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## CATION RETENTION (EXCHANGE) IN SOILS

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Probably the most important and distinctive property of soils is that they can retain ions and release them slowly to the soil solution and to plants. The retention prevents concentrations that are too high and too low. The evolution of plants has taken advantage of this buffered range of ion concentrations that soils make available in the soil solution. Over most of the earth's surface, the availability of these ions in the soil solution is adequate, but not necessarily ideal, for plants. Crop and horticultural plants and a desire for maximum yield place greater demands on the soil and may require adjusting the native soil solution. Adjustments by fertilization, liming, and salt removal are usually temporary. The soil and climate tend to return the soil to its native state.

Ion retention is actually ion exchange. Soils give up other ions,  $H^+$  or  $OH^-$  and  $HCO_3^-$ , in equal amounts to those retained. When trace ions are removed from the soil solution, the ion exchange to the soil solution is often unnoticed. The retention of organic, nonionic substances usually results in their degradation by soil microbes and conversion to  $CO_2$  and water. This chapter is concerned with the exchange, the retention and release, of cations between soil particles and the soil solution.

Soil chemistry has stressed cation retention and exchange and has almost ignored anion retention and exchange. This unfortunate bias is because the clay particles of most soils of Europe and North America have a net negative charge. The amount of cation exchange is therefore greater than anion exchange. Had soil chemistry begun in Australia, in soils of volcanic parent material, or in highly weathered tropical soils the bias might be toward anion exchange and retention. Soils have both a negative charge that retains cations and a positive charge that retains anions. We usually measure the soil's net charge and that is usually negative.

Cation retention by soils can be roughly divided into the weaker electrostatic interaction of soil particles with the alkali and alkaline earth cations and the soil's stronger

chemical bonding with trivalent and transition metal cations. Chemical bonding is the interaction of polyvalent cations with  $O^{2-}$  and  $OH^-$  ligands of aluminosilicates, hydroxyoxides, and phosphates, plus retention of weak Lewis acids by soil organic matter. Chemical bonding, also called precipitation or strong adsorption, is discussed in Chapter 3 and is related to the dissolution–precipitation reactions of classical chemistry. The weaker, electrostatic retention of ions is distinctive to soils and colloidal systems and creates the major reservoir of the essential macroelement cations for plants and all living organisms. Some generalizations can be made about the attraction, exchange, and retention of cations by soils:

1. Relatively weak (electrostatic) attraction—alkali and alkaline earth cations (mainly Ca, Mg, K, and Na)

Nonspecific, depends mostly on the concentration ratios on the solid vs. the soil solution and on the ion charge ratio. Some clay minerals prefer one ion over others.

Reactions are fast and reversible; time scale is seconds and minutes.

Amount of retention depends on soil's cation exchange capacity, the negative charge of soil particles.

Largely due to aluminosilicate clay minerals plus soil organic matter.

2. Strong (chemical bonding) attraction—H, Al, Be, Ti, transition metal, and “heavy metal” cations

Specific, that is, the strength of attraction depends mostly on the cation's water solubility and the amount of that cation on the surfaces of soil particles.

Reaction time scale is rapid at first, but continues at ever-slower rates for long periods.

Amount of retention depends on soil pH rather than on the charge properties of soil clays.

Aluminosilicates are less important, Fe and Mn oxides are more important, in this retention than in electrostatic cation retention. The retention is generally much stronger than that predicted by aqueous solubility products.

Mechanisms of retention are complex and grade gradually from one to another.

Organic matter increases the range of sorptivity, possibly by adding soft Lewis base character.

Amorphous materials retain more than crystalline.

## 8.1 ELECTROSTATIC CATION RETENTION (CATION EXCHANGE)

*Exchangeable ions* are those ions replaced by neutral salt solutions flowing through soils. *Soluble salts* are removed by water alone. Salt solutions also exchange anions



from soils, but because soil colloids are mostly negatively charged, generally more cations exchange than anions. The major exchangeable cations are, in order of decreasing amounts,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . The retention helps prevent leaching losses during weathering; plants exchange for these cations and absorb them by releasing  $\text{H}^+$ .

In humid and temperate region soils, most of the plant-available alkaline earth and alkali metal cations neutralize the soil's negative charge. A typical agricultural loam soil contains about 20 000–30 000  $\text{kg ha}^{-1}$  of exchangeable cations in its root zone (0.5 m depth). Roughly 80% is Ca, 15% is Mg, 4% is K, and 1% is Na. As soil acidity increases,  $\text{Al}^{3+}$  and  $\text{H}^+$  are also exchangeable on soil surfaces. Arid soils may contain salts considerably in excess of the charge-neutralizing cations. Exchangeable cations and soil solution salts are very important to plant productivity and are easily manipulated by liming, irrigation, and fertilization. Hence, cation exchange has long been an important part of soil chemistry research.

Thompson and Way conducted the first recorded studies of cation exchange in Rothamsted, England, in 1850. They showed that passing an ammonium sulfate solution through soil columns leached calcium sulfate out of the soil. The predominant cation in the aqueous solution had changed from ammonium to calcium because of cation exchange in the soil. Thompson and Way showed that the exchange was very fast and reversible, and that the amount of ammonium ion retained equaled the amount of calcium released. Subsequent work has refined and supported these findings and has measured the cation exchange capacities of soil and soil components, the relative affinities of soils and their components for various cations, and the effects of changing soil pH on exchange reactions.

Cations in soils are roughly in three major categories: solid phase, exchangeable, and soluble. Weathering and organic decay release cations that vary in charge, size, and polarizability, so they respond differently to the soil surfaces and other ions they encounter in the soil solution. Small, polyvalent ions tend to reprecipitate/adsorb in soils by forming strong chemical bonds with aluminosilicate and hydroxyoxide surfaces. Larger, lower-charge cations (mainly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) instead associate more weakly with surfaces of the solid phase and are the exchangeable ions. The largest, lowest-charge cations ( $\text{K}^+$  and  $\text{Na}^+$ ) are weaker competitors for surface charge neutralization and tend to dominate in the *bulk soil solution* away from the charged surfaces (the soluble ions). Weathering tends to remove the soluble and exchangeable ions from soils.

The distribution of major exchangeable cations in productive agricultural soils is generally  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ \approx \text{Na}^+$ . The composition of the exchangeable cations in different soils tends to be much more uniform than the composition of the parent material rocks from which the soils are derived. The general effect of soil reactions is to smooth out the differences between soil parent materials and inputs, and to create a relatively uniform distribution of exchangeable ions for plant growth.

The soil-forming factors can modify the distribution of exchangeable cations from this desired state. Table 8.1 shows examples of exchangeable cations found in a wide variety of soils. The Merced soil has high exchangeable Na because it is poorly drained in an arid climate, it has no drainage to the sea, and upwelling water from a



**Table 8.1. CEC values and major exchangeable cations of selected soils<sup>a</sup>**

Soils	pH	CEC (mmol kg <sup>-1</sup> )	Exchangeable Cations (% of Total)				
			Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	H <sup>+</sup> (Al <sup>3+</sup> ) <sup>b</sup>
Average of agricultural soils (Netherlands)	7.0	383	79.0	13.0	2.0	6.0	—
Average of agricultural soils (California)	7.0	203	65.6	26.3	5.5	2.6	—
Chernozem or Mollisol (Russia)	7.0	561	84.3	11.0	1.6	3.0	—
Sodic Merced soil (California)	10.0	189	0.0	0.0	5.0	95.0	0.0
Lanna soil, unlimed (Sweden)	4.6	173	48.0	15.7	1.8	0.9	33.6
Lanna soil, limed (Sweden)	5.9	200	69.6	11.1	1.5	0.5	17.3

<sup>a</sup>From F. E. Bear, ed. 1964. *Chemistry in the Soil*, 2d ed. American Chemical Society, Washington, DC, p. 167.

<sup>b</sup>Probably includes some titratable acidity (Chapter 10.)

high water table evaporates at the surface. Under those conditions Ca precipitates as CaCO<sub>3</sub>, Mg, and K can form secondary soil minerals, leaving Na as the major cation. Exchangeable Na may exceed K in the Netherlands soils because of atmospheric inputs of NaCl from the nearby ocean. The high Mg<sup>2+</sup> content of the California soils may reflect the high-Mg content of rocks found in volcanic and geologically active regions. Exchangeable Al<sup>3+</sup> is present in appreciable quantities in acid soils (pH < 5.5), such as the Lanna soil in Sweden. This soil is formed from granitic rocks in dense forest under conditions of slowly weatherable parent material, high rainfall, good drainage, and organic acids from organic matter decomposition. This strongly acid soil (pH < 4) contains considerable exchangeable Al and some exchangeable H<sup>+</sup>.

Productive agricultural soils are characteristically Ca dominated. One important part of sustainable agriculture is to maintain Ca dominance. Despite the wide range of soil-forming factors in Table 8.1, Ca is the predominant cation in all but the extremely sodic (and barren) Merced soil.

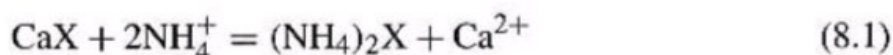
The sum of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Al<sup>3+</sup> generally equals, for practical purposes, the soil's *cation exchange capacity* (CEC). The CEC varies from 10 mmol(+) kg<sup>-1</sup> for coarse-textured soils to 500 to 600 mmol(+) kg<sup>-1</sup> for fine-textured soils containing large amounts of 2:1 layer silicate minerals and organic matter.

In 1850, Thompson and Way found cation exchange to be reversible, *stoichiometric* (the amount released, as moles of ion charge, equals the amount retained), and rapid. Since then some refinements have been studied and some exceptions have been found, but their results are still generally valid. Although cations are preferred



in varying degrees by soil colloids, even strongly adsorbed cations can normally be replaced by manipulating solution conditions. An exception to this generalization of reversibility is the preferential retention of many polyvalent cations (especially trace metals, weak Lewis acids) by soil organic matter. Such cations, which are thought to be partially covalently bonded, can be displaced only by other polyvalent cations capable of forming even stronger covalent bonds. Other exceptions include cation fixation reactions, described later in this chapter; cases where large organic cations, such as the pesticides paraquat and diquat, are physically prevented (steric hindrance) from approaching certain interlayer exchange sites; and cases where multivalent cations are preferentially adsorbed because they can simultaneously balance several closely adjacent exchange sites.

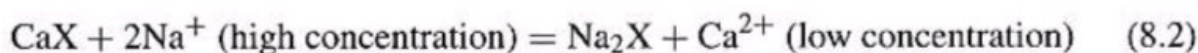
Because cation exchange reactions are stoichiometric, the sum of all exchangeable cations present at a given pH and CEC varies little or not at all with cation species. For example, consider the exchange reaction



where X designates a cation exchanger. Two ammonium ions replace one calcium ion to preserve the stoichiometry of the reaction. Exchangeable cation composition and CEC values normally are expressed as moles of ion charge  $\text{kg}^{-1}$ , formerly meq/100 g (milliequivalents per 100 g).

Exchange reactions are also rapid. The exchange step itself is virtually instantaneous. The rate-limiting step often is ion diffusion to or from the colloid surface. This is particularly true under field conditions, where ions may have to move through tortuous pores or through relatively thick, stagnant water films on soil colloid surfaces to reach an exchange site. The need for diffusion can produce *hysteresis* (the extent or speed of reaction depends on direction of the reaction) for some ion exchange reactions. Under laboratory conditions, samples normally are shaken during exchange reactions, to speed ion movement and to minimize the thickness of stagnant water layers on soil particle surfaces.

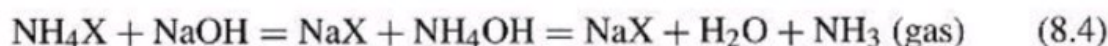
Because of their reversibility, cation exchange reactions can be driven forward or reverse by manipulating the relative concentrations of reactants and products. In the laboratory, common techniques for driving the reactions toward completion are to use high ( $\geq 1 \text{ M}$ ) concentrations of exchanging cations and to maintain low concentrations of product cations by leaching or repeated washings:



to form insoluble precipitates



or to form volatile gases





For exchange between cations of differing charge, diluting the solution favors retention of the more highly charged cation. For example, Eq. 8.1 has a reaction coefficient  $k$ :

$$k = \frac{[(\text{NH}_4)_2\text{X}][\text{Ca}^{2+}]}{[\text{CaX}][\text{NH}_4^+]^2} \quad (8.5)$$

where brackets indicate concentrations ( $\text{mol L}^{-1}$  or  $\text{mol kg}^{-1}$ ) rather than activities. Rearranging Eq. 8.5 gives a typical cation exchange equation:

$$\frac{[(\text{NH}_4)_2\text{X}]}{[\text{CaX}]} = k \frac{[\text{NH}_4^+]^2}{[\text{Ca}^{2+}]} \quad (8.6)$$

Because of the squared term on the right of Eq. 8.6, the ratio of ammonium to calcium in the colloid's double layer changes with total, as well as relative, salt concentration of the bulk solution. This dependence of cation exchange on cation valence has been termed the *valence dilution effect*. As an example, consider a solution having  $[\text{NH}_4^+] = [\text{Ca}^{2+}] = 1 \text{ mmol L}^{-1}$ . The ratio  $[\text{NH}_4^+]^2/[\text{Ca}^{2+}]$  in this case equals  $1^2/1$ , or  $1 \text{ mmol L}^{-1}$ . Upon tenfold dilution, the ratio is  $[0.1]^2/[0.1]$ , or  $0.1 \text{ mmol L}^{-1}$ . Hence, the ratio of ammonium to calcium on the colloid decreases with dilution (Table 8.2). The total quantities, but not the concentrations, of replacing ions remained constant. Table 8.2 shows the absence of a dilution effect for cations of the same valence. The percentage of calcium replaced by barium remained virtually constant, but that replaced by ammonium decreased with decreasing salt concentration.

Exchanging one cation for another in the presence of a third (*complementary*) cation also becomes easier as the retention strength of the third cation increases. For example, replacing calcium by ammonium is easier from a  $\text{Ca}^{2+}\text{-Al}^{3+}$  soil than from  $\text{Ca}^{2+}\text{-Na}^+$  soil. The fraction of the CEC satisfied by the tightly bound Al is in effect blocked off, and the Ca and ammonium ions compete for a smaller number of exchange sites.

**Table 8.2. Replacement of exchangeable calcium from 1 mmol of montmorillonite exchange sites by a constant amount (1 mmole of ion charge) of barium or ammonium, at varying replacing-cation concentrations<sup>a</sup>**

Solution Added		Percent $\text{Ca}^{2+}$ Replaced by:	
liters	mol charge $\text{L}^{-1}$	$\text{Ba}^{2+}$	$\text{NH}_4^+$
0.025	0.04	49.7	29.8
0.100	0.01	50.2	20.8
0.200	0.005	50.8	16.6
0.400	0.0025	52.7	15.2

<sup>a</sup> Adapted from P. Schachtschabel. 1940. *Kolloid-Beihefte*. 51:199-276.

### 8.1.1 Exchange Selectivity

The attraction of cations for negatively charged colloid surfaces is qualitatively described by electrostatic attraction and repulsion, following Coulomb's law (Appendix 8.1). A major limitation of this simple electrostatic approach, however, is its failure to predict differences in preference or selectivity of colloid surfaces for cations of the same valence. Such preference is related to the relative hydrated sizes or to the relative energies of hydration of the various cations. Ions of smaller dehydrated radius have a greater density of charge per unit volume. Hence, they attract waters of hydration more strongly and have a larger hydrated radius. An ion of larger hydrated radius is held less tightly by coulombic attraction. Partially dehydrated ions can approach the surfaces more closely and generally are retained quite tightly by soil colloid particles.

These generalizations arise from data such as in Table 8.3. The data were generated by saturating a montmorillonite suspension with a given ion and then measuring the quantity of that ion released when a symmetry (amount equal to the CEC) of either  $\text{NH}_4\text{Cl}$  or  $\text{KCl}$  was added.

The most important factor determining the relative extent of adsorption or desorption of a given ion is its valence. Divalent ions in general are retained more strongly than monovalent ions, trivalent ions are retained even more strongly, and quadrivalent ions such as thorium  $\text{Th}^{4+}$  are essentially unreplaced by an equivalent amount of  $\text{KCl}$ .

Within a given valence series, the degree of replaceability of an ion decreases as its dehydrated radius increases. An apparent exception is the " $\text{H}^+$ " ion. Monovalent

**Table 8.3. Relation of ion charge and ion size to ion retention<sup>a</sup>**

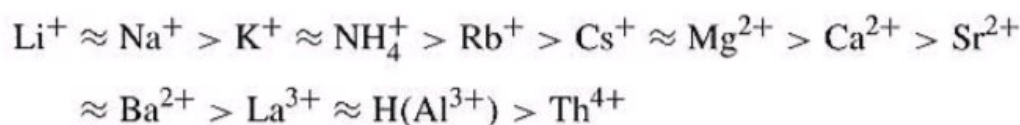
Ion	Crystallographic (Dehydrated) Radius (nm)	% Released by $\text{NH}_4^+$ or $\text{K}^+$
$\text{Li}^+$	0.068	68
$\text{Na}^+$	0.097	67
$\text{K}^+$	0.133	49
$\text{NH}_4^+$	0.143	50
$\text{Rb}^+$	0.147	37
$\text{Cs}^+$	0.167	31
" $\text{H}^+$ " ( $\text{Al}^{3+}$ )	(?)	15
$\text{Mg}^{2+}$	0.066	31
$\text{Ca}^{2+}$	0.099	29
$\text{Sr}^{2+}$	0.112	26
$\text{Ba}^{2+}$	0.134	27
$\text{Al}^{3+}$	0.051	15
$\text{La}^{3+}$	0.102	14
$\text{Th}^{4+}$	0.102	2

<sup>a</sup>Modified from H. Jenny and R. F. Reitemeier, 1935. Reprinted with permission from *J. Phys. Chem.* **39**:593–604. Copyright by the American Chemical Society.



“hydrogen” in this case behaves more like trivalent lanthanum. Work with acid soils and clays since the early 1950s has demonstrated that “hydrogen” clays are unstable and rapidly decompose to produce aluminium-saturated clays. Hence, the “H<sup>+</sup>” entry of Table 8.3 probably represents Al<sup>3+</sup>.

Relative ion replaceability, or ease of removal from specific colloids, has been called the *lyotropic series*. For example, the data of Table 8.3 could be written as

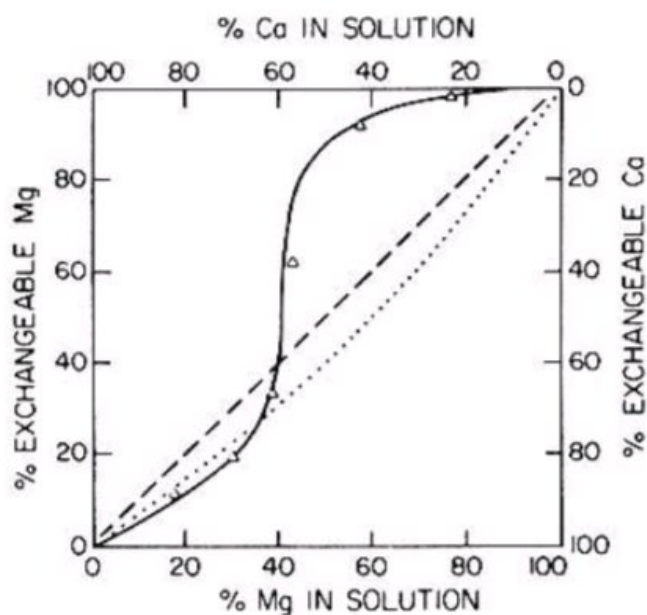


in order of increasing strength of retention by montmorillonite. The order of the lyotropic series is explainable if the cations at the colloid surface include a layer of specifically adsorbed or partially dehydrated cations, the so-called Stern layer (Appendix 8.1). The composition of the Stern layer can be estimated from coulombic calculations if individual ion characteristics (e.g., hydrated radius and polarizability) are considered.

Soil colloids of high charge density, that is, of high charge or CEC per unit surface area, generally have the greatest preference for highly charged cations. For example, vermiculite normally retains more Ca than does montmorillonite from a mixed Na<sup>+</sup>–Ca<sup>2+</sup> solution. Hence montmorillonite has a higher exchangeable Na percentage than vermiculite at the same bulk-solution Na and Ca concentrations. The monovalent cations NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> are often exceptions to this generalization, because of their unusually strong preference by mica and vermiculite (discussed in greater detail below). Partially covalent bonding and/or complex formation may contribute to a similar preference of soils high in organic matter for many polyvalent cations. Raising soil pH can also change cation selectivity by increasing soil CEC and thus increasing the preference for polyvalent versus monovalent ions.

In addition to coulombic preferences related to ion size, certain colloids exhibit unusually high preferences for specific cations. An example is the high exchangeable magnesium content of vermiculite. Hydrated Mg<sup>2+</sup> apparently fits so well into the water network between partially expanded sheets of vermiculite that Mg is preferred over a wide concentration range (Fig. 8.1). The dashed line in the figure indicates no ion preference by the colloid, and the dotted line shows a more typical case of Ca<sup>2+</sup>–Mg<sup>2+</sup> exchange with an exchange coefficient of 1.5. At low Mg<sup>2+</sup> concentrations, vermiculite prefers Ca over Mg because the hydrated Mg<sup>2+</sup> is larger than hydrated Ca<sup>2+</sup>. As soon as enough Mg (>40%) is present in solution to exert a significant effect on the interlattice water network, the curve shifts to a pronounced preference for Mg. Although normal soil solutions have relatively high Ca<sup>2+</sup>/Mg<sup>2+</sup> ratios, the crossover on the figure occurs at Ca<sup>2+</sup>/Mg<sup>2+</sup> ratios that are attainable under some natural conditions. These conditions can occur when calcium carbonate is precipitating, when former marine sediments are contributing soluble salts, or when high Mg micas are weathering to vermiculite. Vermiculite then is an excellent scavenger of Mg ions and becomes nearly saturated with Mg even when exposed to appreciable Ca concentrations and/or monovalent cations. To replace the Mg from natural





**FIGURE 8.1.** Ca–Mg exchange in a vermiculite suspension. The dashed line represents an exchange constant of 1.0 (no preference); dotted line represents a Ca–Mg exchange constant of 1.5. (From F. F. Peterson et. al. 1965. *Soil Sci. Soc. Am. Proc.* 29:327.)

vermiculites, the mineral must be repeatedly leached with high concentrations of a replacing ion. This procedure lowers the relative Mg concentration below the point of preferential adsorption.

Another case of high preference for a particular ion is the preference of vermiculites and of weathered edges of trioctahedral micas for K and similar exchangeable cations. Mica weathers to a vermiculite-like mineral with a decrease in layer charge accompanying the weathering process. Traditionally, the preferential adsorption of K,  $\text{NH}_4$ , cesium, and rubidium by such minerals has been attributed to the excellent fit of the ions in the hexagonal or ditrigonal holes on vermiculite surfaces. The process is believed to be activated by the dehydration of large, weakly hydrated ions as adjacent silicate sheets approach one another during thermal motion or drying.

Alternatively, the affinity has been explained by the relative hydration energies of various ions, plus the relative hydration energies of individual cation exchange sites on different minerals. The relatively small hydration energies of K,  $\text{NH}_4$ , Rb, and Cs result in easy dehydration and strong retention. The hydration energy theory explains how  $\text{Ba}^{2+}$ , with essentially the same crystallographic radius as  $\text{NH}_4$ , is not fixed by trioctahedral micas or vermiculite. Barium ions, with their greater energy of hydration, apparently are not readily dehydrated and entrapped by adjacent mineral lattices. Barium also readily rehydrates, forcing the lattices apart when mineral surfaces are rewetted after drying.

Preferential retention of K and  $\text{NH}_4$  by vermiculite and by weathered mica edges is sufficiently dramatic that a sizeable literature has accumulated on this so-called *fixation* reaction. Fixation generally decreases with soil acidification and increases with soil liming. This is attributed to the formation of Al and Fe hydroxide interlayers between mica and vermiculite layer lattices under acid conditions. Such interlayers prevent the lattices from collapsing completely. Lattice collapse is theoretically



necessary to retain fixed cations against exchange by various extracting solutions. Fixation is accentuated by drying.

### 8.1.2 Cation Exchange Equations

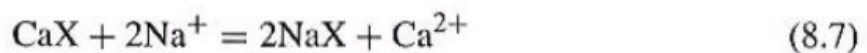
To predict the effects of, for example, irrigation, liming, weathering, fertilization, and acid rain on soils, it is necessary to predict the exchangeable cation composition in equilibrium with this new input. The exchangeable cation chemistry can also provide valuable clues about plant elemental deficiencies or imbalances, rates of toxic metal movement and attenuation, and tendencies toward soil dispersion. Cation exchange equations predict those effects with varying precision.

Several equations describe cation exchange processes. Each has its own set of characteristics and merit. The choice of a particular equation often seems to be subjective, however, and may be based as much on the investigator's background as on any other factor. Lack of familiarity with the units, and of the numerical values of exchange coefficients for other equations are major deterrents to adoption of a more widespread and uniform approach to cation exchange.

Certain limitations are inherent in most cation exchange equations:

1. Cation and anion exchange are considered separately; acknowledging their simultaneous presence is rare.
2. The cation or anion exchanger is assumed to possess constant exchange capacity. Often, however, the capacity varies with the exchangeable ion, with salt concentration, and with pH.
3. Stoichiometric (1 to 1) ion exchange is generally assumed. Apparent exceptions are usually explained by simultaneous adsorption of molecules or by complex ion formation.
4. Complete reversibility is usually assumed.

The most general type of cation exchange relationship is a mass action equation:



resulting in the reaction coefficient

$$k = \frac{(\text{NaX})^2(\text{Ca}^{2+})}{(\text{CaX})(\text{Na}^+)^2} \quad (8.8)$$

where X denotes the exchangeable form of the cation and parentheses denote activities of soluble or exchangeable cations. The major problem in all exchange equations is evaluating the activity of the exchangeable cations, since their activities cannot be measured or calculated precisely. Equation 8.8 can be rearranged to

$$\frac{(\text{NaX})^2}{(\text{CaX})} = k \frac{(\text{Na}^+)^2}{(\text{Ca}^{2+})} \quad (8.9)$$



This has been termed a *Kerr*-type exchange equation. Kerr used ion concentrations in place of ion activities, thus tacitly assuming concentrations and activities to be directly proportional. Nevertheless, the equation often holds fairly well over narrow concentration ranges. The activity coefficient of the divalent cation is more concentration dependent than that of the monovalent cation, but the monovalent cation activity coefficient is squared, offsetting much of this variation. The ion activity ratio in the soil solution, therefore, may be roughly proportional to the concentration ratios in the soil solution over an appreciable range.

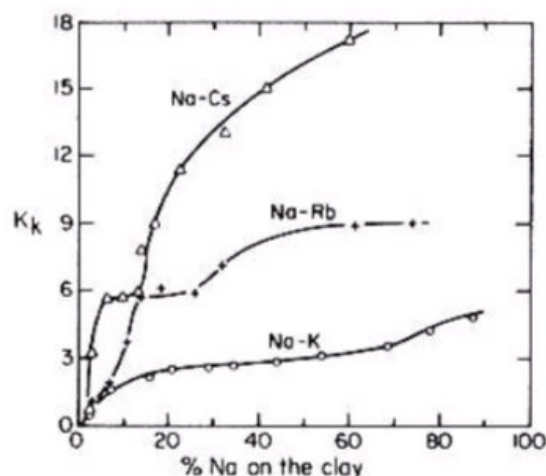
Ion activities in aqueous solution can be estimated from Debye–Hueckel theory (Eq. 3.16) or approximated by measurements with specific-ion electrodes. The more difficult problem of estimating the activities of adsorbed cations is still unanswered. Different assumptions for estimating the activities of exchangeable ions have resulted in the several cation exchange equations that are commonly used for exchange between ions of different valence. All of these exchange equations reduce to the Kerr equation (8.9) when ions are the same valence. The goal of each equation is to provide a relatively uniform exchange “constant” (more correctly, *exchange coefficient*) over a wide range of exchangeable cation compositions. The difficulty of this, even for ions of the same valence, is apparent from the Kerr equation “constants” plotted in Fig. 8.2. The exchange coefficient is approximately constant only over a limited concentration range for Na–K exchange and over even more restricted ranges for Na–Rb exchange. Such variability limits the practical usefulness of most exchange equations to relatively small ranges.

The *Gapon* equation, proposed in 1933, has found considerable use:

$$\frac{[\text{NaX}]}{[\text{Ca}_{1/2}\text{X}]} = k_G \frac{[\text{Na}]}{[\text{Ca}]^{1/2}} \quad (8.10)$$

where exchangeable-cation concentrations are in mmoles of charge per gram (or kilogram), and soluble-cation concentrations are in millimoles (or moles) per liter.

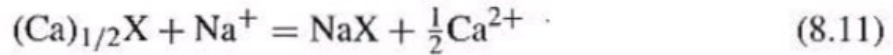
The Gapon equation also uses concentrations rather than activities for the soluble ions, and writes the mass action equation with chemically equivalent quantities both



**FIGURE 8.2.** Selectivity coefficient  $K_k$  versus exchangeable ion composition for an attapulgite clay. (From C. E. Marshall and G. Garcia. 1959. *J. Phys. Chem.* 63:1663.)



for colloid exchange sites and exchanging cations. The Gapon equation corresponds to the following chemical reaction:



It differs from the square root of the Kerr equation by including the term  $[\text{Ca}_{1/2}\text{X}]$  rather than  $[\text{CaX}]^{1/2}$ . As was discussed for Eq. 8.9, the successful use of concentration ratios in solution, instead of activity ratios, is fortuitous over fairly narrow (though important) ranges of soluble-ion composition. One example, Na–Ca exchange, is important in irrigated regions. Dispersion and physical deterioration of many soils occur if exchangeable Na becomes too high. The Gapon equation is unsatisfactory if applied over the entire range of Na–Ca compositions, but works fairly well over the range of compositions of most interest to irrigated agriculture. The Gapon exchange coefficient is fairly uniform from 0 to 40% exchangeable sodium for many irrigated soils of the western United States, at  $k_G = 0.010$  to  $0.015$   $(\text{Lmmol}^{-1})^{1/2}$ .

Other cation-exchange equations are discussed in Appendix 8.2. Most of these have a better theoretical basis than the Gapon equation, but few are as simple to apply or visualize. Many workers are willing to sacrifice a little theoretical rigor to gain some simplicity in a cation-exchange equation. The Gapon and the Kerr equations are the simplest the ion-exchange equations. Gapon adequately predicts cation-exchange behavior over practical ranges for many soil systems.

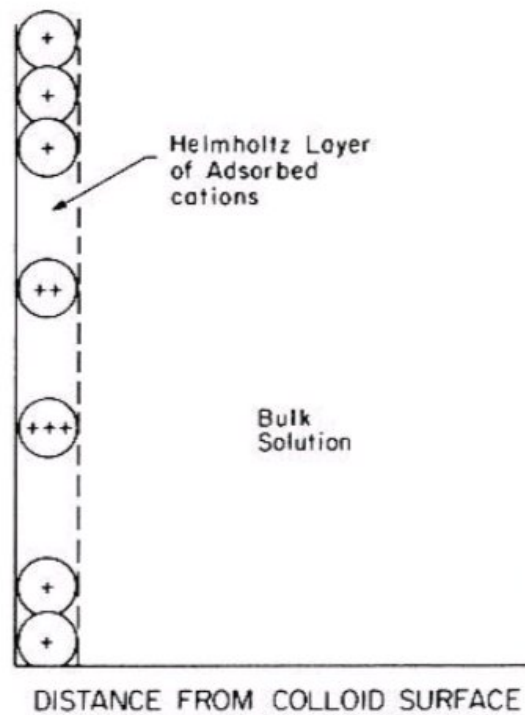
### 8.1.3 Diffuse Double Layer

In air-dry soils, the exchangeable ions can be considered to reside directly on the surface of the colloid (Fig. 8.3). The negative charges of soil clays and the layer of exchangeable cations make up two slightly separated layers, called a *Helmholtz double layer*. When water is present, however, the cations are no longer so tightly held on the surface. The electrostatic attraction of cations is counteracted somewhat by diffusion into the aqueous solution. Diffusion tries to equalize the concentration throughout the aqueous phase. Figure 8.4 shows the net result of electrostatic attraction versus diffusion of cations at two bulk solution salt concentrations, ignoring any anion effects. The cation concentration decreases with distance from the negatively charged surface. The colloid's negative charge is neutralized by a swarm of positive ions in the aqueous phase, the diffuse double layer (DDL).

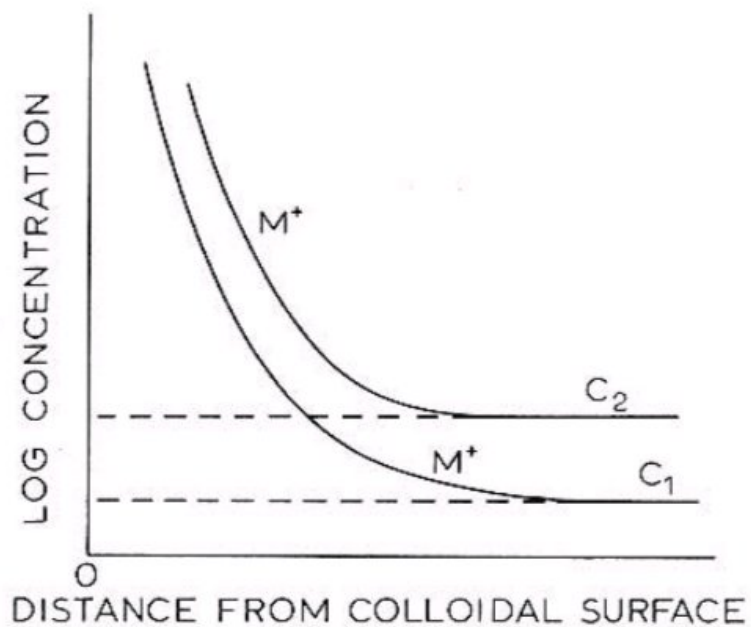
Increasing the salt concentration from  $C_1$  to  $C_2$  reduces the tendency for diffusion away from the surface and thus shrinks the DDL. The thickness of the DDL is loosely defined as the distance over which the solution concentration is affected by the colloid's charge. The solution outside the DDL is termed the *bulk solution*.

Anion repulsion within the DDL also neutralizes the colloid's negative charge by increasing the net positive charge within the DDL. Figure 8.5 shows how anions are repelled by the colloid's charge. Assuming for the moment that cations do not affect the anion distribution, the anion concentration outside the DDL,  $C_3$ , is then higher than if no repulsion occurred,  $C_0$ . Since ion charges in the bulk solution must



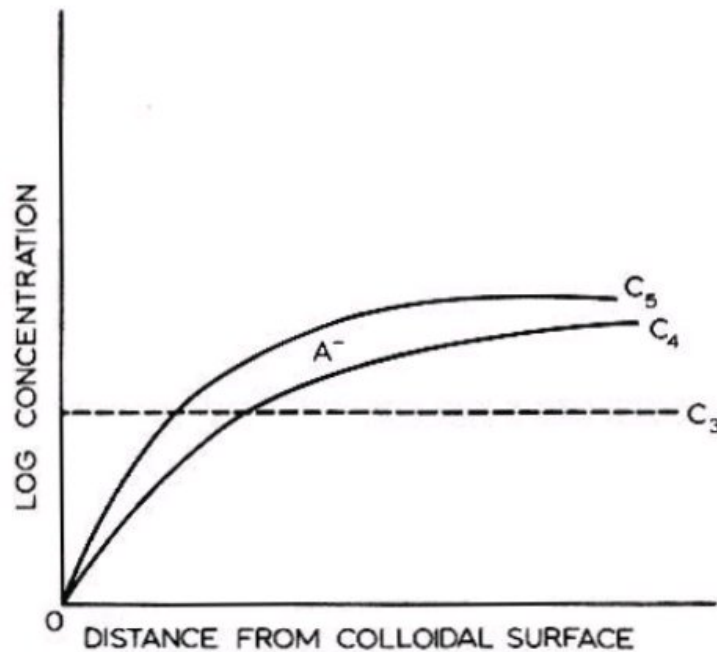


**FIGURE 8.3.** Distribution of monovalent cations and anions near the surface of a typical montmorillonite particle according to the Helmholtz model. (Adapted from D. R. Neilsen et al. 1972. *Soil Water*, p. 45, by permission of the American Society of Agronomy and Soil Science Society of America.)



**FIGURE 8.4.** The distribution of cations away from a negatively charged soil surface at two cation concentrations, with effects of anions disregarded. The cation exchange capacity is proportional to the area between the curves and their corresponding dashed lines.





**FIGURE 8.5.** Distribution of anions near a negatively charged surface at two anion concentrations,  $C_4$  and  $C_5$ , disregarding cation effects.

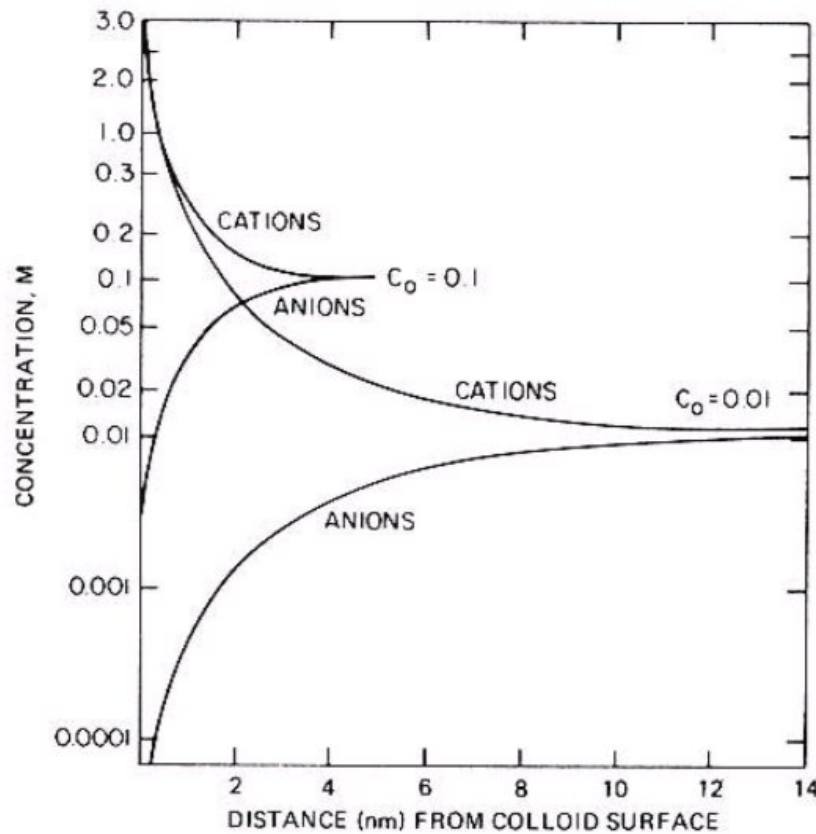
balance, this means that anion repulsion increases the salt concentration in the bulk solution. Increasing the anion concentration to  $C_4$  shrinks the DDL, as it did for cation attraction, though in this case the effect arises from increased anion diffusion toward the surface. The effect of anion repulsion is mostly interesting in the laboratory, because the contribution of anion repulsion to soil behavior is small except when bulk solution salt concentrations are  $> 1$  M, where few organisms can survive.

Figure 8.6 shows the combined result of cation attraction, anion repulsion, and ion diffusion on the cation and anion distribution next to a negatively charged particle. The solution near the surface has an excess of cations and a deficit of anions. The thickness of the DDL decreases with increasing cation or anion charge. The effect of anion charge is less significant, because fewer anions are in the DDL. The DDL shrinks with increasing cation charge because fewer ions are necessary for charge neutralization and the more highly charged cations are attracted more strongly to the colloid. Diffusion, on the other hand, results from ion concentrations rather than ion charge.

Table 8.4 gives values for an arbitrary double-layer “thickness” for monovalent and divalent cations at three bulk solution salt concentrations. Double-layer thickness varies inversely with the square root of the bulk solution salt concentration or the valence of the exchangeable cation. These thicknesses are small compared to the diameters of soil pores, which are on the order of 1000 to 50 000 nm, but they are of the same magnitude as water film thicknesses in relatively dry soils.

If the DDL contained only those cations necessary to neutralize the colloid charge, the anion concentration would be zero within the DDL. Because diffusion continually drives anions toward the colloid surface, however, the total negative charge within the DDL is that of the anions plus the colloid’s charge. Cations within the DDL must neutralize both sources of negative charge. The cations that neutralize





**FIGURE 8.6.** Distribution of monovalent cations and anions near the surface of a montmorillonite particle. (Adapted from D. R. Nielsen et al. 1972. *Soil Water*, p. 45, by permission of the American Society of Agronomy and the Soil Science Society of America.)

the colloid charge are “exchangeable”; the remainder are “soluble,” because they neutralize the anions that have diffused into the DDL. The total positive charge in the DDL must exactly equal the total negative charge of that region. For positively charged colloids, the behavior of cations and anions in the DDL and bulk solution are reversed. Anions are attracted to the surfaces and cations are repelled.

**Table 8.4.** Approximate “thickness” of a typical soil colloid double layer as a function of electrolyte concentration<sup>a</sup>

Bulk-Solution Concentration of Cations (mol charge L <sup>-1</sup> )	“Thickness” of the Double Layer (nm) for:	
	Monovalent Cations	Divalent Cations
10 <sup>-5</sup>	10	5
10 <sup>-3</sup>	1	0.5
10 <sup>-1</sup>	0.1	0.005

<sup>a</sup> Adapted from H. Van Olphen. 1963. *An Introduction to Clay Colloid Chemistry*. Interscience, New York. Reprinted by permission of John Wiley & Sons, Inc.



## 8.2 STRONGLY-RETAINED CATIONS

The strongly retained cations in soils include many of the essential microelements and also the "toxic" cations. The concentrations of these ions in the soil solution are low and they are apparently retained by two means. One group is the cations that in aqueous solutions precipitate as insoluble oxides and hydroxyoxides. The root zone of a typical agricultural soil might contain as much as 300 000 kg ha<sup>-1</sup> of Fe and Al, but their plant availability is only a few kg ha<sup>-1</sup>.

The second and smaller group is those cations that also are insoluble in pure aqueous solutions, but that tend to associate in soils with soil organic matter and sulfide. These cations are the weak and intermediate Lewis acids of Table 3-7—Cu<sup>1-2+</sup>, Cd<sup>2+</sup>, Hg<sup>1-2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Fe<sup>2+</sup>. Soil retains these cations by hydroxyoxide precipitation/adsorption and by soil organic matter adsorption in varying degrees. The amounts of the weak Lewis acids in soils are small; the root zone contains on average about 300 kg ha<sup>-1</sup> of Pb and <1 kg ha<sup>-1</sup> of Cd and Hg but the variation is large. The amounts of these ions absorbed by plants is a tiny fraction of the total.

Soil retention of strongly retained ions generally increases with pH. Above pH 7, the effect of increasing pH on ion movement, plant availability, and chemical extractability lessens. Molybdenum is an exception: MoO<sup>2-</sup> reacts strongly with Ca<sup>2+</sup> and precipitates at higher pHs. If these ions are added to soils, as in municipal and industrial wastes, contaminated water, fly ash, and so on, most tests have shown that the amounts retained and the strength of that retention increases with time. The amounts retained and the strength of retention increase rapidly at first; the rate then slows over periods ranging from days to months.

The generalization that heavy metal retention increases with time may be wrong for weak Lewis acids applied in organic wastes to soils. One recent experiment with Mo, Zn, and Cd added to soils in sewage sludge showed that their plant availability remained unchanged for many years after application. The plant uptake of these ions was linearly proportional to soil content even after 23 years since the last addition. The amount of Zn available was 0.5 to 3% of that added initially. The amount of available Cd was 4 to 18% of that added. The reasons for the long-term and high availability in this case is uncertain.

### 8.2.1 Oxide-Retained Cations

The relative retention of divalent ions by amorphous Fe hydroxyoxides is



Retention of the divalent cations by Al hydroxide is slightly different:



Retention by silica is



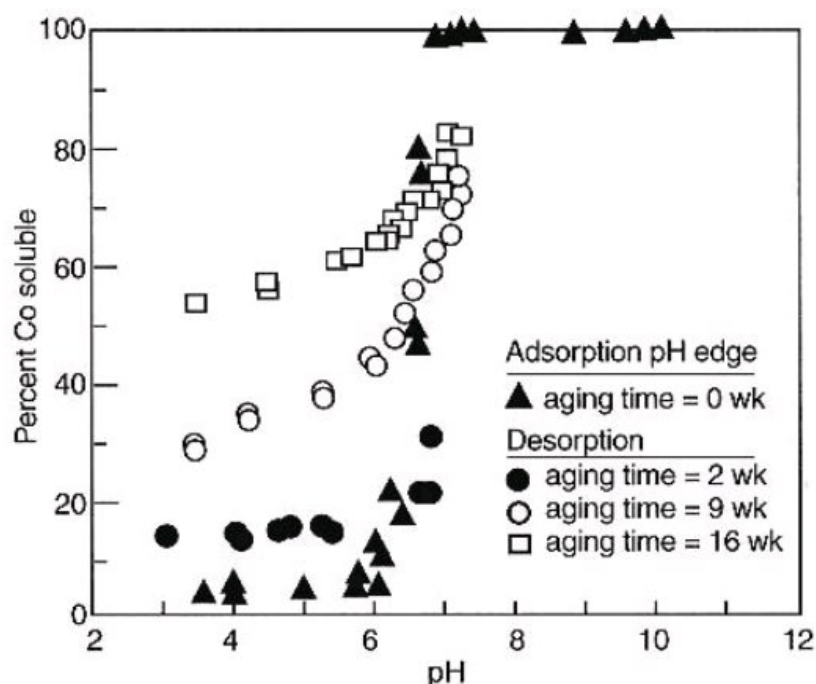


Although differing in detail, the retention by these three major soil components is rather similar. The measurements were done in the absence of organic matter or sulfide ions, so only the attraction to  $O^{2-}$ -dominated surfaces was determined.

The retention by silicate and hydroxyoxide minerals and surfaces is by  $O^{2-}$  ions. Since the oxide ion interacts strongly with  $H^+$ , the cation retention is strongly pH dependent. Figure 8.7 illustrates both the pH and time dependence of the retention of  $Co^{2+}$  by Fe hydroxyoxide. At  $pH < 6$ , the amount of  $Co^{2+}$  retained by Fe hydroxyoxide increased with pH and time. At  $pH > 6.5$ ,  $Co^{2+}$  retention was complete within 2 weeks.

The initial retention shown by the black triangles is low as acidity decreased to pH 7, whereupon retention increased sharply, the so-called *adsorption edge*. When the solid was treated later with acid, the amount of  $Co^{2+}$  released back to the solution was less than the amount added, and the release decreased as time of aging the Co-Fe hydroxyoxide mixture increased. Other ions react similarly with silicates and hydroxyoxides. The pH of the adsorption edge and the effect of time differ somewhat, but the behavior is rather general. Plant deficiencies of these essential microelements, such as Fe chlorosis and Zn deficiency, may occur above soil pH 8. The deficiencies have been noted in fruit and nut trees and in some varieties of sorghum. The deficiencies are in arid regions under irrigation in which the faster growth puts a greater stress on soil availability. Native plants growing under native conditions do not show deficiency symptoms. Plant deficiencies are more complicated than simple soil unavailability, but the deficiencies can usually be overcome by acidifying the soil.

Conversely, when the concentrations of these cations are too high—Al toxicity in acid soils or Fe and Mn toxicity in rice paddies—raising the soil pH by liming is ef-



**FIGURE 8.7.** Fractional adsorption of  $Co^{2+}$  to hydrous Fe-oxide (HFO) as a function of pH and HFO- $Co^{2+}$  aging time. (From C. C. Ainsworth, J. L. Pilou, P. L. Gassman, and W. G. vander Aluys. 1994. *Soil Sci. Soc. Am. J.* 58:1615.)



fective. Since  $O^{2-}$  ligands are so prevalent in soils, they can retain/adsorb/precipitate large amounts of these ions if  $pH > 6$ . Changing the soil pH or foliar spraying to circumvent the soils is generally more effective than adding these microelements as soil fertilizers. That also means that soil pollution by these ions is readily overcome by increasing the soil pH. The ions are immobile and unavailable for plant or microbial uptake. Liming contaminated soils, covering them with clean soil, or mixing them with clean soil underneath, is often sufficient to overcome any hazards. Regulatory agencies realize that the mere presence of an ion in soils does not necessarily constitute a hazard to humans. Soils have a high capacity to reduce high additions of these elements to their plant availability in native soils.

The retention of this group increases, that is, mobility and plant availability decreases, rapidly at first and the rate slows with time. This behavior is similar to diffusion and suggests that the mechanism is the slow transfer of surface ions into the weathered layer on soil particles. The initial rate is rapid because the surface concentration is relatively high and the diffusion path length is short. As diffusion inward proceeds, the surface concentration decreases and the diffusion path length increases. The shallower concentration gradient slows the rate of further cation diffusion.

Although the cations retained primarily by aluminosilicates and hydroxyoxides in soils, that is, the hard Lewis acids, are controlled by interaction with  $O^{2-}$  and  $OH^-$  ligands on soil particle surfaces, the aqueous solubility of these cations is usually much less than that predicted by the solubility products of their pure hydroxyoxides. The big differences between solubility products and ion activity products (IAP) indicate that soils retain the cations more strongly than their own pure hydroxyoxides. How soils can accomplish this is still uncertain. Although the cations fit better into their own hydroxyoxide structures than into aluminosilicate or major Al, Fe, Mn, and Ti hydroxyoxide structures, soils nonetheless retain the ions very strongly.

One school of thought maintains that certain "sites" on soil surfaces can retain these cations strongly; radiographs show the cations are both bunched and spread out on soil surfaces. Another school suggests that these adsorption sites are where the cations can mix as solid solutions with the other ions on the surfaces. The free energy of mixing on the surfaces (Appendix 3.2) is responsible for the strong retention rather than any uniquely favorable adsorption spots on soil particle surfaces. In any case, soil retention can reduce the aqueous solubility of these ions to well below that in equilibrium with their pure hydroxyoxides.

The models that predict soil solution concentrations by their oxide/hydroxyoxide or other solubility products ( $K_{sp}$ ) have usually been only qualitatively successful. Predictions of aquated Al and Fe concentrations have sometimes been successful, probably because their hydroxyoxides were a major component of the solid phase and therefore unaffected by the effects of solid solution mixing. For trace metals, the models have been less successful. In some cases the measured IAP has been similar to the  $K_{sp}$  of a pure solid that has not yet been identified in soils. Pb solubility in the soil solution has been linked to the solubility of Pb phosphate, for example. This must still be tested by measuring the Pb response to added phosphate to see if the agreement of IAP and  $K_{sp}$  is coincidental rather than causal.



Another approach is simply to statistically relate the ion concentration in the soil solution to the total amount in the soil. In 100 British soils, the Pb concentration in the extracted soil solution closely followed the following equation:

$$\log \text{Pb}_{\text{total}} - \log \text{Pb}_{\text{soilsolution}} = 1.30 + 0.55\text{pH} \quad (8.12)$$

In 30 British soils, the soil Cd concentrations followed

$$\log \text{Cd}_{\text{total}} - 1.09\text{Cd}_{\text{soilsolution}} = 1.11 + 0.38\text{pH} \quad (8.13)$$

Such relations depend on the analytical procedure employed. The relations do not support one retention mechanism over another but are useful for regulatory purposes. The soil solution concentrations ranged from 3.6 to 3600  $\mu\text{g Pb L}^{-1}$  and 2.7 to 1280  $\mu\text{g Cd L}^{-1}$ . The amounts in the extracted solutions were less than 1% of the total amounts in the soils, indicating how effective soils are in reducing availability of these toxic ions. Although several retention mechanisms may be involved for Pb and Cd, all the mechanisms apparently respond to pH. Neither equation supports the generalization of increasing retention with time.

### 8.2.2 Cations Retained by Soil Organic Matter

The soft Lewis acids (Section 3.5)—Cd, Cu, Zn, Hg,  $\text{Pb}^{2+}$ , and to a lesser extent  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ —tend to be more affected by soil organic matter and sulfide. Some generalities about these cations are the following:

1. Soil retention is less pH sensitive than for hard Lewis acids.
2. Retention may be less time dependent.
3. Fraction retained, and strength of retention, decreases as concentration increases.
4. The ion activity products of the cation's hydroxyoxide are less than their hydroxyoxide solubility products.

Although soft Lewis bases are associated with reducing (anaerobic, low oxygen) conditions, normal (aerobic) soils contain sufficient amounts of organic matter to retain the low amounts of these trace metal ions in soils.

The soft Lewis acids and bases are among the very toxic ions. The soft Lewis acid–base situation that has created considerable concern is in municipal and industrial landfills. The worry is that the strong reducing conditions will create soluble soft Lewis acid–base ions, complex ions and molecules that will leach out of the landfills and into groundwater. To counteract this problem, clay and plastic liners are being installed beneath landfills and water-impermeable caps are being placed above the landfills to entomb the wastes. The slow migration of ions beneath natural swamps, another strongly reducing condition, suggests that the severity of the problem may be exaggerated. The problem, however, has made people more aware of proper and



improper use of soil as a disposal/recycling medium. The idea of entombing our wastes in "secure" landfills seems naive; wise treatment would seem to be a better alternative.

## APPENDIX 8.1 DIFFUSE DOUBLE-LAYER THEORY

The *Guoy–Chapman* theory, derived concurrently by them in the early 1900s, is the basis of describing the DDL on charged colloid surfaces. Their assumptions are similar to those used later and more successfully by Debye and Hueckel to describe ion activities in the much simpler case of aqueous solutions. Gouy–Chapman theory assumes that (1) exchangeable cations exist as point charges, (2) colloid surfaces are planar and essentially infinite in extent, and (3) surface charge is distributed uniformly over the entire colloid surface. These assumptions inaccurately describe actual systems, but the theory of the DDL works surprisingly well for soil colloids. Apparently, many of the errors inherent in the assumptions tend to cancel each other.

Cations are attracted toward, and anions are repelled from, negatively charged soil colloids. Such interactions follow Coulomb's law:

$$F = \frac{qq'K}{Dr^2} \quad (8.14)$$

where  $F$  is the force of attraction or repulsion (newtons),  $q$  and  $q'$  are the electrical charges (coulombs),  $K$  is a proportionality constant ( $= 8.9 \times 10^9$  for these SI units),  $r$  is the distance of charge separation (meters), and  $D$  is the dielectric constant ( $= 78$  for water at  $25^\circ\text{C}$ ). The strength of ion retention or repulsion increases with increasing ion charge, with increasing colloid charge, and with decreasing distance between the colloid surface and either the source of charge or the soluble ion.

The increased cation concentration in the DDL develops a countertendency for cation diffusion away from the surface. The diffusion tends to equalize cation concentrations throughout the solution phase. Combining the equations for cation attraction and diffusion yields the Boltzmann equation:

$$\frac{C}{C_0} = \exp\left(-Ze\frac{\psi}{kT}\right) \quad (8.15)$$

where  $C$  is the concentration of an ion at a specified distance from the charged surface,  $C_0$  is the concentration of the ion in the bulk solution,  $Z$  is the valence of the ion,  $e$  is the unit of electronic charge,  $\psi$  is the electrical potential of the colloid at the specified distance,  $k$  is the Boltzmann constant (the gas constant per molecule), and  $T$  is the absolute temperature. Equation 8.15 describes the distributions of both cations and anions in the double layer, provided that  $\psi$  is made negative because of the net negative charge of most soil colloids.

The treatment of double-layer phenomena is straightforward when the change of electric potential with distance from the colloid surface can be adequately estimated. This distribution can be considered to arise from the termination of individual lines of



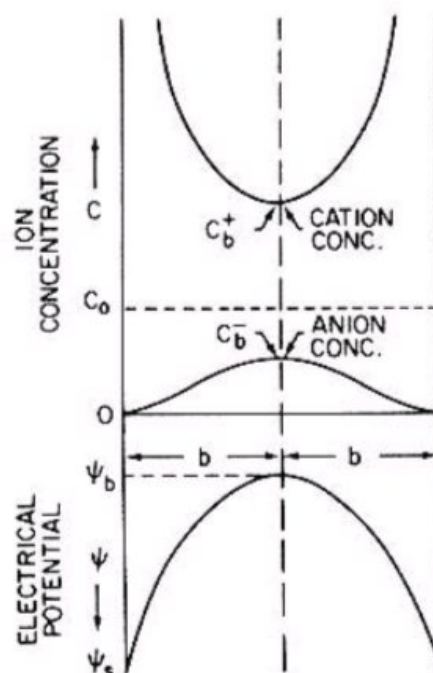
force from the colloid when they encounter cations in the double layer. Solutions of the equations describing electric potential distribution are, however, mathematically complex.

The DDL is generally treated quantitatively in either of two ways. The more standard approach is to regard soil colloids as having constant surface charge but variable surface potential (constant charge colloids). The distribution of potential thus varies with bulk solution salt concentration and with average valence of the counter (exchangeable) ions, but the charge (CEC) of the soil remains constant.

A second approach is to treat the colloid as having constant surface potential but variable surface charge (*constant potential colloids*). This behavior is common for colloids such as gold sols or glass surfaces and for soils having predominantly pH-dependent charge. In most soils, however, the main potential-determining ions are H and OH ions. Hence, the charge remains virtually constant as long as the pH is held constant, unless the salt concentration or the exchangeable cation composition changes markedly. Unlike for variable potential colloids, the charge of constant potential colloids varies appreciably and predictably with the salt concentration of the bulk solution. Adsorption of certain anions can also change the colloid charge.

Hydroxyoxide surfaces often appear to have concentration-dependent anion exchange capacities, but such behavior can also be explained by the collapse of the double layer at high salt concentrations. Under these conditions, positively charged sites are no longer masked by the DDLs of the predominantly negatively charged soil matrix.

Fully expanded double layers are rare in field soils. Double-layer expansion normally is restricted to thin water films on colloid surfaces or by interactions with double layers on adjacent soil particles within aggregates. Figure 8.8 represents such



**FIGURE 8.8.** Electrical potential and ion concentration between interacting negatively charged platelets.



a restricted double layer. The distributions of cations, anions, and electrical potential in Fig. 8.8 are assumed to be symmetrical between two vertical colloid particles. The cation concentration decreases to  $C_b^+$ , and the anion concentration increases to  $C_b^-$ , the solute concentrations at the midplane between adjacent particles. Similarly, the electrical potential varies from  $A_s$ , the *surface potential* of the colloid, to  $\psi_b$ , the *midplane electric potential*. The excess of cations at the midplane compared to the bulk solution causes an osmotic gradient. This, in turn, causes water imbibition, or swelling, of the colloid. Water imbibition continues until the tendency to swell is balanced by interparticle bonds; that is, until the osmotic potential at the midplane equals that in the bulk solution, or until swelling is retarded by the lack of additional water. For most soils, obvious swelling of the entire matrix is uncommon, but it can be pronounced for highly montmorillonitic soils, such as Vertisols.

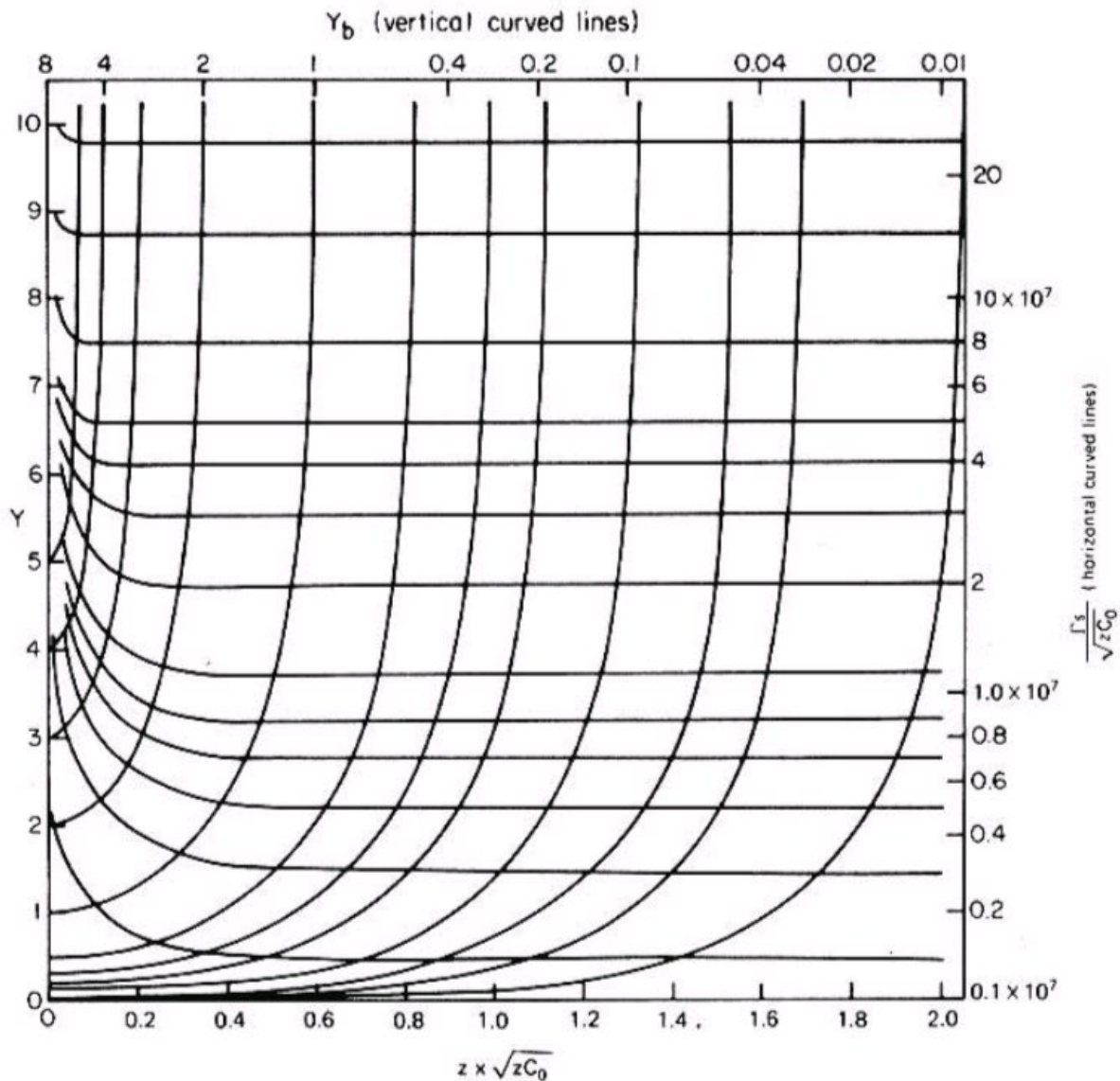
In theory, one can calculate the distribution of electric potential within the double layer for any combination of colloid charge, salt concentration, counter-ion valence and interparticle distance. The Boltzmann equation (8.15) can then be used to calculate cation and anion distributions. From such distributions, cation exchange, colloid swelling, and anion repulsion can be inferred but the calculations are complex, tedious, and often only approximate.

In practice, a set of curves developed by Kemper and Quirk (Fig. 8.10), yields approximate electric potentials as a function of distance from the colloid surface. Such potentials can then be substituted directly into the Boltzmann equation to infer cation and anion distributions.  $Y_b$  is the scaled electric potential (equal to  $-Ze\psi/kT$  of Eq. 8.15) at the midplane between interacting colloids,  $\Gamma$  is the surface charge density in coulombs  $m^{-2}$  (96.5 times the ratio of CEC, in mmoles charge  $kg^{-1}$ , divided by the specific surface, in  $m^2 kg^{-1}$ ),  $Z$  is the valence of the exchangeable cation,  $C_0$  is the molar salt concentration in the bulk solution, and  $x$  is the distance (in nm) from the midplane between colloids to the plane at which the ion concentration is to be calculated.

Figure 8.9 is designed for partially expanding (interacting) double layers. A value of  $Y_b = 0.01$ , however, is normally a satisfactory approximation for noninteracting colloid surfaces. To estimate the thickness of the water film, move across the figure from right to left on the line representing  $\Gamma_s/(C_0)^{1/2}$  axis to obtain the distance from midplane to surface ( $x$ ). When the distance to the midplane is known and  $Y_b$  is to be estimated, on the other hand, move from right to left across the figure on a  $\Gamma_b/(C_0)^{1/2}$  line to the appropriate value of  $Zx(C_0)^{1/2}$ . Then estimate  $Y_b$  by interpolating between  $Y_b$  lines.

In either of the above cases, the intersection of horizontal and vertical lines, when projected horizontally onto the  $Y$  axis, determines the surface potential  $Y_s$ . Values of the electric potential for the system can vary only between  $Y_b$  and  $Y_s$ . The  $Y_b$  line then yields values of  $Y$  corresponding to selected  $x$  values. The cation and anion concentrations can then be calculated as functions of distance from the colloid surface or from the midplane between interacting colloids by using these  $Y$  values and Eq. 8.15. When estimating anion distributions from the Boltzmann equation,  $Y$  must first be multiplied by  $Z_{(-)}/Z_{(+)}$  to obtain values that decrease appropriately with proximity to the colloid surface.



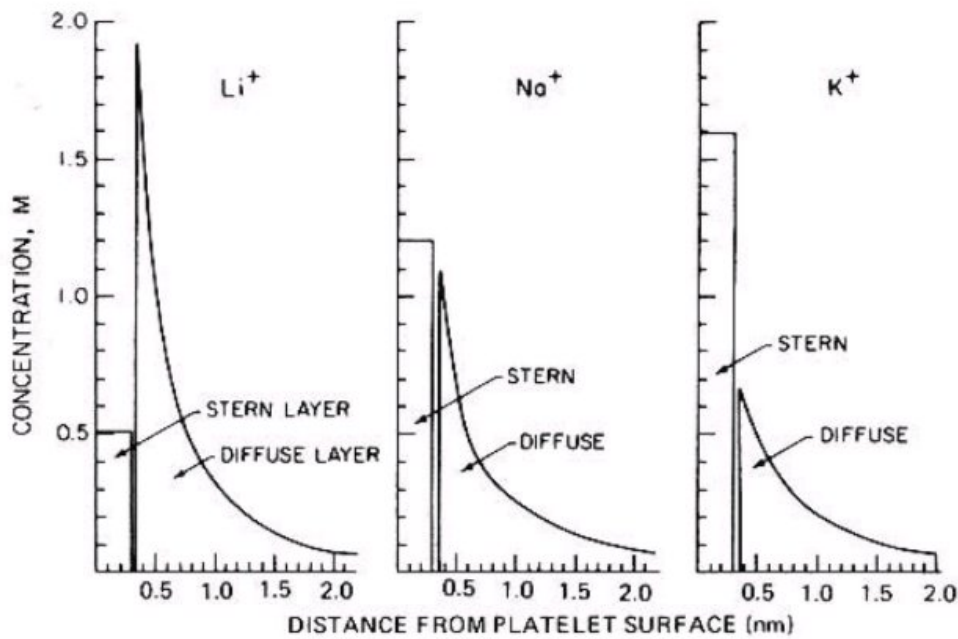


**FIGURE 8.9.** Scaled potential ( $Y_b = Ze\psi/kT$ ) as a function of solution concentration and of distance from the midplane, charge density, and soil colloid surfaces. (From W. D. Kemper and W. P. Quirk. 1970. *Soil Sci. Soc. Am. Proc.* **34**:347–350.)

To derive Fig. 8.9, Kemper and Quirk assumed symmetric electrolytes (e.g., NaCl and CaSO<sub>4</sub>, but not CaCl<sub>2</sub>). Such an assumption is unreasonable for many soil solutions, but causes relatively minor errors in most cases. The effects of symmetric versus nonsymmetric electrolytes on electrical potential distribution are considerably less than the effects of ion valence, total salt concentration, or surface charge density.

Stern improved the Gouy–Chapman theory of the DDL by assuming that some ions are tightly retained immediately next to colloid surfaces in a layer of specifically adsorbed or Stern-layer cations. The double layer is diffuse beyond this layer. A satisfactory approximation of the Stern model can be made by assuming that the specifically adsorbed ions quantitatively reduce the surface density of the colloid. The diffuse portion of the double layer then is assumed to develop on a colloid surface of correspondingly reduced charge density. Sample Stern-modification calculations for a series of monovalent cations are shown in Fig. 8.10. Relatively few of the





**FIGURE 8.10.** Calculated cation distributions near a mineral surface. (From I. Shainberg and W. D. Kemper, 1966. *Soil Sci. Soc. Am. Proc.* 30:707–713.)

strongly hydrated lithium ions are strongly adsorbed in the Stern layer. Most lithium ions are in the diffuse layer instead. The opposite trend is evident for the weakly hydrated potassium ions. Shainberg and Kemper treated the implications and applications of the model, and consequences of its assumptions, during the mid 1960s.

## APPENDIX 8.2 CATION EXCHANGE EQUATIONS

As indicated in Section 8.4, the primary difference between various cation exchange equations is their differing treatment of the activities of exchangeable cations. Vanselow, for example, assumed that the activities of exchangeable cations were proportional to their mole fractions. This is equivalent to saying that ions on soil colloid surfaces behave as if in ideal solution (Appendix 3.2). The mole fraction of an ion in a binary system is

$$\text{mole fraction of species } a = \frac{n_a}{n_a + n_b} \quad (8.16)$$

where  $n$  is the number of moles per unit volume or per unit mass. Substituting this assumption into a Kerr-type expression (Eq. 8.8), yields the *Vanselow–Argersinger* equation for monovalent–divalent cation exchange

$$\frac{[\text{NaX}]^2}{[\text{CaX}][\text{NaX} + \text{CaX}]} = K_v \frac{(\text{Na}^+)^2}{(\text{Ca}^{2+})} \quad (8.17)$$

Here brackets indicate exchangeable ion concentrations ( $\text{mmol kg}^{-1}$ ) and parentheses denote soluble ion activities ( $\text{mmol L}^{-1}$ ). Since the left-hand side of the equation



is dimensionless,  $K_v$  has units of  $L \text{ mmol}^{-1}$ . The Vanselow–Argersinger equation has been used extensively to characterize cation exchange on simple, relatively uniform exchangers. In the surface chemistry literature, this equation has been used to calculate so-called *thermodynamic exchange constants*. However, these constants generally are simply averaged values of Vanselow coefficients over a range of exchangeable and soluble ion compositions. They rarely describe the ion distribution at any specific composition precisely.

Davis developed an equation similar to the Vanselow equation from statistical thermodynamics. Electrostatic forces between colloid surfaces and adsorbed cations were calculated for various surface configurations of charge sites. These sites were assumed to be neutralized by individual adsorbed ions. Hence, the model resembles most closely the Helmholtz model of the double layer with the charge of cations on the surface assumed to be just equal to the number of colloid charges. The resultant equation is

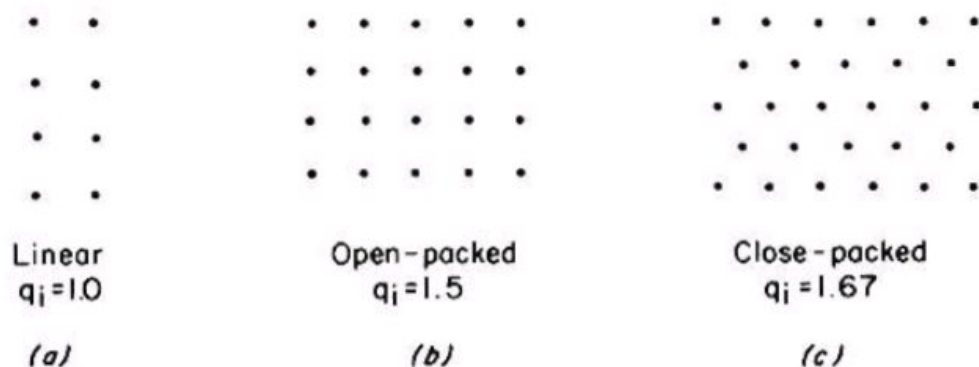
$$\frac{[\text{NaX}]^2}{[\text{Ca}][\text{NaX} + q_{\text{Ca}}\text{CaX}]} = K_d \frac{(\text{Na}^+)^2}{(\text{Ca}^{2+})} \quad (8.18)$$

where

$$q_{\text{Ca}} = Z_{\text{Ca}} - \frac{2Z_{\text{Ca}}}{Y} + \frac{2}{Y} \quad (8.19)$$

Here  $Y$  is the number of nearest-neighbor (closest) charge sites, and  $Z$  the cation valence. The main difference between the Davis equation (8.18) and the Vanselow equation (8.16) is the specific ion factor  $q_i$  for the divalent cation. For monovalent ions,  $q_i$  is unity.

Despite the entirely different theoretical bases of the Davis and Vanselow equations, each produces essentially the same expression for ion exchange. Values for the specific ion factor ( $q_i$ ) include 1.0 for a linear array of cation exchange sites (two nearest-neighbor exchange sites), and 1.67 for a close-packed array (six nearest-neighbor sites) (Fig. 8.11). The linear array gives results that are numerically equal to the Vanselow equation. Krishnamoorthy and Overstreet tested several configurations and concluded that a large number of soils behaved as if the exchange sites were in



**FIGURE 8.11.** Surface arrays of cation exchange sites used in the Davis (statistical thermodynamics) equation for cation exchange.



open-packed array ( $q_i = 1.5$ ). Because Davis delayed publishing his work, Eq. 8.18 has sometimes been called the *Krishnamoorthy–Overstreet* equation instead.

Eriksson and Bolt used another approach to develop the Eriksson, or *double layer, exchange equation*:

$$\frac{\Gamma_1}{\Gamma} = \frac{r}{\Gamma\sqrt{\beta}} \sinh^{-1} \frac{\Gamma\sqrt{\beta}}{r + 4v_d\sqrt{M_2}} \quad (8.20)$$

where  $\Gamma$  is the colloid charge density ( $\text{mmol}(-) \text{m}^{-2}$ );  $\Gamma_1$  is the portion of the charge neutralized by the monovalent cation;  $r$  is the reduced ratio ( $= M_1/(M_2)^{1/2}$ ), where  $M_1$  and  $M_2$  are the activities of monovalent and divalent cations in the bulk solution;  $\beta$  is a constant equal to  $1.08 \times 10^{20} \text{ mmol}^{-1}$  for aqueous systems at  $25^\circ \text{C}$ ; and  $v_d = \cosh Y_b$  (the hyperbolic cosine of  $\exp -Ze\psi/kT$ ) from Eq. 8.15 at the midplane between adjacent colloid particles). In practice,  $v_d$  commonly is set equal to unity. This is equivalent to no interaction between adjacent particles or to infinite interparticle distance (realistically, to a particle separation of a few tens of nanometers).

An advantage of the double-layer equation is that it calculates ion distributions entirely from physically measurable parameters, such as CEC, surface area, and bulk solution solute concentrations. Disadvantages are that these measurements are rather involved, and that the inverse hyperbolic sine makes it difficult to visualize the effects and implications of changes on cation exchange. Generally, experimental surface charge densities for soils and clays must be multiplied by a factor of 1.2 to 1.4 to make experimental results and this equation's predictions agree satisfactorily. The need for this modification may result either from errors in the surface area estimates or because different portions of the surface affect the exchange capacity and surface area measurements differently. Nonetheless, Eq. 8.20 permits a wide variety of calculations almost entirely from measurable soil properties. The Kerr, Vanselow, and Davis equations, in contrast, require measurement of empirical exchange coefficients for different sets of experimental conditions to make such predictions.

Workers at the U.S. Salinity Laboratory substituted the sum of Ca plus Mg for the exchangeable and bulk-solution Ca concentrations in the Gapon equation (8.10). This yields

$$\frac{[\text{NaX}]}{[\text{CaX} + \text{MgX}]} = k \frac{[\text{Na}^+]}{[\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}} \quad (8.21)$$

The  $[\text{Ca}^{2+} + \text{Mg}^{2+}]$  term was necessary because many early water analyses did not distinguish between the two ions. The left side of Eq. 8.21 was termed the ESR (exchangeable sodium ratio). The solution concentration ratio on the right side was termed the SAR (sodium adsorption ratio). The SAR is written as  $[\text{Na}^+]/([\text{Ca}^{2+} + \text{Mg}^{2+}]/2)^{1/2}$  when the concentration units are millimoles of charge per liter. The reduced ratio ( $r$ ) of the double-layer exchange equation (8.19) is equal to the SAR divided by  $(1000)^{1/2}$ .

From analyses of saturation extracts and exchangeable cation concentrations for a large number of soils from the western United States, the statistical relation of ESR



and SAR was found to be

$$\text{ESR} = -0.01 + 0.015 (\text{SAR}) \quad (8.22)$$

This is equivalent to the Gapon equation, with an exchange constant of 0.015, except for the small negative intercept. For many applications, the intercept is negligible. Soils outside the principal irrigated portions of the western United States, such as the irrigated tropics, may have Gapon constants appreciably different from 0.015.

Another early approach to ion exchange was that of the *Donnan* equilibrium. This concept described a system in which a solution and suspension were separated by a membrane that is permeable to ions but impermeable to the exchanger or clay. An example is filter paper separating a soil suspension and its extract. In a "micro-Donnan" system, each soil colloid particle with its ion swarm is regarded as being separated from the bulk solution by an imaginary membrane. Basic Donnan equilibria apply to homovalent exchange in soils and can also be used to explain dilution effects during exchange between ions of different valence.

*Eriksson* applied Donnan equilibrium calculations to heterovalent exchange, reasoning that clays in a salt solution could be thought of as an ion species restricted from free diffusion. His equation was

$$\frac{(B)_i}{(A)_i^2} = \frac{(B)_o}{(A)_o^A} \quad (8.23)$$

where *i* and *o* refer to ions inside the clay phase and outside (in the bulk solution). This is equivalent to a Kerr equation with  $K_K = 1$ . Concentrations were multiplied by activity coefficients for the solution phase, and calculated from the amount of ad-

**Table 8.5. A comparison of exchange coefficients for several cation exchange equations, as calculated from the ammonium–calcium exchange data of Table 8.2**

Equation	Exchange Coefficient at an Ammonium Concentration of:			
	0.04 M	0.01 M	0.005 M	0.0025 M
Kerr (using concentrations)	$1.91 \times 10^{-3}$	$1.81 \times 10^{-3}$	$1.58 \times 10^{-3}$	$2.30 \times 10^{-3}$
Kerr (using solution activities)	$1.33 \times 10^{-3}$	$1.51 \times 10^{-3}$	$1.37 \times 10^{-3}$	$2.07 \times 10^{-3}$
Gapon (using concentrations)	1.77	1.07	0.97	1.17
Vanselow	2.22	2.50	2.35	3.60
Davis ( $q_{ca} = 1.5$ )	1.75	1.88	1.73	2.63
Davis ( $q_{ca} = 1.67$ )	1.63	1.73	1.59	2.41
	Exchangeable $\text{NH}_4^+$ Percentage			
Eriksson				
Predicted <sup>a</sup>	26.1	20.2	17.9	14.4
Measured	29.8	20.8	16.6	15.2

<sup>a</sup> Assuming a surface area of  $800 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ .



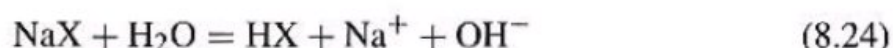
sorbed ions divided by the volume of exchanger for ions in the adsorbed phase. This fixed the activity coefficients for the adsorbed-phase ions as well. Today, Donnan equilibrium is used only as a first approximation to DDL theory. The main objection to Donnan theory is the large error involved in predicting concentrations at varying distances from the particle surface with a single ion ratio. Donnan theory predicts only an average activity ratio, which may err by a factor of two or more. Other criticisms have arisen from its inability to adequately predict the properties of clay suspensions.

Table 8.5 compares different exchange coefficients calculated from the data for ammonium–calcium exchange in Table 8.2. The simple Gapon equation (8.10) yields the most uniform exchange coefficient for this set of data; the Eriksson equation's predictions also agree well with the measured values. Bond and Verburg (1997) applied the various ion equations to the more complicated case of ternary (Ca–K–Na). Their slight modifications of the 1918 work by Rothmund and Kornfeld yielded the most consistent exchange coefficients in their study. Snyder and Cavallaro (1997) applied a single-phase mixture approach to  $\text{NH}_4^+$ – $\text{Ba}^{2+}$ – $\text{La}^{3+}$  exchange on clays.

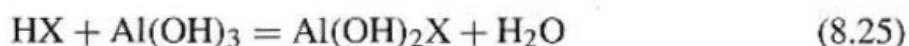
### APPENDIX 8.3 DETERMINATION OF CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS

When cation exchange relations are measured, both the total and the relative quantities of the exchangeable cations are required. To determine the total quantity of exchangeable cations, the cation exchange reaction is normally forced toward completion by either of two approaches. In one, the soil sample is exhaustively leached with a solution that contains a replacement, or index, cation to be placed on all exchange sites. Ions removed by the leaching are then analyzed to determine the initial exchangeable cation composition. A second approach involves repeated batch washings (several cycles of adding replacement cation, shaking, centrifuging, and decanting the supernatant solution). Analysis of the combined supernatant solutions yields the amounts of exchangeable ions initially present. The large excess of replacing ion in each batch-washing step drives the reaction toward completion.

In determining the CEC, a soil saturated with a single index ion is washed free of soluble salts, often with alcohol to keep the soil flocculated and to prevent loss of the index cation by hydrolysis:



where X represents the clay and  $\text{Na}^+$  is the index cation. The  $\text{H}^+$  clay is unstable and rapidly breaks down:



Hydrolysis would yield a low estimate of the CEC. The index cation is then extracted from the soil with still another salt solution and measured to give the CEC.



The salt used to furnish the index cation should be relatively soluble in the alcohol used for sample washing. The low solubility of NaCl in ethanol has been a frequently overlooked source of error. The salt then dissolves during the subsequent extraction step and yields an anomalously high CEC value. Soils containing large quantities of hydroxyoxide or amorphous minerals may also retain salts in particle micropores, so that washing does not completely remove the salts. This also yields high CEC values.

To eliminate the problems associated with the washing step, Okazaki, Smith, and Moodie proposed a CEC procedure in which salts are not removed between the index cation saturation and extraction steps. Rather, the anion of the salt providing the index cation is analyzed in the final extract. In accordance with electrical neutrality, the CEC is then equal to the total quantity of index cations removed during extraction minus the quantity of index anions removed simultaneously. The main potential source of error from this procedure arises from anion repulsion, if the quantity of index salt remaining after saturation is merely calculated from the weight of solution retained and its initial (or average) concentration. This error minimized if the index solution is lowered to approximately 0.1 M during the final two saturation washes. The error is eliminated if the quantities of index salt are analytically determined instead.

The concentration of the index salt solution should not be high. Early measurements using 1 M salt solutions, to insure complete replacement and flocculation, yielded low CEC measurements because anion repulsion is significant at these concentrations and neutralized a significant portion of the colloid's charge. The CEC measurement is one of many examples in soil chemistry of the complexity of a seemingly simple experiment.

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## QUESTIONS AND PROBLEMS

- The following distribution of cations and anions exists near a soil colloid surface:

Distance	4.0 nm	3.0 nm	2.0 nm	1.0 nm	0.5 nm	0.25 nm
Cation concentration (mol(+) L <sup>-1</sup> )	0.10	0.12	0.17	0.35	1.0	2.0
Anion concentration (mol(-) L <sup>-1</sup> )	0.10	0.08	0.06	0.04	0.01	0.00



Assuming that the excess of cations reported for each increment represents the entire increment (e.g., that the cation concentration is  $2.0 \text{ mol charge L}^{-1}$  from the colloid surface to  $0.375 \text{ nm}$  from the surface, etc.), estimate the CEC for a colloid having  $800 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$  of reactive surface (Ans. =  $12.0 \text{ mmol charge kg}^{-1}$ ).

2. Based on the data of Table 8.4, what proportion of the cross-sectional area of a cylindrical soil pore of radius  $15 \mu\text{m}$  is influenced by the electric double layer if monovalent ions predominate at a salt concentration of  $10^{-1} \text{ M}$ ?
3. If all water of an unsaturated soil at 20% water content is spread uniformly over  $100 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$  of reactive surface, what proportion of that water is influenced by the electric double layer for the chemical conditions specified in Problem 2?
4. A soil is equilibrated with a solution of  $\text{SAR} = 20$ . Based on the Gapon equation, what would be its equilibrium exchangeable sodium percentage (ESP)? If the soil had instead been equilibrated with the same solution diluted fivefold with salt-free water, what would have been the corresponding SAR and ESP values?
5. Generate a selectivity diagram similar to Figure 8.1 for two cations (A and B) having Kerr-type coefficients of
  - (a) 0.5
  - (b) 1.0
  - (c) 2.0
6. A vermiculitic surface soil has the ability to fix  $25 \text{ mmol kg}^{-1}$  of  $\text{K}^+$  or  $\text{NH}_4^+$ . What rate of  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{KCl}$  fertilizer (in  $\text{kg ha}^{-1}$ ) would be required to saturate this fixation capacity for a 30-cm depth of soil?
7. The CEC is being estimated by the Okazaki, Smith, and Moodie procedure. If 5 g of soil retain 3 g  $0.1 \text{ M}(+)$  index solution after centrifugation and decanting, and if the total index cation retained is subsequently determined to be  $1.6 \text{ mmol}(+)$ , what is the CEC of the sample? Based on the anion distribution of Problem 1, what percentage error is contributed in this case by anion exclusion, if the soil has a reactive surface area of  $200 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ ?
8. Based on layer lattice thickness estimates from Chapter 4, what is the relative attraction for a dehydrated  $\text{K}^+$  ion residing directly on the mineral surface of a tetrahedrally substituted 2:1 mineral when compared to an octahedrally substituted 2:1 mineral?
9. For a mineral of  $\text{CEC} = 100 \text{ mmol}(+) \text{ kg}^{-1}$  and surface area =  $800 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ , saturated with a monovalent cation at a salt concentration of  $0.001 \text{ M}$ , use Fig. 8.8 to estimate the distance from the mineral surface to the midplane if  $Y_b = 0.01$ , as well as the values of  $Y (= Ze\psi/kT)$  at 0.5, 2, 5, 10, and 30 nm from the mineral surface.



10. Using the  $Y$  values from Problem 9, calculate the corresponding cation and anion concentration at the specified distances from the mineral surface.
11. Verify the calculations of Table 8.5.
12. Explain in your own words the differences between the Helmholtz, Guoy–Chapman, and Stern models of the double layer.
13. Explain the valence dilution effect.
14. For a CEC procedure that uses  $\text{Na}^+$  as the index cation,  $\text{H}_2\text{O}$ /ethanol as the wash solvent, and  $\text{Mg}^{2+}$  as the displacing cation, discuss the effect of each of the following on CEC measurements:
  - (a) Hydrolysis due to excess washing
  - (b) Presence of large amounts of lime or gypsum in the soil
  - (c) Incomplete index–cation saturation
  - (d) Precipitation of an insoluble  $\text{Na}^+$  salt in the ethanol
  - (e) Incomplete removal of the index cation by  $\text{Mg}^{2+}$
15. For a solution of  $\text{SAR} = 40$  and a total salt concentration of  $0.01 \text{ mol}(+) \text{ L}^{-1}$ , calculate ESP if  $k = 0.015$ .