

A Review of Chemical Solute Transport Models

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This paper presents a review of groundwater models capable of simulating solute transport (*i.e.* advection-dispersion) and equilibrium chemistry processes.

Introductory, basic model components are discussed including a physical and a chemical model component and the coupling between the two components. However, emphasis is placed on the chemical model component, since this represents the recent addition to solute transport modeling.

Several ways exist of formulating either model component. For the physical model component this may include a continuous description based on the governing mass balance equations or a discontinuous description by a mixing cell approach. For the chemical model component, *i.e.* processes such as ion exchange, adsorption, complexation, precipitation/dissolution and open/closed carbonate system reactions, local equilibrium is usually assumed. The assumption of local equilibrium is investigated. The relation between the continuous formulation and a coupling/decoupling of the physical and chemical components and the resulting nature of the mathematical problem and its numerical strategy is briefly discussed.

In all, 27 models have been surveyed in terms of their physical and chemical model components, their verification and applicability to field scale problems. Due to a lack of actual field applications it has not been possible to evaluate all models in natural settings and hence, each model will, in theory, be valid when the constraints given by the assumptions and limitations taken in developing the model are met.

The models show great diversity with respect to complexity and general applicability to field scale problems. Most of the models were developed for specific purposes and it is difficult to point out one or more »general« models. However, it may be concluded that there exist many ways of formulating a model both with respect to transport and chemical calculations, but also to numerical techniques.

Many of the models are very complex and future research should be directed towards validation studies of these models on a field scale, rather than developing still more complex models.

Introduction

It is often desirable to be able to predict movement of chemical species through soils and aquifers, for example in the case of subsurface contamination, recharge of surface water and treated wastewater or design and management of irrigation schemes in arid and semi-arid areas. To this end, predictive tools in the form of mathematical models have been developed to simulate the mechanisms responsible for the movement of chemical species, *i.e.* advection, dispersion and chemical reactions. Different research disciplines have contributed such as, soil science, groundwater hydrology and geochemistry, quite often resulting in segmented research. For example, the focal point in the early development of unsaturated zone models was the chemical reactions coupled with simple mass transport calculations, while, at the same time, saturated zone models were developed which considered all species as non-reactive and hence, only affected by advective-dispersive processes. These early models all considered only a limited number of species and only few chemical reactions. However, during the past decade more and more complex models have evolved capable of simulating multispecies interaction and movement through soils and aquifers. The development and use of these models has become an interdisciplinary challenge (Abriola 1987).

This paper reviews solute transport models based on equilibrium chemistry. Focus is on the chemical submodels since these represent »new« additions to mass transport models. Field validation studies are still few in number and hence, the necessary background for critically reviewing the models currently is not present. However, it is expected that these models will find increased use in the years to come yielding valuable experience on practical applicability of solute transport models. The purpose of this paper is to survey the state-of-the-art of available chemical equilibrium solute transport models. Reviews exist in the literature, however, they have either been restricted to certain types of models or do not contain the more recent developments (which have been substantial). In addition, they do not present details about the model structure and included chemical submodels. Anderson (1979) reviewed primarily advection-dispersion models for the saturated zone, while Oster (1982) found 55 flow and/or transport models for the unsaturated zone and selected ten for more careful study. The review by Anderson (1979) concluded on a decade of the practical use of advection-dispersion models in field scale problems and introduced the next decade of adding chemical reactions by presenting models which included simple geochemistry. The review by Oster (1982) did not focus on the chemical reactions. Van Genuchten (1978) reviewed models for both zones, some including simple chemistry, which were applicable to landfill disposal siting. Rao and Jessup (1982) surveyed models able to simulate pesticide dynamics in soils affected by equilibrium or kinetic adsorption and/or degradation. Travis and Etnier (1981) studied the incorporation of various adsorption isotherms into transport models and gave several examples of the application

of these models. Jury (1982) reviewed different unsaturated zone models with and without chemical calculations and gave examples of their use in design and management of irrigation schemes. A review prepared by Batelle Pacific Northwest Labs for EPRI (1984a, 1984b, 1986) evaluated hydrologic and equilibrium chemistry codes that were of interest to the electric power industry. State-of-the-art-codes in each area were investigated for the potential coupling into one comprehensive geohydrochemical model. All models except one in this overview were screened out because of the lack of generality. Recently, Abriola (1987) reviewed the last four years of model development including geochemical, sorption, biological transformation, immiscible phase transport, fractured media and dispersion models. A detailed explanation of each group of models was precluded. A similar review in construction, but with the scope of providing a synthesis of findings rather than a general survey is found in Naymik (1987). As in Abriola (1987), no detailed description of the key models is provided. However, seven recent practical applications are cited to illustrate the variety of modeling procedures. No extensive geochemical modeling was performed in the applications. A short review of equilibrium and non-equilibrium transport models for the unsaturated zone were given by Nielsen *et al.* (1986).

The reviews by Sposito (1985) and Nordstrom *et al.* (1979) specifically deal with the chemical submodels.

All chemical solute transport models consist basically of a physical and a chemical model component. Although the emphasis of this review is on the chemical aspects, the physical component cannot be ignored. A complex chemical model may only be of limited use if not coupled to an appropriate physical model.

The first part of this review contains basic descriptions of various physical and chemical equilibrium models and of their coupling. This is followed by a survey of actual models found in the literature, including complex and simple models for the saturated and unsaturated zone.

The present review is not exhaustive, however, it represents the state-of-the-art of transport and equilibrium chemistry modeling, as well as the history of model development. It covers material published up to and including December 1987.

The Physical Model Component

The physical model is defined here as a mathematical description of the flow and transport phenomena in the saturated or unsaturated zone of the soil/aquifer system with focus on the transport equation. This can be formulated as either mass transport models based on the governing mass balance equations or as mixing cell models.

Mass Transport Models

Following Rubin (1983) the mass balance equation is for a certain chemical entity

and for a certain given space domain of the porous medium

$$\frac{\partial m^T}{\partial t} = - \frac{\partial q^T}{\partial x} + S^T \quad (1)$$

where m^T and q^T is the total mass stored and total mass flux of the chemical entity, respectively, and S^T is the total source/sink term.

The nature of the chemical reactions affects all three terms in Eq. (1) and the choice of a fundamental variable. Rubin (1983) divided all chemical reactions into two groups; those with »sufficiently fast« and reversible reactions and those with »insufficiently fast« and/or irreversible reactions. The first group characterizes equilibrium reactions and the last group kinetically dominated reactions. Although the first group will be of primary interest later in this context, it is important to discuss both groups here.

Consider the last group of chemical reactions. Since these are kinetically dominated and can be irreversible, the mass of each reaction participant is either depleted or produced. Hence, Eq. (1) must track the mass of each individual species in time and space, *i.e.* species such as free ions, complexes, sorbed ions or minerals. Here, $m^T = \theta C_i$, where θ is the volumetric moisture content and C_i the concentration of the individual species. Also q^T is the flux of dissolved mass of the individual species given by $q^T = q_i$, where

$$q_i = - D \frac{\partial C_i}{\partial x} + Q C_i \quad (2)$$

D is a constant coefficient of longitudinal dispersion and Q is a constant, volume flux of water. The last S^T term of Eq. (1) accounts for the aqueous chemical reactions. Each mass balance equation must be coupled to one rate equation, see Rubin (1983) for examples.

In equilibrium chemistry, it is possible to define fundamental variables that are reaction invariant. In Rubin (1983) these are called »tenads«. In an open system, changes in the global mass of a tenad are only caused by the differences in entering and leaving fluxes of the tenads mobile form. Similar definitions have been given by Parkhurst *et al.* (1980) where the fundamental variables are described as »master species« and in Westall *et al.* (1976) as »components«. From this definition it is clear that if the chemical reactions are of the kinetic and irreversible type no tenads can be defined. In equilibrium chemistry m^T is then the sum of mass of the tenad within all species that contain the tenad. Similar, q^T is the sum of mass fluxes of all mobile species that contain the tenad. Since the mass of tenads are reaction invariant S^T must be equal to zero.

As stated in Rubin (1983), the tenads are usually equivalent to the chemical elements that remain as elements during chemical reactions, *i.e.* the tenads are the fundamental building blocks in the chemical species as well as free ions. So, by writing the mass balance equations in terms of tenads and not species the number

of equations are reduced to the number of tenads. An example is given by Cederberg *et al.* (1985). They considered a multicomponent solution consisting of bromide, chloride and cadmium. Together with their complexes and sorbed species a total of 13 species was identified. The tenads or components are here given by the free ions of bromide (Br^-), chloride (Cl^-) and cadmium (Cd^{++}). It was then possible to reduce the originally 13 mass species transport equations to three mass tenad transport equations. A similar, but less complicated example, is given by Lewis *et al.* (1987). The savings in computer time is obvious.

In an equilibrium system with N species and M tenads, $(N-M)$ chemical reaction equations (see later) are needed to constitute a set of N equations with N unknowns. A brief description of this set of equations is given in the section on coupling between the physical and chemical model component.

Although Eqs. (1)-(2) allow for spatial variation of θ , D and Q most models consider fixed values of these parameters.

Mixing Cell Models

Discontinuous models are represented by mixing cell or plate models. Here, the flow regime is divided into a number of cells (plates) and advective transport is simulated by a simple plugflow and dispersive transport by mixing mass from each cell with masses from the neighbouring cells. These two processes alternate (*i.e.*, they are discontinuous). First, the cell solution is moved downflow with the average fluid velocity and afterwards mixing of masses takes place. It is clear that this method does not treat the dispersion phenomenon from a physical point of view.

Spatial Dimensions of Models

Eqs. (1)-(2) are valid for a one-dimensional system. In the case of vertical transport in the unsaturated zone this may be adequate, however, the underlying aquifer is a three-dimensional system and Eq. (1) must be transformed accordingly. Two-dimensional areal (*i.e.* with instantaneously vertical mixing) or cross-sectional models may suffice in some cases.

Models designed to simulate the transport of solutes in groundwater reservoirs are generally one or two-dimensional. This imposes limitation on the practical use of these models. However, as many researchers note, the conceptual scheme behind the proposed models can easily be extended to two or three dimensions. There have, to our knowledge, been no evidence of this in the literature.

Chemical Model Component

Before any attempt to use chemical models based on equilibrium theory, this fundamental assumption must be investigated. Therefore, the first task will be to explain some of the assumptions and call attention to the research performed in this area, along with the presentation of a basic chemical equilibrium component

model.

Again, using the definition of tenads it is possible to set up chemical tenad mass balances. The chemical reactions for the formation of all other aqueous species can then be specified in terms of the tenads (Plummer *et al.* 1983)

Local Equilibrium Assumption

In chemical equilibrium modeling it is assumed that all chemical reactions proceed instantaneously to equilibrium. This perception of the chemical processes is often referred to as the local equilibrium assumption (LEA).

Chemical reactions can be classified as either homogeneous reactions involving only one phase, such as complexation or heterogeneous reactions involving at least two phases, such as precipitation, dissolution and ion exchange (Rubin 1983). Both types of reactions can be characterized by their reaction rates. At any given point in the soil-water system, LEA is valid only if the pore water flow rate is »slow enough« relative to the reaction rates of all the chemical processes. In other words, all chemical reactions must attain equilibrium before the dissolved solutes are transported away.

Several researchers have recently tried to assess the impact of physical and chemical parameters on the validity of the LEA, because, whenever applicable, the approach may include advantages such as more readily available equilibrium constants than kinetic data and a generally more simple mathematical description of the chemical processes (James and Rubin 1979; Rubin 1983; Jennings and Kirkner 1984; Valocchi 1985; Parker and Valocchi 1986; Valocchi 1986; Jennings 1987; Bahr and Rubin 1987).

The above cited works are theoretical, except James and Rubin (1979), who carried out a series of soil column experiments and found that an equilibrium model failed to describe the effluent breakthrough curves for higher pore water velocities. It was concluded that the LEA was only valid when the hydrodynamic dispersion coefficient was comparable to the estimated diffusion coefficient. However, Valocchi (1985) found evidence in the literature that the equilibrium theory was successful in situations where the hydrodynamic dispersion coefficient was higher than the diffusion coefficient and also for higher pore water velocities. In a series of papers Valocchi (1985, 1986) and Parker and Valocchi (1986) have defined criteria for the validity of the LEA based upon basic system parameters (*e.g.* pore water velocity, dispersion coefficient, sorption rate, boundary conditions, pumping rate). Likewise, Jennings and Kirkner (1984) and Jennings (1987) defined criteria based on an error norm expressing the error introduced if finite reaction rates are assumed to be infinite. A more fundamental approach is taken by Bahr and Rubin (1987) introducing the method of separation of the kinetically influenced term (SKIT). Herein, the tenad based mass balance equations are a sum of the LEA formulation and the kinetically influenced terms. By identification of conditions where the kinetic terms are of no influence the LEA applicability can be

evaluated. All of the above attempts in defining criteria for the validity of the LEA have only considered surface reactions (sorption or ion exchange) except Jennings and Kirkner (1984) who included complexation. No attempt, apparently, has been made to include precipitation/dissolution. These latter processes may cause problems, because of often very slow kinetics (Rubin 1983; Willis and Rubin 1987).

Basic Chemical Equilibrium Reactions

Chemical reactions of interest in soil and groundwater systems may include cation exchange, adsorption, complexation, precipitation/dissolution and the open/closed carbonate system. Assuming that the LEA is valid, the equilibrium state of the system can be expressed by algebraic equations, e.g. $K = C_i^p C_j^m C_k^n$ where K is an equilibrium constant, p , m , n , known integers and C_i , C_j , C_k are the activities of the dissolved or adsorbed species. The activities may be replaced by concentrations in dilute systems.

Nordstrom *et al.* (1979) have summarized different ways of treating this approach and discussed its limitations. They emphasize that the largest single source of error is the reliability of the equilibrium constants, but they also noted that activity coefficients are approximated only by semi-empirical equations.

In the following, a short description of the above processes is given. This will include the relevant equilibrium equations and, where possible, a discussion of observed reaction rates (to be considered when justifying the use of the LEA), and the reliability of the equilibrium constants. The description will, by no means, be general in the sense that all possible chemical reactions are covered, however, it should be clear how diverse a chemical equilibrium model can be formulated.

Apparently only one attempt has been made to model redox processes (Walsh *et al.* 1984). This is an area that may be of particular interest in context with waste disposal sites, where various redox environments may be present in the aquifer.

Cation Exchange

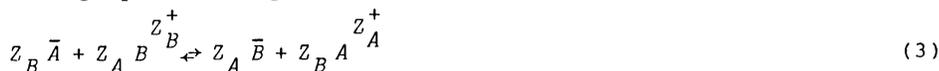
Cation exchange is usually modeled according to a constant charge or a constant potential model.

The constant charge model assumes that a fixed charge imbalance exists on the surface of the sorbing substrate, due to an isomorphic substitution of ions of lower valency. This is the case for many clay minerals, where Si and Al have been substituted by cations of lower valence, resulting in a negative surface charge, which is neutralized by sorption of cations. One disadvantage is that sorption of cations and anions must be treated separately.

The constant potential model is usually considered a more realistic treatment of natural sorbing substrates whose surface charge is not constant but a function of pH. An example could be that of an oxide surface which is partly hydroxylized. The constant potential model can be described by a surface complexation model where the sorption sites are treated as additional complexing ligands that may

compete for dissolved ionic species. These additional complexing ligands can be treated as acids in order to model the pH sensitivity.

The constant charge model has been preferred by most researchers, despite its limitations, with considerable success. Here, the exchange process is considered as a partition of ions between two phases with a sharp and distinct boundary. The following equilibrium is given



where A, B are the two exchanging ions, a bar denotes the adsorbed phase and Z denotes the valency.

Using the principles of chemical thermodynamics, the equilibrium state can be expressed by a mass action formula

$$K_{B/A} = \left(\frac{\bar{a}_B}{a_B} \right)^{Z_A} \left(\frac{a_A}{\bar{a}_A} \right)^{Z_B} \quad (4)$$

where $K_{B/A}$ is the thermodynamic equilibrium constant and \bar{a}_i, a_i is the activity of sorbed and dissolved ion i , respectively.

The problem of exchange equilibrium is now reduced to specifying the activities of ion A and B in both phases. This poses no problem for the solution phase, but no exact theory exists to estimate activities in the sorbed phase, although they can be determined experimentally (Bolt 1967; Jensen and Babcock 1973).

Bolt (1967) reviewed various exchange equations used in soil science and Table 1 lists some of the equations used in model studies. A number of other expressions exist, *e.g.* the Kielland function, the Rothmund – Kornfeld and the Donnan equations (Helfferich 1962). In general, the activity of an adsorbed ion is given by its equivalent or molefraction, and the equilibrium constant is now termed a selectivity coefficient, since one cannot expect it to be a constant under varying conditions (*e.g.* exchanger saturation or ionic strength). The Gaines-Thomas equation can be derived from thermodynamics, the Kerr equation is valid only for homoivalent exchange, while the similar Vanselow equation allows for heterovalent exchange. The Davis equation considers the probability of placement of cations with different valency on a regular array of negative pointcharges as supposed to be present on the exchanger surface. This equation is valid only for heterovalent exchange, here mono (B)-divalent (A). The Gapon equation was originally introduced as an empirical description of Na-Ca exchange, however, Sposito and Mattigod (1977) and Harmsen (1979) gave it some thermodynamic justification.

For practical application it is important to select the equation where the selectivity coefficient shows the greatest constancy under varying ionic strength and exchange saturation (Jensen and Babcock 1973; Jensen 1972). Bruggenwert and Kamhorst (1979) list several selectivity coefficients found in the literature. Ion exchange reactions are usually introduced to describe the behaviour of the cations

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Table 1 – Selected Ion Exchange Equations. The structural relationships between the various equations are discussed by Harmsen (1979).

Kerr:	$K_K = \frac{M_B}{\alpha_B} \frac{\alpha_A}{M_A}$
Vanselow:	$K_V \equiv \left(\frac{M_B}{\alpha_B} \right)^{Z_A} \left(\frac{\alpha_A}{M_A} \right)^{Z_B}$
Gaines-Thomas:	$K_{GT} \equiv \left(\frac{N_B}{\alpha_B} \right)^{Z_A} \left(\frac{\alpha_A}{N_A} \right)^{Z_B}$
Davis:	$K_D \equiv \left(\frac{\alpha_A}{M_A (M_B + 2 \left(\frac{n-1}{n} \right) M_A)} \right) \left(\frac{M_B}{\alpha_B} \right)^2$
with $n \equiv 4$ (i.e., square array) the equation reduces to;	
Davis-Krishnamorthy-Overstreet:	$K_{DKO} = \left(\frac{\alpha_A}{M_A (M_B + \frac{3}{2} M_A)} \right) \left(\frac{M_B}{\alpha_B} \right)^2$
Gapon:	$K_G = \frac{N_B}{\alpha_B} \frac{\alpha_A^{1/Z_A}}{N_A}$

$a_i \equiv$ solution activity, $N_i \equiv$ equivalent fraction, $M_i \equiv$ mole fraction, $Z_i =$ valency, $n =$ assumed number of nearest neighbours

Na^+ , K^+ , Mg^{2+} and Ca^{2+} , but also ammonium (NH_4^+), lithium (Li^+) and several radioactive species have been subject to ion exchange modeling.

Ion exchange is generally very rapid. Grove and Wood (1979) found that exchange between the soil particle surface and a solution comprising Ca, Mg and Na ions was completed within two minutes while Reardon *et al.* (1983) found that 20 minutes was sufficient time for equilibration. Sears and Langmuir (1982) suggested that equilibrium may be attained in tens of seconds to 48 hours. Sparks and Jardine (1984) found in their attempt to describe the kinetics of K-Ca exchange an equilibration time of approximately 35-250 minutes depending on the type of mineral. These equilibration times are very short compared with average flow velocities in soil and groundwater systems.

Adsorption

Adsorption is the process whereby solutes adhere to the surface of soil particles. In their study, Travis and Etnier (1981), reviewed the incorporation of various adsorption isotherms into transport models, and in Table 2 is found a listing of the most common adsorption isotherms. The linear and Freundlich isotherms are characterized by having no maximum adsorption capacity. All isotherms are single-species except the competitive Langmuir isotherm, which resembles the ion exchange process, where adsorption of one ion must be accompanied by desorption

Table 2 – Summary of equilibrium adsorption isotherms.

Adsorption Isotherm	Equation
Linear	$S = K_d C$
Freundlich	$S = K C^N$
Langmuir	$S = kbC/(1+kC)$
Langmuir Two-Surface	$S = (k_1 b_1 C / (1 + k_1 C)) + (k_2 b_2 C / (1 + k_2 C))$
Competitive Langmuir	$(C_1 / C_2) / S = (b_2 / k_1 b_1) + (C_1 / b_2 C_2)$

S = sorbed species	K_d = distribution coefficient	K_i = bond strength
C_i = dissolved species	b_i = maximum capacity of sorbed solute	K, N = constants

of the other ion. In the Langmuir isotherms, b is the maximum amount of sorbed solute on the soil and k is a measure of the bond strength holding the sorbed solute on the soil surface. In case the surface has two types of different bond energies, the two-surface isotherm can be used.

The choice of which adsorption isotherm to use is difficult. Travis and Etnier (1981) gave many examples on successful/unsuccesful use of the various isotherms in modeling studies of transport of different species.

Adsorption isotherms have been applied for numerous chemical species, *e.g.* heavy metals, specific organic compounds and phosphate. In most cases the adsorption process is kinetically fast with rates comparable to those found for ion exchange.

The adsorption parameters found in the literature should only be used after careful examination since they only apply to conditions comparable to those for which they are determined. This, of course, is general for all use of borrowed data, but it is especially warranted in the case of adsorption, since various other ions present in higher concentrations directly affect the parameter values.

Complexation

Some constituents in the dissolved phase are present almost entirely in the free ionic form (*e.g.* Cl^-). However, other ions like calcium and magnesium are also present in charged and uncharged inorganic associations. These associations, known as complexes or ion pairs, are due to the electrostatic attraction between the ions of opposite charge.

The possible number of complexes that can form in the soil environment is large. However, in the concentration ranges found in actual cases, relatively few complexes, excluding unspecific complexation by dissolved organic matter, are of practical significance. Complexation is a very fast process, with equilibration times in seconds. Most complexes involve only two ions and the equilibrium relation for such a reaction can be found in Table 3. Here, the reaction is written as a formation and the strength of the complex is expressed by the equilibrium constant or stability constant. The literature is relatively rich in stability constants. Useful compilations

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Table 3 – Equilibrium reactions for complexation (two ions), precipitation/dissolution (three ions) and an open/closed carbonate system.

Reaction type	Equilibrium Relation	Mass action Equation
Complexation	$i A^{Z_A} + j B^{Z_B} \rightleftharpoons A_i B_j^{(iZ_A + jZ_B)}$	$\frac{[C_{AB}^i]}{[C_A]^i [C_B]^j} = K_{AB}^C$
Precipitation/ Dissolution	$A_i B_j C_k \rightleftharpoons i A^{Z_A} + j B^{Z_B} + k C^{Z_C}$	$[C_A]^i [C_B]^j [C_C]^k = K_{ABC}^S ; iZ_A + jZ_B + kZ_C = 0$
Carbonate System		
<i>Closed</i>	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} \equiv K_1$
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \equiv K_2$
	$H_2O \rightleftharpoons H^+ + OH^-$	$[H^+][OH^-] \equiv K_w$
<i>Open</i>	As for closed system + $CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$	$K_{CO_2} P_{CO_2} = [H_2CO_3]$

A, B, C : Involved ions i, j, k : no. of moles K : equilibrium constants (confer text)
 Z_i : Valency $[C_i]$: Activity of species P_{CO_2} : partial pressure of CO_2

have been made by Sillén and Martell (1964, 1971) and for the speciation program GEOCHEM by Sposito and Mattigod (1980).

Precipitation/Dissolution

Free ionic species in the dissolved phase may also exist in equilibrium with a solid phase. Unlike the complexation process, solids may involve more than two ions *e.g.* dolomite $CaMg(CO_3)_2$.

Chemical reactions involving a solid phase are quite often slower than reactions between dissolved species. This is associated with the formation of the solid, which depends on at least two processes: nucleation and crystal growth. Nucleation is the interaction between ions or molecules forming a cluster in order to exceed an activation energy barrier. Thereafter the crystal growth stage begins depositing material on the nuclei. In some cases nucleation is not taking place and the solution will be oversaturated with respect to the free ions (the solubility product is exceeded). Foreign solids may act as a catalyst for the nucleation process by reducing the energy barrier and are often needed to start the process. The growth of crystals occurs in successive reaction steps and impurities in the dissolved phase may at this stage have a profound effect in limiting the overall process.

An equilibrium relation involving three ions is shown in Table 3. The activity of a solid is taken as unity. Here, it is written as a dissociation. The equilibrium constant is better known as the solubility product.

The nature of the precipitation/dissolution process makes it almost impossible to deduce anything about the rates of reaction and time to reach equilibrium in real soils. Several authors indicate that observed levels of supersaturation may be caused by slow kinetics, *e.g.* Suarez (1977) and Nicholson *et al.* (1983) found that the soil solution may have to rise to a level of supersaturation for calcite to precipitate in many natural hydrogeologic settings. On the basis of a number of well water analyses, Suarez (1977) proposed a new solubility product for calcite. Grove and Wood (1979) observed also a supersaturated carbonate solution and suggested that the cause could be slow reaction rate or unexplained soil water interactions. White *et al.* (1984) explained observed calcite supersaturation as being caused by suppressed nucleation kinetics from the coexistence of other aqueous species. Solubility products can be found in *e.g.* Sillén and Martell (1964, 1971) and Sposito and Mattigod (1980).

Open/Closed Carbonate System Equilibria

To explain chemical equilibria, which involve carbonate minerals like calcite (CaCO_3) or dolomite $\text{CaMg}(\text{CO}_3)_2$ a distinction between an open or closed system must be made. The unsaturated zone is a good example of an open system. Decay of organic matter and respiration of plant roots, continuously produces CO_2 to the soil atmosphere. Equilibrium between CO_2 in the gas and aqueous phase will thus lead to the generation of dissolved carbonic acid (H_2CO_3) that reacts with soluble minerals. A closed system can be characterized by that below the groundwater table. Here, no soil atmosphere is present and due to the low diffusion coefficient of CO_2 in water and lack of organic matter, no substantial production or replenishment will take place.

Simplified carbonate systems have been studied extensively (*e.g.* Garrels and Christ 1965; Freeze and Cherry 1979). These systems contain only calcite or dolomite. In Table 3 the general equilibrium relations are presented for open/closed carbonate systems. Basically, they include the first and second dissociation of carbonic acid and the stability of water for both systems and in addition for the open system, Henry's law for the interaction of gaseous and dissolved CO_2 .

It is worth noting that the open system calculations require either knowledge of the distribution of CO_2 in the soil profile or computation of production and transport of CO_2 in the system.

Coupling Between Physical and Chemical Model Components

The physical and chemical model can be coupled by two distinct methods.

In the first method (one-step) a system of partial differential and algebraic equations are solved simultaneously. Here, the mass action expressions from the chemical reactions are inserted directly into Eq (1). The mathematical nature of the resulting problem and its solution strategy is dependent here on the nature of

the chemical reactions. These models are also called integrated transport/chemistry models (Abriola 1987).

Different alternatives are possible for solving this system of equations. In its simplest form, exemplified by Lai and Jurinak (1971, 1972), a system with two exchanging cations can be described by one equation, when considering one ion as a complementary ion to the other because of the stoichiometric nature of the process. This equation was solved by finite difference techniques. In the more advanced form, the full set of equations, including several processes, were solved by finite element techniques (*e.g.* Rubin and James 1973; Valocchi 1981; Jennings *et al.* 1982). A different technique which also solves the total set of equations simultaneously, but does not insert the chemical mass action expressions directly into Eq. (1), was developed by Miller and Benson (1983). This set of differential/algebraic equations, was solved by finite differences and a Newton-Raphson iteration technique.

The second method (two-step) of coupling the chemical and physical model solves the chemical reactions isolated (decoupled) from the governing transport equations. These models are also called modularized chemistry models (Abriola 1987). The method consist then of two steps. First step assumes all species are non-reactive and hence, transported according to a simple advection-dispersion process. Second step solves the algebraic system of chemical equations by an iterative procedure. These two steps can also be treated by different techniques. The solution of the advection-dispersion equations can be approximated by standard numerical techniques; finite difference or finite element (*e.g.* Grove and Wood 1979; Cederberg *et al.* 1985). Nordstrom *et al.* (1979) discuss various iteration procedures (*e.g.* successive approximation or Newton-Raphson) to solve the set of chemical equations.

There are several variations or hybrids of both methods. Cederberg *et al.* (1985) formulate their model in terms of components (tenads) to reduce the number of mass transport equations, but utilize a two-step method. Process separation is taken care of by iterating between the two sets of equations. Narasimhan *et al.* (1986) use an equilibrium reaction path model (PHREEQE) to evaluate a *time-dependent* source-sink term in an explicit solution procedure. Lewis *et al.* (1987) developed a model which combines features of both coupling methods.

Models which solve the physical set of equations by a mixing cell or plate model all utilize the two-step method.

The two methods have different advantages. The first method secures that all processes (physical and chemical) occur simultaneously, while the second method is flexible because the separation of physical and chemical processes makes it easy to delete or add processes. In general, it is recognized that the two-step method is the most competitive in terms of computer cost and flexibility when dealing with complex systems (Abriola 1987; EPRI 1986). However, this conclusion is problem dependent.

Models from the Literature

Chemical solute transport models reported in the literature are discussed in the following with focus on the chemical submodels. Attention is also paid to model validation and possible field applications.

The survey is not exhaustive. The choice of which models to include has been based on several factors. First of all, the survey will show the historical trend in developing more and more complex models, however, secondly it has also been the intention to include recently developed simple models, which may prove to be sufficient in many cases. Models that have been applied to field cases have been given a high priority, because they often reveal unavoidable model limitations and because application and practical use is the ultimate goal for model development.

For convenience, the models are presented as either saturated or unsaturated zone models. The structure of the physical model and the coupling to the chemical model are normally not discussed. However, these details are given in Tables 4-5, which is a full summation of most of the models.

Saturated Zone Models

Lai and Jurinak

Lai and Jurinak (1971, 1972) and Jurinak *et al.* (1973) developed a model to simulate binary (*i.e.* two ions), homovalent, cation exchange involving a general non-linear exchange function. Other chemical processes were not considered. The exchange function was based on a separation factor and Kielland function and are of a semiempiric nature. It offers flexibility when solving for a variety of exchange isotherms, because it includes concentration dependent equilibrium constants. The model was validated against column experiments with reasonable success. First, the general exchange function was fitted to the data describing the adsorption isotherm, and secondly, this function was used to predict concentration profiles.

Rubin and James

In their classical paper Rubin and James (1973) treated the problem of multi-species ion exchange. The purpose was to introduce a "basic methodological framework" from which a more general model could be developed (*e.g.* incorporating two or three dimensions, transient solutions, kinetically-controlled ion exchange or other equilibrium chemistry). The ion exchange process was described by a mass action or a Gapon equation. Several hypothetical sample cases were simulated, which included the following effects on the transport of cations; (a) dispersion coefficient and exchange capacity, (b) two-layered medium with different exchange capacities, (c) difference in total normality between displacing and initial solution, (d) gypsum dissolution and, (e) mass action vs. Gapon equation. Although there was no validation of the model, it was concluded that the Galerkin finite element method was an efficient technique to solve the highly non-linear system of partial differential equations.

Chemical Solute Transport Models

van Beek and Pal

Beek and Pal (1978) developed a model to simulate the transport of sodium, calcium and sulphate in a system where dispersion could be neglected. The model considers ion exchange (Gapon equation), complexation and precipitation/dissolution of CaSO_4 . A soil column experiment consisting of a synthetic exchanger was used to validate the model. The selectivity coefficient for Ca-Na exchange was calculated from an experimental exchange isotherm. Agreement between simulated and observed values was good. Deviations were explained as caused by neglecting the dispersion process.

Valocchi et al.

Valocchi (1981) and Valocchi *et al.* (1981a, 1981b) implemented the same numerical scheme as Rubin and James (1973) to simulate the transport of cations in a field experiment with the direct injection of advanced treated municipal effluent into an aquifer. Only ion exchange was considered. In Valocchi (1981) and Valocchi *et al.* (1981a), a comprehensive chromatographic analysis was developed for the *a priori* characterization of key concentration profile features. Simulated concentration profiles were then compared with the analysis. The case studies included both homovalent and heterovalent exchange in binary and ternary (*i.e.* three ions) systems. For all cases, the model was able to predict the location of profile fronts and plateaus. This only gave a “qualitative” validation, but impressive results were also achieved for the field experiment. Advanced treated municipal effluent was injected into a shallow aquifer and the model was set up to describe two-dimensional areal transport including a solution to the groundwater equation. The exchange, using a Gaines-Thomas expression, between four major cations (Ca, Mg, Na, NH_4) was simulated using laboratory determined parameters (*i.e.* selectivity coefficients, CEC). Good agreement was found between simulated and actual breakthrough for all cations except NH_4 , even though the actual breakthrough showed several profile fronts and plateaus.

Miller and Benson

Miller and Benson (1983) developed a model including ion exchange, aqueous complexation and dissociation of water. Ion exchange is described by a Vanselow equation for basis solutes and complexes. The model was validated on the field experiment by Valocchi (1981) with good results and furthermore, hypothetical sorption cases showed that using a linear sorption model (constant distribution coefficient) is inadequate when surface site competition is taking place between the involved ions. Additional examples showed the combined effects of all processes on the migration of strontium.

Grove, Stollenwerk and Kipp

The model by Kipp *et al.* (1986) is an example of the potential use of a simple, one-dimensional transport model. The purpose of the model was to estimate clean out

times for the decontamination of strontium 90 in an unconfined aquifer. The model considers only ion exchange reactions and decay of strontium 90. From laboratory experiments it was concluded that other major cations (Ca, Mg, K and Na) and the strontium concentration affect sorption of strontium 90. However, since Ca comprised about 90 % of the equivalents in the cation solution and the concentration of strontium was much less than the total concentration of other cations, all cations except strontium 90 were lumped into one component B. Hence, only divalent-divalent exchange between B and strontium 90 was considered. Total ion concentration was a function of time and space and had to be considered. Radioactive decay of strontium 90 had a negligible effect on the total ion concentration, which then could be treated as a conservative species. A sensitivity analysis of the involved parameters in this simplified model yielded a range of clean out times for the contaminated aquifer.

It was concluded, as in other model studies, that the use of a linear sorption model with constant distribution coefficient is inadequate when the sorption process depends on other competing species and the total ion concentration.

A model, similar to the one used by Kipp *et al.* (1986), was developed by Grove and Stollenwerk (1984). In addition to ion exchange and radioactive decay, the model includes Langmuir and Freundlich adsorption. The model was checked against analytical solutions in two ways. For linear sorption and first order decay a direct comparison is possible. Introducing non-linear sorption/exchange makes it impossible to compare directly, however, by adjusting the non-linear isotherm to approach the linear isotherm, the numerical solution should approach the analytical solution. The model proved successful in both ways.

Jennings, Kirkner and Theis

Jennings *et al.* (1982) developed a model not only comprising ion exchange but also soluble complexation in a multicomponent system. The ion exchange process is described by a surface complexation model in which the active surface sites are treated as an acid to model the pH sensitivity of the exchange capacity. The pH must be known and is treated as an independent variable. The model was not validated against any experiments, but by considering only a simple case of soluble complexation (two metals and one ligand allowed to form one complex) the simulated results could be compared with an analytical solution. Furthermore, the effects of the physical parameters (velocity, dispersion coefficient, space and time discretization) on the complexation process were investigated. It was concluded that a desired accuracy was possible with appropriate space and time discretization. Examples illustrating the sorption process and the combined complexation-sorption process were also given.

The following two models are hybrid formulations of the two methods of coupling the physical and chemical model components (although they are classified as two-step models in Table 4). This is so because the models are formulated in terms

of tenads and the non-linearity and coupling in and between the mass transport equations are retained. However, chemical calculations are performed separately. Iterations between the two sets of equations are carried out.

The first model (Kirkner *et al.* 1984) considers a three-component system with ion-exchange and soluble complexation. Ion exchange is described by a general mass action expression and incorporated into the transport equation as an implicit function of total soluble concentration. The model was tested on the same hypothetical examples as in Rubin and James (1973), but with the addition of the effects of including the complexation process.

The second model by Kirkner *et al.* (1985) is interesting in the fact that it, besides equilibrium ion exchange, incorporates sorption kinetics in the form of a dynamic Langmuir isotherm. No other processes are included. The dynamic Langmuir isotherm accounts for multi-species competition for the sorptive sites. If the local equilibrium assumption is valid, the isotherm is steady and reduces to the linear or two-surface Langmuir isotherm (equivalent to an exchange process) in a single and two-component system, respectively. The model was verified against an analytical solution for single-component transport with sorption kinetics. The results were good. A soil column experiment with cadmium and nickel was also simulated. Using experimentally determined parameters and assuming a steady Langmuir isotherm, large discrepancies between observed and predicted values were seen. This was explained by non-equilibrium conditions, and employing the dynamic Langmuir isotherm and calibrating the rate constants yielded better results.

Reardon, Dance and Schulz

In connection with a case study of the migration of contaminants in the groundwater at a landfill at Borden, Ontario, Dance and Reardon (1983) developed a model which included the following processes; ion exchange, complexation and closed carbonate calcite dissolution/precipitation. Ion exchange was described by a Gaines-Thomas equation and complexation was allowed between all ion pairs of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , with SO_4^{2-} , HCO_3^- and CO_3^{2-} . These processes, together with calcite equilibrium, formed 26 equilibrium equations in 26 unknowns. Selectivity coefficients and exchange capacities were determined by Reardon *et al.* (1983), while the practical solubility product of calcite suggested by Suarez (1977) was used. One-dimensional flow was assumed at the test site (approximately 8 m in flow direction). In this study calcite reaction rates were investigated but were of no influence. Comparison between predicted and observed values was possible 0.75 and 1.75 m downstream from the injection point. The model predicted, with good agreement, the release of Ca and Mg at the expense of Na and K (slightly and strongly retarded, respectively). However, the model underestimated the dissolved Mg concentration at 0.75 m and it was suggested that Mg exchange was not appropriately accounted for.

Schulz and Reardon (1983) developed a model similar to the model by Dance

and Reardon (1983). However, they tried to simulate the physical transport of solutes more closely than Dance and Reardon (1983). The sacrifice was a more simple chemical model, *e.g.* no complexation is allowed. The model considers only one-dimensional flow, but two-dimensional transport, *i.e.* lateral and longitudinal dispersion is included. Model results were compared with field results for the Borden test site. However, because the observed dispersivity coefficients increased by nearly an order of magnitude over 11 m of flow distance and the model requires fixed values, only results within a short distance from the source could be simulated. A quantitative comparison was only possible for Cl^- in plan view, but the same observations for areal transport of Ca, Mg, Na and K, as in Dance and Reardon (1983), were also seen.

Grove and Wood

In a study of the effects of artificial recharge on the chemical composition of the soil-water system, Grove and Wood (1979) developed a model that accounted for ion exchange, precipitation/dissolution and complexation. Mg-Ca exchange and Na-Ca exchange were described by a mass action and Davis-Krishnamoorthy equation, respectively. Gypsum was the only solid that could precipitate/dissolve because in a column experiment no carbonate precipitation was observed, even though the water was supersaturated with calcium carbonate. Complexation included CaSO_4° and MgSO_4° . Laboratory determined parameters were used to simulate soil column and field experiments. Good agreement was achieved for the column experiment. The field site consisted of a recharge facility, where a saturated, one-dimensional infiltration was assumed down to the water table 35 m below the surface. Sampling took place at 0.6, 1.9 and 7.9 m. Comparison between predicted and observed values showed good agreement at 1.9 m, however at 0.6 m the agreement was less good and at 7.9 m large discrepancies were observed.

Walsh et al.

Walsh *et al.* (1984) developed a mixing cell model coupled to a comprehensive equilibrium chemistry model. The mass transport equation was formulated in terms of total soluble concentration and solved by an explicit, backward-in-space finite difference scheme. In effect, this scheme is a mixing cell model. The cell solution entering a downstream cell is known (backwards-in-space) and the immobile concentrations (minerals) in that cell are also known (explicit), and hence, no iteration between the sets of transport and chemical equations is necessary. The chemical component accounts for complexation, precipitation/dissolution, redox processes and adsorption. In redox processes, conservation of electrons are invoked and the total concentration of electrons is transported according to the advection-dispersion equation. Of special interest in applying the model was the study of precipitation/dissolution waves (fronts). Based on a four element simulation, "scalable" problems were identified. If the correct mineral sequence (waves, fronts) is known, then, together with the "downstream equilibrium" and "coher-

ence” condition, the problem is scalable. The downstream equilibrium condition states that whenever a solid disappears across a wave (assumed a step function) the aqueous phase concentrations are saturated with respect to that solid even though the solid itself is not present in the downstream region. Hence, this constraint apply for the downstream region. The coherence condition states that all elements are transported with the same velocity. If a problem is scalable great savings in computer resources can be achieved. If changes in injection and initial conditions do not alter the sequence of minerals, then only one computer run is necessary. All other problems may then be solved from a scalable problem set of algebraic equations. An example of a scalable problem is presented as uranium roll front deposition. The time required to form an ore deposit is in tens of millions of years. A simulation period of this order is not possible. However, by assuming some intermediate condition a relative shorter period was sufficient. By using the scalable property all other intermediate time conditions could be calculated. Chemical reactions between 26 minerals and 60 aqueous species were accounted for. Redox processes were a dominant reaction. The deposition history agreed qualitatively well with what was expected.

Bryant *et al.* (1986) included ion exchange of an arbitrary number of aqueous species on an arbitrary number of both insoluble and soluble exchangers in the model presented above. Their primary interest was to study the combined effects of ion exchange and precipitation/dissolution waves in alkaline flooding of oil recovery. First, the ion exchange calculations were validated by simulating a sodium-calcium exchange experiment. Model results agreed favourably with observations. Second, hypothetical examples concluded that the individual ion exchange or precipitation/dissolution wave phenomena cannot be superimposed, but rather a complex set of plateaus and waves was observed. These examples neglected dispersion. Finally, the model was applied to alkaline flooding in an oil-bearing core. Generally, the model simulated the qualitative features of pH loss and dissolution, however, the results were conservative estimates. The latter was explained as being due to kinetic limitations on silica dissolution. In these examples ten minerals, 18 aqueous and three sorbing species were accounted for.

Cederberg, Street and Leckie

To test the applicability and effectiveness of a two-step method, Cederberg *et al.* (1985) coupled two previously developed models. However, in contrast to other two-step models, the decoupled set of equations were not solved sequentially but rather by iterating between the two sets. The chemical submodel MICROQL, a scaled down version of MINEQL (Westall 1976) accounts for various processes, here exemplified by sorption, ion exchange, aqueous complexation, and dissociation of water. Sorption and ion exchange are modeled by either a surface complexation or a constant charge model. Iteration between the two sets of equations was established by considering total species concentrations. The full model was tested

on hypothetical cadmium transport cases and the field experiment by Valocchi (1981). Sorption of cadmium was modeled by the surface complexation model, while the constant charge model was used to describe ion exchange between the major species in the field experiment. The latter showed close agreement between simulated and observed breakthrough curves.

Narasimhan et al.

A model study of the contamination of a shallow aquifer as a result of the infiltration of uranium mill tailings water lead to the development of a three-stage model (Narasimhan *et al.* 1986). In the first stage, time-dependent fluid potentials, fluid saturations and infiltration rates were calculated. These results acted as input to stage two which consisted of the migration of species in the unsaturated zone and of a dynamic mixing of the infiltrating water and the ground water. A program DYNAMIX was developed for this stage. Here, a multiple-species, advective-dispersive transport model was coupled to an existing geochemical equilibrium model PHREEQE (Parkhurst *et al.* 1980). At the third stage, non-reactive, single-species transport was calculated in order to predict plume migration. Due to a high pH-difference between tailings water and the ground water, mineral precipitation/dissolution processes were considered the most important and the mixing of waters was treated as a titration process. It was not computationally feasible to apply DYNAMIX to the entire study area, hence, stage two involved only the tailings pile area and the aquifer immediately below, while, in stage three, no chemical reactions outside this area and only single-species transport were considered. In the case study, stage two and three were linked by calculating gypsum precipitation-rates in stage two and using them as input to stage three to predict sulphate plume migration in the tailings pile area. Outside this area precipitation-rates were set equal to zero and hence, sulphate was transported conservatively. Observed values for sulphate, pH and Fe concentrations in the unsaturated zone and sulphate plume contours were available to validate the model. The model predicted no species precipitation in the unsaturated zone and a comparison between simulated and observed values were good for pH, while some discrepancy existed for sulphate and Fe. Comparison of sulphate plumes after twenty years from the time of mill abandonment showed reasonable agreement. This comprehensive study made use of numerical models, which all handled flow in three-dimensions and can account for heterogeneities. As a result of computational time limitations due to the complex set of models, some restrictions had to be made. Conservative sulphate transport in stage three has already been mentioned and furthermore, the unsaturated zone aquifer volume below the tailings area (800m × 350 m × 10 m) had to be divided into only seven elemental volumes in stage two.

van Ommen

A mixing cell model developed by van Ommen (1985) was applied to the field experiment by Valocchi *et al.* (1981). The mixing of masses was calculated on the

basis of known intervals of residence times between the cells given that the streamlines are known *a priori*. As opposed to Valocchi *et al.* (1981) the Gapon and Kerr equations were used. On the basis of the aquifer geometry and injection rate in the experiment, interval of residence times and cell geometry could be specified. Comparing the model results and observations revealed that a quite satisfactory agreement was achieved. Using only five cells proved slightly better than using ten cells. A major advantage of this method is its simplicity, however, it lacks a physical meaning of the dispersion coefficient.

Appelo and Willemsen

A more comprehensive chemical mixing cell model was developed by Appelo and Willemsen (1987) by attaching the EQ3/6 equilibrium code (Wolery 1982) to a mixing cell model. The equilibrium code was modified to include a Gapon ion exchange reaction. The model was applied to investigate dispersive intrusion of salt water into a fresh water aquifer and diffusion from a stagnant salt water body. The dispersive flow situation was that of a field situation, where streamlines were known *a priori*. The simulations allowed for the estimation of the location of the fresh-salt water interface and documented the buffering effects by cation exchange on the water composition upon salt water intrusion.

Lewis et al.

A model considering aqueous complexation and either sorption or ion exchange were developed by Lewis *et al.* (1987). The model is a hybrid between the two methods of coupling the physical and chemical component, but has been classified in Table 4 as a two-step method. Most notably, this model uses a promising solution strategy that is compatible with existing non-reactive transport codes. An iterative solution procedure (Picard scheme) secures that all non-linear effects are accounted for, while still keeping chemical calculations separate. The basic transport model was a modified version of SUTRA (Voss 1984). Linear sorption or binary ion exchange together with complexation were investigated in one and two-dimensional hypothetical settings. The model is limited to few simple, but important chemical reactions.

Unsaturated Zone Models

Routson and Serne

Routson and Serne (1972) developed a model to predict the potential movement of trace solutes in soil systems. The model considered macrosolute and microsolute chemistry. A microsolute is defined as one whose presence does not measurably affect the sorption either of other microsolute or of the macrosolutes. However, the solution concentration of the ions present in macro-amounts does affect the sorption of microsolute. Macro model chemistry included sorption, ion exchange, complexation, dissolution, and precipitation, while micro solute chemistry was simulated by an empirical method. In this context only macrosolute chemistry is of

interest.

Ion exchange was described by an empirical corrected mass action expression, similar to the Rothmund and Kornfeld equation (Harmsen 1979). An empirical activity correction parameter must be estimated from batch experiments. Two slightly soluble salts and one complex ion formation were also included in the macro model. These were gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), limestone (CaCO_3), and undissociated calcium sulphate (CaSO_4°). The carbonate system was modeled by assuming the system open and using Henry's law. Column studies were conducted to validate the model. System parameters (e.g. column length, flow rate, soil type and saturation) were varied in each experiment. Strontium or cesium was used as micro solutes, while Na^+ , Ca^{2+} , Mg^{2+} and K^+ acted as macrosolutes. Generally, comparison between simulated and observed values showed better agreement for the microsolutes than the macrosolutes.

Dutt et al.

Early work by Dutt (1962, 1964) Dutt and Anderson (1962), Dutt and Doneen (1963), Dutt and Tanji (1962), Dutt *et al.* (1972b), Tanji *et al.* (1967), Paul *et al.* (1966) laid the foundation for a comprehensive model developed by Dutt *et al.* (1972a). While these early models considered only saturated flow, ion exchange of Ca and Mg and solubility of gypsum, Dutt *et al.* (1972a) extended these models to also account for unsaturated conditions, nitrogen transformations in the soil, evapotranspiration and withdrawal of nitrogen by plants. Furthermore, a relation between the moisture flow and the biological-chemical programme was established to be able to simulate the dynamics of the various processes. Ca-Mg and Na-NH₄ exchange were described by a mass action equation, while a Gapon equation was used for Ca-Na exchange. Experimental data were needed to describe the reaction of CaCO₃ at various moisture levels. It was found that the H₂CO₃ content varied with different soils and moisture levels. This variation was incorporated into a solubility product parameter, K' , and a nearly linear relationship between the logarithm of K' and moisture level was found. For gypsum and undissociated CaSO₄[°], the usual solubility product and stability constant were used. The model was validated using two experiments. First, at batch experiment (no moisture flow) with no nitrogen transformations and plant uptake was simulated. A comparison between simulated and observed exchangeable concentrations (Ca^{2+} , Mg^{2+} and Na^+) showed good agreement. Next, a lysimeter study (with moisture flow) was simulated including all processes. Large discrepancies existed between predicted and observed values for plant uptake of nitrogen and organic-nitrogen content in the soil profile. Comparison of the salt content was not performed.

Tanji et al.

Tanji *et al.* (1972) extended previous models by Dutt (1964) Dutt and Tanji (1962) and Tanji *et al.* (1967). Simplistic assumptions were made for water contents, since leaching was taken to be at field capacity, neglecting the infiltration and redistribu-

tion process of soil water from variations in application of irrigation water. The chemical equilibrium calculations included gypsum solubility, complexes of CaSO_4° , MgSO_4° , and NaSO_4^- , ion exchange between Na, Ca, Mg and Langmuir adsorption of boron. Ca-Mg and Na-Ca ion exchange were described by a mass action and Davis-Krishnamoorthy-Overstreet equation, respectively. A field leaching study was simulated with reasonable agreement between predicted and observed values. Deviations were ascribed the simple flow model. The model was found well suited for estimating the amount of water and gypsum needed to reclaim sodium-affected profiles.

Jury et al.

Jury *et al.* (1978) developed a transient model, which included a water and salt transport model and an approximate solution to the transport equilibrium problem. This approximate solution resembles the two-step method, since it only periodically restores equilibrium. However, as the frequency of restoration calculations increase, the solution will approach the two-step method. By only restoring equilibrium periodically computer time is saved. The model includes complexation, precipitation, dissolution, cation exchange and the carbonate system. A mass action equation was used for Ca-Mg exchange and a sodium adsorption ratio (SAR) for Na-Ca-Mg exchange. The model was used to simulate the effect of the chemical processes on the time needed to reach a steady state between infiltrating water and the soil system. Jury and Pratt (1980) used the model to estimate the salt burden of irrigation drainage waters as compared to two other models; a proportional model which only includes mixing and a steady state model based on the same equilibrium model as used in the transient model. Large differences existed in the prediction between the three models. Shaviv and Jury (1986) modified the model to include changes in potassium selectivity.

Robbins et al.

Robbins *et al.* (1980a) combined a salt flow model with a chemical equilibrium model to describe transient salt movement in soils. Chemical calculations accounted for complexation, lime and gypsum solubility and exchange equilibria. The soil system was assumed open with respect to CO_2 governed by the soil pH. However, the soil was considered sufficiently buffered that the pH at a given depth is constant. Ion exchange was described by a modified Gapon expression (Robbins *et al.* 1980b). The model was developed so that precipitation/dissolution and exchange processes could be turned on or off if needed. The result from a lysimeter study showed that satisfactory results only were achieved when both chemical precipitation and cation exchange were considered.

Melamed et al.

Melamed *et al.* (1977) added a source-sink term to the transport equation to simulate precipitation/dissolution processes. Ion exchange was neglected because

salt movement was treated in terms of total salinity. The source-sink term was adjusted to predict observed values, however, simulation of a field leaching study was not satisfactory.

van Genuchten, Wierenga and others

The following group of models all combine a physical non-equilibrium transport model with a chemical equilibrium model. Here, physical non-equilibrium is present because the soil matrix is thought of as consisting of a mobile and an immobile zone, where diffusive mass transfer takes place between the two zones. The transport of solutes is then influenced by the mass transfer rate between the two zones. The group of models shows great diversity with respect to which process is assumed the most dominant. One of the first models was proposed by van Genuchten and Wierenga (1976) and this later became the foundation for other models. Here, diffusive mass transfer was assumed to be proportional to the concentration difference between the two zones. Chemical equilibrium is described by a simple linear exchange isotherm. This system can be solved analytically. Nkedi-Kizza *et al.* (1983) evaluated this type of model with a similar model where no immobile zones were present against observed breakthrough curves.

Several extensions of this model have been made. Mansell *et al.* (1986) use a Gaines-Thomas exchange relationship instead of a linear exchange and also include concentration dependent selectivity coefficients. Eijkeren and Loch (1984) utilize a Gapon equation. A more comprehensive model was developed by Förster (1986). Here, the model by van Genuchten and Wierenga (1976) was coupled to an equilibrium model which accounted for ion exchange, complexation and precipitation of one salt. The purpose of the model was to simulate the effect of acid rain on the soil environment. Sorption/desorption of hydrogen and aluminium and precipitation of AlOH_2SO_4 were the main processes. The model by Nkedi-Kizza *et al.* (1982) is slightly different from the model by van Genuchten and Wierenga (1976), in that diffusive mass transfer follows Fick's second law of diffusion.

Danish Hydraulic Institute

A comprehensive solute transport model consisting of several submodels was proposed by DHI (1986). The basic transport model accounts for one-dimensional advection and two-dimensional dispersion. The latter allows for simulation of transport of solutes from area and line sources, and in addition, a coneshaped spreading of solutes from a point source by solving the transport equation in polar coordinates. When desired or needed the following submodels are easily attached; (a) transient calculation of moisture content and water flow, (b) addition of immobile water (c) chemical equilibrium/non-equilibrium reactions, (d) plant uptake and (e) oxygen transport and consumption. Chemical equilibrium is assumed for ion exchange (Gaines-Thomas), complexation, precipitation/dissolution, the open carbonate system and adsorption, while non-equilibrium reactions are possible only for adsorption. This submodel also includes first order decay or production.

Chemical Solute Transport Models

By attaching submodels (b) and (c), the model was validated against observed breakthrough curves from a column experiment with reasonable success. A hypothetical example showing the models applicability to aid in managing irrigation schemes was carried out by attaching submodels (a), (c) and (d).

Conclusion

From Tables 4 and 5 it is possible to compare all the models and draw conclusions about the state-of-the-art of transport and equilibrium chemistry modeling. It is clear that this selected group of models shows great diversity with respect to complexity and general applicability to field scale problems. This conclusion rests on the fact that many of the models were developed for a specific purpose, and thus, are only as complex as needed. Some of these models are so purpose specific that their general applicability is very limited. It is therefore difficult to point out models formulated in such a general way, that they are applicable to a wide range of problems and systems.

Table 4 = Description of physical component and coupling to chemical component for selected models.

Reference	Saturated	Unsaturated	Flow	Transport	Spatial dim. of transport	Num. method to solve transp.	One step	Two step
Lai & Jurinak (1971)	x		-	MBE	1	FDM	x	
Rubin & James (1973)	x		-	MBE	1	FEM	x	
Valocchi (1981)	x		(+) ^{a)}	MBE	(2) ^{a)}	FEM	x	
Jennings <i>et al.</i> (1982)	x		-	MBE	1	FEM	x	
Miller & Benson (1983)	x		-	MBE	1	FDM/NR	x	
Kipp <i>et al.</i> (1986)	x		-	MBE	1	FDM	x	
Grove & Stollenwerk (1984)	x		-	MBE	1	FDM	x	
van Beek & Pal (1978)	x		-	(MBE) ^{b)}	1	FDM		x
Grove & Wood (1979)	x		-	MBE	1	FDM		x
Dance & Reardon (1983)	x		-	MIX	1	-		x
Schulz & Reardon (1983)	x		-	Analytical-MIX	2	(Analytical)		x
Kirkner <i>et al.</i> (1984)	x		-	MBE	1	FEM		x
Walsh <i>et al.</i> (1984)	x		-	MIX	1	FDM		x
van Ommen (1985)	x		-	MIX	1	FDM		x
Kirkner <i>et al.</i> (1985)	x		-	MBE	1	FEM		x
Cederberg <i>et al.</i> (1985)	x		-	MBE	1	FEM		x
Bryant <i>et al.</i> (1986)	x		-	MIX	1	FDM		x
Narasimhan <i>et al.</i> (1986)	x	x	+	MBE	3	IFDM		x
Appelo & Willemssen (1987)	x		-	MIX	1	-		x
Lewis <i>et al.</i> (1987)	x		-	MBE	2	FEM		x
Routson & Serne (1972)		x	-	MIX	1	-		x
Dutt <i>et al.</i> (1972a)		x	+	MIX	1	-		x
Tanji <i>et al.</i> (1972)		x	-	MIX	1	-		x
Jury <i>et al.</i> (1978)		x	+	MBE	1	FDM		x
Robbins <i>et al.</i> (1980)		x	+	MBE	1	FDM		x
Melamed <i>et al.</i> (1977)		x	-	MBE	1	FDM		x
DHI (1986)		x	+	MBE	2	FDM		x

^{a)} Included to simulate field experiment

^{b)} Neglects physical hydrodynamic dispersion

MBE = Mass Balance Equation

MIX = Mixing Cell Model

FDM = Finite Difference Method

FEM = Finite Element Method

NR = Newton-Raphson

IFDM = Integrated Finite Difference Method

Table 5 - Description of Chemical Component and Validation Methods for Selected Models

Reference	Aqueous Activity Correction	Complexation	Precipitation Dissolution	Ion Exchange - Adsorption ^{a)}	Carbonate System	Validation ^{b)}	Comments
Lai & Jurinak (1971)	-	-	(-)*	Kielland	-	A-SC	*Included in Jurinak et al. (1973)
Rubin & James (1973)	-	-	(-)*	Gaines-Thomas	-	-	*Can be included
Valocchi (1981)	(Davies)*	-	-	Gaines-Thomas	-	A-SC-FIELD	*Can be included
Jennings <i>et al.</i> (1982)	-	+	-	Surface Complexa.	-	-	
Miller & Benson (1983)	Davies	+	-	Vanselow	-	FIELD*	*From Valocchi
Kipp <i>et al.</i> (1986)	-	-	-	Mass action	-	-	+radioact.decay
Grove & Stollenwerk (1984)	-	-	-	Mass action Langmuir Freundlich	-	A	+first order rate reaction
van Beek & Pal (1978)	Davies	+	+	Gapon	-	SC*	*Synthetic
Grove & Wood (1979)	Debye-Hückel	+	+	Mass action DKO ^{d)}	-	SC-FIELD	
Dance & Reardon (1983)	-	+	+	Gaines-Thomas	-	FIELD	
Schulz & Reardon (1983)	+	-	+	Gaines-Thomas	Closed	FIELD	*Expression not given
Kirkner <i>et al.</i> (1984)	+	+	-	Mass action	-	-	Examples from Rubin & James (1973)
Walsh <i>et al.</i> (1984)	+	+	+	Adsorption (Not given)	-	-	Includes redox processes

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van Ommen (1985)	Davies	-	-	-	Gapon/Kerr	-	A-FIELD*	*From Valocchi
Kirkner <i>et al.</i> (1985)	-	+	-	-	Langmuir*	-	A-SC	*Includes kinetics
Cederberg <i>et al.</i> (1985)	+	+	+	+	Surface Complex*	-	FIELD**	*From MICROQL **From Valocchi
Bryant <i>et al.</i> (1986)	+	+	+	+	Mass Action Mass action	-	SC	See also Walsh <i>et al.</i> (1984)
Narasimhan <i>et al.</i> (1986)	-	-	+	+	Adsorption	-	FIELD	*From PHREEQE
Appelo and Willemssen (1987)	-*	-*	-*	-*	Gapon*	-	FIELD	*From EQ3/6 (or can be included)
Lewis <i>et al.</i> (1987)	-	+	-	-	Mass action	-	A	
Routson & Serne (1972)	Davies	+	+	+	Rothmund- Kornfeld	Open	SC	
Dutt <i>et al.</i> (1972a)	Debye- Hückel	+	+	+	Mass action	Open	BATCH	
Tanji <i>et al.</i> (1972)	Davies	+	+	+	Gapon Mass action	-	FIELD FIELD*	*Field basins
Jury <i>et al.</i> (1978)	-	+	+	+	DKO ^{a)} Mass action	Open	-	
Robbins <i>et al.</i> (1980)	Davies	+	+	+	SAR ^{a)} Gapon	Open	SC*	*Lysimeter tanks
Melamed <i>et al.</i> (1977)	-	-	+	+	-	-	SC-FIELD	*Incl. kinetics
DHI (1986)	Davies	+	+	+	Gaines-Thomas	Open	SC	+other submodels

a) Structural agreement; see also text (DKO=Davies-Krishnamoorthy-Overstreet; SAR = Sodium Adsorption Ratio)

b) A ≡ analytical, SC ≡ Soil Column Experiment, BATCH ≡ Batch Experiment, FIELD = FIELD Experiment

Table 4 shows that all models except one have been developed for one medium, either the saturated or the unsaturated zone. Only Narasimhan *et al.* (1986) is an example of the potential use of these models in both zones. Few models are capable of solving the flow equation. Generally, this is not crucial, because it can be assumed that the flow and transport equations can be solved independently and hence, these transport models can be linked to flow models (see *e.g.* Oster 1982). As mentioned earlier, most models are also one-dimensional. This might be adequate for the unsaturated zone, however, for the saturated zone it is a great limitation.

Table 5 clearly underlines the point that most of these models are developed for a specific purpose, *e.g.* some processes were omitted because they were of no importance and specific appropriate ion exchange equations were chosen. Table 5 also shows the lack of field validation studies. The field experiments that appear in the table have been »short scale« experiments with maximum transport distances of 20 m, and more typically less than 10 m. Furthermore, all models utilize a subset of the equilibrium equations outlined in Tables 1-3. The number of solutes to include is problem dependent. Until recently, most models have been single component with fairly simple chemical processes, but Table 5 shows that more advanced models accounting for several interacting components and complicated reactions have emerged.

Based on this survey, it is felt that future research should be directed towards more field scale validation studies with present models rather than developing still more complex models. Future field experiments should be based on "short" and "long" scale experiments in order to determine whether geochemical processes are accurately represented by the present chemical submodels (Tables 1-3), compared to the variability and uncertainty emerging from expanding the scale on the cost of data intensity. In doing so, one must also try to develop more practical guidelines to investigate the validity of the local equilibrium assumption or identify other processes. It is clear that, with the present models, these may have to be expanded to two and three dimensions. However, with the development of faster computers this should be a possible task. When these validation studies have been carried out it should be possible to critically evaluate these models, as has been done with advection-dispersion models (Anderson 1979).

Finally, one might get an answer to the question whether it is possible to develop a "general" model or if it is better to continue to develop "specific" models. Today, there have been a few attempts to develop "general" models (*e.g.* Cederberg *et al.* 1985; Narasimhan *et al.* 1986). These models consist of complex flow, transport and chemical submodels which, beforehand, have been developed independently of each other, and then coupled into one model. However, one major drawback is that the input data required by these models are enormous and that they may prove to be inefficient with respect to computer time. Also, in EPRI (1986) it is concluded that the coupling of state-of-the-art hydrologic and geochemical codes is still

premature. So with that in mind, it is encouraging to see from Tables 4-5 that there are numbers of ways to design and formulate transport and equilibrium chemistry models.

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