

## 2 MATHEMATICAL MODEL

This Chapter provides a description of the governing equations that are the basis for the MOUSER models. A Notation list is given at the end of the Chapter.

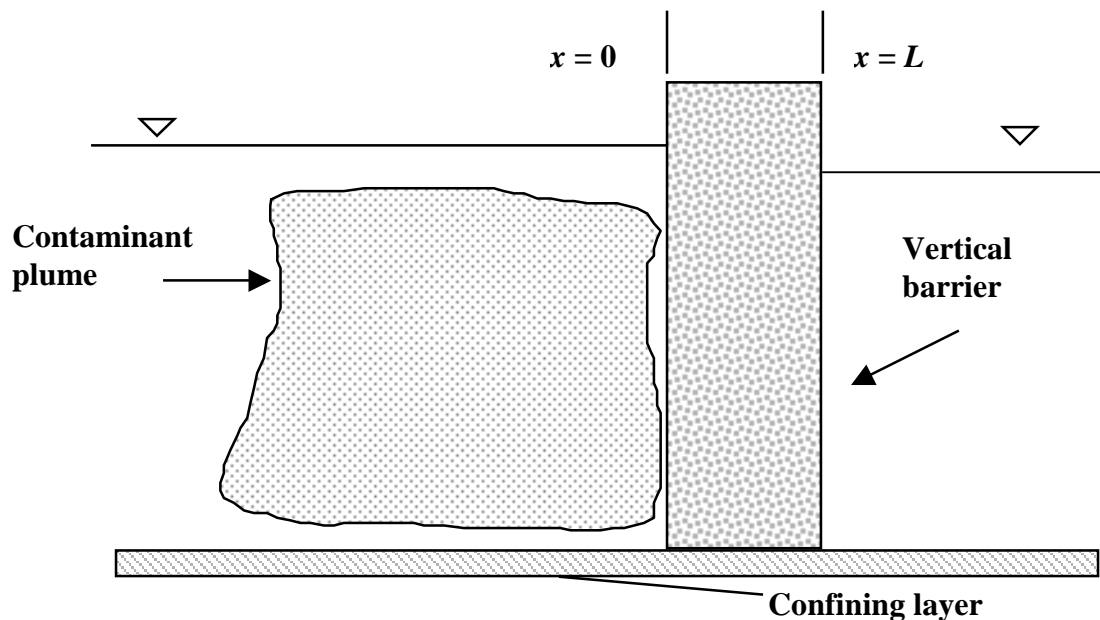
### 2.1 Advective-dispersive-reactive equation

While originally intended for the analysis of low permeability media, the models implemented in MOUSER are applicable to any physical system described by the one-dimensional form of the advective-dispersive-reactive (ADR) equation and the specified boundary conditions. The general form of the ADRE used in this work is:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \mu_a C - \frac{\rho_b}{n} \frac{\partial S}{\partial t} - \frac{\rho_b}{n} \mu_s S \quad (2.1)$$

where  $C$  is the dissolved phase resident contaminant concentration,  $t$  is time,  $x$  is distance from the domain entrance,  $v$  is the fluid velocity in the  $x$ -direction,  $D$  is the dispersion coefficient (includes hydrodynamic dispersion and molecular diffusion),  $\mu_a$  and  $\mu_s$  are first-order decay coefficients for the aqueous and sorbed phases, respectively,  $\rho_b$  is the bulk density,  $n$  is the porosity, and  $S$  is the sorbed phase mass fraction.  $S$  is understood to incorporate the contaminant mass residing in all immobile compartments, except for separate nonaqueous phase liquids (NAPL), which are assumed to be absent.

A schematic of a typical application (a vertical barrier) showing the coordinate system is included in Figure 2.1. Other applications are discussed in Chapter 4.



**Figure 2.1 Schematic of a typical barrier or treatment wall application**

The velocity may be specified directly or computed from one of the following expressions of Darcy's Law:

$$v = -\frac{Ki}{n} \quad (2.2a)$$

$$v = -\frac{Q}{nA} \quad (2.2a)$$

$$v = -\frac{q}{n} \quad (2.2b)$$

where  $K$  is the hydraulic conductivity of the porous medium,  $i$  is the average hydraulic gradient across the domain,  $Q$  is the total volumetric flow into the domain,  $A$  is the total cross-sectional area normal to flow, and  $q$  is the specific discharge (Darcy velocity) into the domain, .

The dispersion coefficient is a lumped parameter that represents the combined effects of molecular diffusion and hydrodynamic mixing:

$$D = a_l v + \frac{D_d}{H_p} \quad (2.3)$$

where  $a_l$  is the barrier longitudinal dispersivity,  $D_d$  is the contaminant liquid diffusion coefficient, and  $H_p$  is the diffusion hindrance factor. The interpretation of these parameters is discussed in Chapter 4.

## 2.2 Initial conditions

Most of the models implemented in MOUSER incorporate a uniform concentration initial condition:

$$C(x, t = 0) = C_i \quad (2.4)$$

where  $C_i$  is the initial contaminant concentration within the domain. Many of the particular models require  $C_i = 0$ .

## 2.3 Entrance boundary conditions

Two boundary conditions (BCs) are required to solve the one-dimensional ADRE. The selection of the appropriate BCs depends upon the system geometry and the degree of advection dominance, which can be considered in terms of the dimensionless Peclet number ( $Pe$ ):

$$Pe = \frac{vL}{D} \quad (2.5)$$

where  $L$  is the domain length.

The *entrance* BC defines the condition at  $x = 0$ . Several alternatives are implemented in MOUSER, which facilitates application to a variety of advection- and diffusion-dominated scenarios.

### 2.3.1 Constant concentration

For many problems of interest, it is common to specify the entrance boundary as a constant concentration:

$$C(x = 0, t) = C_0 \quad (2.6)$$

where  $C_0$  is the concentration at the entrance boundary.

### 2.3.2 Danckwerts

For advection-dominated transport in laboratory columns, several researchers have argued that the following 3rd-type “Danckwerts” BC is most appropriate (e.g., Danckwerts, 1953):

$$C(0, t) = C_0 - \frac{D}{v} \frac{\partial C}{\partial x}(0, t) \quad (2.7)$$

Eq. 2.7 was developed by performing a mass balance across the domain entrance and is interpreted to represent a transition from pure advection to advective-dispersive transport.

### 2.3.3 Finite mass

In analyzing of contaminant migration across a landfill liner, Rowe and Booker (1985) defined a boundary condition based on a declining source of contaminant mass within the landfill. Such a condition may be generalized to a vertical barrier or laboratory column by assuming a fixed initial mass of contaminant within a mixing zone at the domain entrance, expressed as:

$$C(0, t) = C_0 - \frac{1}{H_f} \int_0^t \left[ vC(0, \zeta) - D \frac{\partial C}{\partial x}(0, \zeta) \right] d\zeta \quad (2.8)$$

where  $C_0$  is the initial concentration in the mixing zone and  $H_f$  is the width in the  $x$ -direction of the mixing zone (corrected by the ratio of the mixing zone porosity to the domain porosity, if different).

While such the condition represented by Eq. 2.8 does not account for concentration gradients or fluctuations within the entrance mixing zone, it may be more realistic than the assumption of an unchanging contaminant concentration at the domain entrance.

### 2.3.4 Declining concentration

When a contaminant is subject to a first-order decay and the entrance zone is not replenished by an active source, the BC is expressed by:

$$C(0,t) = C_0 \exp(-\lambda_s t) \quad (2.9)$$

where  $\lambda_s$  is the decay coefficient for the contaminant source (not necessarily the same as the domain interior).

A general time-varying condition may also be defined. For convenience, a second-order polynomial is used in MOUSER:

$$C(0,t) = C_0 + P_1 t + P_2 t^2 \quad (2.10)$$

where  $C_0$  is the initial entrance concentration, and  $P_1$ , and  $P_2$  are known constants.

## 2.4 Exit boundary conditions

The *exit* BC is defined at  $x = L$ . As with the entrance BC, there are several options supported by MOUSER. In general, the importance of the exit BC is highly dependent on the degree of advection-dominance. For low flow systems (diffusion-dominated) the solutions are highly sensitive to the specified exit condition. A schematic of several of the more common conditions is shown in Figure 2.2.

### 2.4.1 Constant concentration

A constant concentration may be assumed at the domain exit:

$$C(L,t) = C_L \quad (2.11)$$

where  $C_L$  is the constant concentration outside the barrier.

Eq. 2.11 was originally implemented to address the scenario where the influence of advection is much greater on the exit side of a low permeability barrier (versus the interior of the barrier), resulting in a zero concentration condition. The numerical version of MOUSER has been extended to allow the specification of any nonnegative concentration. The zero concentration exit BC (Figure 2.2b) implies that the contaminant is rapidly transported away from the domain as it emerges, and may be referred to as a “perfect flushing” condition. For low permeability barriers, such a condition is very conservative in that it results in the maximum concentration gradient at the barrier boundary, providing a greater driving force for diffusion.

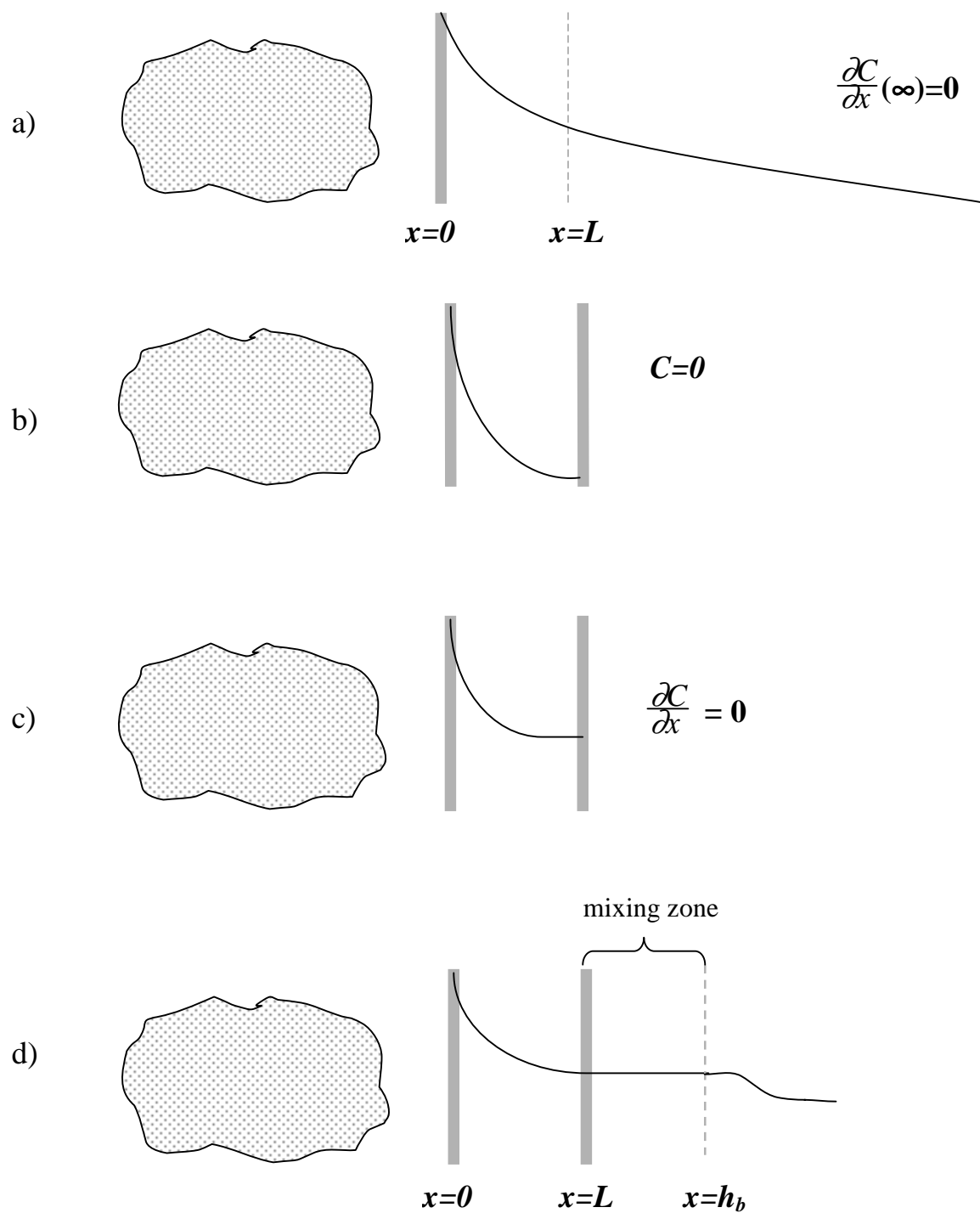


Figure 2.2 Schematic of exit boundary conditions for constant concentration source and moderate  $Pe$  (a = zero concentration, b = semi-infinite, c = zero gradient, d = mixing zone)

### 2.4.2 Semi-infinite domain

A popular strategy for modeling transport in porous media is to set the domain boundary at infinity, resulting in a condition that can be modeled by:

$$\frac{\partial C}{\partial x}(\infty, t) = 0 \quad (2.12)$$

The implication of the semi-infinite condition (Figure 2.2a) is that the exit boundary has negligible impact on transport; i.e., the medium behaves as if it were continuous at the boundary. This condition is reasonable if the transport conditions on the exit side of the domain are comparable to conditions within the domain.

### 2.4.3 Zero gradient

For laboratory-scale problems characterized by advection-dominated transport, some investigators have advocated a zero gradient condition for the exit boundary (e.g., Brenner, 1961):

$$\frac{\partial C}{\partial x}(L, t) = 0 \quad (2.13)$$

For laboratory columns, there is disagreement regarding the merits of the above condition (Figure 2.2c) versus the semi-infinite condition (Eq. 2.12). For conditions where diffusive transport dominates, this condition is usually inapplicable because it implies a zero concentration gradient and consequently no diffusive flux at the domain exit.

### 2.4.4 Exit mixing zone

For landfill applications, Rowe and Booker (1985) proposed the following exit condition:

$$C(L, t) = \frac{1}{n_b h_b} \int_0^t \left[ v C(L, \zeta) - \frac{\partial C}{\partial x}(L, \zeta) \right] d\zeta - \int_0^t \frac{v_b C(L, \zeta)}{n_b W_b} \quad (2.14)$$

where  $n_b$  is the porosity of a completely mixed transition zone adjacent to the barrier exit,  $h_b$  is the  $x$ -dimension of the transition zone,  $W_b$  is the lateral dimension of the transition zone, and  $v_b$  is the velocity of groundwater flushing the transition zone.

While less intuitively meaningful when applied to a vertical wall or column, Eq. 2.14 (Figure 2.2d) provides for some flexibility in adjusting the boundary condition between the limiting conditions of zero concentration and zero gradient. As the ratio  $v_b/W_b$  is decreased, the boundary condition converges to the zero gradient condition, while as  $v_b/W_b$  is increased, the condition converges to a constant zero concentration boundary. A more detailed discussion of

this condition for barrier applications is included in Chapter 4. A discussion of slurry wall applications is also provided by Rabideau and Khandelwal (1998b).

## 2.5 Single solute sorption models

### 2.5.1 Equilibrium models

When mass transfer between the aqueous and stationary phases is represented as an equilibrium (i.e., fast) process, the ADRE can be reduced to:

$$R_f \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \mu_a C - \frac{\rho_b}{n} \mu_s S \quad (2.15)$$

where  $R_f$  is the retardation factor, defined as:

$$R_f = 1 + \frac{\rho_b}{n} \left( \frac{\partial S}{\partial C} \right) \quad (2.16)$$

with the form of the partial derivative dependent on the specified isotherm expression.

MOUSER provides several options for nonlinear sorption, including the 1-parameter (linear) isotherm, the 2-parameter Freundlich and Langmuir isotherms, and the 3-parameter Toth isotherm (e.g., Kinniburgh, 1986):

$$\text{Linear} \quad S_e = K_d C \quad (2.17)$$

$$\text{Freundlich} \quad S_e = K_F C^{n_F} \quad (2.18)$$

$$\text{Langmuir} \quad S_e = \frac{b Q_0 C}{1 + b C} \quad (2.19)$$

$$\text{Toth} \quad S_e = \frac{b Q_0 C}{\left[ 1 + (b C)^{n_T} \right]^{1/n_T}} \quad (2.20)$$

where  $S_e$  is the sorbed phase concentration in equilibrium with the dissolved concentration  $C$ ,  $K_d$  is the linear distribution coefficient,  $K_F$  and  $n_F$  are the Freundlich parameters,  $Q_0$  and  $b$  are parameters used in both the Langmuir and Toth isotherms, and  $n_T$  is the third Toth parameter.

Substitution of any of the nonlinear expressions (Eqs. 2.18-2.20) into the ADRE (Eq. 2.1) results in a retardation factor (Eq. 2.16) that is a function of the concentration, rendering the governing partial differential equation nonlinear and necessitating the use of a numerical solution technique. When the linear isotherm is specified, the governing ADRE remains linear (and more amenable to analytical solution). For the linear case, the retardation factor reduces to:

$$R_f = 1 + \frac{\rho_b K_d}{n} \quad (2.21)$$

All three isotherms reduce to the linear expression for certain values of the parameters (e.g.,  $n_F = 1$  for the Freundlich case).

### 2.5.2 Nonequilibrium models

Under conditions where the sorption reaction is not well represented as an equilibrium process, a first-order mass transfer model may be used:

$$\frac{\partial S}{\partial t} = \alpha(S_e - S) \quad (2.22)$$

where  $\alpha$  is the sorption rate coefficient, and the form of  $S_e$  dependent on the specified isotherm.

An alternative model for linear nonequilibrium considers sorption and desorption as simultaneous chemical reactions, each characterized by a respective rate coefficient, expressed as:

$$\frac{\partial S}{\partial t} = k_f C - k_r S \quad (2.23)$$

where  $k_f$  and  $k_r$  are forward (sorption) and reverse (desorption) rate coefficients, respectively. For linear sorption, Eq. 2.22 and Eq. 2.23 are mathematically equivalent if  $\alpha$  is equated to  $k_r$  and  $K_d$  is equated to  $k_f/k_r$ . For this reason, subsequent discussions of nonequilibrium sorption are considered in terms of the more general Eq. 2.22.

### 2.5.3 Effective decay

The single solute ADR equation includes decay in both the aqueous and solid phases. When a linear isotherm is applicable, the decay terms can be combined into a single “effective” decay constant, leading to a simplified equation in which the sorbed phase is eliminated:

$$R_f \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \lambda C \quad (2.24)$$

with:

$$\lambda = \mu_a + \frac{\rho_b K_d}{n} \mu_s \quad (2.25)$$



## 2.6 Multi-solute models

The current implementation of MOUSER includes two models that involve multi-solute interactions: 1) parent-daughter decay chains, and 2) competitive cation exchange.

### 2.6.1 Decay chain

For some applications of interest, consideration of the production and transport of decay products may be necessary. For this scenario, an ADR equation must be developed for each solute:

$$\frac{\partial C_i}{\partial t} + \frac{\rho_b}{n} \frac{\partial S_i}{\partial t} = -v \frac{\partial C_i}{\partial x} + D \frac{\partial^2 C_i}{\partial x^2} - \lambda_i C_i + \beta_{i-1} \lambda_{i-1} C_{i-1} \quad (2.26)$$

where the subscript  $i$  refers to the reaction product generated by the decay of solute  $i-1$ , and  $\beta$  is a production coefficient that can be decomposed as:

$$\beta_{i-1} = (f'_{i-1})(\chi_{i-1}) \quad (2.27)$$

where  $f'_{i-1}$  is the fraction of parent  $i$  undergoing sequential degradation to form transformation product  $i-1$ , and  $\chi_{i-1}$  is the stoichiometric conversion factor for the reaction.

Two key simplifications are imposed by the form of Eq. 2.26: 1) the velocity and dispersion terms are assumed equal for all solutes, and 2) decay is assumed to occur only in the aqueous phase.

### 2.6.2 Competitive cation exchange

In addition to the single-solute sorption models previously considered, MOUSER includes an option for a competitive cation exchange model. In the current implementation, binary equilibrium relationships are expressed in terms of the “reference solute”  $C_1$ , which is assumed to be monovalent. For each of the remaining solutes, the governing equilibrium relationship is expressed using the Gaines-Thomas convention

$$K_{Na,i} = \left( \frac{a_{Na}}{y_{Na}} \right)^m \left( \frac{y_i}{a_i} \right) \quad (2.28)$$

where  $a$  represents the aqueous phase activity,  $y$  is the sorbed phase activity,  $m$  is the charge of solute  $i$ , and  $K_{Na,i}$  is the equilibrium constant.

The aqueous phase activity is the product of the concentration and an activity correction based on the Davies equation (e.g., Stumm and Morgan, 1998):

$$a_i = 0.5z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) c_i \quad (2.29)$$

where  $c_i$  is the solute molar concentration and  $I$  is the ionic strength.

In MOUSER, the independent variables are typically restricted to the cations of interest, and the ionic strength is calculated by:

$$I = 0.5 \sum_j c_j z_j^2 + An \quad (2.30)$$

where  $z_j$  is the charge associated with cation  $j$ , and  $An$  is the background anion ionic strength (supplied as input to the model).

The sorbed phase activity is calculated using the Gaines-Thomas convention:

$$y_i = \frac{q_i N_i}{Q} \quad (2.31)$$

where  $q$  is the sorbed phase mass fraction (moles/kg) of species  $i$ ,  $N$  is the equivalents per mole, and  $Q$  is the total cation exchange capacity (eq/kg).

The cation exchange capacity is calculated from the initial sorbed ion concentrations:

$$Q = \sum_i m_i q_{i0} \quad (2.32)$$

where  $q_{i0}$  is the initial sorbed phase mass fraction for species  $i$ .

## 2.7 Contaminant flux

Solutions of the ADR equation for advection-dominated problems are usually expressed in terms of spatial and temporal concentration profiles. As discussed in Chapter 1, a flux-based solution may be of greater interest for diffusion-dominated problems. The governing expression for the instantaneous contaminant flux ( $f$ ):

$$f = nvC - nD \frac{\partial C}{\partial x} \quad (2.33)$$

where  $f$  has units of mass per area per time.

Eq. 2.33 is usually evaluated at the domain exit ( $x = L$ ). The cumulative mass released from the domain is readily evaluated by analytical or numerical integration of the flux expression:

$$m_{cum} = \int_0^t \left( nvC - nD \frac{\partial C}{\partial x} \right) \bigg|_{x=L} d\tau \quad (2.34)$$

where  $m_{cum}$  is the cumulative mass per unit area crossing the plane of interest ( $x = L$ ) during the time period of interest ( $t$ ).

## 2.7 Sorbed concentrations

For some problems of interest, MOUSER can be configured to output the sorbed or total concentrations. The sorbed phase mass fraction ( $S$ ) is computed using the appropriate sorption model. For the cation exchange model, the following conversion is used:

$$S = 1000 Mq \quad (2.35)$$

where the sorbed phase mass fractions  $S$  and  $q$  are typically expressed in mg/kg and moles/kg, respectively and  $M$  is the solute molecular weight.

The total concentration ( $C_T$ ) includes both the aqueous concentration and sorbed mass fraction, and corresponds more closely to concentrations that might be measured by extraction procedures performed on soil samples from the field or experimental columns. The following expression is used to calculate  $C_T$ :

$$C_T = \frac{nC + \rho_b S}{\rho_b} \quad (2.36)$$

## 2.10 Solution methods and limitations

MOUSER utilizes a common input format and three computational approaches for solving the ADR: (1) analytical (closed-form) solutions for concentration and flux, including solutions that require numerical integration and/or differentiation, (2) “finite layer” solutions for concentration and flux, based on a numerical inversion of the Laplace-transformed solutions, and (3) numerical solutions for concentration and flux, based on a split-operator grid-based (finite element or finite difference) solution. The user may specify the desired solution technique in the input. If the user specifies input parameters incompatible with the available solution algorithms, an error message is generated.

### 2.10.1 Analytical solutions

Closed-form solutions are available for a number of idealized scenarios, as delineated in Chapter 7 and Appendix I. In general, the following conditions are not addressed by the analytical models:

- Multi-solute parent/daughter decay or cation exchange
- Nonlinear sorption isotherms

- Mixing-zone or zero-gradient exit boundary conditions

Where feasible, the use of an analytical solution is usually desirable because of faster computation and greater accuracy.

### 2.10.2 *Finite layer solutions*

The “finite layer” solutions are based on the numerical inversion of the Laplace-transformed solution, as developed by extensions to the algorithms of Rowe and Booker (1985), who popularized the term. Details of the method are described in Chapter 8 and Appendix II. The finite layer algorithms incorporate most of the available boundary condition combinations, as well as the formation and transport of reaction products. As with the analytical model, sorption is considered only for the case of a single-solute linear isotherm. Also, nonzero initial conditions are not supported in the current version.

In general, the finite layer algorithms are very accurate and require reduced computation because temporal and spatial discretization are not required. They are typically used when the required boundary conditions are not supported by the analytical models, or for multi-solute scenarios that incorporate linear isotherms.

### 2.10.3 *Numerical solutions*

The current numerical model is based on a split-operator finite element method, as described by Miller and Rabideau (1993) and Rabideau and Khandelwal (1998a). Although the numerical model typically requires considerably more computational time than the other methods, the split-operator approach is well suited for the consideration of nonlinear reactions. The current implementation incorporates all of the features associated with the other models, with the additional capability of handling nonlinear isotherms. The primary advantage of the numerical model is the capability of extension to other nonlinear reactions, as well as nonuniform parameter distributions. Details of the numerical model are provided in Chapter 9 and Appendices III-IV. The primary disadvantage of the numerical solution is the lengthy execution times required for some problems.

At the time of this writing, two additional numerical modules are under development: 1) an explicit finite difference algorithm, and 2) a second-order *total variation diminishing* scheme. Because these explicit algorithms are being implemented for primary application in a parallel computing environment, several approaches are implemented for the various reactions. Further details regarding these algorithms will be included in Part II of the User's Manual as they become available.

**NOTATION**

$\zeta$	integration variable
$\alpha$	sorption rate coefficient ( $T^{-1}$ )
$\beta$	fractional production coefficient
$\lambda_a$	lumped first-order decay coefficient ( $T^{-1}$ )
$\lambda_s$	decay coefficient for the contaminant source ( $T^{-1}$ )
$\rho_b$	bulk density ( $M L^{-3}$ )
$\mu_a$	first-order decay coefficient for the aqueous phase ( $T^{-1}$ )
$\mu_s$	first-order decay coefficient for the sorbed phase ( $T^{-1}$ )
$\chi$	stoichiometric conversion factor
$A$	area ( $L^2$ )
$An$	background anionic activity for cation exchange model (moles/liter)
$a_l$	longitudinal dispersivity ( $L$ )
$b$	Langmuir and Toth isotherm parameter (dimensionless)
$B$	vertical thickness of the aquifer ( $L$ )
$C$	dissolved phase contaminant concentration ( $ML^{-3}$ )
$C_i$	initial concentration ( $M L^{-3}$ )
$C_0$	concentration at the entrance boundary ( $M L^{-3}$ )
$Cr$	Courant number (dimensionless)
$D$	dispersion coefficient ( $L^2T^{-1}$ )
$Da_I$	type 1 Damkohler number (dimensionless)
$Da_{II}$	type 2 Damkohler number (dimensionless)
$D_d$	contaminant liquid diffusion coefficient ( $L^2T^{-1}$ )
$D$	dispersion coefficient ( $L^2T^{-1}$ )
$f$	instantaneous contaminant flux ( $MT^{-1}L^{-2}$ )
$f'_{i-1}$	fraction of parent undergoing sequential degradation
$h_b$	x-dimension of the transition zone ( $L$ )
$H_f$	the width in the x-direction ( $L$ )
$H_p$	diffusion hindrance factor (dimensionless)
$i$	hydraulic gradient (dimensionless)
$K$	hydraulic conductivity ( $LT^{-1}$ )
$K_d$	linear distribution coefficient ( $L^3M^{-1}$ )
$k_f$	forward (sorption) rate coefficient
$K_f$	Freundlich parameter (dimensionless)
$k_r$	reverse (desorption) rate coefficient
$L$	domain thickness ( $L$ )
$M$	solute molecular weight (g/mole)
$m_{cum}$	cumulative mass per unit area ( $ML^{-2}$ )
$n$	porosity (dimensionless)
$n_a$	porosity of aquifer (dimensionless)
$n_b$	porosity of exit mixing zone (dimensionless)
$n_f$	Freundlich parameter (dimensionless)
$n_T$	third Toth parameter (dimensionless)

$Pe$	Peclet number (dimensionless)
$q$	sorbed phase mass fraction for cation exchange (moles/g)
$Q$	pumping rate ( $L^3T^{-1}$ )
$Q_0$	Langmuir and Toth isotherm parameter (dimensionless)
$R_a$	aquifer retardation factor (dimensionless)
$R_f$	retardation factor (dimensionless)
$R_s$	retardation factor for the source zone (dimensionless)
$S$	sorbed phase mass fraction (dimensionless, typically mg/kg)
$S_e$	sorbed phase mass fraction in equilibrium with $C$ (dimensionless)
$t$	time (T)
$V$	volume of the pore fluid in the source zone ( $L^3$ )
$v$	fluid velocity in barrier ( $LT^{-1}$ )
$v_a$	fluid velocity in the aquifer ( $LT^{-1}$ )
$v_b$	velocity of groundwater flushing the exit mixing zone ( $LT^{-1}$ )
$W_b$	lateral dimension of the exit mixing zone (L)
$x$	distance (L)
$x_a$	distance from exit face of the barrier (L)
$z$	charge associated with cationic species