KINDS OF CHEMICAL AMELIORATION

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Contents

Summary

Soil cation exchange properties and their diagnostic parameters, as well as soil acidity and alkalinity as properties limiting plant growth and agricultural production, are briefly described.

Details are given of the kinds of chemical amelioration: chemical amendments for the reclamation of acid soils (liming materials), different chemical amendments for the reclamation of alkaline (alkali/sodic/solonetz soils and soda-saline soils), and artificial soil-structure-forming substances (soil conditioners). Calculation of amendment rates, methods of application, and different aspects of the effective use of the above three groups of chemical amendments are discussed.

1. Cation Exchange Complex of the Soil

The cation exchange complex of the soil is the complex of finely dispersed (<0.001 μm) mineral, organic, and organo-mineral compounds developed during the soil forming process, and partly inherited from the parent rock.

The cation exchange complex (mainly the soil colloid particles) defines the physico-chemical adsorption (cation exchange) ability of the soil. It plays a substantial role in the soil forming processes, and determines a number of soil properties (physical and physico-chemical properties, water, air, nutrient, and microbial regimes) on which fertility depends.

Study of the cation exchange complex of the soil is important to determine the most effective measures and methods of soil amelioration (e.g. liming of acid soils, gypsum application in solonetz soils).

1.1. Exchangeable Cations

On the negatively charged surface of soil colloids, cations of the soil solution are chiefly bound with electrostatic forces. They can be displaced by other cations from the solution (cation exchange). The main cations involved in the ion exchange processes of the soil are: Ca^{2+}, Mg^{2+}, Na^+, K^+, and sometimes NH_4^+, as well as H^+, Al^{3+} (and Fe^{3+}). Exchangeable cations and their composition in the soil cation exchange complex control the pH of the soil solution and have a strong influence, directly and/or indirectly, on a wide range of soil properties.

The dominance of basic cations results in neutral or alkaline soil reaction (pH > 7); exhangeable H^+, Al^{3+}, and Fe^{3+} can be found only at acidic reaction (low pH) in the soil. When basic cations prevail, the soil is “base saturated”; otherwise it is “unsaturated”. In the practice of soil science, the amount of exchangeable cations is given in $\text{cmol}_c\ \text{kg}^{-1}$ (or meq 100g^{-1} soil). The sum of basic exchangeable cations, S_{cat}, is also often used for characterizing the cation exchange properties of soils.

1.2. Cation Exchange Capacity

The value of the Cation Exchange Capacity (CEC) (in cmol kg^{-1} or meq $100g^{-1}$) expresses the total amount of exchangeable cations adsorbed by the soil at a given pH value.

The relative amount (%) of exchangeable cations is also important for diagnosis of the physico-chemical properties of different types of soils. For example: exchangeable Na^{+} CEC^{-1} x100 = ESP (Exchangeable Sodium Percentage) is one of the main diagnostic parameters of alkali (sodic/solonetzic and soda-saline) soils. The value of base saturation: $V\% = S_{cat}\ CEC^{-1}$ x100 gives the relative amount of basic cations in the soil cation exchange complex. As low base saturation (V% < 80) is connected with acidic soil reaction, V% is one of the diagnostic parameters of acidic soils. Details on the physico-chemical characteristics and properties of the soil are given in *Chemical Amelioration of Soils*.

2. Acidity and Alkalinity of Soils: Their Diagnostic Parameters

The chemical reaction of the soil influences the chemical, physical and biological processes, and thus affects soil formation, changes in soil properties, and the availability to plants of nutrient elements. The following properties play a role in the formation of soil reaction (pH value): the quantity and composition of salts dissolved in the liquid phase, quantity and quality of organic and mineral acids, composition and ratio of exchangeable cations, base saturation of soil colloids, CO_2 content of the soil's gas phase (and the amount dissolved in the soil moisture), carbonate content of the soil, and oxidation-reduction processes.

2.1. Soil Acidity

Soil acidity is one of the most important chemical properties of many soils. It increases the amount of hydrogen ions in the soil solution and the accumulation of adsorbed hydrogen and aluminum ions in the soil cation exchange complex. Two forms of soil acidity are distinguished (their amount and ratio is in accordance with the actual chemical equilibrium in the soil): actual (active) acidity and potential acidity. Actual acidity, connected with the increase of hydrogen ions in the soil's liquid phase, is expressed by the pH value of the soil solution. Potential acidity occurs as either exchangeable or hydrolytic acidity. Exchangeable acidity is caused by the accumulation of hydrogen and aluminum ions. It is expressed as the pH value measured in a salt solution (mainly KCl), and/or given in cmol. kg^{-1} soil. Hydrolytic acidity is caused by the amounts of hydrogen ions that are most strongly adsorbed on the soil; these can be displaced from the cation exchange complex with cations of the solution of hydrolytic alkali salts. The diagnostic parameters of soil acidity are usually: the pH measured in a soil suspension prepared with molar KCl solution (1:2, or 1: 2.5 ratio), and the hydrolytic acidity (acidimetric titration of soil- Ca acetate solution extract). More details are given below.

2.2. Soil Alkalinity

Alkalinity is caused by the prevalence of salts capable of alkaline hydrolysis (mainly sodium carbonate) in the soil and/or by the hydrolysis of basic exchangeable cations (mainly Na^+) into the soil solution. Alkalinity is one of the main properties of several groups of salt-affected (alkali/sodic/solonetzic, and soda-saline) soils. The diagnostic parameters of soil alkalinity are: soil pH (measured in soil paste or suspension of different soil-water ratios) and the amount of free sodium carbonate determined from soil-water extracts by alkalimetric titration (its value is given as a percentage or in mg 100 g^{-1}). More details are given below.

Soils can be grouped according to their pH values, as follows:

	pH_{H2O}
Strongly acidic	<4.5
Acidic	4.5–5.5
Slightly acidic	5.5–6.8
Neutral	6.8–7.2
Slightly alkaline	7.2–8.5
Alkaline	8.5–9.0
Strongly alkaline	> 9.0

The most acidic soils are some organic (peat, and different kinds of marshy) soils and podsols; podsolic and non-podsolic forest soils are moderately acidic, while some kinds of sandy soils are slightly acidic. To the alkali soils belong highly calcareous soils, and different type of alkali soils (sodic/solonetz soils, soda alkali soils). Highest alkalinity can be measured in soils containing free sodium carbonate. Details on the chemistry and nature of soil acidity and alkalinity are given in *Chemical Amelioration of Soils* and in the lower-level articles *Soil Adsorption Complex, Soil Acidity and Soil Alkalinity, Amelioration of Alkali(Sodic/Solonetz) Soils*, and *Amelioration of Alkali(Soda-Saline) Soils.*

3. Acidity and Alkalinity as Properties Limiting Soil Fertility

3.1. Water-Physical, Chemical, and Biological Properties of Acid Soils Unfavorable for Plant Growth and Agricultural Production

Plant growth and agricultural production in acid soils may be affected directly and indirectly, often simultaneously, by the following:

- Formation of agronomically favorable soil structure becomes less likely.
- Water-physical properties are poor (decrease of water capacity, water infiltration and permeability). Stagnant water can more easily form on the soil surface.
- There is a deficiency of Ca and Mg in the soil, due to the leaching out of these elements.
- Harmful chemical reduction processes increase, leading to unfavorable changes in nutrient solubility and the availability of macro- and micronutrients.
- There is increased solubility and accumulation of certain toxic elements affecting plant metabolism.
- Conditions for humus formation are less favorable, and the amount of agronomically valuable humus compounds decreases.

- There is low activity of useful microbes due to the acid medium in the soil, decrease of the intensity of N binding and nitrification.

Soil acidity is a complex phenomenon, from both the qualitative and quantitative point of view. Its effects are rather complex and can vary according to seasons and over longer periods.

Through the above soil properties and processes, under field conditions, high acidity can lead to overmoistening in the soil, increasing the negative effects on crop yield. It decreases the effectiveness of mineral fertilizers and limits the possibility of crop cultivation.

3.2. Water-Physical, Chemical, and Biological Properties of Alkali Soils Unfavorable for Plant Growth and Crop Production

Plant growth and agricultural production (yield, and/or quality of crops) in alkali soils may be affected by any of the following:

- poor water and air permeability as a result of high dispersion of soil aggregates and clay particles,
- low availability of water due to poor conductance from the lower soil layers,
- a hard crust on the surface layer that greatly hinders seedling emergence and reduces the germination percentage and thus plant population,
- deficiency of Ca, since nearly all the soluble and exchangeable Ca is precipitated as insoluble $CaCO_{3,}$
- excess of Na, which is toxic per se to the plants and causes imbalance due to antagonic effect on K and Ca nutrition,
- toxic concentration of HCO_3^- and CO_3^{2-} ions,
- decreased solubility and availability of micronutrients such as Zn and Fe, due to high pH, $CaCO_3$, and soluble HCO_3^- and CO_3^{2-} ions,
- increased solubility of certain toxic elements such as F, Se, and Mo in plants,
- low activity of useful microbes due to high pH and excess exchangeable Na, and
- continuous loss of fertile topsoil due to wind and water erosion.

Under field conditions, plant growth is adversely affected by a combination of the above factors; the extent depends upon the amount of exchangeable sodium, pH, nature and stage of the crop growth, environmental conditions, and overall management level.

3.3. Chemical Composition of Soil and the Efficiency of Organic and Mineral Fertilizers

The humus and nutrient status of acidic and alkali soils is of secondary importance for soil fertility. If the soil is strongly acidic or contains high amount of salts capable of alkaline hydrolysis and/or exchangeable sodium, these factors reduce soil fertility almost independently of the humus and nutrient status. This does not mean that the nutrient requirements of plants grown on these soils can be ignored. On the contrary: proper agrotechnics and fertilization are always necessary. However, these measures can be effective only if the main factors limiting the fertility are previously altered.

In the case of acid soils, parallel liming and agrotechnical measures are the preconditions for mineral and organic fertilizers to be effective. For example, one of the effects of liming is to change the solubility of several chemical soil constituents, including complex formations. Its importance can be illustrated by the way it hinders the mobilization of iron compounds, which leads to a decrease in phosphorus fixation, and thus to an increase in the efficiency of phosphorus fertilizers.

In the case of alkaline soils (alkali/solonetz soils and soda-saline soils), chemical amelioration with acidulants and Ca-containing amendments, associated with leaching of water soluble salts from the root zone and/or the use of proper agrotechnics, is essential to guarantee the efficiency of fertilizers.

3.4. Tolerance of Plants to Soil Acidity and Alkalinity

Crops vary widely in their tolerance of extreme soil reactions. Crop tolerance depends upon the nature of the plant, stage of growth, soil fertility, climatic conditions, and other factors, so only relative tolerance can be given.

Soil acidity limits the variety of crops to be cultivated. Rye, oats, barley, potatoes, soybeans, different types of clovers, and sudangrass can tolerate slight acidity.

Among crops in general, rice and other cereals are more tolerant, to soil alkalinity (soil ESP) than legumes as they require less Ca, availability of which is a limiting factor in alkali soils. Crops that can withstand excess moisture conditions are generally more tolerant to alkali conditions. Among cultivated crops, rice is most tolerant to soil ESP. It is followed by sugarbeet and teosinte. Wheat, barley, and oats are moderately tolerant. Legumes, such as gram, mash, lentils, and different kinds of pea are very sensitive and their yield decreases significantly even when soil ESP is less than 15. Sesbania is an exception among the leguminous crops as it can grow at ESP up to 50, without any reduction in yield. It is hence an excellent crop for green manure in alkali soils. Among oilseed crops, all except groundnut are moderately tolerant to soil ESP. The relative tolerance to soil ESP among the green fodder crops decreases in the following order: teosinte, oats, shaftal, lucerne (alfalfa), turnips, berseem. Some of the natural grasses, such as Karnal grass, Rhoades grass, and Bermuda grass, are very tolerant to soil sodicity and in fact grow normally under high alkali conditions. Grasses also ameliorate the soil and thus, after few years of their cultivation, other field crops can be grown in certain conditions, without the addition of amendments.

4. Kinds of Chemical Amelioration: Chemical Amendments

Chemical amelioration is the system of methods to improve disadvantageous soil chemical or physical properties by adding chemical compounds (amendments) to the soil in order to increase crop yields and/or reduce environmental damage. The kinds of chemical amelioration to be used are determined by: the amount of macro and micronutrients, plant requirements on mineral salts, soil acidity, soil alkalinity, soil salinity, and the microbiological activity. Chemical amelioration can be divided into three types: control of soil acidity, control of salinity-alkalinity, and control of soil structure (soil conditioning).

Chemical amendments are:

- Chemical substances used to improve the physico-chemical properties of acidic or alkaline (alkali/sodic/solonetzic or soda-saline) soils. They affect the soil chemical reaction (pH), and the composition and ratio of basic cations in the soil solution and in the soil cation exchange complex. As soil chemical amendments, materials containing the following chemical compounds are used: $CaCO_3$ (lime), $CaSO_4$ (gypsum), $CaCl_2$ (calcium chloride), H_2SO_4 (sulfuric acid) and others (see below).

- Chemical substances used to improve the soil structure (artificial soil conditioners), increase porosity, and improve infiltration properties and water permeability.

Chemical amendments are usually added into the plough layer and/or to the underlying soil horizon.

4.1. Chemical Amendments and the Reclamation of Acid Soils (Liming Materials)

Liming soil is an ancient agricultural practice. The use of lime was referred to in the first and second centuries BC. A great deal of knowledge has been accumulated over the centuries, on materials, methods, effects, crop response, amendment effectiveness, economics, and so on in the agriculture of countries where liming of soil has been continuously practiced (mostly those in humid and semihumid regions). The role of liming has become more important in the last decades with the extension of soil acidification due to various industrial activities, and with the use of physiologically acid mineral fertilizers and of ameliorated fields.

For liming, those materials can be used, whose Ca and Mg compounds are capable of neutralizing soil acidity.

The mechanism through which $CaCO_3$ reacts with acid soils is complex. The rates of neutralization and final reaction products are not known with certainty, although the influence of factors such as the amount of soil acidity, and the particle size and the reactivity of liming materials have been studied extensively. The generalized overall reaction of lime with an acid soil may be written as:

$$2Al_{(soil)} + 3\,CaCO_3 + H_2O \rightarrow 3\,Ca_{(soil)} + 2Al(OH)_3 + 3CO_2\uparrow \qquad (1)$$

Liming materials include limestone, (both calcitic and dolomitic), burnt lime, hydrated lime, marl, shells, and different by-products such as slag.

The rate of reaction of liming materials with soils varies considerably. It depends on the source of liming material, the solubility of the material, the rate of removal of OH^- ions, the rate of the hydrolysis of Al^{3+} and Fe^{3+}, partial pressure of CO_2, particle size, soil mixing, and environmental factors (e.g. temperature and moisture).

Limestone is the most commonly used liming material. It may be calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), or a mixture of these two minerals. Pure dolomite has equal molecular ratios of $CaCO_3$ and $MgCO_3$; on a weight basis, it consists of 54.3% $CaCO_3$

and 45.7% $MgCO_3$ (with 21.7% Ca and 13.1% Mg since the molecular weight of Mg is less than that of Ca). Agricultural limestone is usually a mixture of calcite and dolomite that has been crushed so that it is sufficiently fine to react with the soil.

Agricultural marl is a soft deposit usually found in poorly drained low lying areas (its $CaCO_3$ content is: 25–50%). It is an amorphous material that is powdery when dry and very finely divided, and should react rapidly with the soil. Bog (lake) lime consist of calcium carbonate.

Industrial by-products are cheaper materials. They often also contain useful macro and micronutrients. Three different form of slags are used as agricultural liming materials: blast furnace slag, used mainly to neutralizing soil acidity and supply Ca and Mg; open hearth slag, which is used because of its high Mn content in addition to its liming effect; basic slag, which contains phosphorus that is readily accessible to crops.

Miscellaneous materials used for liming include:

- various shells;
- flue dust from cement plants; containing 40–60% CaO and up to 40% K, it has high acid neutralizing capacity;
- lime from pollution control systems;
- refuse lime from sugar beet factories (which contains up to 70% $CaCO_3$, 10–15% organic matter, 0.3–0.5% nitrogen, 0.4–0.7% P_2O_5 and 0.1–0.8% K_2O), paper mills, calcium carbide plants, rock wool plants, water softening plants; and
- by-product lime from lead mines.

These materials are used in areas close to the point where they are produced. They are generally finely pulverized so they react rapidly with the soil. Burned lime and hydrated lime, which were the first liming materials used, are still applied.

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Bibliography

Adams F. (ed.) (1984). *Soil Acidity and Liming*, 2nd edn. 568 pp. Agronomy Monograph No 12. Madison WI: American Society of Agronomy Inc. [This describes the chemistry of soil acidity, liming materials and practices.]

Ben-Hur M. and Keren R. (1997). Polymer effects on water filtration and soil aggregation. *Soil Science of America Journal*. **61**(2), 565–570.

Chhabra R. P. (1996) *Soil Salinity and Water Quality*. 284 pp. New Delhi, India: Oxford and IBH Publishing. [Management of alkali soils, irrigation and salinity control are discussed.]

Im Sang Jo, et al.(1997). Development of plastic emulsion as a soil conditioner and its effect in soil improvement. *RDA Journal of Agro-environmental Sciences.* **39**(2), 8-13.

Oster J.D. (1982). Gypsum usage in irrigated agriculture: a review. *Fertilizer Research.* **3**, 73–89. [A broad review of the use of gypsum for the reclamation of alkaline soil is given.]

Scheffer P. and Schachschabel P. (1992). *Bodenkunde 14*. Aufl. Stuttgart: Springer. [In German] [This is a textbook on general Soil Science, where the chemistry of soil acidity and alkalinity is thoroughly discussed.]

Sumner M.E. and Naidu R. (eds.) (1998). *Sodic Soils: Distribution, Properties, Management and Environmental Conditions*. 207 pp. Oxford, UK: Oxford University Press. [This gives information about the distribution, properties, and amelioration of alkali/sodic/solonetz, and soda-saline soils.]

Suarez D.L., Simunek J., and Guzy M. (1996). Practical model for predicting soil salinity and sodicity under transient conditions. *Proceedings of the International Workshop on Integrated Soil Management for Sustainable Use of Salt Affected Soils*. BSWM Diliman, Quezon City, Manila, (The Philippines), 6–10 November, 1995. (ed. A. T. Ayoub (UNEP), A. M. Mashali (FAO), M. Redly (ISSS)). 39–55. 237 pp. Budapest, Hungary. [This is a discussion of physical and chemical processes affecting the transport of major ions.]

Szabolcs I. (1989). *Salt Affected Soils*. 274 pp. Boca Raton, FL: CRC. [This is a general review on the distribution, genesis, properties and classification of saline and alkali soils. The problems of their management are also outlined.]

Tanji K. (ed.) (1990). Agricultural Salinity Assessment and Management. 619 pp. New York: American Society of Civil Engineers. [This is a manual that integrates contemporary concepts and managements for agricultural water and salinity problems.]

Biographical Sketches

Marianna Redly is senior soil scientist at the Research Institute of Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences. Budapest, Hungary. She was born in 1933. Her academic background is physical and colloid chemistry. She defended her doctor's theses from the cation exchange properties of alkali soils. She is the author of about 40 papers on the laboratory methods of determining the diagnostic parameters of saline and alkali soils, and on the description and modeling of physico-chemical processes in alkali soils. She acted between 1986-1994, as vice chairperson, and between 1994-1998, as the chairperson of the Subcommission of Salt Affected Soils of the International Soil Science Society.

Valentina Fedorovna Utkaeva was born in 1949. In 1973, she graduated from the Department of Biology and Soil Science, Moscow State University. In 1978, she defended her Candidate theses devoted to the application of different structuring agents for the improvement of soil physical properties. At present, she is a senior researcher at the Department of Soil Physics and Soil Reclamation, V.V. Dokuchaev Soil Science Institute. She is the author of about 50 papers on agrophysical soil properties and methods of improving them.