6 Hydrogeochemical and Geochemical-Hydraulic Models and Model Concepts

6.0 Introduction

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In the priority programme all research groups were encouraged to develop and use model concepts and computer models to evaluate the measured data. Notwithstanding the fact that models cover a very wide range of sophistication, computer models are extremely helpful for the description of the complex geochemical reaction systems, especially in combination with the transport processes in the unsaturated or saturated zones. Thus, the different sections in this chapter cover models that combine geochemical black boxes with different flow systems, models that use geochemical measurements for the calibration of flow systems, models that combine geochemical reaction systems with flow systems and models which try to achieve a better understanding of calculated saturated indices in seepage and ground water.

For most natural waters the calcite-carbonate system controls the usually high concentrations of dissolved calcium and hydrogen carbonate as well as the pH value and a variety of other dissolved components. At the beginning of the priority programme the dissolution and precipitation processes of carbonates for most researchers seemed to be important as well, and simple enough to achieve a quantitative understanding of the system including the reaction kinetics. The different laboratory studies and field measurements on carbonate systems, presented in Chapter 3 of this volume, are evaluated in the Sections 6.1.1, 6.1.2 and 6.2.2 of Chapter 6, which deal with the modelling of carbonate systems.

In Section 6.1.1 Dreybrodt applies his theory of calcite dissolution kinetics (Sect. 3.1.1) with a realistic flow system through a fracture aquifer in carbonate rocks. The result is a deterministic model that predicts the development of a natural karst system in a geological time scale. For this combination it is necessary to apply the theory of calcite dissolution kinetics which could only be tested in short-time laboratory experiments on a process in a time which is orders of magnitudes longer. The realistic results for the time necessary for the development for a karst system are a reliable proof for the validity of the kinetic theory and show that for the first time a geological/geochemical process is quantitatively understood.

The Sections 6.1.2 (Eichinger, Merkel and Udluft) and 6.2.1 (Schulz) refer to sections in Chapter 3 describing the laboratory experiments and field measurements on the calcite-carbonate system in the unsaturated zone. Besides different locations of the field studies, the differences between both sections lie especially in the
regarded time scale. Whereas in Section 6.2.2 the calcite weathering is described by Schulz as a long-term process in its dependency on seepage velocity, calcite dissolution, mass balance and cation exchange reactions, in Section 6.2.2 Eichinger, Merkel and Udluft simulated the annual variations of dissolved carbonate in seepage water as dependent on climatic variations, seepage velocity and CO₂ produced by microbiological activities. The comparison between the measured concentrations of dissolved carbonate and calcium with the simulated concentrations of these ions shows that the entire process of the calcite-carbonate system in the unsaturated zone is well understood in its major and minor controls.

The release rate of feldspars measured in three different laboratory experimental setups (Sect. 4.3.2, this Vol.) are discussed in Section 6.1.3 (Dahmke, Matthess, Petersen and Schenk) with respect to the influence of grain sizes, flow rates, premineralization and pH changes. These evaluations are connected with the laboratory observations on the influence of organic ligands (Sect. 2.9, this Vol.), and are helpful for the discussion of the field observations (Sect. 4.3.2, this Vol.).

In Section 6.2.5 (Strebel, Böttcher and Duynisveld), a model is presented which attaches more importance to the flow system and the mass balance of components, while treating geochemical reactions only as source or sink terms in the calculations. The model uses in a one-dimensional tube or in a two-dimensional vertical cross-section for the simulation of the physical transport in groundwater. A mass balance for chloride as a conservative tracer is used as a test for the model. In comparison with the nitrate and sulfate concentrations, it is necessary to incorporate sink or source terms in the calculations which are used to quantify the microbiological reactions in groundwater for these constituents.

In Section 6.2.2 (Bugner and Mull) the development of sulfate concentrations in groundwater, including microbiological decomposition, was simulated for an unconfined aquifer of gravel and sands. In order to identify a vertical cross-section through the aquifer, first a three-dimensional groundwater flow model was calculated. For the unidirectional flow in the two-dimensional mass transport model with curvilinear elements the velocity data of the three-dimensional groundwater flow model were used. After a calibration of the model using environmental isotopes, the sulfate reduction was incorporated by using a time-dependent exponential reaction kinetics comparable to that of a radioactive decay. Obviously, in this model the physical transport is much more sophisticated than geochemical reactions, since the major aim of the authors was to find a physical transport model which allows the incorporation of even more complex reactions. Thus, this model shows how, in future work, complex flow situations could be combined with different multicomponent geochemical reactions.

The models of the Sections 6.2.3 (Dörr, Schlosser, Stute and Sonntag) and 6.2.4 (Forster, Loosli and Weise) deal with the description of groundwater flow systems using different isotope measurements. In these models geochemical reactions are not regarded and importance is attached only to the determination of residence times of groundwater in the aquifer and to the calibration of groundwater transport models. Both sections show quite clearly to what extent isotope techniques today are useful and necessary for this purpose.

Using the data of three test areas in Section 6.3 (Kölling and Schulz), mineral saturations were calculated with different geochemical equilibrium models like