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ABSTRACT

For a long time, earth scientists have qualitatively recognized that mineral assemblages in soils and rocks conform to established principles of chemistry. In the early 1960's geochemists began systematizing this knowledge by developing quantitative thermodynamic models based on equilibrium considerations. These models have since been coupled with advective-dispersive-diffusive transport models, already developed by ground-water hydrologists. Spurred by a need for handling difficult environmental issues related to ground-water contamination, these models are being improved, refined and applied to realistic problems of interest. There is little doubt that these models will play an important role in solving important problems of engineering as well as science over the coming years. Even as these models are being used practically, there is scope for their improvement and many challenges lie ahead. In addition to improving the conceptual basis of the governing equations, much remains to be done to incorporate kinetic processes and biological mediation into extant chemical equilibrium models. Much also remain to be learned about the limits to which model predictability can be reasonably taken.

INTRODUCTION

The geochemical evolution of ground-water systems is of major interest in many disciplines, as for example, contaminant hydrology, economic geology, pedology, soil hydrology and so on. It is now recognized by researchers in these and related fields that the evolution in space and time of any chemical constituent in a ground-water system cannot be understood in isolation. Rather, it must be seen in the context of its interactions with the other chemical constituents, both in the aqueous phase and in coexisting fluid and solid phases. The collective understanding of the *transformation (or mass transfer)* of chemical constituents from one phase to another and the *transport* of constituents within the coexisting aqueous and solid phases is commonly known as *reactive chemical transport.*

The present status of reactive chemical transport in the earth sciences has been profoundly influenced by two parallel developments over the past thirty years or so, which have gradually merged. In the field of ground-water hydrology, increasing concerns about pollution of drinking water supplies diverted the attention of ground-water hydrologists to the study of the transport of

chemicals by the moving water from their preoccupation with merely finding economic supplies of fresh water. This interest soon led to the inevitable development of quantitative models necessary for solving practical problems. The earliest of these models (Higgins, 1959, Ogata, 1961, Baetslé, 1967) dealt with the transport of a single chemical species, subjected to adsorption. However, it was soon realized that these models were grossly inadequate to understand the mutually interactive behavior of many chemical constituents. Consequently, considerable attention is now being devoted by ground -water hydrologists to the modeling of reactive chemical transport involving the simultaneous transport of many chemical constituents.

Meanwhile, the early 1960's also witnessed the formal, quantitative application by geochemists of the principles of thermodynamics in understanding the evolution of hydrothermal mineral deposits, rock weathering and diagenesis (Garrels and Christ, 1965). Researchers soon introduced (e.g. Helgeson et al., 1970) the first computational tools to implement the principles of equilibrium thermodynamics to quantify homogeneous reactions (that is, reactions within a given phase such as a titration) as well as heterogeneous reactions (that is, reactions involving different phases such as fluid-solid interactions) leading to precipitation and dissolution. These tools continue to be refined by geochemists.

Following these pioneering developments, there has been a very fruitful integration of the transport models of the ground- water hydrologists and the chemical transformation models of the geochemists. This integration has been catalyzed by developments in the field of digital computers.

In a qualitative way, geologists have long recognized the manifestations of fluid-fluid interactions and fluid-solid interactions in the field, conforming to recognized principles of chemistry. One outstanding example of this is the supergene enrichment of disseminated porphyry copper deposits, characterized by zones of oxidation/leaching (the gossan) and zones of reduction/enrichment (enriched blanket). Roll-front deposits of uranium and vanadium constitute another outstanding example of field manifestation of oxidation and reduction. Other examples could easily be added.

Although the qualitative recognition helped understand broad patterns of geochemical zonation in soils and rocks on the basis of equilibrium chemistry, it was inadequate in two main ways; it could not quantify the spatially observed distributions of the chemical constituents in terms of the causative factors and it could not estimate the *magnitude of time* involved in the evolution of the hydrogeochemical system. It is in this context of second-order knowledge that reactive chemical transport models assume relevance. Thus, quantification and validation pose the greatest challenges to reactive chemical transport modeling in ground-water systems. By the term validation, we mean the assertion that the processes simulated in the model actually correspond to those in the field.

The purpose of this paper is to broadly assess the current status of knowledge in modeling reactive chemical transport and to identify the challenges that lie ahead. This work is not intended to be a critical review of the literature. The references cited are not comprehensive and are primarily drawn from the American literature. The authors recognize that many active contributions have been made on this subject by researchers in Europe and elsewhere. In the present work we restrict ourselves to ground-water systems characterized by low temperatures (< 100 ° C).

CURRENT KNOWLEDGE

The most general reactive chemical transport models currently available in the literature consider the simultaneous transport of dissolved chemical constituents subject to fluid-fluid interactions (mixing of ground waters) and fluid-solid interactions. As examples one may cite,

Dutt et. al. (1972), Grove and Wood, 1979, Rubin, 1983, Miller and Benson, 1983, Cederberg, 1985, Lichtner, 1985, Narasimhan et. al., 1986, Carnahan, 1987 and Liu and Narasimhan, 1989a. Because of the computational efforts needed in harnessing the geochemical processes, attention is devoted at the present time mainly to the steady-state ground water flow field under isothermal conditions. In considering fluid-solid interactions, two broad cataegories of processes have been considered; those dictated by equilibrium thermodynamics and those involving surface processes (sorption, ion-exchange).

A key task of these transport-transformation codes is to couple the multiple species chemical reactions with transport. This task has been handled by researchers in two broad ways. In one (e.g. Miller and Benson, 1983, Lichtner, 1985, Carnahan, 1987) the transport modules and the chemical reaction modules are developed by the same researcher and these are fully coupled. In the other (e.g. Narasimhan et al., 1986), advantage is taken of sophisticated geochemical models independently developed by others which are then coupled with existing transport models. Geochemical simulators developed by Wigley, 1977, Wolery, 1979, Parkhurst et al, 1980, and Peterson et al., 1987 are widely used in the study of hydrogeochemical systems.

Chemical reactions do not attain equilibrium instantaneously and equilibrium models are in themselves not adequate to simulate many natural hydrogeochemical systems. Having achieved a measure of success with the development of equilibrium geochemical models, researchers are beginning to turn their attention towards introducing kinetic or rate-controlling processes in their models.

Reactive chemical transport models have been used in the literature to obtain qualitative and semi-quantitative insights into systems at are otherwise too complicated to visualize simplistically (e.g. Liu and Narasimhan, 1989b). In the fields of economic geology and soil science, particular mineral assemblages observed in the field and their parentage have been accounted for by reactive chemical transport models (e.g. Brimhall et al., 1985, Ague, 1987). Such models have have also been able to account for the diverse rates of migration of different chemical species in contaminated ground-water systems. These ventures have also demonstrated clearly that reactive chemical transport models have the potential to become realistic tools of quantitative analysis of observations in the field.

On a quantitative level, attempts have been made to use these models for the engineering design for the geochemical remediation of contaminated ground water systems and for the environmental regulation of such systems. The success of these ventures must at best be considered as limited. The strongest motivation to improve the quantitative accuracy stems from a need to solve environmental engineering problems of considerable socio-political sensitivity. Among the difficulties faced in the application of reactive chemical transport models, the following are noteworthy. Many constituents, particularly certain metals, are toxic in trace quantities. Therefore, the models are ideally required to predict very small quantities of certain elements ($<<$ 1 ppm) often in the presence of large concentrations of many others. Secondly, the time scale of engineering prediction is becoming larger than ever before (centuries to millenia) due to stringent environmental regulations. Thirdly, in order to meet licensing requirements, the models must be strictly verified and validated. A fourth difficulty stems from the fact that because of the sensitive interrelationships that exist between the various chemical species, even within a simple ground-water system, much attention is usually needed even to set up the computational geochemical problem before it can be solved. As a result, much remains to be learned about the practical application of these newly developed models to field situations,

The difficulties mentioned above arise due to two broad reasons: information needed as input for the model and the nature of the model itself. We now turn to these issues.

INPUT FOR THE MODEL

Chemical Transformations

To simulate chemical reactions, a geochemical data base consisting of two broad categories of quantitative information is needed. The first relates to interactions, i.e. the thermodynamics of the system. The second relates to the factors that control the time-dependence (deviation from equilibrium or kinetics) of chemical reactions.

Briefly stated, the parameters needed for the system at equilibrium are as follows: the standard state molal properties of water-miscible inorganic and organic species (i.e. heat capacity, entropy, enthalpy of formation) at 298 ° K from which Gibb's free energy or dissolution constants may be obtained as a function of temperature. Means are needed to calculate these properties under other-than- standard state conditions; that is, the extension of these properties to systems of strong mixed electrolytes. Most ground waters are relatively dilute, requiring only simple electrolyte models to calculate the thermodynamic properties of aqueous species, such as the extended forms of Debye-Huckel equation. However, in a surprising number of problems strong brines or industrial effluents encountered. These require much more sophisticated models such as that developed by Pitzer and his coworkers (e.g. Pitzer, 1977). In addition,thermodynamic properties of solid phases and means of quantifying adsorption exchange on mineral surfaces and ion exchange in clays and their temperature dependance must be known.

The time-dependence of chemical reactions (non-equilibrium processes) can be divided conveniently into two parts: kinetics of chemical interactions and external rate-controlling processes.

By the phrase kinetics of chemical interactions, we denote those processes such as energy transfer, reconstitution of chemical bonds and so on that are intrinsic to the chemical reactions. In practice, kinetics of reactions are defined by appropriate rate constants, consistent with experimental observations of the reaction rate. The kinetics of precipitation are often catalyzed by inorganic and biological agents. These include oxidation/reduction processes and kinetic processes in metastable systems under secular equilibrium. These systems exist because a given reaction may often involve many intermediate reaction steps, each of which requires a finite rate constant.

In many hydrogeological systems, both natural and modified by anthropogenic causes, ground waters become supersaturated with respect to many metastable or unstable solid phases. Such is the case during the weathering of glasses, the diagenesis of arkosic sediments, the leaching of fly-ash from thermal power plants, or during the leaching of high level radioactive waste, where not only is the waste highly reactive, but radiation-induced oxidation/reduction reactions may dramatically perturb the system from equilibrium. In all these cases the system approaches equilibrium through a sequence of metastable states, in which the least super saturated phases are the first to precipitate. These dissolve subsequently and precipitate another sequence of metastable phases and the process is repeated until thermodynamic equilibrium is attained. Ostwald (1897) was the first to recognize the phenomenon. Unfortunately, currently available reactive chemical transport models are ill-equipped simulate this common phemomenon, since they implicitly assume equilibration with respect to the most soluble phases unless artificial constraints are introduced to suppress their appearance during a simulation.

By the phrase external rate-controlling processes, we imply physical factors that are external to chemical interactions which modify chemical reaction rate. Consider, for example, the titration of two solutions for which thorough mixing is a prerequisite. In the laboratory, mixing is achieved by physically stirring the mixture. In geological media, however, mixing has to be

achieved purely by advective transport (hydrodynamic dispersion) and molecular diffusion. Both these are time-dependent processes which introduce a time-lag to chemical equilibration. In regard to fluid-solid interactions involving precipitation and dissolution, the transfer of constituents is mostly dictated by bidirectional diffusion. This diffusion rate is not only controlled by the surface to volume ratio of the particles but also by the generation of thin layers of new materials on the grain surfaces which may profoundly alter the diffusion rate. A related, but poorly understood process is that of mixing due to bioturbation. Although, in general, mixing and diffusion are transport processes, in the present context we restrict ourselves to transport on a local scale that directly influence chemical reaction rates.

Thirdly, sorption and ion-exchange interactions between the fluid and the solid are known to be a function of the availability of active sites on the solid surface that favor the exchange process. The availability of these sites is dictated by a combination of the intrinsic property of the mineral grain itself (an external process) as well as the oxidation state, pH of the pore fluid and the availability of other species (a kinetic process). Finally, even in low temperature ground-water systems, the parameters that control sorption and ion exchange are temperature sensitive.

At the present time, our ability to handle input data on chemical transformations is hampered by two limitations. First, the thermodynamic data bases on equilibrium chemistry and kinetics are still evolving. Much remains to be done to refine these data bases and to extend them to a broader range of environmental conditions. Compared to equilibrium chemistry, our data base on chemical kinetics is perhaps even more primitive. Second, it is critical that the initial state of the hydrogeochemical system be consistently described in terms of water chemistry, gas-phase composition and solid phase chemistry. Often, available information on these aspects is poor, inconsistent or inadequate. This may be attributed partly to the fact that some parameters such as the oxidation state of *in situ* ground water are extremely difficult to measure even under ideal conditions. Consequently, using available data in credible modeling exercises at present demands considerable geochemistry expertise and skill.

Chemical Transport

Whereas chemical transformations transfer chemical constituents into and out of the aqueous phase, chemical transport causes them to be distributed in space and in time. A majority of currently available models give consideration to transport of dissolved constituents by advection, hydrodynamic dispersion and molecular dispersion in the aqueous phase. In addition, some of these models also provide for diffusion into the solid phase. Over the past few years the transport of sorbed constituents by colloidal particles and suspended organisms has also been proposed as a transport mechanism and is important in some situations.

In dynamic ground-water systems, the most dominant transport mechanism is advection and the associated phenomenon of hydrodynamic dispersion. Therefore, the most important input information for the transport problem is a description of the fluid flow field in terms of flow tubes and fluid fluxes or in terms of the spatial distribution of fluid velocities. However, because of the nature of Darcy's Law, these describe macroscopic averages on a scale larger than the one in which advective mixing takes place. Consequently, these fields are too coarse to resolve the effects of the finer scale mixing that dictates the spatial dispersal of constituents. Despite skepticism about its conceptual adequacy, the hydrodynamic dispersion coefficient is the most widely used parameter which seeks to quantify finer scale hydrodynamic mixing. It is now generally accepted that heterogeneities in material distributions dictate the nature and magnitude of hydrodynamic dispersion. In practice, greatest difficulties arise in describing the heterogeneities of a given system in sufficient detail and to associate, with each material, realistic coefficients of dispersion. These coefficients are dependent on the spatial scale and duration of

experimentation, and are difficult to extrapolate in time and space even under controlled conditions.

Seemingly, molecular diffusion is much easier to handle than hydrodynamic dispersion, although both have the same mathematical form. The molecular diffusion coefficients of aqueous species in water are known or can be predicted with reasonable precision and these values can be applied in a relatively well constrained manner to geologic media by accounting for effects of porosity and tortuosity. Often, the magnitude of molecular diffusion may be two to three orders of magnitude smaller than that of hydrodynamic dispersion and superficially one may be inclined to ignore this process. However, in heterogeneous media in which lenses of low permeability materials and dead-end pores occur in significant populations, the large surface areas available for diffusion and the existence of large concentration gradients at a local level may greatly enhance the role of molecular diffusion in comparison to hydrodynamic dispersion. Indeed, during large scale, long duration transport of constituents in slow-moving groundwater, hydrodynamic dispersion will invariably incorporate effects of molecular diffusion.

A major difficulty that is common both to transformation processes as well as transport processes is that of averaging. Chemical reactions take place on a scale of 10 Å at the molecular level and on a scale of up to 100 Å on a colloidal level. Compared to this , pore level mixing occurs on a scale of microns to millimeters and formation heterogeneities come into play on a scale of centimeters to meters. As a result, it is extremely difficult to define realistic "average" input parameters on a macroscopic scale of modeling, which, while making the computational problem tractable, do not mask the important features of the system dictated by the finer scale processes.

This difficulty of scales has been approached by researchers in two different ways. In the multi-continua approach, components of the system that respond at different time scales are grouped into separate continua and these continua are loosely coupled to each other by appropriate coupling criteria. Alternatively, the scale problem is being approached by many researchers from the view point of uncertainty. To study uncertainty, then, geostatistical methods and the theory of probability are employed. These evolving methods are currently being tested on simple field systems in regard to the transport equation. They are yet to be extended to transformation equations involving equilibrium and non-equilibrium thermodynamics and kinetics.

THE MODEL ITSELF

Most currently used reactive chemical transport models employ either the finite difference method or the finite element method for solving the transport equation. In so far as the transport equation is concerned these approaches have been well-tested and can be relied upon to provide good solutions if sufficient care is taken in the design of the mesh. The coupling between the transport equation and multiple-species geochemical calculations may be either full or partial. In the case of full coupling, both equations are solved simultaneously, while in the partial coupling approach, the transport equation and the transformation equations are solved sequentially within each time step. Because of the number of variables to be calculated for each mesh point, the fully coupled approach introduces highly non-linear equations which are more computation-intensive in their solution than the other approach.

A fundamental limitation of all reactive transport models is that no known method is currently available to verify them for mathematical consistency. No mathematical theory is currently available for the purpose. The best that can be done at the present time is to "benchmark" independently developed models against one another by solving identical problems. Much judgement is needed in interpreting computational results,

Thanks to research motivated by environmental considerations, many attempts are under way to validate reactive chemical transport models. The task of validation is to evaluate the closeness between the processes and parameters simulated by the model and the system that is actually simulated. Considering the many variables involved in multiple-species reactive chemical transport, and the number of spatial and temporal locations at which they need to measured, it appears that even a near-complete validation of field systems would involve prohibitive efforts. Recognizing this, more modest attempts are made to partially validate the models. On the practical side, one point that merits attention is the role played by the measuring instruments. One would suspect that soil-water samplers, piezometers and wells will significantly affect downstream chemical concentrations, The role of measuring instruments is often overlooked in the construction of mathematical models for reactive chemical transport.

CHALLENGES

Natural hydrogeochemical systems are extremely difficult to access and characterize. Physico-chemical processes occur in these systems over widely different spatial and temporal scales. The classical cause-effect models which we use to analyze these systems are intrinsically data-intensive. The qualitative credibility of these models to explain naturally observed features of soils, mineral assemblages and rocks is beyond dispute. Yet, the moment attempts are made to extract quantitative predictions from these models, many difficulties arise. These difficulties transcend the spectacular developments in computer technology. Even our currently available computers (not to speak of the coming generations of new machines) possess enough capabilities to process, store and portray data on hydrogeochemical systems as we currently visualize them. Yet, we are grossly limited in our ability to generate meaningful input information that can be processed by the machine.

This difficulty arises due to conceptual as well as practical limitations. There probably exists a point beyond which our cause-effect models may defy improvement and it would make little sense to attempt to acquire more data; for, the very act of data collection may change the system. This point will define the ultimate resolution of the reactive chemical transport models to answer questions. Unless our classical cause-effect model undergoes drastic change or is replaced by something very different, the best we can do is to refine the models as far as possible and then to develop an expertise in extrapolating the less than perfect model results to formulate important decisions related to the natural system.

Thus, the challenges that lie ahead in regard to reactive chemical transport relate to concepts, data acquisition and model application.

Conceptual

Almost all our models of reactive chemical transport are based on the premise that the transport and transformation equations are accurately represented by a set of coupled partial differential equations and that these equations are solved approximately by the appropriate numerical techniques. In the absence of an alternative, this paradigm will guide the refinement of the currently used models over the coming years.

Yet, heterogeneity and scale have come to be recognized in the earth sciences as the two most distinctive attributes of earth systems that profoundly influence all physico-chemical processes. In trying to comprehend dynamic processes in such systems, the notions of a point and of continuity become less important than macroscopic subdomains. The traditional foundation of the differential equation has served extremely well in dealing with homogeneous media

involving simple geometries. For such systems, the differential equation can be solved and the solution verified. However, we are unable to solve the equation when heterogeneity is dominant and when several interacting processes occur together. Consequently, we are unable to strictly verify any of our reactive chemical transport results. Purely from a logical view point this is very disconcerting because the essence of modern science is testability.

Therefore, even as we push our current models to the limits of their capabilities, there is a need to examine whether new conceptual models can be formulated that go beyond the classical basis of continuum mechanics to realistically describe heterogeneous systems involving coupled processes on different spatial and temporal scales. Such models would naturally incorporate the role of instruments which are used to observe the system. This aspect is extremely important for, what we see is determined by what the instruments will let us see.

As accuracy of model prediction assumes increased importance, the need to develop improved models for simulating time-dependent reactions (chemical kinetics) also becomes very important. The challenges in this regard arise in two ways. First, kinetic effects involve a variety of processes such as bond reconstitution, intermediate metastable reactions, catalysis and so on. A major finding in geochemistry is the realization that biological organisms may play an extremely important role in many kinetic processes in ground water. Very little is known about the actual mechanisms during this biological mediation. Deciphering and parametrizing these mechanisms in a fashion that is amenable to the structure of existing models is in itself a challenging task.

Data Bases

One of the concerns frequently expressed by observational geochemists is that model calculations may be futile without adequate data bases. Assembling a reliable data base, both for equilibrium reactions and for kinetic processes is complicated not only by the vast number of chemical reactions that need to be experimentally quantified but also the difficulties and cost in conducting the experiments. The task is further complicated by the fact that parameters determined from experiments of simple reactions will have to be used in the context of several mutually interacting reactions. New advances in theoretical thermodynamics may be needed to aid in this extrapolation.

Essentially, data base development involves inverting experimental data to estimate physical and chemical parameters. This task is relatively easy in the case of well-controlled laboratory experiments. However, in dealing with complex natural systems, it is often necessary to generate parameters when the system is not fully defined. In interpretating experiments involving many coupled reactions, numerical models are powerful tools. Indeed one challenging area of research is to use mathematical models to design, conduct and interpret experiments of increasing complexity. This can provide new opportunities for breaking down the distinctions between experimentalists and computationalists and between the laboratory and the field.

The long term dynamics of hydrogeochemical systems cannot be realistically understood without considering the influence of chemical reactions on the fluid flow field. Emerging models will pay increased attention to reactive chemical transport in the presence of transient fluid flow. Perhaps the single most important mechanism in this regard is permeability. Precipitation at pore constrictions can profoundly alter permeability. In some systems, a rapid decrease in permeability will induce the build up of pore pressures, which may in turn influence the course of chemical reactions. At the present time, we do have the ability to computationally model these processes; however, we have very little knowledge of the actual magnitudes involved. We lack the observational basis.

Model Applications

At the present, the greatest motivation for research in reactive chemical transport comes from a need to solve problems related to ground-water contamination. There exists a growing need to develop user-friendly models which can be used to assess contamination, design remedial actions and monitor their performance. These engineering tasks are constrained by limitations of resources and time leading to limited data availability. It is a challenge to bring the power of reactive chemical transport models to solve these important engineering problems. Much remains to be learned about the judicious application of models of varying complexity to practical field problems under conditions of limited data availability. Underlying this challenge is the deeper question of the limits of utility of the cause-effect models.

From the point of view of scientific curiosity, a major challenge is to quantify the time scales in which hydrogeochemical processes occur within the earth's crust, be it related to the evolution of a soil profile, the origin of a mineral deposit or a sedimentary bed. On a geological time scale, one has to quantitatively consider a combination of several factors including the volumes of circulating fluids, the fluid-solid interactions and their kinetics, and the feed back of the chemical reactions on the field of fluid flow.

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