CHAPTER III

CONCEPTUAL APPROACH

3.1. CONCEPTUAL MODEL

The starting point to propose a conceptual model of clogging is to understand the physics of the problem. Clogging refers to the modification of porosity or infiltration area as a result of a combination of the following five elementary processes (PÉREZ-PARICIO & CARRERA, 1999a):
- attachment/detachment of suspended particles;
- bacterial growth;
- precipitation/dissolution of minerals;
- formation/dissolution of gas;
- compaction of the clogging layer.

The five individual processes have to be included in the mathematical framework. But this is not sufficient, since it is necessary to transform those processes into porosity changes. Clogging occurs when the concentration of the so-called generic minerals increases (diminishes), leading to a reduction in porosity and an equivalent diminution (increment) of intrinsic permeability. Generic minerals are the solid phases causing clogging. In this model, they include retained particles, bacteria and *true* or precipitated minerals. All of them are solids attached to the porous matrix.

Temperature is also a key factor affecting water viscosity, the rate of kinetic chemical reactions and the rate of growth of microbial populations. Table 3.1. contains a summary of the main species[a], basic laws and how clogging is considered in the model. Basically, the porous medium is assimilated to a continuum formed by three phases: liquid, solid and gas (Figure 3.1.). The liquid phase includes water, dissolved gas, suspended particles and dissolved species (solutes). Bacteria are not currently considered in the liquid phase because they are most frequently attached to the solid matrix and, from the point of view of clogging, mobile bacteria are not relevant. As mentioned in Chapter 2, only about 1 % or less of bacteria are in suspension and transported with groundwater. The solid phase contains the matrix, attached bacteria (and biofilm) and particles, and precipitated minerals. The gaseous phase contains gaseous species, mostly oxygen, carbon dioxide, water vapour and nitrogen.

Evaluating clogging consists of solving the following conceptual steps sequentially:
1. Liquid and gas pressures are calculated. Hydraulic gradients and Darcy's velocities are subsequently obtained for chemical computations.
2. Suspended particles, heat (temperature, which is assumed identical for the three phases) and solutes are transported throughout the medium. All of them are referred to as mobile species.
3. Processes of attachment/detachment of particles, bacterial growth/die-off and mineral precipitation/dissolution are kinetically evaluated based on the concentrations of the aqueous,

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[a] A chemical system is formed by atomic constituents or elements. A chemical species is defined as any chemical entity that can be distinguished from the rest by one of the following properties: (1) its elemental composition and (2) the phase at which it is present. This means that carbon dioxide in the gaseous phase, $CO_{2(g)}$, is different than dissolved carbon dioxide, $CO_{2(l)}$. But not all species are required to fully characterise a chemical system. The subset of species that is strictly needed to describe the system (basis of the system) can be arbitrarily chosen among all species. In principle, the atomic constituents could serve as a set of components, but this would be useless from the practical perspective. Instead, it is convenient to select a subset of the chemical species, known as primary species.

mobile species. The concentration of generic minerals is, thus, dependent on the concentration of mobile species.

4. Porosity is updated according to the changes of generic minerals concentration.
5. Intrinsic permeability is also updated through Kozeny-Carman equation.
6. The cycle is repeated for the next time increment.

Table 3.1. Main features of the proposed conceptual model that is the basis of the code.

|	LIQUID	GAS	SOLID

SPECIES	• Water
	• MOBILE SPECIES:
	  -Dissolved gases
	  -Suspended particles
	  -Solutes (dissolved)
		-Gaseous species	Aquifer matrix
			GENERIC MINERALS:
			  -Retained particles
			  -Attached bacteria
			  -True minerals

BASIC LAWS	• Flow: Darcy's law • Exchange with gas: • Henry's law • Dispersion: Fick's law • Mass conservation of all species	• Flow: Darcy's law • Exchange with the liquid: Henry's law	Sink/source kinetic terms: particles bacteria minerals

CLOGGING	• Clogging-agents
	  Carried by liquid
	• Permeability:
	  Function of porosity
	  and saturation degree
		The presence of gas reduces water saturation	Porosity reduced by:
			-Retained particles
			-Bacterial growth
			-Precipitation of minerals
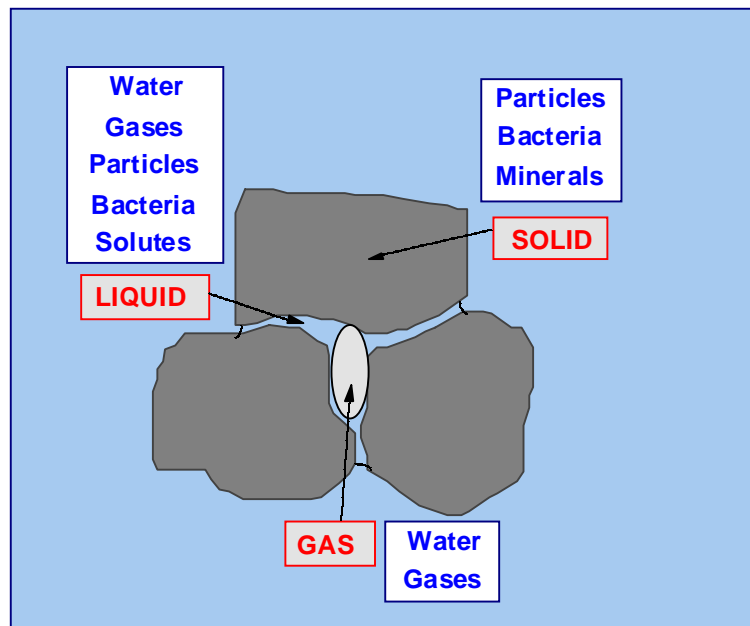
Figure 3.1. Schematic plot of the considered phases and species.
The conceptual model includes three phases (liquid, solid and gas, in upper case), each of them containing different species (lower case).

3.2. MATHEMATICAL FRAMEWORK

This section presents a summary of the basic equations. A classical deterministic approach was selected to translate the conceptual model into a mathematical model. Mass balance equations have been written for the different components[b] within the aquifer.

In this way, liquid and gas pressures are obtained first by appropriate water and gas balances, together with the vector of solid displacement (provided that compaction/deformation is significant) and the temperature (assuming the same temperature for the three phases at a given point). Then, reactive transport of solutes and suspended particles follows. Reactive transport can take place under equilibrium and kinetic conditions. The latter is particularly important for clogging, because it implies that rate-controlled relationships must be used, as concentration changes of generic minerals commonly proceed at a finite rate. Generic minerals include retained particles, bacteria and precipitated (true) minerals.

As a consequence, the change in concentration of the generic minerals is a function of:
- The concentration of the catalysts, which accelerate reaction rates.
- The concentration of other mobile species that slow down or inhibit reactions. For instance, anaerobic bacteria are extremely sensitive to the presence of oxygen.
- Empirical parameters, such as surface area, kinetic rates, etc.

In general terms, it is important to note the main features of the model:
1. Three phases are considered: aqueous, gas and solid. Each one contains various species.
2. Flow of liquid and gas phases determined by Darcy's Law.
3. Deformation of the solid matrix. Solid displacements are calculated for a given (user-selected) mechanical constitutive model.
4. Transport of suspended particles, chemical species (solutes) and heat using the advection-dispersion equation with reactive terms. Bacteria are not transported, but grow attached to the medium at the present stage of the model.
5. Kinetic approach for attachment/detachment of particles, for precipitation/dissolution of species (also possible in equilibrium) and for bacterial growth attached to the matrix. Both heterogeneous (between different phases) and homogeneous reactions can be dealt with.
6. Intrinsic permeability changes are obtained from porosity variations by means of the equation of Kozeny-Carman.

The mathematical framework is presented in the next paragraphs. Prior to describing the specific equations that control the kinetics of generic minerals, the basic equations governing flow and transport are described in the first section (3.2.1.). Gas flow and compaction are included in this description. Then, section 3.2.2 presents a compact formulation, derived by SAALTINK ET AL. (1998a), that simplifies the notation of the model equations. The adopted formulation allows to write the transport equation and the chemical reactions in a concise way by using the tensor notation. Finally, section 3.2.3. gives all the details needed to characterise the kinetics of physical, biological and chemical clogging. and how they affect the properties of the porous medium. It will be shown that reactions affecting generic minerals –attachment/detachment of particles, growth/decay of bacteria and precipitation/dissolution of minerals- can be described by means of a unique, generalised equation.

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[b] Components are defined in such a way that every species can be uniquely represented as a combination of one or more components. The total mass of a component can be distributed over the various chemical species. For instance, in a classical carbonated system the total mass of calcium is distributed over two species: calcium ion and calcium carbonate. The mass of a component equals the analytical determination.

3.2.1. BASIC EQUATIONS

Liquid and gas pressures are obtained by performing mass balances of water and air within the porous medium. The mass balance affects components, not phases. For instance, a mass balance for water is made, which means that water it includes water in different species (in the liquid, gas and solid phase). In general, it can be expressed as follows:

$$\frac{\partial}{\partial t}\left[\rho_l w_l^j S_l \phi + \rho_g w_g^j S_g \phi + \rho_s w_s^j (1-\phi)\right] +$$
$$+ \nabla \cdot \begin{bmatrix} \rho_l w_l^j \mathbf{q}_l + \rho_l w_l^j S_l \phi \mathbf{u} - \mathbf{D}_l^j \nabla w_l^j + \\ \rho_g w_g^j \mathbf{q}_g + \rho_g w_g^j S_g \phi \mathbf{u} - \mathbf{D}_g^j \nabla w_g^j + \\ \rho_s w_s^j (1-\phi)\mathbf{u} - \mathbf{D}_s^j \nabla w_s^j \end{bmatrix} = f_{s/s}^j \qquad [3.1.]$$

where the superscript *j* refers to the component (water or air) and subscript α indicates the phase (where $\alpha=l,g,s$ stands for the liquid, gas or solid, respectively). The rest of variables are the phase density, ρ_α [ML^{-3}]; the mass fraction of species per unit mass of phase, w_α^j [L^0]; the degree of saturation, S_α [L^0]; Darcy's velocity, $\mathbf{q}_\alpha$ [LT^{-1}]; porosity, ϕ [L^0]; the dispersion tensor times density, $\mathbf{D}_\alpha^j$ [ML^{-1}T^{-1}]; the displacement velocity of the aquifer matrix due to the deformation of the solid skeleton, $\mathbf{u}$ [LT^{-1}]; and a sink/source term, $f_{s/s}^j$ [ML^{-3}T^{-1}].

As for the balance of momentum for the porous medium, it reduces to the equation of stress equilibrium if inertial terms are neglected (OLIVELLA ET AL., 1994):

$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{b} = \mathbf{0} \qquad [3.2.]$$

where $\boldsymbol{\sigma}$ [ML^{-1}T^{-2}] is the stress tensor and $\mathbf{b}$ [ML^{-2}T^{-2}] is the vector of body forces (per unit volume). By providing an adequate constitutive model, equation [3.2.] can be transformed into an expression in terms of the solid velocities, fluid pressures and temperature. Here it is only interesting to note that such a model leads to a compatibility condition between the total strain rate and solid velocities (**u**), as indicated in Chapter II.

Heat transport is evaluated by means of an energy balance within the system, for the three phases. Here, this is mathematically written in terms of internal energy. Provided that temperature is the same for all phases, a unique equation for total energy (per unit volume) is required:

$$\frac{\partial}{\partial t}\left[E_l \rho_l S_l \phi + E_g \rho_g S_g \phi + E_s \rho_s (1-\phi)\right] +$$
$$+ \nabla \cdot \begin{bmatrix} -\lambda \nabla T + \mathbf{j}'_{El} + E_l \rho_l S_l \phi\, \mathbf{u} + \mathbf{j}'_{Eg} + \\ E_g \rho_g S_g \phi\, \mathbf{u} + \mathbf{j}'_{Es} + E_s \rho_s S_s (1-\phi)\, \mathbf{u} \end{bmatrix} = f_{s/s}^E \qquad [3.3.]$$

where E_α [L^{2}T^{-2}] is the specific internal energy corresponding to each phase; λ [MLT^{-3}K^{-1}] is the tensor of thermal conductivity, defined in Fourier's law; T [K] is absolute temperature; $f_{s/s}^E$ [ML^{-1}T^{-3}] accounts for sink/source terms, and $\mathbf{j}'_{E\alpha}$ [MT^{-3}] represents the advective energy fluxes for phase α with respect to the solid phase. They are defined as follows:

$$\mathbf{j}'_{El} = \mathbf{j}_l^h E_l^h + \mathbf{j}_l^w E_l^w + \mathbf{j}_l^a E_l^a = (\mathbf{i}_l^h + w_l^h \rho_l \mathbf{q}_l) E_l^h + (\mathbf{i}_l^w + w_l^w \rho_l \mathbf{q}_l) E_l^w + (w_l^a \rho_l \mathbf{q}_l) E_l^a$$

$$\mathbf{j}'_{Eg} = \mathbf{j}_l^w E_g^w + \mathbf{j}_l^a E_g^a = (\mathbf{i}_g^w + w_g^w \rho_g \mathbf{q}_g) E_g^w + (\mathbf{i}_g^w + w_g^w \rho_g \mathbf{q}_g) E_g^w \qquad [3.4.]$$

$$\mathbf{j}'_{Es} = \mathbf{j}_s^h E_s^h + \mathbf{j}_s^w E_s^w = \mathbf{i}_s^h E_s^h + \mathbf{i}_s^w E_s^w$$

where E_α^j [$L^2 \cdot T^{-2}$] is the specific internal energy of species j ($j=a,w,h$) within phase α ($\alpha=l,g,s$) and $\mathbf{i}_\alpha^j$ [$M \cdot T^{-3}$] is the nonadvective flux of species j in phase α. Further details are given in Olivella et al. (1994), but it is enough to explain that the sum of nonadvective fluxes within each phase is constraint according by the following equation:

$$\sum_j \mathbf{i}_\alpha^j = \mathbf{0} \qquad [3.5.]$$

The final type of equations is the mass balance of mobile species or classical transport equation. If component j is only present in the liquid phase, the following mass balance can be written per unit of aquifer volume:

$$\frac{\partial}{\partial t}\left[w_l^j \rho_l S_l \phi\right] + \nabla\left[w_l^j \rho_l \mathbf{q}_l + w_l^j \rho_l S_l \phi \mathbf{u} - D_l^j \nabla w_l^j\right] = f_{s/s}^j + \sum_{m=1}^{N_{eq}} S_{eq}^{mj} r_{eq}^m + \sum_{m=1}^{N_{kin}} S_{kin}^{mj} r_{kin}^m \qquad [3.6.]$$

The first term in equation [3.6.] represents storage variation. The second term comprises fluid flux due to advection, solid deformation and dispersion. The right-hand side includes the external sink/source of species j, $f_{s/s}^j$ [$ML^{-3}T^{-1}$], and an additional sink/source term, r_{eq} and r_{kin} [$ML^{-3}T^{-1}$], which account for the N_{eq} chemical reactions in equilibrium and the N_{kin} kinetics reactions, respectively; superscript m refers to the generic mineral. Stoichiometric coefficients, expressed by S_{eq} and S_{kin}, link mineral (equilibrium or kinetic) concentration changes to solute concentration changes. These reaction rates, in general, depend on the concentration of aqueous species and generic minerals. The choice of equilibrium or kinetics is a function of the velocity of reactions compared to flow velocity. If reactions are sufficiently fast, then equilibrium can be assumed; on the contrary, if the rate of reaction is a limiting factor, then kinetics has to be incorporated into the characterisation of the model.

Next, recalling the concept of total derivative, it is possible to rewrite [3.6.] in the following form:

$$\frac{D}{Dt}\left[w_l^j \rho_l S_l \phi\right] + \nabla\left[w_l^j \rho_l \mathbf{q}_l - D_l^j \nabla w_l^j\right] + \left[w_l^j \rho_l S_l \phi\right] \nabla \mathbf{u} = f_{s/s}^j + \sum_{m=1}^{N_{eq}} S_{eq}^{mj} r_{eq}^m + \sum_{m=1}^{N_{kin}} S_{kin}^{mj} r_{kin}^m \qquad [3.7.]$$

where the total or material derivative is defined by $\dfrac{D}{Dt} = \dfrac{\partial}{\partial t} + \mathbf{u} \cdot \nabla$

Developing the bracketed terms, we come to next expression:

$$\rho_l S_l \phi \frac{D w_l^j}{Dt} = \nabla\left[D_l^j \nabla w_l^j\right] - \rho_l \mathbf{q}_l \nabla w_l^j + f_{s/s}^j + \sum_{m=1}^{N_{eq}} S_{eq}^{mj} r_{eq}^m + \sum_{m=1}^{N_{kin}} S_{kin}^{mj} r_{kin}^m -$$
$$- w_l^j \left\{ \left[\frac{D}{Dt}(\rho_l S_l \phi) + \nabla(\rho_l \mathbf{q}_l) \right] + (\rho_l S_l \phi) \nabla \cdot \mathbf{u} \right\} \qquad [3.8.]$$

Finally, if the flow equation is applied to the water component (*j=w* in equation [3.1.]) and only the aqueous contribution is considered, then equation [3.1.] transforms into:

$$\frac{\partial}{\partial t}\left[\rho_1 w_1^w S_1 \phi\right] + \nabla \cdot \left[\rho_1 w_1^w \mathbf{q}_1 + \rho_1 w_1^w S_1 \phi\, \mathbf{u} - \mathbf{D}_1^w \nabla w_1^w\right] = f_{s/s}^w \qquad [3.9.]$$

Under the common assumption that $w_1^w \approx 1$, it is immediate that $f_{s/s}^w$ can be substituted into the last term of Equation [3.8.] to yield the final form of the transport equation,

$$\rho_1 S_1 \phi \frac{D w_1^j}{Dt} = \nabla\left[\mathbf{D}_1^j \nabla w_1^j\right] - \rho_1 \mathbf{q}_1 \nabla w_1^j + f_{s/s}^w\left[w_{i/o}^j - w_1^j\right] + \sum_{m=1}^{N_{eq}} S_{eq}^{mj} r_{eq}^m + \sum_{m=1}^{N_{kin}} S_{kin}^{mj} r_{kin}^m \qquad [3.10.]$$

where $w_{i/o}^j$ refers to the prescribed input/output of particles into/from the system, $f_{s/s}^w w_{i/o}^j = f_{s/s}^j$, which can be applied to Artificial Recharge.

3.2.2. A MORE COMPACT NOMENCLATURE FOR REACTIVE TRANSPORT

Equation [3.10.] is written in accordance with the classical reactive transport theory. The formulation implemented in the code makes use, though, of a more concise formulation in tensorial form (SAALTINK ET AL, 1998a and SAALTINK, 1999). Equation [3.10.] can be rewritten like this:

$$\frac{D\mathbf{w}_1}{Dt} = \mathbf{M}\cdot\Gamma(\mathbf{w}_1) + \mathbf{S}_{eq}\cdot\mathbf{r}_{eq} + \mathbf{S}_{kin}\cdot\mathbf{r}_{kin} \qquad [3.11.]$$

where $\mathbf{w}_1$ is the vector of all aqueous species; $\mathbf{M}$ is a diagonal matrix that controls whether the species is mobile or immobile; Γ is a linear operator comprising the advection, dispersion and prescribed sink/source terms; $\mathbf{S}_{eq}$ and $\mathbf{S}_{kin}$ are the stoichiometric matrices for equilibrium and kinetic reactions; and $\mathbf{r}_{eq}$ and $\mathbf{r}_{kin}$ are the vectors of reaction rates for equilibrium and kinetic reactions, respectively. All proportionality factors have been included into the different matrices.

The method applied by SAALTINK ET AL. (1998a) consists in reducing the number of unknowns from the initial number of species (N_{spe}) to the reduced primary species, $N_{spe}-N_{eq}-N_{ca}$, i.e. the initial number minus the number of chemical equilibrium reactions (N_{eq}) and the number of constant activity species (N_{ca}). This is carried out in two steps:
(1) Eliminating the term of equilibrium reaction rates by means of the component matrix, $\mathbf{U}$. This matrix relates the total concentration of the components to the concentration of dissolved species. Every species can be uniquely represented as a combination of one or more components (YEH & TRIPATHI, 1989). An important feature is that all primary species consist of only one component. The component matrix can be split up into different parts, each referring to a group of species: $\mathbf{U}_{aqu}$, $\mathbf{U}_{ads}$ and $\mathbf{U}_{min}$ are, respectively, the component matrices for dissolved, sorbed and mineral species.
(2) Eliminating the concentrations of constant activity species through an elimination matrix, $\mathbf{E}$., which is the kernel of the component matrix for mineral species, i.e. $\mathbf{E}\cdot\mathbf{U}_{min}=\mathbf{0}$.

With these manipulations, equation [3.11.] finally becomes:

$$\mathbf{E}\,\mathbf{U}_{aqu}\,\frac{D\,\mathbf{w}_l^{aqu}(\mathbf{w}_l^{pri})}{D\,t} = \mathbf{E}\,\mathbf{U}_{aqu}\mathbf{M}\,\Gamma(\mathbf{w}_l^{aqu}(\mathbf{w}_l^{pri})) + \mathbf{E}\,\mathbf{U}\,\mathbf{S}_{kin}^t\cdot\mathbf{r}_{kin}(\mathbf{w}_l^{pri}) \qquad [3.12.]$$

where $\mathbf{w}_l^{aqu}$ is the vector of aqueous (dissolved) species and $\mathbf{w}_l^{pri}$ is the vector of reduced primary species that are the degrees of freedom of the system.

3.2.3. SPECIFIC KINETIC EQUATIONS

This section focuses on the reactive expressions for physical, biological and chemical clogging, as well as equations to update porosity and intrinsic permeability as a result of changes in the system.

In general, the mass balance for a generic mineral m can be expressed as follows:

$$\frac{\partial w_s^m}{\partial t} + \nabla\cdot\left[w_s^m\mathbf{u}\right] = f_{s/s}^m(\mathbf{w}) \qquad [3.13.]$$

where the sink/source term of the generic mineral, $f_{s/s}^m$ may depend on the concentration of all chemical species of the system, as indicated by the vector $\mathbf{w}$. This production/decay term is intimately associated to the sink/source term of the aqueous species in Equation [3.10.], which was denoted r_{kin} for kinetics reactions such as the ones investigated here. Notice that the mineral concentration is now expressed per unit bulk volume of the aquifer for the sake of simplicity.

After a simple algebraic manipulation and the use of the definition of the total derivative, it is possible to obtain the generic form of the equation for mineral m:

$$\frac{D\,w_s^m}{D\,t} = -\left[\nabla\cdot\mathbf{u}\right]w_s^m + f_{s/s}^m(\mathbf{w}) \qquad [3.14.]$$

Therefore, the problem restricts to defining the explicit mathematical expression of the production/decay ($f_{s/s}^m$) term for each type of generic mineral. This is done in section 3.2.2.1. for physical clogging, section 3.2.2.2. for biological clogging and section 3.2.2.3. for chemical clogging. Superscripts p, x and m, respectively, are used for particles, bacteria and precipitated minerals..

3.2.3.1. *Physical Clogging*

The model adopts a classical macroscopic equation (RAJAGOPALAN & CHU, 1982; ADIN & REBHUN, 1987) to quantify the attachment/detachment of particles,

$$f_{s/s}^p(w_l^i) = \frac{\partial w_s^p}{\partial t} = \lambda_a' w_l^p - \lambda_d' w_s^p \qquad [3.15.]$$

where superscript p applies to particles. λ_a' [T^{-1}] and λ_d' [T^{-1}] are the attachment and detachment coefficients. The mathematical form of both coefficients, with the form implemented in the model, is explained below.

- *Attachment*

As discussed in Chapter 2, attachment can be caused by six different mechanisms. The relative importance of such mechanisms is dictated by the particle size (diameter). Three categories of particles can be distinguished based on this criterion:

(1) Large particles, whose diameter is larger than 30 μm, are primarily subjected to volumetric forces such as inertia, sedimentation and interception.

(2) Mean particles, whose diameter is smaller than 1 μm, are basically affected by surface forces. These include Brownan diffusion, van der Waals (attractive) forces and electrokinetic forces.

(3) Intermediate particles. They can be affected by both volumetric and surface forces, since their mean diameter lies between 1 and 30 μm.

A conjecture in the present work is that the effect of each of the six previous mechanisms is additive in the model. Both the transport and the attachment mechanisms (Chapter 2) are treated as pure attachment mechanisms, since this distinction is arbitrary (BOYD & GHOSH, 1974). Mathematically, the attachment coefficient in Equation [3.15.], K_a, is expressed as the sum of interception, inertia, sedimentation, Brownian diffusion, van der Waals forces and electrokinetic forces:

$$\lambda'_a = \frac{\lambda'_{att}}{d_g}\left\{ \left(\frac{d_p}{d_g}\right)^{n_{INT}} + \left(d_p^{3/2}\right) + \left(\frac{g\,\phi_0\,(\rho_s - \rho_l)\,d_p^2}{18\mu_l|q|\,d_g}\right) + \right.$$
$$\left. + \left(\frac{\phi_0\,K_B T}{\mu_l\,d_p\,d_g|q|}\right)^{2/3} + \left(d_p^2\right) + \left(\frac{Q_{PV}\,d_g - 6\,Q_{PS}}{\mu_l\,d_p|q|\,/\phi_0}\right)\right\}$$

[3.16.]

where λ'_{att} [LT^{-1}] is the velocity of attachment; d_p [L] is the mean diameter size of suspended particles; d_g [L] is the mean diameter size of matrix grains; n_{INT} [L^0] is an empirical coefficient that lies between 0.5 and 2.0; g [LT^{-2}] is gravity; ϕ_0 [L^0] is the initial porosity, at time t=0; ρ_p and ρ_l [ML^{-3}] are the particles and liquid density; μ_l [ML^{-1}T^{-1}] is the dynamic viscosity of the liquid; K_B [ML^{2}T^{-2}K^{-1}] is Boltzmann's constant; Q_{PV} [CL^{-3}] is volumetric charge times the charge of one particle; and Q_{PS} [CL^{-2}] is the surface charge density times the charge of one suspended particle.

Strictly speaking, a proportionality factor should multiply the terms describing inertia (second addend in 3.16.) and van der Waals forces (fifth addend), but it has been eliminated and included into the velocity of attachment.

The form of each term in Equation [3.15.] is based on empirical and theoretical evidence obtained from filtration theory. The parameters affecting each of these terms and the empirical dependencies or theoretical formulations are written in Table 3.2.

Table 3.2. Mathematical dependence of each attachment mechanism on the initial filter coefficient (IWASAKI, 1937). This table shows either mathematical relationships or the predicted dependence of the filter coefficient with some properties of the system (after BOYD & GHOSH, 1974).

	Mechanism	EQUATION for λ_0 [L^{-1}]	Predicted dependence
1	INTERCEPTION	$\lambda_0 = A \dfrac{1}{d_g} \left(\dfrac{d_p}{d_g} \right)^{n_{INT}}$	
2	INERTIA		$\lambda_0 \propto \left(d_p^{3/2} \right)$
3	SEDIMENTATION	$\lambda_0 = \dfrac{A}{d_g} \dfrac{g\, \phi_0\, (\rho_p - \rho_1)\, d_p^2}{18 \mu_1 |q|}$	
4	BROWNIAN DIFFUSION	$\lambda_0 = \dfrac{A}{d_g} \left(\dfrac{\phi_0\, K_B T}{\mu_1 d_p d_g |q|} \right)^{2/3}$	
5	LONDON-VAN DER WAALS FORCES		$\lambda_0 \propto \left(d_p^2 \right)$
6	ELECTROKINETIC FORCES	$\lambda_0 = \dfrac{A}{d_g} \left(\dfrac{Q_{PV}\, d_g - 6\, Q_{PS}}{\mu_1 d_p |q| / \phi_0} \right)$	

- *The Detachment Term*

In this conceptual model detachment may depends on (1) hydrodynamic changes, expressed through modifications in hydraulic gradients; and (2) hydrochemical changes -specifically, variations in ionic strength and pH of the solution-. This can be mathematically expressed by:

$$\lambda'_d = \lambda'_{det} \cdot \left\{ 1 + A_{pH} \frac{\partial pH}{\partial t} - A_{IS} \frac{\partial IS}{\partial t} + A_J \frac{\partial J}{\partial t} \right\} \cdot \delta_{\phi \phi_{crit}} \qquad [3.17.]$$

where λ'_{det} [T^{-1}] is the specific detachment velocity; A_k [L^0] is a parameter for each of the three involved variables (pH; the ionic strength, IS; and the hydraulic gradient, J); δ is a step function defined as 0 when $\phi > \phi_{crit}$ and 1 elsewhere, ϕ_{crit} being a threshold value below which hydrodynamic and hydrochemical forces are capable of detaching particles. Detachment rate incorporates some field observations such as the positive correlation with pH and hydraulic changes, and its negative correlation with ionic strength changes (MC DOWELL-BOYER ET AL., 1986).

3.2.3.2. *Biological Clogging*

Bacteria need three major inputs for synthesis and metabolism (CHAPELLE, 1992):
1. Energy. Microorganisms employ three basic strategies for obtaining energy: (1) photosynthesis, i.e. the use of light in surface environments; (2) chemolithotrophy, which refers to the use of reduced inorganic chemicals (H_2, H_2S, Fe^{+2}, NH_3) as electron donors; (3) heterotrophy, or utilising organic compounds as electron donors. This third group is the most common in subsurface environments.

2. Organic carbon. This is necessary both for energy and growth. Heterotrophic organisms use organic carbon, whilst inorganic carbon is consumed by autotrophic organisms.
3. Electrons to store and carry the energetic compounds. Bacteria

The availability of these sources determines how bacteria survive and reproduce within the porous medium. This is often quantified through a generic empirical relationship, which expresses the net rate of heterotrophic bacterial growth as a function of two terms:
1. Energy needed for cell synthesis through the oxidation of organic matter.
2. Endogenous maintenance, at the expense of bacteria, when there is no food available (lysis).

These two mechanisms have to be included in the mathematical model. Bacterial growth can be described by means of a generalised Monod equation, whilst a first-order decay law is adopted to account for lysis (LICHTNER ET AL., 1996):

$$f_{s/s}^{x}(\mathbf{w}) = \left.\frac{\partial w_s^x}{\partial t}\right|_{net} = \left.\frac{\partial w_s^x}{\partial t}\right|_{growth} - \left.\frac{\partial w_s^x}{\partial t}\right|_{dieoff} = \left\{\mu_{max}\prod_{i=l}^{N_{sec}}\frac{g_1^i\ w_l^i+g_2^i}{w_l^i+g_3^i} - \mu_{dec}\right\}w_s^x \qquad [3.18.]$$

where μ_{max} [T^{-1}] is the maximum growth rate; g_1^i [L^0] is a coefficient that equals 1 if species w_l^j acts as a catalyst and 0 when it inhibits growth of bacteria species; g_2^i [L^0] equals 0 when species w_l^j is a catalyst and another (empirical) value when it is an inhibitor; g_3^i [L^0] is the half-saturation constant for the electron donor; and μ_{dec} [T^{-1}] denotes the die-off coefficient. N_{SEC} is the number of electron acceptors and donors or other limiting compounds (inhibitors) that play a role in bacterial growth..

The die-off fraction of bacteria must be taken into account from the clogging point of view. As for the impact of bacteria on the concentration of the chemical species, only the term related to bacterial growth has to be accounted for because die-off is assumed to be independent of the presence/absence of chemical species. This is why the sink/source term for mobile species in Equation [3.10.] is not identical to the production/decay rate of minerals in the case of bacteria. When dealing with bacteria, the right value of r_{kin} is:

$$r_{kin}^{x}(\mathbf{w}) = \left.\frac{\partial w_s^x}{\partial t}\right|_{growth} = \left\{\mu_{max}\prod_{i=l}^{N_{sec}}\frac{g_1^i\ w_l^i+g_2^i}{w_l^i+g_3^i}\right\}w_s^x \qquad [3.19.]$$

The adopted model is termed macroscopic, in contrast to biofilm models. Bacteria tend to form a so-called biofilm, which is mainly formed by water (around 80 %), organic matter (18 %) and inorganic compounds (ca. 2 %). This biofilm obstructs the pore volume, thus enhancing clogging. The biofilm is indirectly accounted for when updating the porosity, as shown in section 3.2.2.4., assuming that the composition of the biofilm remains constant and is proportional to bacterial concentration. In this model it is implicitly assumed that all microrganisms are exposed to the substrate concentrations in the liquid, whilst biofilm models account for the resistance at the interface liquid-colonies. In fact, there are few circumstances for which the added complication of a full biofilm model is justified (LICHTNER ET AL., 1996; HOLM, 1999).

3.2.3.3. *Chemical Clogging*

Chemical reactions can be classified as a function of two different concepts: its relative rate with respect to water flow, and the phases involved. According to the relative rate, fast reactions are

considered at equilibrium, while slow reactions must be studied from a kinetic point of view. Thus, kinetics is only a relative concept, depending on the reference magnitude (in our case, water velocity). As for the phases involved, reactions affecting only dissolved species are said to be homogeneous, whilst reactions such as precipitation/dissolution (i.e., exchange between the solid phase -a mineral- and a dissolved species) are termed heterogeneous.

Equilibrium reactions establish a relationship among the concentrations of the involved dissolved species by means of stoichiometric coefficients and thermodynamic constants. Mathematically, equilibrium reactions are described through the Mass Action Law. This equation does not specify the mass transfer needed to achieve equilibrium, i.e. there is no mathematical expression for the reaction rates of equilibrium reactions. This is why the rates of equilibrium reactions have to be removed from the reactive transport equations through algebraic manipulations. A full description of this topic, which was outlined in section 3.2.2. is beyond the scope of this paper (see SAALTINK ET AL., 1998a).

Kinetics models have experienced a spectacular development during the last years, reflecting an increasing interest and concern about environmental issues. A general expression for heterogeneous kinetics (precipitation/dissolution) for a mineral *m* is used in our model (SAALTINK ET AL. 1997):

$$f_{s/s}^m(w_1^i) = \zeta_m \, a_s \, \exp\left[-\frac{Ea_m}{RT}\right] \cdot \sum_{j=1}^{N_{kin}} \left\{ R^{mj} \prod_{i=1}^{N_{aqu}} \left(w_1^i\right)^{p_{mj}^i} \left[\Omega_m^{\theta_{mj}} - 1\right]^{\eta_{mj}} \right\}$$ [3.20.]

where ζ_m [L^0] is a constant that takes on a +1 value for precipitation and a -1 for dissolution; Ea_m [ML^2T^{-2}] is the activation energy of the reaction, ranging between 30 and 80 kJ/mol for most minerals (LASAGA, 1984); T [K] is the absolute temperature; R^{mj} [LT^{-1}] is the experimental rate constant for precipitation/dissolution, which depends on the N_{kin} different catalytic terms; a_s [L^{-1}] is the specific surface area of the mineral; N_{aqu} is the number of aqueous species; p_{mj}^i is an empirical exponent that relates a mineral *m* with the catalyst *i* for a given kinetic path *j*; Ω_m is the saturation index of mineral *m*; and θ_{mj} and η_{mj} are two additional experimental parameters (often taken as 1) for the mineral *m* and kinetic path *j*.

3.2.3.4. *Generalisation of the specific kinetic equations*

Kinetic reactions can be expressed in a compact way. Equation [3.14.] can be generalised as follows:

$$\frac{Dw_s^m}{Dt} = \psi_a(\mathbf{w}) + \psi_d(\mathbf{w}) \cdot w_s^m$$ [3.21.]

where ψ_a [T^{-1}] and ψ_d [T^{-1}] are two functions of the concentration of mobile species, i.e. the generalised attachment and detachment terms. Table 3.3. contains a summary of the explicit form of both functions for each type of mineral.

Table 3.3. Explicit form of the generalised attachment and detachment terms for generic minerals as a function of the specific mineral type (suspended particles, bacteria, or 'true' minerals).

	GENERALISED ATTACHMENT TERM $\psi_a(w)$ [T^{-1}]	GENERALISED DETACHMENT TERM $\psi_b(w)$ [T^{-1}]	CLOGGING FACTOR* Φ_m [M^{-1}L^{-3}]
ATTACHED PARTICLES	$\lambda'_a w_l^j$ λ'_a defined in equation [3.16.] and Table 3.2.	$\left\{-[\nabla \cdot \mathbf{u}] - \lambda'_d\right\}$ λ'_d is defined in equation [3.17.]	$\beta_s \cdot [\rho_s]^{-1}$
FIXED BACTERIA	0	$\left\{-[\nabla \cdot \mathbf{u}] + \mu_{max} \prod_{i=1}^{N_{sec}} \frac{g_1^i w_l^i + g_2^i}{w_l^i + g_3^i}\right\} - \mu_{dec}(w_s^x)^k$ The last addend is not accounted for in the sink/source term of mobile species	$\beta_x \cdot [\rho_x]^{-1}$
TRUE MINERALS	$\zeta_m a_s \exp\left[-\frac{Ea_m}{RT}\right] \cdot$ $\sum_{j=1}^{N_{kin}} \left\{ k_{mj} \prod_{i=1}^{N_{aqu}} \left(w_l^i\right)^{p_{mj}^i} \left[\Omega_m^{\theta_{mj}} - 1\right]^{\eta_{mj}} \right\}$	$\left\{-[\nabla \cdot \mathbf{u}]\right\}$	$\beta_m \cdot [\rho_m]^{-1}$

*The clogging factor is expressed as the ratio of a fitting parameter, β_m [L^0], termed apparent clogging factor of mineral m, and the density of the mineral, ρ_m [M·L^{-3}]. Contrary to the rest of minerals, the density of bacteria is not easy to determine; therefore, the product is used for calibration.

Mineral concentrations are finally computed based on their chemical behaviour. The concentration of a kinetic mineral is obtained with the help of a first-order approximation:

$$(w_s^m)^{k+1} = (w_s^m)^k + r_{kin}^m \cdot (t^{k+1} - t^k) \qquad [3.22.]$$

The concentrations of minerals in equilibrium are calculated through algebraic operations, yielding an expression as a function of dissolved species.

3.2.3.5. *Changes in the Porous Medium Properties*

Porosity is assumed to be a linear function of the concentration of retained particles, bacteria (biofilm) and *true* minerals, i.e. the generic minerals. If the concentration of generic minerals increases then porosity will diminish. This is expressed by the following equation:

$$\frac{\partial \phi}{\partial t} = -[\rho_l S_l \phi] \cdot \sum_m \Phi_m \frac{\partial w_s^m}{\partial t} \qquad [3.23.]$$

where Φ_m [L^0] is a proportionality factor relating porosity changes to concentrations of generic minerals. It is termed clogging factor and is defined for each mineral type in Table 3.3.

The final effect of these processes and the porosity variation is that the intrinsic permeability of the aquifer changes. There exist different ways of relating the intrinsic permeability with certain properties of the medium, such as the grain size distribution, tortuosity, connectivity of pores and

material-type (Chapter II). Classical approaches use porosity and other lumped parameters, like the Kozeny-Carman relationship:

$$\mathbf{k} = \mathbf{k}_0 \, \frac{\phi^3}{(1-\phi)^2} \frac{(1-\phi_0)^2}{\phi_0^3} \qquad\qquad [3.24.]$$

where $\mathbf{k}$ and $\mathbf{k}_0$ [L^2] are the updated and initial intrinsic permeability tensors; and ϕ and ϕ_0 are the updated and initial porosity values.