FOREWORD

This slide set, entitled "Cation Exchange Properties of Soils," and the written comments about each slide, were prepared by a special committee in Division S-2, Soil Chemistry, of the Soil Science Society of America, Inc., with Dr. E. O. McLean serving as chairman. Reproduction of the slides and of the accompanying booklet was undertaken by the Headquarters Office in behalf of the Society, specifically for classroom use. The slides and booklet provide background material which can be used to supplement or complement other sources of information used in teaching cation exchange properties of soils.

The slide set on "Cation Exchange Properties of Soils" is the first of what is expected to be a series of sets concerning the study of soils which will be prepared and distributed by the Soil Science Society of America. This project consisting of producing and distributing various slide sets on subjects in soil science had its origins from what is known as the S572 Slide Coordination Committee. When the committee was originally appointed its charge was to compile a list of sets of slides from various sources which were available and to distribute this list to interested persons. At the time, the Society did not distribute the slide sets per se; if an individual was interested in a particular slide set, he wrote directly to the person or company which offered the set. Since this procedure at times caused confusion, and in some cases delays in obtaining the needed slides, the Executive Committee of the Soil Science Society of America, in 1973, authorized the initiation of a project whereby the Society would collect various slide sets and make them available at a modest price. The Headquarters Office staff was authorized by the Soil Science Society of America to handle the production, distribution, and promotion of these slide sets.

It is the goal of the Soil Science Society of America to assemble a number of slide sets for classroom use. These slide sets will be, in some cases, assembled by specific committees appointed to develop a slide set on a particular subject. In other instances, an already existing slide set will be obtained, reproduced, and distributed by the Society. A broad range of subjects is expected to be covered. Committees will periodically review the slide sets for the purpose of updating them as needed.

Since this is an initial effort on a long term project, the criticisms and suggestions for improvement by the users of this slide set are welcomed. Furthermore, suggestions for additional slide sets are invited. Contributions of slide sets or individual slides which could be considered for insertion into a slide set on a particular subject will be appreciated.

March 1974

Matthias Stelly
Executive Vice President

-- A Few Words of Explanation --

This set of slides on "Cation Exchange Properties of Soils" was prepared and assembled by a Committee composed of the persons named below. This Committee was appointed in accordance with action taken by the Board of Directors of the Soil Science Society of America in late 1969 calling for appointment of slide committees in each Division of the Society. Upon instruction by Dr. C. I. Rich then president of SSSA, Dr. A. L. Page, Chairman of Division S-2 selected those to serve on the Committee.

After considerable correspondence and one meeting, the Committee selected this topic for development of a slide set and began work on it as early as August 1970. It represents much effort by committee members as well as their associates. Most of the material on the slides has been assembled for this purpose from various sources, including original publications, many of which are cited.

The slide set is considered to be neither all-inclusive nor all-exclusive. A person using it may wish to add to it some of his own slides, or delete from it some of those supplied. Also, the comments about each slide are not intended to be all-inclusive of what might be said in each case. Instead, this information is background material which one can use to supplement or complement the obvious things he may wish to point out in the slide.

Generally we have attempted to keep the diagrams and charts on each slide as brief and simple as possible. However, this principle has been violated in a few instances where it was felt that an audience would gain more from seeing a comparison of two situations presented side by side than from seeing each on separate slides.

Division S-2 Slide Committee
Murray Dawson
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18. The effect of the loss and gain of potassium on the exposure of internal surface and the resulting cation exchange capacity of soil clays is indicated. Some decrease in charge density and less than complete crystal expansion probably account for less than theoretical CEC of 240 meq per 100 grams. The trapping (fixing) of K^+ in the wedge-shaped spaces of the clays is a well-known phenomenon when K is added to soils.

19. The effect of the loss and gain of potassium on the exposure of internal surfaces and the resulting cation exchange capacity of soil clays is indicated. Charge density is markedly decreased by oxidation of divalent iron to trivalent iron and by incorporation of H^+ ions into the clay crystal. Correspondingly lower CECs of the clays result. The iron often substitutes for Al in the octahedral layer of the 2:1 clays.

20. The effect of potassium fixation (lattice-trapped K) on the permanent charge CEC is here illustrated in a vermiculite clay* and a Sierra surface soil. The total CEC was not pH-dependent in the vermiculite but was in the soil. The pH-dependency of CEC of the soil is an effect of the organic matter. Since the <u>change</u> in CEC in both the vermiculite and the soil was constant with pH, the lattice trapped K merely inactivated permanent charges (SSSAP 28:199).

21. In addition to permanent charges previously considered, pH-dependent charges result when H ions dissociate from hydroxyl groups of the mineral. Since these OH groups are attached to different cations or combinations thereof causing different degrees of bonding of the H to the O, the H ions dissociate at different pH levels. Even different individuals of a given group dissociate progressively through a considerable pH range. The pK_1 values indicated are the approximate pH levels where half the H^+ is dissociated from that particular group. Because of the wide range in pK_1 values and progressive dissociation within each group, additional pH-dependent charges gradually increase through a wide range in pH. (7th Int. Cong. Soil Sci. 2:445).

22. pH-dependent charges also result from the dissociation of H from OH groups in organic matter. Several of the more common functional groups illustrate the pronounced pH-dependency of CEC of organic matter. Since no permanent charge CEC exists in organic matter, the effects of pH-dependent CEC are generally much more striking than in clay minerals. (Soil Sci. 91:341).

23. The constituent hydroxyls of the carboxyl groups of amino acids in soil organic matter are a source of pH-dependent charge. Whether the amino acids are expressed as acids, or as zwitterions in which the H from the hydroxyl group moves to the amino group making the latter (+) charged and the former (-) charged, the effect is the same, i. e., K is adsorbed to the pH-dependent (-) charge and H ions are neutralized by the OH ions from the base added.

24. Amorphous inorganic soil colloids such as allophane often have very large cation exchange capacities. Some of these charges are pH-dependent; others are of the permanent type. The latter result from substitution of Al^{3+} for Si^{4+} in silica-oxygen tetrahedra, while pH-dependent charges result both from dissociations of H ions from hydroxyl groups and from partial or complete neutralization of positively charged hydroxy-aluminum polymers obstructing negative charges (permanent type). (N. Z. J. Sci. 3:563).

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* Unexpanded mica in this vermiculite may account for lower CEC than that in slide 18.

CATION EXCHANGE PROPERTIES OF SOILS

Slide No.

Comments

1\. Various mechanisms regulate the reactivity and plant availability of ions in soils. The composition of the soil solution is a consequence of the tie-up and release of ions through these mechanisms. Indeed, one can think of the soil solution as containing all the ions of the soil except those removed by these mechanisms, the latter then serving as reservoirs for regulating the reactivity of the various ions. It shall be our purpose here to examine only the cation adsorption and desorption as a mechanism regulating reactivity of cations in soils.

2\. Understanding cation exchange properties of soils requires a knowledge of the source of negative charges effective for adsorption and desorption of cations which we call cation exchange. Two basic types of rectangular solids make up the constituent units of clay minerals. These are the tetrahedron and the octahedron. The tetrahedron has four sides and four corners. It can be thought of as a pyramid with a triangular base.

3\. A tetrahedron results when the centers of four spheres such as oxygen atoms closely packed together are connected by lines. The space between the oxygen atoms can be occupied by a small cation such as silicon to form the silicon-oxygen tetrahedron of clay minerals. Additional tetrahedra form by oxygen ions being shared with silicon ions in adjacent tetrahedra. The resulting tetrahedral layer is a "lattice" with every second line of oxygens having every second oxygen ion missing. This provides an opening for another ion of similar size such as K to be incorporated into the lattice.

4\. The octahedron has six sides and six corners. It can be thought of as a double pyramid with a square base and an apex both above and below the base. An octahedron results when the centers of six spheres such as oxygen atoms closely packed together are connected by lines. (Actually the oxygen atoms may have very small hydrogen ions attached forming hydroxyl ions). The space between the oxygen atoms of an octahedron is a little larger than that in a tetrahedron and is generally occupied by an aluminum atom forming the aluminum-hydroxyl octahedron.

5\. Since additional negative charges of the oxygen atoms remain unneutralized when one octahedron is formed, additional octahedra form resulting in an octahedral layer. The octahedral layer of kaolinite has a bottom layer of oxygens (and hydroxyls) while that of gibbsite has both top and bottom layers of hydroxyls.

6\. Kaolinite clay is composed of one tetrahedral layer and one octahedral layer. Hence it is called a 1:1 clay. The middle oxygen-hydroxyl layer is shared as part of both the tetrahedral and octahedral layers.

7\. Two kaolinite layers are bonded together by O-H-O bonds called hydrogen bonding which makes the separation of the two units of kaolinite relatively difficult. The characteristic C-axis spacing of the kaolinite clay, i. e., the vertical distance from one repeating unit to the next is 7.2 A.

8. Illite clay is composed of one tetrahedral layer on both the top and bottom of the clay with an octahedral layer sandwiched between. Hence it is called a 2:1 clay. The two middle oxygen-hydroxyl layers are shared as part of both the tetrahedral and octahedral layers both top and bottom. Note some substitution of aluminum for silicon in the tetrahedral layer. The term <u>illite</u> may soon give way to <u>mica</u> or <u>hydrous mica</u>.

9. Two illite layers are bonded together by O-K-O bonds, the K^+ having gone into the structure along with Al^{3+} to replace Si^{4+} normally found in the tetrahedra. This K bonding prevents the swelling apart of the illite clay. The C-axis spacing of illite is 10A.

10. Montmorillonite clay is also a 2:1 clay, but it has some substitutions of Mg^{2+} for Al^{3+} in the octahedral layer.

11. Unlike illite clay, montmorillonite has less K^+ remaining to cement the layers together, hence it swells apart upon wetting exposing internal surfaces where negative charges adsorb and desorb cations from the solution. These negative charges are those from the oxygen ions not neutralized by tetrahedral or octahedral cations. Since these charges are effective for cation exchange at all pH levels, they are called permanent charges, or cation exchange capacity resulting therefrom is called permanent charge CEC. Prior to weathering of K from the clay, these charges were most likely neutralized by K^+ ions. The montmorillonite clay has a variable C-axis spacing depending upon how much water or other polar liquid is present to swell it apart.

12. Cations tend to hydrate in water. Here a cation is hydrated with six water molecules.

13. A montmorillonite clay here has two exchangeable cations each hydrated with six molecules of water.

14. A lattice layer composed of 28 molecules of water is shown.

15. Two lattice layers of water molecules on a 2:1 clay such as occurs in the hydration of Mg to form vermiculite or of Al to form chlorite. The C-axis spacing is 14A.

16. The source of permanent charge cation exchange capacity to which reference has previously been made, i.e., substitution of Al^{3+} (& K^+) for Si^{4+} to form mica, illite (hydrous mica), and beidellite is shown. The unsubstituted pyrophyllite mineral is used as a reference to indicate the precise balance of (-) and (+) charges and the shared layers of oxygen-hydroxyls in the tetrahedral and octahedral layers. The substitutions of one Al^{3+} (& 1 K^+) for one Si^{4+} in both silica layers balance the charge initially. But upon weathering the K^+ free so that other cations can exchange for them, a net negative charge of 2 results which is the source of the permanent charge cation exchange capacity of these clays.

17. The source of permanent charge cation exchange capacity: substitution of Mg^{2+} (& K^+) for Al^{3+} to form montmorillonite is shown. The substitution of one or more Mg^{2+} (& an equal number of K^+) in the alumina layer balances the charge initially. But upon weathering K^+ free so that other cations can exchange for them, a net negative charge of one or more results which is the source of the permanent charge cation exchange capacity of this clay.

25. The pH-dependency of net charge of several selected clays is illustrated here. The percentage pH-dependent charge obviously depends on the relative magnitude of the net charge. The CEC of montmorillonite is 11% pH-dependent between pH 4.8 and 7.6; that of illite is 33%, and that of the allophanic Taupo soil clay is all pH-dependent in this pH range. (N. Z. J. Sci. 3:563).

26. The CEC's of whole soils and the contributions of clay and organic matter at different pH's are shown. The change in CEC of the clay increased 1.7 times in the range pH 2.5 to 8.0, while that of the organic matter increased nearly 6 fold. As a consequence, organic matter which contributed only 19% to the CEC of the whole soils at pH 2.5 contributed 45% to the total at pH 8.0 (SSSAP 27:517).

27. The effective CEC (K adsorbed from KCl extraction) of unlimed and limed soils of varying organic matter contents is shown. In the unlimed soils CEC was low and did not increase much with organic matter. Liming to near neutrality increased the effective CEC, and the increase was progressively greater with increased organic matter content. Evidently the cation exchange sites of the organic matter in the unlimed soils were inactivated by Al in other forms than that exchangeable. (SSSAP 29:370).

28. Soil organic matter has a number of functional groups which may be involved in the chelation of metal cations such as Al, Fe, Zn, Mn, Cu, etc. This mechanism usually bonds the cation sufficiently strong to prevent normal cation exchange. In general, only other cations which are also chelated by the same functional groups are able to displace chelated cations. Whether or not chelated cations are available to plants depends on such things as relative bonding strength of the chelate, plant species (its own chelation mechanisms), pH of the system, and solubility of the metal-chelate complex.

29. Soil mineral particles may combine with organic complexing groups to complex or chelate the metal cations.

30. It is now evident that several mechanisms may obstruct or otherwise decrease the effective cation exchange capacities of soils as the pH is changed. These mechanisms may be regarded as pH-dependent obstructions of both permanent and pH-dependent charges. By addition of OH^- or increasing the pH, additional cations can be adsorbed and desorbed by the soil. (SSSAP 31:473).

31. A schematic diagram is shown to illustrate how both pH-dependent and permanent charges may be inactivated by hydroxy-aluminum polymers or by chelation or complexation under strongly acid conditions. Less acid soils or those made so by liming have less inactivation of charges, hence larger effective CEC. pH-dependent charges are shown here schematically as longer and thus weaker bonds for basic cations than permanent charges.

32. The concept of the Donnan Equilibrium has been used to examine the relative bonding of cations to cation exchange sites of soil particles. It has been particularly valuable for assessing the interaction of permanent and pH-dependent charges on cationic activities in systems at various basic cation saturation ratios and base saturation levels. The suspension phase is confined from the equilibrium solution phase by a membrane or other constraint. The relative contribution of soil-dissociated cations to the total activity in the suspension phase can be assessed. Also, the soil retention of the cations in the suspension phase can be quite revealing of bonding energies of cations (or inversely, of their activities).

33. A schematic diagram is shown of pH-dependent and permanent charges of bentonite (montmorillonite) and illite clays as they appear to affect cationic fractions active. At 90% Ca-10% Rb saturations of bentonite Ca preempts the stronger permanent charges causing most of the Rb to counter pH-dependent charges. Only a small portion of the Ca counters pH-dependent charges. With 10% H-clay added to inactivate the pH-dependent charges, the fraction of Rb decreases 9-fold while Ca decreases 4 1/2-fold. Similar changes occur in the illite clay, but much more H-clay is required to inactivate the higher percentage of pH-dependent charge. (SSSAP 33:392).

34. The retention of calcium in the clay phase of Donnan-type systems indicates that practically all of the Ca not retained by the clay phase is related to pH-dependent charges. With 0% H added considerable Ca was free to move from both clay phases at high Ca saturations, but when 10% H was added to the bentonite clay to inactivate pH-dependent charges, a very high percentage of the Ca was retained at all Ca saturations. In illite which has 33% pH-dependent CEC, more than 30% H was required to reach a point where maximum retention occurred at all Ca saturations. (SSSAP 33:392).

35. The distribution of Ca and of Rb in 3-phase Donan systems where equal numbers of exchange sites are provided in each clay and both separated from a common dialysis solution is revealing. Bentonite has a stronger attraction for Ca than has illite. As a result, more Ca is retained in the bentonite at all Ca saturation levels. With Rb, illite shows strongly preferential bonding (fixation) for Rb at low (Rb) saturations. But at higher Rb saturations bentonite adsorbs more Rb than illite. (SSSAP 33:392).

36. The exchangeability of cations such as K is largely a consequence of the strength of bonding of the two ions which exchange places as well as that of the accompanying ion adsorbed to the colloidal surface. These strengths of bonds are reflected in an effective oscillation volume. Thus when a symmetry concentration of NH_4Cl is added to a colloid 50% saturated with a weakly bonded cation such as Na and 50% saturated with K, most of the NH_4 goes to displace Na and less remains to displace K. On the other hand, when a symmetry concentration of NH_4Cl is added to the colloid 50% saturated with strongly bonded Ca and 50% saturated with K, only a little of the NH_4 goes to displace Ca leaving most of it to displace K. Thus at the same level of K saturation several times as much K may be displaced when accompanied by a strongly bonded complement as when accompanied by a weakly bonded complement. (Soil Sci. 48:443).

37. The percentage of K displaced by 1S of HCl in the presence of three complementary ions at all K: complementary ion saturations of the clay is shown. (Soil Sci. 48:443).

38. The percentage of K displaceable when cations of various valencies and hydration sizes are added at different symmetry amounts is shown. The reason is obvious why Ba^{++} is often used as a displacing cation in preference to ions such as Li^{+}. However, other divalent cations may be less subject to fixation in the clay lattice than is Ba.

39. Preferential bonding of one cation over another by exchange sites is demonstrated when a relatively higher proportion of the one cation is adsorbed from a two-cation leaching solution passed through columns of soil. Here preferential bonding of Ca over Sr is manifested by an Ap horizon soil with organic matter present while slight preference of Sr over Ca is evidenced by a B_{21} horizon. (Soil Sci. 107:206).

40. Relative differences in equivalent fraction of cations in solution versus equivalent fractions adsorbed is affected by the sequence of exchange. The ease of displacement of a cation from an exchange site often depends on the order in which it was adsorbed to a colloid relative to that of a complementary ion. This phenomena seems to be related to exchanges of cations on internal surfaces where space is restricted.

41. The soil cation exchange capacity is a buffer against both acids and bases. The soil CEC is normally a mixture of weak acid and its salt. Hence H ions are removed from solution by exchange for basic cations, while OH ions are neutralized by reaction with H ions replaced by basic metal cations. Both H and OH ions are also dissipated by reaction with the hydroxy-aluminum polymers.

42. The type of acidic cations adsorbed to the soil CEC has marked effect on the pH of the soil at a given degree of neutralization of the total acidity present. For example, at 60% neutralization the pH differs 4 full pH units depending on whether the acid is hydronium ions (H_3O^+) or polymerized hydroxy-Al $(Al\text{-}OH)_n^{2n+}$, i.e., pH 3.4 vs. 7.4.

43. The percentage calcium saturation of the CEC of soil colloids markedly affects the plant availability and HCl-displaceability of Ca from these colloids. Indeed, Ca uptake from all colloids at all Ca saturations by soybeans was highly correlated with that displaced by a symmetry amount of HCl. Since this relationship did not occur for Ca displaced with $BaCl_2$, this is undoubtedly a consequence of equally effective Ca displacement by HCl and H-roots from H-preferring, pH-dependent charges made progressively more active at higher Ca saturation. (Soil Sci. 59: 207).

44. The inactivation of pH-dependent charges by H-saturations of bentonite and illite clays has marked effects on both Ca fractions active and uptake by soybean roots, which in turn are highly correlated. (SSSAP 33:397).

45. The soil CEC is a reservoir for plant-available nutrients. The action is at the interface where soil colloid meets root colloid in a bath of soil solution! Our challenge is to focus on the action by some type of instant replay with the aim of developing a better understanding of the game being played.