir and the random sequential adsorption (RSA). The simplest Langmuir blocking function was produced by analogy with the Langmuir expression for molecular adsorption [194-197]:

$$B(\theta) = 1 - \varphi\theta \quad (33)$$

where  $\varphi$  is the normalized collector surface area which is blocked by an attached particle, namely the ratio of the average excluded area to the projected particle area  $\pi r_s^2$ . Parameter  $\varphi$  is also referred to as the parameter of excluded area. It can be inferred from the limit of

$B(\theta) = 0$  that  $\varphi$  equals to the reciprocal of the maximum surface coverage  $\theta_{\max}$  or the jamming limit.

The Langmuir blocking function is usually applied for the description of adsorption of the point-sized molecules, such as solute ions. Such a function may be insufficient to describe deposition of the finite-sized colloidal particles [195, 197]. A more advanced blocking function accounting for the areal dimension and interaction of the attached particles is desirable for colloid filtration processes. Schaaf and Tabot proposed an expression of the blocking function based on the random sequential adsorption mechanism [197]. Their blocking function is based on a virial expansion of the surface exclusion to third order in density and may be applied to “hard” spheres attached to flat surfaces. This expression was generalized onto the double-layer interactions (“soft”) between colloids and onto more complex collector geometry [195, 198]:

$$B(\theta) = 1 - 4(\theta_{\infty}\varphi\theta) + \frac{6\sqrt{3}}{\pi}(\theta_{\infty}\varphi\theta)^2 + \left(\frac{40}{\sqrt{3}\pi} - \frac{176}{3\pi^2}\right)(\theta_{\infty}\varphi\theta)^3 \quad (34)$$

where  $\theta_{\infty}$  is the jamming limit for hard spheres. This extended blocking function applies to only surface coverage below 80% of  $\theta_{\max}$ . For the coverage above this value, separate expression is applied [195, 198]:

$$B(\theta) = \frac{(1 - \varphi\theta)^3}{2m^2\varphi^3} \quad (35)$$

where  $m$  is the jamming limit slope which can be determined from the experimental breakthrough curves [195].

### 3.5. Surface Charge Heterogeneity

Most natural and engineered porous media exhibit surface charges when immersed in water or water solutions of the different salts [199]. The origins of the surface charges include the ionic substitution within the crystal lattice of minerals, complexation or ionization of surface functional groups, or specific adsorption of ions onto solid surfaces [1, 200]. The internal surfaces of the porous media are inherently heterogeneous due to physical and chemical imperfections, such as cracks, edges, lattice defects, and chemical impurities [12, 13, 201]. The natural porous media may also possess a composite structure consisting of different minerals [202]. The second type of surface charge heterogeneity stems from colloid surface roughness and colloid size distribution.

#### 3.5.1. Geochemical Heterogeneity

The effects of surface charge heterogeneity in porous media have been introduced into the classical CFT via nominal surface potential [1, 12, 73, 203, 204]. The nominal potential is

a homogeneous analog of the heterogeneously charged surface. It is equal to the potential of a homogeneous surface which exhibits the same double-layer interactions as the heterogeneous surface considered. The nominal potential is determined by the distribution of the surface potentials at different sites of the surface. There are two approaches to characterize the surface charge distribution: patchwise heterogeneity and random heterogeneity [73].

In the patchwise heterogeneity approach, the surface sites in the porous medium are grouped into macroscopic patches, each of which can be deemed to a homogeneous surface [73, 203]. It is assumed that the patches are isolated homogeneous surfaces in contact with the bulk solution. Interactions at the patch boundaries are neglected.

In the random heterogeneity approach, the equipotential sites are assumed to be distributed randomly over the entire surface [73, 203]. A random distribution can be applied to the collectors that do not possess obvious large patches, such as glass beads and other amorphous materials. A truncated normal distribution of the surface potentials (without unphysical negative “tail”) is most often used in this approach.

The nominal surface potential is calculated as the mean surface potential of the heterogeneous surface. The resulted nominal surface potential can be used for calculating the overall single collector removal efficiency. The single collector removal efficiency for the geochemically heterogeneous medium can be calculated by:

$$\eta = \sum_i \lambda_i \eta_i, \quad (36)$$

for the patchwise heterogeneity, or

$$\eta = \int \eta(\Phi) p(\Phi) d\Phi, \quad (37)$$

for the random heterogeneity, where  $\lambda_i$  is the surface fraction of *i*th patch for the patchwise heterogeneity, and  $p(\Phi)$  is the distribution of surface potentials for the random heterogeneity. The calculation of single collector removal efficiency can be coupled with the blocking dynamics, where a blocking function is assigned to each patch [12, 204].

It was shown by Elimelech and his co-authors [204] that the most sensitive factor that controls the deposition behavior is the geochemical heterogeneity determined by parameters  $\lambda_i$  in Equation (36) and distribution  $p(\Phi)$  in Equation (37). The deposition behavior is relatively insensitive to the ionic strength and the mineral grain surface potentials [204].

It is worth mentioning that geochemical heterogeneity of the porous surface alone does not give rise to non-exponential deposition from a strictly monodisperse suspension, since only one filtration coefficient enters the mass balance equation.

In practice, even the best prepared monodisperse suspensions possess a certain degree of polydispersity. This creates a possibility for the different particles to interact with the different parts of the heterogeneous surface and, thus, to be filtered in different ways. This mechanism is usually assumed to create hyperexponential deposition profiles even during filtration of seemingly uniform suspensions in microscopically heterogeneous porous media.

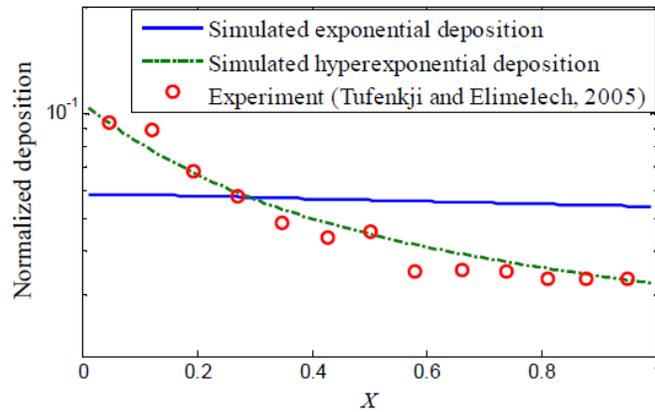


Figure 5. Simulated exponential and hyperexponential deposition [104] and experimental deposition [103].

### 3.5.2. Particle Population Heterogeneity

As discussed above, particles may be captured via the secondary energy minimum under unfavorable attachment conditions. The resulted collision efficiency is several orders of magnitude larger than that predicted from accounting only for the primary energy minimum and matches the experimental observation better [92-94, 101, 103, 120]. A nominal potential as a homogeneous analogue can be applied to incorporate the geochemical heterogeneity effects. In spite of this improvement, the predicted deposition decays are still exponential. Meanwhile, hyperexponential deposition profiles are observed in the presence of repulsive double-layer interactions [101, 103, 110, 205, 206]. The exponential deposition is revealed as a straight line in the logarithmic plot, while hyperexponential deposition is depicted by a concave line, as illustrated in Figure 5. Exponential decay of deposition is the standard solution to the advection-dispersion equation with a single sink term for the deposition, as seen in Equation (24).

It was demonstrated by a number of authors that hyperexponentiality of the deposition profiles can be explained by the surface charge heterogeneity of particles [101, 103-105, 207, 208]. A more general approach to the deposition rates accounts for the particle capture via heterogeneous energy minima. The particle population should be represented by at least two kinds of particles, one of which is subject to faster deposition (e.g. via the secondary energy minimum) and the other deposits slower (e.g. via the primary energy minimum).

A bimodal distribution of the filtration coefficients is typically applied to describe this type of heterogeneity.

Other distributions, such as log-normal in (38) and power-law in (39), can also produce similar hyperexponential deposition profiles:

$$p(\lambda) = \frac{1}{\lambda\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln \lambda - \mu)^2}{2\sigma^2}\right] \quad (38)$$

$$p(\lambda) = \lambda^{-b} \quad (39)$$

Here,  $p(\lambda)$  is the probability density function (PDF),  $\mu$  and  $\sigma$  are the mean and the standard deviation for the log-normal distribution.  $b$  is the power in the power-law distribution controlling the shape of the PDF curve.

Instead of a single deposition rate for the whole particle population, a separate transport equation for each kind of particles (corresponding to each separate value of the filtration coefficient).

Many authors [101, 103-105, 186, 207, 208] conclude that the distribution of filtration coefficients is sufficient and necessary to produce the hyperexponential deposition decay caused by the surface and the surface charge heterogeneity. Apart from the colloid deposition in geochemically heterogeneous porous media, the particle population heterogeneity approach can be also applied to describe particles with a wide size distribution and particle surface roughness.

The particle population approach can express the heterogeneity effects directly while the nominal potential approach can only resemble the heterogeneous population with a homogeneous analogue.

### 3.6. Physical Heterogeneity

#### 3.6.1. Straining

Another explanation for the deposition hyperexponentiality is the straining of the particles due to the physical heterogeneity at the pore scale [79, 81, 109, 115, 118, 121, 209]. Straining is the physical screening of particles by the porous medium, such as particle retention at the collector-collector contacts/constrictions. The retention of particles is enhanced in the low-velocity or stagnant zones.

Straining is often accompanied by the size exclusion, where the particles of the different sizes retain or deposit with the different rates. These phenomena are often treated as connected and even identical, although, strictly speaking, this is not always the case.

Straining and size exclusion are neglected in many traditional studies of colloid filtration at the collector scale, since they require analysis of the heterogeneous particle population. Pore scale observations, on the other hand, show that straining plays a significant role in the porous media with irregular-shaped pores or under unfavorable attachment conditions [55, 84, 109, 135, 210, 211]. Torque analysis at the pore scale can identify regions favorable for straining. Constrictions and grain-grain contacts, where flow may be slow or stagnant, are observed to be such regions. As a consequence, pore geometry and collector surface roughness determine the degree of straining.

Classical filtration theories treated the straining of particles as a pure physical phenomenon [95, 96, 212, 213]. A number of authors focused on the effects of colloid sizes, pore sizes, and pore geometry on the straining phenomena [95, 109, 118, 126, 212-214]. Geometrical models were developed to describe straining as a physical process [95, 212, 213]. The predicted straining threshold ratio  $r_s / r_c$  ranged from 0.05 to 0.154. However, it was found in the experiments that the straining effects could be significant even when the ratio  $r_s / r_c$  is as small as 0.002~0.008 [109, 118, 126, 214].

On the macro-level, colloid filtration with straining may be modeled by a dual-permeability model [122] or a physical non-equilibrium model [134], which accounts for the particles flowing in the high-velocity and the low-velocity regions, respectively. In the works [155-157], size exclusion is described as a random process involving interacting distributed populations of particles and pores. The simplest approach to account for straining in colloid filtration is based on the consideration of the accessibility of pore networks. Bradford and his co-authors [121] expressed the straining rate as a function of the penetration depth:

$$\frac{\rho_b}{\phi} \frac{\partial s}{\partial t} = (\psi_{att} k_{att} + \psi_{str} k_{str}) c \quad (40)$$

where  $\psi_{att}$  is a dimensionless parameter accounting for attachment ripening, blocking (such as the blocking function  $B(\theta)$ ), and others  $k_{att}$  and  $k_{str}$  are attachment and straining rate constants.  $\psi_{str}$  is a parameter of straining depending on the depth:

$$\psi_{str} = \left( \frac{2r_c + x}{2r_c} \right)^{-\omega} \quad (41)$$

where  $\omega$  is a fitting parameter that controls the shape of the spatial distribution of deposition. The depth dependency is explained in the following way: Straining of particles causes the blocking of the thin pores close to the inlet. It re-directs the colloid flow to a network of larger pores, resulting in bypassing thin pores at the downstream. As a consequence, the straining effect is strongest at the inlet ( $x=0$ ,  $\psi_{str} = 1$ ), and it decreases with depth. It was suggested in [118, 121, 215] that an integral model involving both straining and attachment is more realistic, especially in the system with intermediate particle and collector sizes.

As discussed above, the geometrical models based on the physical description of straining failed to predict the straining threshold ratio. On the other hand, a number of authors [79, 115, 135, 216] noticed that straining was also influenced by the chemical conditions, along with physical. In [136], we proposed an approach to colloid migration based on both the attachment conditions and hydrodynamics. Under unfavorable attachment conditions, the attached particles via weak association (secondary energy minimum) are subject to hydrodynamic drag from the fluid and migrate to the region that is chemically (attachment via the primary minimum) and physically (straining) favorable for deposition [3, 112, 135, 136]. The approach for incorporating straining effects into the CFT should take into account both the physical and the chemical factors influencing the process, such as the pore and particle size distributions, hydrodynamics, and solution chemistry.

### 3.6.2. Non-Fickian Transport

The third explanation for the deposition hyperexponentiality is distribution of the particle times of flight and residence times, resulting in the non-Fickian character of particle

dispersion in porous media [11, 104, 105, 125, 217-222]. This mechanism is to some extent similar to the physical straining, since they both consider longer residence times for the particles in low-velocity regions. However, the non-Fickian transfer mechanism describes also particles that travel faster than the average particle velocity, as seen in Figure 6. As a result, the non-Fickian transport gives rise to more dispersed breakthrough curves for pulse injection and hyperexponential deposition profiles [104, 105, 123, 217, 218].

Two approaches have been commonly applied for modeling the non-Fickian transport of colloids in porous media: the continuous time random walk (CTRW) approach and the elliptic equation approach as an important reduction of the CTRW [104, 105, 217-219, 223]. The CTRW approach, as many other developments in stochastic processes, has started from the famous works of Einstein, Langevin and Smoluchowski about Brownian motion of the particles [224-227] (see extensive discussion in Ref. [228]).

In terms of physical effects, a major difference between the CTRW and the previously considered approaches is consideration of the particle residence time distribution accounting for the small-scale heterogeneity effects on the transport.

The CTRW theory has been extensively applied to describe the non-Fickian transport of tracers in porous media [10, 11, 117, 124, 125, 221]. Colloid transport and particle deposition were considered in several CTRW works, mainly, based on the elliptic equation approach [104, 105, 123, 217, 218, 220]. The CTRW approach was capable of describing some phenomena that were previously interpreted as the action of the different other physical mechanisms. In particular, the long tails in the breakthrough curves were usually interpreted as a result of reversible deposition [111, 112]. The deposition hyperexponentiality could also be interpreted as a result of straining [79-81, 114, 115]. The effect of non-Fickian transport provides alternative or additional explanation for these experimental observations.

Until now, the physical picture of particle deposition adopted within stochastic approaches was rather incomplete. Such phenomena as migration of deposited particles or distinction between strained and attached particles have not been considered. A more comprehensive stochastic model that can incorporate the migration of deposition, the straining, and the non-Fickian transport effects is desirable.

It has been shown that the CTRW description of tracer and particle flow may be reduced into an elliptic partial differential equation in the limit of infinitely many infinitesimal step lengths and residence times [217].

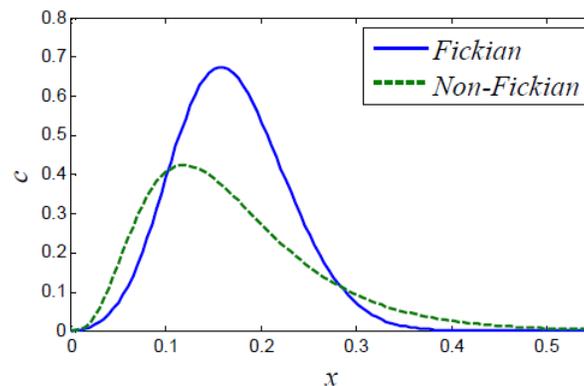


Figure 6. Concentration distribution of a pulse injection.

Unlike the full CTRW approach, such an equation needs only characteristic information from the residence time distribution, the variance and the mean value. As a result, the elliptic equation can be solved numerically and even analytically for some 1-D flow problems [123, 218]. The elliptic equation for transport is given by [217, 218]:

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} + D_t \frac{\partial^2 c}{\partial t^2} - \frac{\rho_b}{\phi} \frac{\partial s}{\partial t} \quad (42)$$

where  $D_t$  is called the temporal dispersion coefficient, which is defined as the ratio between the variance and the mean of the particle residence time distribution. Furthermore, the elliptic equation was coupled with the distribution of filtration coefficients representing the particle population heterogeneity [104, 105].

Experimental verifications of the stochastic approach were extensively discussed in Refs [10, 11, 104, 105, 124, 125, 220-223], although most of the CTRW applications were to the tracer flows. A growing body of evidence shows that the CTRW is able to catch the three important effects that were observed in experiments [10, 11, 223] and in the nature [124, 220, 221], but cannot be adequately described by the ADE: 1) Under pulse injection, the maximum of concentration moves slower than the flow rate of the carrying fluid; 2) The concentration distribution around the maximum is asymmetric, and 3) The forward “tail” of the concentration distribution contains much more particles and decreases much slower than predicted by the traditional approach. The authors showed that the elliptic equation approach excels the Fickian approach in matching both the breakthrough curves and deposition profiles for highly heterogeneous porous media.

For nearly homogeneous or slightly heterogeneous porous media, the elliptic or CTRW formalism is not necessary, but the particle distribution should sometimes be introduced for modeling the deposition curves. This requires the application of the population balance approach [104, 105].

### 3.7. Migration of Deposited Particles

Release and migration of deposited colloids, such as microorganisms in aquifers and clay fines in oil reservoirs, is of considerable importance in some environmental and engineering applications. For example, detachment of pathogenic microbes can pose great risk to public health [22-31]. Migration of reservoir fines during water flooding can cause severe permeability damage, which subsequently reduces injectivity and productivity of the injection and production wells, correspondingly [34-38, 229, 230].

#### 3.7.1. Mechanisms of Colloid Release

Colloid release in environmental systems has been attributed to physical, chemical, or biological processes. Particles may also be produced from the erosion of porous media, such as acid treatment for well stimulation in oil reservoirs [231-234].

Specifically, physical perturbations of the rock in the course of reservoir development include drilling wells, sampling, rapid infiltration, waterflooding, water production, and

others [235-237]. Chemical perturbations include increase of pH, decrease of salinity, generation of surfactants, and others [34-37, 40, 229, 238-243]. Generation of surfactants is also regarded as a biological perturbation since surfactants may be produced by microbes [40, 243]. Bacteria-forming large aggregates at grain-grain contacts which are re-entrained by flowing fluid is another example of biological perturbation [80].

At the collector scale, a study of colloid release usually focuses on the torques exerted on the attached particles [9, 35, 216, 241, 244, 245]. It has been demonstrated that the balance of the hydrodynamic torque, the lifting torque, the resisting adhesive torque and the torque of the gravity force determines whether the particles attached to the pore walls will be immobilized and re-entrained into the carrying fluid, as seen in Figure 7. The erosion number, a dimensionless parameter indicating the ratio between the torques for the detachment and the attachment of particles, can be expressed in the following way:

$$\varepsilon = \frac{F_l l_n + F_d l_d}{(F_e + F_g) l_n} \quad (43)$$

where  $F_l, F_d, F_e$ , and  $F_g$  are respectively the lifting force, the hydrodynamic drag, the electrostatic force, and the gravity exerting on the particles attached to the pore walls.  $l_d$  and  $l_n$  are respectively the levers of drag and normal forces.

A mechanistic model has been proposed by Bedrikovetsky and his co-workers [241, 245] to express the maximum deposition concentration as a function of the particle size, the pore size, the ionic strength, the fluid velocity and a number of other factors. The model assumes that the attached particles will release if the detachment torques are larger than the adhesive torques ( $\varepsilon > 1$ ). A good agreement has been observed between the model prediction and the experimental injectivity decline [245].

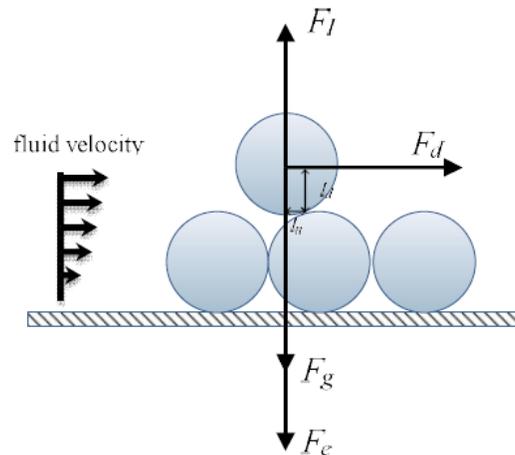


Figure 7. Forces exerted on the attached particles.

### 3.7.2. Effects of Colloid Migration

At the pore scale, the migration of colloids is often coupled with other processes, such as re-entraining back into fluid and straining at throats and constrictions, as seen in Figure 8. As a result, the released particles may be re-entrained by the bulk fluid and migrate further to the downstream or subsequently strained at thin pore throats. The release of attached particles may give rise to permeability increase to a small degree, while the subsequent straining usually causes severe permeability damage [34, 37, 229, 240, 246].

It has been shown by Bedrikovetsky and his co-authors [240] and Yuan and Shapiro [229] that the effects of fines migration induced by low salinity waterflooding may be used as a mobility control technique to alter the flow field in layer-cake petroleum reservoirs.

In the cases where deposited colloids are associated with low-solubility contaminants in water and straining is insignificant, the re-entrainment of deposited colloids is a major reason for the long distance migration of the contaminant, such as the migration of plutonium associated particles observed in [16]. It can be inferred from the torque balance analysis (43) that the larger particles attached to the collector surface are more subject to release and migration under unfavorable attachment conditions.

In such cases, long tails of the breakthrough curves after the end of particle injection are usually observed, while the deposition concentration may be non-monotonously distributed along the column [80, 111, 135, 136]. In the cited works, migration of released colloids is described as a third particle population migrating with a different rate and probably re-entrapped.

Such a model captures non-monotonous particle deposition profiles. Bradford and his co-workers [80] found that the colloid release is not limited to the attached particles (in their study, bacteria *E. coli*), but may also stem from large *E. coli* aggregates at straining sites.

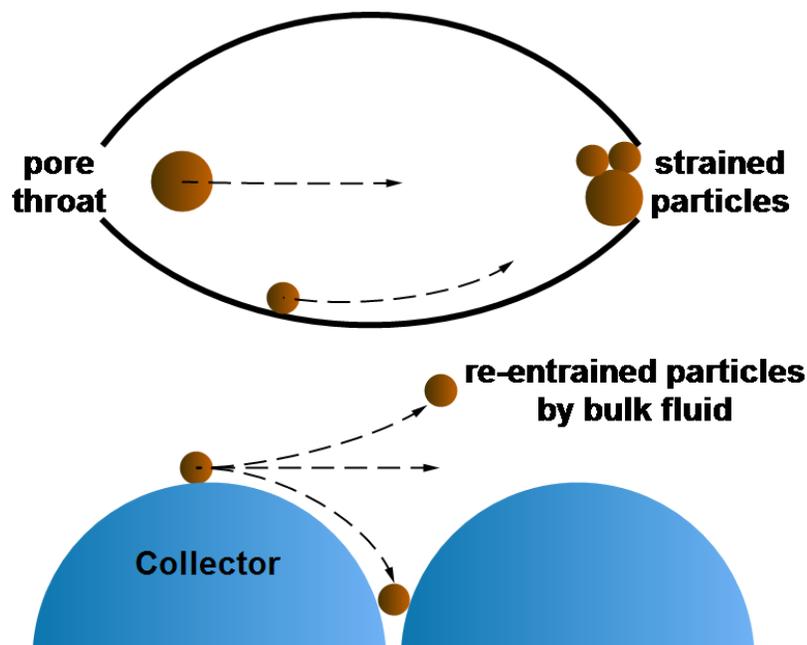


Figure 8. Migration of deposition coupled with other processes.

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