

---

# 10 Soil Reaction

## 10.1 DEFINITION AND IMPORTANCE

The *soil reaction* is a term used to indicate the acid–base reactions in soils (Brady, 1974, 1990; Logsdon et al., 2008; Tisdale and Nelson, 1975). Although the extent of the soil's acid–base reaction is commonly expressed in terms of soil pH, the use of the terms acidic pH (Chorover, 2006), neutral pH, and basic pH is incorrect. Soil pH values are plain numbers from 0 to 14, which are derived from the hydrogen ion activity in  $-\log$  form. Therefore, the term *soil reaction* can be used to simplify and avoid this problem. Accordingly, it is more appropriate to use the terms *soils with acid, neutral, or basic reaction* or, if desired, *soils with low pH* or *soils with high pH*.

Brady and Weil (1996, 2008) consider the soil reaction a master variable that affects most of the soil properties. They believe that pH will not only affect the chemical and biological properties of soils, but will also affect the physical properties, including air and water movement in soils. The latter is subject to arguments, because many questions will arise on the issue of pH dependency of air and water movement in soils. It is very difficult to provide a direct scientific basis for differences in the flow of water and air in soils at low and high pH. Nevertheless, the soil reaction can be considered a *master determinant*, instead of a master variable, in controlling plant growth and crop production. The effect of the acid–base reactions in soils is manifested directly or indirectly on the growth of plants. Directly,  $H^+$  ions are reported to have a toxic effect on plants when present in high concentrations. Indirectly, the soil reaction may influence plant growth through its effect on solubility and availability of plant nutrients. The changing phosphate concentration with soil pH, as discussed in the preceding chapter, is one example. Another good example is the concentration of micronutrients reaching toxic or adequate levels with changing soil pH. Many soil chemical and biological reactions can occur only at specific soil reactions. The rate of decomposition of soil minerals and organic matter is influenced by the soil reaction. Weathering of primary minerals is promoted by low soil pH, because sufficient amounts of protons are required for hydrolysis to occur. The  $H^+$  ions are consumed by the hydrolysis reaction, and  $OH^-$  ions are produced, making the soil solution become more basic (Birkeland, 1974; Wild, 1993). Formation of clay minerals depends on specific soil reactions. The solubility of alumina and silica is markedly affected by pH. At pH less than 4, alumina is considered to become more soluble than silica. On the other hand, between pH 5 and 9, alumina is practically insoluble, whereas silica becomes increasingly soluble. Such a condition may lead to differential leaching of silica, and the consequent formation of kaolinite, gibbsite, and bauxite (Ollier, 1975). On the other hand, smectite is more likely to be formed in a soil reaction favoring the presence of adequate amounts of silica.

Another chemical property influenced by soil pH is the exchange reaction, especially in soils with variable charges (Theng, 1980). However, exchange reactions are not the reason for soil acidity, but, depending on pH, are accumulating more  $H^+$  ions through exchange processes.

The transformation of  $NH_4^+$  into  $NO_3^-$ , called nitrification, is considered the most pH-sensitive biochemical reaction in soils. Nitrification in forest soils is noted to occur below pH 4 but has not been found to take place below pH 6 in solution cultures (Paul and Clark, 1989).

The soil reaction is also an important, if not a determining, factor in environmental issues. It controls the fate of inorganic and organic pollutants in soils, by affecting their degradation or decomposition, solubility, and precipitation by formation of complex compounds, and many more. Adsorption of heavy metals by soil colloids increases with increased pH. Depending upon the pH,



the organic pollutant can be present in the soil solution in the cationic, anionic, or molecular form. The form in which it occurs determines the rate and degree of adsorption and, hence, its mobility in soil. The importance of the concept of surface acidity was discussed earlier in this connection of adsorption of organic compounds (see Section 7.1).

The colloidal particles in soils can also behave as acid or base. Hydrogen or Al-saturated clays usually behave as an acid and may react with bases.

## 10.2 ACID–BASE CHEMISTRY

To understand, study, and apply the acid–base concept, it is important to first define an acid and a base. Three major concepts of acids and bases are available: Arrhenius, Brønsted–Lowry, and Lewis. Other less used concepts also exist—for example, Usanovich, Lux–Flood, and Pearson (Volpe and Siboni, 2006). The latter three are not used too often due to their ambiguity but will be addressed briefly below for completeness.

### 10.2.1 THE ARRHENIUS CONCEPT

The concept of Arrhenius developed between 1880 and 1890, stated that an acid is a compound that contains hydrogen. In aqueous solution, the acid yields hydrogen ions ( $H^+$ ). The hydrogen ion is in fact a bare proton, without the electron connected to it in the hydrogen atom. Therefore, the terms *hydrogen ion* and *proton* are often used interchangeably. Free hydrogen ions do not exist in the soil solution but exist only attached to water molecules, forming *hydronium ions*,  $H_3O^+$ . Because of the many complications introduced by the use of  $H_3O^+$  in writing chemical reactions, for simplicity it is customary to use  $H^+$  only.

Acids that can dissociate one, two, three, and more protons are often referred to as *mono-*, *di-*, *tri-*, and *polyprotic* acids, respectively. Compounds that can both dissociate or add a proton are called *amphiprotic* (Greek: *amphi* means “both”) compounds. Water is an example of an amphiprotic compound because it can dissociate, though very weakly, a proton and accept a proton to form a hydronium ion, as illustrated by the following reactions:



This reaction, called *autoprotolysis*, occurs to such an extent that only very small amounts of hydronium and hydroxyl ions are produced. Refined analyses reported values of  $1 \times 10^{-7} M$  for  $H_3O^+$  and  $OH^-$  ions in pure water at 25°C.

A base, on the other hand, is a compound containing hydroxide (OH) groups that dissociate in aqueous solution as hydroxyl ions ( $OH^-$ ). A basic solution is also called an alkaline solution.

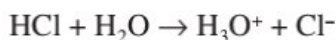
The Arrhenius concept is essentially valid only for the definition of acids. Almost all acids contain hydrogen and dissociate  $H^+$  ions. However, Arrhenius’ definition of a base limits the bases to only compounds containing hydroxide groups. It is currently known that ammonia ( $NH_3$ ) and many other organic substances exhibit characteristics of base compounds.

### 10.2.2 THE BRØNSTED–LOWRY CONCEPT

Brønsted and Lowry defined independently, in 1923, that an *acid* is a compound capable of donating a proton (*proton donor*). On the other hand, any compound capable of accepting a proton is considered a *base* (*proton acceptor*). This acid–base concept is also known as the *proton concept*.

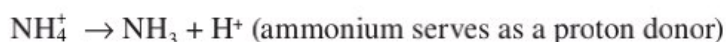
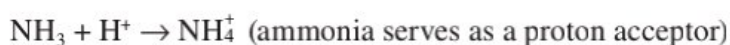
Therefore, HCl is an acid. However, after dissociation, the remaining  $\text{Cl}^-$  ion is then a base, because it can accept a proton. This type of acid–base pair is called a *conjugate pair*, with the  $\text{Cl}^-$  ion being the conjugate base of the acid HCl.

If HCl is dissolved in water, the following reaction occurs:



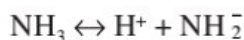
$\text{H}_3\text{O}^+$  was previously called a *hydronium ion*. Because hydronium is formed by adsorption of a proton by the water molecule, water is a proton acceptor. Consequently, water can be considered a base. The reaction to the left will not occur ( $\leftarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ ), because  $\text{H}_2\text{O}$  is a stronger proton acceptor than proton donor.

According to this proton concept, ammonia ( $\text{NH}_3$ ) is then a base, and the ammonium ion ( $\text{NH}_4^+$ ) is called an acid, because of their reactions as illustrated below:



As is the case with HCl, this ( $\text{NH}_4^+ - \text{NH}_3$ ) pair is also a conjugate acid–base pair, with  $\text{NH}_3$  as the conjugate base of the acid  $\text{NH}_4^+$ .

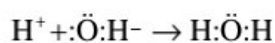
However, ammonia can also function as an acid, because it can dissociate according to the following reaction:



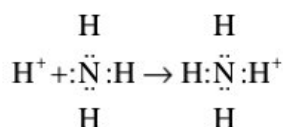
The amide ( $\text{NH}_2^-$ ) ion is the conjugate base to the acid  $\text{NH}_3$ . With a base stronger than itself,  $\text{NH}_3$  will behave as an acid, but with an acid stronger than itself, it will react as a base. Such a compound was previously called an amphiprotic compound.

### 10.2.3 THE LEWIS CONCEPT

According to this theory, also developed in 1923, an acid is a compound that can accept an electron pair (*electron-pair acceptor*). A base is a compound that can donate an electron pair (*electron-pair donor*). Hence, any substance that has an unshared pair of electrons is a base, and any compound that can react with that pair of electrons is an acid. This is also called the *electron concept*. The following serves as an example:



In this reaction, the  $\text{H}^+$  ion accepts an electron pair. The proton is then the acid and the bonding is called a *covalent bond*. The hydroxyl ion donates the electron pair and is considered the base. Another example is as follows:





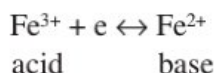
Again, the  $H^+$  ion accepts an electron pair and is the acid. Ammonia,  $NH_3$ , is then the base, because it donates the electron pair.

#### 10.2.4 THE USANOVICH CONCEPT

This concept that was developed by a Russian scientist, Michael Usanovich, in 1934 (Volpe and Siboni, 2006) is defined as follows:

1. Acid as a compound that reacts with a base, and in the process accepts electrons or anions or gives up cations.
2. Base as a compound that reacts with an acid, giving up electrons or anions or combines with cations.

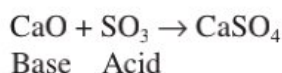
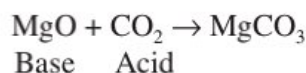
Usanovich is of the opinion that all compounds in the reduced state are bases, whereas all compounds in the oxidized state are acids. The following example illustrates Usanovich acid–base theory:



The reaction above shows the relationship of Usanovich's theory with the redox concept that was quoted in the literature by the confusing statement of an "overlap of the redox concept."

#### 10.2.5 THE LUX AND FLOOD CONCEPT

Herman Lux developed his acid-base concept in 1937 (Lux, 1939), which in 1947 was rediscovered by Hakon Flood (see Flood and Forland, 1947, p. 592). In their opinion, "an acid is an oxide ion acceptor, whereas a base is an oxide ion donor." This can be illustrated by Lux's (1939, p. 303) examples as follows:



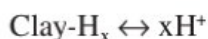
#### 10.2.6 THE PEARSON CONCEPT

Pearson (1963) developed the *HSAB* or *hard soft acid base concept* (see also Volpe and Siboni, 2006). *Hard* refers to a chemical species with a small radius, which is highly charged and weakly polarized, whereas *soft* refers to a chemical species with a large radius that is low in charge and strongly polarized. For example,  $H^+$  is a hard acid, whereas  $Ag^+$  is a weak acid. A hard base is  $OH^-$ , whereas a soft base is  $I^-$ . It finds occasional applications in transition metal chemistry and in ligand exchange reactions. This will be addressed in Section 12.1.

### 10.3 APPLICATION IN SOILS

In studying the three major theories, perhaps it can be noted that in the soil solution at one time both the Brønsted–Lowry and the Lewis theories can be applied. However, at another time, the Arrhenius and Brønsted–Lowry theories are more suitable to describe the condition. Reactions with clay minerals perhaps follow more the Brønsted–Lowry concept, whereas complex reactions involving organic matter apply only to the Lewis theory.

If clay can adsorb and dissociate protons as illustrated by the reaction:



where  $H_x$  is the number of adsorbed  $\text{H}^+$ , we can assume that soil clays can

1. Accept  $\text{H}^+$ : According to the Brønsted–Lowry concept, clay is then a base.
2. Dissociate  $\text{H}^+$ : Applying again the Brønsted–Lowry theory, clay is an acid.

Hence, clay behaves as an amphoteric compound.

## 10.4 FORMULATION OF SOIL ACIDITY AND ALKALINITY

### 10.4.1 Soil pH

The theories of Arrhenius and Brønsted–Lowry in combination must be applied to characterize acid and alkaline conditions in soils. In acid soils, more  $\text{H}^+$  than  $\text{OH}^-$  ions are present. On the other hand, a basic soil has in its soil solution more  $\text{OH}^-$  than  $\text{H}^+$  ions. A soil with a neutral reaction contains equal amounts of  $\text{H}^+$  and  $\text{OH}^-$  ions. To characterize these conditions, the term *soil pH* is used. The term pH was introduced by Sørensen in 1909 while he was working on problems in brewing beer, where the fermentation reactions involved are very sensitive to the  $\text{H}^+$  ion concentration. It is defined as:

$$\text{pH} = \log 1/(a_{\text{H}^+}) = -\log a_{\text{H}^+} \quad (10.1)$$

where  $a_{\text{H}^+}$  is the activity of  $\text{H}^+$  ions.

However, frequently, it is more convenient to use  $\text{H}^+$  ion concentration rather than activity. In dilute conditions  $a_{\text{H}^+}$  equals  $(\text{H}^+)$ , and Equation 10.1 becomes:

$$\text{pH} = \log 1/(\text{H}^+) = -\log(\text{H}^+)$$

where  $-\log = \text{p}$ .

A simple term, pH, is now available for describing soil acidity by saying only that the pH is 7, instead of saying the  $\text{H}^+$  ion concentration is  $1 \times 10^{-7} \text{ M}$ . Application of this pH concept in the *auto-protolysis* or dissociation of pure water gives the following relationships. As discussed in Chapter 4, the ion product of water is:

$$K_w = C_{\text{H}^+} \times C_{\text{OH}^-} = 10^{-14} \text{ at } 25^\circ\text{C}$$

By taking the  $-\log$ , this equation changes into:

$$-\log K_w = -\log C_{\text{H}^+} + -\log C_{\text{OH}^-} = -\log 10^{-14}$$

or

$$\text{p}K_w = \text{pH} + \text{pOH} = 14 \quad (10.2)$$

in which  $\text{p} = -\log$ .

Equation 10.2 states that  $\text{pH} + \text{pOH} = \text{constant}$ , and conversion of one into another is a simple matter. Therefore, in describing soil acidity or soil alkalinity, it is not necessary to determine both



pH and pOH. If pH is known, pOH, or the  $-\log$  of the hydroxyl ion concentration, can be calculated using Equation 10.2.

We can see from the formulations above that the pH concept or the term soil acidity describes both the  $H^+$  and  $OH^-$  ion concentrations. If the soil solution contains 1 mole of  $H^+$  ions per liter (or  $1 \times 10^{-0} M$ ), then the soil  $pH = -\log 10^{-0} = 0$ , which constitutes the extreme limit of soil acidity, and consequently,  $pOH = 14$ . This means that the soil is very strongly acid, because the concentration of hydroxyl ions is  $1 \times 10^{-14}$  mol/L, which is an extremely low concentration. However, the number of actual  $OH^-$  ions per liter is still large. Avogadro's number is  $6 \times 10^{23}$ , so a concentration of  $1 \times 10^{-14}$  mol/L corresponds to  $6 \times 10^9$   $OH^-$  ions, which is 6,000,000,000  $OH^-$  ions/L.

When, on the other hand, the soil solution contains 1 mole of  $OH^-$  ions per liter (or  $1 \times 10^{-0} M$ ), the  $pOH = 0$ , and the  $pH = 14$ , indicating the extreme alkaline limit of pH. In this case, the  $H^+$  ion concentration is extremely small, though the absolute number of  $H^+$  ions, amounting to  $6 \times 10^9$  ions per liter, is still large.

### 10.4.2 ACIDITY CONSTANT

According to the Brønsted–Lowry concept, the following acid–base relationship is valid:



This is a dissociation reaction; therefore, at equilibrium we have

$$K_A = [(H^+)(\text{base})]/(\text{acid})$$

in which  $K_A$  is the *acidity constant*. This was formerly called  $K_a$  or the ionization constant, but some books still use the term *acid dissociation constant*. Application of the pH concept in this equation gives:

$$pK_A = [pH - \log (\text{base})]/-\log (\text{acid})$$

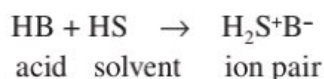
Rearranging gives

$$pH = pK_A + \log [(\text{base})/(\text{acid})]$$

This is the Henderson–Hasselbalch equation discussed in Section 4.13, and such a conclusion is supported by Anslyn and Dougherty (2005). The above derived equation also means that for a given ratio of concentrations (or activities) of an acid and its conjugated base, the pH has a fixed value (Novozamsky et al., 1976). When  $(\text{base}) = (\text{acid})$ ,  $\log[(\text{base})/(\text{acid})] = 0$ ; hence,  $pH = pK_A$ . In aqueous solutions, the  $pK_A$  generally ranges from  $\leq -2$  to  $\geq 12$ . A strong acid has a  $pK_A \leq -2$ , whereas a weak acid exhibits a  $pK_A$  between 2 and 7. On the other hand, a weak base is characterized by a  $pK_A$  between 7 and 10, whereas a strong base is characterized by a  $pK_A \geq 12$ . Consequently,  $H_3PO_4$ —a polyprotic acid with three  $K_A$  values—is a strong acid at  $K_{A1}$  but has to be considered a weak acid at  $K_{A2}$  and at  $K_{A3}$  falls even into the category of a weak base (see Section 4.16).

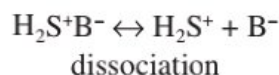
### 10.4.3 ACID STRENGTH AND ION PAIRS

The strength of an acid HB depends on the reaction of the acid with the solvent:



This reaction results in ionization of the acid and conjugated base. In most electrolytes, the resulting component ions do not completely dissociate from each other. The cations and anions are strongly attracted to each other, and a large part behaves as if it is not ionized. These ions present in association are called *ion pairs* (Davies, 1962). The degree of ionization is dependent on the relative alkaline strengths of the conjugated base and the solvent.

The dissociation of an ion pair into its component ions can be illustrated as follows:



The degree of dissociation depends on the dielectric constant of the solvent. The dielectric constant is the ratio of the capacity of an electric condenser in a vacuum and in the solvent,  $\epsilon = C_v/C_s$ .

By combining the two foregoing reactions, the dissociation constant ( $K_a$ ) of HB can be written as:

$$K_a = \frac{[(\text{H}_2\text{S}^+)(\text{B}^-)]}{[(\text{HB}) + (\text{H}_2\text{S}^+\text{B}^-)]}$$

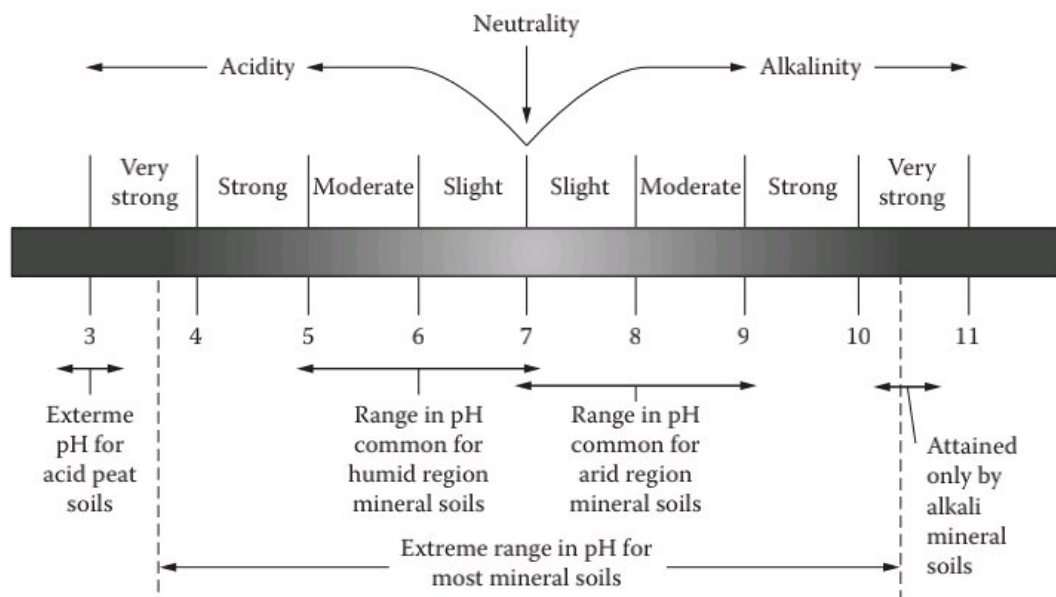
The value for  $K_a$  is used as a quantitative measurement of the strength of the acid.

## 10.5 CONCEPTS OF SOIL ACIDITY

### 10.5.1 SOIL pH RANGE

On the basis of their relative degree of acidity, the soils are divided into several acidity or alkalinity classes, as shown in Figure 10.1. As stated before, such a classification enables the use of proper terms for indicating acid–base conditions in soils. Instead of applying inaccurate terms, such as acid pH, neutral pH, basic pH, and the like, the use of the terms slightly, moderately, strongly, and very strongly acid (or basic) soil is more appropriate. By using them, the pH range is known.

Acid soils ( $\text{pH} < 7$ ) are usually common in humid regions. In these soils, the concentration of  $\text{H}^+$  ions exceeds that of  $\text{OH}^-$  ions. Most plants grow best in soils with a slightly acid reaction. In this pH range, nearly all plant nutrients are available in optimal amounts. Soils with a  $\text{pH} < 6$  will



**FIGURE 10.1** Soil pH ranges and soil reaction classes. (From Brady, N. C., *The Nature and Properties of Soils*, 8th ed., Figure 17-3, 463, MacMillan, New York, 1974. Reprinted and electronically produced by permission of Pearson Education, Inc., Upper Saddle River, NJ.)



more likely be deficient in some of the available nutrients for optimal plant growth. Calcium, Mg, and K are especially deficient in acid soils. In strongly and very strongly acid soils, Al, Fe, and Mn may exist in toxic quantities because of their increased solubilities. In addition, these elements will react with phosphates to form insoluble phosphates, as discussed in Section 9.3, on phosphate retention and fixation. Alkaline soils ( $\text{pH} > 7$ ) occur mostly in semiarid to arid regions. Because of the alkaline reaction, the soils contain low amounts of soluble Al, Fe, and Mn, due to formation and subsequent precipitation of insoluble Al, Fe, and Mn hydroxides. The micronutrients, Fe, Mn, Cu, and Zn, are usually unavailable or are available in quantities insufficient for plant growth. Severe micronutrient deficiency will most likely occur in moderately to strongly basic soils. In general, high pH and available Ca content are closely related, but there are exceptions, especially when Na is present. In strongly alkaline soils, phosphate fixation is again a problem due to formation of insoluble tricalcium phosphates.

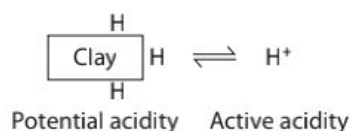
### 10.5.2 ACTIVE VERSUS POTENTIAL ACIDITY

A number of compounds contribute to the development of acidic and basic soil reactions. Inorganic acids and organic acids, produced by the decomposition of soil organic matter, are common soil constituents that may affect soil acidity. Water is a source for a small amount of  $\text{H}^+$  ions. Autoprotolysis of water yields hydronium ions in concentrations of  $1 \times 10^{-7}$  moles per liter (at  $25^\circ\text{C}$ ). Respiration of plant roots yields  $\text{CO}_2$  that will produce  $\text{H}_2\text{CO}_3$  in water. Nitrification is an additional biochemical source for  $\text{H}^+$  ions in soils. Cation exchange reactions are often considered to make the soils more acid by loosing bases through exchange with  $\text{H}^+$  ions already present in soils, but cation exchange is neither a source nor a producer of  $\text{H}^+$  ions. Through the loss of bases by exchange, it is accumulating  $\text{H}^+$  ions, and therefore affecting reserve acidity.

The  $\text{H}^+$  ions may be present in soils as adsorbed  $\text{H}^+$  ions on the surface of the colloidal complex, or as free  $\text{H}^+$  ions in the soil solution. The portion of  $\text{H}^+$  ions adsorbed by the clay complex becomes exchangeable  $\text{H}^+$  ions. The exchangeable  $\text{H}^+$  ions dissociate into free  $\text{H}^+$  ions, and the amount adsorbed is usually in equilibrium with the amount free in solution. The chemical conditions created produce a chemical environment showing two types of soil acidities, as illustrated in Figure 10.2.

The types of  $\text{H}^+$  ions and the degree of ionization and dissociation into the soil solution determine the nature of soil acidity. The adsorbed, reserve, or exchangeable  $\text{H}^+$  ions are the reasons for the development of *potential*, *reserve*, or *exchange acidity*. The magnitude of the latter can be determined by titration of the soil. The free  $\text{H}^+$  ions create the *active acidity*. Active acidity is measured and expressed as soil pH. This is the type of soil acidity upon which plant growth reacts. However, the tendency exists today to call this exchange acidity *salt replaceable acidity*, which is related especially to exchangeable  $\text{Al}^{3+}$  that can be replaced by unbuffered salt solutions (e.g., KCl) (Chesworth, 2008). However, this is more a type of *potential acidity* because it requires hydrolysis of  $\text{Al}^{3+}$  to produce the  $\text{H}^+$  ions that are the true sources for soil acidity.

Taken together, the active and potential acidity make up the *total soil acidity*. The free  $\text{H}^+$  ion concentration of the soil solution at any particular time is relatively very small compared to the reserve or exchangeable  $\text{H}^+$  concentration. Most soil chemists indicate that the potential acidity may be 1000 times greater than the active acidity in acid sandy soils, and it may be even 50,000 to



**FIGURE 10.2** Relationship between active acidity and potential acidity. The latter is also called reserve or exchange acidity, because adsorbed  $\text{H}^+$  ions are  $\text{H}^+$  ions in reserve and are at the same time exchangeable.



100,000 times larger in acid clayey soils. In humid region soils, the removal of bases from the colloidal material, especially calcium, occurs constantly through ion exchange. Rainfall is sufficiently high to provide large amounts of water for leaching most of the bases from the soil. Their places on the colloidal complexes are taken by  $H^+$  ions.

The soil pH can be influenced only when sufficient amounts of lime are added to neutralize the total acidity. The greater the cation exchange capacity of the soil, the greater the reserve or potential acidity, and the more difficult it is to reduce the total acidity. This resistance to change in soil reaction is called the *buffer capacity*.

Brady and Weil (1996) reported a third type of soil acidity that they called *residual acidity*. It is defined as soil acidity that remains after active and exchange acidity have been neutralized. They believe that residual acidity is associated with aluminum hydroxy ions and with  $Al^{3+}$  and  $H^+$  ions that are bound in nonexchangeable forms by organic matter and silicate clays. Chesworth (2008) calls this “the remaining soil acidity that cannot be replaced by an unbuffered salt solution” (p. 10).

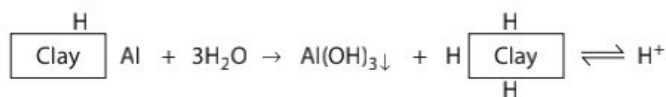
Aluminum hydroxy ions  $Al(OH)^{2+}$  and  $Al(OH)^+$  are the products of hydrolysis of  $Al^{3+}$  ions, which in turn are subject to hydrolysis, releasing  $H^+$  ions during the reaction. This will be discussed in detail in Section 10.5. According to current concepts, aluminum ions and their hydrolysis products are the primary sources of  $H^+$  ions in soils for both active and potential acidity. If free  $Al^{3+}$  ions can be considered contributors to the creation of residual acidity, then their hydrolysis products will also be important substances affecting in a similar fashion residual acidity. Nonexchangeable Al bound by organic matter is perhaps the only source for production of  $H^+$  ions creating the residual acidity. However, it is subject to many arguments, because this Al is known to be present in chelate form, and the stability of Al-humic acid chelates is pH dependent. Hydrolysis of chelated  $Al^{3+}$  depends upon its release into free  $Al^{3+}$  ions. In clay minerals, the only nonexchangeable bound Al is structural Al in the octahedrons, which can only be released after saturation of the clay complex with  $H^+$  ions. This reaction will cause a gradual destruction or decomposition of the clay mineral and is likely to occur only in extreme acid reactions not normally found in ordinary soil conditions. On the other hand, the substitution of Ca and Mg for octahedral Al or, in other words, the destruction of clay minerals by liming, has not been known to occur.

The most important types of nonexchangeable  $H^+$  ions bound to soil organic matter are the OH groups in carbohydrates, which do not contribute to production of  $H^+$  ions to any appreciable extent. However, the functional groups of humic acids and other organic acids can dissociate their  $H^+$  ions. Such dissociation is dependent upon pH and was discussed in detail in Section 5.9.

Nonexchangeable  $H^+$  ions bound to clay minerals are present as structural OH groups attached to the Al octahedrons. Only at high pH values will the exposed OH groups dissociate their hydrogen atoms. It is not yet known whether the nonexposed OH groups, located in the interior of the crystal, are also subject to a similar dissociation reaction. Dissociation of exposed OH groups on mineral surfaces was discussed in Chapter 6 as the major reason for the development of variable negative charges. They are, therefore, exchangeable at high soil pH. Whether the release of these  $H^+$  ions contributes to the residual acidity is a matter of conjecture.

### 10.5.3 NONSELECTIVE AND PREFERENTIAL ADSORPTION OF HYDROGEN IONS BY SOILS

Bolt (1976) distinguishes two types of adsorption of  $H^+$  ions by soil colloids—*nonselective* and *preferential adsorption*. Soil colloids, such as clay, adsorb  $H^+$  ions by the nonselective process. They accumulate on the charged surface as a swarm of counterions. The relative proportion can be estimated with the Gapon equation. Nonexchangeable  $H^+$  ions bound to clay are only present as structural OH groups attached to the Al octahedrons in the clay mineral. As indicated before, these hydroxyl groups, when exposed on the surface of the mineral, can dissociate their  $H^+$  ions at very high pH, increasing in this way the negative variable charges of the clays. In contrast to clay



**FIGURE 10.3** Theoretical reaction of the release of Al from a H–Al–clay, producing H<sup>+</sup> ions.

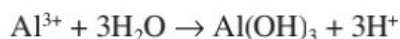
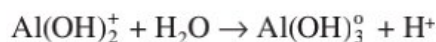
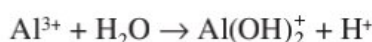
minerals, organic colloids exhibit preferential adsorption of H<sup>+</sup> ions. The organic compounds contain acidic groups, such as carboxyl and phenolic hydroxyl groups, which are highly selective for association with protons. The adsorbed H<sup>+</sup> ions are, then, considered part of the functional groups, and are located on the surface. Bolt (1976) considered them more difficult to exchange against other cations. It was shown that the exchange reaction is pH dependent.

## 10.6 THE ROLE OF ALUMINUM IN SOIL ACIDITY

Most clay particles interact with H<sup>+</sup> ions. Evidence is available that hydrogen-saturated clay undergoes a spontaneous decomposition. The hydrogen ion penetrates the octahedral layer and replaces the Al atoms. The Al released is then adsorbed by the clay complex and a H–Al–clay complex is formed rapidly. The Al<sup>3+</sup> ions may hydrolyze and produce H<sup>+</sup> ions as illustrated in the reaction shown in Figure 10.3. This reaction contributes toward increasing the H<sup>+</sup> ion concentration in soils. The magnitude of the change in pH is related to the Al concentration expressed in terms of the *aluminum potential*, pAl, which can be explained as follows. The exact reaction processes of hydrolysis of free Al<sup>3+</sup> ions are, however, more complicated than illustrated in Figure 10.3, because Al<sup>3+</sup> cannot exist as a free ion too long. As soon as an Al<sup>3+</sup> ion is present in the soil solution, it is quickly surrounded by six molecules of H<sub>2</sub>O in octahedral coordination, forming Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. This ion is called an *aluminum hexahydronium ion*, which is the Al compound that undergoes hydrolysis:



The hydrolysis process continues further in a stepwise process according to the reactions as illustrated below. For simplicity, the Al monomers are customarily written in these reactions without their coordinated water:



Applying the mass action to the total or final reaction above gives:

$$K_h = [\text{Al}(\text{OH})_3](\text{H}^+)^3 / [\text{Al}^{3+}(\text{H}_2\text{O})^3]$$

where  $K_h$  is the hydrolysis constant. By considering Al(OH)<sub>3</sub> and H<sub>2</sub>O pure compounds at standard states, their activity equals unity. Hence, the equation can be converted into:

$$K_h = (\text{H}^+)^3 / (\text{Al}^{3+})$$



By taking  $-\log$ , the equation becomes:

$$-\log K_h = -\log (H^+)^3 - [-\log (Al^{3+})]$$

Substituting p for  $-\log$  gives:

$$pK_h = 3pH - pAl^{3+}$$

or

$$3pH = pK_h + pAl^{3+}$$

Division by 3 gives:

$$pH = \frac{1}{3}pK_h + \frac{1}{3}pAl^{3+}$$

The equation above, commonly called the *aluminum potential*, shows the relationship between pH and Al activity in soils. The degree of change in soil pH is, accordingly, dependent upon the aluminum concentration as expressed in terms of the aluminum potential. Once again, the author realizes that the equations above have been derived from ion activity products; hence, the term *aluminum potential* may not be acceptable for some (Chesworth, 2008). However, the name is now common knowledge and is used by most soil scientists as is the case with the *phosphate potential*. (See Section 9.7.3.) But in all fairness, the term *potential* not only relates to electric charges as implied by Chesworth (2008), but it also has the connotation of various degrees of possibilities capable of developing into actuality (*Merriam-Webster*, 1973). In this case, it is possible to determine the pH from the Al activity values; in other words, the equation has the potential to be used in predicting soil pH.

Polymerization of the Al-monomers,  $Al(OH)^{2+}$ , yields dimeric Al-hydroxides (Figure 10.4). As illustrated in Figure 10.4, oxolation reaction of Al-hydroxide polymers also increases the  $H^+$  ion concentration of the soil solution.

From the discussion above, it is clear that monomeric aluminum ions ( $Al^{3+}$ ) adsorbed electrostatically on the negatively charged surfaces of clay minerals can be released by exchange with other cations. They hydrolyze in solution, forming a series of Al-hydroxy compounds while releasing protons at the same time. The hydrolysis products are reabsorbed by the clay minerals, causing increased hydrolysis and production of more  $H^+$  ions. Acid soils are, therefore, high in soluble aluminum accompanied by a complex series of its hydrolysis products in the form of Al-hydroxy substances. As indicated above, the degree of change in pH is controlled by the aluminum potential. In line of this concept, Kennedy (1992) presents a hypothesis that aluminum compounds in acid soils are in fact pH buffers. Free  $Al^{3+}$ , released by exchange of adsorbed Al into the soil

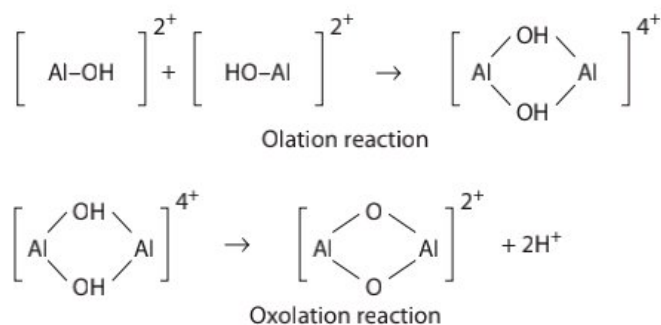
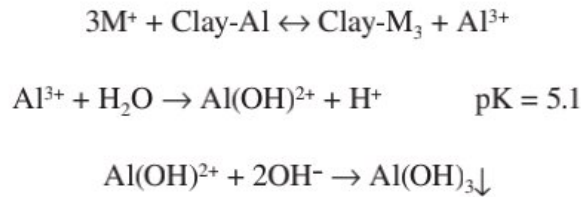


FIGURE 10.4 Polymerization of aluminum monomers.

solution, yields  $H^+$  upon hydrolysis. When the latter is not reabsorbed on the clay complex, but instead is neutralized by liming, the aluminum hydroxy ions are precipitated as insoluble aluminum hydroxides:



However, more  $H^+$  ions can be produced if more Al can be released from the exchange sites to replace the amounts lost, and the soil pH then remains unaffected. Therefore, exchangeable Al concentration can be considered as a source of *reserve acidity* in the same sense as the concept of reserve acidity based on exchangeable  $H^+$  concentrations. Because the hydrolysis of aluminum hydroxy compounds occurs at  $\text{pK} = 5.1$ , the buffering effect is felt at a soil  $\text{pH} \leq 5.1$ .

Kennedy (1992) believes that similar reactions are valid for  $\text{Fe}^{3+}$  ions. Free  $\text{Fe}^{3+}$  ions, released into the soil solution from the exchange sites on the clay surfaces, are also important sources of protons. When these protons happen to be neutralized by liming, the soil pH can only be maintained if more Fe can be moved from the exchange sites into the soil solution. Because the hydrolysis of  $\text{Fe}^{3+}$  occurs at a  $\text{pK}$  equal to 2.2, the buffering effect occurs at even lower soil pH values, and hence is unrealistic or nonpractical for normal soils.

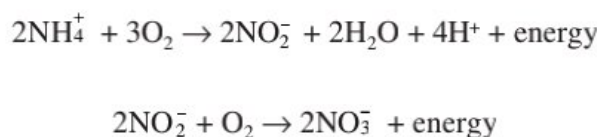
In view of the basic principles in aluminum chemistry as discussed above, it is perhaps accurate to say that the aluminum monomers, dimers, and polymers are more important in affecting potential and active acidity, rather than affecting residual acidity.

## 10.7 THE ROLE OF FERTILIZERS, SULFUR, PYRITE, N FIXATION, AND ACID RAIN IN SOIL ACIDITY

In addition to the aforementioned processes, both potential and active acidity can also be increased by human activities in agriculture and industry. The use of fertilizers to increase crop production in agriculture, the production of *mine spoils* containing pyrite in the coal industry, and emission of pollutant gases contributing to acid rain by the factories and power plants are *anthropogenic sources of  $H^+$  ions*.

### 10.7.1 AMMONIUM FERTILIZERS

Rising demands in food production pressurized by the rapidly increasing world population have stimulated the use of fertilizers. On the basis of their effect on soil pH, chemical fertilizers can for convenience be distinguished into *acid-forming*, *basic-forming*, and *neutral* fertilizers. All ammonium fertilizers are acid-forming fertilizers, because they decrease the soil pH. Basic-forming fertilizers, on the other hand, such as  $\text{NaNO}_3$ , may increase soil pH, and the application of neutral fertilizers has no effect on pH. Large applications of ammonium fertilizers are increasing the  $H^+$  concentrations in soils. In a normal healthy soil, ammonium ions will be attacked by microorganisms and oxidized into nitrate ions according to the following reactions:





As indicated in an earlier chapter, the oxidation of ammonium into nitrate, called *nitrification*, occurs in two steps. In the first step, the conversion of ammonium into nitrite, by the bacteria *Nitrosomonas* sp., produces four protons (see the first reaction above), which may increase soil acidity. In the second and final step, nitrite is oxidized into nitrate by the *Nitrobacter* sp. bacteria. Sparks (2002), quoting data from the literature, indicated that soil acidification due to nitrification of applied N to the amounts of 50 to 200 kg N per ha was 4 to 16 times greater than the effect of acid rain. Unfortunately not much more information is available on the effect of nitrification on soil pH, and only a few researchers have addressed it casually (Gowariker et al., 2009; Rengel, 2003). On the other hand, the literature abounds with studies of the effect of pH on the process of nitrification.

### 10.7.1.1 Equivalent Acidity and Acidity Index

The amount of acidity created by commercial fertilizers is usually expressed in terms of *equivalent acidity*, which is defined as the amount of lime required per unit amount of fertilizers used to bring the soil pH back to prefertilizer application levels. This is also called the *acidity index* by Gowariker et al. (2009) and should not be confused with the *acidity constant* (see Section 10.4.2). Values for equivalent acidities of major chemical fertilizers are shown in Table 10.1. As can be noticed, the values of equivalent acidities can be positive or negative in sign. For example, the equivalent acidity of ammonium nitrate equals 593. This means that the use of 1000 kg (or 2000 lb) of  $\text{NH}_4\text{NO}_3$  will decrease the soil pH to a point where 593 kg (or 1188 lb) of lime ( $\text{CaCO}_3$ ) are needed to restore the original pH. Therefore, the equivalent (or potential) acidity of 1000 kg (or 1 ton equals 2000 lb) of ammonium nitrate equals 593 (or 1188).

In contrast, the equivalent acidity of  $\text{NaNO}_3$  is  $-292$  (or  $-583$ ), which means that the use of 1000 kg (or 2000 lb) of  $\text{NaNO}_3$  will increase the pH to a point that (literally) 292 kg (or 583 lb) of  $\text{CaCO}_3$  must be taken out of the soil to restore soil pH to prefertilizer level.

Kennedy (1992) believes that nitrification of nitrogenous fertilizers will increase soil acidity, but never to the full extent expected from the nitrification reactions. Only one-half of the acidity expected from the nitrification reaction will be developed. This is caused by (1) the simultaneous uptake of nitrogen by plants (e.g., nitrate), (2) loss of  $\text{NH}_3$  by volatilization from soil, and (3) denitrification. Denitrification processes consume one proton per nitrate converted to  $\text{N}_2$ .

**TABLE 10.1**  
**Equivalent Acidity of Major Commercial Fertilizers**

Fertilizer	Equivalent Acidity	
	Per 1000 kg	Per 2000 lb
Ammonium nitrate, $\text{NH}_4\text{NO}_3$	593	1188
Ammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$	724	1450
Anhydrous ammonia, $\text{NH}_3$	70	140
Muriate of potash, $\text{KCl}$	—	—
Nitrate of soda, $\text{NaNO}_3$	$-292$	$-583$
Sulfate of ammonia, $(\text{NH}_4)_2\text{SO}_4$	1099	2200
Sulfate of potash, $\text{K}_2\text{SO}_4$	—	—
Superphosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$	—	—
Urea, $\text{CO}(\text{NH}_2)_2$	749	1500
Triple superphosphate	—	—

### 10.7.2 PHOSPHATE FERTILIZERS

Application of monocalcium phosphate and superphosphate is also noted to increase soil acidity, although their equivalent acidity values are not listed in Table 10.1. Hydrolysis of superphosphate will yield orthophosphoric acid:



Being an acid, o-phosphoric acid will dissociate its proton in the soil solution, which decreases soil pH. The effect will occur particularly in soils where superphosphate is applied in bands. In crop production, the acidification effect is considered a temporary effect (Kennedy, 1992), because eventually the phosphate concentration will be reduced by plant uptake, or leaching, or by sorption and fixation reactions.

The use of superphosphate may also be of advantage in reducing the pH of alkaline soils and in buffering against increasing alkalinity.

### 10.7.3 ELEMENTAL SULFUR

Elemental sulfur, S, has often been used in crop production and horticultural operations to produce an acid growing environment needed by certain plants. The soils in tea plantations are frequently acidified by adding sulfur, and soils for growing azaleas, rhododendrons, and blueberries often received treatments of  $\text{FeSO}_4$ . Oxidation of sulfur produces sulfuric acid, which increases the  $\text{H}^+$  ion concentration in the soil solution. The oxidation reaction can be illustrated as follows:

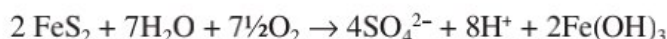


In soils, such a reaction is made possible by the presence of sulfur-oxidizing bacteria. In addition to creating acid media for acid-loving plants, the use of S to decrease soil pH is often desirable in alkaline and saline soils. In this case, elemental S is usually applied in combination with fertilizers, such as *S-coated urea*.

Emission of sulfur in the atmosphere by natural causes or by industry is a major contributor of acid rain, which will be discussed in a later section.

### 10.7.4 PYRITE ( $\text{FeS}_2$ )

Oxidation of pyrite,  $\text{FeS}_2$ , a sulfur mineral, produces sulfuric acid,  $\text{H}_2\text{SO}_4$ , which dissociates its protons in the soil solution. The reaction can be illustrated as follows:



This reaction produces eight protons and contributes toward increasing soil acidity. According to Stevenson (1986), the oxidation of pyrite is partly chemical and partly biochemical and yields  $\text{FeSO}_4$ , not  $\text{Fe}(\text{OH})_3$  as shown by the reaction above.

The process is of special importance in soils of coastal regions affected by the tide, and in soils derived from *mine spoils* or *mine tailings*. Drainage of tidal marshes causes oxidation of  $\text{FeS}_2$ . The sulfates from seawater are the sources of sulfides in the deltaic and coastal marshes. In inland swamps, the sulfides are derived from oxidation of sulfates from the surrounding rocks.

Coal contains large amounts of sulfur in the form of pyrite and organic sulfur. The residue of coal mines, called *mine spoil*, left behind on the land is rich in pyrite, which is subject to oxidation



in nature, creating extremely acid conditions in soils. One recent dramatic example of this problem is the pH reported of soils derived from mine spoils in Hungary, which was in the range of  $\text{pH}_{\text{KCl}} = 3.20$  to  $3.26$  (Simon, 2005). Compounded by the Cd, Cu, Pb, and Zn toxic concentrations of 7.1, 120, 2154, and 605 mg/kg, respectively, the soil was a real head-sore for crop production. However, Simon (2005) reported that by adding lime to increase the soil pH to 5, the soil became suitable for use as potting soil. Simon also claimed that *phytostabilization* of the toxic metals by growing red fescue have reduced the risk considerably of contaminating the food chain. What he meant was *phytoextraction*—a category of *phytoremediation* of soils—of the toxic elements by red fescue (see Tan, 2009).

The use of coal as an energy source will also oxidize the pyrite minerals and the organic sulfur, increasing emission into the atmosphere of sulfur dioxide gas. The latter is known to be an important contributor to acid rain, as will be discussed in Section 10.6.6.

### 10.7.5 BIOLOGICAL NITROGEN FIXATION

The effect of biological nitrogen fixation on soil acidity is a controversial issue. Most people realize the impact of soil pH on biological N fixation, in particular by legumes, but not the other way around. These legumes and their root rhizobia are generally very susceptible to soil pH and are noted to grow well only at the pH range of 5 to 8 (Leigh, 2002). The perception that biological nitrogen fixation increases soil acidity originates from growing legume-based pastures in Australia. The soils in areas with significant winter rainfall have been noted to become strongly acidic after growing legume-based pastures for an extended period of time. Kennedy (1992) believes that ammonia levels increase considerably in the soil due to ammonification of organic-N from nitrogen fixation. In a soil ecosystem where the level of inorganic nitrogen is in excess to that needed by the growing plants, this excess of ammonium will be nitrified, adding significant amounts of  $\text{H}^+$  ions to the soil solution. Kennedy (1992) argues that the process of nitrogen fixation alone does not contribute directly toward increasing the  $\text{H}^+$  ion concentration in soils, but it is the product in the form of organic-N released into the soil that has precisely a similar effect as the reaction of acid-forming fertilizers.

### 10.7.6 ACID PRECIPITATION

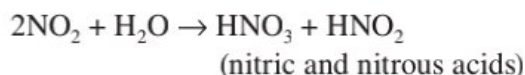
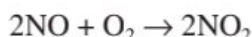
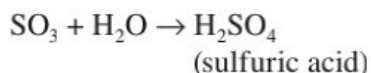
Acid precipitation, also known as *acid rain*, is caused by the conversion of nitrogen oxide and sulfur dioxide gases into strong acids. Alewell (2003) calls it also *acid deposition* and defines it as “the acidification of soils and the ecosystem by the acid input from the atmosphere due to human activities by burning fossil fuel” (p. 83). However, it should be realized that the process creating acid rains can also involve natural processes that occur frequently during thunderstorms and in regions with active volcanism. Wildfires and bushfires also contribute to the emission of gases contributing to acid rain. Carbon monoxide, nitrogen oxide, and sulfur oxide gases are released into the air by all of these activities and contribute to acid rain and acid soils in the region. However, emission of these pollutant gases into the atmosphere by human activity is often in excess to that created by natural causes and is today one of the most urgent issues of the century. The enhanced and continuous production of unwanted gases, generated by the combustion of fuel from motor vehicles, electric power production, space heating and cooling, and disposal of refuse, has become of global concern. In the United States alone, it was estimated, in 1965, that those anthropogenic processes have produced and released into the air 72 million tons of carbon monoxide, 26 million tons of sulfur dioxides, and 13 million tons of nitrogen oxides (Manahan, 1975, 2009). Kennedy (1992) quotes that nitrogen oxides are produced at the rate of 50 million tons annually. In central Europe, anthropogenic emissions of pollutant gases exceed natural emissions by a factor of 10. In clean air, nitric oxide is known



to have a half-life of a few days, but in polluted air it may be converted rapidly into nitrogen dioxide, which is soluble in water.

These gases are very harmful to the environment, plant growth, and human health. Carbon monoxide is very toxic for animals and human beings. It displaces oxygen from hemoglobin and reduces the capacity of blood to carry oxygen. The latter results in suffocation. Exposure to high levels of sulfur dioxide gas may cause *leaf necrosis* in plants. There is now evidence that nitrogen oxide gases, produced not only by industry but also by supersonic and space transport, may be harmful to the ozone layer of the stratosphere. From the standpoint of acid rain, carbon monoxide is of less significance than sulfur dioxides and nitrogen oxides.

Oxidation of sulfur dioxides and nitrogen oxides in the air and subsequent dissolution of the oxidation products in raindrops produce sulfuric acids, nitric acids, and their salts. Not only are these acids very corrosive, but they also result in a decrease in pH of the rainwater. The salts of these acids have been implicated in the formation of *turbid haze* or fog covering industrial towns in the Midwest and California. The processes of formation of acids can be illustrated by the following reactions:



These reactions are, in reality, very complex, and it is believed they are catalyzed by the presence of ozone. Sulfuric, nitric, and nitrous acids are strong acids and will dissociate their protons in water droplets of fog or rain. Because of this, the pH of rainwater or water in fog may decrease to two or lower. However, until now a lot of confusion existed on the pH as a result of acid rain. As of 2000, acid rain in the United States is considered to have a pH of  $\pm 4.3$  (Tan, 2009). The deposition of these acids in cloud and fog water is called by Alewell (2003) *occult deposition*. Alewell also distinguished between (1) *wet deposition*, which pertains to the above, and (2) *dry deposition*, which he defines as “the transport from the atmosphere of particulates and gaseous contaminants directly on land, water and plant surfaces in the absence of real precipitation or rain” (p. 83).

Acid rain has become of increasing concern today in Europe and North America because of the *die-back* of forest trees, a harmful process also known as *forest decline*. Acid rain has been implicated in defoliation of the forest in Germany, though direct evidence has not been presented. Development of fine roots in Scandinavian spruce has been noted to be restricted in the surface soil because of increased soil acidity. Yellowing of the needles and thinning of the crowns were thought to be symptoms of chronic water stress and magnesium deficiency as a result of the degrading environment (Kennedy, 1992). This yellowing of spruce needles has also been noted in the early 1970s in Czechoslovakia and the *Fichtelgebirge* of Northeast Bavaria (Germany) as the result of Mg deficiency. However, it is more likely that all these symptoms are caused by Al toxicity, due to increased solubility of alumina compounds in acid soils. Reports have also indicated that the increased acidity of lake water in the Adirondacks of the United States, because of acid rain, has contributed to *fish kill*, because most fish are sensitive to pH below 4.5. Key organisms of the food chain supporting lake trout will disappear at pH 5.8, whereas the ability of fish to reproduce may be impaired as early as pH 5.8 (Kennedy, 1992). Because of reproductive failure, salmon and brown trout are expected to disappear altogether at pH 5. However, the Great Lakes have been reported to possess an internal buffer capacity. The buffering reaction is a biological process through respiration of



nitrate (denitrification) and sulfate. The rate of buffering is noted to be proportional to the sulfate and nitrate concentration in lake water (Kennedy, 1992).

The effect of acid rain is of a less serious nature in soils than in lake water. Soils exhibit a cation exchange capacity (CEC) that provides them with a buffering complex to adsorb the excess protons from acid rain. However, prolonged impact by acid rain can saturate the buffer capacity of soils, which eventually increases soil acidity. This is especially critical in sandy soils that are weakly buffered by nature. Soils of calcareous origin may be able to neutralize the effect of acid rain due to its high pH and high base content. Alewell (2003) believes that the acid input to soils under forest cover is also affected by what he calls *canopy interaction*, which involves *through-fall*—water dripping down from tree canopies—and *stem flow*. The author claims that leaching of nutrients from through-fall and stem flow is far greater than by incident rains.

Two methods were proposed to control the effect of acid rain on soil acidity: cleaning the emissions in industry and in motor vehicles and liming the soils, or both. For example, the primary source of enhanced production of sulfur dioxide gas is coal. The sulfur in the coal is present as pyrite,  $\text{FeS}_2$ , and as organic sulfur. Upon burning of the coal, the pyrite minerals are oxidized and sulfur dioxide is produced as discussed above. Removing the S from the coal before use in the ovens to keep sulfur dioxide emissions at relatively low level is an option, but it is still a costly process. The effect of acid rain in soils is usually controlled by liming the soils. In Scandinavia, acidification of lakes is neutralized by spraying lake water with  $\text{CaCO}_3$  or  $\text{Ca(OH)}_2$  slurries.

## 10.8 BUFFERING CAPACITY OF SOILS

Chemically, a buffer solution is defined as one that resists a change in pH on addition of acid or alkali. Buffer solutions contain compounds that react with acid or base so that the  $\text{H}^+$  ion concentration in the solution remains constant. In soils, the clay and humic fractions act as a buffer system. As discussed previously, the soil cation exchange complex creates the development of active and potential acidity. The potential acidity will maintain the equilibrium with the active acidity. If the active  $\text{H}^+$  ion concentration is neutralized by the addition of lime, the potential acidity will release exchangeable  $\text{H}^+$  ions into the soil solution to restore the equilibrium, and no change in soil reaction occurs until the reserve in  $\text{H}^+$  is exhausted. The magnitude of the potential acidity usually far exceeds that of the active acidity. It was noted that in sandy soil, reserve acidity was 1000 times greater than active acidity. In clay soils with high organic matter content, reserve acidity was even 50,000 to 100,000 times greater than active acidity. Therefore, buffering capacity is greater in clay soils than in sandy soils. The larger is the buffer capacity, the larger is the amount of lime needed to raise the soil pH to the desired level.

The concept of buffering capacity of soils is not limited to the soil's resistance to changes in soil reaction. The soil can also act as a filter for dissolved and colloidal contaminants. It may act as a sieve, or during the passage through the topsoil, the aerated condition may oxidize and mineralize, in particular, the organic compounds. The ions released by mineralization are adsorbed by the soil's adsorption complex and prevented from reaching the groundwater.

## 10.9 ELECTROMETRIC MEASUREMENT OF SOIL pH

The determination of soil pH is now conducted with a glass electrode. It consists of a thin glass bulb containing dilute HCl, into which is inserted an Ag-AgCl wire, serving as the electrode with a fixed voltage (Figure 10.5). When the glass bulb is immersed in a soil solution, a potential difference develops between the solution in the bulb and the soil solution outside the bulb. This potential  $E$  is formulated by the *Nernst equation*:

$$E = (RT/nF) \log (K/M^{n+})$$

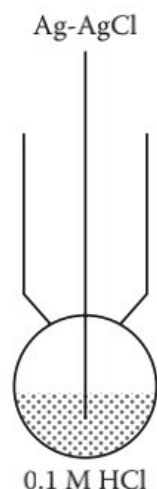


FIGURE 10.5 A schematic diagram of a glass electrode.

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $n$  is the valence,  $F$  is the Faraday constant,  $K$  is a constant, and  $M$  is the activity of ions to be measured with  $n+$  valence.

$E$  is called the *half-cell potential* and cannot be measured alone. If the glass electrode is placed against a reference electrode (usually a calomel electrode), the potential difference between the two ( $E - E_{\text{cal}}$ ) is measurable.

Before any pH measurement, the two electrodes have to be placed first in a solution of known pH (e.g., usually a solution with a  $\text{H}^+$  ion concentration = 1 g/L). This is called *standardizing* the electrodes and the pH meter. The overall potential of the total cell  $E_o$  equals  $E - E_{\text{cal}}$  and is formulated as follows:

$$E_o = [(RT/F) \log (K/1)] - E_{\text{cal}} \quad (10.3)$$

If the two electrodes are now placed in the solution with the unknown  $\text{H}^+$  ion concentration, the potential  $E_c$  is:

$$E_c = [(RT/F) \log (K/\text{H}^+)] - E_{\text{cal}} \quad (10.4)$$

Subtracting Equation 10.3 from Equation 10.4 gives

$$E_c - E_o = (RT/F) [\log (K/\text{H}^+) - \log K]$$

$$E_c - E_o = (RT/F) \log (1/\text{H}^+)$$

or

$$E_c - E_o = (RT/F) \text{pH}$$

Because  $RT/F = 0.0591$  at  $25^\circ\text{C}$ ,

$$\text{pH} = (E_c - E_o)/0.0591 \quad (10.5)$$

This means that for a change of one pH unit, the potential will change with 0.0591 volts. The soil pH can be measured in several ways. It can be measured in a water extract of soil, aqueous soil suspension, KCl-soil suspension, or  $\text{CaCl}_2$ -soil suspension.



### 10.9.1 MEASUREMENT OF pH IN WATER EXTRACT

Soil and water are mixed in a 1:1 or 1:2 (weight/volume) ratio and stirred thoroughly for 15 minutes, after which the supernatant is collected by centrifugation for pH measurement. The pH value obtained usually increases with increased volume of water used. The increase in pH is caused by the dilution of the  $H^+$  ion concentration in the solution. Therefore, the smallest soil/water ratio that can be used without producing technical difficulties is preferred in this method of pH measurement.

### 10.9.2 MEASUREMENT OF pH IN SOIL SUSPENSION

Soil and water are also mixed in a 1:1 or 1:2 ratio and then stirred for 15 minutes, after which the pH is directly measured in the soil suspension. As with the previous method, the value obtained will also change with increased dilution by the use of wider soil/water ratios. Some workers prefer to use a saturated soil paste. However, in sandy soils the contact between the electrode and the soil solution is decreased, and the chance to damage the electrode is increased. The value obtained is considered to be closer to the true pH value in nature than the supernatant pH. It is often lower in value than the soil pH measured in its supernatant solution. This is caused by the suspension effect, which will be discussed below.

### 10.9.3 MEASUREMENT OF pH IN A KCl SOLUTION

For this method, the soil is mixed with a 1 M KCl solution in a 1:1 or 1:2 ratio. The pH is measured directly in the soil suspension. This type of measurement will yield a more stable result than with the two other previously discussed methods. It is sometimes referred to as the *buffered pH*. In acid soils, the pH value obtained is usually lower than that measured with the other methods above. The use of  $pH_{KCl}$  will provide better information concerning the chemical properties of the system (Moore and Loeppert, 1987). It is believed that the KCl-pH reflects closely the CEC and the cationic composition of the exchange complex.

### 10.9.4 MEASUREMENT OF pH IN A $CaCl_2$ SOLUTION

The soil is mixed with a 0.1 M  $CaCl_2$  solution using a 1:1 or 1:2 soil-to-solution ratio, and the pH is measured in the  $CaCl_2$  suspension. This type of measurement is often used in conjunction with the determination of the *lime potential*, which will be discussed separately below.

## 10.10 SUSPENSION EFFECT IN SOIL pH MEASUREMENT

In the pH measurement, the reference and indicator electrodes are immersed in a heterogeneous soil suspension composed of dispersed solid particles in an aqueous solution. If the solid particles are allowed to settle, the pH can be measured in the supernatant liquid or in the sediment. Placement of the electrode pair in the supernatant gives a higher pH reading than placement of the electrodes in the sediment. This difference in soil pH reading is called the *suspension effect*.

Stirring the soil suspension before measurement will not solve the problem, because the latter procedure gives unstable readings. According to Bolt et al. (1976), the reference electrode should be placed in the supernatant. The position of the glass electrode is considered immaterial at the equilibrium condition. This is rather strange because the electrode pair then measures the supernatant pH if both electrodes are placed in the supernatant. The glass electrode should more likely be placed in the sediment.

## 10.11 LIME POTENTIAL

It is apparent from the foregoing discussions that measurements of soil pH can give highly variable results, because they are affected by several factors, including suspension effect, soil/water ratios, and electrolyte levels. Schofield and Taylor (1955) proposed the use of 0.1 M CaCl<sub>2</sub> solutions for obtaining stable readings in pH measurements. However, instead of using single ion activity measurements, Schofield and Taylor (1955) suggested the use of ion activity ratios for determination of soil acidity and base saturation. If the soil exchange complex is saturated with both H<sup>+</sup> and Ca<sup>2+</sup> ions, at equilibrium Schofield's ratio law says that:

$$H^+/\sqrt{Ca^{2+}} = \text{constant}$$

By taking  $-\log$ , this ratio changes to

$$-\log H^+/\sqrt{Ca^{2+}} = \text{constant}$$

$$(-\log H^+) - (-\log \sqrt{Ca^{2+}}) = \text{constant}$$

or

$$pH - \frac{1}{2}pCa = \text{constant} \quad (10.6)$$

This equation is called the *lime potential*. It characterizes the composition of the exchange complex relative to its saturation by H<sup>+</sup> and Ca<sup>2+</sup> ions. Many of the methods for determination of the lime requirement take into consideration the lime potential. The equation says that a change in pH is dependent on the Ca<sup>2+</sup> concentration expressed as the calcium potential ( $pH = \frac{1}{2}pCa + \text{constant}$ ), and as discussed in Section 10.5, the term potential is viable.

## 10.12 THE NEED FOR ACIDIC SOIL REACTIONS

Usually, soil fertility is improved by liming acid soils to pH 6 to 7. Most plants grow well in this pH range. At this soil reaction, available Ca, Mg, and P concentrations are adequate for plant growth. The levels of micronutrient contents in the soil solution are sufficient. Both fungal and bacterial activity are also present.

However, in certain cases it is desirable to maintain a strong to moderately acid condition for plant growth. Some ornamental plants (e.g., azaleas and rhododendrons) require acid soil reactions for optimum growth. Pine trees also grow better in acid soils. Other crops that are grown in acid soils are blueberries, pineapples, and Irish potatoes. With potatoes, the acid condition will reduce the development of potato scab, a disease caused by actinomycetes, which affects the quality of the potatoes. Tea is also grown frequently in acid soils.

A number of compounds can be used to maintain or intensify soil acidity. Acid organic matter (e.g., pine needles) or chemical compounds such as S powder or FeSO<sub>4</sub> can be mixed with the soil to produce the acid reaction. The role of these compounds in contributing to the H<sup>+</sup> ions concentration was discussed in Section 10.6.

## 10.13 SOIL REACTIONS IN SALINE AND SODIC SOILS

### 10.13.1 SALINIZATION

Saline and sodic soils, today called *Aridisols*, are soils of arid regions where the average precipitation is less than 500 mm (20 in.) annually. The amount of H<sub>2</sub>O coming from the precipitation is

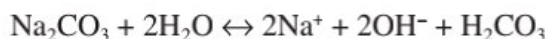


insufficient to neutralize the amount of H<sub>2</sub>O lost by evaporation and evapotranspiration. As the water is evaporated in the atmosphere, the salts are left behind in the soil. The process of accumulation of soluble salts in these soils is called *salinization*. The salts are mostly NaCl, Na<sub>2</sub>SO<sub>4</sub>, CaCO<sub>3</sub>, and MgCO<sub>3</sub>. In the past, the soils developed were called *saline soils*, *white alkali soils*, or *solonchaks*. They belong to the zonal-type soils. Salinization can also occur locally and develops the intrazonal type of saline soils (e.g., soils reclaimed from the sea bottom) and soils in coastal areas affected by the tide.

### 10.13.2 SODICATION AND ALKALINIZATION

The addition of salts to the soil may result in saturating the soil's exchange complex with Na. The process of progressively increasing the Na saturation of the soils exchange complex is called *sodication*. The soils formed are called *sodic soils*, *solods*, *solonetz*, or *black alkali soils*. If these soils occur only in small areas (in small localized spots), they are often called *slick spots*.

Kamphorst and Bolt (1976) reported that sodication does not necessarily yield a rise in soil pH. Many sodic soils are neutral in reaction, whereas a number of solonetzic soils are even acid in reaction. In sodic soils with a neutral soil reaction, the Na salts are neutral salts such as NaCl. The strong alkaline reaction (pH = 10) of most sodic soils is caused by alkalization. The latter is due to hydrolysis of Na<sup>+</sup> ions or Na<sub>2</sub>CO<sub>3</sub> compounds:



The OH<sup>-</sup> ions produced will increase the soil pH, whereas the Na<sup>+</sup> is saturating the exchange complex. The latter, in turn, may undergo hydrolysis, which also contributes toward increasing the OH<sup>-</sup> ion concentration in the soil:



## 10.14 CHEMICAL CHARACTERIZATION OF SALINE AND SODIC SOILS

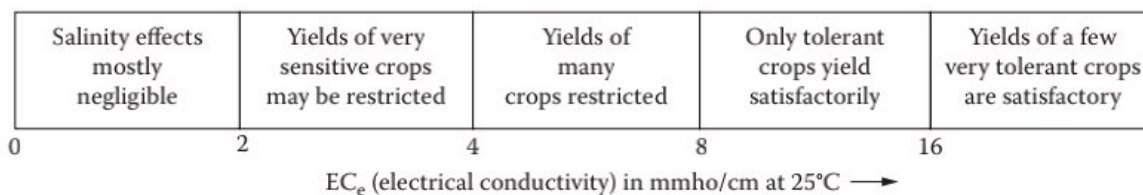
It is apparent from the foregoing that soil pH is not a good method for characterization of these soils. The saline soils have a soil pH = 8.5 or lower. The sodic soils may possess a soil pH = 10, and some of the soils may be neutral, whereas others are acid in reaction. To distinguish saline and sodic soils from other soils, the U.S. Salinity Laboratory (Richards, 1954) proposed to use as criteria soluble salt and exchangeable Na<sup>+</sup> content. These parameters are expressed in terms of electrical conductivity (EC<sub>e</sub>) for salt content and exchangeable sodium percentage (ESP) for exchangeable Na<sup>+</sup> content. The salinity of the soil is found by measuring the EC<sub>e</sub> in *millimho per centimeter (mmho/cm)* of the soil's saturated extract. In the International System of Units (SI) system, the unit *decisiemen/m* is used, but because *mmho/cm = decisiemen/m*, the conversion is a simple matter. The ESP analysis is conducted by suction and filtration of a water-saturated soil paste. The exchangeable sodium percentage is then calculated using the following formula:

$$\text{ESP} = (\text{exchangeable Na}^+ / \Sigma \text{exchangeable cations}) \times 100\%$$

Based on ESP and EC<sub>e</sub> values, three groups of soils are recognized: (1) *saline soils*, (2) *saline-alkali soils*, and (3) *nonsaline-alkali (sodic) soils*.

The *saline soils* are characterized by EC<sub>e</sub> > 4 mmho/cm at 25°C, and ESP < 15%. Dispersion of saline soils occurs at ESP = 15%. The soil pH is ordinarily less than 8.5. Because of the presence of excess salts and low amounts of Na<sup>+</sup> ions in exchange position, these soils are usually in a flocculated state, and their permeability is considered to be equal or higher than the two other soils.





**FIGURE 10.6** The degree of salinity, as expressed in EC<sub>e</sub> values, on yields of crops according to the U.S. Salinity Laboratory. (Adapted from Richards, L. A., ed., *Diagnosis and Improvement of Saline and Alkali Soils*, USDA Agriculture Handbook No. 60, U.S. Government Printing Office, Washington, DC, 1954.)

The *saline-alkali soils* are soils with EC<sub>e</sub> > 4 mmho/cm at 25°C, and ESP > 15%. These soils have both free salts and exchangeable Na<sup>+</sup>. As long as excess salts are present, the soil is flocculated, and the pH is normally ≤8.5. When the soils are leached, the free salt content decreases, and the soil reaction may become strongly alkaline (pH > 8.5) because of hydrolysis of the exchangeable Na<sup>+</sup>.

*Nonsaline-alkali soils* are characterized by EC<sub>e</sub> < 4 mmho/cm at 25°C and ESP > 15%. Most of the Na<sup>+</sup> is in exchangeable form, and very small amounts of free salts are present in the soil solution. The soil pH ranges from 8.5 to 10. As a result of irrigation, strongly alkaline conditions may develop in these soils, and pH values reaching 10 are common.

The selection of the *critical value for EC<sub>e</sub>* at 4 mmho/cm was reported to be based on the expected salt damage to crops. The EC<sub>e</sub> value of 4 mmho/cm originated with Schofield in 1942, who considered the soil to be saline at 4 mmho/cm or above. At the latter values, the yield of many crops is restricted. Kamphorst and Bolt (1976) indicated that an EC<sub>e</sub> of 4 mmhos/cm corresponded to an osmotic pressure at field capacity of 5 bars. At EC<sub>e</sub> values between 2 and 4 mmho/cm, only very sensitive crops will be affected, and at values below 2 mmho/cm the effect of salinity is negligibly small (Figure 10.6). However, different opinions exist on the critical EC<sub>e</sub> value, because several authors indicated that cotton, wheat, and soybeans are growing well in soils at EC<sub>e</sub> values of 7.7, 6, and 5 mmho/cm, respectively (Fipps, 2003; Rhoades et al., 1992). Perhaps these crops can be grouped as salt-tolerant crops. Sugar beet is another crop that is considered salt tolerant.

The decision to use an ESP value of 15% is also arbitrary, because no sharp changes in soil properties have been observed as the degree of saturation of the exchange complex with Na<sup>+</sup> ions is increased. Moreover, different crops will react differently to the same ESP value (Kamphorst and Bolt, 1976; Richards, 1954). The U.S. Salinity Laboratory has used, from history and experience, the ESP = 15% as a boundary limit to distinguish nonalkali from alkali soils.

### 10.15 EFFECT OF SALINIZATION AND SODICATION ON PLANT GROWTH

The accumulation of soluble salts in soils severely inhibits plant growth. It induces plasmolysis (see Section 7.6), by which H<sub>2</sub>O moves out of the plant into the soil solution. Most scientists only realize the danger of the osmotic effect to crops brought about by salinization. However, according to Stewart and Howell (2003), the following special ion effect can also be very harmful to growing crops. The Na<sup>+</sup> and Cl<sup>-</sup> ions are taken up and move with the transpiration flow from roots to leaf tissues where they accumulate. Stewart and coworker indicate that older leaves exhibit greater transpiration than younger leaves; hence, the tips and margins, in particular, of the older leaves will develop injury first due to accumulation of the above. They firmly believe that the combined osmotic and this special ion effect are perhaps even more harmful than the guidelines for salt tolerance would have indicated.

Another important effect is that the presence of high amounts of Na<sup>+</sup> ions may keep the soil particles suspended. Upon drying, the soil may cake, and crust formation develops at the surface. The latter decreases soil porosity, and aeration is severely inhibited. Of equal importance is the high pH in many of the soils which reduces the availability of many micronutrients. These soils frequently encounter Fe, Cu, Zn, or Mn deficiencies.



**TABLE 10.2**  
**Index of Salinity Hazard in EC<sub>e</sub> Values**

Salinity Hazard	EC <sub>e</sub> (mmho/cm at 25°C)
Low	<0.75
Medium	0.75–1.5
High	1.5–3
Very high	>3.0

In the opinion of Sparks (2002), three parameters or equations are available for the determination of sodic hazards. They are the SAR (sodium adsorption ratio), ESR (exchangeable sodium ratio), and ESP (exchangeable sodium percentage). The present author believes that a big difference exists between salinity and sodic hazards. Sodic refers mainly to the issue of Na (sodic) ions, whereas salinity refers to a broader spectrum where not only sodium, but also pH, osmosis, and so forth, are included. Hence, a distinction is made below by addressing them separately, which will expose the issue clearly.

## 10.16 IRRIGATION OF SALINE AND SODIC SOILS

Reclamation and management of the saline and sodic soils are based mainly on proper irrigation and drainage, on the exchange of Na<sup>+</sup> for Ca<sup>2+</sup> on the exchange complex, and on the use of salt-tolerant crops.

### 10.16.1 SALINITY HAZARDS

To make saline soils arable, leaching of excess salts by irrigation is usually conducted. A proper drainage method and the use of irrigation water with the proper salt quality are necessary. In this respect, the electrical conductivity EC<sub>e</sub> is frequently used as an index for salinization hazard. The hazard of salinization is considered low if irrigation water used has an EC<sub>e</sub> < 0.75 mmho/cm (Richards, 1954; Taylor and Ashcroft, 1972) (see Table 10.2).

In arid regions, salinization is a natural phenomenon. Therefore, the chances for salinization are considered very high if water with EC<sub>e</sub> = 3.0 or higher is used for irrigation over many years, even on nonsaline soils.

### 10.16.2 HAZARDS OF SODICATION

The hazard of sodication is usually estimated by the use of the sodium adsorption ratio (SAR). The SAR formula varies somewhat according to different authors. The formula, as originally presented by the U.S. Salinity Laboratory, is as follows (El-Swaify, 1979; Richards, 1954):

$$\text{SAR} = (\text{Na}^+) / \sqrt{[(\text{Ca}^{2+} + \text{Mg}^{2+})/2]} \quad (10.7)$$

However, Janzen (1993) and Sparks (2002) give a slightly different version for SAR:

$$\text{SAR} = (\text{Na}^+) / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})} \quad (10.8)$$

The concentration of Na<sup>+</sup> and Ca<sup>2+</sup> + Mg<sup>2+</sup> can be expressed in millimoles per liter (Janzen, 1993; Kamphorst and Bolt, 1976) or in milliequivalents per liter (El-Swaify, 1979; Taylor and Ashcroft,

1972). Sparks (2002) also indicates that total concentrations are used in Equation 10.8, and not activities; hence, SAR does not express the effects of ion pair or complex formation that influence changes in free ion concentration and activities. He also claims that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are treated as similar ion species. Perhaps these are more academic problems, because in practice the concentrations of  $\text{Ca}^{2+}$  in soils are generally substantially higher than those of  $\text{Mg}^{2+}$  ions. Sparks also suggests that Equation 10.8 be simplified into the following:

$$(\text{Na-soil})/[\text{CEC} - (\text{Na-soil})] = k_G \text{ SAR} = \text{ESR} \quad (10.9)$$

where  $k_G \text{ SAR}$  equals the modified Gapon selectivity coefficient.

It is up to the readers whether Equation 10.9 is a simpler version than Equation 10.8. Anyway, no agreement seems to exist either on the formula or the units to be used, creating in this way considerable confusion on the proper determination of SAR. For most soils, El-Swaify (1979) believes that SAR is related linearly to ESP.

Because the sodic soils are highly saturated with  $\text{Na}^+$  ions, it is necessary to use irrigation water with low SAR values on these soils. It is sometimes suggested to add gypsum to the irrigation water. But most often the gypsum is plowed under in the soil. This may ensure the development of low SAR values of the water in the soil. The  $\text{Ca}^{2+}$  may, at the same time, replace  $\text{Na}^+$  from the exchange complex. Theoretically, any soluble Ca compound that will not affect soil pH can be used together with irrigation water to reduce the SAR value and exchange the  $\text{Na}^+$  ions.

## 10.17 SALT BALANCE AND LEACHING RATIO

Irrigation will sometimes only wet the soil. This is a potential danger for salt buildup. In the management of saline and sodic soils, the salt balance is taken into account. The latter means that the amount of salt brought into the soil must equal the amount of salt leached out of the soil. Therefore, more water must be applied over that needed to wet the soil. The additional water, used for leaching, is called the *leaching requirement* (LR) (Bernstein and Francois, 1973):

$$\text{LR} = \text{EC}_{\text{iw}}/\text{EC}_{\text{dw}}$$

where  $\text{EC}_{\text{iw}}$  is the electrical conductivity of irrigation water, and  $\text{EC}_{\text{dw}}$  is the electrical conductivity of saturation extract of saline soil which exhibited 50% decrease in yield.

If the irrigation water increases in salinity over the years, the value of LR becomes larger. Bernstein and Francois (1973) suggested managing irrigation in such a way that the major water needs of crops are supplied at the minimum salinity level of the irrigation water.

## 10.18 IRRIGATION-INDUCED SALINIZATION AND SODICATION

The hazard of salinization and sodication is perhaps not limited to semiarid and arid region soils. Currently, it is common practice to also use supplementary irrigation in areas with measurable rainy seasons. With easy access to water from the huge underground aquifers in the southern coastal plain region of the United States, large areas are now continuously being irrigated by the center pivot sprinkle system. No adequate disposal systems of the used irrigation water have yet been devised. The irrigation water reaching the soil is allowed to percolate naturally through the soil and return to the groundwater in a more concentrated condition. A large part of the irrigation water may, perhaps, also evaporate, leaving the salts in the surface soil. No investigations have yet been done on the potential hazard of salinization and sodication by the use of this water. The danger of salinization and sodication is somewhat reduced by the presence of a humid climate. However, over many years, one can expect a reduction in the quality of this irrigation water by the use of high amounts of fertilizers and in the absence of a proper drainage and disposal system.