

CHEMICAL AMELIORATION OF SOILS

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Summary

The objects and goals of chemical amelioration of soils are defined. The concepts of cation-exchange complex and acid–base properties of soils are explained. The nature of soil acidity and alkalinity and theoretical backgrounds of chemical amelioration of soils are considered. The factors limiting the fertility of acid, salt-affected, and alkaline soils, including specific solonetzic (sodic) and soda-saline soils, and the soils of coastal areas are outlined. Specific measures to ameliorate these soils, ecological consequences of chemical amelioration, and necessary environmental conservation measures are discussed.

1. Introduction. Definition of Concepts. Goals and Tasks of Chemical Amelioration

Chemical amelioration is the collective term for a system of measures aimed at improving chemical, physical, and other properties of soils on the basis of regulation of acid–base and ion-exchange soil processes via addition of various chemical additives. As a rule, chemical amelioration is performed in combination with other kinds of soil amelioration, e.g., agrotechnical, hydrotechnical, phytomelioration, etc. In this case, we can speak about the complex (multiple) amelioration of soils.

Agrotechnical amelioration is aimed at improving the water and air regimes of soils and their structural state. This is achieved by means of special tillage operations, leveling of the surface, and other measures (see *Agrotechnical Amelioration*).

Phytomelioration (bioremediation) is used to amend soil properties and regimes by exploiting the ameliorative capacities of herbaceous and arboreal species adapted to particular environmental conditions (e.g., frost-tolerant, salt-tolerant, drought-tolerant, alkali-tolerant, hydrophilous, etc.) (see *Phytomelioration*).

Hydrotechnical amelioration is directed toward the control of water, air, and salt regimes of soils by means of special engineering constructions, drainage and irrigation systems, water storage basins, dams, etc. (see *Irrigation for Sustainable Development*)

Application of different kinds of ameliorative measures ensures the maximum efficiency of amelioration.

The main objects of chemical amelioration are acid and alkaline soils. The simplest way to judge the soil acidity or alkalinity is to determine the reaction, or pH, of the water suspension or a saturated paste prepared from the soil (pH denotes the negative logarithm of the activity of H^+ ions in the solution; $pH = -\lg a_{H^+}$). Ranges in pH are: for acid soils, <6.5; for neutral soils, 6.6–7.3; for slightly and moderately alkaline soils, 7.3–8.3 (8.5); for strongly alkaline (alkali) soil, >8.3 (8.5). Neutral and slightly alkaline soils usually do not require chemical amelioration.

Acid soils are typical of areas with a wet climate; most of them are found in the boreal and tropical forest zones. A special place in the group of acid soil belongs to the soils of sea coasts, estuaries, marshes, and river deltas in tropical regions subjected to periodic inundation by sea water. These are extremely acid ($\text{pH} < 3.5$) sulfate-containing soils. Chemical amelioration of acid soils is aimed at neutralization of soil acidity. It should be applied not only to strongly, moderately, and slightly acid soils, but even to the neutral soils of croplands with unbalanced removal of calcium (see *Amelioration of Acid Soils*).

Alkali soils, as well as acid soils, require ameliorative measures for their efficient utilization. Alkali soils are widespread in subarid and arid regions (forest-steppe, steppe, dry steppe, and desert zones) in all parts of the world. Alkali soils are subdivided into two subgroups: (a) Solonchic soils (Alkali Sodic) soils and (b) Alkali Soda-Saline soils (see *Amelioration of Alkali (Soda-Saline) Soils* and *Amelioration of Alkali (Sodic, Solonchic) Soils*). In turn, Alkali soils are included into a larger group of Salt-Affected soils.

Chemical amelioration of both acid and alkaline and soils is aimed at changing the composition of exchangeable bases in the adsorption complex of these soils and regulating the actual reaction of soil solutions. The main points of the processes that take place in soils during the application of chemical additives are discussed below.

2. Soil Adsorption Complex, Soil Acidity, and Soil Alkalinity

2.1. Cation-Exchange Complex, Ion Exchange, and Ion Selectivity

The collection of mineral, organic, and organo-mineral solid-phase soil substances capable of ion exchange and taken as a whole is called soil cation-exchange complex or soil adsorption complex (SAC). Cation-exchange processes take place on negatively charged sites of SAC and play an important role in the genesis of acid, alkaline, and saline soils.

The particles composing SAC may carry both permanent and variable charges. Permanent charges are conditioned by isomorphic substitutions in crystal lattices of clay minerals. Their quantity is determined by structural peculiarities of clay minerals and does not depend on pH conditions. Variable charges are often called pH-dependent charges. They appear as a result of ionization of functional groups of soil organic substances and surface OH-groups of oxides and hydroxides. The intensity of ionization increases with the rise in pH and depends on many factors.

Negative charges of SAC are compensated by positively charged ions that are called exchangeable cations. Exchangeable cations can be replaced from SAC by the cations of surrounding solution. This process is called the cation exchange. Cation-exchange reactions are reversible and follow the equivalent proportions' principle. Thus, cation exchange is a reversible process that takes place between closely contacting solid and liquid phases of heterogeneous systems.

The composition of exchangeable cations is an important characteristic of the soil that

controls many soil properties. It depends on the properties of SAC and the composition of soil solution.

The prediction of these changes is based on quantitative regularities of cation distribution between the SAC and the soil solution. These regularities can be described by several equations based on the mass action principle applied to soil ion-exchange systems.

These equations allow one to find the coefficients of selectivity of cation exchange showing the ability of the soil for preferential adsorption of certain cations from the soil solution.

In the case of exchange between Ca^{2+} ion of the SAC and Na^+ ion of the soil solution, the coefficient of selectivity can be found according to the Gapon equation:

$$K = \frac{\bar{c}_{\text{Na}} \cdot a_{\text{Ca}}^{1/2}}{\bar{c}_{\text{Ca}} \cdot a_{\text{Na}}}, \quad (1)$$

where a_{Ca} and a_{Na} are the activities of corresponding cations in the solution and \bar{c} is the cation concentration in the SAC.

In contrast to thermodynamic equilibrium constants, the coefficients of selectivity vary in dependence on a number of factors, including the content of exchangeable cations in the SAC, the ion strength of soil solution, the concentrations of other cations in the soil solution, and the presence of complex-forming anions in the solution.

In the case of exchange reactions between Ca of the SAC and Na of the soil solution, we can expect the predominant adsorption of Na if the selectivity coefficient is higher than 1. Mathematical modeling is widely used for the prediction of cation-exchange processes.

Cation-exchange processes play a key role in functioning of saline soils. In particular, the substitution of sodium for exchangeable calcium leads to the development of solonchaks; the reverse process (the replacement of exchangeable sodium by the calcium of CaCO_3) can lead to the appearance of soda and formation of alkali (soda-saline) soils.

Cation-exchange processes affect the structure and water-physical properties of soils. Thus, an increase in the proportion of exchangeable sodium among the exchangeable cations of SAC leads to peptization of fine fractions and worsens the water and air regimes of soils, etc. Cation-exchange processes also affect chemical properties of soils, their acidity and alkalinity, the mobility of organic substances, soil fertility, and the capacity of soils to fix toxic substances.

At the same time, by affecting the ion-exchange processes via addition of chemical additives, we can change soil properties in the desired way. Cation exchange lies in the basis of chemical amelioration of acid soils via substitution of Ca^{2+} ions of lime for exchangeable H^+ and Al^{3+} of soil SAC; substituting Ca^{2+} ions of gypsum for

exchangeable Na^+ , we can reclaim alkali soils.

2.2. Acid-Base Properties of Soils

Acidity and alkalinity exert tremendous impacts on the properties and functioning of soils and biogeocenoses as a whole. They affect the development of plants, the mobility of nutrients in the soil and their availability for plants, the exchange capacity and composition of exchangeable cations, the activity of soil biota, soil physical properties, etc. At the same time, acid–base properties are very dynamic. They can alter in the process of agricultural management and under other impacts. One of the main goals of chemical amelioration is to regulate the acid–base properties of soils.

Soil acidity may be regarded as an ability of the soil to act as an acid, i.e., to be a donor of protons. Soil alkalinity denotes the ability of the soil to accept protons. Thus, the acid–base properties of soil characterize soil behavior with respect to protons (H^+ ions).

Soil acidity and alkalinity may be estimated from data on pH values of various soil systems (extracts, suspensions, pastes) that characterize the activity (concentration) of H^+ ions in the liquid phase on one hand, and from data on the potential acidity and total alkalinity that characterize the whole amount of acidic and basic components contained in the soil and capable of transition from the solid soil phase into the liquid phase on the other hand.

Soil acidity is mainly conditioned by the cations that produce H^+ ions in the course of their hydrolysis; soil alkalinity is related to the presence of anions of weak acids that accept protons from the water producing OH^- ions.



In dependence on the composition of cations and anions soils may acquire acid, neutral, or alkaline reaction.

To characterize soil acidity or alkalinity, the sources of the components with acid or base properties and the degree of manifestation of these properties in the soil are studied separately.

2.2.1. The Nature of Soil Acidity

Soil acidity may be caused by the presence of hydrogen-containing acids and cations with distinct acid properties. The degree of manifestation of acid properties by these components in water solutions is characterized by the acidity constants, or the constants of dissociation, K_a (Table 1). The higher the constant, the lower the pH at which dissociation (the release of a proton into the liquid phase) takes place, and the more significant the impact of the acidic component on the pH of the soil solution. The so-called strong acids are completely dissociated and manifest acid properties at any pH

values.

In most soils, acid properties are created by weak and strong mineral acids, organic acids, and various aluminum compounds (see Table 1). Such cations as Na^+ , Ca^{2+} , and Mg^{2+} have such low acidity constants that they do not display acid properties.

Equations	$\lg K_a$
$\text{Fe}^{3+} + \text{H}_2\text{O} \Leftrightarrow \text{FeOH}^{2+} + \text{H}^+$	-2.19
$\text{Al}^{3+} + \text{H}_2\text{O} \Leftrightarrow \text{AlOH}^{2+} + \text{H}^+$	-5.02
$\text{Al}^{3+} + 2\text{H}_2\text{O} \Leftrightarrow \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-10.02
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \Leftrightarrow \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-7.70
$13\text{Al}^{3+} + 28\text{H}_2\text{O} \Leftrightarrow \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+} + 32\text{H}^+$	-98.73
$\text{Fe}^{2+} + \text{H}_2\text{O} \Leftrightarrow \text{FeOH}^+ + \text{H}^+$	-6.74
$\text{Mg}^{2+} + \text{H}_2\text{O} \Leftrightarrow \text{MgOH}^+ + \text{H}^+$	-11.45
$\text{Ca}^{2+} + \text{H}_2\text{O} \Leftrightarrow \text{CaOH}^+ + \text{H}^+$	-12.70
$\text{Na}^+ + \text{H}_2\text{O} \Leftrightarrow \text{NaOH}^0 + \text{H}^+$	-14.20

Table 1. Equations and equilibrium constants of chemical reactions (acidity constants, $\lg K_a$)

Strong mineral acids, in particular, nitric acid produced by microorganisms in the course of nitrification, usually have very low concentrations in soils. However, in some soils, e.g., in pyrite-containing soils, the oxidation of pyrite leads to the appearance of sulfuric acid in relatively high concentrations.

Among weak acids, the most significant role belongs to carbonic acid produced during respiration of soil microorganisms and released from roots.

Organic acids are produced by microorganisms and enter the soil with root exudates and plant litter (e.g., acetic, citric, and oxalic acids). Besides, soils contain humic and fulvic acids and some other specific organic compounds bearing acidic functional groups. However, in soils, most of these groups are tightly bound with aluminum, iron, and clay minerals, so that just a small portion of functional groups is capable of dissociation with the release of protons.

Usually, negatively charged surfaces of clay minerals do not carry exchangeable H^+ ions as most of them are easily replaced by the cations of aluminum, iron, or magnesium from the crystal lattice of minerals. Thus, the share of H^+ ions among the components responsible for acid properties of mineral soils is usually rather small. At the same time, this ion may play a significant role in the acidity of organic (in particular, peaty (histic)) horizons.

In spite of the fact that in most soils the content of hydrogen-containing acids is relatively low, the role of these acids in the formation of acid soils cannot be overestimated. Indeed, it is hydrogen-containing acids (especially, organic acids and carbonic acid) that interact with soil minerals in the process of acid soil formation,

increasing the mobility of the main components of soil acidity, cations. In the developed acid soil, most of the initial protons in the soil solution become fixed in the soil mass. Instead, cations and aluminum compounds appear in the soil solution and play the major role in soil acidity.

Aluminum compounds manifest their acid properties as a result of hydrolysis. Table 1 contains the equations of several reactions of the hydrolysis of Al^{3+} ion with the formation of aluminum hydroxycomplexes and the release of protons into the soil solution. Hence, some part of H^+ ions contained in soil solutions are produced not in course of dissociation of hydrogen-containing acids, but in the course of hydrolysis of aluminum compounds. The products of aluminum hydrolysis are represented by a range of various hydroxycomplexes, including mononuclear (AlOH^{2+} , $\text{Al}(\text{OH})_2^+$) and polynuclear (with several atoms of aluminum, e.g., $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_6(\text{OH})_{12}^{6+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) compounds. Some of these hydroxocomplexes are subjected to further hydrolysis with the formation of new polymerized products having a larger OH/Al ratio. As a rule, the larger the OH/Al ratio, the weaker the acid properties of the products of hydrolysis. Simultaneous reactions of hydrolysis and complex formation lead to the appearance of mixed hydroxy- and oxy-hydroxycomplexes of aluminum, silicon, and organic compounds. In many cases, the formation of hydroxycomplexes of aluminum is a reversible reaction so it may control the acid-base buffering of soils.

The components with acid properties may be present in the soil solution, and/or be adsorbed on the surface of soil particles, form complex compounds with organic substances, and form separate solid-phase compounds, e.g., amorphous hydroxides of aluminum. In dependence on the composition and state of these components in the soil, several kinds of soil acidity can be distinguished.

Aluminum (Al^{3+}) ions, hydroxocomplexes of aluminum, and hydrogen-containing acids are the main acid components in the soil solution. They dictate the actual acidity of the soil, which can be judged from pH values of soil suspensions. Actual acidity depends not only on the content of acid compounds, but also on their ability to release H^+ ions characterized by the acidity constants (Table 1).

Acid components connected with the solid phase are responsible for potential soil acidity. They may be present in exchange positions or be firmly adsorbed on the surface of soil particles. To distinguish between these two groups of acid components in the solid phase, the notions of exchangeable and pH-dependent acidity may be introduced. The pH-dependent acidity is often called the nonexchangeable or titratable acidity.

Exchangeable acidity can be determined via soil treatment with unbuffered salt solutions at relatively low pH values that are determined by soil properties. It characterizes the amount of exchangeable Al^{3+} and H^+ ions adsorbed on the surface of soil particles.

The pH-dependent acidity is determined at higher pH values, upon which weakly acid components of the soil are capable of dissociation (hydrolysis) with the release of H^+ ions. These components include tightly adsorbed hydroxocomplexes of iron and aluminum, solid-phase organic compounds with acidic functional groups, allophanes,

etc. Usually, under the action of buffered salt solutions, these components remain in the solid phase releasing H⁺ ion into the soil solution. Buffered salt solutions with pH 8.3 are often used for the determination of pH-dependent acidity. Such a value of pH is characteristic of the soils in the equilibrium state with CaCO₃.

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Biographical Sketches

Pankova, Yevgenia Ivanovna, was born in 1932. In 1955, she graduated from the Geographical Department, Moscow State University with a diploma in soil geography and environmental geochemistry. Starting from that time, her scientific career has been connected with the Dokuchaev Soil Science Institute. At present, she is the leading researcher of the Department of the Genesis and Amelioration of Salt-Affected Soils, Doctor of Agricultural Sciences, corresponding member of the Russian Ecological Academy. She is the author of more than 200 works, including five monographs, devoted to the genesis, mapping, and monitoring of salt-affected soils.

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