

Part VII

Physicochemical Description and Mathematical Formulation of Sorption Processes

Apart from dissolution/precipitation reactions, most physicochemical interactions accompanying subsurface solute transport are generally referred to as adsorption or sorption reactions. These involve the loss of chemical components from an aqueous to a contiguous solid/mineral phase. In many cases, sorption is the most significant chemical process affecting the mobility of contaminants in the subsurface. Adsorption reactions are discussed primarily in terms of intermolecular interactions between a solute and solid phases, and can be generally categorized as either physical adsorption, chemisorption, or electrostatic adsorption (Sparks 2003; Encyclopedia of Surface and Colloid Science et al. 2006).

Weak molecular forces, such as Van der Waals forces, provide the driving force for physical adsorption, while chemical reactions form chemical bonds between the compound and the surface of the solid in chemisorption. Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange. Interphase interactions can be described also as a series of surface complexation reactions between dissolved ions and mineral surface, as well as specific adsorption. Specific adsorption is an interaction stronger than the electrostatic interaction ascribed to exchange reactions. The nature of the forces involved in the specific adsorption of ions at the mineral-matrix/pore-solution interface is not always fairly well identified.

The process in which chemicals become associated with solid phases is often referred to as *sorption*, especially when one is not sure whether one is dealing with adsorption (attraction and bonding onto a two-dimensional surface) or absorption in which the solute is taken up into a three-dimensional matrix (Cantrell et al. 2002; Sparks 2003). In our analysis we do not emphasize the difference between sorption and adsorption terms. In majority of cases they are believed to be synonymous.

The most common models consider sorption as instantaneous and reversible processes. However, these assumptions are not always valid for natural soils and aquifer materials: kinetic effects are sometimes observed and significant differences may occur between sorption and desorption processes, resulting in irreversible reactions or very slow desorption kinetics.

The sorption process is particularly important for the transport of contaminants with mobile aqueous phase in the subsurface environment. Sorption of dissolved contaminants onto the soil and rock matrix results in slower transport (retardation) of contaminants relative to water velocity and a decrease in solute concentration. On the other hand, adsorption onto mobile colloids present in groundwater typically enhances the transport of contaminants traditionally considered as strongly sorbing species having low potential for mobility, e.g., actinides. The degree to which colloids enhance the transport depends on the adsorption–desorption kinetics (see Part IX).