

## Chapter 7: Sorption and Ion Exchange Reactions

In the above chapters, we have traced the evolution of water quality by weathering and redox processes. Here we will look at a third process by which the geochemistry of water evolves – surface reactions between dissolved species and clay minerals, iron oxyhydroxides and organics substances. These reactions generally involve cations because the solid surfaces or substrates on which reaction takes place are for the most part bristling with negative charges. Protons,  $H^+$ , also exchange with negative surface charges, and so cation exchange reactions are pH sensitive. Surface reactions differ from mineral dissolution and precipitation reactions in that they do not generally advance mineral growth or dissolution. Nonetheless, they have the ability to alter the geochemistry of a solution.

Two types of surface reactions can be considered. One is the alteration of the major cation composition of the water by an exchange cations between the solution and a solid surface. In this case, a major cation such as  $Ca^{2+}$  will attach electrostatically to the surface, displacing others such as  $Na^+$  from the surface into solution. These are *cation exchange reactions* and are stoichiometrically balanced. This exchange causes a change in the geochemical facies of both the solution and the surface. Cation exchange is a mechanism that describes bulk changes in the geochemistry of groundwater.

The second type of surface reaction involves the *adsorption* of trace solutes onto a solid surface and *desorption* from a surface into solution. Here the approach is based on the distribution of the single species between the solution and the surface, rather than on the exchange of two species between the solution and the surface. Sorption reactions are most suited to modeling the transport of contaminants in water.

Intrinsically, all such surface reactions can be considered sorption reactions. In practice, the term sorption is used to describe the reaction of trace solutes and contaminants with mineral and organic surfaces, while cation exchange describes the change in major ion composition by exchange with surfaces. In both cases, the density of negative charges on the solid surface – its exchange capacity – is of primary importance.

### EXCHANGE SURFACES IN SEDIMENTS, SOILS AND AQUIFERS

Sorption and exchange reactions are enhanced by the reactivity of solid surfaces in contact with the solution. As mineral free energies are greatest along growth surfaces, boundaries and imperfections where uncoordinated oxygen atoms are positioned, it follows that the smallest minerals and grains are the most reactive in sorption and exchange processes. Similarly, non-crystalline solids such as amorphous ferric iron oxyhydroxides, colloidal particles and organic matter possess high electropotential charges on their surfaces. Studying their importance in sorption and exchange reactions merits a review of their compositions.

#### *Surface charge*

The surfaces of structured minerals, amorphous oxides and organic compounds are composed of reaction sites where composite ions of the solid are exposed to the solution. Unlike ions below the surface, surface ions are not fully coordinated and so maintain an electrostatic charge. In most solids, it is oxygen ions that populate the surface, providing a net negative charge. In the absence of other cations, negative charges can be balanced by protons,  $H^+$ , which adsorb and desorb from surface charge sites. Accordingly, the pH of the pore waters affects the net surface charge of a solid, and thus its exchange capacity. In the case of quartz, the charge of the surface oxygen atom in a Si–O layer will vary, depending on pH:



The pH at which a surface has an overall charge of zero is known as its zero point of charge or ZPC. The high cation exchange capacities for which silicate clay minerals are known comes from the low ZPC of Si, which allows a negative surface charge at pH values above about 3. For the iron and aluminum hydroxides, the ZPC occurs at much higher pH, and so have a negative surface charge at neutral pH (Fig. 7-1).

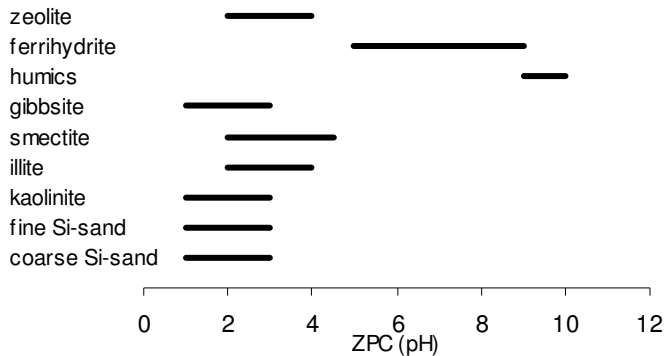


Fig. 7-1 Zero point of charge (ZPC) for common solids in soils.

### Clay minerals

Clay minerals are classified by their structure and chemistry, both of which affect their capacity to exchange cations with surface and groundwaters. Structurally, they comprise sheets of Si and Al oxides as tetrahedral layers – sheets of  $\text{Si}^{4+}$  coordinated with  $\text{O}^{2-}$  in a tetrahedron structure, and octahedral layers – layers of  $\text{Al}^{3+}$  coordinated with  $\text{O}^{2-}$  (also called the gibbsite [ $\text{Al}(\text{OH})_3$ ] layer) (Fig. 7-2). In some clays, Al is replaced by Mg (the brucite [ $\text{Mg}(\text{OH})_2$ ] layer). Oxygens in the octahedral layer coordinate with Si in the tetrahedral layer, bonding them into two (oct–tet) or three (tet–oct–tet) layer sheets. The sheets are joined by weak van der Waals bonds to build a single crystal.

Common clays from the three principal groups and their basic chemical formula include the following, with their general chemical formula showing common substitutions (Mg,Fe,Al) and *interlayer* cations in italics.

- **kaolinite** [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] – a two-layer clay that forms in humid climates from acid weathering of granites. Note that kaolinite has no interlayer positions, which limits its ion exchange capacity to surface charge sites. Other two layer clays include serpentine in which a brucite layer replaces the gibbsite layer
- **smectite** (*Na,Ca*<sub>0.5</sub>)(Mg,Fe,Al)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> – three layer clays that form from weathering of mafic (Fe, Mg and Ca rich, K-poor rocks). These clays, and particularly the Na-montmorillonite variety, swell from the uptake of water to satisfy excess negative charges when Na and Ca are leached from interlayer positions. This gives the smectite clays a high cation exchange capacity. Other common three layer clays include pyrophyllite (the pure three layer clay with no substitutions), talc (brucite replacing gibbsite) and chlorite (three layer units with brucite layers, often Fe-rich).
- **illite** [ $\text{K}(\text{Fe,Mg,Al})_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ ] – also a three layer clay that forms from weathering of potassic rocks. Unlike smectites, the interlayer ion,  $\text{K}^+$ , is firmly positioned and stabilizes the structure, and so reduces its cation exchange capacity.

Variations occur due to substitutions for Si and Al. For example,  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  can replace  $\text{Al}^{3+}$  although this leaves a net negative charge for the layer. Similarly,  $\text{Al}^{3+}$  can replace  $\text{Si}^{4+}$  in the tetrahedral layer, again leaving a charge imbalance. Further, the oxygen atoms on the surface of individual clay crystals, and on

their edges maintain a net negative charge. The negative charges from substitutions within the layers can be satisfied by cations that fill *interlayer* positions. The surface negative charges can be balanced by adsorbing cations from pore waters.

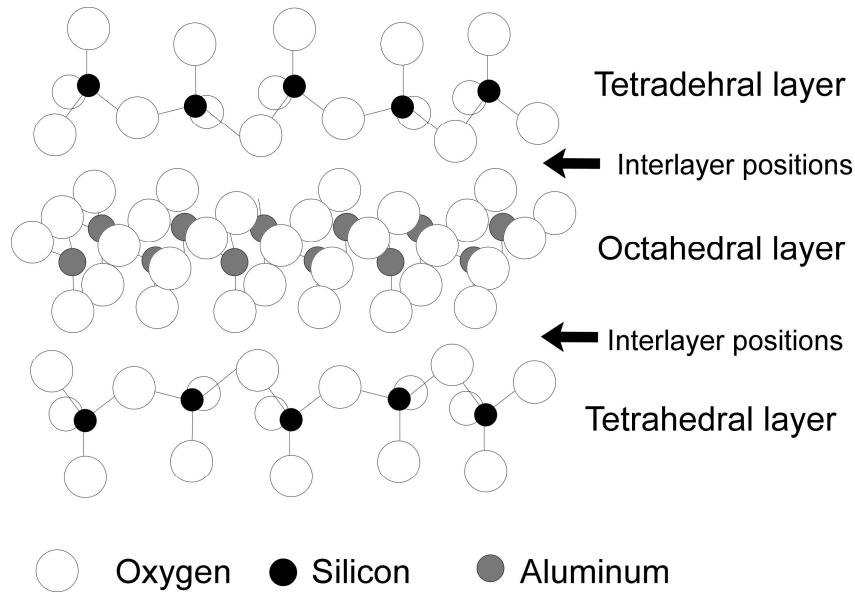


Fig. 7-2 Tetrahedral (silicate) and octahedral (gibbsite) layers of clay minerals

Clay minerals occur on the fracture surfaces in primary silicate rocks, where weathering occurs. Clays also develop through weathering of clastic material such as feldspar-rich sands and glacial till. Alternatively, clay minerals can be allocthonous, transported and deposited with coarser grained sediment as clayey sand or till. Shaley laminations present in limestone and sandstone aquifers, and fractured, weathered shale sequences are also geological settings where circulating meteoric waters can experience ion exchange reactions with clay minerals.

### ***Humic substances***

Humic substances are the principal organic component of soils, and develop through the biodegradation of vegetation. They are heterogeneous, high molecular weight C–O–H–(N, S) compounds that are soluble only at higher pH and give the dark brown color to soils and wetland waters. Humic acids are soluble above pH 2, while lighter weight fulvic acid is soluble at all pHs. Humin is the solid, refractory component, which is strongly adsorbed to soil minerals and insoluble at all pHs. Humic substances make up the greater fraction of dissolved organic carbon in groundwaters and surface waters.

Structurally, humic substances are three-dimensional networks of aromatic rings and carbon chains that are fringed with various functional groups including carboxyl (–COOH) and phenol (–OH). These groups can shed their  $H^+$ , providing negative sites for other cations in the pore waters (Fig. 7-3).

## 7-4 Chapter 7 Ion Exchange Reactions

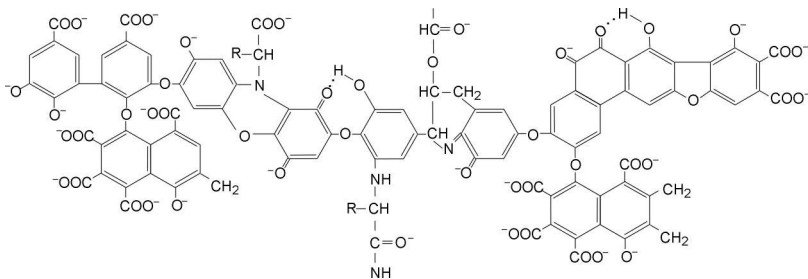


Fig. 7-3 Schematic diagram of humic matter showing negatively charged exchange sites which can be occupied by H<sup>+</sup> in low pH waters, by major cations from solution, or trace metals.

### *Iron and manganese oxihydroxides*

The third principal type solid substrate for sorption reactions is iron oxihydroxide or ferrihydrite, which is essentially an amorphous and hydrated ferric iron oxide. Crystalline forms include goethite [FeOOH], and hematite [Fe<sub>2</sub>O<sub>3</sub>]. Iron and manganese are released by the weathering of mafic minerals such as biotite, amphiboles and pyroxenes or by oxidation of sulfides such as pyrite. Under oxidizing conditions and neutral pH, iron occurs as Fe<sup>3+</sup> and is highly insoluble (see Chapter 6). Similarly, manganese is soluble only under reducing or acidic conditions. In soils and aquifers, amorphous forms dominate as coatings on mineral grains and partially filling porosity.

Oxygen atoms on ferrihydrite surfaces are not fully coordinated with Fe<sup>3+</sup> and so retain a negative charge. While protons can coordinate with them to form a surface hydroxide, there is increasing competition for these sites under neutral to high pH conditions. As a result, such amorphous and semi-crystalline solids represent excellent substrates for cation exchange and adsorption of trace metals.

### *Colloids*

One of the most effective media for adsorption of metals from solution is that of colloids – small (< 10 μm), non-crystalline particles of mineral or organic composition dispersed in water. In most natural waters, mineral colloids are typically oxides of Si, Fe, Mn or Al. Their small size and high surface area combined with their non-crystalline structure engenders a very high, negative surface charge. In fresh waters, electrostatic repulsion precludes flocculation whereas in saline waters such as seawater, this effect is suppressed and colloids will flocculate and settle out of solution. In waters where colloids remain in suspension, they can be transported by advection. Adsorbed cations will, in this case, also be transported, although they are technically not in solution and can be filtered with appropriate membrane filters (usually with filter membranes of 0.2 to 0.1 μm).

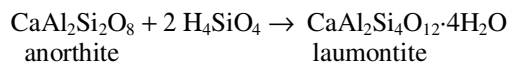
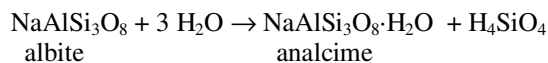
Dissolved organic compounds in natural waters can also form colloids. Tea-colored waters are typically rich in humic colloids, and demonstrate the characteristic of colloids to absorb and disperse certain wavelengths of light. The high negative charge found on the edges of many dissolved organic compounds allows these colloids adsorption and complexation properties similar to their inorganic counterparts.

The high negative surface charge on colloids allows the adsorption of heavy metals and other contaminants onto their surfaces. Thus, the total amount of lead, for example, which could be held in solution by adsorption onto colloids can far exceed the its concentration as say Pb<sup>2+</sup> or as a complex such as lead hydroxide, PbOH<sup>+</sup> in solution.

### *Zeolites*

The zeolites are low-temperature tectosilicates (like feldspars) with an open crystal structure formed by silica tetrahedra linked corner to corner. They occur as a product of weathering of volcanic rocks and

feldspar-rich sediments under conditions of high pH and high salinity. Their porous structure allows the incorporation of considerable amounts of hydration water. Charge deficiencies are caused by replacement of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$ . This allows incorporation of cations such as  $\text{Ca}^{2+}$  or  $\text{Na}^+$  during zeolite formation according to weathering reactions such as:



Both unbalanced charge deficiencies and the high surface area of these minerals make them excellent substrates for cation exchange. Combined with their open water-filled lattice, zeolites are important industrial minerals used as molecular sieves to purify waters and gases.

## CATION EXCHANGE

The simplest form of sorption involves the reversible exchange of cations between water and the surface of a solid. Surface reactivity is largely generated by oxygen ions coordinated with Si, Al or Fe cations, which generate a negative electrostatic potential on the surface. Each oxygen atom can then be considered as a potential exchange site. The negative charges can be satisfied by sorption of protons, which provides pH buffering. As ionic strength is increased, there is increased competition for these exchange sites by other cations in solution. Because protons and cations are held only by weak electrostatic attraction, they can be displaced by other cations in solution, which may have a greater electrostatic charge or simply a higher concentration in solution. This is the basis of cation exchange.

### *Equilibrium exchange and the double layer*

The solid-aqueous interface where cation exchange takes place is a complicated environment, with differing types of exchange sites, hydration and dehydration reactions, and ion diffusion all playing a role in exchange. The most versatile model for cation exchange involves a double layer of cations electrostatically bound to the clay surface (

Fig. 7-4). The electrostatic potential is greatest along the negatively-charged surface, and maintains a “fixed” or hard layer of unhydrated cations. These are inner-sphere complexes. Outward from the fixed layer, the electrostatic potential decreases, creating a “diffuse” layer characterized by a cation excess over anions that diminishes with distance. Cations within the diffuse layer are free to move as their electrostatic attraction is considerably less than in the fixed layer. The thickness of this layer increases in more dilute solutions, and essentially decreases the pore volume available to anions. This effect of anion-exclusion decreases with salinity due to the high concentration of cations that narrow the zone over the clay’s negatively-charged surface from which anions are repelled.

Ions in both layers can exchange with the adjacent solution, although cations in the diffuse layer can be expected to exchange more readily than inner sphere cations. Under steady-state conditions, an equilibrium is established between the solution and the surface that governs the concentration of adsorbed cations according to their concentration in solution.

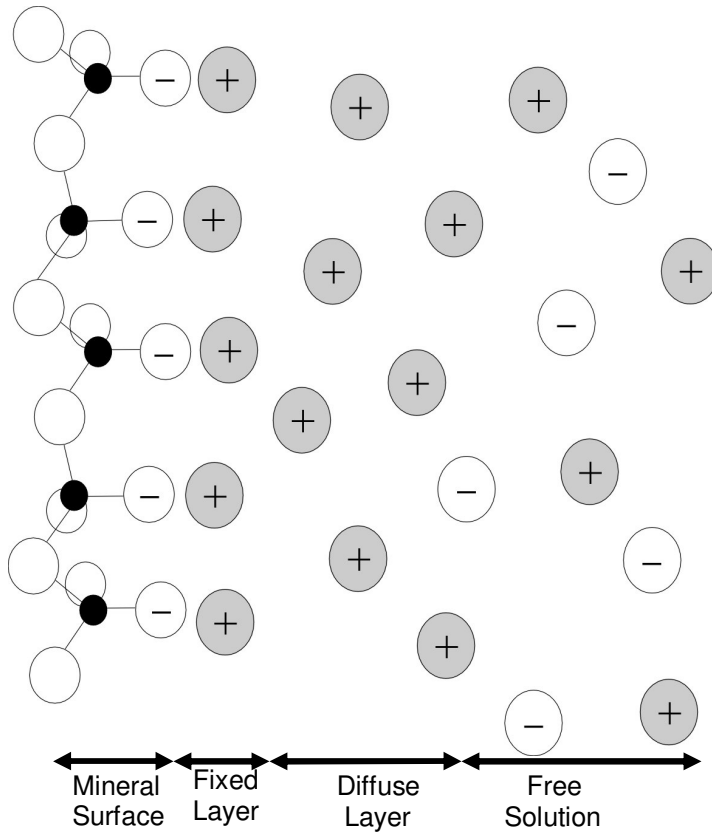
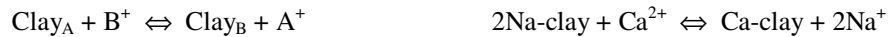


Fig. 7-4 Double layer model of the negative charge distribution on a clay mineral and cations attached at exchange sites.

**Selectivity coefficient**

The exchange of a cation in solution with another adsorbed to a clay surface can be represented by the reaction:



The reaction constant is known as the selectivity coefficient,

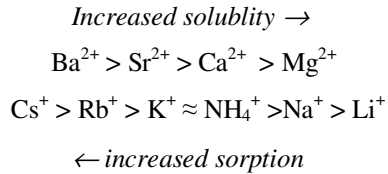
$$K_{A-B} = \frac{[\text{Clay}_A] \cdot [B^+]}{[\text{Clay}_B] \cdot [A^+]} \qquad K_{\text{Na-Ca}} = \frac{[\text{Clay}_{\text{Na}}]^2 \cdot [\text{Ca}^{2+}]}{[\text{Clay}_{\text{Ca}}] \cdot [\text{Na}^+]^2}$$

The activities of the dissolved cations are determined from ionic strength and activity coefficients. The adsorbed cation activities are most easily considered by their molar fraction of the total clay surface, hence:

$$[\text{Clay}_A] = \frac{\text{moles } A^+ \text{ on clay}}{\text{moles } A^+ + B^+ \text{ on clay}} \qquad [\text{Clay}_{\text{Na}}] = \frac{\text{moles } \text{Na}^+ \text{ on clay}}{\text{moles } \text{Na}^+ + \text{Ca}^{2+} \text{ on clay}}$$

In high ionic strength waters where monovalent  $\text{Na}^+$  tends to dominate (e.g. seawater), more  $\text{Na}^+$  will reside on exchange sites. Displacement with a lower salinity  $\text{Ca}^{2+}$ -groundwater will produce a new equilibrium with more  $\text{Ca}^{2+}$  on the clays. The distribution is then governed by the selectivity coefficient determined for this system. Unlike solubility constants ( $K$ ) for pure minerals, selectivity coefficients are specific to the clay and water types, and so will differ for each system.

Each cation has its own selectivity or tendency for sorption onto a charged surface. This characteristic relates to the surface charge of the cation, and the stability of its hydration sheath, which reduces its electrostatic interaction. Divalent cations have a greater tendency for exchange than monovalent ions. Cations with smaller hydrated radii (Table 2-1) are also more readily adsorbed. The order of selectivity for adsorption of the major monovalent and divalent cations are:



While the selectivity coefficient can be determined for any cation exchange reaction, it is less of a constant than an empirical value incorporating the heterogeneities of the surface in question and the bulk ion geochemistry of the solution and ionic strength. Thus, the exchange of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  for example between solution and a clay surface will be affected also by other cations in solution, and by the ionic strength of the solution.

### ***Cation exchange capacity***

The capacity for clay or other solid substrates to exchange cations with solution is an important characteristic with respect to the geochemical evolution of groundwater. Relatively inert media such as quartz sand or fractured crystalline rock offer little in the way of exchange sites for reaction with the solution. However, the presence of clays or ferrihydrite coatings on quartz and feldspar grains greatly increases their cation exchange capacity or CEC. Measuring CEC is important in soil studies where the conversion of Ca-clays to Na-clays can adversely affect permeability and drainage. It can also be important in water quality studies where cation exchange can affect the concentrations of potential contaminants such as fluoride.

The cation exchange capacity of a soil represents the number of exchange sites per unit dry weight of sample. Formally, it is measured by saturating the sample's exchange sites with a 1 molar ammonium acetate solution at pH 7 and analyzing the release of  $\text{NH}_4^+$  following equilibration with a (usually)  $\text{Na}^+$  solution. CEC is expressed as meq/100g dry sample. It is not a rigorous analysis, with variations due to differences in pH and initial geochemistry of the soil. It does, however, provide a reasonable indication of the potential for exchange.

Of the principal clay groups identified above, smectites have the highest CEC, with values between 50 and 150 meq/100 g. Montmorillonite is a good example of a smectite clay with particularly high CEC due to leaching of Na from interlayer positions. By contrast,  $\text{K}^+$  is retained in interlayer positions of illite clays, reducing their CEC to less than 50 meq/100 g. Kaolinites have tightly spaced layers with no interlayer cations, and so have low CEC, generally less than 10 meq/100 g.

The cation exchange capacity of ferric iron oxyhydroxides (ferrihydrite) is even greater than that of smectite clays, with values often exceeding 500 to 700 meq/100 g. However, this is the case only at neutral to high pH. As pH becomes more acidic,  $\text{H}^+$  competes effectively for exchange sites. Below ~ pH 4, ferrihydrite becomes increasingly soluble, and it retains no capacity for cation

exchange. Similarly, zeolites and humic substances have high cation exchange capacities in the range of 100 to 500 meq/100 g.

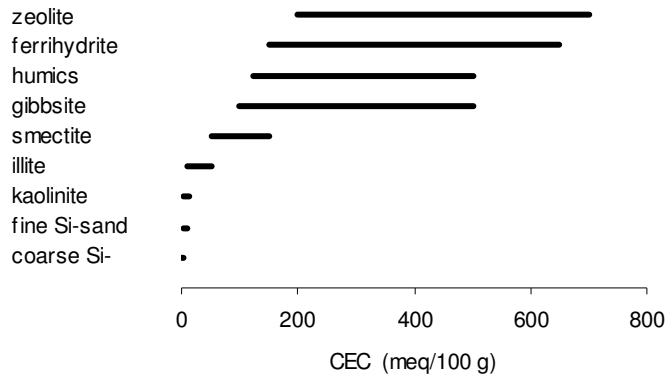


Fig. 7-5 Cation exchange capacity of the major natural inorganic and organic materials.

### *Cation exchange in groundwaters*

Geochemical evolution in groundwater can often be attributed to cation exchange. However, cation exchange is often invoked to account for geochemical evolution where the hydrogeological setting does not support it. Two principal prerequisite must exist:

- (i) An extensive mineral or organic substrate of high cation exchange capacity must be present, with which the groundwater can react. Reactive material can be found in aquifers or in soils and overburden through which recharge may take place, occurring as coatings on grains or as accumulations within the porosity. Consideration must be given to hydraulic conductivity, which is greatly reduced by the presence of clay minerals, oxyhydroxides and organics.
- (ii) A change in conditions that has moved the geochemical environment away from equilibrium. Under equilibrium conditions, the distribution of cations between a solution of given cation composition and the exchange surface is controlled by the selectivity coefficient for that clay-solution system. Groundwater entering this environment will have the same composition as that flowing out, and the clay will have constant cation composition. When a new solution with different geochemistry enters this setting, the process of cation exchange will move the system towards a new equilibrium between the solution and medium.

Such shifts to non-equilibrium conditions can occur by new groundwaters entering the aquifer such as saline intrusion of coastal aquifers, road salt contamination, or the discharge of waste water. Non-equilibrium conditions are also generated by a change in groundwater flow paths through new material. Examples include erosion and uplift, allowing groundwater circulation through deeper bedrock horizons, and the reestablishment of groundwater flow through previously inundated (marine) sediments.

The example of road salt contamination is useful. Take the case where groundwater recharge takes place through a shallow glacial till with interstitial clay as a product of weathering. Groundwater in the till will likely have a Ca-HCO<sub>3</sub> geochemical facies, produced through dissolution of carbonates and feldspars, perhaps with minor Na<sup>+</sup>. Over time, clays in the till will become loaded with Ca<sup>2+</sup>, as the dominant cation with the advantage of a divalent charge. One spring, the



excessive use of road salt has caused a plume of Na-Cl water to infiltrate the till. The Na<sup>+</sup>-rich solution is no longer in equilibrium with the Ca-clays, and Na<sup>+</sup> begins to displace Ca<sup>2+</sup> into solution. The spring groundwater moving through the till begins to evolve from a Na-Cl water to a Ca-Cl water. If Na-Cl waters continue to infiltrate through the till, they will eventually re-establish an equilibrium with the clays, converting them from Ca-clays to Na-clays. At this point, the groundwaters discharging below the till will evolve from a Ca-Cl water back to a Na-Cl water. If the original Ca-HCO<sub>3</sub> groundwaters reestablish in the recharge zone, then the deeper groundwater will evolve towards a Na-HCO<sub>3</sub> facies as Ca<sup>2+</sup> replaces Na<sup>+</sup> on the clays, and eventually to a Ca-HCO<sub>3</sub> water. Key to this process, however, is the transient geochemical condition in the recharge environment which generated non-equilibrium conditions, and the evolution back to equilibrium.

## SORPTION

Like cation exchange, ion sorption is the reversible exchange of a given solute between the solution and a charge-bearing surface. Unlike cation exchange, it is treated as an equilibrium distribution of the solute between these two phases rather than the competitive exchange of two cations for surface exchange sites. Typically sorption is used to model the mobility of a solute such as trace metals (e.g. Cd or Pb), radionuclides (<sup>90</sup>Sr or <sup>137</sup>Cs) or organic compounds (perhaps MTBE or TCE) present at low-concentration in groundwater. Sorption of some fraction of the solute onto solid surfaces in the soil or aquifer lowers its aqueous concentration, but does not necessarily alter the major ion geochemistry of the bulk solution. By coupling reversible sorption of a trace solute with groundwater flow, a contaminant plume will move more slowly than the advecting groundwater. The sorption phenomenon can be calculated and modeled by measuring the equilibrium distribution of the solute between the solid and solution at different concentrations, and representing the results by a mathematical relationship. As temperature will affect the degree of sorption, the measurements are made for constant temperature, resulting in sorption isotherms.

### *The Sorption Isotherm*

The degree of sorption of a given solute onto a mineral or organic surface is affected by the geochemistry of the solution and the characteristics of the charged surface, making it difficult to predict. It can be measured, however, by mixing a test solution with an initial concentration of the solute, C<sup>o</sup>, with an measured amount of the solid material. The loss from solution is what adsorbed onto the solids:

$$S \text{ (mg/g)} = (C^o - C) \cdot (L \text{ sample}) / (\text{g soil})$$

At equilibrium, the adsorbed amount will be proportional to the concentration in solution, C, with a proportionality constant known as the distribution coefficient, K<sub>d</sub>, where:

$$K_d = S/C$$

Batch tests are carried out at different initial concentrations to characterize K<sub>d</sub> over a range of solute concentrations. Multiple tests would not be necessary if the adsorbed to aqueous concentration was constant and the system was linear, and it might be over a limited concentration range. However, at higher concentrations the number of unfilled sorption sites is diminished, and K<sub>d</sub> generally becomes smaller (less sorption), requiring batch tests to be carried out over the anticipated concentration range. The resulting sorption curve can then be represented by an equation and used for predicting concentrations as the solute moves with groundwater. Three relationships are used. A simple linear isotherm can be drawn through batch test data from the origin, yielding a slope which is equal to K<sub>d</sub>:

$$S = K_d C$$

The Freundlich model uses an exponential function to characterize data which show a reduction of sorption with increasing concentration:

$$S = KC^n$$

The Langmuir model for sorption assumes an equilibrium constant that relates the number of filled sorption sites to the number of remaining unfilled sites and the solute concentration. This way, as the concentration goes up, the amount sorbed is constrained to a maximum number of sorption sites,  $S_{max}$ .

$$S = \frac{S_{max} \cdot KC}{1 + KC}$$

For all,  $K_d$  is the slope of the line at any given point, with the units of mass ratio over concentration (i.e. mg/g over mg/L or L/g). A large  $K_d$  indicates that the solute is strongly sorbed onto the material, whereas lower values indicate that the solute is more conservative and so not readily affected by sorption. Chloride, for example, is considered to be a conservative tracer and so would have a  $K_d$  very close to 0. Thorium, Th, by contrast, has a strong affinity for surfaces and is strongly sorbed, with almost no aqueous concentration and a very high  $K_d$ . Take for example these batch test data for  $Cd^{2+}$  on a clay loam soil, using a solution volume of 25 ml and 100 g of soil:

Initial concentration $C^o$ (mg/L)	Final concentration $C$ (mg/L)	Adsorbed concentration $S$ (mg/g)	$K_d$
27.2	0.092	0.678	7.4
50.8	0.182	1.27	7.0
75.0	0.284	1.87	6.6
150	1.39	3.94	2.7
100	2.86	4.93	1.7

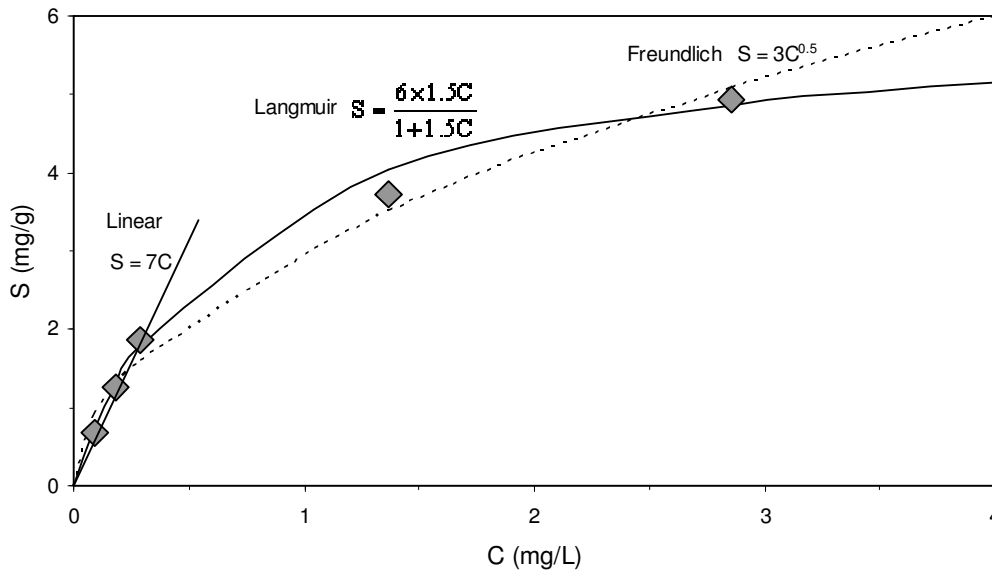


Fig. 7-6 Best fit isotherms for batch test data testing the adsorption of  $Cd^{2+}$  onto a clay loam. The low  $C$  data are best modeled with a simple linear isotherm, while at higher concentrations, the limited number of exchange sites must be accounted for by a Freundlich or better still is a Langmuir isotherm with a  $S_{max}$  of 6 mg/g and  $K$  of 1.5.