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2287

PART TWO: EFFECTS OF SALTS ON SOILS

CHAPTER 3

THE CHEMISTRY OF SALT-AFFECTED SOILS AND WATERS

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INTRODUCTION

This chapter describes the origins of salts in soil and water and the major pathways by which they accumulate in soils, particularly in soils of arid regions. The basic chemistry of soil-water systems is described, with a focus on the most common salts and the complex chemical interactions within various soil types and combinations of dissolved minerals and salts in the soil solution. Basic methods for calculating salt concentrations are described for a number of different salts, and the complex interactions of salts and variables, such as pH are described.

ORIGIN OF SALT IN SOIL AND WATER

The primary source of salts in soil and waters is the continuous geochemical weathering of rocks that form the upper strata of the earth's continental crust. It represents one step in the geochemical exchange of matter between the land, oceans, crust, and mantle that has been in existence throughout geologic time.

Weathering

Because most rocks have formed under high temperature and pressure, the constituent minerals usually are thermodynamically unstable when exposed to atmospheric conditions. Weathering is a spontaneous process that transforms primary minerals into other minerals that are more stable at the earth's surface. This process is, of course, critical to understanding soil formation and release of salts over geologic time. In most instances the rates of silicate reaction are slow, as there are important kinetic constraints. As a result, silicate weathering influences salt chemical composition and initial salt load but is not important at the management time scale. The reagents involved in geochemical weathering include atmospheric water, oxygen, and carbon dioxide. The biosphere enhances weathering because of its increased levels of CO_2, organic matter, and biological activity. Organic matter can serve as a reducing agent and a source of organic acids, which promote weathering and cation migration through complexation.

Three types of reactions describe the chemical weathering of rock-forming minerals: congruent dissolution, incongruent dissolution, and reduction-oxidation (redox) reactions. Some of these reactions are reversible, denoted with the ↔ symbol, and some are irreversible, denoted by the → symbol.

Congruent dissolution

In this reaction, the solution products exist in the same proportion as they occur in the mineral, that is,

$$\textit{Mineral} \rightarrow \textit{soluble species}$$

Examples of congruent weathering processes are

$$CaCO_3\ \text{(calcite)} + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3-1}$$

$$SiO_2\ \text{(quartz)} + 2H_2O \leftrightarrow H_4SiO_4 \tag{3-2}$$

Most, but not all, minerals that release salt in soils dissolve congruently. These include chloride, sulfate, and most carbonate salts.

Incongruent dissolution

In this reaction, part of the mineral dissolves and leaves behind a secondary solid phase (secondary aluminosilicate clay minerals) that differs in composition from the original mineral:

$$\begin{gathered} 2NaAlSi_3O_8\ \text{(albite)} + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4\ \text{(kaolinite)} + \\ 4SiO_2\ \text{(quartz)} + 2Na^+ + 2OH^- \end{gathered} \tag{3-3}$$

$$\begin{gathered} 3KA1Si_3O_8\ \text{(orthoclase)} + 2CO_2 + 14H_2O \rightarrow 2K^+ + \\ 2HCO_3^- + 6H_4SiO_4 + KA1Si_3O_{10}(OH)_2\ \text{(mica)} + 4H_2O \end{gathered} \tag{3-4}$$

The silicate minerals, including those found in soils, control the earth surface chemistry under natural conditions over geologic time. However, the silicate dissolution reactions are mostly so slow under natural conditions (Suarez and Wood 1996) that they can be neglected in terms of anthropogenic time scales for salt loading and prediction of soil-solution composition under arid and semiarid lands.

Redox reactions

Changes in the oxidation states of minerals modifies the weathering process. Redox reactions between ions dissolved in solution and minerals in contact with that solution often influence the pH of the solution and subsequently its composition, for example,

$$\text{FeS}_2\text{(pyrite)} + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3\text{(s)} + 4\text{H}^+ + 2\text{SO}_4^{2-} \tag{3-5}$$

In this reaction, the protons produced have a strong local influence on subsequent weathering and salt release. Oxidation of reduced S materials (including elemental S) has been used in reclamation of calcareous sodic soils. In this instance, the reactions

$$2\text{S} + 3\text{O}_2 \leftrightarrow 2\text{SO}_3 \tag{3-6}$$

$$\text{SO}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{H}^+ + \text{SO}_4^{2-} \tag{3-7}$$

occur slowly, releasing H^+ that in turn reacts with the calcite in the soil,

$$\text{CaCO}_3 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \tag{3-8}$$

resulting in net release of Ca^{2+} and SO_4^{2-}. Reaction of the acid produced in Eq. 3-5 would result in a similar solution composition. In the absence of carbonates, silicates would slowly dissolve, releasing cations from the minerals, with the protons neutralizing the hydroxols released from weathering.

Climate and Landscape Effects

Although weathering is continuous and occurs universally, the intensity and extent of the weathering reactions strongly reflect the influence of climate. The presence of water is most important to the weathering process. It serves as a reactant in mineral transformation and is the medium that transports dissolved and suspended matter from the system. The transport of the weathering products depends on sufficient rainfall to move the soluble salts through the surface soil into the groundwater, eventually into rivers, and, ultimately, the oceans. The oceans' chemical composition reflects the constant inflow of salt from the land masses as modified by chemical interaction with the oceanic sediments, evaporation, volcanic outgassing, and aerosol transport.

Salt-affected soils are natural components of arid landscapes. Their presence directly correlates with limited rainfall, that is, in arid landscapes the evapotranspiration (ET) greatly exceeds precipitation throughout most of the year. Lack of moisture limits the intensity of the chemical weathering of minerals. Lack of moisture also limits the movement of the product of weathering (salts), and the secondary minerals formed often are constrained to a localized area. In subhumid and humid areas, the properties of the parent rock largely dictate the properties of the soils formed and most solutes are displaced from the watershed in drainage. Most arid-zone soils are classified under two soil orders: entisols, soils that have little or no development of pedogenic horizons; and aridisols, soils that do not have water available to mesophytic plants for long periods and contain only small amounts of organic material.

Because water serves as the principal transport vehicle for salts, salinity is closely linked to lowlands or depressions into which water drains and accumulates. Salinization is enhanced when restricted soil drainage promotes a high water table and the balance of mineralized groundwater is regulated by the evaporation of water, transpiration, or both, rather than by surface runoff and drainage. Areas of impeded drainage vary in size from a fraction of a hectare to thousands of square kilometers, such as Utah's Great Salt Lake basin and Pakistan's Indus Plain.

Fossil or Secondary Deposits

Throughout geologic time, saline seas have inundated large areas of present-day continents. These submerged areas have subsequently been uplifted. The resulting geologic formations provide parent material for soils as well as outcrops and underlying saline strata to soils or other formations, all of which are important zones of contact for salt loading of surface and groundwater. The secondary deposits (sedimentary rocks) formed from inland seas and weathering of continental rock during inundation are the major sources of salinity and sodicity. The term "fossil salt" has been used to describe the salinity of these deposits. These deposits, mobilized by irrigation and rainfall, are the major sources of salt loading in western U.S. surface waters.

A good example of a secondary saline deposit that markedly affects the salinity of a region is the Mancos shale formation in the upper Colorado River basin. This formation, deposited in inland seas in the late Cretaceous epoch, reaches a maximum thickness of about 2,000 m

(Williams 1975). Mancos shale forms an extensive belt of erodible outcrops and underlying strata in southern Wyoming, eastern Utah, and western Colorado. This formation is a major contributor to the salt load in the Colorado River.

Atmospheric Deposition

The atmospheric deposition of salt can be of localized importance. Dry and wet aerosol fallout contributes up to 100 kg/y-ha to 200 kg/y-ha along sea coasts and from about 10 kg/y-ha to 20 kg/y-ha in the interior. The composition of atmospheric salt deposition varies with distance from the source. The salt is predominately an NaCl-type at the coast, consistent with the composition of the oceans. It becomes proportionately greater in Ca^{2+} and SO_4^{2-} ions as the air mass moves inland. Atmospheric contributions to the salt load of arid lands can be from 10% to 25% of the total yearly contribution of weathering (Bresler et al. 1982), but are a much smaller contributor in regions with saline geologic materials.

In the overall picture of salinization of soils, the contribution of atmospheric salt is often overlooked, but it is a factor that must be considered in highly weathered landscapes that have poor drainage. A case in point is a large area of saline soils in western Australia. The source of the salts is attributed to long-term inputs from rain in combination with limited drainage and concentration of the salts by surface evaporation and extraction of water by tree roots and subsequent transpiration, leaving most of the salt in the unsaturated zone.

Anthropogenic Activities

Soils made saline by humans are of major historical and economic importance. Industrialization has increased the atmospheric loading of gaseous nitrogen and sulfur components, both of which result in acidic fallout, which intensifies the soil mineral weathering rate. This impact is of importance primarily in nonsaline areas. Energy-related mining activities have brought to the surface saline and sodic materials that, if left in the ground, would have had little effect on the environment. At the surface in the presence of rain, they are mobilized and contribute to salt loading of surface and shallow groundwaters. Most recently, development of coal bed methane resources in the western United States has resulted in pumping of saline groundwater to dewater the methane-containing materials. Discharge of these waters into natural drainage ways increases salt concentrations in receiving surface waters, while surface application increases surface salinity.

Agriculture, both irrigated and nonirrigated, has had a dramatic effect on salt distribution in the terrestrial system. All irrigation water contains salt in varying amounts and differing types. During ET the plant extracts water with a much lower salt content than in the water source. The majority of the salt (85%–95%) applied in the irrigation water is left behind in the remaining water, inevitably resulting in a drainage water more saline than the applied water. For example, for every 100 mg/L salt in irrigation water, one megagram of salt is added per ha-m of applied water.

If one ha-m of water with a salt concentration of 850 mg/L is applied to a crop during the growing season, 8.5 megagrams (8,500 kg or about 9.4 tons) of salts are added. Without salinity management, salts will eventually accumulate in the rhizosphere and affect crop yield.

Management of salinity in the rootzone requires application of quantities of water above the actual water use of the crop (for leaching). Inevitably, more water is transported down into the unsaturated and shallow groundwater, thus greatly increasing the mobilization of salts present in those zones. The rate of mineral weathering, primarily gypsum, calcite, and dolomite, is also enhanced by the larger volumes of water passed through the soil under irrigation. The control of salinity or sodicity in the rhizosphere and in surface or ground waters receiving drainage waters is, therefore, closely associated with soil and water management practices.

MEASUREMENT OF SALINITY

The chemical and physical properties of a salt-affected soil reflect the amount and type of salt present. Although the use of salinity sensors in the field is increasingly common (see Chapter 10), laboratory analysis of aqueous extracts of soil is still the most common technique for assessing salinity and other potential hazards.

One of the earliest methods for determining the amount of dissolved salts is based on evaporating a given volume of water or soil extract and measuring the weight of the residue. The result is called the total dissolved solids (TDS) and the dimensions are mg/L. This method, although still used, has been largely replaced by a more convenient measurement of the electrical resistance of the solution, or its reciprocal, the electrical conductance (EC).

The current-carrying capacity of a solution is proportional to the concentration of ions in the solution. The electrical conductance is measured in reciprocal ohms (ohms^{-1}), also known as mhos. In SI units, mhos are designated as siemens (S).

Measurements of conductivity are typically made in a cell containing two electrodes of defined geometry. An electric potential is imposed across the electrodes and the resistance of the solution between the electrodes is measured. The results are multiplied by a "cell constant" to correct for variations in cell geometry, allowing all data to be reported as specific EC. The EC is commonly reported per unit volume (1 cm^3) of solution in siemens (S) per cm, at 25 °C. Alternatively, EC can be measured using a four-electrode configuration, whereby a known potential is imposed on the two outer electrodes and the potential is measured between the two inner electrodes. This configuration has the advantage of being less sensitive to changes in the surface conductance of the electrodes, and is useful for measurements of soil conductivity in the field (see Chapter 10).

The siemen is too large for measuring electrical conductance in most natural systems. Hence, the working unit is often the decisiemen ($S \times 10^{-1}$). Because the basic length in the SI convention is the meter, the preferred dimension for EC is decisiemens per meter (dS/m). The units relationship is as follows: dS/m = mS/cm = mmhos/cm where mmhos/cm (millimhos per cm) are the traditional and now-obsolete dimensions for EC.

Saturation Extract

A variety of soil/water ratios can be used to obtain an aqueous extract from a soil sample. Therefore, a standard extraction method must be used if saline-soil chemical data are to be compared. Because the amount of water that a soil holds at saturation (saturation percentage, SP) is related to a number of soil parameters, such as texture, surface area, clay content, and cation exchange capacity (Merrill et al. 1987), one widely used technique is to obtain an extract by vacuum filtration of a saturated soil paste made with distilled or deionized water (U.S. Salinity Laboratory 1954). This extract is then analyzed for electrical conductivity (EC_e) and soluble constituents of interest. Higher-water-content extracts (soil/water ratios of 1:1, 1:2, 1:5) are easier and faster to prepare, but their solution compositions are less related to those at field moisture condition than those of the saturation pastes and are generally not recommended. As increasing amounts of water are added, there is an increasing importance of mineral dissolution (primarily gypsum and carbonates), cation exchange, and anion desorption on solution composition and EC. However, when only relative salinity changes are of interest, and in the absence of gypsum, the lower soil/water ratios can be used to advantage. Correction of the composition from one water content to another can be made by use of the *Extract Chem* program (Suarez and Taber 2007). This computer model considers cation exchange, calcite and gypsum dissolution/precipitation, and boron (B) adsorption/desorption, as related to changes in water content.

The value of EC is sensitive to the temperature of the solution. The change in EC with temperature depends on the mineral composition of the dissolved salts. However, the correction for natural waters is about a 1.9% increase in EC for each degree increase in solution temperature in the range of 15 °C to 35 °C. The EC data are usually normalized to a temperature of 25 °C for a meaningful comparison among samples. A temperature correction to 25 °C (EC_{25}) can be approximated by

$$EC_{25} = EC_t - 0.019(t - 25)EC_t \qquad (3\text{-}9)$$

where EC_t = the value at temperature t. Temperature-compensated EC probes make a similar correction of EC.

Predicting Electrical Conductivity from Ionic Composition

Theoretical and empirical approaches have been used to predict the EC of a solution from its composition. An example of the theoretical approach is a model based on Kohlrauch's Law of independent migration of ions (Harned and Owen 1958), in which each ion contributes to the current-carrying ability of an electrolyte solution. The equation used is

$$EC = \sum EC_i = \sum_i \frac{c_i(\lambda_i^0 - \beta\sqrt{c_i})}{1{,}000} \qquad (3\text{-}10)$$

where EC = the specific conductance (dS/m); EC_i = the ionic specific conductance (dS/m) summed over all ith species in solution; c_i = the concentration of the ith ion ($mmol_c/L$); λ_i^0 = the ionic equivalent conductance ($cm^2\ S/mol_c$) at infinite dilution; and β is an empirical interactive parameter obtained by plotting the ionic equivalent conductance of the ith ion (λ_i expressed in $cm^2\ S\ mol_c^{-1}$) versus $(c_i)^{1/2}$. For relatively dilute mixtures, β ranges in value from 2 to 9, with an average of 5.5 (Tanji and Biggar 1972). Values of λ_i^0 can be obtained from standard textbooks on electrochemistry and physical chemistry.

A more accurate, but mathematically more complex, model based on the modified Onsanger-Fuoss equation and corrected for ion pair formation (which will be discussed later) gives reasonable agreement (± 8%) between calculated and measured EC up to 15 dS/m (Marion and Babcock 1976; Tanji 1969). Marion and Babcock (1976) also developed an empirical approach relating measured specific conductance (EC in dS/m) to total soluble salt concentration (TSS in $mmol_c/L$) and ionic concentration (C in $mmol_c/L$), where C is corrected for ion pairs. In the absence of ion complexation, TSS = C. The derived relationship was determined on a composite database obtained from soil extracts, river waters, and pure salt solutions. The equations, suitable for most purposes, are

$$\log C = 0.955 + 1.039 \log EC \quad r^2 = 0.997 \qquad (3\text{-}11)$$

$$\log TSS = 0.990 + 1.055 \log EC \quad r = 0.993 \qquad (3\text{-}12)$$

Equation 3-11 should be used instead of the empirical relationship (U.S. Salinity Laboratory 1954):

$$\text{TSS (mmol}_c\text{/L)} = 10\ \text{EC (dS/m)} \qquad (3\text{-}13)$$

McNeal et al. (1970) developed a more detailed empirical relationship with improved predictive capability of EC (generally within ±5%, listed as Method 3 in their publication), suitable for inclusion in spreadsheets or computer models. This calculation of EC from solution composition is used in the *Extract Chem* computer model and in the *SWS* model used for management of salt-affected soils (see Chapter 28).

CHEMISTRY OF SALT-AFFECTED SOIL SOLUTIONS

Major cations in salt-affected soils are Na^+, Ca^{2+}, Mg^{2+}, and, to a lesser extent, K^+. The major anions are Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, and, at high pH, CO_3^{2-}. The ions HCO_3^- and CO_3^{2-} are usually reported together as carbonate alkalinity. Under high pH conditions (>8.5), elevated concentrations of B can result in a significant contribution to alkalinity [dissociation constant for boric acid (pK_a) is 9.2]. Other ions that are sometimes present under anaerobic conditions, but usually neglected from a salinity viewpoint, include NH_4^+, NO_2^-, and organic anions (such as acetate). When analyzing high-organic-content waters (such as waste waters), these anions of weak organic acids will also contribute to titratable alkalinity, which needs to be corrected if carbonate alkalinity is to be reported.

Dissolution and precipitation of minerals often determine the composition of the soil solution. The degree of saturation of the soil solution with respect to a particular solid phase can be evaluated from the ion activities. The activity concept accounts for the nonideal behavior of ions in solution. Activities can be calculated from solution concentrations and ionic strength as follows:

$$a_i = \gamma_i m_i \qquad (3\text{-}14)$$

where γ_i is the activity coefficient and m_i is expressed in molal units (moles/kg solvent) concentration of the ith ion. Activities and activity coefficients are dimensionless, since m_i is actually the ratio m_i/m_0 where m_0 is the standard state molal concentration (1.0). Except for very saline solutions, the assumption that $m_i = M_i$ (moles/L of solution) is reasonable. The activity coefficients are, in turn, related to the ionic strength, I, defined by

$$I = 0.5 \sum_i m_i z_i^2 \qquad (3\text{-}15)$$

where z = the valence of the ith ion. The summation in Eq. 3-15 is for all charged species in solution. An empirical relationship between EC and ionic strength suitable for most natural waters is given by

$$I = 0.0127\ \mathrm{EC} \qquad (3\text{-}16)$$

where EC is in dS/m at 25 °C (Griffin and Jurinak 1973).

The activity coefficients of individual ions are necessary for calculation of the mineral saturation status of a water. The most utilized method of calculating activity coefficients is by applying the Davies equation (Stumm and Morgan 1996):

$$\log \gamma_i = 0.509\, z_i^2 \left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right] \qquad (3\text{-}17)$$

Note that this equation uses the term $-0.2I$ instead of $-0.3I$ as originally proposed by Davies. This equation is reported as valid when $I < 0.5$ and water at 25 °C is the solvent, but substantial errors occur above $I = 0.1$; also, the equation does not consider differences in activity coefficients with ions of the same charge. A better estimate of activity coefficients can be obtained by a modified version of the extended Debye-Huckel equation (Truesdell and Jones 1974),

$$\log \gamma_i = A\, z_i^2 \left[\frac{\sqrt{I}}{1 + Ba_i\sqrt{I}} \right] + b_i I \qquad (3\text{-}18)$$

where A is equal to 0.509 and B is equal to 0.33 at 25 °C and a_i and b_i are ion-specific adjustable parameters fitted from mean salt calculations (Truesdell and Jones 1974). The coefficients based on Eq. 3-18 can be obtained from Fig. 3-1. Individual ion activities can then be estimated from concentration data using Eq. 3-14. This equation is used in *WATEQ* (Truesdell and Jones 1974), *UNSATCHEM* (Suarez and Šimůnek 1997), and available as an option in *PHREEQC* version 2 (Parkhurst and Apello 1999), among others. The *WATEQ* and *PHREEQC* models are available from the U.S. Geological Survey website and *UNSATCHEM* from the ARS-USDA Salinity Laboratory website. The equation is stated as valid to $I = 4.0$, but this is based on NaCl as the background electrolyte; in mixed electrolyte solutions, the limit is around $I = 0.3$–0.5 depending on the actual solution composition. At higher ionic strength it is recommended to use the Pitzer expressions (Pitzer 1979) with the Harvie et al. (1981) species constants.

Equally as important as the specific model chosen for the absolute accuracy of the activity coefficient calculation is internal consistency in

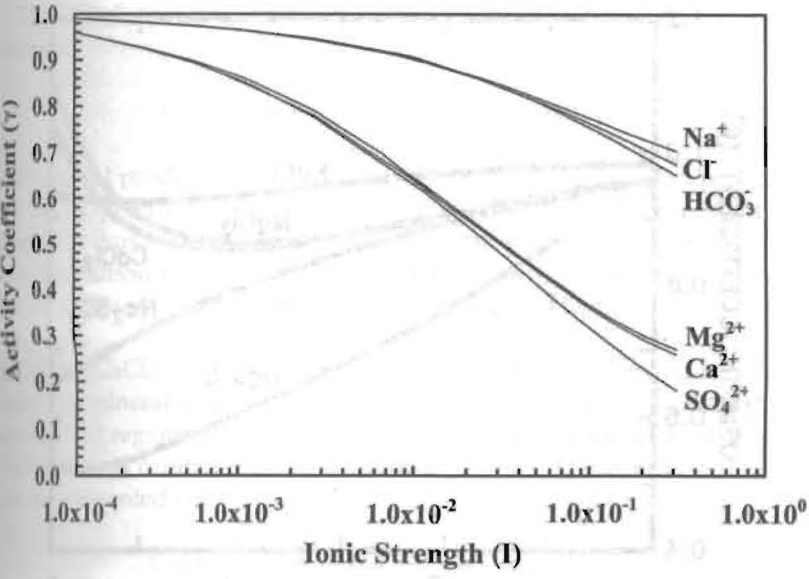

FIGURE 3-1. *Calculation of activity coefficients as related to ionic strength using a extended version of the Debye-Huckel equation. From Butler (1964).*

the database used for the calculations. Many thermodynamic constants have been derived from solubility experiments; thus, the derived solubility product (K_{sp}) values depend on the chemical speciation model used. For this reason the activity calculation model needs to use the same activity coefficient calculations and ion association model and constants as used to generate the database (Suarez 1998).

Salt-tolerance data for crops usually are expressed as a function of osmotic potential, $-\tau_o$, where τ_o = the soil solution's osmotic pressure. The osmotic pressure, in kPa, can be calculated from

$$\tau_o = 2480 \sum_i m_i \upsilon_i \phi_i \tag{3-19}$$

where ϕ_i = the osmotic coefficient of the ith salt and υ = the stochiometric number of ions yielded by the salt. The ϕ value for each salt can be obtained by using the salt's total concentration (Fig. 3-2). The approximate relationship between τ_o and EC at 25 °C, is

$$\tau_o\ (\text{kpa}) \approx -\ 0.40\ \text{EC} \tag{3-20}$$

where EC is in dS/m. The commonly used proportionality constant of 0.36 is for τ_o data obtained at 0 °C (U.S. Salinity Laboratory 1954).

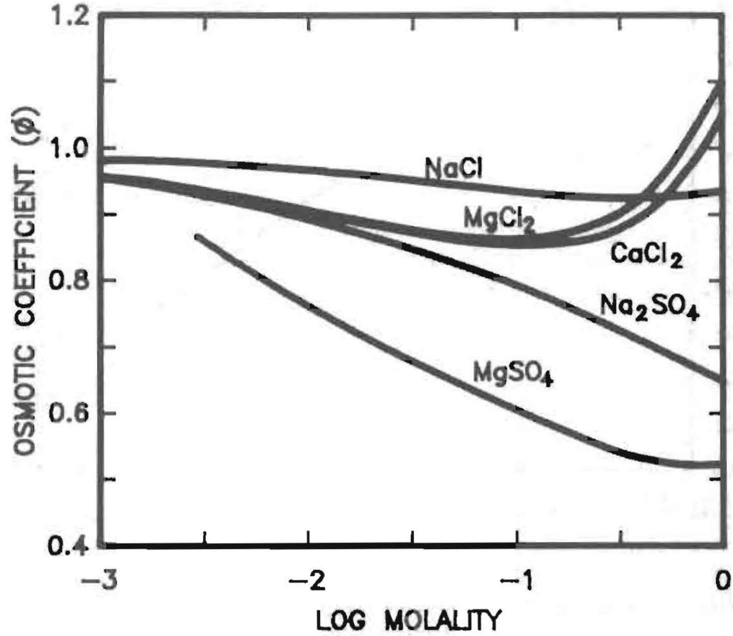

FIGURE 3-2. Osmotic coefficients of electrolytes at 25 °C. From Robinson and Stokes (1959).

Salt and pH Effect on Chemical Mass Action

The general mass action equation for any reaction is

$$aA + bB \leftrightarrow cC + dD \tag{3-21}$$

where the lowercase letters are the stochiometric coefficients and uppercase letters represent chemical symbols.

In Eq. 3-21, the thermodynamic equilibrium constant for the general reaction is

$$K_{eq} = \frac{(C)^c (D)^d}{(A)^a (B)^b} \tag{3-22}$$

where ( ) represents activities as defined in Eq. 3-14. This convention is generally used in soil chemical publications. In the chemical and geochemical literature, [ ] is used to denote activities; in this chapter [ ] denotes concentrations.

The dissolution of carbon dioxide in water is represented by the reactions

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (3\text{-}23)$$

Biological production and diffusion (water content-dependent) control the CO_2 concentration in soil air. The CO_2 concentration of the soil solution is thus assumed to be independent of water quality or precipitation-dissolution reactions (i.e., an open system). Equation 3-23 shows that an increase in CO_2 results in a production of H^+ and, thus, a reduction in pH.

Calcite ($CaCO_3$) is a source of calcium commonly found in most arid soils. This mineral is important because much of the soil-solution's chemistry in arid regions can be defined in the context of the CO_2—$CaCO_3$—H_2O system in combination with cation exchange. The dissolution of calcite is represented by

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad (3\text{-}24)$$

An increase in aqueous CO_2 concentration shifts the reaction to the right. This increases the Ca^{2+} concentration and alkalinity of the solution. The presence of ions other than Ca^{2+} or HCO_3^- increases the ionic strength, which, in turn, decreases the ionic activity coefficients of Ca^{2+}, HCO_3^-, and CO_3^{2-}. This, known as the ionic strength effect, increases the solubility of $CaCO_3$.

Dolomite, $CaMg(CO_3)_2$, is sometimes present in arid soils, usually derived from carbonate geologic materials. Its solubility is very similar to that of calcite (expressed as a double carbonate mineral), but its dissolution rate is very slow and its precipitation negligible over time frames of agricultural interest. Soils with native dolomite almost always contain calcite. The dissolution reaction is

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3 \qquad (3\text{-}25)$$

We do not consider this reaction to be reversible as it does not form over time frames of interest to agriculture. Gypsum ($CaSO_4 \cdot 2H_2O$) is another mineral that may be found naturally in arid soils. It is frequently added as a soil amendment as a calcium source to reclaim sodic soils and thus maintain or enhance soil permeability. It is moderately soluble and readily precipitated when its solubility is exceeded, such as when irrigating with a high-sulfate water. The dissolution reaction for gypsum is

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (3\text{-}26)$$

Addition of salts that contain ions, such as Na^+, Mg^{2+}, Cl^-, and NO_3^-, enhances the solubility of gypsum by the ionic strength effect. Adding salts that contain either Ca^{2+} or SO_4^{2+} decreases gypsum solubility by the common ion effect. For example, gypsum solubility is greatly reduced in the presence of water containing large amounts of Na_2SO_4 or $MgSO_4$ salt. At constant temperature, the solubility product, K_{sp}, of gypsum is invariant, that is, assuming the activities of H_2O and solid-phase gypsum are unity, the product of the activities (Ca^{2+}) (SO_4^{2-}) is constant, even though the concentrations of the constituent ions in solution increase.

Gypsum's solubility is also increased by ion association (the formation of soluble ion pairs and complexes). The concentration of ion pairs can constitute an important percentage of the total ions in a saline solution. For example, in a system of pure gypsum dissolved in water, the concentration of free Ca^{2+} ion is 10 mmol/L, but the total Ca concentration in solution is 15 mmol/L. The difference between the two concentrations is the presence of 5 mmol/L of the $CaSO_4^0$ ion pair in the solution phase. Because the formation of $CaSO_4^0$ requires both Ca^{2+} and SO_4^{2-} ions, gypsum solubility increases as ion association occurs.

The formation of ion pairs is prevalent between multiple valence ions and, to a lesser extent, mono- and multivalent ions. It is relatively minor for monovalent–monovalent interactions. Ion association can best be considered as a way to fit nonideal behavior among ions rather than as actual physical entities with chemical significance. These always reduce the activity of the free ions and, hence, they enhance the solubility of minerals. These speciation corrections are needed to accurately estimate the soil-solution composition of salt-affected systems when the ion association model is used, but they are not utilized in the Pitzer formulations.

Addition of neutral salts can nonetheless affect the soil-solution pH. For example, the addition of gypsum to a solution saturated with respect to calcite increases the Ca ion concentration, causing additional $CaCO_3$ to precipitate, reducing the bulk solution alkalinity, and decreasing the solution pH. However, the solubility of gypsum is not pH-dependent. Adding sulfuric acid to a soil suppresses gypsum solubility due to the common ion effect, rather than the effect of the acidity. However, the net result of adding gypsum or gypsum + sulfuric acid is similar in the presence of soil calcite. Conversely, Eq. 3-24 shows that $CaCO_3$ solubility is pH-dependent. Addition of acid reduces the alkalinity of the solution and allows $CaCO_3$ to dissolve until equilibrium is reestablished.

Chemical Composition of Surface and Ground Waters

The composition of surface and ground water varies greatly in arid regions. Table 3-1 shows data selected from saturation extracts of salt-

TABLE 3-1. Chemical Characteristics of Saturation Extracts of Salt-Affected Soils, Well Waters, and River Waters Analyzed at U.S. Salinity Laboratory

		Number of Samples (1)	Mean (2)	Median (3)	10% less than (4)	90% less than (5)
(a) $\mathrm{mmol_c/L}$						
Ca	Sat. Ext.	139	27.8	10.6	1.4	71.8
	Well	115	5.9	3.1	0.8	14.5
	River	68	4.7	3.4	1.0	10.9
Mg	Sat. Ext.	139	22.2	8.0	1.1	79.1
	Well	115	4.3	1.5	0.5	15.3
	River	61	3.6	2.2	0.6	9.2
Na	Sat. Ext.	139	93.2	53.5	1.8	219
	Well	115	15.8	6.6	0.8	44.8
	River	58	7.5	3.7	0.7	18.9
K	Sat. Ext.	128	1.6	0.5	0.1	2.2
	Well	101	0.6	0.1	0.01	0.9
	River	30	0.3	0.2	0.06	0.5
SO_4	Sat. Ext.	134	400	29.4	3.7	94.1
	Well	23	6.7	3.6	0.4	15.4
	River	58	6.7	4.1	0.3	19.0
Cl	Sat. Ext.	139	95.5	34.8	1.4	281
	Well	115	15.0	2.5	0.2	54.2
	River	58	5.9	1.5	0.2	20.7
HCO_3	Sat. Ext.	139	8.3	3.0	1.2	10.3
	Well	115	4.9	4.1	1.9	8.2
	River	58	3.3	3.0	1.7	5.7
(b) (dS/m)						
EC	Sat. Ext.	134	12.9	8.8	1.1	33.7
	Well	115	2.4	1.2	0.3	7.3
	River	58	1.4	0.92	0.3	3.2
(c) $(\mathrm{mmol/L})^{0.5}$						
SAR	Sat. Ext.	139	38.5	15.1	0.9	56.1
	Well	115	6.6	4.7	0.6	16.5
	River	58	3.3	2.4	0.7	7.4

EC, electrical conductance; SAR, sodium adsorption ratio; Sat. Ext., saturation extract affected soils, well waters, and surface waters analyzed at the U.S. Salinity Laboratory. The data represent samples obtained throughout the world.

The soil extracts were more saline and more sodic than the well waters and surface waters. This reflects the effects of ET and mineral dissolution in the soil. With increasing salinity, Na predominates over Ca because Na salts are more soluble than Ca salts. The importance of Na is also reflected in the increasing sodium adsorption ratio (SAR).

These data also show that Cl is the dominant anion in saline waters, whereas SO_4 and Cl are prevalent in dilute solutions. This reflects the influence of limited solubility of gypsum and precipitation as the waters are concentrated by ET.

The increase in the Mg/Ca ratio reflects the fact that Mg salts are more soluble than Ca salts. In general, the ratio Ca/HCO_3 is also >1.0 (when concentrations are expressed in $mmol_c/L$). A Ca/HCO_3 ratio of less than 1.0 poses a special sodicity hazard because, when such waters are concentrated by ET, calcite precipitates, the Ca concentration decreases, and the HCO_3 increases. The smaller the Ca/HCO_3 ratio, the greater the sodicity hazard.

Surface Chemistry

Clay minerals

Incongruent weathering processes in soils result in the production of soluble salts and, more importantly, the formation of secondary aluminosilicate clay minerals. These secondary clays are what give soils their ion-exchange and adsorptive properties. Because weathering processes differ in response to changing environmental conditions, and because weathering products from one reaction may simultaneously participate as reactants in other, different reactions, a given soil often contains a wide range of clay minerals. For the same reasons, a given clay type typically exhibits a wide range of chemical composition and physical properties.

With their plate-like shape and small particle size, clay minerals exhibit large specific surface areas (m^2/kg). This, coupled with their permanent charge and their pH-dependent charge, causes the colloidal clay fraction to be the center of chemical activity in the soil. The permanent charge is the result of structural substitution of cations of lesser charge (primarily Al^{3+} for Si^{4+}), resulting in net negative charge at the surface. The pH-dependent charge (broken bonds at the surface) is most important on the mineral edges. In addition, the colloidal hydrous oxides of iron and aluminium (the stable end-products of weathering) enhance the adsorptive and exchange capacity of soils.

Table 3-2 gives the qualitative unit cell formulae, the range of the cation exchange capacities (CEC), and specific surface areas for three clay minerals commonly found in arid soils. Textbooks on soil mineralogy can be consulted for more information on crystal structure and properties (Dixon and Weed 1989).

TABLE 3-2. Properties of Common Soil Clays

Clay (1)	Formula (General) (2)	Surface Area ($10^4 m^2/kg$) (3)	CEC ($cmol_c/kg$) (4)
Smectite (montmorillonite)	$Si_8(Al,Mg)_4O_{20}(OH)_4$	60–80	80–120
Mica (illite)	$K(Al,Si)_8(Al,Fe,Mg)_4O_{20}(OH)_4$	10–20	20–40
Kaolin (kaolinite)	$SiAl_4O_{10}(OH)_8$	1–2	3–6

CEC, cation exchange capacity

Although inorganic aspects of the soil matrix are emphasized here, the colloidal (<0.2 μm) organic matter fraction of a soil cannot be overlooked. In some soils, the effect of organic matter is more important than the inorganic-fraction processes. The organic matter has exchange properties, with extreme affinity for Ca (affecting the overall Ca–Na selectivity of soils) as well as variable charge, allowing for buffering of solution pH.

The diffuse double layer

The diffuse double layer (DDL) model developed from basic electrostatic theory describes electrochemical phenomena at the charged solid–liquid interface. The charge associated with a given surface is viewed as a layer, with an adjacent diffuse layer of oppositely charged ions, known as counter ions, in solution. The layer of counter ions maintains a charge in solution that is equal and opposite to the net charge of the mineral-surface layer. Various forces influence the diffuse nature of the counter ions: electrostatic attraction, which draws them toward the charged surface, repulsion among the ions and thermal energy, which tends to equalize the concentration of ions in the system and draw the counter ions back into the bulk solution, as well as close-range van der Waals forces.

Applying the DDL model to the clay-mineral surface allows one to predict the distribution of cations (counter ions) and anions (co-ions) at the charged mineral interface. It is an alternate approach to the mass action model (discussed later) for describing the exchange phenomena in soils.

Many physical properties of soils can be modeled as an interaction between DDLs of soil clay particles. The degree and nature of interaction is determined by the effective thickness of the DDL, which can be estimated with the K parameter in units of cm^{-1}:

$$K = \sqrt{\frac{8\pi e^2 z^2 n^0}{D \Diamond k \Diamond T}} \qquad (3\text{-}27)$$

where e = the electron charge (coulomb/ion); z = the valence of the counter ion, n^0 is the electrolyte concentration in the bulk solution (ion/cm^3); D = the dielectric constant (coulomb/V/cm); k = the Boltzmann constant (V coulomb/K/ion); and T = absolute temperature (K). The effective thickness of the DDL is $1/K$, which has units of cm.

Compression of the DDL (the desired condition for soil stability) is promoted by (1) increasing the valence of the counter ion, (2) increasing the concentration of the bulk solution, or (3) reducing the dielectric constant of the medium. The first two factors can be readily altered by processes, such as application of a calcium amendment or leaching. Leaching is necessary for salinity control; however, a reduction in salt concentration expands the DDL and thus reduces aggregate stability. Addition of a calcium source (such as gypsum) increases both the concentration of the bulk solution and provides addition of a divalent ion, both of which compress the DDL. Compression of the DDL allows for increased soil stability because, at specified distances, there is a reduction in the repulsive forces between clay particles, thus enabling closer approach of individual clay particles, resulting in aggregation. Aggregation of soil particles results in beneficial soil properties, including development of larger pores, thus enhancing permeability, as well as improving soil tilth. Several excellent references discuss at length the DDL theory and applications (Bolt 1979; Bresler et al. 1982; Singh and Uehara 1998).

Anion exclusion

The DDL model has successfully predicted anion exclusion, the negative adsorption of ions from the clay–water interface. Anions excluded from the double layer must be associated with cations to maintain solution electroneutrality. This increases the apparent concentration of soluble cations in solution.

Figure 3-3 shows how the concentration of counter ions (n_+) and anions (n_-) vary with distance in the DDL of a negatively charged particle. Assuming a 1:1 symmetrical salt, e.g., NaCl, in the bulk solution (infinite distance from the surface), the concentration of the electrolyte n^0 equals n_+ or n_-. This is represented by the dashed line in the figure. The excess of cations (α_+), which neutralizes both the surface charge and the anions in the DDL, is given by area ABCDEF. The amount of anions (α_-) in the DDL is given by area AEF. Total surface charge (α_{tot}), equivalent to CEC, is given by

$$\text{CEC} = \alpha_{\text{tot}} = \alpha_+ - \alpha_- \tag{3-28}$$

$$\text{CEC} = \text{surface cation excess} + \text{anion exclusion} \tag{3-29}$$

where e = the electron charge (coulomb/ion); z = the valence of the counter ion, n^0 is the electrolyte concentration in the bulk solution (ion/cm^3); D = the dielectric constant (coulomb/V/cm); k = the Boltzmann constant (V coulomb/K/ion); and T = absolute temperature (K). The effective thickness of the DDL is $1/K$, which has units of cm.

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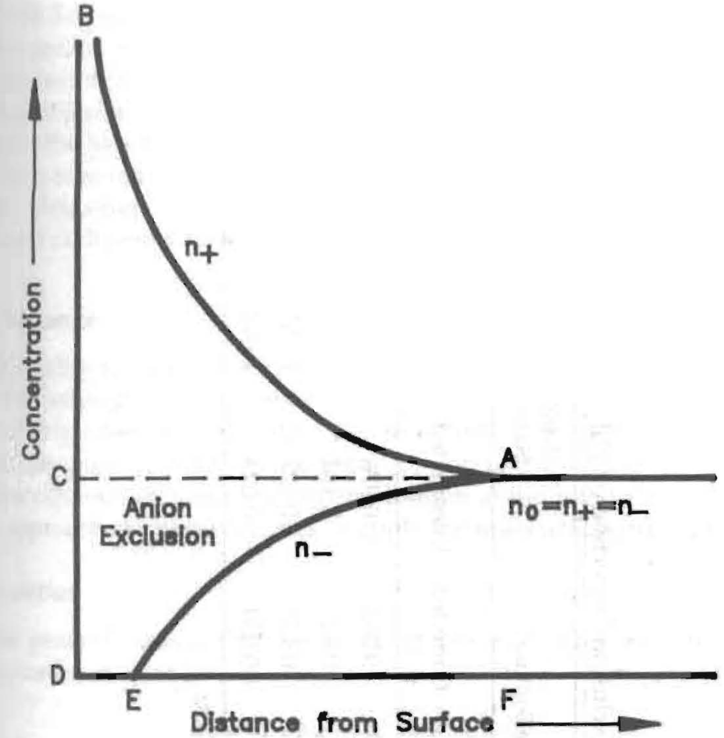

FIGURE 3-3. Charge distribution in diffuse double layer (DDL) of a negatively charged particle.

The CEC is equal to the area *ABCDEF* − area *AEF*, which equals the area *ABCDE*, where anion exclusion is measured by the increase of anion concentration in the contacting solution. The CEC is equal to the surface cation excess (total exchangeable cations) only when anion exclusion is negligible. This occurs at low electrolyte concentrations. Increasing electrolyte concentration compresses the DDL and increases anion exclusion. The correction for anion exclusion becomes significant above approximately 10 dS/m at 25 °C.

Bower and Hatcher (1962) reported the effect of the anion exclusion correction on exchangeable sodium percentage, ESP, where ESP = NaX · 100/*CEC*. The units of NaX and CEC are mol_c/kg). Table 3-3 shows selected data from their study. To correct for anion exclusion, they determined the Cl concentration in the saturation extract. The Cl concentration in the whole soil was determined by extensive leaching. The soluble cation content of the saturation extract was then multiplied by the ratio, $\text{Cl}_{\text{leaching}}/\text{Cl}_{\text{extract}}$.

TABLE 3-3. Anion Exclusion Correction on ESP

			Chloride[a]		Soluble Sodium[a]		Exchangeable Sodium[a]		ESP (Percentage)	
Soil (1)	SP (2)	EC_e (dS/m) (3)	Saturation Extracts (4)	Corrected (5)	Uncorrected (6)	Corrected (7)	Uncorrected (8)	Corrected (9)	Uncorrected (10)	Corrected (11)
1	101	9.0	0.078	0.068	0.071	0.062	0.076	0.085	21	23
2	60	67.4	0.406	0.368	0.464	0.420	0.184	0.228	60	75
3	57	32.3	0.074	0.061	0.165	0.135	0.027	0.057	13	27
4	59	17.7	0.033	0.026	0.076	0.059	0.023	0.040	12	21

[a] Chloride, soluble sodium, and exchangeable sodium are given in $\mathrm{mol_c/kg}$.

ESP, exchangeable sodium percentage

From Bower and Hatcher (1962).

Table 3-3 indicates a marked increase in Na ion preference by the exchanger, as seen by the ESP, after correction. This underscores the importance of considering anion exclusion in high-salinity environments. Anion exclusion fostered the concept known as the apparent exclusion volume, the hypothetical volume of water near the surface that must be insoluble to anions to account for the bulk solution's anion concentration. When calculating anion exclusion, the mathematically simpler concept of apparent exclusion volume is often used.

Ion Exchange

The ability to predict the distribution of ions between the soil solution and the exchanger phase is vital to the management of salt-affected soils, particularly when dealing with a potential sodic hazard. The complexity of the clay mineral fraction and the multi-ion nature of the soil solution make a rigorous definition of ion distribution in the soil difficult. A common approach to ion exchange is to apply the mass action principle.

Mass action

The general mass action equation for describing ion exchange in a binary cation system is

$$bAX_a + aBA^{b+} \leftrightarrow aBX_b + bA^{a+} \tag{3-30}$$

where X = one mole of negative charge on the exchanger; a = the valence of cation A; and b = the valence of cation B. Ion concentrations are in mol/L. When $a = b$, the exchange is homovalent. When $a \neq b$, the exchange is heterovalent. Applying the general exchange equation to Ca/Na exchange, where $a = 2$ and $b = 1$, gives

$$\mathrm{Ca}X_2 + 2\mathrm{Na}^+ \leftrightarrow 2\mathrm{Na}X + \mathrm{Ca}^{2+} \tag{3-31}$$

The thermodynamic equilibrium constant is

$$K_{eq} = \frac{(\mathrm{Na}X)^2(\mathrm{Ca}^{2+})}{(\mathrm{Ca}X_2)(\mathrm{Na}^+)^2} \tag{3-32}$$

where ( ) signifies activities in both solution and exchanger phase. The method for calculating activities of ions in solution is well established (Stumm and Morgan 1996), but determining the activities of ions in the exchanger phase is difficult and subject to question. A simple mass action approach, which gives the selectivity coefficient, can be used to calculate the ion distribution between the solution and adsorbed phase.

For Ca/Na exchange (Eq. 3-31), the selectivity coefficient k_s is

$$k_s = \frac{[\mathrm{NaX}]^2[\mathrm{Ca}^{2+}]}{[\mathrm{CaX}][\mathrm{Na}^+]^2} \tag{3-33}$$

where [ ] signifies concentrations units in both the solution and exchanger phases. The ion concentration in the exchanger phase is expressed in units of equivalent fraction, using the Gapon convention, or, less frequently, the mole fraction, using the Vanselow convention. These terms are related, but they produce different values for the selectivity coefficient (Sposito 1977).

Although not a true thermodynamic constant, the variability of k_s is often small. Using the equivalent fraction, E_i, for the adsorbed ion concentration and mol/L for the solution concentration, Eq. 3-33 becomes

$$k_s = \frac{[E_{\mathrm{Na}}]^2[\mathrm{Ca}^{2+}]}{[E_{\mathrm{Ca}}][\mathrm{Na}^+]^2} \tag{3-34}$$

where $E_i = iX/\mathrm{CEC}$ and both iX and CEC have the units of $\mathrm{cmol}_c/\mathrm{kg}$ ($\mathrm{cmol}_c/\mathrm{kg}$ is equivalent to the formerly popular units of meq/100 g).

Levy and Hillel (1968) found the k_s value for this exchange reaction to be constant over a wide range of E_{Na} values (i.e., $E_{\mathrm{Na}} \approx 0.1$ to 0.7) for typical Israeli soils. The magnitude of the k_s, however, varied between soils.

The Gapon constant

The Gapon exchange reaction has been widely used in salinity and sodicity studies. The original expression for Ca/Na exchange is

$$\mathrm{Ca}_{1/2}X + \mathrm{Na}^+ \leftrightarrow \mathrm{Na}X + 1/2\,\mathrm{Ca}^{2+} \tag{3-35}$$

where solution concentration is in mol/L and exchange ion concentration is in $\mathrm{cmol}_c/\mathrm{kg}$. At equilibrium, we can write

$$k_g = \frac{[\mathrm{Na}X][\mathrm{Ca}^{2-}]^{1/2}}{[\mathrm{Ca}_{1/2}X][\mathrm{Na}^+]} \tag{3-36}$$

where k_g = the Gapon selectivity coefficient, often assumed to be constant. The ratio of adsorbed ions is

$$\frac{[\mathrm{Na}X]}{[\mathrm{Ca}_{1/2}X]} = kg\frac{[\mathrm{Na}^+]}{[\mathrm{Ca}^{2+}]^{1/2}} \tag{3-37}$$

where the units of k_g are $(\mathrm{mol/L})^{-1/2}$. The U.S. Salinity Laboratory (1954) further assumed that Mg behaves similarly to Ca in the adsorbed phase and modified the Gapon equation to the following:

$$\frac{[\mathrm{NaX}]}{[\mathrm{CaX}+\mathrm{MgX}]}=k_g'\frac{[\mathrm{Na}^+]}{[\mathrm{Ca}+\mathrm{Mg}]^{1/2}}=k_g'\,\mathrm{SAR} \tag{3-38}$$

where k_g' = the modified Gapon selectivity coefficient $(\mathrm{mmol/L})^{-1/2}$; and SAR = the sodium adsorption ratio, defined as

$$\mathrm{SAR}=\frac{[\mathrm{Na}]}{[\mathrm{Ca}+\mathrm{Mg}]^{1/2}} \tag{3-39}$$

where total analytical concentrations are used (mmol/L) with no account of ion association. Because Ca, Mg, and Na are the most common exchangeable cations in arid soils, Eq. 3-38 may be simplified to

$$\frac{[\mathrm{Na}X]}{\mathrm{CEC}-[\mathrm{Na}X]}=k_g'\mathrm{SAR}=\mathrm{ESR} \tag{3-40}$$

where ESR is called the exchangeable sodium ratio. In terms of the ESP, Eq. 3-40 becomes

$$\frac{[\mathrm{ESP}]}{[100+\mathrm{ESP}]}=k_g'\mathrm{SAR}=\mathrm{ESR} \tag{3-41}$$

where ESP = NaX 100/CEC. Because obtaining reliable exchangeable ion data is difficult (Amrhein and Suarez 1990), the SAR of the soil solution or extract has become the principle parameter for diagnosing sodic hazards in soils.

The value of k_g' is determined by the regression (slope) of the ESR–SAR relationship, which is linear. A value of k_g' = 0.015 $(\mathrm{mmol/L})^{-1/2}$ is widely used. It is useful in field studies when the ESR $\leq$ 30. Correspondingly, as a rough approximation in this sodicity range, the value of SAR and ESP are assumed equal (U.S. Salinity Laboratory 1954). More recent studies, however, indicate that numerous factors influence the ESR–SAR couple and the value of k_g' ranges from 0.016 $(\mathrm{mmol/L})^{-1/2}$ to 0.008 $(\mathrm{mmol/L})^{-1/2}$. This suggests that, to be accurate, k_g' should be estimated using data specific to the site under study (Doering and Willis 1980; Jurinak et al. 1984).

Effect of salinity on ion exchange

If the soil solution is concentrated by a factor ΔC, maintaining the same ionic ratios, the initial SAR increased by the factor $(\Delta C)^{1/2}$:

$$\mathrm{SAR}_{\mathrm{final}} = (\Delta C)^{1/2} \cdot \mathrm{SAR}_{\mathrm{initial}} \tag{3-42}$$

Thus, if the concentration is increased by a factor of 3 and no chemical precipitation occurs, $\mathrm{SAR}_{\mathrm{final}} = (3)^{1/2}\ \mathrm{SAR}_{\mathrm{initial}}$. Increasing soil salinity increases the SAR, and if k_g' remains constant, then ESR and ESP must increase. There is little evidence for a change in selectivity with increasing salinity (Amrhein and Suarez 1991), hence no practical need to consider solution activity coefficients and ion pairs for cation exchange calculations.

As an example, assume a soil is irrigated with water of EC = 1.5 dS/m and SAR = 8 $(\mathrm{mmol/L})^{1/2}$. Assuming an ET concentration factor of 3 in the rootzone, and using Eq. 3-42, the SAR of the soil solution will then be 13.9 $(\mathrm{mmol/L})^{1/2}$. Applying the Gapon convention and assuming that k_g' is constant and equal to 0.015 $(\mathrm{mmol/L})^{-1/2}$, the steady-state ESR of the soil is 0.21 (ESP = 17.4). If ET increases the concentration factor to 6, the SAR will then equal 19.6 $(\mathrm{mmol/L})^{1/2}$, and the ESR increases to 0.29 (ESP = 22.5). Thus, if the selectivity coefficient remains the same, an increase in the concentration of the equilibrium solution increases the affinity of the clay fraction for monovalent cations, and dilution increases the affinity for divalent cations.

Ion demixing

Early theories of cation exchange assumed exchangeable ions were randomly distributed at the clay surface. More recent evidence suggests, however, that random distribution is rare for expanding lattice clays. Instead, divalent ions are preferentially adsorbed in the interlayer spaces and monovalent ions are adsorbed on the edges and planar surfaces. This phenomenon, referred to as ion demixing, affects a soil's response to relatively low amounts of exchangeable sodium (see Chapter 5).

Rhizosphere Chemistry in Salt-Affected Soils

The composition of soil water depends on the composition of irrigation and rain water; chemical reactions, such as dissolution, precipitation, adsorption, and exchange; and the extent to which ET concentrates the water. Predicting the chemistry of a soil solution is difficult due to the dynamic nature of the system. For a more convenient prediction we often assume (though it may be far from true) that steady-state conditions exist.

When assuming steady-state conditions, ion exchange is viewed as a static condition affected only by ET and precipitation-dissolution reactions. It is also assumed that Na, Mg, K, and Cl do not undergo chemical reactions (other than exchange). Concentrations of these ions can be estimated by multiplying their initial concentrations in the applied water, C_w, by the ratio of the water consumed to water applied.

Magnesium carbonates

In the rhizosphere, many soil waters are supersaturated with respect to dolomite, $CaMg(CO_3)_2$, and possibly magnesite, $MgCO_3$. Dolomite is not considered a sink for Mg because of the kinetic constraints on precipitation existing in rhizosphere environments. Although dolomite has approximately the same molar solubility as calcite, the rate at which it dissolves is about 70 times slower. The result is that dolomite contributes Ca to the soil solution but, in the absence of calcite, is extremely slow to reach equilibrium with a soil solution. Because dolomite does not precipitate readily from the soil solution, whereas calcite does, the Mg/Ca ratio increases as the leaching fraction is reduced.

Magnesite precipitation in soils has not been documented. The solubility of magnesite is in dispute, but pure solutions may attain (Mg^{2+}) values of about 60 to 180 times greater (at pH 9.5 and 8.5, respectively, depending also on the alkalinity) than the (Ca^{2+}) values before another magnesium carbonate, hydromagnesite $(Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O)$ precipitates. Before either dolomite or Mg-carbonate minerals form, Mg will most likely form a Mg-silicate mineral, such as sepiolite, $MgSi_3O_6(OH)$. Co-precipitation with Ca is also another sink for Mg because, depending on the Ca/Mg ratio, the precipitated calcite will often contain 3% to 7% Mg substitution for Ca.

Calcium carbonate

The dissolution and precipitation of $CaCO_3$ influences rhizosphere chemistry. Indeed, calcite reaction is generally assumed to dominate the chemistry of the soil solution in arid-zone soils. Studies show that calcite is usually supersaturated in waters in and below the rootzone, and the mean value of the ion activity product (IAP) of $(Ca^{2+})(CO_3^{2-})$ equals 10^{-8} (Suarez 1977; Suarez et al. 1992), that is,

$$(Ca^{2+})(CO_3^{2-}) = 10^{-8.0} \tag{3-43}$$

This measured IAP does not imply that soil calcite is thermodynamically unstable (K_{sp} of calcite is $10^{-8.47}$ at 25 °C). Rather, it appears that this supersaturation reflects a kinetic aspect associated with calcite crystal growth. At an IAP value of $10^{-8.0}$ calcite is sufficiently supersaturated that heterogeneous nucleation occurs. Once calcite nucleates in the soil, calcite crystal growth is inhibited by dissolved organic carbon in the soil water and the value of $10^{-8.0}$ corresponds to the value at which calcite precipitates via heterogeneous nucleation (Lebron and Suarez 1996; 1998). Soil solutions remain in a metastable condition at this IAP value (threefold supersaturated with respect to calcite), so it can be used as an apparent solubility constant for predictive purposes.

Since CO_3^{2-} is usually a minor species in solution, calcite solubility can more conveniently be represented by expressing it in terms of HCO_3^-:

$$K'' = \frac{(Ca^{2+})(HCO_3^-)^2}{P_{CO_2}} \tag{3-44}$$

When P_{CO_2} is expressed in kilopascals (1 atm = 101 kPa) and a calcite thermodynamic K_{sp} of $10^{-8.47}$ is used, the theoretical value of $K'' = 10^{-8.0}$. If the apparent solubility product of calcite (Eq. 3-43) is used in Eq. 3-44 for predictive purposes, then the value of K'' increases to $10^{-7.5}$. In that situation, Eq. 3-45 loses its thermodynamic significance. Computer programs, such as *Extract Chem* (Chapter 26) are available for calculating equilibrium Ca^{2+} and HCO_3^- concentrations and activities. A graphical method, based on solution of the following equation, is also available (Suarez 1982):

$$(Ca^{2-} - x)(HCO_3^- - 2x)^2 = \frac{10^{-7.5} P_{CO_2}}{\gamma_{Ca^{2+}} \gamma^2_{HCO_3^-}} \tag{3-45}$$

where x = the amount of Ca that is precipitated or dissolved. No correction for ion association is made, so the results are only approximate. In the absence of specific data for the rhizosphere, use P_{CO_2} = 1 kPa (0.01 atm) for sandy soils and 5 kPa (0.05 atm) for clay soils.

The adjusted sodium adsorption ratio

As discussed earlier, the SAR relationship is useful for estimating the ESP of the soil. The SAR of soil water, assuming steady-state conditions, is determined from the composition of the irrigation water, after correcting for ET and $CaCO_3$ precipitation or dissolution.

An adjustment to the SAR of irrigation water is often made to incorporate the changes in Ca that will occur when the water is equilibrated with calcite. Various methods are used to adjust the SAR of waters, several of which are in error. The preferred method is to calculate the equilibrium Ca concentration in the water (Ca_{eq} in mmol/L) and use in the following equation (Suarez 1981):

$$SAR_{adj} = \frac{Na_{iw}}{\sqrt{Mg_{iw} + Ca_{eq})}} \qquad (3\text{-}46)$$

where Na_{iw} and Mg_{iw} are concentrations of Na and Mg (mmol/L), respectively, in the applied water. The Ca_{eq} is the Ca value in equilibrium with calcium carbonate, and can best be obtained by use of chemical speciation models, such as *Extract Chem*. This correction will result in a downward adjustment of the SAR if the initial irrigation water is undersaturated with respect to calcite. More commonly, surface irrigation waters in arid lands are already reacted with carbonates and a $(Ca^{2+})(CO_3^{2-})$ IAP at or greater than $10^{-8.0}$. In this instance an adjustment to SAR is not needed.

The SAR correction is most important when using groundwaters or waste waters for irrigation. In this instance the waters are generally equilibrated at higher concentrations of CO_2 and, upon exposure to the air, will degas CO_2 and the solution will precipitate calcite, thus increasing the SAR.

An alternate equation for calculating SAR_{adj} is

$$SAR_{adj} = \frac{Na_{iw}}{\sqrt{Mg_{iw} + 0.215X(P_{CO_2})^{1/3}}} \qquad (3\text{-}47)$$

where P_{CO_2} is in kPa and X values are found in Table 3-4 (Suarez 1981) using the molar HCO_3/Ca ratio and ionic strength values for the irrigation water. The P_{CO_2} for surface waters can be set to around twice atmospheric (i.e., $10^{-3.14}$ atm or 0.072 kPa).

The same concepts can be used to estimate the equilibrium SAR in the rhizosphere. In this instance Eq. 3-47 is modified to

$$SAR_{adj} = \frac{Na_{iw}F_c}{\sqrt{Mg_{iw}F_c + 0.215X(P_{CO_2})^{1/3}}} \qquad (3\text{-}48)$$

The concentration factor F_c equals 1/L, in which L = the leaching fraction. Its value depends on the soil depth.

TABLE 3-4. X-Values for Various HCO_3/Ca Mole Ratios and Ionic Strengths

	Ionic Strength (I)[a]														
HCO_3/Ca (1)	0.001 (2)	0.005 (3)	0.01 (4)	0.02 (5)	0.03 (6)	0.04 (7)	0.05 (8)	0.07 (9)	0.1 (10)	0.15 (11)	0.2 (12)	0.25 (13)	0.3 (14)	0.4 (15)	0.5 (16)
0.1	73.4	79.6	84.1	90.0	94.4	97.9	101.0	106.0	112.0	120.0	125.0	130.0	133.0	139.0	144.0
0.2	46.2	50.1	53.0	56.7	59.5	61.7	63.6	66.8	70.5	75.3	78.8	81.7	84.0	87.9	90.4
0.3	35.3	38.2	40.4	43.3	45.4	47.1	48.5	51.0	53.8	57.5	60.1	62.3	64.1	67.0	69.0
0.4	29.1	31.6	33.4	35.7	37.5	38.9	40.1	42.1	44.4	47.4	49.6	51.5	52.9	55.3	57.0
0.5	25.1	27.2	28.8	30.8	32.3	33.5	34.5	36.3	38.3	40.9	42.8	44.3	45.6	47.6	49.1
0.6	22.2	24.1	25.5	27.3	28.6	29.7	30.6	32.1	33.9	36.2	37.9	39.3	40.4	42.2	43.5
0.7	20.1	21.7	23.0	24.6	25.8	26.8	27.6	29.0	30.6	32.7	34.2	35.4	36.4	38.1	39.2
0.8	18.3	19.9	21.0	22.5	23.6	24.5	25.2	26.5	28.0	29.9	31.3	32.4	33.3	34.8	35.9
0.9	17.0	18.4	19.4	20.8	21.8	22.6	23.3	24.5	25.9	27.6	28.9	30.0	30.8	32.2	33.2
1.0	15.8	17.1	18.1	19.4	20.3	21.1	21.8	22.8	24.1	25.8	26.9	27.9	28.9	30.0	30.9
1.5	12.1	13.1	13.8	14.8	15.5	16.1	16.6	17.4	18.4	19.7	20.6	21.3	21.9	22.9	23.6
2.0	9.96	10.8	11.4	12.2	12.8	13.3	13.7	14.4	15.2	16.2	17.0	17.6	18.1	18.9	19.5
2.5	8.58	9.31	9.84	10.5	11.0	11.5	11.8	12.4	13.1	14.0	14.6	15.2	15.6	16.3	16.8
3.0	7.60	8.24	8.71	9.33	9.78	10.1	10.5	11.0	11.6	12.4	13.0	13.4	13.8	14.4	14.9
3.5	6.86	7.44	7.86	8.42	8.82	9.15	9.44	9.91	10.5	11.2	11.7	21.1	12.5	13.0	13.4
4.0	6.27	6.80	7.19	7.70	8.07	8.37	8.63	9.06	9.57	10.2	10.7	11.1	11.4	11.9	12.3
4.5	5.80	6.29	6.65	7.12	7.46	7.74	7.98	8.38	8.85	9.45	9.88	10.2	10.2	11.0	11.3
5.0	5.41	5.86	6.20	6.63	6.96	7.22	7.44	7.81	8.25	8.81	9.21	9.55	9.83	10.3	10.6
6.0	4.79	5.19	5.49	5.87	6.16	6.39	6.59	6.92	7.30	7.80	8.16	8.46	8.70	9.09	9.37
7.0	4.31	4.68	4.95	5.30	5.56	5.77	5.95	6.24	6.59	7.04	7.36	7.63	7.85	8.20	8.45
8.0	3.95	4.29	4.53	4.85	5.09	5.28	5.44	5.71	6.03	6.44	6.74	6.98	7.18	7.50	7.73
9.0	3.65	3.96	4.19	4.48	4.70	4.88	5.03	5.28	5.57	5.95	6.23	6.46	6.64	6.94	7.15
10.0	3.41	3.69	3.90	4.18	4.38	4.55	4.69	4.92	5.20	5.55	5.80	6.02	6.19	6.46	6.66

[a] I = 0.0127 EC (mol/L)

From Suarez (1981).

SUMMARY

The salt-mineral composition of the soil solution results from numerous, interdependent, multiphase chemical interactions, including dissolution and precipitation of minerals, formation of inorganic and organic coordination compounds in solution, adsorption of ions and ligands onto the surfaces of minerals and organic compounds, exchange of ions between clay-mineral surfaces and the solution phase, transport of compounds between the gas and liquid phases, and reduction and oxidation of ions and minerals. This list suggests not only the complexity of the system, but also the need for conceptual geochemical computer models to predict the composition of the soil solution as affected by man's activities. Geochemical models can be linked with soil-water flow models, plant growth models, and other models to predict solute migration in soils.

Numerous geochemical models are available. An abbreviated list includes *PHREEQC* (Parkhurst and Appelo 1999) *MINEQL* (Westall et al. 1976), *EQ3/EQ6* (Wolery 1979; 1983) and *MINTEQ* (Allison et al. 1990; HydroGeologic Inc. and Allison Geoscience Consultants, Inc. 1999). They represent the current state-of-the-art in computer simulation of soil-solution chemistry. The *UNSATCHEM* model (Suarez and Šimůnek 1997) incorporates a variably saturated water flow model with major ion chemistry, B adsorption, plant water uptake, and yield predictions related to salinity.

REFERENCES

Allison, J. D., Brown, D. S., and Novo-Gradac, K. J. (1990). *MINTEQA2/PRODEFA2: A geochemical assessment model for environmental systems: Version 3.0 user's manual*, Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Ga.

Amhrein, C., and Suarez, D. L. (1990). "A procedure for determining sodium-calcium exchange selectivity in calcareous and gypsiferous soils." *Soil Sci. Soc. Am. J.*, 54, 999–1007.

———. (1991). "Sodium-calcium exchange with anion exclusion and weathering corrections." *Soil Sci. Soc. Am., J.* 55, 698–706.

Bolt, G. H. (1979). *Soil chemistry, B: Physico-chemical models*, Elsevier Scientific Publishing Co., New York.

Bower, C. A., and Hatcher, J. T. (1962). "Characterization of salt-affected soils with respect to sodium." *Soil Sci.*, 93, 275–280.

Bresler, E., McNeal, B. L., and Carter, D. L. (1982). *Saline and sodic soils*, Springer-Verlag, New York.

Butler, J. N. (1964). *Ionic equilibrium, a mathematical approach*, Addison-Wesley, Boston.

Dixon, J. B., and Weed, S. B. (eds.). (1989). *Minerals in soil environments*, 2nd ed., Soil Science Society of America Book Series No. 1, Soil Science Society of America, Madison, Wisc.

Doering, E. J., and Willis, W. O. (1980). "Effect of soil solution concentration on cation exchange relationships." *Proc., International Symposium on Salt-Affected Soils, Karnal, India.*

Griffin, R. A., and Jurinak, J. J. (1973). "Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts." *Soil Sci.,* 116, 26–30.

Harned, H. S., and Owen, B. B. (1958). *The physical chemistry of electrolyte solutions,* Reinhold Publishers, New York.

Harvie, C. E., Moller, N., and Weare, J. H. (1981). "The prediction of mineral solubilities in natural waters: The $\text{Na-K-Mg-Ca-H-Cl-SO}_4\text{-OH-HCO}_3\text{-CO}_3\text{-H}_2\text{O}$ system to high ionic strength." *Geochim. Cosmochim. Acta,* 48, 723–751.

HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. (1999). *MINTEQA2/PRODEFA2: A geochemical assessment model for environmental systems, Version 4.0 user's manual,* Environmental Research Laboratory, Office of Research and Development. U.S. Environmental Protection Agency, Athens Ga., www.epa.gov/ceampubl/mmedia/minteq/, accessed January 15, 2011.

Jurinak, J. J., Amrhein, C., and Wagenet, R. J. (1984). "Sodic hazard: The effect of SAR and salinity in soils and overburden materials." *Soil Science,* 137, 152–158.

Lebron, I., and Suarez, D. L. (1996). "Calcite nucleation and precipitation kinetics as affected by dissolved organic matter at 25 °C and pH >7.5." *Geochim. Cosmochim. Acta,* 60, 2765–2776.

———. (1998). "Kinetics and mechanisms of precipitation of calcite as affected by P_{CO_2} and organic ligands at 25 °C. *Geochim. Cosmochim. Acta,* 62, 405–416.

Levy, R., and Hillel, D. (1968). "Thermodynamic equilibrium constants of sodium-calcium exchange in some Israel soils." *Soil Sci.,* 106, 393–398.

Marion, G. M., and Babcock, K. L. (1976). "Predicting specific conductance and salt concentration of dilute aqueous solution." *Soil Sci.,* 122, 181–187.

McNeal, B. L., Oster, J. D, and Hatcher, J. T. (1970). "Calculation of electrical conductivity from solution composition data as an aid to in-situ estimation of soil salinity." *Soil Sci.,* 110, 405–414.

Merrill, S. D., Deutsch, J. R., and Pole, M. W. (1987). "Saturation percentage," in *Reclaiming mine soils and overburden in the western United States,* D. R. Williams and G. E. Schuman, eds., Soil Conservation Society America, Ankeny, Iowa.

Parkhurst, D. L. and Appelo, C. A. (1999). *User's guide to PHREEQC (ver 2): A computer program for speciation, batch reaction, one dimensional transport, and inverse geochemical calculations.* U.S. Geol. Survey Water Resources Investigations Report 99-4259. U.S. Geological Survey, Denver, Colo.

Pitzer, K. S. (1979). *Activity coefficients in electrolyte solutions,* Chapter 7, CRC Press, Boca Raton, Fla.

Robinson, R. A., and Stokes, J. J. (1959). *Electrolyte solutions,* 2nd ed., Butterworth and Co., London.

Singh, U., and Uehara, G. (1998). "Electrochemistry of the double layer," in *Soil physical chemistry,* 2nd ed., D. Sparks, ed., Chapter 1, CRC Press, Boca Raton, Fla.

Sposito, G. (1977). "The Gapon and Vanselow selectivity coefficients." *Soil Sci. Soc. Am. J,.* 41, 1205–1206.

Stumm, W., and Morgan, J. J. (1996). *Aquatic chemistry*, 3rd ed., John Wiley and Sons, New York.

Suarez, D. L. (1977). "Ion activity products of calcium carbonate in waters below the rootzone." *Soil Sci. Soc. Am. J.*, 41, 310–315.

——. (1981). "Relation between pH_c and sodium adsorption ratio (SAR) and an alternative method of estimating SAR of soil or drainage waters." *Soil Sci. Soc. Am. J.*, 45, 469–475.

——. (1982). "Graphical calculation of ion concentrations in $CaCO_3$ and/or gypsum soil solutions." *J. Environ. Qual.*, 11, 302–308.

——. (1998). "Thermodynamics of the soil solution," in *Soil physical chemistry*, 2nd ed., D. Sparks, ed., Chapter 3, CRC Press, Boca Raton, Fla.

Suarez, D.L. and J. Šimůnek. (1997). "UNSATCHEM: Unsaturated water and solute transport model with equilibrium and kinetic chemistry." *Soil Sci. Soc. Am. J.*, 61, 1633–1646.

Suarez, D. L., and Taber, P. (2007). "Extract Chem: Numerical software package for estimating changes in solution composition due to changes in soil water content," http://ars.usda.gov/Services/docs.htm?docid=14567, accessed January 15, 2011.

Suarez, D. L., and Wood, J. D. (1996). "Short and long term weathering rates of a feldspar fraction isolated from an arid zone soil." *Chem. Geol.*, 132, 143–150.

Suarez, D. L., Wood, J. D., and Ibrahim, I. (1992). "Reevaluation of calcite supersaturation in soils." *Soil Sci. Soc. Am. J.*, 56, 1776–1784.

Tanji, K. K. (1969). "Predicting specific conductance from electrolytic properties and ion association in some aqueous solutions." *Soil Sci. Soc. Am. Proc.*, 33, 887–889.

Tanji, K. K., and Biggar, J. W. (1972). "Specific conductance models for natural waters and soil solutions of limited salinity levels." *Water Resource Res.*, 8, 145–153.

Truesdell, A. H., and Jones, B. F. (1974). "WATEQ, a computer program for the calculating chemical equilibria of natural waters." *J. Res. U.S. Geol. Surv.*, 2, 233–248.

U.S. Salinity Laboratory. (1954). *Diagnosis and improvement of saline and alkali soils*, U.S. Department of Agriculture Handbook No. 60, U.S. Government Printing Office, Washington, D.C.

Westall, J. C., Zachary, J. L., and Morel, F. M. (1976). *MINEQL: A computer program for calculation of chemical equilibrium composition of aqueous systems*, Tech Note 18, Dept. Civil Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

Williams, J. S. (1975). *The natural salinity of the Colorado River*, Occasional Paper 7, Utah Water Research Laboratory, Logan, Utah.

Wolery, T. J. (1979). *Calculation of chemical equilibrium between aqueous solution and minerals: The EQ3/6 software package*, UCRL-52658, Lawrence Livermore Lab., University of California, Livermore, Calif.

——. (1983). *EQ3NR: A computer program for geochemical aqueous speciation-solubility calculations*, Lawrence Livermore Lab., University of California, Livermore, Calif.

NOTATION

A, B, C = chemical symbols
a = valence of cation A
a, b, c = stoichiometric coefficients
b = valence of cation B
c_i = concentration of the ith ion
D = dielectric constant
e = electron charge
EC = specific conductance
EC_i = ionic specific conductance
EC_t = value at temperature t
ESR = exchangeable sodium ratio
ET = evapotranspiration
F_c = concentration factor
K' = solubility product for calcite
k = Boltzmann constant
k_g = Gapon selectivity coefficient
k_g' = modified Gapon selectivity coefficient
L = leaching fraction
Mg_{iw}, = concentration of Mg in applied water
m_i = molal concentration of the ith ion
Na_{iw} = concentration of Na in applied water
n^0 = electrolyte concentration in the bulk solution
SAR = sodium adsorption ratio
T = absolute temperature
TSS = total soluble salt concentration
X = one mole of negative charge on the exchanger
x = amount of Ca precipitated or dissolved
z = valence of the counter ion
β = empirical interactive parameter
γ_i = activity coefficient
λ_i^o = ionic equivalent conductance at infinite dilution
ϕ = osmotic coefficient of the ith salt
( ) = activities
[ ] = concentrations

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