# Ion-Exchange Minerals and Disposal of Radioactive Wastes— A Survey of Literature

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# ION-EXCHANGE MINERALS AND DISPOSAL OF RADIOACTIVE WASTES—A SURVEY OF LITERATURE

## By B. P. ROBINSON

**ABSTRACT**

A review of the literature on ion-exchange theory, naturally occurring ion-exchange minerals, and the role of ion exchange in the disposal of radioactive wastes is presented. Ion-exchange theory is discussed in terms of colloid science, thermodynamics, reaction kinetics, reaction mechanisms, and adsorption equations.

Ion exchange may be defined as the exchange of an ion held by an electrical charge near the surface of an exchange mineral with an ion present in a solution in which the exchange mineral is immersed. Ion-exchange reactions follow the law of mass action with the reactions being restricted by the number of exchange sites on the mineral and by the bond strength between the exchangeable cations and the mineral surface. Crystalline structure of the exchange minerals and the chemical composition of the solution in contact with the mineral influence the ion-exchange reaction.

Clay minerals and other ion-exchange minerals, including glauconite, ultramarines, and zeolites are discussed in terms of origin, nomenclature, composition, structure, and exchange capacities. The origin of clay minerals is explained by various factors. These include leaching of certain elements from older minerals, complete replacement of a mineral, devitrification of a volcanic glass, crystallization of colloid material, direct precipitation from solutions, and reactions between older minerals and solutions. Older literature on clay minerals includes some misnomers of nomenclature. The modern student, having the advantages of better instruments and improved analytical techniques, has made progress in correcting this situation.

Structurally the clay minerals are considered to consist of a colloidal, silicate-layer lattice in which the layers are composed of planes of silica-oxygen tetrahedrons and planes of aluminum, iron, or magnesium atoms surrounded by six oxygen atoms or hydroxyl groups arranged as octahedrons.

Ion-exchange capacities generally are measured in chemical equivalents adsorbed per 100 grams of exchange mineral at pH 7. Because of differences in structure and in chemical composition of clay minerals, their exchange capacities are reported over a range. Some of the exchange capacities reported in the literature are kaolinite, 3–15; halloysite ($2H_2O$), 5–10; halloysite ($4H_2O$), 40–50; montmorillonite, 70–100; illite, 10–40; vermiculite, 100–150; glauconite, 11–20; and attapulgite, 20–30.

The control of radioactive wastes has been described as adequate but expensive at the present time. However, the condition of adequacy could change in the foreseeable future unless additional means of disposal become available. Some of the major technical considerations associated with the radioactive waste disposal problem include the following (Wolman and others, 1956):

1. Nuclear fuel characteristics and processing associated with them.
2. Recovery of specific isotopes from wastes and use of them to help defray disposal costs.

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3. Proper selection of sites for nuclear plants.
4. A detailed quantitative evaluation of the environments selected to receive radioactive materials.
5. Suitable means of handling and transporting highly radioactive materials.

On the basis of available literature, it appears that practical means for the permanent disposal of high-level radioactive wastes that may be encountered with an expanding nuclear industry remain to be discovered.

## INTRODUCTION

### PURPOSE AND SCOPE OF STUDY

The U.S. Geological Survey has the responsibility of conducting a continuing study of the water resources of the Nation.   This includes a study of the chemistry of the elements in the hydrosphere.   This paper is primarily concerned with the phenomenon of ion exchange, one of the many chemical processes occurring in the hydrosphere. Accordingly, a comprehensive literature survey has been made of clay minerals and other naturally occurring silicate minerals exhibiting the phenomenon of ion exchange.   These minerals are of interest not only for their ion-exchange property but also for their possible adaptability to radioactive waste disposal.

### ION-EXCHANGE PROPERTY OF MINERALS

Examples of the fundamental and practical importance of ion exchange exist all about us.   Growing plants in the soil depend upon cation exchange.   Weathering processes involve the liberation of alkalies and alkaline earths, which may take part in exchange reactions.   Changes in the chemical composition of water occur through cation exchange.   The sodium concentration in sea water is largely the result of the cation-exchange properties of clay minerals that have accumulated in the sea.   The plastic properties of a soil or clay vary with the degree to which sodium or calcium is the dominant exchangeable cation.

It has been said that all inorganic minerals of extreme fineness possess a small exchange capacity as a result of broken bonds (Grim, 1953b, p. 131–132).   However, only such minerals as clays, naturally occurring zeolites, glauconites, greensand, and ultramarines are commonly thought of as cation-exchange materials.   The usual list of clay minerals exhibiting ion exchange includes the following groups: kaolinite, halloysite, montmorillonite, illite (hydrous mica), vermiculite, chlorite, and sepiolite–attapulgite–palygorskite.   Of these, the montmorillonites are noted for the highest cation-exchange capacity.

Marshall (1949, p. 26–27) offered the following list of zeolites: natrolite, mesolite, scolecite, edingtonite, thomsonite, heulandite, analcite, chabazite, and gmelinite.

Various glauconite minerals are known to exist, but exact formulas have not yet been determined for them. They are known to be of marine origin (Grim, 1953b, p. 353) and have been found to approach the illites in structure (Smulikowski, 1954).

The ultramarines were classified under four groups by Marshall (1949, p. 26–27), as follows: sodalite, helvite, ultramarine, and scapolite.

Other suggested general references on ion-exchange materials include Deitz' (1956) "Bibliography of Solid Adsorbents 1943-1953," a review of ion exchangers made by Deuel and Hutschneker (1954), and a general study of ion exchangers made by Malquori (1948).

Ion exchange is an important geochemical process affecting the quality of water. Many ions may be removed from natural waters by means of this process. The clay minerals exhibit a marked capacity for the exchange of cations. Without this phenomenon serious poisoning of the oceans by such elements as copper, selenium, arsenic, and lead could result. Waterlot (1955) noted that ion exchange in clay beds overlying the Cobrieux limestone (France) changes the water progressively from one rich in calcium and magnesium to one nearly free of these elements and high in sodium.

Ion exchange not only influences the migration of elements but also can be of value in the discovery of laws affecting the relations of elements. Although geochemistry will not be discussed in detail in this paper, a few references on the subject are suggested. These include Clarke, 1924; Goldschmidt, 1954; Mason, 1952; Rankama and Sahama, 1950; and Vernadsky, 1924.

## RADIOACTIVE WASTE DISPOSAL

Radioactive contaminants created by bomb tests and by nuclear processing plants can enter water supplies as fallout material, as low-level wastes being dumped into streams or as a result of accidents whereby storage facilities or processing plants release them. Radioactive contaminants differ from the usual industrial plant wastes in that they emit radiation. There is no known method for neutralizing radioactivity; therefore the wastes must be either diluted and dispersed or concentrated and stored (Straub, 1956). Radioactive isotopes disintegrate and thus lose their activity with time, the length of time depending upon the given isotope and its half-life.

One of several methods of concentrating radioactive wastes consists of "fixing" them on montmorillonite clay to minimize the amount leached out by subsequent exposure to water during confinement by underground burial (Ginell, 1952).

Other methods suggested for disposal of radioactive wastes include confinement in geologic formations (Lieberman, 1955), in dry oil wells (Aiken, 1954), and in abandoned mines (Rodger, 1954).

Whatever the method for handling these wastes, be it direct disposal into the ground, dilution disposal into flowing streams and lakes, or other means of disposal, much remains to be learned about the behavior of the radioactivity after disposal.   Will it stay relatively near its original confinement area or will it migrate and possibly contaminate underground waters?   Answers to these and other questions are needed before adequate methods for disposing of radioactive wastes can be devised.

## ACKNOWLEDGMENTS

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## ADSORPTION AND ION EXCHANGE: GENERAL

Adsorption is most commonly thought of in terms of an accumulation of substances at an interface.   It can  be said to occur at all surfaces as in the cases of adsorption of gases by solids, adsorption of dyes from solution by solids, and adsorption of cations on ionic lattices as in naturally occurring clay minerals.   Adsorbed substances may be the products of reaction or of hydrolysis, unaltered molecules, or ions (McBain, 1950, p. 38).   Adsorption, as in the case of condensing gas molecules on a solid surface, differs from adsorption of cations as on ionic lattices of clay minerals.   In the former case gas molecules are held by Van der Waals forces.   In the latter case the cations on ionic lattices are held by electrostatic forces.   Adsorption from solution is more commonly observed than adsorption of gases.   Adsorption or ion exchange as in the case of cation exchange between natural waters and clay minerals is of particular interest in this paper.

An understanding of adsorption and ion exchange involves a study of colloids, a study of the two fundamental approaches applicable to chemical phenomena, namely, thermodynamics and kinetics, and a study of reaction mechanisms.   These will be considered in succeeding paragraphs.

## COLLOID SCIENCE

One hundred years have passed since Graham proposed the term "colloid" in 1861, but colloid science has had to wait until the present generation to receive its just recognition.   The term was introduced to identify certain substances (albumin, gelatin, glue, and silicic acid) used by Graham in diffusion studies (Glasstone, 1940, p. 1206).   All of the substances exhibited a very slow rate of diffusion through a parchment membrane.   Today the colloidal condition is thought of as comprising any substance and any medium.

## COLLOIDS DEFINED

The term "colloid" has been defined more specifically by Jirgensons and Straumanis (1954, p. 1) as follows:

Colloids are substances consisting of a homogeneous medium and of particles dispersed therein. India ink, the milky dispersions of sulphur, clays and humus, a soapy shaving cream, glue and blood serums, are all examples of colloids. The dispersed entities may eventually be large molecules.

## CLASSIFICATION OF COLLOIDS

All colloidal systems or sols (as they are often called) are classed as inorganic or organic, depending on their chemical composition. They may be further broken down into hydrosols and organosols, depending on the dispersing medium. If water is the dispersing medium, the colloid is a hydrosol, of which there are two types: hydrophylic and hydrophobic. The first type is characterized by a strong interaction between particles and water molecules that tends to make a stable colloid. The other type has no such strong attraction between particles and water molecules and is much less stable. If an organic liquid such as alcohol, ether, or benzene, for example, is the dispersing medium, the colloid is an organosol.

## SIZE OF COLLOIDAL PARTICLES

Colloids can be said to exist in a state of fine subdivision, ranging in size from a true solution on the one hand to a true suspension on the other. An approximate size range of $10^{-3}$ to $10^{-6}$ mm was suggested for colloidal particles by Mason (1952, p. 147). Bragg (1937b) described them as too small for the microscope and too large for usual X-ray methods.

## EXAMPLES OF COLLOIDS

Several types of colloid systems or disperse systems, as they are generally called, are known. They include the following: solid/gas (smoke), liquid/gas (fog), liquid/liquid (emulsion), and solid/liquid (sols, gels, pastes). The solid/liquid type is of great importance to geochemistry.

## PROPERTIES OF COLLOIDS

A better understanding of colloids is possible if some consideration is given to their properties and characteristics.

### STRUCTURE AND ELECTRIC CHARGE

Both crystalline and amorphous colloids are known, although most inorganic colloids are crystalline.

Colloidal particles are characterized by an electric charge. Some colloids are known to exist with either a positive or negative charge, depending on the environment. Colloidal particles of the soil usually carry a negative charge. Ferric hydroxide is an example of such a

colloid. A few of the most important colloids are listed in Mason (1952, p. 148).

The origin of the charge on colloidal clay particles has been explained by various investigators. Mukherjee (1921) reported the charge as being due to the adsorption of a common ion. He claimed that electrostatic forces are strong enough to account for the adsorption. Baver (1956, p. 24–29), Gapon (1946), Hauser and Le Beau (1946), and Hauser and Colombo (1954) explained the charge in terms of Helmholtz's "double layer." According to this theory, replaceable adsorbed cations are found on the surface of clay minerals. In other words, clay particles are colloidal anions with the corresponding cations adsorbed on the surface. One colloidal-clay particle can adsorb many cations. Thus, it may be considered as a negatively charged nucleus surrounded by positively charged ions.

McBain (1950, p. 195) challenged the accuracy of the double-layer theory explanation. He believed that the distance between the charges on particles and surfaces makes them practically independent of each other. In addition he doubted that the conductivity observed for surfaces can be accounted for by an outer diffuse ionic atmosphere.

Kiefer (1947) attributed the charge on colloidal particles to dissociation and (or) adsorption of ions. By mathematical analysis, he showed that, for the dissociation process, the charge and electrophoretic velocity increase with dilution; whereas, for the adsorption process, both approach zero with dilution.

Particle charge and stability are closely related and usually require the presence of a small amount of an electrolyte, the most important of which are organic compounds (British Patent 689,692, 1953). Excessive amounts of electrolytes cause the colloids to precipitate or coagulate. Humus colloids seem to exert a stabilizing influence on inorganic colloids in the geochemical environment (Mason, 1952, p. 148–149).

### STABILITY OF COLLOIDS

Another distinguishing property of the colloidal state is its metastability or its degree of stability (McBain, 1950, p. 195). Any change in the particle size will result in a change in the total surface area and a change in the free energy of the system, so that all colloids are theoretically unstable (Mason, 1952, p. 148–149).

Stabilization of a colloid is referred to as deflocculation, dispersion, or peptization throughout the literature.

Speil (1940) explained deflocculation on the basis of the Gouy-Freundlich double-layer theory of water hulls around kaolinite particles. The OH$^-$ is supposed to be selectively adsorbed on the broken

edges of the crystals with $Na^+$ counter ions. When more $OH^-$ is added than can be adsorbed on the crystal, an excess occurs in the free water and profoundly changes the forces between the particles.

The mechanism of peptization is related to the distribution of those components responsible for the difference of the osmotic pressure in the region near the surface of the colloid particles (methoric spaces) as compared with the osmotic pressure in the bulk solution, according to Tezak (1952). Peptization results when the concentration of ions and molecules of the dissolved component in the methoric spaces is greater than in the interior of the solution, and the difference in osmotic pressure tends to separate the particles. Conversely, with a smaller concentration of ions and molecules of the dissolved component in the methoric spaces, the equilibrium distribution of the ions and molecules could be reached by the colloidal particles approaching each other, thus giving a coagulated system.

Duclaux (1946, p. 514–517) proposed that inorganic colloids are stabilized by condensation with multivalent negative ions rather than by mere physical adsorption.

Baver (1956, p. 24–29) and Jenny and Reitemeier (1935) explained stability of various clay suspensions in terms of cation-exchange capacity of the clay and the energy with which the adsorbed cations are held against the inner layer of the double layer. As the exchange capacity increases, so does the stability; whereas, with increasing energy of adsorption, the stability decreases.

In a series of papers the Russian, Gedroiz (1912–22), made some outstanding contributions to soil science. According to Gedroiz (1922), all salts, acids, and bases can bring about the flocculation of colloidally divided substances. He pointed out that cations of the electrolyte generally will be the flocculating agents, since soil colloids commonly carry a negative charge. Flocculation takes place when the concentration of a given electrolyte exceeds a certain quantity which he called the "electrolytic limit."

The flocculating power of various cations increases with increasing valences and atomic weights, except for $H^+$, which has higher flocculating power than that of the other monovalent metals. Presence of the smallest possible quantities of $H^+$, in combination with other cations, diminishes the amounts of other cations needed for flocculation of negative colloids (Gedroiz, 1922).

Rabinerson (1938) suggested that in the coagulation of colloids there is a difference between those particles whose electric properties are the same in all directions and those with a nonuniform distribution in charge. In the first case, a compact precipitate forms; in the second, a gel.

In tests with colloidal clay from Hesperia sandy loam, Mazurak (1953) found that both concentration of cation and time of shaking affected the aggregation obtained. H-saturated clays were the most water stable, but $Ca^{+2}$ decreased water stability.

Wiklander and Hallgren (1944–45) found a pronounced difference in the effect of the alkali ions and that of bivalent ions on the dispersion of soil colloids. Soil samples saturated with bivalent ions were much more resistant to dispersion.

Haissinsky and Gluzbarg (1951) studied the effect of ionizing radiation on colloidal solutions. Positively charged copper and negatively charged gold and silver aqueous colloidal solutions were exposed to radiation. The positively charged copper colloidal solution was coagulated, whereas the gold and silver solutions were stabilized. The authors attribute the observed effect to the formation of free radicals, hydroxyl groups, from water. The hydroxyl groups then affect the double layer of the sol particles, stabilizing the negatively charged sols and coagulating the positively charged ones.

Shukla (1944) explained the dispersion of soil colloids produced by shaking calcium soil with the carbonates of alkali metals as due to the gradual replacement of exchangeable calcium by alkali cations. But as the concentration of the free salt increases in the dispersion medium, the alkali cations tend to coagulate the soil by compressing the double layer surrounding the dispersed particles.

From studies made on colloidal solutions in concentrated electrolytes, Voet (1936) concluded that the influence of electrolytes on colloids is more complicated than formerly thought. For example, a small quantity of electrolyte is necessary to form the double layer and stabilize a hydrophobic sol; whereas, a somewhat larger quantity produces coagulation. Finally, the sol can be stabilized again by adding an even higher concentration of electrolyte which shows that a colloidal system can have two stable and two unstable zones, depending on the concentration of the electrolyte.

Powell (1954) and Lauderdale (1951) discussed the effect of pH on coagulation. A pH of 5.5 is considered by Powell to be an optimum value for coagulation. Lauderdale found that a pH of 11.3 gave optimum results in the removal of radioactive wastes through phosphate precipitation.

Sharov (1939) suggested that students of soil colloids like Vageler, Kelley, and Jenny, who consider the disperse system not only as a unit by itself (physicochemical interaction of two phases) but as also involving an extraneous third component, are in error. By the third-component idea, colloids essentially are mechanical mixtures of the fundamental phases, and of the adsorbed ions or substances, or impurities sticking to the colloid.

## OTHER REFERENCES

Other suggested references on colloids include: Caldwell and Marshall (1942), Freundlich (1926, p. 216–217), Glasstone (1940, p. 1172–1257), Hauser (1939), Iler (1955, p. 181–232), Kinet (1943), Paneth (1948), and Phelps (1947).

A number of reviews are also available including the following: Alexander (1947, p. 1–52), Antipov-Karataev (1940), Atkinson (1943), Broughton (1953), Hauser (1945, p. 287–321; 1955a, p. 2–9; 1955b, p. 8), Holdridge (1953), Hopu (1943), Mattson (1954), Milligan and Mill (1955), Nagelschmidt (1944), Schweitzer and Jackson (no date), and Troelstra (1954).

## THERMODYNAMICS AND ADSORPTION

Mason (1952, p. 59) described thermodynamic systems as being characterized by certain fundamental properties which may be classified as (a) extensive and (b) intensive. Examples of extensive properties include mass, volume, and entropy. They depend upon the amount of matter in the system. Intensive properties include temperature, pressure, and chemical potential, all of which are independent of the amount of matter present in the system.

The total energy of a thermodynamic system is called its internal energy. It consists essentially of the sum of the thermal, mechanical, electrical, and chemical energies (Mason, 1952, p. 60). While absolute values of these quantities generally cannot be obtained, changes in the quantities can be obtained. Thermodynamics, then, is concerned with these changes; that is, the initial and final states of a system and the equilibrium conditions and criteria for evaluating them (Encyclopedia of Chemical Technology, 1953, v. 11, p. 570).

Goldschmidt (1954, p. 3) suggested that modern thermodynamics, and particularly the concept of free energy, makes possible the prediction of the distribution of elements and their compounds between liquid and gaseous phases at any temperature and pressure, provided their thermodynamical constant is known.

Eley (1947, p. 54) considered thermodynamics as concerned with systems in equilibrium whose properties do not change with time. Time effects—diffusion rates, rates of flow or creep—do not fall within its province.

Thus, while thermodynamics cannot predict the rate at which a reaction will proceed nor describe the mechanism of the reaction, conditions under which certain geochemical processes may occur can be predicted even though the reactions cannot be reproduced experimentally.

## FREE ENERGY AND EQUILIBRIUM

A better understanding of thermodynamics can be had from a consideration of the relationship between free energy and the equilibrium of a thermodynamic system. The brief discussion that follows is based on Mason (1952, p. 60–64).

Free energy has been defined by the Helmholtz and Gibbs equations as follows:

$$\text{Free energy} = E - TS \text{ (Helmholtz)}$$

$$\text{Free energy} = E - TS + PV \text{ (Gibbs)}$$

in which

$E$ = internal energy of the system

$TS$ = (Absolute temperature $\times$ entropy) = Thermal energy

$PV$ = (Pressure $\times$ volume) = Mechanical energy

The free energy of a reaction determines its state of equilibrium. For a reversible reaction at equilibrium, the free energy of the reactants is equal to the free energy of the products. A necessary condition for a chemical reaction to proceed spontaneously is that the total free energy of the reaction products be less than the free energy of the reactants. Thus, knowing the free-energy change of a reaction, one can predict whether or not it will occur.

The free-energy change of a chemical reaction can be difficult to obtain experimentally. However, the problem becomes simplified if it is assumed that both products and reactants are in their standard states and heat-capacity data are available. The molar free energies of formation of many chemical compounds are now known in their standard states. The free-energy change is simply the sum of the free energies of the reaction products minus the sum of the free energies of the reacting substances. When working with silicates, though, one is handicapped in that but few data on the free energies of silicates are available.

Thus, thermodynamics provides a general approach to problems of stability, equilibrium, and chemical change.

## EXPERIMENTAL STUDIES

A number of investigators have studied the thermodynamics of exchange adsorption in clay minerals and other exchange materials. Amphlett and McDonald (1956) studied the uptake of $Cs^+$ and $Sr^{+2}$ on a lower greensand soil. Isotherms were obtained for the system $Cs^+$–$Sr^{+2}$ soil at two different ionic concentrations, and from these, the thermodynamic equilibrium constant was calculated for the exchange reaction—

$$2CsE + Sr^{+2} \rightleftharpoons SrE_2 + 2Cs^+,$$
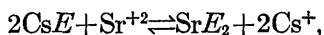
in which $E$ represents solid-phase material.

This and other thermodynamic data were compared with those of other workers on montmorillonite.

Gaines and Thomas (1953), in studies on clay-mineral adsorption, formulated expressions for thermodynamic-equilibrium constants for ion-exchange equilibria of models defined in terms of operational variables.

Gregor (1949), with his thermodynamic theory of exchange processes, predicted ion-exchange phenomena—in particular, distribution constants—from measurable physical quantities that are defined apart from the exchange processes themselves. In a qualitative comparison between theory and experiment, reasonably good agreement was obtained for the limited number of cases presented.

Marshall and Upchurch (1953), in plant-growth studies with soybeans, explained uptake of a particular cation as being governed in part by the free-energy change in the reaction between root in acid media and the exchanger.

Thomas and Gaines (1954) wrote theoretical equations for describing exchange isotherms and for determining equilibrium constants in studies on the system: montmorillonite–cesium–strontium.

Faucher and Thomas (1954) studied the ion-exchange equilibria between a montmorillonite clay and K–Cs from chloride solutions by chromatographic and other methods. Results of their experiments indicate that the total concentration of the salt in solution has no influence on the shape of the isotherm up to 0.4M. The results are summarized in terms of equilibrium constants and activity coefficients for the mixed-clay phase.

Woodruff (1955) presented theoretical consideration for the evaluation of the free-energy change that accompanies an exchange of cations between a clay and a solution. Working with Putnam clay, he found a change of about $-3,000$ calories per chemical equivalent in the exchange of potassium for calcium when the cations were present in the ratios characteristic of productive soils.

Studies of cation-exchange reactions with clay minerals by Cutler and Cook (1953a; 1953b) showed that at least three equilibrium reactions are involved in cation exchange. These are equilibrium between (a) active and inactive sites, (b) free and adsorbed $H^+$ ions, and (c) free and adsorbed cations other than $H^+$ ions. Free-energy computations support the accuracy of the derived equilibrium constants.

Kiselev (1945) applied Gibb's fundamental equations for bulk phases and surface layers to a study of the work and heat of adsorp-

tion.  He described the work (and heat) of adsorption from solution as being equal to the sum of the work (heat) of wetting of adsorbent by pure solvent, the work (heat) of adsorption from solution of the solute, and displacement of the solvent by the latter, and work (heat) of dilution of the solution.

### OTHER REFERENCES

For further discussion on thermodynamics and adsorption, the reader is referred to standard textbooks of thermodynamics and to Bower and others (1957), Flood (1955), "Encyclopedia of Chemical Technology" (1953, v. 11, p. 570–585), Jurinak and Bauer (1956), and Kiselev (1946).

## REACTION KINETICS

### FUNCTION OF KINETICS

Thermodynamics predicts the sign of reaction velocity, but it cannot give the magnitude of velocity (Turner and Verhoogen, 1951, p. 38).  Thus we turn to chemical kinetics for an explanation of reaction rates.

Chemical reactions are known to occur at definite rates depending upon conditions such as concentration of reactants, temperature, radiation, and presence of a catalyst or inhibitor.  Reactions may be so rapid as to appear instantaneous, as in the neutralization of a strong acid by a strong base, or so slow at ordinary temperatures that no detectable change is noticeable for many years, as in the combination of hydrogen and oxygen.  Thus chemical kinetics may be said to consist of the study of the rates of reaction processes which occur with measurable velocities between these two extremes and at temperatures that are easily accessible in the laboratory (Glasstone, 1940, p. 1024).

### ORDER OF RATE EQUATIONS

Reactions are classified as first order, second order, and third order, depending upon whether the reaction rate is dependent upon the concentrations of one or more substances.  If the reaction rate is unaffected by concentration, it is classified as a zero-order reaction.  Glasstone (1940, p. 1045) referred to literature mention of higher order reactions (even as high as eight), but he also stated that it is unlikely that any single step or mechanism in such a reaction involves processes higher than third order.

Reactions generally consist of a combination of the several orders rather than one particular order.  They may consist of (a) consecutive reactions in which the overall reaction passes through a series of steps, (b) reverse reactions, and (c) side reactions, the latter being particularly common in organic chemistry (Kittsley, 1955, p. 104–105).  Glasstone (1940, p. 1045) and Turner and Verhoogen (1951,

p. 40) pointed out that it is the slowest stage that determines the overall rate of the whole process.

### DIFFUSION EFFECT ON REACTION RATE

Turner and Verhoogen (1951, p. 40) expressed the belief that the velocity of diffusion of reactants and their products is the rate-determining factor in many processes of geological importance. Kunin (1958, p. 49) speculated on the mechanism of ion exchange by tracing the path of an individual ion in the bulk solution to its destination in a resin phase. The ion diffuses through the bulk solution until it reaches a stagnant solution layer near the resin phase. It then passes through that layer into the resin structure and diffuses through restricted and water-filled pores until it reaches an exchange site. Exchange occurs and the replaced ion retraces the path taken by the entering ion.

Studies of clay minerals and zeolite by Wiegner (1936) might be considered with Kunin's discussion in mind. Wiegner considered that the location of the exchange groups determines the ion exchange rate in silicates. The zeolite cation exchanger chabazite, for example, with exchange sites accessible only through very small pores, has a low rate of exchange. Kaolinite in contrast, with exchange sites at the surface and edge of platelike sheets, attains equilibrium almost instantaneously.

### TEMPERATURE EFFECT AND THE ARRHENIUS EQUATION

A better understanding of the mechanics of rate processes can be gained from a study of the influence of temperature on these rates. The Arrhenius equation (proposed in 1889) is considered the most satisfactory method for expressing the influence of temperature on reaction velocity. It is represented as follows:

$$k = Pe^{-\frac{E}{RT}}$$

where the symbols are—

$k =$ Rate constant

$E =$ Energy of activation or heat of activation (it is a constant and represents the energy per mole that a particle must acquire before it can enter into the reaction).

$e =$ Base of natural logarithms, 2.71828

$R =$ Molar gas constant

$T =$ Absolute temperature

$e^{-\frac{E}{RT}} =$ The fraction of all particles possessing $E$ at a given time

$P =$ A frequency factor representing the number of particles entering into the reaction per unit of time

The Arrhenius equation may be transposed to the simpler logarithmic form

$$\log k = -\frac{E}{2.303R} \times \frac{1}{T} + \text{Constant}$$

Thus, it can be seen that for a given reaction the log of the rate is proportional to the reciprocal of the absolute temperature, and the slope of the line is dependent upon the energy of activation.

The Arrhenius equation is applicable to homogeneous gas reactions, to heterogeneous processes, and to reactions in solution.

It is apparent that if absolute calculations of reaction rates are to be made, the energy of activation and the frequency factor must be obtained. A semiempirical method for calculating the energy of activation was discussed by Glasstone and others (1941, p. 4).

Calculation of the frequency factor also was discussed by Glasstone and others (1941, p. 10–11). The calculation is based on the assumption of a critical intermediate stage in chemical reactions and other rate processes. This critical stage (activated complex) generally occurs at the maximum potential energy value. It is assumed to be an ordinary molecule having all the usual thermodynamic properties except that motion along the reaction coordinates leads to decomposition at a definite rate.

### PARTITION FUNCTIONS

Partition functions have been used in a statistical treatment of reaction rates. For a given molecule the partition function $F$ is a measure of the probability of the occurrence of that molecule in a specified volume and is the sum of the $e^{-E/kT}$ terms for all forms of energy possessed by the molecule.

In the term $e^{-E/kT}$, the symbols are—

  $e = 2.71828$
  $E =$ Energy of molecule
  $k =$ Boltzman constant
  $T =$ Absolute temperature

If the dimensions of the molecule and its normal vibration frequencies are known, the partition function can be calculated with a fair degree of accuracy (Glasstone and others, 1941, p. 14–15). Partition functions are of importance because from them thermodynamic quantities such as equilibrium constants, free energies, and entropies can be obtained (op. cit., 1941, p. 169).

### EXPERIMENTAL STUDIES

Bauman and Eichhorn (1947) observed that it is difficult to make a fundamental study of the mechanism, equilibrium, and rate of ion-exchange reactions of such exchange materials as naturally occurring

greensand, clay, bentonite, peat, sulfonated coal, lignite and tannin. This is true because of the wide variety of ion-active groups and variations in the structure of individual particles. This observation is emphasized by the dearth of literature on the reaction rate of ion exchange for clays, greensand, and other naturally occurring exchange materials.

Some equations for describing the process of ion exchange between a flowing salt solution and an exchanger were derived by Thomas (1944). These equations have been extended and applied to various mass transfer processes, including the case for ion exchange, where any proportion of the two ionic species are initially present uniformly on the exchanger and in the solution applied (Hiester and Vermeulen, 1952; Opler and Hiester, 1954; and Vermeulen and Hiester, 1954). Bower and others (1957) applied the equations to the study of the distributions of dissolved and adsorbed cations in soil columns as functions of depth and volume of solution applied. For the exchange of ions of equal valence, the following type of rate equation was used:

$$\left(\frac{\partial q_A}{\partial \tau}\right)_z = k \left[ c_A q_B - \frac{1}{K} q_A c_B \right]$$

At equilibrium $(\partial q_A/\partial \tau)_z = 0$ and this gives a mass action type exchange equation:

$$K = \frac{q_A c_B}{q_B c_A}$$

For the exchange between a univalent cation $A$ and a divalent cation $B$, the following type of equation was used:

$$\frac{q_A c_B}{q_B c_A} = K\sqrt{2c_B}$$

The symbols for the preceding equations are identified as follows:

$c_A, c_B$ = Concentration of cation species $A$ or $B$ in the solution phase at a specified point in the column, in milliequivalents per milliliter.

$k$ = Exchange rate constant, milliliters per milliequivalent per minute.

$K$ = Exchange equilibrium constant, dimensionless.

$q_A, q_B$ = Concentration of cation $A$ or $B$ in the adsorbed phase at a specified point in the column, milliequivalents per gram.

$\tau$ = Time, minutes.

$z$ = Depth of soil, centimeters.

Experimental results agreed quite satisfactorily with those predicted by the equations for both equal and unequal valence ion pairs.

Grim (1953b, p. 136–137) discussed cation-exchange rates in clay minerals and zeolites. He points out that various factors—particular clay mineral, nature and concentration of cations, nature and concen-

tration of anions—influence the rate of cation exchange. Kaolinite has about the most rapid rate of exchange for clay minerals, being almost instantaneous. Montmorillonites, attapulgite, and illite have slower rates of exchange, with the latter requiring hours to reach completion. Chloritic clay minerals probably have a rate of exchange similar to illites, and vermiculite should exhibit a rate of exchange similar to montmorillonite. Rate of exchange in some zeolites is slower than for the clay minerals.

The different rates of exchange exhibited by the various clay minerals likely is due to their differing crystal structures. The rapid exchange rate exhibited by kaolinite might be explained by exchange occurring on the edges of particles. Exchange in montmorillonite occurs primarily between layers and in attapulgite in channels. Thus the slower exchange rate of the latter two clays might be explained by the time required for penetration between layers and into the channels.

Wiklander (1955a, p. 126–127) commented on the rate of ion exchange based on experiments by Way, Gedroiz, Hissink, Wiegner, and others. His conclusions of the rates of exchange for various clays are similar to those outlined by Grim (1953b, p. 136–137).

Tsyurpa's (1946) results on cation-exchange rates support Grim's (1953b, p. 136–137) belief that kaolinite has the most rapid rate of exchange of the clay minerals.

Other investigators have reported on reaction rates for inorganic exchange materials. Cernescu (1931) observed that clays establish an exchange equilibrium in 5 minutes, whereas in tests with a siliceous cation exchanger and chabazite reaction periods of 10 and 92 days respectively were required. Using Oak Ridge clay, which is composed mainly of montmorillonite and kaolinite, Lacy (1954) found that a contact time of 15 minutes was sufficient for easy-to-remove radioactive isotopes, whereas more difficult ones required 90 minutes. McHenry (1956b) reported that reactions between a composite Hanford soil and cesium ions attain adsorption equilibrium within a few minutes for a given set of conditions. Gedroiz (1914) found that equilibrium was established in 3 minutes of shaking time in tests using 50 grams of a chernozem soil and 500 ml of $1N$ ammonium chloride. Later Gedroiz (1919) found that equilibrium was established within 1 to 5 minutes in tests in which 10 grams of soils was shaken for varying periods of time with 100 ml of $1N$ solutions of ammonium chloride, sodium chloride, and potassium chloride. Borland and Reitemeier (1950) used radioactive $Ca^{45}$ to demonstrate that equilibration of calcium between the solution and solid fractions of aqueous systems of kaolinite, halloysite, hydrous mica, beidellite, and montorillonite is complete, or virtually so, after shaking for

½ to 1 hour.   Techniques used did not permit the study of shorter periods.

Much work has been done on reaction rates of synthetic resins. Some of those studies may be helpful in studying reaction rates of clay minerals and other naturally occurring cation exchangers.

## REACTION MECHANISMS

### TYPES OF ADSORPTION

Various types of adsorption are discussed in the literature, but the two most commonly mentioned are referred to as physical and chemical (Glasstone, 1940, p. 1179; Mason, 1952, p. 149; McBain, 1950, p. 38; Trapnell, 1955, p. 1–4).

### PHYSICAL

Physical adsorption is characterized by relatively small heats of adsorption, relatively weak van der Wall force of attraction, condensed gas molecules on solid surface, and a reversible equilibrium between a solid and a gas that is rapidly attained when temperature pressure are changed.   Several layers of molecules can be adsorbed on a solid by the physical type adsorption (McBain, 1950, p. 38).

### CHEMISORPTION

The understanding of chemisorption or chemical adsorption is of more recent origin than that of physical adsorption.   Haber (1914) and Langmuir (1915) described it in terms of unsaturated chemical forces at the surface of a solid body.   Similarly, McBain (1950, p. 38) characterized chemisorption in terms of strong valence bonds and monomolecular layers.   Due to its high activation energy, chemisorption sometimes is referred to as activated adsorption (Taylor cited in Glasstone, 1940, p. 179).

McBain (1950, p. 52) discussed chemical adsorption in terms of Fajan's rules.   According to this approach, an ion must form a difficultly soluble or weakly ionized compound with the oppositely charged ion of the lattice in order to be strongly adsorbed on an equivalent compound of the salt type.   Thus cation adsorption is raised by charging the surface negatively and is lowered by charging the surface positively.

Kolthoff (1936) in his study of adsorption on ionic lattices discussed five different examples of adsorption:

1.   Adsorption of a salt having an ion in common with the lattice: adsorption of potential-determining ions.
2.   Exchange adsorption between lattice ions in the surface and foreign ions from the solution.
3.   Exchange between adsorbed counter ions and foreign ions in the solution.
4.   Molecular adsorption on nonelectrolytes and true adsorption of salts.
5.   Activated adsorption.

## OTHER TYPES

McBain (1950, p. 49) suggested the term persorption for applying to the adsorptive properties of dehydrated zeolites such as chabazite.

Hauser (1939, p. 142–143) described an electric theory of adsorption. It suggests that adsorption energy decreases rapidly with distance and that adsorption of molecules on crystalline surfaces depends on the size, shape, and distance between molecules.

Muto (1942, p. 104–107) explained adsorption of surface-active electrolytes in terms of Coulomb forces. For example, when surface-active ions are adsorbed, Coulomb repulsion between similar ions and the repulsion due to the jump of the dielectric constant at the interface act to reduce adsorption. Ions of opposite charge in solution assemble close to the adsorption layers and counterbalance the effect. Muto has derived an adsorption formula based on the assumption that the adsorption layer is a continuous distribution of electricity.

Notable contributions on the power of soil colloids to exchange cations have been made by Gedroiz (1922) who described adsorptive power of the soil as its power ability to retain substances dissolved or suspended in water. He considers adsorption by the soil as consisting of the five following forms: mechanical, physical, physicochemical, chemical, and biological.

The first of these, mechanical adsorption, is demonstrated by water-suspended particles of such size that they cannot pass through a porous soil but are filtered out.

Physical adsorption is explained in terms of surface tension and the fundamental law of colloid science. These are discussed elsewhere in the paper by Gedroiz (1922) under "Surface tension."

The term physiochemical adsorption is applied to cation exchange in soils by Gedroiz (1922). He cites historic terminology in using zeolitic bases for alumino silicates and compares this type of adsorption with physical adsorption as follows:

Physical:
1. A substance adsorbed from solution remains in the dissolved condition, but is to a certain extent connected with the solid particle.
2. Whole molecules are adsorbed.
3. Distribution of concentration of the soil solution changes.

Physiochemical:
1. A substance adsorbed from solution passes into the soil as a solid phase. The substances are not water soluble.
2. Only the cation is adsorbed.
3. Concentration of soil solution does not change quantitatively, only qualitatively.

Gedroiz (1922) considered cation exchange in the soil attributable to both organic humates and alumino silicates or zeolite bases.

Chemical adsorption (Gedroiz, 1922) is based on a purely chemical reaction of mutual exchange and on the ability of anions and cations to give difficultly soluble compounds.

The extraction of various substances from the soil solution by organisms is termed biological adsorption by Gedroiz (1922). Nitrifying bacteria are an example of this form of adsorption.

The reader is referred to Harris (1953, 1954, 1955) for recent reviews on adsorption.

## ADSORPTION EQUATIONS AND EXCHANGE EQUILIBRIUM

Attempts have been made to apply various equations to the study of adsorption and cation-exchange equilibriums (Davis, 1945; Grim, 1953b, p. 154; Kelley, 1948, p. 40–50; Krishnamurti, 1954; Magistad and others, 1944; Marshall, 1949, p. 124–125; McBain 1950, p. 40; and Saidel, 1943). These equations represent three specific avenues of approach to a quantitative expression of adsorption and cation exchange and have been classified by Grim (1953b, p. 154) and Marshall (1949, p. 124–125) as follows:

1. Empirical equations based on adsorption isotherms.
2. Mass-action (thermodynamic) approach.
3. Kinetic-theory approach.

### EMPIRICAL EQUATIONS

The classical adsorption isotherm, or Freundlich equation, was derived originally from the adsorption of a gas by a solid (Kelley, 1948, p. 40). It may be applied to cation exchange when identified as follows:

$$M = kc^{1/n} \tag{1}$$

where

$M$ = weight of cations adsorbed from a solution at equilibrium with a known weight of exchange material,

$k$ and $n$ = constants,

$c$ = cations remaining in solution.

The equation applies fairly well over a limited range of concentration.

Langmuir (1918) proposed the following type of equation for the adsorption of a monomolecular layer of gas by a solid:

$$M = \frac{abp}{1 + ap} \tag{2}$$

where

$M$ = gas molecules adsorbed,

$a$ and $b$ = constants,

$p$ = pressure.

Derivations of this equation were presented by Langmuir (1918) and Dunken (1940). The equation, by proper definition of quantities, can be written to apply to exchange adsorption.

Another modification of the Freundlich equation was proposed by Wiegner and Jenny (1927). Their equation has the following form:

$$a\text{-}b = k\left(\frac{b}{a\text{-}b}\right)^{1/p} \tag{3}$$

where
  $a\text{-}b$ = weight of cations adsorbed per given weight of soil,
  $b$ = remaining concentration of cations in solution at equilibrium,
  $a$ = concentration of salt solution at start of exchange process,
  $k$ and $p$ = constants.

Vageler and Waltersdorf (1930) explained the exchange process by the following equation:

$$a = \frac{s}{1 + \frac{z}{b}} \tag{4}$$

where
  $a$ = cation mass adsorbed per gram of adsorbent,
  $b$ = equivalents of initial salt solution used per gram of adsorbent,
  $s$ = exchange capacity of adsorbent,
  $z$ = constant called the half value by Vageler. When half of the exchangeable cations ($s/2$) have been replaced, $z/b = 1$.

Barkan (1940) reported that the adsorption isotherm can be used to determine the exchange acidity of the soil.

Högfeldt (1955, p. 151) reviewed empirical equations (representing cation exchange equilibrium) of the following authors: Kroeker, Vageler, Weisz, Boedeker, Freundlich, Wiegner and Jenny, Van Dranen, Rothmund-Kornfeld, and Yamabe and Sato. Three different kinds of equilibrium quotient curves are recorded in the literature: falling curves, rising curves, and curves showing maximum or minimum. Of the empirical equations reviewed, only Freundlich's is capable of representing all of these types.

Mokrushin (1945) showed how such basic equations of colloid chemistry as Gibbs' adsorption equation, the Langmuir and Freundlich adsorption equations, and others can be deduced by use of the Maxwell-Boltzman equation.

In the foregoing empirical adsorption equations, the assumption is made that cation exchange can be represented algebraically over a considerable range. Marshall and Gupta (1933) applied these equations to a wide range of concentrations for beidellite and montmorillonite clays and found none entirely satisfactory. The application of these empirical equations is limited by such variables as nature of the clay mineral, nature of ion, ionic concentration, clay concentration, and others, according to Grim (1953b, p. 154). Different explanations for the departure from linearity of adsorption isotherms for small degrees of surface filling were reviewed by Zel'dovich (1949).

## MASS-ACTION EQUATIONS

Ion exchange is considered a chemical process in which a reaction between a solution phase and an exchange material occurs.  Given the amount of exchangeable cations on the exchange material and the composition of the original solution, one can assume that at equilibrium the amounts in solution and in exchangeable form can be calculated from a chemical analysis of the filtrate (Kelley, 1948, p. 42).  Vanselow (1932b) calculated relative activity coefficients of mixed electrolytes from data obtained in this manner.

Similarly, Magistad and others (1944) expressed the belief that exchange reactions follow chemical laws and that equilibrium exists between the proportion of each cation on an exchange complex and relative concentration of these cations in the solution phase.

This idea conflicts with the diffuse double-layer concept in which adsorbed ions and solution ions are not definable as separate entities (Kelley, 1948, p. 42).  On the basis of the double-layer theory, cation exchange is merely the rearrangement of cations and cannot be considered a chemical reaction in the opinion of Davis (1945).  Davis has critically analyzed the significance of the cation-exchange equilibrium concept and has suggested that the entire concept as a true thermodynamic equilibrium is not valid.

Marshall and Gupta (1933) expressed doubt that cation exchange can be described in terms of the mass-action law.  Data obtained by them did not agree with the mass-action law when applied to mass-action equations of various investigators.  Of Kerr's theory involving the coexistence of two types of clay at equilibrium, these authors point out that many assumptions are made.  For example, Kerr assumed that the two clays exist independently in solution, behaving as weak electrolytes, while the concentrations of the cations are assumed to bear a constant relation to their thermodynamic activities.

Various investigators have recognized that a law of mass action is strictly applicable only to activities and not to concentrations of ions.  Activities were calculated by Magistad and coworkers (1944) and by Marshall and Gupta (1933), but their utility is limited according to Davis (1945).  He pointed out that only in the case of the very weak electrolytes whose ionic concentrations are small does the activity represent a measure of the true degree of dissociation, and then only an approximate measure.

Davis suggested that an equation of the form

$$Na\text{-}clay + K^+ \rightleftharpoons K\text{-}clay + Na^+ \tag{5}$$

may be interpreted as representing a definite chemical reaction occurring at the time of mixing.  For this interpretation to be valid,

both Na-clay and K-clay would have to be completely undissociated complexes, according to him.    In his opinion, it is doubtful that any colloidal materials exhibiting the cation-exchange property are completely undissociated.

Other investigators (Kerr, 1928; Magistad and others, 1944; Vanselow, 1932a) expressed satisfaction with the approximate agreement between one equation or another and their experimental results.

Magistad and others (1944) studied the effects of the following factors on the equilibrium constant $k$ as calculated by equations of Kerr, Vanselow, and Gapon: ratios of competing ions in solution, volume, size of soil sample, concentration, and temperature.    Gapon's equation gave the best fit.    According to the authors, each of the equations gives a satisfactory explanation of the shift in equilibrium with dilution.    They point out that there was indication of appreciable amounts of cations being dissolved from soil minerals and that the dissolved cations influenced equilibriums.

Kerr (1928) wrote equilibrium equations for cation exchange between ions of equal valence and between ions of unequal valence. Cation exchange between ions of equal valence may be represented as follows:

$$KE + Na^+ \rightleftharpoons NaE + K^+ \tag{6}$$
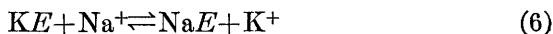
$E$ represents solid-phase material.    Kerr's equilibrium equation for this exchange reaction is:

$$\frac{[NaE][K^+]}{[KE][Na^+]} = k \tag{7}$$

Cation exchange between cations of unequal valence may be represented as follows:

$$CaE + 2K^+ \rightleftharpoons 2KE + Ca^{+2} \tag{8}$$
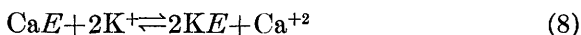
Kerr's equilibrium equation for this exchange reaction is:

$$\frac{[KE]^2[Ca^{+2}]}{[CaE][K^+]^2} = k \tag{9}$$

Although in all mass-action expressions, the quantities in brackets should denote activities, Kerr has used concentrations, assuming that activities and concentrations are essentially equal (Kerr, 1928). Kelley (1948, p. 43) questioned this assumption.    He explains that the assumption happens to work satisfactorily for sodium chloride and potassium chloride because their activity coefficients are close to unity.    But, as he points out, calcium chloride represents a different situation in that its coefficient in dilute solutions is considerably less

than unity.   Also, its activity coefficient exhibits more rapid change as the concentration changes than does that of potassium chloride or sodium chloride.

Vanselow (1932a) also questioned the validity of Kerr's assumption that active and actual concentrations are equal.   According to him, if this were true, then the substances $NaE$ and $KE$ in the equation

$$KE + Na^+ \rightleftharpoons NaE + K^+ \tag{10}$$
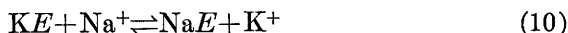
would behave as if in true solution and have activity coefficients of unity.   Vanselow suggests that if $NaE$ and $KE$ could form a continuous series of mixed crystals, their activities would no longer be unity, but each would have an activity equal to its mole fraction in the mixed crystal.   Thus, the activities of $NaE$ and $KE$ would be

$$[NaE] = \left( \frac{NaE}{NaE + KE} \right) \tag{11}$$

and

$$[KE] = \left( \frac{KE}{NaE + KE} \right); \tag{12}$$

or, for monovalent cations, Kerr's equation (7) can be written:

$$\frac{(NaE)[K^+]}{(KE)[Na^+]} = k. \tag{13}$$

Although neither monovalent nor divalent cation pairs permit one to distinguish between the mixed-crystal hypothesis and Kerr's hypothesis, the use of two dissimilar cations does.   Vanselow (1932a) studied the reaction between a solution of ammonium chloride and a calcium-saturated material.   The reaction may be represented as follows:

$$2NH_4E + Ca^{+2} \rightleftharpoons CaE_2 + 2NH_4^+, \tag{14}$$
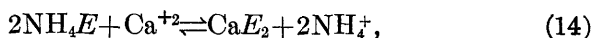
and the equilibrium condition in terms of the activities of the four constituents is

$$\frac{[NH_4^+]^2[CaE_2]}{[Ca^{+2}][NH_4E]^2} = k. \tag{15}$$

Vanselow (1932a) noted that since the solutions used in his work were dilute and of nearly constant ionic strength, any error introduced by the omission of activity coefficients for ammonium chloride and calcium chloride solutions would remain approximately constant for all of the experiments.   By following the idea of Kerr (1928) and

assuming the particles of the substances behave as if in true solution with an activity coefficient of unity, we also get equation 15. For the mixed-crystal hypothesis, activities of the two forms of substances are represented by

$$[NH_4E] = \left(\frac{NH_4}{NH_4E + CaE_2}\right) \tag{16}$$

and

$$[CaE_2] = \left(\frac{CaE_2}{NH_4E + CaE_2}\right) \tag{17}$$

Thus, by process of substitution, equation (15) takes the form

$$\frac{[NH_4^+]^2}{[Ca^{+2}]} \frac{(CaE_2)(CaE_2 + NH_4E)}{(NH_4)^2} = k \tag{18}$$

and the two equilibrium equations are found to differ by the factor $(CaE_2 + NH_4E)$.

Rios and Ruiz (1954) derived an equation for ion-exchange equilibrium based on kinetic considerations. For cations of equal valence, the equation is represented as follows:

$$K_a' = a_X n + a_Y ad / a_Y n + a_X ad \tag{19}$$

$$= \frac{K_Y r_X}{K_X r_Y} \tag{20}$$

where

>    $X$ and $Y$ = cations of equal valence,
>        $a$ = the ionic activity,
>        $r$ = the hydrated ionic radius,
>        $n$ = the number of moles in solution.

The activity of the adsorbed cation is a function not only of its mole fraction present, but also of the total solution concentration. The calculated value of free energy $\Delta F$ indicates the degree of adsorption of a cation on an exchanger for univalent cations is in the order

$$Li < Na < K < Rb < Cs$$

and for bivalent cations

$$Mg < Ca < Sr < Ba$$

According to the authors, this agrees with experimental data of a Spanish Moroccan montmorillonite and with bibliographic sources.

A statistical exchange equation was developed by Krishnamoorthy and others (1948). It is based on the statistical thermodynamics of Guggenheim (1945). In an interpretation of the equation, Harward and Coleman (1953) suggested that Krishnamoorthy and others (1948) consider a situation in which the exchangeable ions reside in an idealized monolayer and adsorption sites on the exchanger exist as a surface array with each site having four nearest neighbors. They conducted studies on cation distribution in clay-water systems containing small amounts of electrolyte (HCl) to test the ability of mass-action type exchange equations to predict the distributions of metal cations in these systems and showed that the statistical exchange equation may be used to estimate fairly satisfactorily the amounts of $K^+$ and $Ca^{+2}$ in solution when HCl is added to these clay systems.

Gapon (1933) reported an exchange equation applicable to exchange between a liquid and a monomolecular layer of a second liquid adsorbed on a solid. The equation may be written as

$$\frac{C_1 \cdot f_2}{C_2(f_0 - f_2)} = k \tag{21}$$

where

$f_0$ = total surface,
$f_1$ = surface occupied by liquid $C_1$ at equilibrium,
$f_2$ = surface occupied by liquid $C_2$ at equilibrium.

In Gapon's opinion, the amount of a given liquid taken up by a solid through exchange is proportional to the surface occupied by that liquid. He believes that cation exchange and the replacement of one liquid by another from the surface of a solid are analagous.

Although Gapon applied the preceding equilibrium equation only to exchange between monovalent and divalent ions, Kelley (1948, p. 45) applied it to exchange between monovalent ion pairs. He assumed that the total surface $f_0$ is proportional to the exchange capacity and applied the equilibrium equation to the reaction

$$KE + Na^+ \rightleftharpoons NaE + K^+ \tag{22}$$
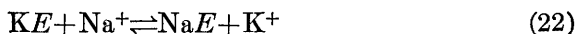
giving

$$\frac{(K^+)(NaE)}{(Na^+)(KE)} = k \tag{23}$$

which has the same form as Kerr's equation for ion pairs of equal valence.

Gapon (1933) represented exchange between monovalent and divalent cations by the equation

$$ECa_{\frac{1}{2}}+NH_4^+ \rightleftharpoons ENH_4+\tfrac{1}{2}Ca^{+2} \tag{24}$$
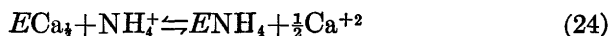
Applying Gapon's equilibrium equation, this gives

$$\frac{(Ca^{+2})^{\frac{1}{2}}(NH_4E)}{(NH_4^+)(NH_4 \text{ ex. cap.}-NH_4E)}=k \tag{25}$$

where cations found in solution are expressed in gram atoms per liter, and exchangeable cations are expressed as gram atoms for a given amount of soil.

Kelley (1948, p. 46) suggested that the following form is preferable to Gapon's exchange reaction cited above:

$$CaE+2NH_4^+ \rightleftharpoons 2NH_4E+Ca^{+2} \tag{26}$$
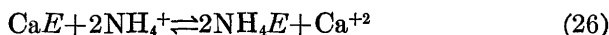
By substitution of proper quantities from equation 26 in Gapon's equilibrium equation, it can be shown to give an equation identical with Kerr's equation for monovalent and divalent ions.

Krishnamoorthy and Overstreet (1950) subjected Gapon's equation to experimental tests with a bentonite clay from Utah, three soil colloids (clays from the Yolo, Hanford, and Aiken soil series), and three synthetic resins. The equation gave very satisfactory constants for ion pairs of equal valence except when the hydrogen ion was involved. The authors suggest that hydrogen ion adsorbed on clays may not behave normally in exchange reactions, because it is not completely dissociated. For monovalent-divalent ion pairs, the equation proved to be unsuitable. These investigators (1949) discussed Gapon's equation in terms of the theory of ionic distribution as applied to mineralogically pure systems in which the ion-exchange process is at equilibrium and is completely reversible.

### KINETIC EQUATIONS

Jenny (1936) considered a quantitative expression of cation exchange in terms of kinetic theory. According to this approach, exchangeable cations held by colloidal clay particles are not at rest but are in a continuous state of thermal agitation and Brownian movement. Cation exchange occurs when a cation in solution comes between the negatively charged inner layer of a colloidal particle and the oscillating outer-layer cation of such a particle. The outer-layer cation then goes into solution as an exchanged cation.

Jenny's equation originally was deduced for a platy colloidal particle (as clays), but it can be applied also to spheres. Furthermore,

it is not restricted to colloidal dimensions or to crystallites. The equation may be written in the following forms:

$$C = \frac{(s+N) \pm \sqrt{(s+N)^2 - 4sN\left(1 - \dfrac{Vc}{Vb}\right)}}{2\left(1 - \dfrac{Vc}{Vb}\right)} \tag{27}$$

and

$$C^2\left(1 - \frac{Vc}{Vb}\right) - C(s+N) + sN = 0 \tag{28}$$

where

$N$=amount of electrolyte added initially (number of ions), $C$=number of cations adsorbed or released at equilibrium, $s$=saturation capacity, $Vc$ and $Vb$=oscillation spaces of the two kinds of adsorbed ions.

Kelley (1948, p. 47) transposed the equation to the following form:

$$\frac{(s-C)(N-C)}{C^2} = \frac{Vc}{Vb} \tag{29}$$

and then applied it to the following reaction:

$$NaE + K^+ \rightleftharpoons KE + Na^+ \tag{30}$$
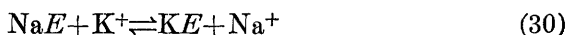
He found that

$$\frac{(K^+)(NaE)}{(Na^+)(KE)} = \frac{Vc}{Vb} = k \tag{31}$$

It can be seen that equation 31 is identical in form with other equations previously cited. Thus, for ions of the same valence, an identical exchange constant is obtained by statistical derivation and by application of the mass law.

Jenny noted that the equation gives good results for the platy structures of soil colloids and bentonite clays where exchange occurs on outside surfaces. The equation has given less satisfactory results with permutites and certain zeolites where exchange occurs in pores and channels. Apparently these materials do not conform to the equation since the ions are so close together that they interfere with each other.

Jenny's kinetic theory of ionic exchange helps to explain the direct exchange which takes place between plant roots and clays without intermediate solution of the ions (Jenny and others, 1939). Grim (1953b, p. 142) suggested that it may be possible for such direct exchange to take place between clay minerals and inorganic materials. Marshall (1949, p. 127) stated that the overlapping of oscillation volumes (Jenny's theory) by adjacent colloidal particles can lead to ion exchange between them, a process which he calls contact exchange.

Davydov and Skoblionok (1953) studied cation exchange on glauconite in mixed media (various mixtures of alcohol and water). The exchange of $Ca^{+2}$ and $Ba^{+2}$ for $Na^+$ and $K^+$ was investigated. The Nikol'skii equation was applied:

$$a = a_m - K^2 a[a/(100 \ Co - a)]^2 \qquad (32)$$

where

    $a$  = the milligram equivalent of the bivalent cation desorbed from 10 gram of adsorbent and equals the quantity of adsorbed univalent cation,

    $a_m$ = the maximum adsorption,

    $Co$ = the initial concentration of univalent cation in millimoles per liter,

    $K$  = the adsorption constant.

The experimental results were presented as isotherms on coordinates $1/a, a/2/(100 \ Co - a)$. Linear-shaped isotherms were obtained showing the applicability of the equation to the system. Addition of a solvent with a small dielectric constant shifted the equilibrium toward displacement of bivalent cation; addition of 50 percent alcohol lowered the equilibrium constant value to half. Additional studies were made by Davydov and Skoblionok (1956) using kaolin, glauconite, and volchonskoite. They found that the displacement of $Ca^{+2}$ by $Li^+$ was more complete as the dielectric constant of the solvent was increased.

### SURFACE TENSION

Surface tension plays an important role in the phenomenon of adsorption. An interesting discussion of surface tension was presented by Jirgensons and Straumanis (1954, p. 47–49). A summary of their discussion follows.

It is commonly accepted that each molecule within a liquid is attracted to other molecules around it. Thus, the forces on these inner liquid molecules are balanced. A different situation exists at the surface of a liquid where the forces of attraction exist only on the liquid side. As a result, surface molecules are pulled into the liquid and the entire outside surface in contact with air is under tension.

Any increase in a liquid's surface area involves the expenditure of some work to take molecules from the bulk of the liquid to the surface. This work, called surface energy, is recovered when the surface area is decreased. (For a discussion on surface energy theory, see Fricke, 1941). Thus, we have the thermodynamic reason for liquids tending to decrease their surface area wherever possible.

Surface tension exists at all interfaces between different phases. Thus, we speak of interfacial energies occurring between solid/liquid, solid/gas, liquid/gas, liquid/liquid, and other combinations of phases.

Surface tension is the work or energy necessary to increase a surface by 1 square centimeter. It can be calculated by the formula

$$\sigma = \frac{\text{surface energy}}{\text{surface area}} \tag{33}$$

where $\sigma$ is surface tension and the units are ergs/cm² or dynes/cm.

Van Nostrand (1947, p. 20) explained surface tension in terms of two dissimilar substances making contact at an interface. Because of inequalities of molecular attraction (cohesion), together with other forces in operation, the shape of the interface is changed until the potential energy of the whole molecular system attains a minimum value.

Gedroiz (1922) used surface tension and the fundamental law of colloid science to explain physical type adsorption. According to the law, a dispersive system tends to diminish its free surface energy. This surface energy is the product of the general surface of the dispersive phase and the surface tension. Thus, there is a tendency for the dispersive system to diminish both its general surface and its surface tension.

### SURFACE-ACTIVE AGENTS

Certain substances when added to a dispersive system diminish the surface tension of the dispersion medium. Surface tension is lowered and positive physical adsorption occurs when a surface-active agent is concentrated in the layer of water adjacent to the surface of the suspended particles. Examples of surface-active materials in aqueous solution are such organic materials as alcohols, aldehydes, fatty acids, esters, amines, terpenes, and camphor.

Surface tension of the dispersion medium may be increased by adding any one of several substances. In this case, the substance is more concentrated in the bulk of the dispersion medium than in the layer adjacent to the suspended particles and this phenomenon is known as negative adsorption. Examples of surface-inactive materials are the soluble inorganic salts and certain organic compounds including those containing many hydroxyl groups such as sugar and glycerin.

A substance may be surface-active in one liquid and inactive in another. For further discussion on this subject the reader is referred to Anson (1946), Fischer (1950, p. 226); Ralston (1946), Schwartz and Perry (1949), and Snell (1943).

### GIBBS' ADSORPTION THEOREM

According to Gedroiz (1922) effects of surface-active agents are explained by Gibbs' theorem developed on the basis of thermo-

dynamics for phenomena of adsorption in gas mixtures. The theorem is expressed by the following formula:

$$U = -\frac{c}{RT} \cdot \frac{ds}{dc} \tag{34}$$

where

$U$ = the excess of substances dissolved in dispersion medium (positive or negative) for every unit of surface of the dispersed phase in comparison with what would have been dissolved in the absence of this surface

$c$  = concentration of substance dissolved in dispersion medium

$T$  = absolute temperature

$R$  = gas constant

$s$  = surface tension

$\frac{ds}{dc}$ = diminution or increase in surface tension with increase in concentration of the dissolved substance.   With diminution, this quantity is negative; with increase, it is positive.

From the formula it follows: (a) if increased concentration of the dissolved substance in the dispersion medium decreases the surface tension, adsorption will be positive, (b) if increased concentration of the dissolved substance in the dispersion medium increases the surface tension, adsorption will be negative.

Physical adsorption may occur when a decrease in surface energy is caused by a diminution in the quantity of surface.   Flocculation of soil particles into larger aggregates is an example of this phenomenon.

### EXPERIMENTAL STUDIES

Gedroiz (1922) cited experimental evidence in support of point a, positive adsorption, in Gibbs' theorem.   His work on negative adsorption gave indefinite results, however.

Bower and Goertzen (1955) studied negative adsorption as defined by Gibbs in 1875.   For three calcium-saturated soils, the negative adsorption of calcium chloride was found to be nearly the same when concentrations in the extract were equivalent.   The values at concentrations of 10, 100, and 1,000 milliequivalents per liter were about $5 \times 10^{-6}$, $35 \times 10^{-6}$, and $290 \times 10^{-6}$ milliequivalent per square meter respectively.   The negative adsorption of sodium chloride and sodium sulfate by sodium-saturated soils was similar to but greater than that of calcium chloride by calcium-saturated soils at equivalent concentrations in the saturation extract.

In an application of Gibbs' fundamental equation to solutions containing both single molecules and micelles, Alexander (1942) found that when $ds/dc = 0$, as at the minimum surface tension, the total adsorption is not necessarily 0, since the vanishing of $ds/dc$ may be due equally well to $c$ (the concentration of single molecules) becoming independent of $C$ (the stoichiometric concentration).   The latter ex-

planation is suggested to explain the apparent anomaly of strong positive adsorption at low surface tension. It is in accord with the experiment and with the results obtained by applying the law of mass action to the single molecule versus micelle equilibrium while it is still based upon Gibbs' fundamental equation.

## CLAY MINERALS

### DEFINITION OF CLAY MINERALS

As mentioned in "The Glossary of Geology" (1957, p. 52) the term clay is used in three distinct senses. This section applies to one of these, clay minerals.

Clay minerals are characterized by a hydrous silicate composition, a finely crystalline structure of the 2-layer type (kaolinite) or 3-layer type (montmorillonite), and exchangeable cations on the surfaces of silicate layers in an amount depending upon the excess negative charge within the composite layer. The cations commonly are calcium and sodium but also may be potassium, magnesium, hydrogen, aluminum, and others. A discussion of the origin, classification, nomenclature, composition and structure of clay minerals follows in succeeding paragraphs.

### ORIGIN OF CLAYS

In the course of geological ages about 4 percent of the igneous rocks in the earth's crust have been weathered to clays, shales, and surface soils (McBain, 1950, p. 377–378). The earth's crust consists of the continental portion, 18 to 25 miles in thickness, and the oceanic portion, 6 to 8 miles in thickness (Gilluly and others, 1959, p. 408).

Ross (1928), in summing up the origin of clay minerals, listed several influencing factors. These include weathering, partial leaching of certain elements from older minerals, complete replacement of a mineral, the devitrification of a volcanic glass, crystallization of colloid material, direct precipitation from solutions, and reactions between older minerals and solutions.

Weaver (1958), in a discussion of the origin of clay minerals in sedimentary rocks, concluded that a majority of them are detrital in origin and are modified only slightly in their depositional environments. X-ray analyses of thousands of sediments indicate that any one of the major clay minerals may be found in abundance in any of the major depositional environments.

Mattson (1930) cited the occurence of the highly silicated and base-saturated soils in the arid regions, the moderately silicated and primarily base-unsaturated soil colloids in the temperate and colder humid regions, and the almost completely desilicated and base-unsaturated soil colloids in the humid tropical regions. He explains

these differences in terms of the following average composition of the lithosphere cited by Clarke (1924); $SiO_2$, 59.08; $Al_2O_3 + Fe_2O_3$, 18.33; CaO, 5.10; MgO, 3.45; $K_2O$, 3.11; $Na_2O$, 3.71; and others, 7.22. In arid regions there is very little loss of material by weathering, most of the products of hydrolysis remaining in the soil and reacting with one another to form a colloidal complex. In regions of greater humidity, the soil is subjected to greater leaching and the cations and the silica are progressively washed out. The relative amounts of leaching depend upon the temperature of the region. There is an accumulation of organic matter in the colder regions resulting in a high-soil acidity. There is no accumulation of humus in the tropics, but more intense weathering and a more nearly neutral reaction occurs as a result. In terms of the foregoing conditions, one would expect to find the soil colloids of the humid, tropical regions to possess a low silica/sesquioxide ratio and the soil colloids of the temperate and cold humid regions, where the soil condition is more acid, to possess a higher silica/sesquioxide ratio.

Clay mineral compositions are intimately related to the conditions under which they form. Extreme weathering conditions and an acid environment give kaolinitic soils. In contrast, the formation of montmorillonite minerals is favored by an alkaline evnironment (Ross and Hendricks, 1945, p. 23).

Other suggested references include Keller (1955), Reiche (1950), Bear (1955, p. ix), and Robinson (1949).

## CLASSIFICATION AND NOMENCLATURE

A study of the literature reveals that classification and nomenclature of clay minerals is still in the development state, although much improvement has been made in recent years. The older literature contains many examples of mineral names erroncoulsy applied to materials believed to be specific minerals. This is not too surprising since these early names were suggested on the basis of chemical and optical data whose validity has been questioned by recent work with new and improved chemical and instrumental techniques (Grim, 1953b, p. 39).

It is not within the scope of this paper to list and discuss all the clay-mineral species found in the literature, but a number of references pertinent to the subject will be mentioned.

### CLASSIFICATION SYSTEMS

Various investigators have devised systems of classification for clay minerals (Brindley, 1955; Grim, 1953b, p. 27; Jasmund, 1950; Troug, 1946; and Weaver, 1953). Any classification system must be

flexible and subject to change as new information becomes available, according to these investigators.

Familiarity with the commonly accepted mineral terminology can be had by studying mineral classification systems such as these. The system outlined by Grim (1953b, p. 27), which is relatively easy to follow, is included (table 1) as an aid in studying the clay-mineral nomenclature.

TABLE 1.—*Classification of the clay minerals* [1]

I   Amorphous
      A.   Allophane group
II   Crystalline
      A.   Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
            1.   Equidimensional
                  a.   Kaolinite group
                      (1).   Kaolinite, nacrite, and others
            2.   Elongate
                  a.   Halloysite group
      B.   Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)
            1.   Expanding lattice
                  a.   Equidimensional
                      (1).   Montmorillonite group
                          (a).   Montmorillonite, sauconite and others
                      (2).   Vermiculite
                  b.   Elongate
                      (1).   Montmorillonite group
                          (a).   Nontronite, saponite, hectorite
            2.   Nonexpanding lattice
                  a.   Illite group
      C.   Regular mixed-layer types (ordered stacking of alternate layers of different types)
            1.   Chlorite group
      D.   Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
            1.   Attapulgite
             2.   Sepiolite
             3.   Palygorskite

[1] From Grim, 1953b, p. 27. (By permission from "Clay minerology," by Ralph E. Grim, Copyright, 1953. McGraw-Hill Book Co., Inc.)

Ross (1960) suggested that the montmorillonite clay group be given under two listings: (a) the dioctahedral including montmorillonite and nontronite and (b) the trioctahedral including saponite, hectorite, and sauconite.

## NOMENCLATURE
### ALLOPHANE

The term allophane, derived from Greek words meaning "to appear" and "other" has long been used to designate amorphous clay materials (Grim, 1953b, p. 27; Kerr and Hamilton, 1949, p. 3).   Dittler (1941b), in studying allophane with the electronmicroscope and the ultramicroscope, found the crystalline clay mineral halloysite present.   Ross and Kerr (1934, p. 145) pointed out that the composition of known amorphous materials in clay varies considerably.   Present usage of the term allophane includes only amorphous material, and it is commonly associated with halloysite (Kerr and Hamilton, 1949, p. 3).

### KAOLINITE GROUP

One of the most outstanding studies of the kaolinite group of clay minerals was that of Ross and Kerr (1931, p. 154).   They described this group as being light in color and low in iron content and having approximately the composition $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$.

According to Ross and Kerr (1931, p. 151), three distinct mineral species, designated kaolinite, dickite, and nacrite, make up the kaolinite group.   Historical origins of these terms and other terms applied to the group (now discredited) are given by Grim (1953b, p. 27–42), Kerr and Hamilton (1949, p. 3), and Ross and Kerr (1931, p. 154–157).

Anauxite is a clay mineral with a structure similar to kaolinite but with a higher silica-alumina ratio frequently approaching 3 (Ross and Kerr, 1931, p. 163).   It is believed to be an interlayer mixture consisting of a double silica layer and a two-layer type of sheet (Grim, 1953b, p. 30).

### HALLOYSITE

Halloysite is the name given by Berthier in 1826 to material  found in pockets of carboniferous limestone near Liége, Belgium according to Grim (1953b, p. 31), and Kerr and Hamilton (1949, p. 30).   Ross and Kerr (1934, p. 135–148) studied the mineral and found it to be crystalline in nature and closely related to kaolinite.   Two types of halloysite are described: one that is light and cottony in texture and another that is dense, nonporous, and resembles porcelain.

Much of the material included as halloysite by Ross and Kerr (1934) has been found to be submicroscopic kaolin.   Porcelainlike material is most commonly halloysite, the other is commonly kaolin (Ross, 1960).

Hofmann and others (1934) reported that two forms of halloysite exist, one being more hydrous than the other.   Mehmel (1935) and Correns and Mehmel (1936) discovered that there are two forms of this clay mineral, one having the same composition as kaolinite and the other differing from kaolinite by $2H_2O$.

Various names have been suggested for halloysite. Alexander and others (1943) called the less hydrous form halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), and other endellite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$). MacEwan (1947) proposed that the name halloysite be applied to all halloysite minerals, with the varying degrees of hydration differentiated by prefixes. He proposed that the nonhydrated form be called metahalloysite. Faust (1955) presented an historical review of halloysite-endellite nomenclature and cited X-ray studies by Brindley and Goodyear (1948) as evidence supporting his belief that $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ is not halloysite but a different clay mineral which he prefers to call endellite. Brindley and Goodyear (1948) found that endellite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) showed spacings from 9.5 to 10.1A for 3½ to 4$H_2O$ and halloysite ($Al_2O3 \cdot 2SiO_2 \cdot 2H_2O$) 7.5 to 7.9A for 2⅕ to 2⅖ $H_2O$. They could obtain no evidence supporting the existance of intermediate halloysite with spacings between 7.9 and 9.5 A.

### MONTMORILLONITE

Two Frenchmen, Damour and Salvetat, in 1847 suggested the name montmorillonite for a hydrous aluminum silicate mineral found at Montmorillon, France (Grim, 1953b, p. 33; Kerr and Hamilton, 1949, p. 45). Both references give an extensive history of the nomenclature of the mineral. Montmorillonite is the essential mineral of bentonite and is widely distributed in soils (Kerr and Hamilton, 1949, p. 45).

In current usage, the name montmorillonite applies to a group of three-layered clay minerals having an expanding lattice (excluding virmiculite) and also as the name of a specified mineral within the group (Grim, 1953b, p. 27).

### VERMICULITE

According to Grim (1953b, p. 35), vermiculite is the name applied by Webb in 1824 to a micalike mineral found near Worcester, Massachusetts. It is derived from the Latin and means worm breeder. Vermiculites have an expanding lattice of a limited degree.

### ILLITE

Illite was proposed as a general term for the micalike clay minerals by Grim and others (1937). Although the term has been widely accepted (Grim, 1953b), its applicability is questioned by Yoder and Eugster (1955). They pointed out that no proof exists that materials now called illite are not all mixed-layer structures.

### CHLORITE

The name chlorite appears to have been used for the first time in about 1800 by Werner (Grim, 1953b, p. 36). It is derived from a Greek word meaning green (Hurlbut, 1952, p. 355).

Palygorskite is the sepiolite-attapulgite isomorphous series that includes a hydrous magnesium silicate end-member, paramontmorillonite, Kerr and Hamilton (1949, p. 48). More specifically, it has been used to designate minerals in this group having a certain amount of aluminum substituting for magnesium. Grim (1942) expressed doubt that such a mineral exists.

Attapulgite was the term applied by De Lapparent (1935) to a clay-mineral constituent from Attapulgus, Ga., and Mormoiron, France. X-ray diffraction patterns for this mineral and montmorillonite are similar, but attapulgite has the higher magnesium content of the two minerals (Kerr and Hamilton, 1949, p. 7).

Sepiolite and meerschaum have long been considered synonomous according to Grim (1953b, p. 37). Meerschaum apparently was used first, having been applied by Werner in about 1789. This term is of German origin and means seafroth, referring to lightness and color.

Sepiolite, first applied in 1847 by Glocker, comes from the Greek word for cuttlefish, of light and porous bones (Grim, 1953b, p. 37).

## COMPOSITION AND STRUCTURE
### OLD CONCEPT

Consideration of some of the older concepts of composition and structure seems worthwhile as an introduction to the modern concepts of clay minerals.

Soil students long believed in the existance of a single pure clay substance—kaolinite or a similar material containing various impurities (Grim, 1953b, p. 12). "Webster's New International Dictionary" (1959) supports this view by its definition of clay, which follows:

"The essential constituent of pure clay, or kaolin, is the mineral kaolinite * * * "

Another belief given wide circulation was that all clay materials consisted of an inorganic-organic colloid complex of an amorphous nature. Van Bemmelen (1888) and Stremme (1911) belonged to this school of thought. They later considered the colloidal fraction to consist of two parts, allophaneton which was soluble in hydrochloric acid, and kaolintin soluble in hot concentrated sulfuric acid but not in hydrochloric acid.

Gedroiz (1922) in his extensive investigations of cation exchange in soils considered the complex as zeolitic material, meaning cation-exchange material rather than zeolite in the mineralogical sense.

One old concept which approaches the present-day clay-mineral concept considered the essential components of soils to be a number of substances rather than a single compound. These substances were thought of as alumino-silicic acids or salts of such acids with definite

composition and structures (Asch and Asch, 1913, p. 15–38; Byers and others, 1935).

Although the small size of clay particles is generally recognized, Oden (1916) is given much of the credit for the idea that particle size is a factor of major importance to clays and that clays can be composed of almost any minerals if they are fine enough. Oden thought of clays as consisting of a heterogeneous mixture of extremely small particles of crystalline and amorphous components, 1 micron or less in size. The modern usage of the term "clay," however, implies more than a particle-size range.

### MODERN CONCEPT

The clay-mineral concept is the so-called modern concept of clay structure and composition. It considers clays as having a colloidal, silicate-layer-lattice type of structure in which the layers are composed of planes of silica-oxygen tetrahedrons and planes of aluminum, iron, or magnesium atoms surrounded by six oxygen atoms or hydroxyl groups arranged as octahedrons (Gregg, 1951, p. 35–38; Kelley, 1948, p. 27; Lacy, 1954).

Grim (1953b, p. 18–19) defined clay minerals as:

* * * essentially hydrous aluminum silicates, with magnesium or iron proxying wholly or in part for the aluminum in some minerals and with alkalies or alkaline earths present as essential constituents in some of them.

Some clay minerals are considered to be colloidal electrolytes. According to Marshall and Krinbill (1942), montmorillonite, beidellite, nontronite, saponite, and attapulgite fit that classification, whereas clays of the illite and kaolin group do not.

Although the clay-mineral concept had been generally accepted by the early 1930's, there were some dissenters. Notable among them was Mattson. Since 1929, Mattson has published a series of papers in Soil Science entitled "Laws of soil colloidal behavior," explaining his acidoid-basoid ratio theory of cation exchange.

Grim (1953b, p. 16) pointed out that the clay-mineral concept is really not so modern, for Le Chatelier and Lowenstein arrived at this same conclusion in 1887 and 1909 respectively. Its lack of acceptance until recent years may be attributed to lack of proof of the concept.

### MODERN STUDIES OF CLAY STRUCTURES

Much of the evidence that led to acceptance of the clay-mineral concept came from Von Laue's discovery of the X-ray diffraction principle in 1912. By the early 1920's X-ray diffraction studies and other advanced methods of study were being applied to clay-mineral structure and composition. Among the first X-ray diffraction

analyses of clays published were those of Hadding (1923). Crystalline material was found in the finest fractions of a series of clays, and there was no wide variety of mineral types in these fractions. Other investigators followed with additional studies on soil composition and structure utilizing X-ray diffraction analyses and obtained similar results (Brindley, 1951a, p. 1–31; Brindley and Robinson, 1951, p. 173–198; Hendricks and Frye, 1930; Kelley and others, 1931; and MacEwan and Amoros, 1950).

By means of careful work with the petrographic microscope and excellent chemical data, Ross and colleagues of the U.S. Geological Survey were able to show that clays consist of crystalline components (clay minerals), only a limited number of which exist (Ross, 1928; Ross and Shannon, 1925, 1926). The use of X-ray diffraction analyses in their work helped to confirm earlier findings just mentioned (Ross and Kerr, 1931).

Goldschmidt and his many coworkers at the mineralogical institutes of the Universities of Oslo and Göttingen made notable contributions on the composition of soils and clays during a period of approximately 20 years, beginning in the early 1920's. Much of their work was done by means of optical and X-ray spectrochemical analyses (Rankama and Sahama, 1950, p. 10).

Berman (1937) presented a discussion on the classification of the natural silicates based on X-ray studies.

Bragg (1949, p. 131, 132, 133, 136) described work on the study of crystal structures by means of X-ray.

Hauser (1955c, p. 442–472) discussed applications of such instruments and methods as the ultramicroscope, the electron microscope, differential thermal analysis, infrared diffraction studies, X-ray diffraction studies, and several other methods and phenomena of colloid science in investigations and studies of clay minerals.

Hambleton and Dodd (1953) described a rapid method of identifying clay-mineral groups. The method utilizes a color test based on the adsorption and oxidation of $p$-amino phenol on clay-mineral surfaces.

Dittler (1941a) summarized research on clays including their identification by the electron microscope.

Robertson (1951) made use of the electron microscope in studies of clay structures and molecular arrangements.

The published work of Pauling (1930a) on X-ray diffraction studies of the crystal structure of micas and related minerals was a milestone in crystal structure studies and the foundation for further studies by other investigators. In his studies of several minerals that were chemically different—(gibbsite, $Al_2(OH)_6$; brucite, $Mg_3(OH)_6$; cristobalite, talc, and kaolinite)—Pauling found that structurally they

were similar in that they gave a unit cell in the plane of cleavage of approximately 5.1 A by 8.8 A. The results suggested that these minerals could be considered as sheet or layer structures. Units were cristobalite, gibbsite, or brucite sheets. With this approach, it was possible to explain the diverse compositions of the mica group.

Other investigators soon made use of Pauling's findings. Gruner in 1932 worked out structures for kaolinite, nacrite, and dickite, all of which have the same composition, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. They differ in displacement of the silica layer in relation to the alumina layer.

The atomic structures of the common clay minerals have been established in considerable detail by the application of Pauling's (1930a) generalizations on the structure of micas. As pointed out by Grim (1953b, p. 43) and Marshall (1949, p. 45), most clay minerals are built up of two structural units. A description of these units (based on Grim, 1953b, p. 43–44) is given in the two succeeding paragraphs.

One unit has octahedral coordination (fig. 1). It consists of two sheets of closely packed oxygen atoms or hydroxyl groups with aluminum, iron, or magnesium atoms in the center of an octahedron made up of six oxygens atoms or hydroxyl groups. Aluminum fills only two-thirds of the possible positions in balancing the structure and forms the gibbsite $[Al_2(OH)_6]$ structure. Magnesium fills all the positions in balancing the structure and forms the brucite $[Mg_3(OH)_6]$ structure. The normal distance between oxygen atoms is 2.6 A for the unit structure of octahedral coordination. The distance between hydroxyl groups is 2.94 A. The unit has a thickness of 5.05 A in clay-mineral structures with a space of about 0.61 A for the atom in octahedral coordination.

The other unit has tetrahedral coordination (fig. 2). Each tetrahedron consists of a silicon atom located at the center of and equidistant from four oxygen atoms or hydroxyl groups, whichever may



(a)             (b)

○ and ◌ = Hydroxyl     ● = Aluminum , magnesium , etc.

FIGURE 1.—Diagrammatic sketches of (a) a single octahedral unit and (b) the sheet structure of the octahedral units, from Grim, 1953b, p. 43. (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright 1953. McGraw-Hill Book Co., Inc.)

(a)                              (b)
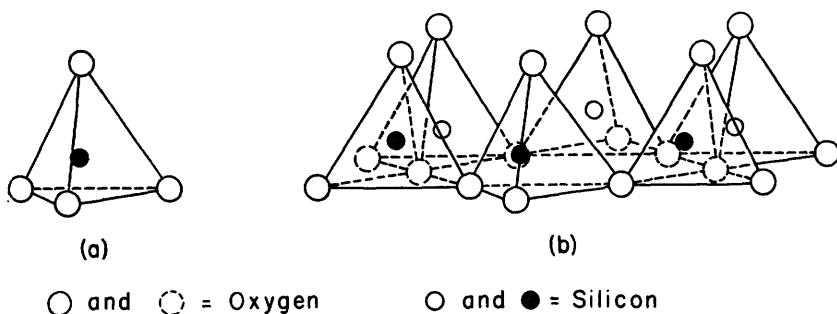
○ and ◌ = Oxygen      ○ and ● = Silicon

FIGURE 2.—Diagrammatic sketches of (a) a single silica tetrahedron and (b) the sheet structure of silica tetrahedrons arranged in a hexagonal network, from Grim, 1953b, p. 44. (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)

be needed to balance the structure. The silica sheet formed from the tetrahedral groups consists of a hexagonal network with the tips of all the tetrahedrons pointing in the same direction and their bases all in the same plane. The sheet has a distance of 2.55 A between oxygen atoms with an available space of 0.55 A for the atom in tetrahedral coordination. The unit has a thickness of 4.93 A in clay-mineral structures.

Other structural units are mentioned in the literature. Marshall (1949, p. 45–47) discussed some variations in the silica sheet structure. In the mineral apophyllite, a derivative of the free compound $(Si_2O_5)H_2$, the $Si_2O_3$ sheet is no longer hexagonal but consists of alternate rings of four and eight tetrahedra. Grim (1953b, p. 44) pointed out that the structural unit of the fibrous clay minerals differs from those noted above. This structural unit resembles the amphiboles and consists of silica tetrahedrons arranged in a double chain of composition $Si_4O_{11}$ (fig. 3).

## STRUCTURE OF ALLOPHANE MINERALS

Not much is known about the variation in composition of allophanes (Grim, 1953b, p. 45). They may be random arrangements of silicon in tetrahedral coordination and metallic atoms in octahedral coordination without any symmetry. However, Dittler (1941a; 1941b) in work with the electron-microscope and the ultramicroscope concluded that allophane is mostly halloysite. Allophane minerals have been described as amorphous to X-ray diffraction by Ross and Kerr (1934, p. 135–148).

## STRUCTURE OF KAOLINITE

The structure of kaolinite is based on Pauling's (1930b) work on the structure of chlorites. Gruner (1932) worked out a structure for kaolinite, which was later revised by Brindley (1951b) and Brindley and Robinson (1945). The structure consists of a single silica tetra-
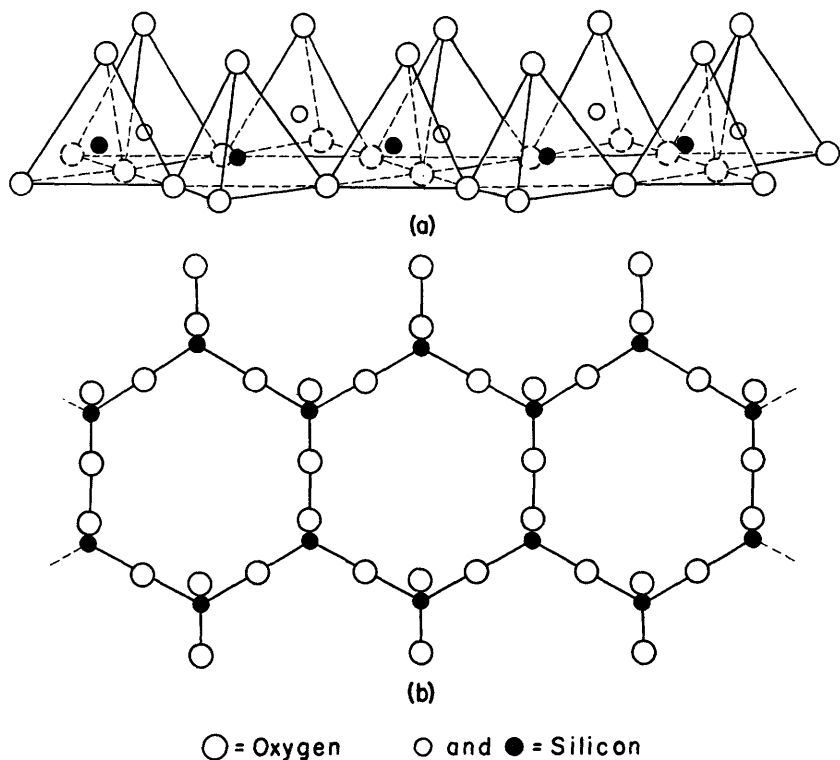
(a)

(b)

◯ = Oxygen      ◯ and ● = Silicon

FIGURE 3.—Diagrammatic sketches of double chains of silica tetrahedrons, as in the amphibole structure type of clay minerals, (a) in perspective, (b) projected on the plane of the base of the tetrahedrons, from Grim, 1953b, p. 45. (By permission from "Clay Mineralogy", by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)

hedral sheet and a single alumina octahedral sheet so combined that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer (Grim, 1953b, p. 46; Marshall, 1949, p. 49) (fig. 4).

Brindley and Robinson (1945) examined the X-ray powder diagram of kaolinite at higher resolution than Gruner (1932) had employed. They found some 70 reflections for kaolinite as compared with the 40 found by Gruner. Although the extra reflections could not be reconciled with a monoclinic cell, they were explained by the following triclinic cell:

$$a = 5.14 \text{ A} \qquad \alpha = 91.8°$$
$$b = 8.93 \text{ A} \qquad \beta = 104.5°$$
$$c = 7.41 \text{ A} \qquad \gamma = 90°$$

This structure differs from Gruner's in being pseudomonoclinic and, having half the height, contains only one SiO, Al-OH sheet.

Kaolinite differs somewhat from the ideal composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, but other members of the kaolinite group (nacrite

○ = Oxygen        ⊙ᴴ = Hydroxyl
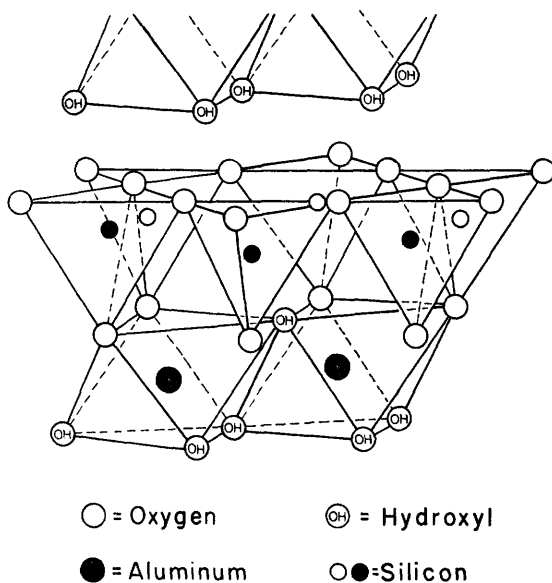
● = Aluminum      ○●=Silicon

FIGURE 4.—Diagrammatic sketch of the kaolinite layer, after Gruner 1932, from Grim, 1953b, p. 46. (By permission from "Clay Mineralogy", by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)

and dickite) correspond closely to this formula (Marshall, 1949, p. 49–50). Charges within the structural units are balanced and the three minerals differ structurally only in the manner of stacking the lattice units (Grim, 1953b, p. 47; Marshall, 1949, p. 50). Slight departure from neutrality in tetrahedral coordination, due to the presence of $Al^{+3}$ for $Si^{+4}$ is compensated for by increase in the number of atoms in octahedral coordination (Hendricks, 1945).

Results of chemical, optical, dehydration, and X-ray studies made by the U.S. Geological Survey on the kaolin minerals were summarized and tabulated by Ross and Kerr (1931).

The close packing of the kaolinite structure does not favor penetration of ions or small molecules between the sheets. The particle edges have unsatisfied valences which result in ionization and cation-exchange reactions.

Stacking of the unit layers of kaolinite was studied by Brindley (1951b, p. 32–75). He found that in successive unit layers, oxygen atoms and hydroxyl groups approach one another in pairs, whether stacked along the c axis (fig. 5) or the a and b axes (fig. 6).

Anauxite is a kaolinite type of clay mineral characterized by a high silica-to-alumina molecular ratio which often approaches 3 (Grim, 1953b, p. 51). Despite much controversy over the structure of anauxite among various investigators, Hendricks (1942) suggested a
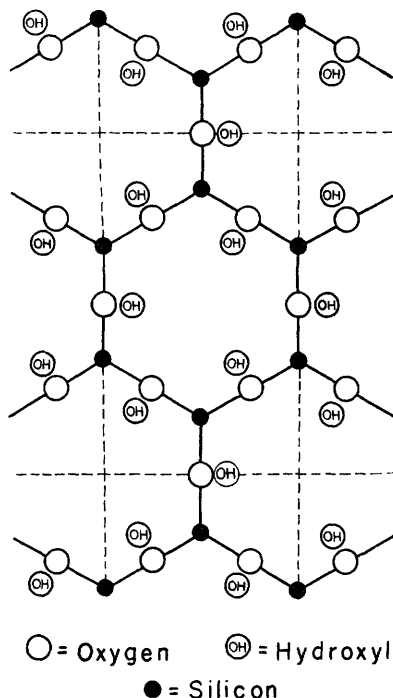
O = Oxygen    (OH) = Hydroxyl

● = Silicon

FIGURE 5.—Projection of O atoms and OH groups of adjacent kaolinite layers on the basal plane after Brindley and Robinson, 1946, p. 199.

structure that seems reasonable. This structure considers anauxite to consist of kaolinite unit layers between which units composed of double-silica tetrahedral sheets are interlayered at random.

### STRUCTURE OF HALLOYSITE

Halloysite is a crystalline material having a structure similar to but distinct from kaolinite (Ross and Kerr, 1934). Two forms of the mineral are known to exist. One having the formula $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$ is called halloysite or hydrated halloysite, and the other, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, is also called halloysite or metahalloysite (Correns and Mehmel, 1936; Hendricks, 1938). Hendricks (1938) suggested that the highly hydrated form consists of kaolinite layers separated from each other by single molecular layers of water. Gregg (1951, p. 35–38) described halloysite as consisting of parallel sheets that are twisted relative to one another, giving random orientation in the c direction. Mehmel (1935) suggested a halloysite structure which consists simply of alternate layers of $Si_2O_3(OH)_2$ and $Al_2(OH)_6$ units. Dehydration of this structure supposedly leaves a structure similar to that of kaolinite minerals (Marshall, 1949, p. 50–51). On the basis of X-ray study, Hendricks and Jefferson (1938a) developed

○ = Oxygen    ⊗ = Hydroxyl

● = Silicon    ○ = Aluminum
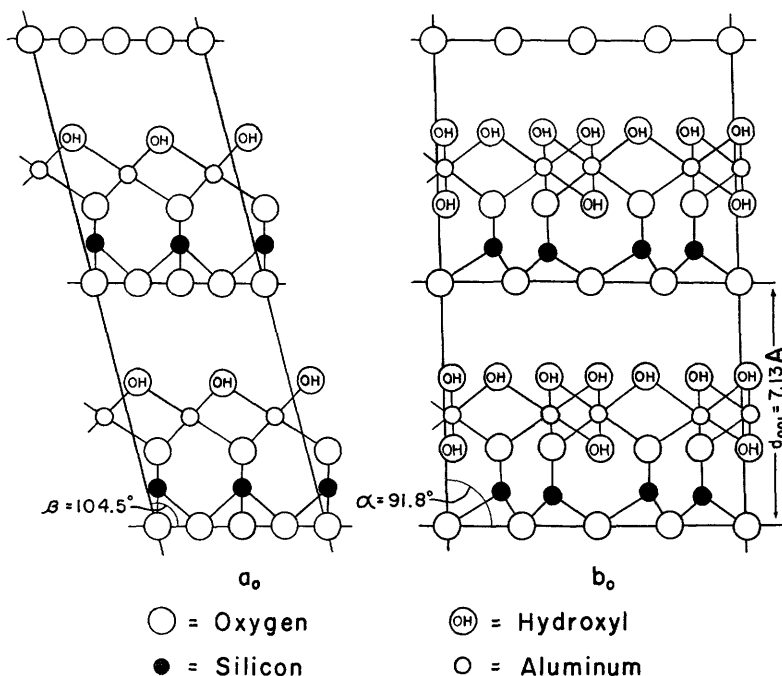
FIGURE 6.—Unit cells of kaolinite showing stacking of layers along the *a* and *b* axes, after Brindley, 1951b, p. 40.

a structure for halloysite $4H_2O$ consisting of alternate layers of kaolinitelike mineral and single layers of water (fig. 7).

### STRUCTURE OF MONTMORILLONITES

Montmorillonites constitute one of the most widely occurring groups of clay minerals known. This group includes numerous minerals of similar structure of which montmorillonite (aluminum silicate with some magnesia and ferric oxide) is the most fully studied (Mac-Ewan, 1951, p. 86-137). They are characterized by an exceedingly fine grain and present a wide variation in composition (Ross and Hendricks, 1945, p. 23-79).

The structure of the montmorillonite unit consists of two silica tetrahedral sheets and a central alumina octahedral sheet. All the tetrahedron tips point toward the center of the unit. The sheets are combined so that a common layer, consisting of the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet, is formed. The oxygen atom rather than the hydroxyl group is common to both the tetrahedral and octahedral sheets (see fig. 8).

An identifying characteristic of the montmorillonite structure is the tendency of the lattice to expand in the *c* direction when polar

Aluminum octahedrons

$\bigcirc, \ominus$ = Oxygen and (or) hydroxyl

$\bigcirc, \ominus$ = Hydrogen

$\bullet$ = Aluminum, magnesium, etc

Water molecules

$\bigcirc$ = Oxygen

$\bigcirc$ = Hydrogen
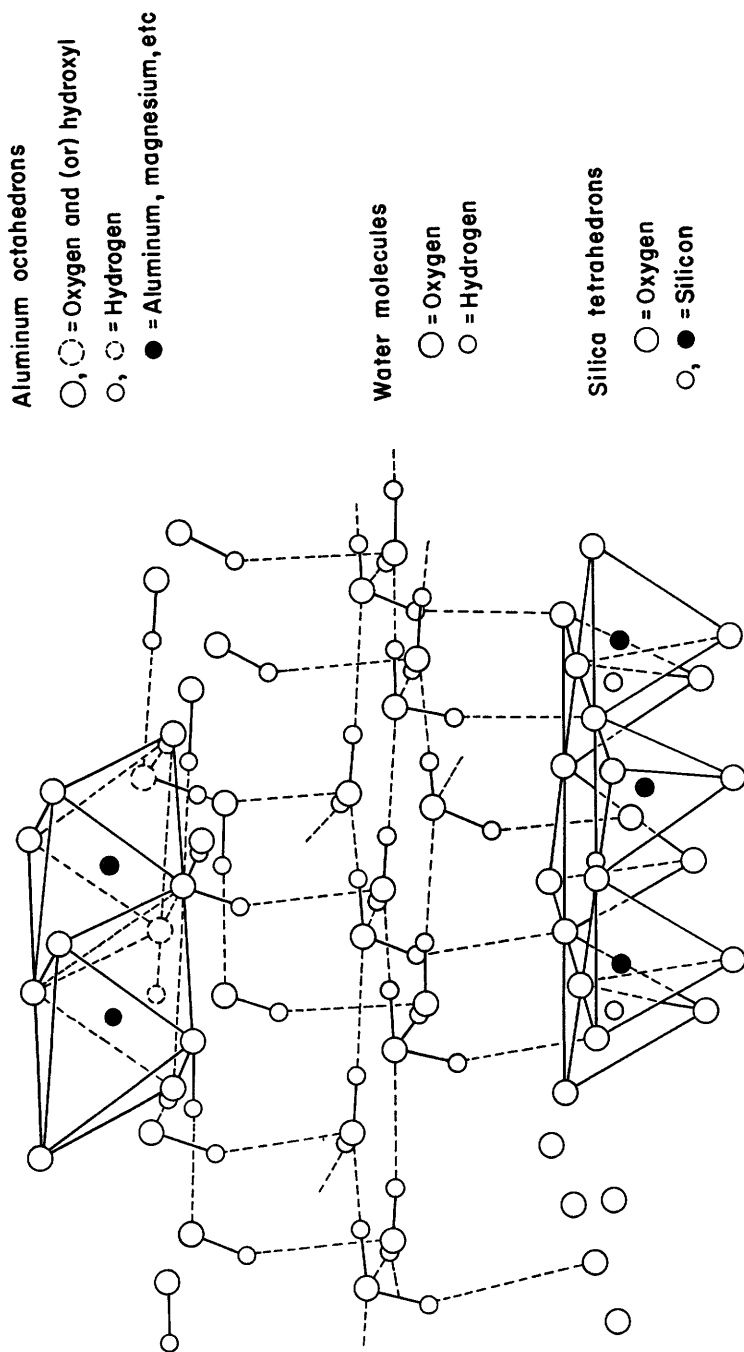
Silica tetrahedrons

$\bigcirc$ = Oxygen

$\bigcirc, \bullet$ = Silicon

FIGURE 7.—Diagrammatic sketch of a portion of the halloysite-4H$_2$O crystal structure showing a silica tetrahedral layer as suggested by Hendricks and Jefferson, 1938, from Grim, 1953b, p. 53. (By permission from Clay Mineralogy, by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)

Exchangeable cations
$nH_2O$

$\bigcirc$ = Oxygen    $\textcircled{\tiny OH}$ = Hydroxyl    $\bullet$ = Aluminum, iron, magnesium

$\bigcirc$ and $\bullet$ = Silicon, occasionally aluminum

FIGURE 8.—Diagrammatic sketch of the Hofmann, Endell, and Wilm crystal structure of mont-morillonite, from Grim, 1953b, p. 56.  (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright, 1953.  McGraw-Hill Book Co., Inc.)

molecules (water and certain organic molecules) penetrate between the unit layers (Gregg, 1951, p. 35–38; Grim, 1953b, p. 56; Iler, 1955, p. 181–232; Ross and Hendricks, 1945, p. 23–79).

Hendricks and others (1940) studied the hydration mechanism of montmorillonite saturated with various cations.  They found that magnesium and other alkaline earth cations pick up six molecules of water that is followed by completion of a water layer of hexagonal-type structure.  At higher humidities, a second water layer of similar structure is formed.  Only three molecules of water were required for hydration of the lithium cation, whereas sodium, potassium, and cesium cations apparently were not hydrated.

A number of investigators have suggested modifications of the montmorillonite structure suggested by Hofmann and others (1933).

Maegdefrau and Hofmann (1937) showed that the unit layers are generally stacked in a random manner in directions $a$ and $b$. McConnell (1950) proposed a modification of the structure of montmorillonite in an attempt to explain the thermochemical properties of that clay. By this modification, hydroxyl groups can occur in the tetrahedral layers as statistical substitutions similar to the substitution of $(OH)_4$ for $SiO_4$ in the garnetoids. The proposed structure concerns only the hexagonal sheet of $Si_2O_5$ groups in which there is occasional substitution of $Al^{+3}$ for $Si^{+4}$. According to McConnell, studies have demonstrated that $(OH)_4$ has a stable configuration as discrete tetrahedra, and 4H is equivalent electrostatically to Si in the garnetoid structures. He assumes that this type of tetrahedral configuration is possible in silicate sheets and extends the consideration to the tetrahedral layers of montmorillonite.

Edelman and Favejee (1940) suggested a structure for montmorillonites in which the direction of successive silica tetrahedrons in both sheets is reversed 180° in direction with respect to one another (figs. 9, 10). This gives a structure in which the silicon atoms are not all in a single plane in the silica tetrahedral sheets. Some substitutions of hydroxyl groups for oxygen atoms in the octahedral sheet are necessary to balance the structure. Doubt is cast on Edelman and Favejee's structure by X-ray diffraction data of Brown (1950) and other chemical data and dehydration studies (Grim, 1953b, p. 62). Forslind (1952) discussed objections raised against the structural theory of Edelman and Favejee. Edelman (1947) suggested a modification of the montmorillonite structure limiting to about 20 percent the number of tetrahedrons inverted.

Montmorillonite's theoretical formula is $(OH)_4Si_8Al_4O_{20} \cdot nH_2O$ (interlayer) if lattice substitutions are disregarded, and the charge distribution for this formula (Grim, 1953b, p. 58) is as follows:

| | | |
|---|---|---|
| 6 $O^{-2}$ | 12$^-$ | |
| 4 $Si^{+4}$ | 16$^+$ | |
| 4 $O^{-2}2(OH)^-$ | 10$^-$ | (Layer common to tetrahedral and octahedral sheets) |
| 4 $Al^{+3}$ | 12$^+$ | |
| 4 $O^{-2}2(OH)^-$ | 10$^-$ | (Layer common to tetrahedral and octahedral sheets) |
| 4 $Si^{+4}$ | 16$^+$ | |
| 6 $O^{-2}$ | 12$^-$ | |

Interlayer of $H_2O$ or other polar molecules

Actually, lattice substitutions cannot be disregarded and various investigators have emphasized that aluminum and possibly phosphorous substitute for silicon in tetrahedral coordination and magnesium, iron, zinc, nickel, lithium, and others for aluminum in the octahedral sheet (Marshall, 1935b; Hendricks, 1942). Furthermore, in montmorillonites, the lattice is always unbalanced as a result of substitutions of ions of different valence in the tetrahedral or octahedral sheets
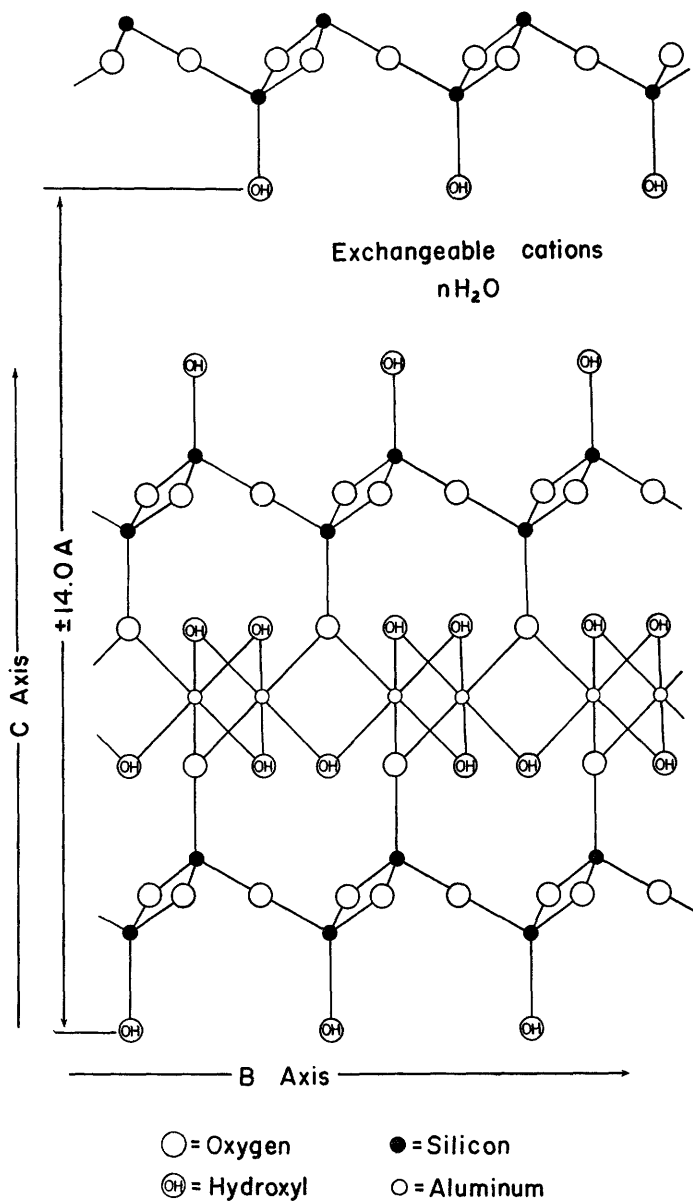
FIGURE 9.—Schematic drawing of the crystal structure of montmorillonite after Edelman and Favejee, 1940, p. 422.

Silica
tetrahedrons

Aluminum
octahedrons

Silica
tetrahedrons

Exchangeable cations
$nH_2O$

FIGURE 10.—Diagrammatic sketch of Edelman and Favejee's crystal structure of montmorillonite, from Grim, 1953b. p. 64. (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.
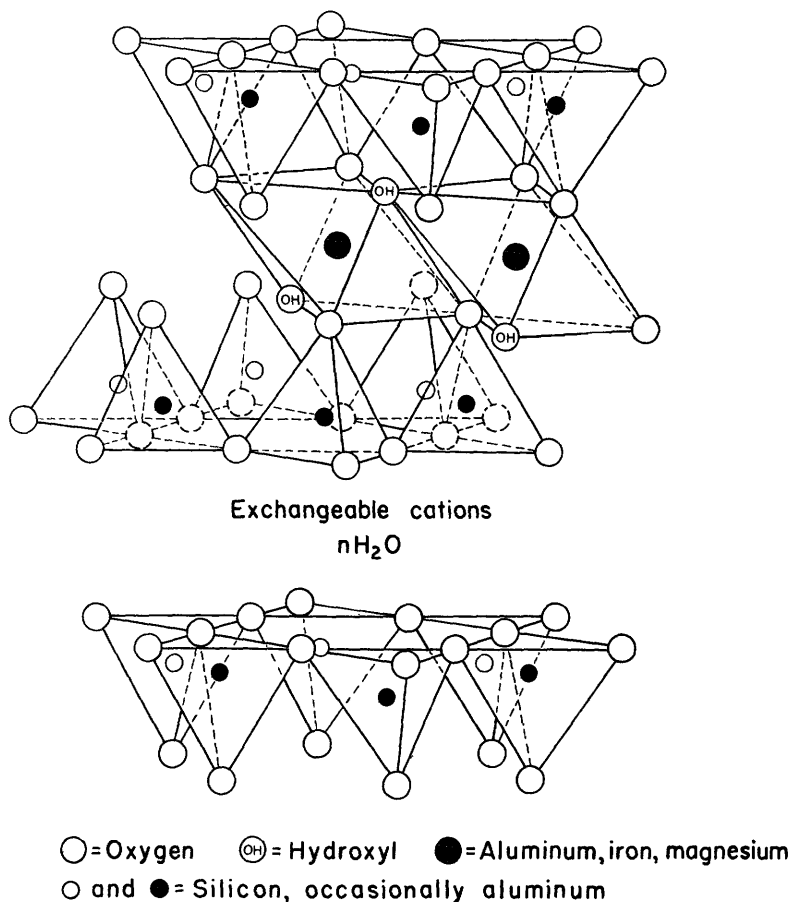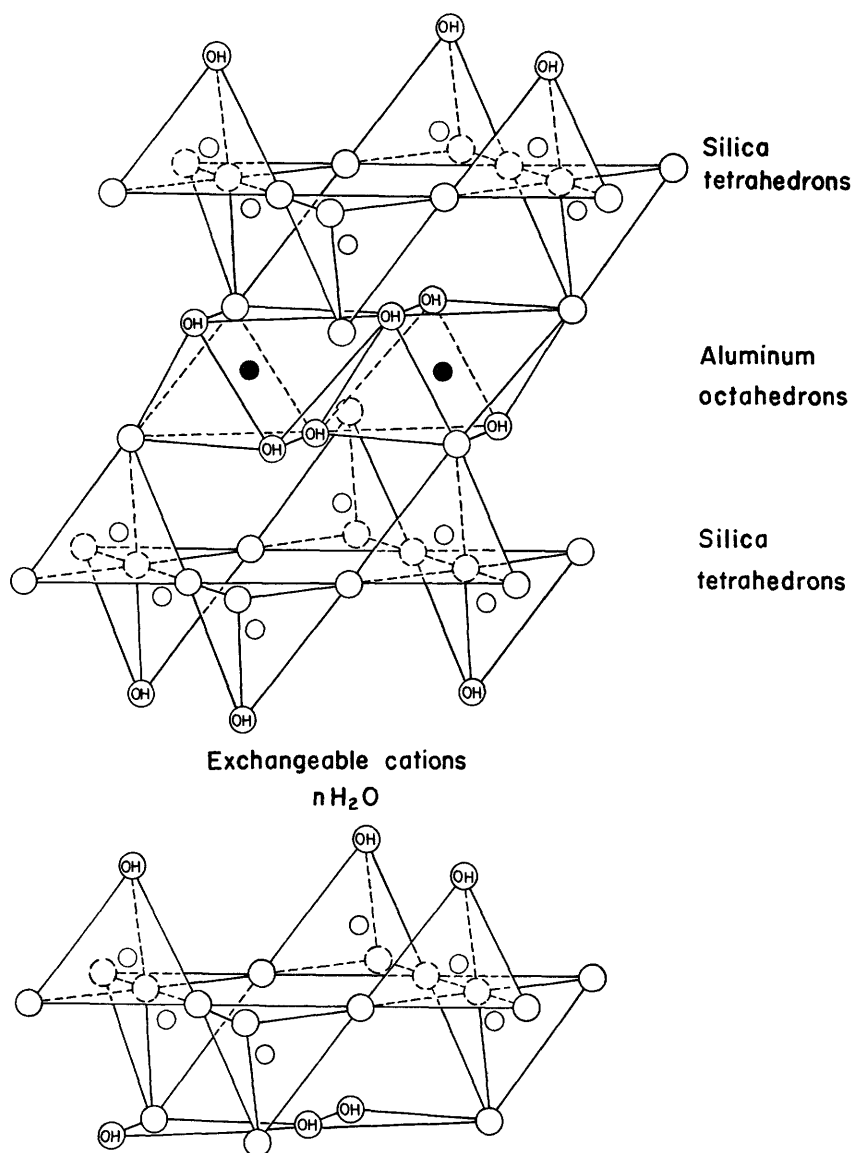
(Grim, 1953b, p. 59).   Montmorillonite has a net charge deficiency of about $0.66^-$ per unit cell, depending on the ionic substitutions within the lattice, which results in a large capacity for adsorption of cations between unit layers and around their edges (Grim, 1953, p. 59).

Osthaus (1954) in chemical determinations of tetrahedral ions in montmorillonite and in nontronite (solubility of iron and aluminum in heated 10 percent hydrochloric acid) attempted to explain the percentage of an ion present by extrapolation of solubility curve slopes to zero.   On the basis of this, he found no substitution for silicon in the tetrahedral layers of montmorillonite.   In the nontronite, solubility curves suggested the presence of iron and aluminum in the tetrahedral layer.

Although beidellite of the montmorillonite group has a theoretical composition similar to that of illites in which $K^+$ is replaced by $Na^+$ or $Ca^{+2}$, Foster (1951) concluded that the concept that montmorillonite and illite are analagous, except for the presence or absence of nonexchangeable $K^+$, is misleading.   Her explanation is that since illites have a much higher total charge and tetrahedral charge than montmorillonites, the removal of $K^+$ would not produce the montmorillonite beidellite.

In discussing the importance of $Mg^{+2}$ in montmorillonite formulas, Foster (1951) cited results to show that the presence of exchangeable $Mg^{+2}$ is more common than generally realized.

Bentonites are a relatively pure type of clay originally found in the western United States (Ross and Hendricks, 1945, p. 64–67), and are in general composed essentially of montmorillonite.   Most bentonites are characterized by having $Ca^{+2}$ as the replaceable cation and by tending to swell but slightly.   A few types having $Na^+$ as the replaceable cation (hectorite and Wyoming bentonites) form a gel-like mass on adsorption of water and tend to stay in suspension indefinitely.

According to Grim (1953b, p. 142) hydrogen clays do not have all exchange positions filled by $H^+$ since $Al^{+3}$ moves in from lattice positions before saturation with $H^+$ can be completed.   Other investigators have pointed out that hydrogen montmorillonites and hydrogen kaolinites are hydrogen-aluminum systems (Paver and Marshall, 1934).

### STRUCTURE OF VERMICULITE

Gruner (1934) is credited with having first worked out the structure of vermiculite.   He describes the structure as consisting of $(OH)_4Mg_6$ $(Si, Al)_8O_{20}$ sheets, similar to mica and talc, with interstratified layers of $8H_2O$ occupying a space close to 4.9 A in thickness.   Work by Hendricks and Jefferson (1938a) confirmed Gruner's conclusions on the structure.   Kerr and Hamilton (1949, p. 65) described the struc-

tural formula of vermiculite as consisting of hydrated mica units less $K_2O$. This can be expanded to $(OH)_2(Mg, Fe)_3(Si, Al, Fe)_4O_{10}4H_2O$.

Vermiculite has a structure similar to that of montmorillonite. Both have an expanding lattice, although vermiculite's maximum of 4.98 A, the thickness of two water molecules (Grim, 1953b, p. 76), is considerably less than the reported 001 spacing of 40 A for sodium montmorillonite immersed in $0.31N$ sodium chloride solution (Norrish and Quirk, 1954). Both vermiculite and montmorillonite adsorb certain organic molecules, differing only in the quantity (Grim, 1953b, p. 76).

Expansion of the mica type of crystal lattice is dependent upon several factors, according to Barshad (1950). He lists ionic radii, valence, total charge of the interlayered cations and the nature of the interlayered substance as factors which determine the extent of the interlayered expansion.

The structure carries a net charge deficiency of 1 to 1.4 per unit cell, resulting from substitutions of $Al^{+3}$ for $Si^{+4}$ in the tetrahedral layer. The charge deficiency on the silica sheet is compensated for by a positive charge on the alumina sheet, which contains an excess of divalent and trivalent cations (Marshall, 1949, p. 51).

There is general disagreement as to the exact structure of water layers in vermiculite (Grim, 1953b, p. 74). Barshad (1949) and Walker (1949) pointed out that the nature of the exchangeable cations must influence the state of the interlayer water since they occur between the mica layers. Walker (1951, p. 199–223) considered water in natural vermiculite to exist in two forms, which he called bound and unbound. The bound water is considered to surround $Mg^{+2}$ as a hydration envelope of six water molecules in the probable form of an octahedral arrangement. The unbound water fills in the space between the octahedral units (fig. 11). Gruner (1939) considered that the water might exist as hydronium ions. Hendricks and Jefferson (1938b) suggested an extended hexagonal network of water molecules (fig. 12). The latter concept was shared by Mathieson and Walker (1954).

The range of composition of vermiculites is not known, but their composition can be like that of some montmorillonites, the two minerals differing only in particle size (Grim, 1953b, p. 35).

### STRUCTURE OF ILLITES

In 1937, "illite" was proposed as a term applicable to micalike clay minerals (Grim and others, 1937). Prior to that time these minerals were known as potash-mica clay minerals (Ross and Kerr, 1931, p. 151–180), sericitelike minerals (Grim and others, 1937), and bravasite (Ross and Hendricks, 1945, p. 23–79). Later Grim and others (1951, p. 138–172) suggested that the term "illite" be applied

A                         B                         C



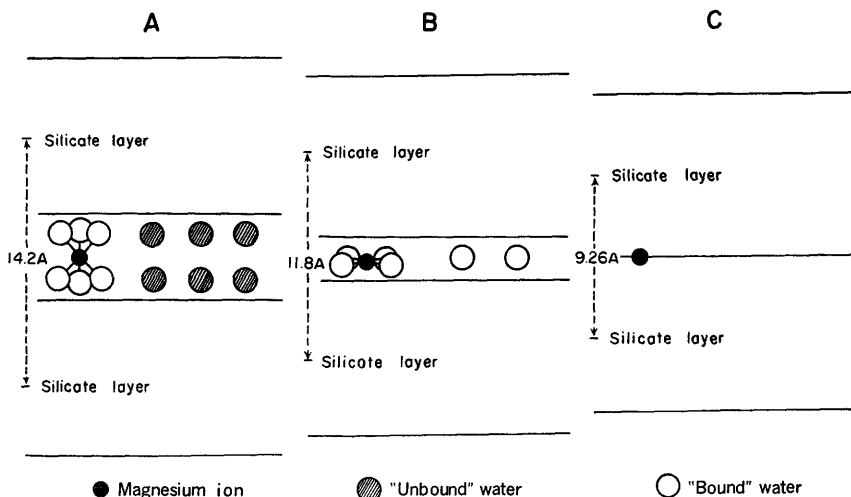● Magnesium ion          ◎ "Unbound" water          ○ "Bound" water

FIGURE 11.—Configuration of the inter-layer water in vermiculite (diagrammatic) from Walker, 1951. *A*, Fully hydrated; *B*, about half hydrated after removal of the "unbound" water. Of the six water molecules in the original hydration shell of magnesium (see *A*) only four are now in actual contact with the ion. *C*, Fully dehydrated with magnesiums in holes in the silicate layers. (By permission from "X-Ray Identification and Structures of Clay Minerals," G. W. Brindley, Editor. Copyright, 1951. Mineralogical Society, London.)

to those clay-mineral micas with less potassium and more water than true micas. Other investigators who have made notable contributions on the structure of illites include Hendricks and Jefferson (1939) and Pauling (1930a).

The basic illite structural unit was described by Grim (1953b, p. 65) as consisting of a layer composed of two silica tetrahedral sheets separated by a central octahedral sheet. Tetrahedrons in each silica sheet are arranged so that their tips point toward the center of the unit and combine with the octahedral sheet in a single layer with replacement of the hydroxyl groups by oxygen atoms.

The structure of the illites is similar to that of montmorillonite, but some differences were noted by Grim (1953b, p. 65-68). For example, some of the silicon atoms are always replaced by aluminum atoms and the charge deficiency is balanced by potassium atoms in illites. Layers are arranged so that the potassium atom is equidistant from 12 oxygen atoms, six of each layer. Also, illite has a charge deficiency, due to substitution, of 1.30-1.50 per unit cell layer compared to about 0.66 for montmorillonite. The seat of the charge deficiency of illite is largely in the outer silica sheets; the montmorillonite charge deficiency is essentially all at the center of the unit layer. The illite structural unit layers do not allow polar ions to enter between their sheets and cause expansion of the lattice in the *c* direction as does montmorillonite.

Examples of the illites include dioctahedral muscovite (fig. 13) with the octahedral sheet populated only by aluminum atoms (Grim,

Silica
tetrahedrons

◯ = Oxygen
◯, ● = Silicon

Water
molecules

◯ = Oxygen
◯ = Hydrogen
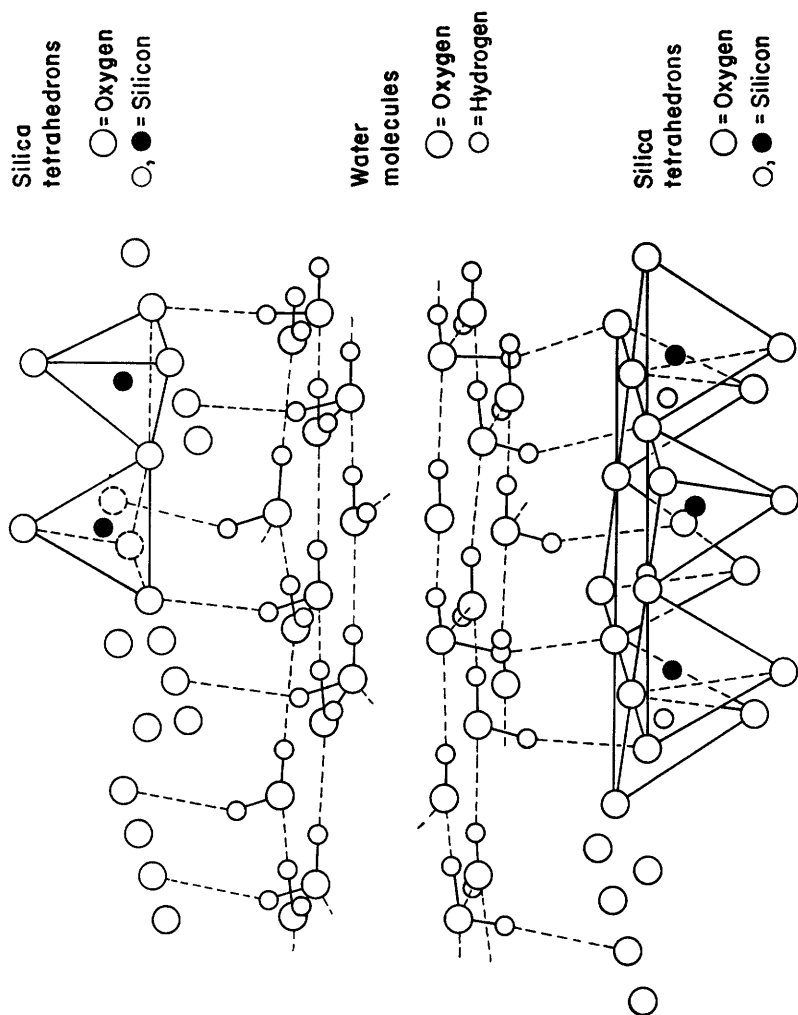
Silica
tetrahedrons

◯ = Oxygen
◯, ● = Silicon



FIGURE 12.—Diagrammatic sketch of a portion of the crystal structure of vermiculite showing layers of water molecules, after Hendricks and Jefferson, 1938, from Grim, 1953b, p. 75. (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)

○ Oxygen , ⊕ Hydroxyl , ● Aluminum, ◯ Potassium

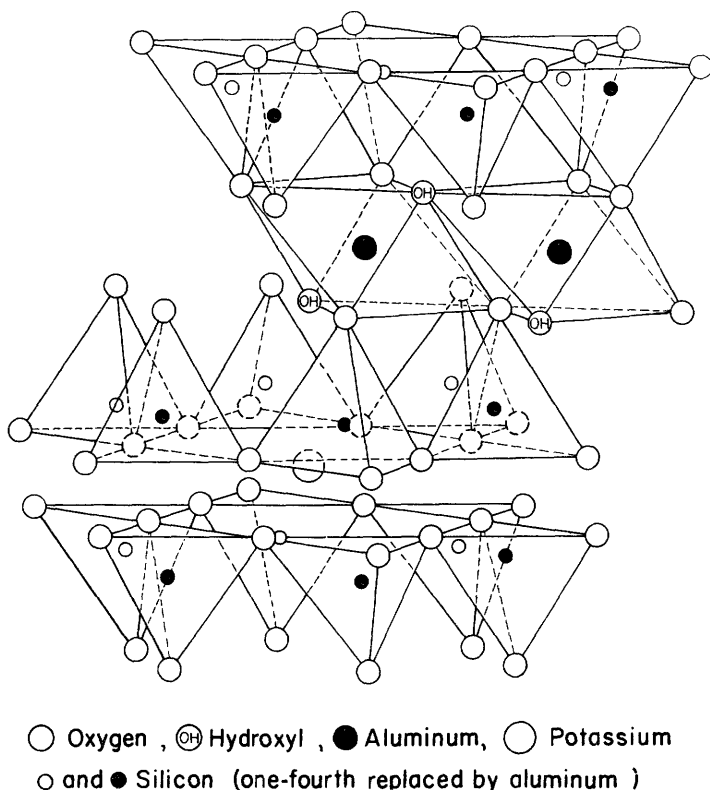○ and ● Silicon  (one-fourth replaced by aluminum )

FIGURE 13.—Diagrammatic sketch of the crystal structure of muscovite, from Grim, 1953b, p. 66.  (By permission from "Clay Mineralogy," by Ralph E. Grim.  Copyright,1953.  McGraw-Hill Book Co., Inc.)

1953b, p. 65); dioctahedral glauconite with considerable replacement of $Al^{+3}$ by $Fe^{+3}$, $Fe^{+2}$, and $Mg^{+2}$ (Hendricks and Ross, 1941); and trioctahedral biotite micas with the octahedral positions populated mostly by $Mg^{+2}$, $Fe^{+2}$, and (or) $Fe^{+3}$ (Grim, 1953b, p. 65).

### STRUCTURE OF CHLORITES

The basic work on chlorite structures was done by Pauling (1930b). Others contributed additional information on the structure of these minerals, however, and have been cited by Grim (1953b, p. 69).

The chlorite structure (figs. 14, 15) was described by Grim (1953b, p. 69–70) as consisting of alternate micalike and brucite layers continuous in the $a$ and $b$ directions and stacked in the $c$ direction with basal cleavage between layers.   Substitution of $Al^{+3}$ for $Si^{+4}$ accounts for a charge deficiency in the mica layer while the substitution of $Al^{+3}$ for $Mg^{+2}$ in the brucite layer results in an excess charge which balances the deficiency of the mica layer.

## STRUCTURE OF ATTAPULGITE–PALYGORSKITE–SEPIOLITE

Much remains to be learned about the structure of this group of clay minerals (Caillère, 1951, p. 224–233; Caillère and Henin, 1951, p. 234–243; Grim, 1953b, p. 77). They all show a variation in relative amounts of aluminum and magnesium but have the same general X-ray diffraction and dehydration characteristics according to Caillère (1936), Longchambon (1937), and Migeon (1936). The important structural element of these minerals according to these investigators is the amphibole double silica chain oriented with its long direction parallel to the c axis. In independent work, Nagelschmidt (1938) concluded that fibrous clay-mineral types consisting of silica chains exist.



$\bigcirc$ = Oxygen      $\ominus$ = Hydroxyl

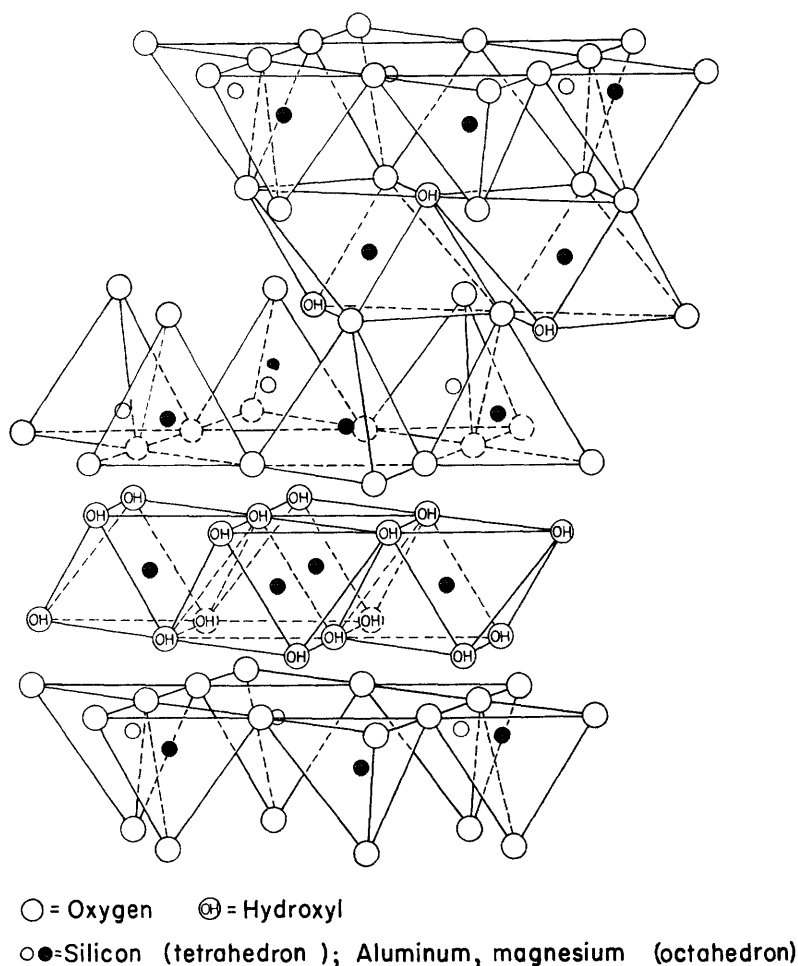$\circ$$\bullet$ = Silicon  (tetrahedron ); Aluminum, magnesium  (octahedron)

FIGURE 14.—Diagrammatic sketch of chlorite structure, after McMurchy, 1934, from Grim, 1953b, p. 70. (By permission from "Clay Mineralogy," by Ralph E. Grim. Copyright, 1953. McGraw-Hill Book Co., Inc.)
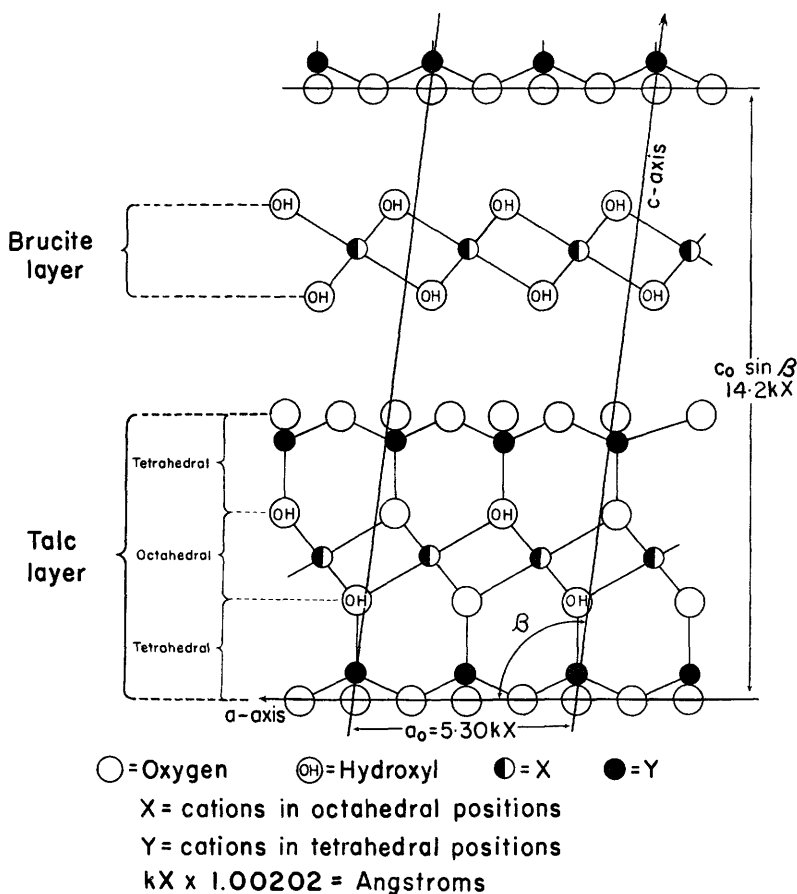
Brucite layer

Talc layer

Tetrahedral

Octahedral

Tetrahedral

c-axis

Co sin $\beta$
14·2kX

$a_0$ = 5·30kX

a-axis

$\bigcirc$ = Oxygen    $\textcircled{OH}$ = Hydroxyl    $\mathbb{O}$ = X    $\bullet$ = Y

X = cations in octahedral positions

Y = cations in tetrahedral positions

kX x 1.00202 = Angstroms

FIGURE 15.—Schematic drawing of the crystal structure of chlorite on the a c plane after McMurchy, 1934, after Brindley and Robinson, 1951, p. 180.

The formula $Si_4O_{11}(Mg \cdot H_2)_3H_2O \cdot 2(H_2O)$ was suggested for sepiolite by Longchambon (1937), while $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ was offered for attapulgite by Bradley (1940). The structure of attapulgite worked out by Bradley is given as figure 16.

It is likely that the general structure of these minerals is the same, but differences in details exist, according to Grim (1953, p. 79).

### STRUCTURE OF MIXED-LAYER CLAY MINERALS

Two different types of mixed-layer structures were described by Grim (1953b, p. 80). They are (a) regular stacking of layers along the $c$ axis and (b) random stacking along the $c$ axis with no uniform pattern of layers. Chlorite with its regular alternation of mica and brucite layers is an example of type (a), and mixed layers of illite and montmorillonite and of vermiculite are particularly common, according

O = H₂O    (OH) = Hydroxyl    O = Mg or Al
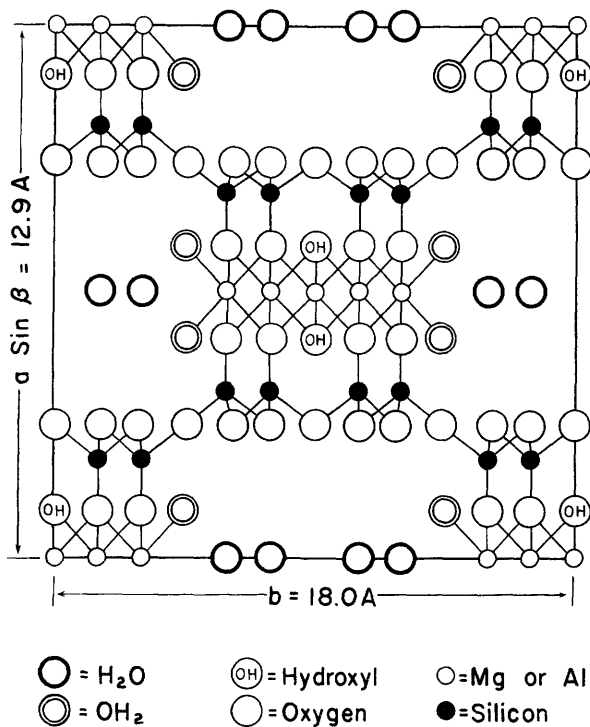◎ = OH₂    ◯ = Oxygen    ● = Silicon

FIGURE 16.—Schematic drawing of the crystal structure of attapulgite, after Bradley, 1940, p. 408.

to the author. Grim points out that a great many of the discredited or questionable clay - mineral species probably are mixed - layer combinations.

Sudo (1955) reported that certain mixed-layer Japanese clays have been found to have long spacings as large as 29.6 A and 26.6 A. They have a very complicated clay-mineral composition, including kaolin minerals, chlorite, sepiolite, and montmorillonite. The long spacings are explained by a regular interstratification between two kinds of lattices selected from among the following:

    1. Montmorillonite lattice with the cell height of 15.4 A.

    2. A magnesium chlorite of 14.5 A.

    3. Sepiolite with 12.7 A.

    4. A new lattice of 14.0 A which is a regular interstratification of gibbsite and silicate layers.

According to Sudo, the 29.6 A spacing agrees well with that of a regular mixed-layer lattice configurated by 15.4-A and 14.0-A cells and the 26.6-A spacing with a regular mixed-layer lattice configurated by 12.7-A and 14.5-A cells.

Methods for calculating clay-mineral formulas from analytical data are given in the literature (Foster, 1951; and Ross and Hendricks, 1945).

Additional references on the structure and composition of clay minerals include the following: Aukland (1956), Bagchi (1946), Bragg (1937b, p. 203–229), Brindley (1955, p. 33–43), Carroll (1959), Clarke (1924), "Encyclopedia of Chemical Technology" (1949, v. 4, p. 24–38), Hauser (1955b, p. 8), Hauser (1955c), Howat (1945), Iberg (1954), Jasmund (1951, p. 7–142), MacEwan (1950, 1952), Nakhira (1953), and Nutting (1943a, 1943b).

## OTHER CATION EXCHANGE MINERALS
### ORIGIN AND NOMENCLATURE
#### GLAUCONITE

The term "glauconite" comes from the Greek, *glaukos*, which means bluish-green or grey.    Glauconite (greensand) is known to form during marine diagenesis under (a) conditions of slow sedimentation, (b) a reducing environment, and (c) in the presence of magnesium and alkalies (Gorbunova, 1950; Grim, 1953b, p. 353; Kitazaki, 1951; Van Nostrand, 1947, p. 654).    Cloud (1955) stated that glauconite forms in cool marine waters at depths of 10 to 40 fathoms, resting on bottom sediments containing reducing matter.

#### ULTRAMARINES

The origin of the name ultramarine goes back to the middle ages when an ore containing blue pigment used by painters was imported into Europe.    Thus, the product became known as ultramarine, which means "beyond the sea" (Van Nostrand, 1947, p. 675).

#### ZEOLITES

This group of crystalline silicates is named for characteristics exhibited by its members.    The term "zeolite" is derived from the Greek words "to boil" and "a stone" (Van Nostrand, 1947, p. 1597). Zeolites are characterized by an easy fusion and a rapid expulsion of water.

Zeolites are hydrous silicates.    They are generally found as secondary minerals filling fissures and cavities in the more basic igneous rocks (Van Nostrand, 1947, p. 1569).

Thugutt (1948; 1949) also discussed the origin of zeolites.    He deduced relationships between zeolites and such primary minerals as feldspars, leucite, and others.

## COMPOSITION AND STRUCTURE

### GLAUCONITE

Glauconite is described by various investigators as a complex hydrous iron and potassium silicate whose exact formula has not yet been determined (Charrin, 1949; Kerr and Hamilton, 1949, p. 25; Van Nostrand, 1947, p. 654). Hendricks and Ross (1941) suggested a representative formula for this mineral which is as follows:

$$(K, Ca_{0.5}, Na)_{0.84}(Al_{0.47}Fe^{+3}_{0.97}Fe^{+2}_{0.19}Mg_{0.40})(Si_{3.65}Al_{0.35})O_{10}(OH)_2.$$
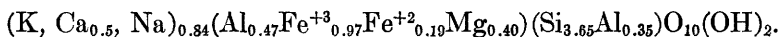
Smulikowski (1954) compared the chemical analyses of 68 glauconites with 67 analyses of illites, hydrous micas, muscovites, phengites, sericites, and biotites. He found that glauconites grade into illites in composition and that the aluminum content in the octahedral layer and the total interlayer cations appear to increase with geological age of the samples.

Hendricks and Ross (1941) reported glauconite as belonging to the dioctahedral group of micas and characterized by replacement of $Al^{+3}$ by $Fe^{+3}$, $Fe^{+2}$ and $Mg^{+2}$. In many instances, less than two-thirds of the possible positions are filled, which results in a charge deficiency in the octahedral sheet as well as in the tetrahedral sheets. Glauconite has been identified as a mica by others, including Gruner (1935) and Sabatier (1949).

### ULTRAMARINES

They are virtually anhydrous aluminum silicates of sodium containing mobile anions (carbonate, chloride, or sulfate) (Marshall, 1949 p. 26). Other cations (calcium, iron, zinc, manganese) may substitute for sodium to give various members of the group.

### ZEOLITES

There is general agreement on the composition and the structure of zeolites. Various investigators have described them as hydrous aluminum silicates which generally contain sodium or calcium and which may contain barium, strontium, magnesium, potassium, and other atoms (Van Nostrand, 1947, p. 1597; Tiselius, 1936; Wells, 1950, p. 571). According to Glemser (1941), the bound water in zeolites is not always easily removed.

Koizumi (1953) investigated the dehydration properties of various zeolites and has classified them according to their dehydration phenomena.

Formulas of the common zeolites are cited in several references (Bragg, 1937a, p. 253–256; Hendricks, 1945; Marshall, 1949, p. 27; Martínez, 1950; Morgante, 1945; Thugutt, 1948; Van Nostrand, 1947, p. 1597).

Thugutt (1948) described the structure of zeolites in terms of a space net consisting of tetrahedra ($SiO_4$) with oxygen atoms in corners and silicon and aluminum atoms in the middle. Oxygen atoms are the joining links between separate tetrahedra.

Other investigators have commented on the structure of zeolites. Eitel (1954, p. 1005–1006) pointed out that the assumed "spongy" or "channel structure" of zeolites has been proved by X-ray structure studies. Marshall (1949, p. 26–27) described zeolites as hydrated three-dimensional structures in which $Al^{+3}$ replacement of $Si^{+4}$ is common. Hendricks (1945) discussed zeolite structures in terms of a rigid framework with all the oxygen atoms shared by two cations having tetrahedral coordination but with an average charge of less than $+4$. He noted that the structure is made microscopically neutral by cations located in the open spaces.

Bragg (1937a, p. 265) described three types of zeolites:

The fibrous zeolites, such as natrolite, $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$, are characterized by chains of linked tetrahedra in which the binding is strong and which are linked laterally at comparatively infrequent intervals. The lamellar zeolites, such as heulandite, $Ca(Al_2Si_7O_{18}) \cdot 6H_2O$, probably consisting of sheets in which the linking is strong, and which are bound together by weak links, perhaps only by cations and water. Analcite, $NaAlSi_2O_6 \cdot H_2O$, and chabazite, $(Ca, Na_2) Al_2Si_4O_{12} \cdot 6H_2O$, are cubic and rhombohedral, respectively, and consist of three-dimensional frameworks of fourfold and sixfold rings of tetrahedra.

## CATION EXCHANGE AND ADSORPTION ON CLAYS AND OTHER EXCHANGE MINERALS

This section of the paper is concerned primarily with the exchange of cations between an aqueous solution and soil colloids.

### DEFINITION

Ion exchange may be defined as the exchange of an ion held by an electrical charge near the surface of an exchange mineral with an ion present in a solution in which the exchange mineral is immersed. The solvent, although generally water, can be other than water. An example of the latter is an exchange system in which alcohol is substituted for water (Magistad and Burgess, 1928 and Wiegner and Jenny, 1927). Also, direct exchange occurs between plant roots and clays (Jenny and others, 1939). Grim (1953b, p. 141) pointed out the probability that exchange reactions can take place in suspensions of high concentration or in the presence of very little water. This is demonstrated (a) by Bradfield's (1932) finding that sodium-saturated clays are able to take up enough barium from barium sulfate to fill about one-fifth of the exchange positions of the clay and (b) by Graham's (1941) finding that hydrogen clay will extract calcium from anorthite by cation exchange. However, data presented by Aderikhin

(1940) on the adsorption of calcium, magnesium, potassium, and hydrogen cations on black soil and podzol showed that the amount of cations adsorbed was directly proportional to the moisture content.

Grim (1953b, p. 128) noted that the term "cation exchange" is used interchangeably with "base exchange," although the first term is more proper technically. "Base exchange" was adopted for use in the time of Thompson (1850) and Way (1850), when it was not known that the $H^+$ cation also could take part in exchange reactions.

Nutting (1931) described cation exchanges in terms of single layers of adsorbed ions, which are practically in chemical combination with the surface.

## CATION EXCHANGE MATERIALS

The exchange of cations is stoichiometric (Grim, 1953b, p. 136; McBain, 1950, p. 51) and the equilibria of exchange reactions are governed by the classical adsorption isotherm.

Some of the substances that exhibit the phenomenon of cation exchange include the following: clay minerals, naturally occurring zeolites, fluoride, humus, cellulose, wool, proteins, alumina, synthetic resins, lignin, living cells, barium sulfate, glass, phosphates, silver chloride, and miscellaneous silicates ("Encyclopedia of Chemical Technology," 1952, p. 1–17). Of this group, the clay minerals, zeolites, and miscellaneous silicates are of primary interest to this report. For a general discussion on various types of ion-exchange materials, the reader is referred to Walton (1941) and Kunin (1958).

## EARLY HISTORY

According to Kelley (1948, p. 1) recognition of the phenomenon of cation exchange is attributed to two Englishmen, Thompson (1850) and Way (1850). Results of their work dating back to 1845 were published in 1850 and 1852. In his first publication, Way (1850) listed several conclusions. They are summarized below.

1. In reactions between soil and salt solutions, calcium in the soil exchanges places with cations in solution, anions remaining in solution unless an insoluble calcium salt is formed.

2. Salts of lime are not adsorbed when filtered through the soil, but $Ca(OH)_2$ and $Ca(HCO_3)_2$ are adsorbed whole (in molecular form) like alkaline compounds of other cations.

3. The clay portion of soil has the power to adsorb cations. Sand, organic matter, calcium carbonate, and free alumina do not possess this power.

4. Preheating of soil diminishes its adsorptive power.

5. Adsorption is a rapid reaction, as between mineral acid and alkalies.

6. Ammonium carbonate and ammonium hydroxide are adsorbed as molecules.

7. Adsorptive power of clay increases with increasing concentration of solution and as the ratio of solution to soil increases.

8. Cation exchange is exhibited with the soil by $K^+$, $Na^+$, and $Mg^{2+}$ in addition to $NH_4^+$.

9. Cation exchange is irreversible.

It is interesting to note that with the exception of conclusions 2, 6, and 9, which were essentially erroneous, the others for the most part have proved to be correct. Organic matter is known, of course, to exhibit the exchange property. Also, calcium ions are not the only exchangeable cations present in the soil.

### CATION EXCHANGE THEORIES

Various explanations of ion exchange have been proposed since Way (1850) performed his experiments on the exchange of cations in the soil. These explanations may be grouped conveniently into three theories: (a) the crystal-lattice theory, (b) the double-layer theory, and (c) the Donnan membrane theory.

The crystal-lattice theory considers all ionic solids as being composed of positively and negatively charged ions in a completely dissociated state. Every ion in a crystal is surrounded by a fixed number of oppositely charged ions and is subject to Coulombic attractive forces. Exchange of a given ion for one of like charge is possible as a result of diminishing the net attractive force binding the ion to its crystal lattice. This can be accomplished by placing the crystal in a polar medium such as water.

Helmholtz (1879) provided the basis for the double-layer theory. Its purpose was to explain the electrokinetic properties of colloids. The Helmholtz double layer consists of two rigid electrical layers analagous to the plates of a condenser. The theory was modified by Gouy (1910) and Stern (1924). They considered a double layer consisting of an inner fixed layer and a diffuse and mobile outer layer of charges. There is no sharp boundary between the two layers, and the concentration of the diffuse layer may be considered as varying constantly and depending on the concentration and pH of the external solution. A change in the concentration of ions in the external solution by addition of a foreign ion upsets the equilibrium and a new equilibrium is obtained.

Other references on the double-layer theory include Bolt, 1955; Hauser and Colombo, 1954; Jenny, 1932; and Kunin, 1958.

The Donnan equilibrium theory is concerned with the state of equilibrium in a system composed of ordinary electrolytes and colloidal

electrolytes separated by a membrane which is impermeable to colloidal particles (Adair, 1947, p. 154–161).

Although none of the three theories presented is completely satisfactory, they all contribute to the understanding of ion exchange.

## ADSORPTION OF POLAR MOLECULES AND GASES BY CLAY MINERALS

Clay minerals have long been used as adsorbents, although their capacity to take up nonpolar molecules is less than that of the best activated charcoal or silica gel (Marshall, 1949, p. 91). Inert gases such as nitrogen are taken up at low temperatures; for this reason they have been used to determine surface areas of clay minerals (Brunauer and others, 1938). According to Marshall (1949, p. 91), little quantitative information on the adsorption of nonpolar vapors at ordinary temperatures is available.

### UPTAKE OF POLAR MOLECULES

#### UPTAKE OF WATER

The uptake of polar molecules by the swelling clays (montmorillonite group) is well known. Among the early workers studying the structure of montmorillonite were Hofmann and others (1933), who showed that the uptake of water by this clay mineral caused an expansion in the direction of the $c$ axis, but no appreciable change in $a$ and $b$ axes.

Various investigators have used the Donnan equilibrium theory as a basis for conclusions concerning swelling, ionic exchange reactions of soils, and hydration (Davis, 1942; Eriksson, 1952; Mattson, 1929; Mattson and Larsson, 1944–1945; Pavlovschi, 1937–1938; Samuelson, 1953; and Whitney and Peech, 1952).

Mattson (1942 described experiments in which pieces of sponge are moistened with an electrolyte solution, washed, and then extracted with a solution of another electrolyte. The resulting ion exchange is described in terms of the Debye-Huckel theory and the Donnan equilibrium system.

The role of the water molecule in clay minerals has been studied by many investigators since the work of Hofmann and others in 1933, but only a few of them can be mentioned here. For montmorillonite, Marshall (1936) suggested that the first water molecules congregate around the exchangeable cation sites between the sheets, and that later additions fill up vacant spaces and finally force the layers farther apart at high vapor pressures. Studies by Hendricks and others (1940) on montmorillonite indicate that certain cations are hydrated while others are not. Mooney and others (1952) in studies on adsorption of water

on montmorillonite found that the adsorption isotherm is dependent on the initial water content.   Gregg (1951) suggested that water is taken up by montmorillonite clays between the sheets and on the outside of crystallites as well.   Ruiz and Gonzales (1955), in studies on the adsorption of water by montmorillonite, interpreted their data as showing three types of water: (a) intermicellar and capillary water, (b) interlaminar water (which causes swelling clays to swell), and (c) osmotic water.   In studies with attapulgite, Chessick and Zettlemoyer (1956) found that as increasing amounts of water were adsorbed (principally on the external surface) an accompanying loss of surface area, as measured by the Harkins-Jura absolute method, occurred.

### UPTAKE OF AMMONIA

Cornet (1943) showed that hydrogen montmorillonite will react with ammonia gas to form ammonium montmorillonite.   At low pressures there is no expansion of the $c$ axis by the adsorbed ammonia, probably because adsorption occurs on the outer surface only.   Expansion of the $c$ axis occurs, presumably, when the ammonia is adsorbed internally.   Zettlemoyer and others (1955) measured nitrogen, ammonia, and water vapor adsorption isotherms on a Wyoming bentonite (montmorillonite).   They found that in the relative pressure range 0.05 to 0.35 (presumably mm) nitrogen and water measured only the external area, whereas ammonia measured the internal area as well.

### ORGANIC POLAR MOLECULES

Bradley (1945), Gregg (1951, p. 35–38), and MacEwan (1948, 1949) showed that a variety of polar organic molecules can be adsorbed on and displace water from basal plane surfaces of montmorillonite. MacEwan (1948, 1949) showed also that these same molecules can be adsorbed by halloysite.   Both Bradley (1945) and MacEwan (1948) concluded that the molecules are held by the clay surface through a C–H . . . O (clay-mineral surface) bond.   Hendricks (1941) showed that in addition to the electrical attraction of the organic cation for the negatively charged silicate surface, strong Van der Waals forces come into play.

## MODERN CONCEPT OF CATION EXCHANGE IN CLAY MINERALS AND EXCHANGE MINERALS

Outlines of the modern concept of cation exchange in clay minerals have been presented by Grim (1953b, p. 132–134), Hendricks (1945), Jenny (1942), and others.   Some of these are discussed in the following section.

### CATION EXCHANGE IN CLAY MINERALS

Cation exchange in clay minerals is due to three causes according to Grim (1953b, p. 132–134).   One cause is broken bonds on the edges

of silica-alumina units resulting in unbalanced charges, which can be balanced by cations. This is the major source of cation-exchange capacity in kaolinite and halloysite clay minerals and is improtant in the illite, chlorite, and sepiolite-palygorskite-attapulgite minerals. Broken bonds cause about 20 percent of the cation exchange in vermiculites and montmorillonites.

A second cause of cation exchange in clay minerals is substitution within the lattice structures. Examples are substitutions of $Al^{+3}$ for $Si^{+4}$ in the tetrahedral sheet, and of lower-valence ions, $Mg^{+2}$, for example, for $Al^{+3}$ in the octahedral sheet. These substitutions result in unbalanced charges, which can be balanced by other lattice changes (hydroxyl group for oxygen atoms) or by adsorbed cations. Substitutions within the lattice account for about 80 percent of the cation-exchange capacity of vermiculites and montmorillonites and may be the cause of some cation-exchange capacity in poorly crystalline examples of illite, chlorite, and sepiolite-palygorskite-attapulgite. Iler (1955, p. 260) described exchange in montmorillonite in a similar manner.

A third cause of cation exchange in clay minerals cited by Grim is the replacement of the hydrogen of exposed hydroxyls by replaceable cations. Although this would apply to all clay minerals, it would be most applicable to kaolinite and halloysite.

Mitra and Rajagopalan (1952) disagreed with the broken-bond hypothesis. They believe that the limiting value of cation-exchange capacity can be explained by the isomorphous and hydroxylic charges.

Hendricks (1942, 1945) attributed cation exchange in clay minerals to two conditions: (a) sheets that are too full for ionic migration through them, and (b) vacancies in one-third of the octahedral coordination positions of the pyrophyllite sheet.

As discussed by McBain (1950, p. 390), cation exchange in clay minerals occurs because of the difference in valence of $Al^{+3}$ substituting for $Si^{+4}$ in the outer layer, or of $Mg^{+2}$ substituting for $Al^{+3}$ in the inner layer. Each of these negative charges on the lattice must be satisfied by free positive ions.

Kingery and others (1955) attributed cation exchange in kaolinite to isomorphous replacement of $Al^{+3}$ in the silica sheet.

Schofield and Samson (1953) advanced the concept that the conventional small cation-exchange capacity of kaolinite is the consequence of a net excess of negative charges on basal surfaces over positive (at lower pH) charges on the edges, the edge charges being sensitive to pH and convertible to negative by abstraction of protons at high pH values.

From studies of 100 mineral specimens of the montmorillonite group of clay minerals, Ross and Hendricks (1941) concluded that

cation exchange in some members of the group is a result of replacement of silicon in the tetrahedral coordination with respect to oxygen by aluminum and in others of replacement among ions having octahedral coordination.

Cation exchange in montmorillonite was discussed further by Ross and Hendricks (1945, p. 23–79). Exchangeable cations in montmorillonite are said to be on the surfaces of the silicate layers. They are generally $Na^+$ and $Ca^{+2}$, but $K^+$, $Mg^{+2}$, $H^+$, and $Al^{+3}$ may be exchangeable. Amounts of exchangeable cations are determined by the excess negative charge within the layer.

Tschapek and Butschkowskyj (1952) have explained the noncompensated bonds in the tetrahedral layers and octahedral layers by the theory that all the interchangeable ions of kaolinite and most of those in montmorillonite are located on the outer edges of the crystals. Noncompensated positive bonds adsorb $OH^-$ and the negative ones adsorb $H^+$, resulting each time (in both cases) in hydroxyl groups whose H is capable of being replaced by a metallic ion. Bagchi (1949) has expressed similar views.

From studies of adsorption and exchange at low concentration, Ganguly (1949) discovered three types of bonding in silicate minerals. He postulated that the sites are exposed $K^+$ sites, broken bonds from silicon atoms exposed on the surface by grinding, and broken bonds from $Al^{+3}$ ions on the surface.

Other suggested references on ion exchange include the following: Barrer (1949); Buehrer (1952); Chatterjee (1949); Lewis (1952); and Thomas and Frysinger (1956).

### CATION EXCHANGE IN GLAUCONITE

Micalike minerals such as glauconite exhibit a relatively low cation-exchange capacity, approximately one-third to one-fourth that of montmorillonite group minerals (Hendricks, 1945). Cations are difficult to exchange between structural sheets in minerals of this type, and cation exchange occurs primarily at the limiting surfaces of the crystals.

Davydov and Skoblionok (1953) studied the adsorption characteristics of glauconite in mixed media. They studied the exchange of $Ca^{+2}$ and $Ba^{+2}$ for $Na^+$ and $K^+$ on the glauconite in water and water-alcohol mixtures containing 30, 50, and 70 weight percent of alcohol. Composition of the solvent did not affect the maximum adsorption by glauconite.

### CATION EXCHANGE IN ULTRAMARINES

Cation exchange takes place inside the channels or pores of these minerals. Marshall (1949, p. 26) suggested that the large anions of ultramarines require fusion with salts for replacement, whereas cations are replaceable from hot, aqueous solutions.

## CATION EXCHANGE IN ZEOLITES

The generally accepted concept of cation exchange in zeolites is the one that considers that exchange occurs in multiconnected voids or channels located within the volume enclosed by a rigid structural framework.

Marshall (1931) distinguished between the type of cation exchange that can occur as a surface reaction with almost all colloidal systems and another, common to zeolites, in which replacement of one cation by another definitely changes optical properties, density, and so forth, of the crystal.

Although they are known to have relatively high cation-exchange capacities, 100 to 300 milliequivalents per 100 grams (Grim, 1953b, p. 132), zeolite exchange capacities are somewhat limited by the fact that large cations, which are commonly adsorbed by expanding lattice clays, cannot enter the open diameters of the zeolite channels (Hendricks, 1945; Eitel, 1954, p. 1020). Russell and Pearce (1943), in preliminary studies of cation exchange by zeolites, found no cation whose valence or size prevented it from entering into cation-exchange reactions.

Various factors influence the cation-exchange capacities of the zeolites. Studies by Zhukov and Brodskaya (1949) indicated that the exchange capacities increase with increasing pH of the exchange solutions. Randall and Cann (1930) used the theory of micelle formation to explain cation exchange in zeolites. According to this theory, all substances forming negative micelles in solution should possess differential cation-exchange properties. In zeolites, the negative ions of the aluminosilicates are considered to form large micelles. Cation exchange in zeolites also seems to vary with temperature. Hey (1932, 1933, 1934, and 1936) noted that all the zeolites studied by him required high temperatures for appreciable reaction.

Silver and other heavy metals can be recovered from sea water or other strong saline solutions by exposing the solutions to iron or manganese-containing zeolites (Brooke, 1953).

## DETERMINATION OF CATION-EXCHANGE CAPACITY

Cation-exchange capacity is generally determined by saturating the clay with ammonium or barium ions and determining the amount held at pH 7 (Grim, 1953b, p. 126). It is expressed as milliequivalents per 100 grams. Kelley and Brown (1924) suggested that the amount of cations taken up by the clay rather than the amount removed from the clay be considered as the cation-exchange capacity. Mattson (1932) pointed out that exchange capacity denotes the total amount of cations that can be exchanged under a given set of conditions. For example, an exchange-capacity determination made

with a neutral solution of a given salt will likely show a lower value than the determination made with an alkaline solution of the same salt. For this reason, Mattson suggested that the pH of the solution should always be stated.

Many investigators, including Chapman and Kelley (1930), Grim (1953b, p. 155), and Kelley and Brown (1925), have stated that the determination of cation-exchange capacity of soils, clay minerals, artificial zeolites, and other substances is not highly precise. This is not difficult to believe after studying the factors influencing cation exchange. Mukherjee and Ganguly (1944) cited three important factors influencing cation exchange: (a) the pH, (b) the nature and concentration of the reacting ion, and (c) the time of interaction.

Many methods have been proposed for the determination of cation-exchange capacity. A few of the more commonly used methods will be discussed.

### AMMONIUM METHOD

Perhaps the most common method is the one that uses the ammonium ion to replace the exchangeable cations in the exchange material. Ammonium salts are used advantageously, as they can be readily decomposed or volatilized and as exchangeable ammonium is not commonly found in the soil or in clay minerals (Kelley, 1948, p. 83).

Peech (1945) described a rapid method of determining exchangeable cations in which the cations are extracted by ammonium acetate solution. Calcium is determined volumetrically as the oxalate, and colorimetric methods utilizing a spectrophotometer are used in the determination of magnesium, potassium, sodium, and manganese.

Kelley and Brown (1934), Kuron and Jung (1940), and Lewis (1950) have used the ammonium acetate method and offer detailed procedures. According to Mehlich (1945) and Pratt and Holowaychuk (1954), leaching with ammonium acetate solution gave lower results than other methods tested.

Graham and Sullivan (1938) suggested that aqueous $1N$ ammonium acetate is a satisfactory leaching agent for most clay bodies; but, for those containing appreciable amounts of calcium carbonate, they recommend that alcoholic ammonium acetate be used.

Sawhney and others (1959) studied the cation-exchange capacity determination of soils as influenced by the cation species. Large fixable potassium cations and small nonfixable calcium cations were used for successive exchange saturation with subsequent replacement by sodium acetate and ammonium acetate leaching solutions. With montmorillonite samples, approximately equal cation-exchange capacity values were obtained for both calcium and potassium saturation and with both replacing solutions. With sample fractions containing appreciable vermiculite, the results were different, The cation-ex-

change capacities obtained with potassium replaced by the ammonium ion of ammonium acetate were much less than the results obtained with the small calcium cations replaced with ammonium or sodium ions of the respective replacing acetate solutions. In addition, calcium replaced by sodium acetate gave noticeably higher values than calcium replaced by ammonium acetate. These results indicate that, although any convenient cation could be used for the determination of total cation-exchange capacity with montmorillonite, any general method for determining cation-exchange capacity of soils should use small cations for both saturation and replacement.

U.S. Department of Agriculture Handbook No. 60 (1954, p. 19–20) notes that some alkali and saline soils fix appreciable amounts of ammonium ion as well as potassium ion under moist conditions. This does not interfere with the extraction of exchangeable cations, but values obtained for cation-exchange capacity by ammonium ion saturation are low by amounts equal to the quantity of ammonium fixed. Soluble salts should not be washed out of the clay or soil prior to extracting the exchangeable cations, because significant changes can take place as a result of dilution and hydrolysis.

The presence of calcium carbonate in the sample does not interfere with the determination of exchangeable magnesium, potassium, and sodium, but the solubility of calcium carbonate must be considered in calculating exchangeable calcium, according to Gedroiz (1918a), in tests made with ammonium chloride.

### BARIUM METHOD

Magistad and Burgess (1928) criticized the ammonium chloride method of Gedroiz (1918a) for determining the cation-exchange capacity of soils containing calcium carbonate. According to them, the amount of calcium dissolved from calcium carbonate cannot be determined accurately, and the constant presence of dissolved calcium prevents the replacing action from going to completion They suggest a method using alcoholic (methyl or ethyl) salt solutions as the displacing agents. A $0.1N$ barium chloride solution in 68 percent ethyl alcohol is recommended. The activity of such a solution approaches that of an aqueous solution, and the solubility of calcium carbonate in the alcoholic solution is extremely low, according to the authors.

Other methods employing the barium cation in the cation-exchange-capacity determination are described in the literature. Martinez (1950) offered a method in which zeolite is saturated with barium cation as barium acetate, followed by leaching with ammonium chloride. Determination of the cation-exchange capacity is calculated from the amount of barium sulfate precipitated in the leaching solution.

Mehlich (1942) described a rapid method for cation-exchange capacity determination of soils that utilizes a well-buffered extracting medium (triethanolamine neutralized to about pH 8.2 with hydrochloric acid) containing about $0.2N$ barium chloride. Sulfate must be absent or results will be high.

### RADIOACTIVE TRACER–CHROMATOGRAM METHOD

Frysinger and Thomas (1955) outlined a method for determination of cation-exchange capacity that relies upon the replacement of exchangeable cations by cesium. The authors have shown that cesium is more strongly held on montmorillonite and attapulgite clays than a large number of univalent and divalent cations including lithium, sodium, potassium, ammonium, rubidium, calcium, strontium, and manganese. Apparently very little work has been done to determine the behavior of cesium in conjunction with cations of higher valence.

With this method, an elution chromatogram is run with cesium chloride solution from a mineral sample distributed on an appropriate inert filter aid. The chromatogram is mapped by following the cesium content of the eluate with a tracer of radioactive cesium-137. Since cesium is more strongly adsorbed than any of the cations generally found in clays and soils, the breakthrough of the chromatographic column is always relatively sharp with the effluent activity rising rapidly to its input value. This is a sure sign that the exchange process is complete, according to the authors. The method is not recommended for exchange materials of low capacity.

### COLORIMETRIC METHOD

A method for the determination of the cation-exchange capacity of soils and other materials involving saturation with divalent manganese was described by Bower and Truog (1940a). After displacement, the manganese is oxidized to permanganic acid and determined colorimetrically. Ormsby and Sand (1954) noted that the pH is critical and must be lower than pH 7 in this determination. Data have been presented by Sand and Ormsby (1954) for the manganese saturation method of determining cation-exchange capacity in mixtures of kaolinite and halloysite.

### MISCELLANEOUS METHODS

Perkins' (1952) method of saturating the clay mineral with either magnesium or calcium acetate, followed by taking the mineral up in an excess of versenate and back-titrating with magnesium acetate at pH 10, is said to show good agreement with the ammonium acetate and ammonium chloride methods.

Robertson and Ward (1951) described a method based on the adsorption of methylene blue for estimating the cation-exchange capacity of clay minerals.

Mortland and Mellor (1954) and de Figueiredo and de Carvalho (1952) suggested conductometric titration methods for determination of cation-exchange capacity in soils. The results are said to compare favorably with the sodium acetate and ammonium acetate procedures on calcareous and acid soils.

A method was described by Holt (1956) in which the soil is saturated with silver ions, excess thiourea is added, and the system is back-titrated with standard $0.01N$ silver nitrate. The end point is detected amperometrically by the use of a rotating platinum microelectrode. Results obtained on 15 soils from 12 states compared favorably with those from ammonium acetate leaching.

Van Olphen (1950) described a method for determining cation-exchange capacity based on emulsification. When cetyltrimethyl ammonium bromide (Lissolamine A) is added to clay sols in successive small amounts, a gradual decrease in stability results and flocculation occurs. Continued addition of the CTAB reverses this behavior and peptization of the clay sols results. The sol will be least stable when the number of CTAB ions added is equal to the number of exchangeable ions on the clay micelle. Although it was not possible to distinguish this point visually, Van Olphen observed that at the equivalence point the coated clay micelle was simultaneously oleophilic (at the lattice surface) and hydrophilic (at the micelle edges). A micelle of such structure would be expected to act as an efficient emulsifier. This idea was verified experimentally by shaking the sols, previously treated with increasing amounts of CTAB, with a paraffinic type of gas oil. A comparatively stable emulsion was formed at a critical concentration of cetyltrimethyl ammonium bromide. Cation-exchange capacities for various clays based on this critical concentration of CTAB showed good agreement with values obtained by the ammonium chloride method.

### REPLACEABILITY OF EXCHANGEABLE CATIONS

From the time of Way (1850), it has been known that under given conditions various cations are not equally replaceable and do not exhibit the same replacing power. This fact is illustrated in replaceability series listed by Gedroiz (1922), Kelley (1948, p. 57–61), Ross and Hendricks (1945, p. 37–39), and Way (1852).

The complexity of exchange reactions is attributable to a number of factors that vary from one clay material to another. The underlying causes of this complexity and variability are not known in

every case.  Certain characteristics of the ion, such as ionic size, valence, hydration, the seat of the exchange position on the clay mineral or the geometrical fit of the cation and the clay mineral are at least partly responsible.  These and other factors influencing cation exchange will be discussed in the section that follows.

## FACTORS INFLUENCING CATION EXCHANGE
### BINDING FORCES

Binding forces within the crystal lattice are an important factor influencing cation exchange.  According to Glasstone (1940, p. 399), the forces that affect the stability of an ionic crystal include (a) electrostatic, or Coulomb, forces whose attraction between ions falls off with the square of the distance; (b) Van der Waals forces with attraction diminishing according to the seventh power of the distance; and (c) interatomic repulsive forces also diminishing rapidly with the distance.

Lacy (1954) and Jenny (1932) attributed the individual behavior of the cations in the exchange process to the magnitude of the Coulombic attraction between negative oxygen atoms of the crystal lattice and adsorbed cations.

Jenny (1932) explained the behavior of hydrogen ion by the strong chemical bonds between adsorbed hydrogen and oxygen and hydroxyl groups of the rigid crystal frame.

In describing adsorption on ionic lattices, Kolthoff (1936) stated that residual valence forces of ions located on the edges are stronger than those on the plane surfaces, and the valence forces of ions located on corners is even stronger than that of ions on the edges.  Thus, the corner lattice ions exhibit the strongest exchange power.

In exchange measurements made with heteroionic bentonites, Ganguly and Mukherjee (1951) reported two categories of cations taking part in the process.  In a binary system, the cation that is introduced first becomes more firmly bound than the one introduced next.

### ACCESSIBILITY OF THE LATTICE IONS

Accessibility of the lattice ions is another factor which influences cation exchange in clay minerals.  Marshall (1948, p. 57–68) found that a single cation may be adsorbed by a clay mineral with a wide range of bonding energies, and that this is related to the position of the silica-alumina packet at which the cation is adsorbed, therefore, on basal surface, edges, or corners.  Kolthoff (1936) and Grim (1953b, p. 135–136) agreed with Marshall's findings.  Lacy (1954) stated that structural differences between clays determine the degree of preferential adsorption or ionic dissociation which gives rise to the exchange capacities.

### IONIZATION OF ADSORBED CATIONS

In ionization studies, Marshall (1948, p. 57; 1949, p. 115; 1950) found that only a small proportion of adsorbed cations is likely to be ionized, the amount ionized depending upon the particular clay, the concentration of the clay-water system, the nature of the cations, the relative concentration of the cations, and the nature of the adsorbed anions. Chatterjee and Marshall (1950) found that, in general, the replaceability was greater the higher the degree of ionization. Davis (1945) noted that few, if any, colloidal materials exhibiting the cation-exchange property are completely undissociated.

Babcock and others (1951) suggested that activity ratios of adsorbed ions, while not uniquely correlated to other values such as degree of saturation or mole fraction, are involved in exchange reactions and can be estimated from ion-exchange relations.

Schuffelen and Middleburg (1953) stated that the relative displacing power of the various exchangeable cations in the soil may be explained by the difference between the ion activity in the outside solution and the inside micellar-ion activity of the clay minerals.

### RELATIVE SIZE OF IONS: HYDRATED AND NONHYDRATED

Magnitude of the ionic radii seems to influence cation exchange in clay minerals according to Jenny and Reitemeier (1935), Mooney and others (1952), and Morel (1954). Grim (1953b, p. 146) noted that for ions of equal valence, the smaller ions are held less tightly than the larger ones. Page and Baver (1939) listed an exception to Grim's statement. Potassium, with an ionic diameter of 2.66 A, can fit into the cavity of the oxygen layer that has about the same size. This makes the potassium difficult to replace. According to Gieseking (1939), minerals of the montmorillonite-beidellite-nontronite type adsorb large substituted $NH_4^+$ ions, giving rise to (001) spacings greater than those of the same minerals saturated with smaller cations such as $Ca^{+2}$ or $H^+$.

Differences of opinion exist on hydrated versus nonhydrated cations in cation exchange. Alten and Kurmies (1931) presented data supporting the idea that all common cations are hydrated. Their data, from investigations carried out in alcohol rather than water, gave a lyotropic replacement series reversed to the usual series in water. This difference is attributed to the difference between hydrated and nonhydrated ionic sizes. Data by Wiegner and Jenny (1927) support this view.

According to Baver (1956, p. 24–29), experimental results indicate that ionic exchange apparently acts opposite to the requirements of Coulomb's law. For example, the small $Li^+$ ion is held with much less energy than the large $Cs^+$ ion. Baver explains this on the basis

of hydration of ions. According to this explanation, the highly hydrated $Li^+$ ion is larger than the weakly hydrated $Cs^+$ ion and, therefore, cannot approach the negative inner layer of the clay particle as closely as the latter. The force of attraction is weak and the ion is easily displaced by others that have greater energies of adsorption.

Grim (1953b, p. 147) credited Wiegner with suggesting that for ions of equal valence, the least hydrated ones have the greatest energy of replacement.

A number of investigators doubt the hydrated-ion theory. Bernal and Fowler (1933) presented data which indicate that not all adsorbed cations are hydrated. Data discussed by Baver (1956, p. 88–90) in connection with swelling of clays do not support the theory that all adsorbed cations are hydrated. Gedroiz (1919) found that the power of $Ca^{+2}$ and $Mg^{+2}$ ions to replace $Ba^{+2}$ ions from barium-saturated chernozem soil exceeded that of the less hydrated $Li^+$ and $Na^+$ ions.

Evidence by Hendricks and others (1940) based on careful dehydration studies, indicates that $Na^+$, $H^+$, and $K^+$ and the trivalent cations are not hydrated when adsorbed by the clay minerals. They suggest that $Ca^{+2}$ and $Mg^{+2}$ are hydrated to $6H_2O$ and that $Li^+$ is hydrated to $3H_2O$. This conflicts with the idea that $Li^+$ and $Na^+$ are among the most highly hydrated cations.

### PARTICLE SIZE (SURFACE AREA)

Numerous references to the relation between particle size of exchange minerals and cation exchange capacity are found in the literature. Grim (1953b, p. 138) has summarized the problem to some extent. He suggested that the clay minerals kaolinite and illite, in which cation exchange is due primarily to broken bonds, would be expected to show an increase in exchange capacity with decreasing particle size. For expanding lattice clay minerals, however, particle size should have little effect on exchange capacity.

Kelley and Jenny (1936) showed that decreased particle size resulting from grinding caused remarkable increases in cation-exchange capacities for biotite, mica, and kaolinite. The latter clay, for example, showed an increase in exchange capacity from 8 milliequivalents per 100 grams at 100 mesh to 57.5 milliequivalents per 100 grams after 48 hours of grinding and 100.5 milliequivalents per 100 grams after 7 days grinding. Kingery and others (1955) also showed that exchange capacity of kaolin varies with particle size.

Mortland and Ericson (1956) reported increasing exchange capacities for kaolinite, illite, and Utah bentonite as ball milling was increased from 1 through 16 hours.

Marshall (1935a) showed that the cation-exchange capacity of unground montmorillonite and beidellite increased very little with decreasing particle size. Later Marshall (1937) found that ground beidellite (Putnam clay) differed from the unground clay in several ways. As a result, he suggested that the original lattice was destroyed by fine grinding and that an amorphous material with properties similar to those of permutites was produced.

Whitt and Baver (1937) presented experimental data on the B horizon of Putnam silt loam from Missouri, indicating that silt 5–20 microns in diameter has about one-tenth the surface properties of clay 1–2 microns in diameter. It has less than one-twentieth the adsorptive capacity of colloidal clay of less than 100 millimicrons diameter.

Perkins (1949) suggested that grinding alters the chemical and physical characteristics of muscovite and bentonite and greatly increases the cation-exchange capacity of muscovite. Cation-exchange capacity is decreased by prolonged grinding, however, indicating decomposition of the mineral.

Data by Caldwell and Marshall (1942) showed that the cation exchange capacities of attapulgite, nontronite, and saponite increased slightly with decreasing particle size.

According to Barshad (1954a), variation in particle size of vermiculite does not affect adsorption of $Mg^{+2}$, $Ca^{+2}$, $Ba^{+2}$, or $Na^+$ ions but strongly affects adsorption of $NH_4^+$ or $K^+$. He suggested that the cation-exchange capacity of vermiculite can be determined more properly by measuring the adsorption of the former cations.

In studies of the cation-exchange capacities of crystalline silicates, Mukherjee and Ganguly (1950) showed that for some minerals the effect of particle size can be correlated with cation-exchange capacity, while for others it cannot.

Johnson and Lawrence (1942), in studies on six monodisperse fractions of kaolinite (mean-particle size ranged from 0.28 to 10.0 microns), found a linear relation between surface area and cation-exchange capacity. Later Johnson (1949) concluded that the exchange capacity of both kaolinite and montmorillonite is a function of the surface that produces their unsatisfied bonds.

Two methods for determining surface area in clays might be of interest at this point. The well-known method of Brunauer and others (1938) depends upon the adsorption of simple molecules, such as nitrogen, at temperatures near their boiling point. More recently the method of Dyal and Hendricks (1950), in which the total surface and the external surface are determined by adsorption reactions with polar molecules such as ethylene glycol, and the internal surface is determined by difference, has been used.

### TEMPERATURE

The literature indicates that temperature generally has but a small effect on cation exchange. In the opinion of Grim (1953b, p. 149, any change in replaceability of cations when heated would be greater for expanding lattice minerals (montmorillonites) than for those minerals (kaolinite and halloysite) whose exchange capacity is due largely to broken bonds. In tests with a Crowley silt loam soil, separate portions of which were saturated with the chlorides of potassium, sodium, calcium, magnesium, and hydrogen respectively, Andrews and Maldonado (1940) found that the amounts of replaceable $K^+$, $Ca^{+2}$, and $H^+$ decreased with prolonged thermal treatment, whereas amounts of $Na^+$ and $Mg^{+2}$ increased. Yusupova (1946) found that montmorillonite, subjected to special thermal conditions over a period of 2 years, showed gradual change in adsorptive properties. De Castro and Rodriguez (1954) found that thermal treatment of a Spanish Moroccan bentonite resulted in a decrease in total exchange capacity.

### VALENCE

According to Grim (1953b, p. 146), the higher the valence of a cation, the greater its replacing power, other things being equal. Hydrogen, which behaves more like a divalent or trivalent cation, is cited as an exception. Investigations by Gapon (1933), Gedroiz (1919), Gieseking and Jenny (1936), Ivanov and Gapon (1941), and Mookerjee and Mukherjee (1953, 1954) support Grim's view.

The different mineral elements in the soil are retained through the action of physicochemical forces, among which the valence bonds of three types (covalent, polar, and ionic) are the most important (Gorbunov, 1940).

Schachtschabel (1940) studied the replaceability of $NH_4^+$ from several clay minerals by using varied concentrations of alkali and alkaline earth chloride solutions. He demonstrated that the effects of concentration vary, depending upon the valence of replacing cation, the particular clay, and the particular cation used. With ammonium-montmorillonite, his data showed that, except for $Rb^+$ and $Cs^+$, all univalent cations were more exchangeable than the divalent cations.

Bower and Truog (1940b) found that exchange-capacity results determined by means of polyvalent cations are significantly higher than when determined by means of monovalent cations.

Investigation of the cation-exchange characteristics of vermiculites by Walker and Milne (1950) showed that $K^+$ and $NH_4^+$ replace $Mg^{+2}$ with difficulty, although $Mg^{+2}$ is readily replaced by $Li^+$ and $Na^+$. In his studies of vermiculites, Barshad (1948) obtained results of a similar nature.

Schachtschabel (1942) concluded from studies made on soils that $K^+$ and $NH_4^+$ are for the most part bound to mica, $Ca^{+2}$ to humus, and $Mg^{+2}$ to montmorillonite.

Kelley (1943) noted that $Ca^{+2}$ generally replaces adsorbed $Na^+$.

Studies by Schuffelen and Middleburg (1953) showed that highly leached acid tropical soil types contain more univalent than divalent cations and more $Mg^{+2}$ than $Ca^{+2}$. The authors interpret this to mean that both a valence effect and activity coefficients play a part in the distribution of exchangeable ions in soils.

### ATOMIC WEIGHT AND ATOMIC NUMBER

Gedroiz (1919) suggested that atomic weight has some influence on exchange of cations when he noted that, for elements of the same valence, replacing power of cations increases with atomic weight. Results obtained by Antipov-Karataev and others (1947) on chernozem soil tend to support Gedroiz.

### CONCENTRATION

The literature reveals that, in general, the replacing power of a cation increases with increasing concentration of the cation in solution. Kelley and Cummins (1921) found that the replacement of $Ca^{+2}$ and $Mg^{+2}$ by $Na^+$ in Placentia light sandy loam from Riverside, Calif., and in a clay loam of the Ramona series from La Habra, Calif., increased with increasing $Na^+$ concentrations. Kelley (1948, p. 56) and Ivanov and Gapon (1941) observed that for cation pairs having the same valence and about the same replacing power, dilution has relatively little effect on exchange, whereas with cations of different replacing power and different valence, dilution produces a noticeable effect on exchange. Similar results have been observed by Melsted and Bray (1947). Gedroiz (1922) found that, although with increased concentration of $NH_4^+$ the amounts of $Ca^{+2}$ and $Mg^{+2}$ that were replaced increased, the amount of increase was not directly proportional to the $NH_4^+$ concentration. Neither was the $Ca^{+2}$ to $Mg^{+2}$ ratio in direct proportion. Damsgaard-Sorenson (1942) suggested that the lower the ratio of a cation to the total amounts of cations, the more strongly is the cation bound to the ion exchanger. Birrell and Gradwell (1956) noted that in tests with soils containing allophane palagonite and amorphous oxides, the cation-exchange capacities were dependent upon concentration of the leaching solution.

Gapon (1943) illustrated the dependence of exchange capacity of zeolites, bentonites, and other exchange materials upon the concentration of $H^+$ and metallic cations by the following equation:

$$S = \alpha + \beta \left[ pH - \left( \frac{1}{n} \right) pM \right],$$

Where the symbols are:

$\alpha$ and $\beta$=constants

$S$=exchange capacity.

$n$=cation valence

$pM$=negative logarithm of cation concentration

Cation exchange from alkaline solutions is represented by

$$S = \alpha' + \beta o.pH \quad ,$$

and from a buffered solution it is

$$S = \alpha'' + \left[\frac{n}{n+1}\right]\beta o\left[pH - \left(\frac{1}{n}\right)pM\right]$$

In testing the adsorption of strontium and cesium by a composite Hanford soil, McHenry (1956a, 1956b) found that the uptake of these cations was a function of their concentration in solution.

A practical example of the importance of concentration effect can be had by considering the cation concentrations of irrigation water. The principal cations are calcium, magnesium, sodium, and potassium. The effect of the cationic constituents of irrigation water on the chemical and physical properties of soils was recognized long before cation exchange reactions were widely understood. For example, it was recognized that an alkali hazard existed in water having a high proportion of sodium cations. Conversely, it was recognized that the hazard was low if calcium and magnesium cations predominated.

Cation-exchange equations can be used for expressing the relation between soluble and exchangeable cations in soils of arid regions, despite difficulties arising from the presence of mixtures of several kinds of cation-exchange materials in soils. Some success has been attained in relating the relative and total concentrations of soluble cations in the saturation extract of soils to the exchangeable-cation composition by using an empirical approach. Two ratios, designated as the sodium-adsorption-ratio and the potassium-adsorption-ratio, are used in discussing the equilibrium relation between soluble and exchangeable cations. These are defined as

$$Na^+ \bigg/ \sqrt{\frac{(Ca^{+2} + Mg^{+2})}{2}}$$

and

$$K^+ \bigg/ \sqrt{\frac{(Ca^{+2} + Mg^{+2})}{2}},$$

respectively, where $Na^+$, $K^+$, $Ca^{+2}$, and $Mg^{+2}$ refer to the concentrations of the designated soluble cations expressed in milliequivalents per liter (U.S. Department of Agriculture, 1954, p. 26).

## pH

The relation between pH and cation-exchange capacity has been studied by many investigators. According to Bacon (1936), Mattson (1932), and other investigators, cation-exchange capacity is a function of pH, and at a given pH the exchange capacity is a definite quantity for a given sample. Kelley (1948, p. 93–94) emphasized the fact that exchangeable cations can be replaced by $H^+$ as well as by $NH_4^+$ or metallic cations, and that, for this reason, the pH of the salt solution used in the determination may have significant influence on the amount of $NH_4^+$ or metallic cations that are adsorbed through exchange. He pointed out that at pH above 7, exchange capacity is found to exceed that at neutrality, being quite marked for kaolinite, halloysite, and organic soils but less pronounced for montmorillonite.

Paramonova and others (1940) showed that cation exchange increased approximately tenfold on change of pH from 2 to 13 in studies on chernozem soil, and the curve expressing this relation is nearly a straight line. A linear relation between pH and magnitude of cation exchange was also reported by Antipov-Karataev and others (1939). In tests with a variety of soils, Hosking (1948) found that cation-exchange capacities increased from a minimum value at pH 5 to a maximum value at pH 9 and then decreased at higher pH values. In studies made on semiarid soils, McGeorge (1945) found that soil pH increased as the percentage of sodium in the exchange complex increased, and the relation between the two was significant and linear. Paramonova (1940) reported that in tests with chernozem, podzol, and glauconite treated with acid, the adsorption capacity for aluminum and barium salts decreased most in chernozem and least in podzol. Data and curves showing the relation between pH and cation-exchange capacity also are presented by Hauser (1955c), Marshall and Krinbill (1942), and Mukherjee and others (1942).

In studies on adsorption of strontium and cesium from a solution of Hanford soil, McHenry (1956a, 1956b) found that pH was one of the influencing factors. For cesium, adsorption at pH 8.0 and higher was relatively unchanged, whereas below pH 8.0 uptake by the soil decreased rapidly with increasing acidity. Straub and Krieger (1954) noted that pH has a decided effect on the removal of radioactive materials from waste solutions by adsorption on clay minerals.

### CLOGGING AT CATION-EXCHANGE POSITIONS

A reduction in cation-exchange capacity has been attributed to the clogging of exchange positions by certain substances. Dion (1944) concluded that ferric oxide in both hydrated and nonhydrated form exhibits a clogging action on clay minerals. Hendricks (1944) suggested that large, flat, organic ions adsorbed on the basal surface of montmorillonite may obstruct the exchange positions.

## HYDROLYSIS

The effects of hydrolysis on cation exchange have been discussed by a number of investigators. Kelley and Brown (1926) concluded that when a soil is leached with a dilute solution of $AlCl_3$, the exchange is effected chiefly by $H^+$ ions formed by hydrolysis rather than by $Al^{+3}$ ions. Lutz (1938) found that the amount of ion adsorbed from $FeCl_3$ by bentonite, expressed as $Fe^{+3}$, equalled about 2.5 times the cation-exchange capacity as determined with a neutral salt. Kelley (1948, p. 80) suggested that exchangeable $Na^+$ tends to be released by hydrolysis. According to Andreatta (1948) the hydrolysis of feldspars helps to explain why so many of the new minerals formed (the clay minerals, for example) have lattice structures. Correns and Von Englehardt (1938) demonstrated that all the ionic components of the aluminosilicates are liberated by hydrolysis as individual ions going into solution.

## HEAT OF WETTING

In experiments with a variety of clays prepared from soils, Anderson and Mattson (1926) found that a linear relation existed between the heat of wetting and the cation-exchange capacity over a considerable range. However, no data were available on pure clays at that time.

## ANIONS

Differences of opinion exist as to whether or not the nature of the anions present influences the replaceability of a given cation. Melsted and Bray (1947) suggested that the soluble anion associated with the cations in leaching solution does not affect the ratio of the cations on the exchange surface but may affect the total amount of cations adsorbed. Neznayko reported in a personal communication to Grim (1953b, p. 146) that he found a variation in the replaceability of $Na^+$ from montmorillonite by $Ca^{+2}$ depending upon whether calcium hydroxide or calcium sulfate was used. Marshall (1949, p. 122) concluded that a considerable variation in cation-exchange capacity occurs when leaching with different neutral salts of a given ion. Jenny and Engabaly (1943) and Marshall (1949, p. 122) suggested that the possibility of the formation of basic salts with the clay and a soluble anion, clay-$Zn(OH)^+$ for example, complicates the question of anion influence on base exchange. Gedroiz (1918b), in summarizing work of Kullenberg on anion influence on cation adsorption concluded that anions have little if any influence on cation adsorption.

Freundlich (1926, p. 216–217), in observing adsorption phenomena in moss and peat, stated that the quantity of adsorbed cations depended on the anion and increased in the series $Cl^-$, $Br^-$, $NO_3^- < SO_4^{-2} < C_2H_3O_2^-$.

## COMPLEMENTARY CATIONS

Studies by Wiklander (1946) showed that the ease of exchange of a given cation is dependent not only on the nature of that cation but also upon the nature of the complementary cations filling the remainder of the exchange positions and the degree of saturation exhibited by the replaced cation. For example $Ca^{+2}$ becomes more difficult to replace as the amount of replaceable $Ca^{+2}$ decreases, whereas $Na^+$ becomes easier to exchange as the concentration of replaceable $Na^+$ decreases. Similar results were obtained by Jenny and Ayers (1939). McHenry (1956a, 1956b) reported that increasing concentrations of complementary cations generally causes a decrease in the adsorption of $Sr^{+2}$ and $Cs^+$.

## SWELLING

In studies of the properties of cation exchange and swelling in a number of clays, Malquari (1942) found that swelling roughly parallels cation exchange in the kaolinite and halloysite clay minerals. No such relation was found for sericite and montmorillonite, however. In similar studies with sodium-saturated montmorillonites from 12 different localities, Foster (1953) could find bo correlation between cation-exchange capacity and swelling.

## ZETA POTENTIAL

Daniels and Alberty (1955, p. 516) described zeta potential as follows:

A charged ion or surface tends to surround itself with an atmosphere of oppositely charged ions. This tendency is partially overcome by the thermal motions of the ions, and so a diffuse-ion atmosphere is formed. The total potential difference between the solid phase and the liquid phase is the thermodynamic potential discussed earlier (p. 411). But when a relative movement of solid and solution phase is produced by the application of an electric field, the surface of the particle carries along with it part of the charge of the atmosphere which is next to the surface. The potential difference between the particle with its adsorbed surface layer and the solution is less than the thermodynamic potential difference and is referred to as the zeta potential. The zeta potential may be modified by changing the nature and concentration of the electrolyte solution. Since the zeta potential is decreased by increasing electrolyte concentration, the electrokinetic effects become smaller at high salt concentrations.

Jenny and Reitemeier (1935) presented data showing that easily exchanged cations cause high zeta potentials. They found that ionic exchange increases approximately as the sixth power of the potentials. At zero zeta potentials, adsorbed cations are held so tightly that exchange is difficult.

## CATION FIXATION

Students of the soil have long known that some cations can be adsorbed by clay minerals in a relatively nonexchangeable or fixed

state.  Such cations include NH$_4^+$ (Barshad, 1954b; Grim, 1953b, p. 152–153; Stanford and Pierre, 1946), Cs$^+$ (Barshad, 1948; and Martin and others, 1946), Li$^+$ (Greene-Kelly, 1955), Rb$^+$ (Barshad, 1948; and Martin and others, 1946), Ba$^{+2}$ (Marshall, 1949, p. 129–130), Mg$^{+2}$ (Grim, 1953b, p. 153), and K$^+$ (Barshad, 1948, 1954b; Fine and others, 1940; Grim, 1953b, p. 152; Joffe and Levine, 1947; Levine and Joffe, 1947; Marshall, 1949, p. 129–130; Martin and others, 1946; Raney and Hoover, 1946; Stanford and Pierre, 1946; Volk, 1934; and Wiklander, 1950).

Potassium, which is the most commonly fixed cation known, has been studied carefully owing to its importance in fertilization of the soil (Grim, 1953b, p. 152).  Fixation of K$^+$ occurs on the basal planes between unit layers in illite (Grim, 1953b, p. 152), montmorillonite (Raney and Hoover, 1946), and vermiculite (Barshad, 1948).  Levine and Joffe (1947) presented evidence supporting this contention.  From work on pyrophyllite, the basic unit of bentonite and montmorillonite, Levine and Joffe (1947) concluded that K$^+$ must first enter the exchange complex before being fixed and that it must be in contact with pyrophyllite over an extended period of time for fixation to occur.  This is necessary because the closeness of the layers makes it difficult for the K$^+$ ions to penetrate between them.  Results of cation-exchange studies on vermiculite, potassic mica, and montmorillonite led Barshad (1954b) to conclude that the magnitude of interlayer charge rather than origin of the charge determines cation fixation.

Fine and others (1940) observed that in most soils of moderately low fertility and soils that have received moderate amounts of potassium fertilizers, there is a tedency for levels of exchangeable K$^+$ to be raised by alternate freezing and thawing.

Volk (1934) and Page and Baver (1939) found that drying of clays favors fixation of cations.

The property of fixation has been shown to be characteristic of illite (Barshad, 1948; and Fine and others, 1940), montmorillonite (Barshad, 1954b; Levine and Joffe, 1947; and Raney and Hoover, 1946), mica (Barshad, 1954b and Wiklander, 1950), and vermiculite (Barshad, 1948; 1954b).  Members of the kaolinite group have practically no power to fix cations, according to Grim (1953b, p. 153), Joffe and Levine (1947), and Marshall (1949, p. 129–130), although Greene-Kelly (1955) reported that Li$^+$ was fixed in kaolinite.  Most fixation of cations in the soil is accounted for in the fixation of K$^+$ by illite, according to Grim (1953b, p. 152).

## ANION EXCHANGE IN CLAY MINERALS

In comparison with cation-exchange phenomena, very little is known about anion exchange. That anion exchange does take place in many clay minerals has been demonstrated by numerous investigators (Barbier and Chabannes, 1948a and 1948b; Buswell and Dudenbostel, 1941; Dean and Rubins, 1947; Dickman and Bray, 1941; Gedroiz, 1918b; Kingery, 1950; McAuliffe and others, 1947; Mehlich, 1950; Russell and Low, 1954; Sieling, 1947; Tyulin and Malomakhova, 1952; and Wey, 1953).

Marshall (1949, p. 130–131) suggested that in clay minerals it is difficult to decide whether the anion exchange is truly adsorbtion or merely a reaction between a hydroxyl group, for example, and an acidic group existing on the surface of the clay mineral.

### TYPES OF ANION EXCHANGE

Three types of anion exchange are recognized in clay minerals (Grim, 1953b, p. 156–158). Replacement of $OH^-$ as by $PO_4^{-3}$ and $F^-$ in kaolinite, is one type of anion exchange. The extent of the reaction in which $OH^-$ is replaced depends on its accessibility. Another type of anion exchange, suggested in a personal communication from Hendricks to Grim (1953b, p. 157) concerns the geometry of the anion in relation to the clay-mineral structural units. Anions such as $PO_4^{-3}$, and $AsO_4^{-3}$, and others, which are of about the same size and geometry as the silica tetrahedron, are adsorbed by fitting onto the edges of the silica tetrahedral sheets and growing as extensions of these sheets. Anions such as $SO_4^{-2}$, $Cl^-$, $NO_3^-$, and others, whose geometry does not fit that of the silica tetrahedral sheets, cannot be so adsorbed. A third type of anion exchange, suggested by Schofield (1940 and 1949), is one in which the clay minerals may have anion-exchange spots on basal-plane surfaces. These would be due to unbalanced charges within the lattice, as, for example, an excess of $Al^{+3}$ in the octahedral positions. Grim (1953b, p. 157) expressed doubts about this theory. It is to be expected that positive and negative deficiencies would balance each other, unless they recurred at considerable distances from each other.

### EXCHANGE ANIONS AND CLAYS

Phosphate exchange probably has been studied the most in the field of anion exchange. The wide interest in the application of phosphate fertilizers helps to explain this fact.

Dean and Rubins (1947) studied anion-exchange reactions of phosphate in acid soils. Comparative tests made at pH 5.7 showed that more phosphate than arsenate was retained by the soils as exchangeable anions and that the exchangeable phosphate was nearly all removed by fluoride, hydroxide, and citrate solutions. However,

some doubt existed about anion exchange being involved in the citrate solution. Soils treated chemically for the removal of free iron oxides showed a reduced anion-exchange capacity.

The role of kaolin in anion adsorption was investigated by Sieling (1947). In tests with $AsO_4^{-3}$ and $PO_4^{-3}$ he found that kaolin adsorbed both anions in practically equivalent amounts from dilute solutions but that the sorbtion of $AsO_4^{-3}$ far exceeded that of $PO_4^{-3}$ from the more concentrated solutions of the two anions. The amount of either anion adsorbed was dependent upon the pH of the equilibrium solution and the initial concentration of the solution. Within the range of 3.0 to 7.0, the lower the pH, the greater the adsorption; and the higher the concentration at any fixed pH, the more the anion was adsorbed per unit of $Al_2O_3$.

In studying the retention of $SO_4^{-3}$ by soils, Barbier and Chabannes (1944) found that this anion was adsorbed by the soil more strongly than $Cl^-$ anions but less strongly than $PO_4^{-3}$ anions.

### FIXATION OF PHOSPHATE IONS

An important characteristic of the phosphate anion is its ability to be fixed in the soil. Fixation can be due to the formation of aluminum and iron phosphates at low pH and due to the formation of phosphates of the alkaline earths at a high pH according to Coleman (1945), Ellis and Truog (1955), Grim (1953b, p. 158), and Laatsch (1941). Other references on phosphate fixation include a review of the subject by Perkins (1945).

#### EFFECT OF GRINDING

Various investigators (Askinazi and Ginsburg, 1950; Black, 1943; Schoen, 1953; and Stout, 1939) have shown that phosphate fixation occurs on the clay minerals. Schoen (1953) obtained results showing that phosphate fixation was 5 percent for nontronite, 53 percent for kaolinite, and 64 percent for halloysite. He also found that by grinding kaolinite and montmorillonite, fixation increased from 19 to 100 percent and from 5 percent to 68 percent, respectively. Black (1943) and Stout (1939) both found that finely ground clay exhibited a higher degree of fixation.

#### EFFECT OF TEMPERATURE

Schoen (1953) described work in which the effect of temperature on phosphate fixation was tested. Fixation increased for kaolinite, halloysite, bentonite, and illite upon heating to 500°C. In illite it also increased at 1,000°C, but in kaolinite, halloysite, and bentonite it decreased at this temperature.

#### EFFECT OF pH

The relation between pH and cation-exchange capacity has been studied by various investigators. According to Bacon (1936),

Mattson (1932), and other investigators, cation-exchange capacity is a function of pH, and at a given pH the exchange capacity is a definite quantity for a given sample. The exchange capacity does vary with different clay minerals and with the nature and concentration of the adsorbed cation.

Kelley (1948, p. 93–94) emphasized that exchangeable cations can be replaced by $H^+$ as well as $NH_4^+$ or metallic cations, and for this reason the pH of the salt solution used in the determination may have significant influence on the amount of cations that are adsorbed through exchange. He pointed out that at pH values above 7, exchange capacity is found to exceed that at neutrality, being quite marked for kaolinite, halloysite, and organic soils while less pronounced for montmorillonite.

Stout (1939) suggested that the relative abilities of kaolinite and bentonite to fix phosphate are related to the hydroxyl ions available for exchange with phosphate ions.

Black (1943) found that finely ground kaolinite showed a maximum fixation at pH 3 to 4, regardless of concentration of phosphate or time of contact employed. Retention in this range was assumed to be indicative of fixation resulting from the replacement by phosphate of the hydroxyl ions on the surface of the clay.

Coleman (1945) found that montmorillonitic and kaolinitic clays fixed almost as much phosphate in 24 hours as in 1 month, within the pH range from 5 to 7, and considerably more phosphate in 1 month than in 24 hours, at pH values below 5.

Wey (1953) found that adsorption of phosphate by calcium- and sodium-montmorillonites is a function of pH. Maximum adsorption was found at pH 5 with little adsorption below pH 3 or above pH 7.

### ANION AND CATION EXCHANGE IN DIFFERENT CLAYS

The degree of both anion and cation exchange in various types of exchange material was discussed by Mehlich (1950). He suggested that minerals having a 2:1 lattice exhibit cation exchange predominantly, while those of hydrated iron and aluminum oxides show essentially anion exchange. Minerals with a 1:1 lattice show both cation and anion exchange. Supporting data were presented by Schoen (1953).

### FACTORS INTERFERING WITH THE STUDY OF ANION EXCHANGE

According to Grim (1953b, p. 156), the study of anion-exchange reactions are difficult because of the possibility of the decomposition of the clay minerals during the course of the reaction. As a case in point, he cites the studies of phosphate adsorption by kaolinite, in which differences of opinion exist as to whether results may be explained by exchange between $OH^-$ ions in the kaolinite lattice and

$PO_4^{-3}$ ions, or by a reaction between the phosphate and alumina as a result of the destruction of the kaolinite lattice.

Another factor complicating anion-exchange studies (Grim, 1953b, p. 158) is the possible formation of insoluble salts with the anions by any free or exchangeable iron, aluminum, or alkaline earths present in the clay.

## OTHER REFERENCES ON ION EXCHANGE

Kunin and McGarvey (1953; 1954; and 1955) prepared extensive reviews on the subject of ion exchange. Nikol'skiĭ and Paramonova (1939) prepared a review of both Russian and non-Russian references on this subject.

## RADIOACTIVE WASTE DISPOSAL
### THE PROBLEM

Since the testing of the first atomic bomb in July 1945, the Nation has experienced a tremendous growth in the production and use of radioactive materials. With this growth have come problems, among the most important of which is the safe handling and disposal of radioactive waste materials. Hatch (1953) noted that radioactive wastes may be accumulating at an estimated rate of $4 \times 10^{11}$ curies per year by 2000 A. D., and thus it is imperative that some practical method of handling these wastes be devised or discovered. Uncontrolled radioactive wastes could be disastrous if they found their way into natural water-supply sources (Jagg, 1957).

All natural waters contain some radioactivity, derived primarily from the radioactive rocks and minerals with which the water has come in contact, but the concentrations are well within the recognized safety limits (Love, 1951).

According to Wolman and Gorman (1956), control of radioactive wastes was adequate but expensive as of 1956. It is apparent, however, that if the atomic industry is to expand further more economical facilities for the handling of radioactive wastes will be required (Ackerman and Lof, 1959, p. 326; Claus, 1956; Hatch and others, 1956; Hayner, 1952; Nesbitt and others, 1952; Wolman and Gorman, 1956; and Wolman and others, 1956).

### RADIOACTIVE WASTES DEFINED

Radioactive wastes may be defined as waste materials containing radioactive substances. Radioactive substances continuously undergo a process of atomic disintegration, with a liberation of energy in one or more of the forms of radiation known as alpha rays, beta rays, and gamma rays. Thus, an element is radioactive when nuclei of individual atoms are unstable and produce some form of these radiations. Since the chemical properties of a given element do not

depend upon nuclear stability, both ordinary and radioactive forms of an element will give the same chemical reactions.

### RADIOACTIVE ELEMENTS

Radioactive elements are generally referred to as naturally radioactive or artificially radioactive, depending upon whether they occur on earth in a natural radioactive state or whether they are produced by bombardment in manmade apparatus. Fifty-eight radionuclides are found in nature, including isotopes of each of the 14 heaviest elements, thallium to plutonium, and isotopes of several of the lighter elements.

Artificial radionuclides were first produced on January 1, 1934. I. Curie and F. Joliot found that boron, aluminum, and magnesium could be made radioactive by bombardment with alpha rays from polonium. By 1954, about 1,000 artificial radionuclides, representing all the elements, had been produced. There are significant differences among the various nuclides. The half-lives, the energy associated with radiated particles and quanta, and the types of radiation involved in the disintegration of the radioactive materials differ from one nuclide to another.

The first atomic bomb was exploded by means of the fission process. Fission means the breakup of a heavy nucleus into two or more lighter fragments. Neutrons are usually emitted in the process. Fission has been produced in a number of nuclides including $U^{235}$, $U^{238}$, $Th^{238}$, and in lighter elements such as bismuth, lead, gold, tantalum, and some rare earths. Fission reactions have been produced by neutrons, protons, deuterons, helium ions, gamma rays, and X-rays.

Although the products of the fission reaction are useful for the radiations that they give off, they also pose a disposal problem for the same reason.

The accompanying table (table 2), based on data in an article by Siegel (1946), appeared in an article by Hayner (1952). It gives the characteristics of the more significant fission products. These include the yield of each isotope expressed as a percentage of the original uranium that has undergone fission.

### UNITS OF MEASUREMENT OF RADIOACTIVITY

The amount of activity of a radioactive substance is measured in terms of the number of disintegrations per second. One common unit of measurement is the curie. It is defined as the amount of a radioactive material undergoing $3.7 \times 10^{10}$ disintegrations per second. This is approximately equivalent to the activity of 1 gram of radium in equilibrium with its disintegration products. The number of gram atoms of an isotope required to make a curie varies with both

TABLE 2.—*Characteristics of significant fission products*

[From Hayner (1952). Reprinted by permission of the copyright owner from Indus. and Eng. Chemistry, v. 44, p. 474 (with modification). Copyright 1952 by the American Chemical Society. Significance for inclusion in this table based on yield of more than 0.5 per cent, a half-life of longer than 40 days, or energy level of over 0.1 million electron volts. These materials might be obtained in large quantities from the byproduct of reactor operations. Arrow indicates decay to radioactive daughter]

| Isotope | Symbol | Yield (percent) | Half-life | Radiation (million electron volts) | |
|---|---|---|---|---|---|
| | | | | Beta energy | Gamma energy |
| Strontium-89 | Sr | 4.6 | 55 days | 1.50 | None. |
| Strontium-90 | Sr | 5.3 | 25 years | .61 | None. |
| ↳Yttrium-90 | Y | | 62 hours | 2.3 | None. |
| Yttrium-91 | Y | 5.4 | 57 days | 1.53 | None. |
| Zirconium-95 | Zr | 6.4 | 65 days | {.39 (98 percent), 1.0 (2 percent)} | }0.73 |
| ↳Niobium-95 | Nb | | 35 days | .15 | .76 |
| Technetium-99 | Tc | 6.2 | $1 \times 10^6$ years | .3 | None. |
| Ruthenium-103 | Ru | 3.7 | 41 days | {.25 (95 percent), .8 (5 percent)} | .5 |
| Ruthenium-106 | Ru | .5 | 1 year | .03 | None. |
| ↳Rhodium-106 | Rh | | 30 seconds | {3.5 (82 percent), 2.3 (18 percent)} | {.51 (17 percent), .73 (17 percent), 1.2 (1 percent)} |
| Cesium-137 | Cs | 6.2 | 33 years | {0.5 (95 percent), 1.19 (5 percent)} | }None. |
| ↳Barium-137 [1] | Ba | | 2.6 minutes | None | .66 |
| Cerium-144 | Ce | 5.3 | 290 days | .35 | None. |
| ↳Praseodymium-144 | Pr | | 17.5 minutes | 3.0 | {.2, 1.2} |
| Promethium-147 | Pm | 2.6 | 4.4 years | .22 | None. |

[1] Metastable state (excited state that changes to ground state without beta emisson).

the half-life and the atomic weight. Suggested references on this subject include Bitter (1950, p. 138–159), Fair and Geyer (1954, p. 881–883), Glasstone (1950, p. 448), Handbook of Chemistry and Physics (1956–1957, p. 396–449) and standard textbooks on nuclear physics and chemistry.

## SOURCES OF RADIOACTIVE WASTES

There are several sources of radioactive-waste products (Aiken, 1954; Ayres, 1951; de Ment, 1951; Gilbert, 1954; Hayner, 1952; Kilcawley and Clark, 1955; Mawson, 1956; Nesbitt and others, 1952; Wolman and others, 1956; and Wolman and Gorman, 1955). They include:

1. Plants producing and processing radioactive materials.
2. Industrial organizations and research laboratories.
3. Fallout and rainout of fission products from nuclear weapons.
4. Nuclear powerplants. Accidental surface spills and failure of underground storage tanks may release large amounts of activity in areas where radioactive materials are handled or stored.

The major source of radioactive-waste products is the plants that process fuels (Glasstone, 1950, p. 515; Wolman and others, 1956).

## CLASSIFICATION OF RADIOACTIVE WASTES

Radioactive wastes are generally classed by the relative amounts of activity that they contain, for example: low-level, intermediate-level, and high-level wastes. The range of values assigned to these classifications varies from one authority to another. Morton and Struxness (1956) identified these three classifications of liquid wastes as follows:

1. Low-level wastes usually consist of large-volume wastes such as accumulate by drainage from laboratory areas and decontamination operations; or water used in basins to shield operators during work with radioactive materials. They contain activity in the range from a trace to about $10^{-3}$ $\mu c/ml$ (microcuries per milliliter).

2. Intermediate-level wastes are generally associated with various chemical processes or relatively large experimental projects. Their activity may be as much as 26 $\mu c/ml$.

3. High-level wastes commonly contain large amounts of dissolved chemical and may be highly acid or alkaline. Their activity ranges from 26 to about $1.3 \times 10^5$ $\mu c/ml$, although activity of some power reactor process wastes will probably be at even higher levels.

Hayner (1952) noted that low-level liquid wastes have been defined arbitrarily by process engineers as those whose radioactivity amounts to less than 1 curie per gallon. This definition includes some wastes that Morton and Struxness (1956) would call high-level wastes.

Geyer and others (1956) described high-level wastes as primarily the manufacturing residues from chemical processing of irradiated reactor fuel elements. All other radioactive wastes come under the classification of low-level wastes according to these investigators.

Wolman and Gorman (1956) described a typical reactor fuel-processing waste (high-level) as having an effective life of about 600 years and radioactivity of 1 to $4 \times 26,420$ $\mu c/ml$ (neutralized).

As mentioned under sources of radioactive wastes, disposal of effluent from nuclear reactors and separation plants presents the biggest problem of all. Such waste products may exist in the gaseous, liquid, or solid states (Glasstone, 1950, p. 515; Gorman, 1949; and Rostenbach, 1956).

### GASEOUS WASTES

Glasstone (1950, p. 515) cited two examples of gaseous radioactive wastes: (a) air that has been used for cooling reactors, and (b) gases formed in the treatment of fission products. The cooling air may contain $C^{14}$, $N^{16}$, $O^{19}$, and $A^{41}$. The most dangerous of these is $A^{41}$ (half-life of 110 minutes), as $N^{16}$ and $O^{19}$ have extremely short half-lives (7.4 seconds and 29.4 seconds, respectively) and are formed in negligible amounts. The amount of $C^{14}$ formed is said by the author to be relatively small.

## LIQUID WASTES

Straub (1956) defined three kinds of liquid wastes at Oak Ridge: (a) metal wastes containing dissolved uranium compounds and which are held for recovery of the uranium, (b) radiochemical wastes from the production and development processes in the laboratory, and (c) process wastes which consist primarily of cooling water and nonradioactive byproducts.

Wolman and Gorman (1956) described a typical high-level waste from reactor fuel processing. It includes such nonradioactive inorganic ions as $Al^{+3}$, $H^+$, $Na^+$, $NO_3^-$, $F^-$, and $SO_4^{-2}$.

Manowitz and Hatch (1954) noted that high-level aqueous waste stream from a typical solvent extraction separation process could consist of such components as the following: corrosion products, fission products, inorganic nitrates, nitric acid, oxidant, soluble materials in the initial uranium, traces of solvent, radiation breakdown products from the solvent, and uranyl nitrate.

The long-lived fission products are known to be the most dangerous (Loutit, 1954, p. 40–42). Of these strontium-90 is one of the most feared because it is a bone seeker and has a long half-life. About 5 percent of fissions give rise to an atom of strotium-90. Others considered of most significance are yttrium, zirconium, niobium, technecium, and ruthenium in the light group, and iodine, cesium, barium, cerium, and the rare earths in the heavy group.

## SOLID WASTES

Solid radioactive wastes include clothing, utensils, bed linens, laboratory animals and plants, and laboratory equipment. These are generally disposed of by burial (Rostenbach, 1956).

## CURRENT METHODS OF HANDLING WASTES

Treatment of radioactive wastes differs from treatment of other wastes. Burning, filtering, or evaporation does not destroy radioactivity. Furthermore, these wastes cannot be neutralized like bases and acids. Only time will render them harmless, and the time required for this varies with the half-life of the material (Straub, 1956; and Warde and Richardson, 1955a).

Radioactive wastes have been handled by two general methods up to the present time. They have been either diluted and released, or concentrated and stored (Aiken, 1954; Hayner, 1952; Miller and others, 1954; and Straub, 1956).

Dilution of high-level radioactive wastes is not practical. Concentration and storage has been used for these wastes (Aiken, 1954; and Straub, 1956).

Low-level wastes do not present a particularly difficult problem of disposal at present, although strict control measures are exercised

with them (Hayner, 1952; and Rostenbach, 1956). Low-level liquid wastes can be diluted with water and a stable isotope of the same element and can then be pumped to the public sewer (Kittrell, 1952) or directly into the ground from operating disposal systems (Warde and Richardson, 1955a).

Tracer studies are a means of evaluating the mixing and travel times of radioactive wastes continuously disposed of in water (Bryant and Geyer, 1958).

The Public Health Service (Palange and others, 1956) has studied the effects of radioactive materials on the physical, chemical, and biological characteristics of the Columbia River and its tributaries, into which reactor cooling waters are discharged. The principal radioisotopes were found to be short-lived beta emitters such as $Cu^{64}$, $Mn^{56}$, $Na^{24}$, $As^{76}$, $Si^{31}$, and $P^{32}$. Radioactive $P^{32}$ accounted for 90 percent or more of the radioactivity in river fish, but less than 2 percent of the radioactivity in the water. From studies made over a period of several years it was found that there were no measurable changes in the physical, chemical, or bacteriological characteristics of the Columbia River as a result of discharge of reactor-cooling waters into the river.

Various natural purification processes may operate to remove the radioactive materials discharged into rivers and lakes, according to Thomas (1956). He lists such mechanisms as precipitation and deposition, adsorption on lake and river bottoms, and biological uptake in aquatic plants and animals.

Small quantities of low-level radioactive wastes are being disposed of at sea, according to Renn (1956b). They include such items as broken glassware, experimental animals, reagents, contaminated equipment, cloths, paper, and liquid waste concentrates. The wastes are enclosed in packages varying in size from 5-gallon drums to 12-ton concrete blocks.

Various investigators (Coppinger and Tomlinson, 1956; Granquist and Tomlinson, 1956; and Patrick, 1956) suggested that the removal of $Cs^{137}$ and $Sr^{90}$ from a waste decreases markedly the time that the self-heating characteristic remains as a practical operating problem.

Gaseous wastes are discharged to the atmosphere through tall stacks after chemical treatment, scrubbing, or filtration (Rostenbach, 1956).

Harris and Weinstein (1956) investigated open-field burning of combustible low-level radioactive wastes. They concluded that no biologically significant contamination, either of the soil or of the air, was created by the incineration.

## PROPOSED METHODS OF HANDLING WASTES

An important condition that must be met by any method of disposal is that the radioactive wastes be stored in such a manner that no radioactivety will be released to the environment (Aiken, 1954). This means that storage must be impervious to winds and water erosion for centuries to come, thus eliminating any possibility of concentration of radioactivity by any of the following; plants (Aiken, 1954; Neel and others, 1953; Nishita and others, 1954; Rediske and Hungate, 1956, p. 354–356; and Rice, 1956); algae (Aiken, 1954 and Rice, 1956); fish (Aiken, 1954; Foster and Davis, 1956, p. 364–367; and Newell and Christenson, 1951); and animals (Aiken, 1954).

A number of the conventional methods used in the treatment and purification of water have been investigated for treatment of radioactive liquid wastes.   Radioactive wastes can be removed from water and obtained in concentrated form by coagulation (Lacy, 1953 and Lauderdale, 1951), precipitation (Lowe and others, 1954 and 1956), filtration (Lauderdale, 1951), evaporation (Manowitz and others, 1955 and Straub, 1951), adsorption (Straub, 1951), and ion exchange (Hatch, 1952, 1953; Hatch and Regan, 1955; Hatch and others, 1956, p. 648–658; Lacy, 1952; and Lauderdale and Emmons, 1951).

Other methods (Straub, 1951) of treating industrial water applicable to the removal of radioactive wastes from water include electrodialysis, metallic displacement or scrubbing, differential volatility, electrolytic separation, solvent extraction, biological separation, and crystallization.

### CHEMICAL METHODS

Straub and others (1956) reported that with the exception of most cations of valence 3, 4, or 5, including the rare-earths group, coagulation is not very effective for the removal of radioactive materials from water.   Downing and others (1953) reported similar results.

Straub (1952) evaluated the simultaneous effects of pH and concentration of radioactivity, turbidity, and coagulant on the removal of radioactive contaminants in tap water.   The more complete removals (more than 50–60 percent) were obtained with larger doses of turbidity and coagulant, and somewhat greater removals were obtained at higher levels of activity.   Substantially greater removals were obtained in alkaline medium than in acid medium.

Christenson and others (1951) obtained good removal of plutonium from laboratory wastes by coagulation with iron and lime.   Complexing agents such as citrates and phosphates interfered with coagulation.

Lacy (1953) reported varied results in the removal of fission products from synthetic mixtures of tap water by coagulation with ferric chloride and limestone.   Over 98 percent of mixtures of $Ce^{141}$, $Ce^{144}$, and $Pr^{144}$ and $Zr^{95}$-$Nb^{95}$ were removed, whereas $Co^{60}$ was difficult to

remove by coagulation. With 100 ppm ferric chloride, 63 percent I[131] was removed. Removal of mixed-fission products containing barium, cerium, cesium, ruthenium, and strontium was in the range of 51 to 59 percent.

Other investigators who have studied the coagulation method of radioactive-waste removal from liquids include the following: Goodgal and others, 1954; Hayner, 1952; Kilcawley and Clark, 1955; Lauderdale, 1952; Morris and Carritt, 1948; Newell and Christenson, 1951; and Straub and others, 1951.

Lauderdale (1952) obtained 99.9 percent removal of $Sr^{89}$ using a modified water-softening process. By this process, carbon dioxide gas was bubbled through a slurry of the waste containing about 1,000 ppm calcium carbonate and some calcium hydroxide. The pH was maintained at 9.8–10.5. In the presence of a minimum of 50 ppm of sodium carbonate, 99.9 percent or more of strontium was removed. Similar results were reported by Straub and others (1956) for lime and soda ash softening.

Lowe and others (1956) studied the removal of radioactive wastes from solution by ferrous sulfide and ferrous ferrocyanide precipitates. Best results were obtained with ferrous sulfide used in conjunction with an adsorbent. Lowe and others (1954) and other workers previously reported success in decontamination of liquid wastes by coprecipitation with ferrous sulfide, ferrous hydroxide, and calcium phosphate.

Using a calcium phosphate flocculation to decontaminate water containing a 2-month-old fission-product mixture, Lauderdale (1951) found that almost all the cerium, yttrium, and zinc were removed from solution by phosphate precipitation. Approximately 10 percent of the tungsten, 67 percent of the antimony, and 95 percent of the strontium were also removed by this treatment. Using kaolinite clay in conjunction with the phosphate, followed by sand filtration, efficiencies of removal greater than 99 percent were obtained. Greatest removals of activity were obtained at high pH (11.3 was optimum) and a ratio of sodium phosphate to calcium hydroxide of 2.2 to 1 (a 46-percent excess of phosphate). Phosphate was found superior to alum and ferric hydroxide in most tests. Results similar to those of Lauderdale were reported by Nesbitt and others (1952) and Straub (1951).

### FILTRATION

The application of the filtration process to decontamination of water supplies and waste solutions has been considered by several investigators (Downing and others, 1953; Gemmell, 1952; Kilcawley and Clark, 1955; Morris and Carritt, 1948; Straub, 1951; and Straub and others, 1956). Successful treatment of low-level liquid wastes by

flow through a settling tank and one of six intermittent sand and gravel filters of about 1 acre each was reported by Gemmell (1952). Activity is said to be removed primarily by the layer of foreign material laid down by sewage with the pure sand removing little if any activity. Straub and others (1956) concluded that sand filters are not very effective in removing radioactivity. They believe that only the radioactivity previously incorporated in floc particles is removed. This explanation agrees with Gedroiz' (1922) definition of mechanical adsorption.

## EVAPORATION

Evaporation is another one of the many methods used in the treatment of industrial wastes that may be applied in the treatment of radioactive liquid wastes. As noted by Hayner (1952) and Straub (1951), evaporation is a means of concentrating the waste by reducing the liquid volume, but it does not solve the problem of disposal.

Manowitz and Hatch (1954) reported a method of disposal in which the evaporated residue is fused with sodium nitrate within disposable containers that can be buried or dropped into the ocean.

## ADSORPTION AND ION EXCHANGE

The phenomena of adsorption and ion exchange have been considered for the decontamination of liquid radioactive wastes. Various adsorbents and exchange materials have been studied, including the following: activated sewage sludge (Kaufman, 1952); clay minerals (Brockett and Placak, 1954; Brookhaven Natl. Lab. Rept. 314, 1954; Gorman, 1949; Holland and Kulp, 1954; Lacy, 1954; Lauderdale and Emmons, 1951; McHenry and others, 1956; Oak Ridge Natl. Lab. Rept. 1488, 1953; Perring, 1956; Rothe, 1940; Stewart, 1953; Straub, 1951; Straub and others, 1951, 1956; Tesdahl and others, 1954; and Theis, 1955); metal-dust slurries (Lacy, 1952); pumice (Christenson and others, 1951 and Newell and Christenson, 1951); celite (Newell and Christenson, 1951); tufa (Christenson and others, 1951); carbon (Lauderdale and Emmons, 1951 and Newell and Christenson, 1951); silt (Carritt and Goodgal, 1953); ferric oxide (Kurbatove and others, 1945); steel wool (Lauderdale and Emmons, 1951); and synthetic resins (Ayres, 1951; Downing and others, 1953; Hayner, 1952; Higgins and Wymer, 1955; Honda and others, 1955; Kilcawley and Clark, 1955; Morris and Carritt, 1948; Nachod and Schubert, 1956, p. 517; Newell and Christenson, 1951; Straub, 1951, 1952; and Straub and others, 1956).

Lacy (1952a) investigated metal slurries and clay slurries as removal agents for radioactivity. In the pH range 7.0–8.3, iron was the best removal agent of the metals tested, followed by zinc, copper, and aluminum. After additional study Lacy (1952b) concluded that water contaminated with radioactive materials from atom bomb

tests can be brought to a safe tolerence level for emergency drinking purposes by a slurrying with powdered metal, followed by conventional coagulation and filtration if the initial beta-gamma activity is not greater than $10^{-2}$ microcuries per milliliter.

Results on tests made with eight different samples of various clays and one sample of Conasauga shale were reported by Brockett and Placak (1954). Clay samples included metabentonites, montmorillonites, halloysite, nontronite, kaolinite, and vermiculite. The results indicate that, except for $Sr^{89}$, the shale (predominantly illite) was as effective as the clays.

Lacy (1954) found that Oak Ridge clay, composed principally of of montmorillonite and kaolinite, when slurried with contaminated water, was quite effective for removing the radioactive materials $Ce^{141}$, $Ce^{144}-Pr^{144}$, $Zr^{95}-Nb^{95}$, $Ba^{140}-La^{140}$, $Sr^{90}-Y^{90}$, and some mixtures of fission products. It was less effective for other mixtures of fission products and for $Ru^{106}-Rh^{106}$. It was also very poor for $I^{131}$. Contact time required varied from 15 minutes for easy-to-remove materials to 90 minutes for the more difficult ones.

In tests with a representative soil sample from the Hanford project, McHenry and others (1956) found that removal of cesium, strontium, yttrium, and cerium are nearly complete where the initial concentration is less than 0.01 of the soil's saturation capacity; that adsorption of plutonium and cesium is least sensitive to pH, and that strontium, yttrium, and cerium are best adsorbed from alkaline systems.

Various investigators have observed the effect of pH on adsorption of radioactive materials. Lacy (1954) stated that the plot of percentage removal of radioactivity from contaminated water by slurried clays showed a sharp increase between pH 4 and 5, and removal was quite effective at higher pH values. Straub and Krieger (1954) observed that pH has a decided influence on removal of $Co^{60}$, $Zn^{65}$, $Se^{75}$, $Ta^{182}$, $Ir^{190}$, and $Tl^{204}$ from waste solutions by clay suspension. Brown, Parker, and Smith (1956) explained the reduction in adsorption of radioactive cations by soil at low pH as due to the competition of $H^{+}$ for available exchange sites. McHenry (1954 and 1955) contended that the adsorption of strontium and cesium cations from solution by a composite Hanford soil is a function of pH. Adsorption of cesium at pH 8.0 and higher is relatively unchanged, but below pH 8.0 uptake by the soil decreases rapidly with increasing acidity.

The ion-exchange method for adsorbing activity is not without limitations. As pointed out by Amphlett and Warren (1956b), the exchange capacity of the medium and the composition of the waste both limit the amount of activity that can be adsorbed. Also, the

presence of appreciable acid concentrations or of polyvalent species such as iron, aluminum, and other elements, in excess will lead to a very poor uptake of active species such as $Cs^{137}$ and $Sr^{90}$.

### FIXATION OF CLAY AND SOILS

A phenomenon that has commanded a considerable amount of attention is the fixation of adsorbed and exchanged radioactive isotopes on soils (Amphlett and Warren; 1956b and Morton, 1955) and on clay minerals, particularly the montmorillonite group of clay minerals (Amphlett and Warren, 1956b; Brookhaven Natl. Lab. Rept. 117, 1951; Brookhaven Natl. Lab. Rept. 219, 1953; Ginell, 1952; Ginell and Simon, 1953; Ginell and others, 1954; Hatch, 1952, 1953; Hatch and Regan, 1955; Hatch and others, 1956; Jensen, 1951, p. 1,500–1,501; Lieberman, 1955; McVay and others, 1956; Simon, 1956; and Thomas and others, 1956). It has been found that radioactive cations adsorbed by a lower greensand soil and by montmorillonite clay can be rendered virtually fixed (or nonleachable) to distilled water or dilute nitric acid (Amphlett and Warren, 1956b). Fixation is accomplished by heating the radioactive clay to approximately 1,000°C. Hatch (1952) reported that 99.9 percent of the activity was retained after washing a montmorillonite clay containing fixed cations with distilled water or dilute nitric acid.

The clay mineral containing the fixed radioactive cations can then be buried in a location that is otherwise suitable for ultimate disposal. A stratum of clay (Jensen, 1951, p. 1500–1501) or possibly the clay silt bed (Hatch, 1953) in the mouth of a river where desired conditions are building up are possible burial sites for hot clay.

Johnson and others (1956) described laboratory experiments devised to determine the temperatures which well-insulated dry clay masses would reach as a function of their surface : volume ratios for various specific energies. They concluded that liquid wastes containing between $10^2$ and $10^3$ curies per gallon may be disposed of in insulated concrete-lined earth pits and will heat spontaneously to temperatures which will insure fixation in clay-flux mixtures.

Continuous flow adsorption and exchange of radioactive cations by montmorillonite, accomplished through the use of exchange columns, were described by Ginell and others (1954). Since a bed of montmorillonite is impervious to fluids, special treatment of the clay mineral is necessary to make it suitable for column use. The clay was prepared at Brookhaven by mixing it with water in the ratio of 10 grams clay to 7.3 grams water and extruding this mix as rods one-thirty-second inch in diameter. The rods, which break into short lengths that pack loosely in the column, are relatively stable in water.

Another method by which montmorillonite clay may be prepared for use in ion-exchange columns was reported by Beirne and others (1955) of Harwell. This method uses hydrolyzed ethyl silicates and temperatures in the range of 200°C to 400°C. Optimum temperature for ion-exchange properties and physical strength is 350°C. Fixation of the adsorbed ion by firing to temperatures of from 900°C to 1,500°C has shown that above 1,500°C less than 0.1 percent of the adsorbed ion is removed by 1M nitric acid.

Two disadvantages in the use of montmorillonite clay for fixation of radioactive wastes were noted by Durham (1957): (1) montmorillonite clay exhibits only cation exchange, and (2) alloy fuel waste with its high ionic strength cuts down the uptake of fission products.

The advantage of using montmorillonite as an adsorbent and an exchanger for fission products have been outlined by various investigators (Ginell and others, 1954; Hatch, 1953; Hatch and Regan, 1955; Hatch and others, 1954; and Jensen, 1951, p. 1500–1501) and include the following: its good capacity for fission products; its ability to fix cations; its stability; its low cost; its availability; and its imperviousness to water.

The possibility that heat produced by the fission products adsorbed by montmorillonite might be used for the self-fixation of fission products was studied by Amphlett and Warren (1956a).

Experiments with montmorillonite clay made in the period 1949–55 demonstrated its capacity for adsorption and fixation of fission products (except ruthenium) according to Hatch and Regan (1955). Similar results were reported by Manowitz and Hatch (1954). High concentration of hydrogen, sodium, or ammonium cations were found by some investigators (Ginell and others, 1954) to be deterimntal to the takeup of fission products by the clay. An optimum pH value of about 4.5 was reported by Manowitz and Hatch (1954). In the opinion of Hatch and Regan (1955), the only serious problem remaining is concerned with the pretreatment of the bulk wastes to eliminate extraneous ion interference. Nitric acid, aluminum nitrate, and zirconium and aluminum fluorides are cited as examples of interfering materials.

Greensands are said to have an advantage over montmorillonite clay for use in column packing. They require no special treatment or preparation for packing, although their exchange capacity is smaller than that of montmorillonite (Glueckauf, 1956).

The possibility of trapping radioactive wastes in ceramic masses was reported by Robinson (1958). He described two compositions that were effective in containing radioactive materials against water leaching. One consisted of a prefred clay unit containing 60 percent vermiculite, 20 percent kaolin, and 20 percent pyrophyllite. A brick

of this composition, when saturated with a radioactive solution, coated with a thin suspension of lead-oxide and clay, and then fired, produced a leachate of very low beta counts after 7 days of leaching. The second composition was a vermiculite concrete made up to contain materials in the following relative amounts: 10 grams of vermiculite, 10 grams of Attasorb HVM, 20 grams portland cement, and 84 milliliters of radioactive waste solution. This composition, when fired to 1,190°C, produced a leachate having a beta count of 10 counts per minute after 10 days of leaching.

### SUGGESTED DISPOSAL SITES

Among the many suggestions made for disposal of high-level radioactive wastes are such extreme ideas as shooting them into space by rockets and dumping them on polar ice caps, but more practical ideas include disposal in the ocean and disposal in the earth (Joseph, 1956).

#### DISPOSAL IN THE OCEAN

The oceans, because of their large volumes ($1,370 \times 10^6$ cu km) (Joseph, 1954), seem to be a logical place in which to dispose of high-level radioactive wastes. Renn (1956b) discussed ocean disposal of such wastes and lists several likely receiving locations in the ocean. They include:

1. So-called deep holes or basins on the ocean bed.
2. Deeply cut canyon beds just off the continental shelf.
3. Ocean bottom muds (and river delta muds).

Glueckauf (1956) proposed a well-balanced disposal and utilization scheme for fission products that includes disposal at sea.

Seligman and others (1956, p. 701–717) described tests made on disposal of radioactive materials into the Irish Sea.

Renn (1956b, p. 718–721) stated that at the time of the International Conference on the Peaceful Uses of Atomic Energy held at Geneva in June 1955 there was no known practical working program for the continuing disposal of high level radioactive wastes. He noted that although detailed analyses of the conditions for safe and economical waste disposal are being made with the aid of leading American oceanographers and waste-disposal specialists, the studies indicate that a number of misapprehensions exist. Thus, additional basic investigations must be made before sea disposal can be recommended.

Aiken (1954), Joseph (1954), and Loutit (1954, p. 40–42) have agreed that mixing of radioactive wastes in the sea is no easy matter. In spite of tides, ocean currents and hurricanes, the sea remains relatively calm and diffusion takes a very long time, according to them. In addition, Aiken (1954) reported that animal, fish, and plant life can reconcentrate the radioactivity through biological processes.

Renn (1956a) stated that ocean disposal of radioactive wastes for specific conditions would appear practical, although further studies of

local mixing patterns in the sea are needed on disposal of free wastes by dilution.

Dropping wastes mixed with concrete into the sea has been considered, according to Rodger (1954).

In spite of the many ideas on sea disposal of radioactive wastes, Lieberman (1955) suggested that the posibilities for disposal of high-level wastes at sea were less practical than possibilities for disposal on land. His reasoning is based on (a) the dearth of quantitative data involving pertinent oceanographic factors; (b) the complex technical problems involved; and (c) the expense of transporting the high-level wastes.

### GROUND DISPOSAL

Disposal of radioactive wastes in the ground offers many possibilities, and this general idea has many supporters. Suggested ground sites include the following:

1. Geologic formations; underground caverns, salt domes, and salt strata, deep permeable formations, and structural troughs (Hess and Thurston, 1958; Joseph, 1956; Kaufman and others, 1956; Lieberman, 1955; Struxness and others, 1956, p. 684–691; Struxness and Blomeke, 1958; Theis, 1955; Warde and Richardson, 1955a; Wolman and Gorman, 1955; and Wolman, 1957).

2. Dry oil wells (Aiken, 1954).

3. Surface pits and trenches (Brown, Parker, and Smith, 1956; Brown and others, 1958; Clark, 1954; Clark and Pohl, 1956; De Laguna and others, 1958; Lieberman, 1955; Mawson, 1956, p. 676–678; Morton and Struxness, 1956; Oak Ridge Natl. Lab. Rept. 1860, 1956; and Struxness and others, 1956, p. 684–691).

4. Abandoned mines (Rodger, 1954).

5. Ground burial before and after confinement in concrete (Aiken, 1954; and Wolman and Gorman, 1955).

6. Clay (Aiken, 1954 and Perring, 1956).

Rodger (1954) suggested desert-area locations as disposal sites for radioactive wastes. The dry climate of the desert would tend to limit the amount of leaching that might occur. The sparse population of the desert areas is another advantage which favors storage of radioactive wastes there.

Ground disposal of liquid radioactive waste products introduces geologic and hydrologic problems (Brown, McConiga, and Rowe, 1956; de Laguna, 1956; McHenry and others, 1956; Morton, 1955; Theis, 1955, 1956a, 1956b; Warde and Richardson, 1955a, 1955b; and Wolman and Gorman, 1955). Ground disposal of such wastes means placing a complex chemical solution into a complex natural environment (Theis, 1956a). The environment could vary from relatively permeable sand formations to relatively impermeable shales.

In a discussion of the geology of the San Juan basin, New Mexico, Repenning (1959) has suggested that the construction of artificial reservoirs in shale has several advantages. One of the most important of these advantages is the practical certainty of confinement of the radioactive wastes. He noted that storage in permeable sandstone would be more suitable from the standpoint of heat control.

The desirable geologic condition would prevent, or at least limit to a slow rate, the release of isotopes thus allowing the radioactivity to decay to a safe level (Warde and Richardson, 1955a; and Wolman and Gorman, 1955). Thus, the suitability of a ground-disposal site cannot be determined until various geologic factors are known (Struxness and others, 1956; and Warde and Richardson, 1955a). Stratigraphy, structure, texture, composition, and cation-exchange capacity are of importance. Such factors as texture and permeability are of particular importance in that they control the rate and direction of liquid flow into the subsurface (Struxness and others, 1956; and Warde and Richardson, 1955a). Nearly all rocks are known to consist of discrete particles cemented together so that there is at least some small degree of permeability for water. Different soils and rocks exhibit varying degrees of permeability. Laboratory tests, for example, have shown that gravel permeability may be 450,000 times that of a clay silt (Warde and Richardson, 1955a).

Normally, ground water rates of flow range from a few feet per day to a few feet per year, depending not only on permeability of the formation, but also on the hydraulic gradient and the temperature (Warde and Richardson, 1955a; Love and White, 1955). Thus, such characteristics of radioactive wastes as their heat-generating capacity, their density, and their chemical properties can affect the underground movement of water (Theis, 1955). It is evident, therefore, that accurate information on the prevailing geologic and hydrologic features of a proposed disposal site is necessary in evaluating the potential hazards to water supply (Warde and Richardson, 1955a).

According to Theis (1956a, p. 679–683) the two isotopes $Cs^{137}$ and $Sr^{90}$, with half-lives at 33 and 25 years respectively and extremely low tolerance levels, increase the hazard of ground disposal tremendously.

Roedder (1957) commented on the possible injection of raw acid aluminum nitrate wastes into ordinary aquifers consisting of approximately 67 percent quartz-group minerals (including chert, flint, jasper, and others); 11.5 percent feldspar; 6.6 percent mica and clay minerals; 11 percent carbonates; and the remaining few percent of miscellaneous minerals. He concluded that such injection would result in the precipitation of aluminum hydroxide gels, effectively blocking further injection. Chemical pretreatment of the waste to prevent the gel formation was suggested.

In investigating the feasibility of the disposal of high-level radioactive wastes by injection into isolated geological formations, Kaufman and others (1956) made studies on columns of clays and oil sand. The results indicate that exchange reactions may retard the advance of radiostrontium concentration fronts to as much as one-fortieth of that of the liquid front. Orcutt and others (1956a and 1956b) reported similar results. They have shown also that ion exchange greatly increases the storage capacity of geological formations.

Mawson (1956, p. 676–678) reported results of tests made at the Canadian ground disposal site where radioactive cooling water was pumped into trenches after the pile accident at Chalk River, December 1952. A volume consisting of approximately 5 x $10^6$ liters of radioactive material in solution and in suspension and containing $10^4$ curies of long-lived fission products was pumped into the sandy soil of the trenches (5 m wide x 3½ m deep x 300 m long). On May 6, 1955, one test hole was drilled 12 m from the edge of the trench and one in the middle of the trench. The first one showed no sign of radioactivity, but the one in the middle of the trench showed radioactivity starting at the bottom of the trench and extending to a depth of 3½ m. Although the core from this hole was not analyzed, a similar core taken about a year earlier showed that most of the radioactivity had been held near the surface in spite of the large volume of water that had washed through the soil.

Struxness and others (1956 studied the disposal of intermediate-level liquid wastes in terrestrial pits. They concluded that such pits offer certain advantages over evaporation and storage in tanks but that some factors need further evaluation before this experience can be applied to high-level liquid wastes. Factors which in their opinion require further evaluation include the following: (a) reaction between soil and waste products; (b) the influence of stable salts and various solvents and complexing agents upon the retainability of radionuclides by the soil; (c) the comparison between the underground flow patterns of waste solutions and ground water; and (d) the passing of critical nuclides through various soil formations.

Orcutt and others (Orcutt, Kaufman, and Klein, 1956; Orcutt, Naor, Klein, and Kaufman, 1956; and Orcutt, Rifai, Klein, and Kaufman, 1957) studied the underground movement of radioactive wastes. From laboratory studies with radiostrontium and several natural exchangers they arrived at the following conclusions: (a) hydraulic dispersion in porous media can be treated mathematically as a random phenomenon; (b) exchange capacities of several connate sands obtained by use of calcium ion traced with $Ca^{45}$ were in good agreement with those obtained by the ammonium acetate method; (c) the relative preference for strontium and calcium was nearly

constant for the various media studied and, with one exception, favored strontium; and (d) the dispersion of a cation front resulting from ion exchange may exceed that attributable to hydraulic effects alone.

Ewing (1958) studied the feasibility of underground disposal of radioactive wastes using $Sr^{89}$ and $Cs^{134}$. A synthesized radioactive waste was introduced into the ground through an injection well and its movement was traced by means of radio assay of samples from monitoring wells at various distances from the injection well. From his studies, Ewing concluded that the movement of $Sr^{90}$ can be predicted with reasonable accuracy. Insufficient data concerning $Cs^{134}$ made a definite conclusion on it impossible.

Thurston (1956) listed five geologic environments, in the order of preference of the Princeton Conference on Disposal of Highlevel Radioactive Waste Products in Geologic Structures, considered for disposal of high-level radioactive wastes. They are as follows: (a) salt domes, salt beds, abandoned salt mines, and cavities excavated in salt; (b) excavations in shale; (c) low-permeable clay beds; (d) deep, abandoned, dry wells; and (e) properly covered shale and clay pits on the surface.

## ECONOMIC EVALUATION OF METHODS FOR PERMANENT DISPOSAL

An economic evaluation of nine proposed methods for the permanent disposal of radioactive waste materials was made by Herrington and others (1953). The preparation of concrete from waste-process streams for subsequent disposal at sea was judged the cheapest and most efficient means of radioactive waste disposal. Two other methods of disposal of the concrete were also considered: (a) burial in a location such as Death Valley, where the annual rainfall is very small and ground water is not near the surface: (b) preleaching of the concrete, the preleach liquor to be returned to the process, and the resultant stable monolith to be buried in a convenient location.

Fusion of powdered dry wastes in sulfur, preparation of ceramics, coprecipitation, and electrolytic deposition of waste materials was rejected as being impractical for industrial use. Dry-well disposal would be practical if the wells to be used were within 100 miles of the waste source. Preparation of a radioactive glass appeared to be too expensive, according to the evaluation.

## REVIEWS ON RADIOACTIVE WASTE DISPOSAL

A number of reviews are available on the subject of radioactive waste disposal. Some of them are included in the list that follows: Curtis (1953); Hedman (1956); Heukelekian (1956); Joseph and Morgan (1954); Kenny (1956); Shannon (1950); Straub (1953, p. 450–470); Theis (1956b); Warde and Richardson (1955b); Research Committee, Federation of Sewage and Industrial Wastes Association, (1959); and Voress and others (1958).

## BIBLIOGRAPHY

Ackerman, E. A., and Lof, G. O. G., 1959, Technology in American water development: Baltimore, Md., Johns Hopkins Press, 710 p.

Adair, G. S., 1947, Membrane equilibrium, *in* Rideal, E. K., ed., Colloid science—a symposium: Brooklyn Chemical Publishing Company, 208 p.

Aderikhin, P. G., 1940, Dynamics of cation adsorption; the adsorption capacity of different soils: Pochvovodenie (U.S.S.R.), no. 2, p. 67–77. (In German.)

Aiken, A. M., 1954, Disposal and uses of fission products: Canadian Chem. Processing, v. 38, p. 98–100.

Alexander, A. E., 1942, Application of the Gibbs adsorption equation to solutions of colloidal electrolytes: Faraday Soc. Trans., v. 38, p. 248–254.

—————— 1947, Surface chemistry and colloids, *in* Rideal, E. K., ed., Colloid Science—a symposium: Brooklyn, N.Y., Chemical Publishing Co., 208 p.

Alexander, L. T., Faust, G. T., Hendricks, S. B., Insley, H., and McMurdie, H. F., 1943, Relationship of the clay minerals halloysite and endellite: Am. Mineralogist, v. 28, p. 1–18.

Alten, F., and Kurmies, B., 1931, Handbuch der Bodenlehre, v. 8: Berlin, Springer, 714 p.

Amphlett, C. B., and McDonald, L. A., 1956, Equilibrium studies on natural ion-exchange minerals; iodine, cesium, and strontium: Jour. Inorg. Nuclear Chemistry, v. 2, p. 403–414.

Amphlett, C. B., and Warren, D. T., 1956a, The temperature distribution in a heated clay block and its application to the problem of fission product disposal: Harwell, England, Atomic Energy Research Establishment, A.E.R.E. C/R 1861, 6 p.

—————— 1956b, Fixation of activity in solid form by adsorption on soils; pt. 1—firing and leaching tests: Harwell, England, Atomic Energy Research Establishment, A.E.R.E. C/R 1686, 9 p.

Anderson, M. S., and Mattson, S., 1926, Properties of soil colloidal material: U.S. Dept. Agriculture Bull. 1452, 47 p.

Andreatta, Ciro, 1948, The formation of layer lattice types in the chemical change of rock-forming minerals: Periodico di mineralogia [Rome], v. 16, p. 269–297.

Andrews, J. S., and Maldonado, J. F., 1940, Effect of temperature upon the base-exchange capacity of clays: Puerto Rico Univ. Jour. Agriculture, v. 24, p. 133–142

Anson, M. L., 1946, Surface-active agents; introduction: New York Acad. Sci. Annals, v. 46, p. 349–350.

Antipov-Karataev, I. N., and Antipova-Karataeva, T. F., 1940, Determination of exchange constants for the soil cations: Pochvovodenie (U.S.S.R.), no. 2, p. 52–65. (In German.)

Antipov-Karataev, I. N., Kader, G. M., and Filippova, V. N., 1947, Nature of the uptake of ions by clays and soils; pt. 3—Uptake of univalent and bivalent cations of chernozem soil and humic acid: Kolloid zhur. [U.S.S.R.], v. 9, p. 315–324. (Chem. Abs., v. 43, 7618[b], 1949.)

Antipov-Karataev, I. N., Onatskii, S. P., and Chernov, V. A., 1939, The laws governing the interaction of clays and soils with electrolytes: Akad. Nauk SSSR, Pochvennogo Inst. Dokuchaev Trudy, v. 20, p. 5–32. (In English.)

Asch, W., and Asch, D., 1913, The silicates in chemistry and commerce: London, Constable and Company, 456 p. (English translation by A. B. Searle.)

Askinazi, D. L., and Ginzburg, K. E., 1950, The role of clay minerals in the soil on the adsorption of phosphate ions: Akad. Nauk SSSR, Pochvennogo Inst. Dokuchaev Trudy, v. 33, p. 20–48. (Chem. Abs., v. 48, 12353[a], 1954.)

Atkinson, H. J., 1943, Soil colloids: Sci. Agriculture, V. 23, p. 273–286.

Aukland, M. F., 1956, Clay mineralogy techniques—a review: Ohio Dept. Nat. Resources, Div. Geol. Survey, Info. Circ. 20, 31 p.

Ayres, J. A., 1951, Treatment of radioactive waste by ion exchange: Indus. and Eng. Chemistry, v. 43, p. 1526–1531.

Babcock, K. L., Davis, L. E., and Overstreet, Roy, 1951, Ionic activities in ion-exchange systems: Soil Sci., v. 72, p. 253–260.

Bacon, R. C., 1936, A study of the laws governing the cation-exchanging properties of a precipitated aluminum silicate: Jour. Phys. Chemistry, v. 40, p. 747–761.

Bagchi, S. N., 1946, The lattice structure of clay minerals: Indian Jour. Physics, v. 20, p. 53–80.

—— 1949, Base-exchange power of clay minerals: Jour. Indian Chem. Soc., v. 26, p. 57–59.

Barbier, Georges, and Chabannes, Jean, 1944, The retention of the sulfate ion in soils: Acad. sci. [Paris] Comptes rendus, v. 218, p. 519–521.

—— 1948a, Role of exchangeable cations in the adsorption of anions by clays: Acad. sci. [Paris] Comptes rendus, v. 226, p. 749–751.

—— 1948b, Relation between adsorption of anions by clays and their flocculation: Acad. sci. [Paris] Comptes rendus, v. 226, p. 1036–1038.

Barkan, Y. G., 1940, The use of the equation of the exchange adsorption isotherm for the determination of the exchange acidity of the soil: Chem. Zentralbl. v. 2, p. 2363.

Barrer, R. M., 1949, Ion exchange in crystals: Soc. chim. France Bull., p. D71–83.

Barshad, Isaac, 1948, Vermiculite and its relation to biotite as revealed by base exchange reactions, differential thermal curves, and water content: Am. Mineralogist, v. 33, p. 655–678.

—— 1949, The nature of lattice expansion and its relation to hydration in montmorillonite and vermiculite: Am. Mineralogist, v. 34, p. 675–684.

—— 1950, The effect of the interlayer cations on the expansion of the mica-type crystal lattice: Am. Mineralogist, v. 35, p. 225–238.

—— 1954a, Cation exchange in micaceous minerals; pt. 1—Replaceability of the interlayer cations of vermiculite with $NH_4^+$ and $K^+$: Soil Sci., v. 77, p. 463–472.

—— 1954b, Cation exchange in micaceous minerals; pt. 2—Replaceability of $NH_4^+$ and $K^+$ from vermiculite, biotite, and montmorillonite: Soil Sci., v. 78, p. 57–76.

Bauman, W. C., and Eichhorn, J., 1947, Fundamental properties of a synthetic cation exchange resin: Am. Chem. Soc. Jour., v. 69, p. 2830–2836.

Baver, L. D., 1956, Soil physics: 3d ed., New York, John Wiley and Sons, 489 p.

Bear, F. E., 1955, Introduction, in Bear, F. E., ed., Chemistry of the soil: New York, Reinhold Publishing Corp., 373 p.

Beirne, T., Grover, J. R., and Hutcheon, J. M., 1955, Bonded montmorillonites for the ultimate disposal of long-lived fission products: Harwell, England, Atomic Energy Research Establishment, A.E.R.E. CE/R 1658, 24 p.

Berman, Harry, 1937, Constitution and classification of the natural silicates: Am. Mineralogist, v. 22, p. 342–408.

Bernal, J. D., and Fowler, R. H., 1933, A theory of water and ionic solution with particular reference to hydrogen and hydroxyl ions: Jour. Chem. Physics, v. 1, p. 515–548.

Birrell, K. S., and Gradwell, M., 1956, Ion-exchange phenomena in some soils containing amorphous mineral constituents: Jour. Soi. Sci., v. 7, p. 130–147.

Bitter, Francis, 1950, Nuclear physics: Cambridge, Mass., Addison-Wesley Press, 200 p.

Black, C. A., 1943, Phosphate fixation by kaolinite and other clays as affected by pH, phosphate concentration, and time of contact: Soil Sci. Soc. America Proc., v. 7, p. 123–133.

Bolt, G. H., 1955, Ion adsorption by clays: Soil Sci., v. 79, p. 267–276.

Borland, J. W., and Reitemeier, R. F., 1950, Kinetic exchange studies on clays with radioactive calcium: Soil Sci., v. 69, p. 251–260.

Bower, C. A., Gardner, W. R., and Goertzen, J. O., 1957, Dynamics of cation exchange in soil columns: Soil Sci. Soc. America Proc., v. 21, p. 20–24.

Bower, C. A., and Goertzen, J. O., 1955, Negative adsorption of salts and soils: Soil Sci. Soc. America Proc., v. 19, p. 147–151.

Bower, C. A., and Truog, Emil, 1940a, Determination of base-exchange capacity of soils and other materials: Indus. and Eng. Chemistry, Anal. Ed., v. 12, p. 411–413.

—— 1940b, Base-exchange capacity determination as influenced by nature of cation employed and formation of basic exchange salts: Soil Sci. Soc. America Proc., v. 5, p. 86–89.

Bradfield, R., 1932, The concentration of cations in clay soils: Jour. Phys. Chemistry, v. 36, p. 340–347.

Bradley, W. F., 1940, The structural scheme of attapulgite: Am. Mineralogist, v. 25, p. 405–410.

—— 1945, Molecular associations between montmorillonite and some polyfunctional organic liquids: Am. Chem. Soc. Jour., v. 67, p. 975–981.

Bragg, W. L., 1949, Crystalline state—a general survey: London, G. Bell and Sons, v.1, 352 p.

—— 1937a, Atomic structure of minerals: Ithaca, N.Y., Cornell Univ. Press, 292 p. [Copyright, 1937. Quoted on p. 60 with permission.]

—— 1937b, Grain structure of solids: Nature, v. 140, p. 954–956.

Brindley, G. W., 1951, Experimental methods, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals, p. 1–31: London,The Mineralogical Society (Clay Minerals Group), 345 p.

—— 1951b, Kaolin minerals, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), p. 32–75.

—— 1955, Structural mineralogy of clays, in Grim, R. E., ed., Natl. Conf. on Clays and Clay Technology, 1st, Berkeley 1952 , Proc.: California Div. Mines Bull., no. 169, p. 33–43.

Brindley, G. W., and Goodyear, J., 1948, X-ray studies of halloysite and metahalloysite; pt. 2—The transition of halloysite to metahalloysite in relation to relative humidity: Mineralog Mag., v. 28, p. 407–422.

Brindley, G. W., and Robinson, Keith, 1945, Structure of kaolinite: Nature, v. 156, p. 661–662.

—— 1946, Randomness in the structures of kaolinitic clay minerals: Faraday Soc. Trans., v. 42B, p. 198–205.

—— 1951, Chlorite minerals, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), p. 173–198.

British Patent 689,692, 1953, Colloidal dispersions of chrysotile.

Brockett, T. W., Jr., and Placak, O. R., 1954, Removal of radioisotopes from waste solutions by soils—soil studies with Conasauga shale, in Indust. Waste Conf. 8th, 1953, Proc.: Purdue Univ. Eng. Ext. Ser. 83, p. 393–409.

Brooke, J. M., 1953, Recovery of heavy metals, U.S. Patent 2,653,089.

Brookhaven National Laboratory, 1951 Quarterly progress report, April 1–June 30: Upton, New York, Associated Universities, Inc., BNL–117, p. 82–93.

——— 1953, Quarterly progress report, October 1–December 31: Upton, New York, Associated Universities, Inc., BNL–219, 56 p.

——— 1954, Quarterly progress report, July 1–September 30: Upton, New York, Associated Universities, Inc., BNL–314, 62p.

Broughton, Geoffrey, 1953, Colloidal and surface phenomena: Indus. and Eng. Chemistry, v. 45, p. 912–932.

Brown, George, 1950, A Fourier investigation of montmorillonite: Clay Minerals Bull., no. 4, p. 109–111.

Brown, R. E., McConiga, N. W., and Rowe, P. P., 1956, Geological and hydrological aspects of the disposal of liquid radioactive wastes: U.S. Atomic Energy Comm.   TID–7517, p. 413–425.

Brown, R. E., Parker, H. M., and Smith, J. M., 1956, Disposal of liquid wastes (radioactive) to the ground, in Internat. Conf. Peaceful Uses of Atomic Energy, Geneva 1955, Proc: New York, United Nations, Pub. 1956 IX. 1. v.9, p. 669–675.

Brown, R. E., Pearce, D. W., de Laguna, W., Struxness, E. G., Horton, J. H., Jr., and Patterson, C. M., 1958, Experience in the disposal of radioactive wastes to the ground, in Internat. Conf. Peaceful Uses of Atomic Energy, 2d, Geneva 1958, Proc.: New York, United Nations, v. 18, p. 95–100.

Braunauer, S., Emmett, P. H., and Teller, Edward, 1938, Adsorption of gases in multimolecular layers: Am. Chem. Soc. Jour., v. 60, p. 309–319.

Bryant, G. T., and Geyer, J. C., 1958, The travel time of radioactive wastes in natural waters: Am. Geophys. Union Trans., v. 39, p. 440–445.

Buehrer, T. F., 1955, Role of chemical properties of clays in soil science, in Grim, R. E., ed., Natl. Conf. Clays and Clay Technology, 1st, Berkeley 1952, Proc.: California Div. Mines Bull. 169, p. 177–187.

Buswell, A. M., and Dudenbostel, B. F., 1941, Spectroscopic studies of base-exchange materials: Am Chem. Soc. Jour., v. 63, p. 2554–2558.

Byers, H. G., Alexander, L. T., and Holmes, R. S., 1935, The composition and constitution of the colloids of certain of the great soils groups: U.S. Dept. Agriculture Tech. Bull. 484, p. 1–38.

Caillère, S., 1936, Étude de quelques silicates magnésiens à facies asbestiforme ou papyrace n'appartenant pas du groupe de l'antigorite: Soc. franc. minéralogie, Bull. v. 59, p. 353–386.

——— 1951, Sepiolite, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), p. 224–233.

Caillère, S., and Henin, S., 1951, Palygorskite-attapulgite, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), p. 234–243.

Caldwell, O. G., and Marshall, C. E., 1942, Some chemical and physical properties of the clay minerals nontronite, attapulgite, and saponite: Missouri Agr. Expt. Sta. Res. Bull. 354, p. 3–51.

Carritt, D. E., and Goodgal, S. H., 1953, The sorptive and zeolitic properties of natural water borne silts, with relation to their capacities to remove, transport, concentrate, and regenerate radioactive waste components in natural waters: U.S. Atomic Energy Comm.   NYO–4591, 97 p.

Carroll, Dorothy, 1959, Ion exchange in clays and other minerals: Geol. Soc. America Bull., v. 70, p. 749–779.

Cernescu, N. C., 1931, Kationenumtausch und Struktur: Inst. Geol. Romaniei Anuar., v. 16, p. 777–859.   (Chem. Abs., v. 29, 3897³, 1935.)

Chapman, H. D., and Kelley, W. P., 1930, The determination of the replaceable bases and the base-exchange capacity of the soils: Soil Sci., v. 30, p. 391–406.

Charrin, V., 1949, Glauconite: Le Génie civil, v. 126, p. 109–110.

Chatterjee, B., 1949, The role of aluminum in the interaction of clays and clay minerals with neutral salts and bases: Indian Chem. Soc. Jour. (Indus. and News ed.), v. 12, p. 81–99.

Chatterjee, B., and Marshall, C. E., 1950, Studies in the ionization of $Mg^{+2}$, $Ca^{+2}$, $Ba^{+2}$ clays: Jour. Phys. Colloid Chemistry, v. 54, p. 671–681.

Chessick, J. J., and Zettlemoyer, A. C., 1956, Studies of the surface chemistry of silicate minerals; pt. 4—Adsorption and heat of wetting measurements of attapulgite: Jour. Phys. Chemistry, v. 60, p. 1181–1184.

Christenson, C. W., Ettinger, M. B., Robeck, G. G., Harman, E. R., Kohr, K. C., and Newell, J. F., 1951, Removal of plutonium from laboratory wastes: Indus. and Eng. Chemistry, v. 43, p. 1509–1515.

Clark, J. R., 1954, Disposal of aqueous radioactive wastes at the Savannah River Plant, in Sanitary Eng. Conf., Baltimore 1954: U.S. Atomic Energy Comm. WASH–275, p. 192–195.

Clark, J. R., and Pohl, H. A., 1956, Earth disposal of radioactive wastes at Savannah River Project, in Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517 (pt. la), p. 162–269.

Clarke, F. W., 1924, The data of geochemistry: 5th ed., U.S. Geol. Survey Bull. 770, 841 p.

Claus, W. D., 1956, Fundamental considerations in the release of large quantities of radioactive wastes to land and sea, in Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956 IX. 1. v. 9, p. 17–18.

Cloud, P. E., Jr., 1955, Physical limits of glauconite formation: Am. Assoc. Petroleum Geologists Bull. 39, p. 485–492.

Coleman, Russell, 1945, Phosphate fixation by montmorillonite and kaolinitic clays: Soil Sci. Soc. America Proc., v. 9, p. 72–78.

Coppinger, E. A., and Tomlinson, R. E., 1956, Heat problems in the disposal of high-level radioactive wastes: U.S. Atomic Energy Comm. TID–7517 (pt. lb), p. 475–492.

Cornet, I., 1943, Sorption of $NH_3$ on montmorillonite clay: Jour. Chem. Physics, v. 11, p. 217–226.

Correns, C. W., and Mehmel, M., 1936, Über den optischen und röntgenographischen Nachweis von Kaolinit, Halloysit, und Montmorillonit: Zeitschr. Kristallographie, v. 94, p. 337–347.

Correns, C. W., and von Englehardt, Wolf, 1938, Weathering of potassium feldspar: Naturw., v. 26, p. 137–138. (Chem. Abs., v. 32, 8306[5], 1938.)

Curtis, Rosalie L., 1953, Decontamination a literature search: U.S. Atomic Energy Comm. Y-964, 32 p.

Cutler, I. B., and Cook, M. A., 1953a, A theory of cation-exchange reactions with clay minerals: Am. Ceramic Soc. Jour., v. 36, p. 165–170.

———— 1953b, Technical report No. VIII on a theory of cation-exchange reactions with clay minerals: U.S. Atomic Energy Comm. AECU–2382, 28 p.

Damsgaard-Sorenson, P., 1942, Cation exchange in the soil: Chem. Zentralbl., v. 1, p. 1231.

Daniels, Farrington, and Alberty, Robert A., 1955, Physical chemistry: New York, John Wiley and Sons, 671 p. [Copyright 1955. Quoted on p. 81 with permission.]

Davis, L. E., 1942, Significance of the Donnan equilibria for soil colloidal systems: Soil Sci., v. 54, p. 199–219.

———— 1945, Theories of base-exchange equilibriums: Soil Sci., v. 59, p. 379–395.

Davydov, A. T., and Skoblionok, R. F., 1953, Exchange adsorption in mixed media; pt. 1—Quantitative rules of cation exchange in mixed media: Nauchno-issled. khim. inst. Trudy, v. 10, p. 195–203. (Chem. Abs., v. 49, 10003$^f$, 1955.)

———— 1956, Exchange adsorption of cations in relation to the dielectric constant of the medium: Kolloid Zhur. [U.S.S.R.], v. 18, p. 163–166 and p. 157–160. (Chem. Abs., v. 51, 10177$^d$ and 13511$^h$. 1957.)

Dean, L. A., and Rubins, E. J., 1947, Anion exchange in soils; pt. 1 —Exchangeable P and the anion-exchange capacity: Soil Sci., v. 63, p. 377–387.

de Castro, A. H., and Rodriguez, Julio, 1954, Changes in surface properties of homionic bentonites on thermal treatment; pt. 1—Total exchange capcaity and rehydration: Anales edafol. y fisiol. vegetal [Madrid], v. 13, p. 225–226.

de Figueiredo, T. P., and de Carvalho, G. M., 1952, Conductometric process for the determination of the sum of the exchangeable bases in soil: Inst. química agrícola Bol., no. 25, p. 7–14.

Deitz, V, R., 1956, Bibliography of solid adsorbents—1943 to 1953: Natl. Bur. Standards Circ. 566.

de Lapparent, Jacques, 1935, Concerning an essential constituent of Fuller's earth: Acad. sci. [Paris] Comptes rendus, v. 201, p. 481–483.

de Laguna, Wallace, 1956, Some biologic factors that influence disposal of radioactive wastes into pits, in Sanitary Eng. Conf., Cincinnati 1955; U.S. Atomic Energy Comm. TID–7517 (pt, 1b), p. 426–456.

de Laguna, Wallace, Cowser, K. E., and Parker F. L., 1958, Disposal of high-level radioactive liquid wastes in terrestrial pits—a sequel, in Internat. Conf. Peaceful Uses Atomic Energy, 2d, Geneva 1958, Proc.: New York, United Nations, v. 18, p.,101–115.

de Ment, Jack, 1951, Removal of radiocative contaminants, U.S. Patent 2,577,514 (Assigned to U.S.A. as represented by U.S. Atomic Energy Comm.).

Deuel, H., and Hutschneker, K., 1954 Selectivity of ion exchangers, in Potassium symposium, Ann. Mtg. Board Tech. Advisers: Zurich, Internat. Potash Inst., p. 41–70. (English summary,) (Chem. Abs., v. 49, 12758$^g$, 1955.)

Dickman, S. R., and Bray, R. H., 1941, Replacement of adsorbed phosphate from kaolinite by fluoride: Soil Sci., v. 52, p. 263–273.

Dion, H. G., 1944, Iron oxide removal from clays and its influence on base-exchange properties and X-ray diffraction patterns of the clays: Soil Sci., v. 58, p. 411–424.

Dittler, Emil, 1941a, New knowledge on the nature of clays: Keram. Rundsch. u. Kunstkeramik, v. 49, p. 307–309 and 327–329. (Ceramic Abs., v. 26, no. 1, p. 20, 1947.)

———— 1941b, More recent knowledge on the nature of clays: Tonindustrie Zeit., v. 65, p. 515, 528. (Ceramic Abs., v. 24, no. 4, p. 80, 1945.)

Downing, A. L., Wheatland, A. B., and Eden G. E., 1953, The removal of radio-isotopes during the treatment of domestic water supplies; pt. 2—Radio-strontium: Inst. Water Engineers, Jour., v. 7, p. 555–572.

Duclaux, J., 1946, The constitution of colloidal particles and adsorption: Recueil des travaux chimiques des Pays-Bas, v. 65, p. 514–517. (Chem. Abs., v. 41, 2978$^a$, 1947.)

Dunken, H., 1940, A simple derivation of the Langmuir adsorption isotherm: Zeitschr. phys. Chem., Abt. A, v. 187, p. 105–106. (Chem. Abs., v. 35, 3138$^3$, 1941.)

Durham, R. W., 1957, Disposal of fission products in glass: Nuclear Eng. and Sci. Conf., 2d., Philadelphia 1957, Paper 57–NESC–54, 5 p.

Dyal, R. S., and Hendricks, S. B., 1950, The surface of clays in polar liquids as a characteristic index: Soil Sci., v. 69, p. 421–432.

Edelman, C. H., 1947, Relations entre les propriétés et la structure de quelques minéraux agileux: Verre et silicates ind., v. 12, p. 3–6.

Edelman, C. H., and Favejee, J. L., 1940, On the crystal structure of montmorillonite and halloysite: Zeitschr. Kristallographie, v. 102, p. 417–431. (In English).

Eitel, Wilhelm, 1954, Silicate hydrates of the zeolite, permutite group, in Phys. Chemistry of the Silicates, Am. Ed., p. 981–1041: Univ. of Chicago Press, 1592 p.

Eley, D. D., 1947, Thermodynamics and colloid systems, in Rideal, E. K., ed., Colloid Sci.—a symposium: Brooklyn, Chemical Publishing Co.

Ellis, Roscoe, Jr., and Truog, Emil, 1955, Phosphate fixation by montmorillonite: Soil Sci. Soc. America Proc., v. 19, p. 451–454.

Encyclopedia of Chemical Technology, 1949, Kirk, R. E., and Othmer, D. F., eds.: New York, The Interscience Encyclopedia, v. 4, p. 24–38.

———1952, Kirk, R. E., and Othmer, D. F., eds.: New York, The Interscience Encyclopedia, v. 8, p. 1–17.

——— 1953, Kirk, R. E., and Othmer, D. F., eds.: New York, The Interscience Encyclopedia, v. 11, p. 570–585.

Eriksson, Erik, 1952, Cation-exchange equilibria on clay minerals: Soil Sci., v. 74, p. 103–113.

Ewing, B. B., 1958, A field test of the movement of radioactive cations through an underground formation: Nuclear Eng. and Sci. Conf., Chicago 1958, Prepr. 64. (Am. Inst. of Chem. Engineers) 37 p.

Fair, G, M., and Geyer, J. C., 1954, Water supply and waste-water dispoasl: New York, John Wiley and Sons, 951 p.

Faucher, J. A., and Thomas, H. C., 1954, Adsorption studies on clay minerals; pt. 4—The system montmorillonite–Ce–K: Jour. Chem. Physics, v. 22, p. 258–261.

Faust, G. T., 1955, The endellite-halloysite nomenclature: Am. Mineralogist, v. 40, p. 1110–1118.

Federation of Sewage and Industrial Wastes Associations, Research Committee, 1959, A review of the literature of 1958 on sewage, waste treatment, and water pollution; pt. 2 —Industrial wastes radioactive: Sewage and Indus. Wastes, v. 31, p. 640–661.

Fine, L. O., Bailey, T. A., and Truog, Emil, 1940, Availability of fixed K as influenced by freezing and thawing: Soil Sci. Soc. America Proc., v. 5, p. 183–186.

Fischer, E. K., 1950, Surface-active agents: New York, John Wiley and Sons, 387 p.

Flood, E. A., 1955, Thermodynamic considerations of surface regions; Surface tension, adsorption, and adsorption hysteresis: Canadian Jour. Chemistry, v. 33, p. 979–1001.

Forslind, E., 1952, The clay-water system; pt. 2—Water adsorption and cation exchange in montmorillonite: Acta Polytechnica, no. 115, Chem. Metall. Series 3, no. 5, p. 3–12.

Foster, M. D., 1951 The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays: Am. Mineralogist, v. 36, p. 717–730.

——— 1953, Geochemical studies of clay minerals; pt. 2—Relation between ionic substitution and swelling in montmorillonites: Am. Mineralogist, v. 38, p. 994–1006.

———— 1954, The relation of illite, beidellite, and montmorillonite, *in* Swineford, Ada, and Plummer, N. V. eds., Natl. Conf. Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.: Natl. Research Council pub. 327, p. 254–263.

Foster, R. F., and Davis, J. J., 1956, The accumulation of radioactive substances in aquatic forms, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, Proc.: New York, United Nations Pub., 1956 IX. 1. v. 13, p. 364–367.

Freundlich, Herbert, 1926, Colloid and capillary chemistry: London, Methuen and Co., 883 p. (Translated from 3d German ed. by H. S. Hatfield.)

Fricke, R., 1941, The fine structure of solids with structural units of colloidal size and their physical and chemical properties: Kolloid-Zeitschr., v. 96, p. 211–227. (Chem. Abs., v. 36, 6394[7], 1942.)

Frysinger, Galen, and Thomas, H. C., 1955, A method for the determination of the cation exchange capacity of clay minerals and soils, *in* Milligan, W. O., ed., Natl. Conf. Clays and Clay Minerals, 3d, Houston 1954, Proc.: Natl. Research Council Pub. 395, p. 239–245.

Gaines, G. L., Jr., and Thomas, H. C., 1953, Adsorption studies on clay minerals; pt. 2—A formulation of the thermodynamics of exchange adsorption: Jour. Chem. Physics, v. 21, p. 714–718.

Ganguly, A. K., 1949, Reactivity of exchange spots of silicate minerals: Sci. and Culture, v. 14, p. 341–342.

———— 1951, Base-exchange capacity of silica and silicate minerals: Jour. Phys. and Colloid Chemistry, v. 55, p. 1417–1428.

Ganguly, A. K., and Mukherjee, S. K., 1951, The cation-exchange behavior of heteroionic and homoionic clays of silicate minerals: Jour. Phys. and Colloid Chemistry, v. 55, p. 1429–1446.

Gapon, E. N., 1933, Theory of exchange adsorption in soils, pt. 1: Zhur. obshch. khim. [U.S.S.R.], v. 3, p. 144–152.

———— 1943, Dependence of the adsorption capacity upon the concentration of H and metallic ions: Zhur. obsch. khim. [U.S.S.R.], v. 13, p. 382–390. (English summary.)

Gapon, E. N., 1946, Ion exchange between solid and liquid phases, pt. 3: Zhur. fiz. khim. [U.S.S.R.], v. 20, p. 297–302. (Chem. Abs., v. 40, 5616[7], 1946.)

Gedroiz, K. K., 1914, Colloidal chemistry as related to soil science; pt. 2—Rapidity of reaction exchange in soil; the colloidal condition of the soil saturated with various bases and the indicator method of determining the colloidal content of the soil: Zhur. opyt. agron. [U.S.S.R.], v. 15, p. 181–205.) Translated by S. A. Waksman and distributed by U.S. Dept. Agriculture.)

———— 1918a, Contribution to the method of determining the zeolitic bases in the soil: Zhur. opyt. agron. [U.S.S.R.], v. 19, p. 226–244. (Translated by S. A. Waksman and distributed by U.S. Dept. Agriculture.)

———— 1918b, Contributions to our knowledge of the absorptive capacity of soils—Rapidity of absorption of cations by soils: Zhur. opyt. agron. [U.S.S.R.], v. 19, p. 269–322. (Translated by S. A. Waksman and distributed by U.S. Dept. Agriculture.)

———— 1919, Contributions to our knowledge of the absorptive capacity of soils—Rapidity of absorption of cations by soils: Zhur. opyt. agron., v. 20, p. 31–58. (Translated by S. A. Waksman and distributed by U.S. Dept. Agriculture.)

———— 1922, On the absorptive power of soils: Petrograd, [Editorial Committee of the People's Commissariat of Agriculture], 56 p. (Translated by S. A. Waksman and distributed by U.S. Dept. Agriculture.)

Gemmell, Lee, 1952, Efficiency of filter beds for treating radioactive wastes: Nucleonics, v. 10, p. 40–42.

Geyer, J. C., MacMurray, L. C., Talboys, A. P., and Brown, H. W., 1956, Low-level radioactive waste disposal, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, in Pub. 1956.1. v. 9, p. 19–23.

Gieseking, J. E., 1939, Mechanics of cation exchange in the montmorillonite-beidellite–notronite type of clay minerals: Soil Sci., v. 47, p. 1–12.

Gieseking, J. E., and Jenny, Hans, 1936, Behavior of polyvalent cations in base exchange: Soil Sci., v. 42, p. 273–280.

Gilbert, F. W., 1954, Decontamination of the Canadian reactor: Chem. Eng. Prog., v. 50, p. 267–271.

Gilluly, James, Waters, A. C., and Woodford, A. O., 1959, Principles of geology: 2d ed., W. H. Freeman and Co., 534 p.

Ginell, W. S., 1952, Disposal of radioactive cations: U.S. Patent 2,616,847 (Assigned to U.S.A. as represented by U.S. Atomic Energy Comm.).

Ginell, W. S., Martin, J. J., and Hatch, L. P., 1954, Ultimate disposal of radioactive wastes: Nucleonics, v. 12, p. 14–18.

Ginell, W. S., and Simon, G. P., 1953, Preparation of tagged spherical clay particles: Nucleonics, v. 11, p. 49–51.

Glasstone, Samuel, 1940, Textbook of physical chemistry: New York, D. Van Nostrand Co., 1289 p.

———— 1950, Sourcebook on atomic energy: New York, D. Van Nostrand Co., 546 p.

Glasstone, Samuel, Laidler, K. J., and Eyring, Henry, 1941, The theory of rate processes: New York, McGraw-Hill Book Co., 611 p.

Glemser, O., 1941, Binding of water in zeolites: Naturw., v. 29, p. 769.

Glossary of geology, 1957: Natl. Research Council Pub. 501, p. 52.

Glueckauf, E., 1956, Long-term aspect of fission product disposal, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, Proc.: New York, United Nations, Pub. 1956.1. v. 9, p. 3–8.

Goldschmidt, V. M., 1954, Geochemistry (Alex Muir, ed.): Oxford, Clarendon Press, 730 p.

Goodgal, Sol, Gloyna, E. F., and Carritt, D. E., 1954, Reduction of radioactivity in water: Am. Water Works Assoc. Jour., v. 46, p. 66–78.

Gorbunov, N. I., 1940, Importance of the nature of the valence bond for the desorption of cations: Pochvovodenie [U.S.S.R.], v. 3, p. 54–66. (In German.)

Gorbunova, L. I., 1950, Comparative study of glauconites: Akad. Nauk SSSR Doklady, v. 70, p. 867–870. (Chem. Abs., v. 44, 8830[a], 1950.)

Gorman, A. E., 1949, Safe disposal of radioactive wastes: Civil Eng., v. 19, p. 29–32.

Gouy, M., 1910, Sur la constitution de la charge électrique á la surface d'un electrolyte: Jour. physique, v. 9, p. 457–468.

Graham, E. R., 1941, Calcium transfer from mineral to plant through colloidal clay: Soil Sci., v. 51, p. 65–71.

Graham, R. P., and Sullivan, J. D., 1938, Critical study of methods of determining exchangeable bases in clays: Am. Ceramic Soc. Jour., v. 21, p. 176–183.

Grandquist, D. P., and Tomlinson, R. E., 1956, Estimated magnitude of waste disposal problems, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1b), p. 400–405.

Greene-Kelly, R., 1955, Lithium adsorption by kaolin minerals: Jour. Phys. Chemistry, v. 59, p. 1151–1152.

Gregg, S. J., 1951, The surface chemistry of solids: New York, Reinhold Pub. Corp., 297 p.

Gregor, H. P., 1949, A general thermodynamic theory of ion-exchange processes, Technical report on ion-exchange project, Polytechnic Inst. Brooklyn, Contract N 6–onr–263, 40 p.   (Nuclear Sci. Abs., v. 9, no. 1, 1955, abs. 116.)

Grim, R. E., 1942, Modern concepts of clay minerals: Jour. Geology, v. 50, no. 3, p. 225–275.

——— 1953a, Ion exchange in relation to some properties of soil-water systems: Am. Soc. Testing Materials Special Pub. 142, p. 3–8.

——— 1953b, Clay Mineralogy: New York, McGraw-Hill Book Co., 384 p. [Copyright 1953.   Quoted, with permission, on pages 33, 37, 47.]

Grim, R. E., Bradley, W. F., and Brown, G., 1951, Mica clay minerals, *in* Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralogical Society (Clay Minerals Group), p. 138–172.

Grim, R. E., Bray, R. M., and Bradley, W. F., 1937, The mica in argillaceous sediments: Am. Mineralogist, v. 22, p. 813–829.

Gruner, J. W., 1932, The crystal structure of kaolinite: Zeitschr. Kristallographie v. 83, p. 75–88.   (In English.)

——— 1934, Vermiculite and hydrobiotite structures: Am. Mineralogist, v. 19, p. 557–575.

——— 1935, The structural relationship of glauconite and mica: Am. Mineralogist, v. 20, p. 699–714.

——— 1939, $NH_4$-mica synthesized from vermiculite: Am. Mineralogist, v. 24, p. 428–433.

Guggenheim, E. A., 1945, Statistical thermodynamics of mixtures with zero energies of mixing: Royal Soc. London Proc., ser. A., v. 183, p. 203–213.

Haber, Fritz, 1914, Modern chemical industry (Hurter memorial lecture): Soc. Chem. Industry Jour., v. 33, no. 2, p. 49–54.

Hadding, A., 1923, Eine roentgenographische Methode kristalline und kryptokristalline Substanzen zu identifizieren: Zeitschr. Kristallographie, v. 58, p. 108–112.

Haissingsky, Moise, and Gluzbarg, W., 1951, The effect of ionizing radiation on colloidal solutions: Acad. sci. [Paris] Comptes rendus, v. 233, p. 1192–1194.

Hambleton, W. W., and Dodd, C. G., 1953, A qualitative color test for rapid identification of the clay mineral groups: Econ. Geology, v. 48, no. 2, p. 139–146.

Handbook of chemistry and physics, 1956–1957: Cleveland, Chem. Rubber Pub. Co.

Harris, B. L., 1953, Eighth annual chemical engineering unit operations review; Adsorption: Indus. and Eng. Chemistry, v. 45, p. 24–31.

——— 1954, Ninth annual chemical engineering unit operations review; Adsorption: Indus. and Eng. Chemistry, v. 46, no. 1, p. 64–72.

——— 1955, Tenth annual review of unit operations in chemical engineering; Adsorption: Indus. and Eng. Chemistry, v. 47, no. 3, pt. 2, p. 508–516.

Harris, W. B., and Weinstein, M. S., 1956, Open field burning of low-level radioactive contaminated combustible wastes, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1a), p. 229–235.

Harward, M. E., and Coleman, N. T., 1953, Ion exchange equilibria in the presence of small amounts of electrolyte: Soil Sci. Soc. America Proc., v. 17, no. 4, p. 339–342.

Hatch, L. P., 1952, Ultimate disposal of radioactive wastes: U.S. Atomic Energy Comm. WASH–129, p. 119–125.

—— 1953, Ultimate disposal of radioactive wastes: Am. Scientist, v. 41, p. 410–421.

Hatch, L. P., and Regan, W. H., Jr., 1955, Concentrating fission products: Nucleonics, v. 13, no. 12, p. 27–29.

Hatch, L. P., Regan, W. H., Manowitz, B., and Hittman, F., 1956, Processes for high-level radioactive waste disposal; in Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1. v. 9, p. 648–658.

Hauser, E. A., 1939, Colloidal phenomena: New York, McGraw-Hill Book Co., 294 p.

—— 1945, Colloid chemistry of clays: Chem. Rev., v. 37, p. 287–321.

—— 1955a, History of colloid science: Jour. Chem. Education, v. 32, p. 2–9.

—— 1955b, Silicic science: New York, D. Van Nostrand Co., 188 p.

—— 1955c, The colloid science of important clay minerals, in Milligan, W. O., ed., Natl. Conf. Clays and Clay Minerals, 3d, Houston 1954, Proc.: Natl. Research Council Pub. 395, p. 442–472.

Hauser, E. A., and Colombo, Umberto, 1954, Colloid science of montmorillonites and bentonites, in Swineford, Ada, and Plummer, N. V., eds., Natl. Conf. Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.: Natl. Research Council Pub. 327, p. 439–461.

Hauser, E. A., and Le Beau, D. S., 1946, Colloid chemistry of clay minerals and clay films, chap. 7 of Alexander, J., ed., Colloid chemistry, v. 6: New York, Reinhold Pub. Corp.

Hayner, J. H., 1952, Atomic energy industry: Indus. and Eng. Chemistry, v. 44, p. 472–476.

Hedman, F. A., 1956, A survey of radioactive waste disposal: CRLR–648, 15 p.

Helmholtz, H. von, 1879, Studien über elektrische Grenzschichten: Ann. Phys. Chemistry, v. 7, p. 337–382.

Hendricks, S. B., 1938, On the structure of the clay minerals—dickite, halloysite, and hydrated halloysite: Am. Mineralogist, v. 23, p. 295–301.

—— 1941, Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to Van der Waals forces: Jour. Phys. Chemistry, v. 45, p. 65–81.

—— 1942, Lattice structure of clay minerals and some properties of clays: Jour. Geology, v. 50, no. 3, p. 276–290.

—— 1945, Base exchange of crystalline silicates: Indus. and Eng. Chemistry, v. 37, no. 7, p. 625–630.

Hendricks, S. B., and Fry, W. H., 1930, The results of X-ray and microscopical examinations of soil: Soil Sci., v. 29, p. 457–478.

Hendricks, S. B., and Jefferson, M. F., 1938a, Crystal structure of vermiculites and mixed vermiculite chlorites: Am. Mineralogist, v. 23, p. 851–862.

—— 1938b, Structures of kaolin and talc-pyrophyllite hydrates and their bearing on water sorption of the clays: Am. Mineralogist, v. 23, p. 863–875.

—— 1939, Polymorphism of the micas with optical measurements: Am. Mineralogist, v. 24, p. 729–771.

Hendricks, S. B., Nelson, R. A., and Alexander, L. T., 1940, Hydration mechanism of the clay mineral montmorillonite saturated with various cations: Am. Chem. Soc. Jour., v. 62, no. 6, p. 1457–1464.

Hendricks, S. B., and Ross, C. S., 1941, Chemical composition and genesis of glauconite and celadonite: Am. Mineralogist, v. 26, no. 12, p. 683–708.

Herrington, A. C., Shaver, R. G., and Sorenson, C. W., 1953, Economic evaluation of permanent disposal of radioactive wastes: Nucleonics, v. 11, no. 9, p. 34–37.

Hess, H. H., and Thurston, W. R., 1958, Disposal of radioactive waste on land: Am. Geophys. Union Trans., v. 39, p. 467–468.

Hey, M. H., 1932a, Studies on the zeolites; pt. 2—Thomsonite (including faroelite) and gonnardite: Mineralog. Mag., v. 23, p. 51.

———— 1932b, Natrolite and metanatrolite: Mineralog. Mag., v. 23, p. 243.

———— 1933, Mesolite: Mineralog. Mag., v. 23, p. 421.

———— 1934, Edingtonite: Mineralog. Mag., v. 23, p. 483.

———— 1936, Scolecite and metascolecite: Mineralog. Mag., v. 24, p. 227.

Heukelekian, H., 1956, A critical review of the literature of 1955 on sewage, waste treatment, and water pollution; Radioactivity waste treatment and disposal: Sewage and Indus. Wastes, v. 28, p. 595–636.

Hiester, N. K., and Vermeulen, T., 1952, Saturation performance of ion-exchange and adsorption columns: Chem. Eng. Prog., v. 48, p. 505–516.

Higgins, I. R., and Wymer, R. G., 1955, Diban, ion exchange waste disposal scheme, pt. 1: U.S. Atomic Energy Comm. ORNL–1984, 17 p.

Hofmann, Ulrich; Endell, Kurdi; and Wilm, Diedrich, 1933, kristallstuktur und quellung von montmorillonit: Zeitschr. Kristallographie, v. 86, p. 340–348.

———— 1934, Rontgenographische und kolloidschemische Untersuchungen über Ton: Zeitschr. Angew. Chem., v. 47, p. 539–547.

Högfeldt, Erik, 1955, Ion-exchange equilibria; pt. 3—Some empirical equations: Acta Chemica Scandinavica, v. 9, p. 151–165.   (In English.)

Holdridge, D. A., 1953, Colloidal and rheological properties of clay: Ceramics Symposium, British Ceramic Soc., p. 60–93.

Holland, H. D., and Kulp, J. L., 1954, The mechanism of removal of ionium and radium from the oceans: Geochim. et Cosmochim. Acta, v. 5, p. 214–224.

Holt, R. F., 1956, Amperometric titration for cation-exchange capacity of soils: Soil Sci., v. 81, p. 121–124.

Honda, Masatake; Sasaki, Yukimi; and Natsume, Haruo, 1955, Ion-exchange separation of fission products: Japan Analyst, v. 4, p. 240–242.   (Chem. Abs., v. 50, 11157$^e$, 1956.)

Hopu, Alexandrina, 1943, Adsorption phenomena: Rev. Stiint. "V. Adamachi" [Romania], v. 29, p. 194–196.   (Chem. Abs., v. 38, 4175$^2$, 1944.)

Hosking, J. S., 1948, The cation-exchange capacity of soils and soil colloids; pt. 1—Variation with H-ion concentration: Council for Sci. and Indus. Research Jour., v. 21, p. 21–37.

Howat, D. D., 1945, Clays: Mine and Quarry Eng., v. 10, p. 55–61.

Hurlbut, Cornelius S., Jr., 1952, Dana's "Manual of Mineralogy," 16th edition: New York, John Wiley and Sons, 530 p.

Iberg, Rolf, 1954, Clay minerals as cation exchangers, *in* Potassium symposium, Ann. Meeting Board Tech. Advisers: Zurich, Internat. Potash Inst., p. 71–79.   (English summary.)

Iler, K., 1955, The colloid chemistry of silica and silicates: Ithaca, Cornell University Press, 324 p.

Ivanov, A. N., and Gapon, E. N., 1941, Ion exchange between solid and liquid phases; pt. 1—Dependence of cation exchange upon dilution: Zhur. fiz. khim. [U.S.S.R.], v. 15, p. 659–664.   (Chem. Abs., v. 36, 4005$^9$, 1942.)

Jagg, Otto, 1957, Radioactivity and water-supply protection: Gas- u. Wasserfach, v. 98, p. 801–803.   (Chem. Abs., v. 51, 17034$^h$, 1957.)

Jasmund, K., 1950, The siliceous clay minerals: Angew. Chem., no. 62, p. 181–182.   (Chem. Abs., v. 44, 8289$^e$, 1950.)

———— 1951, The silicate clay minerals: Angew. Chem. u. Chem.-Ing. Tech., no. 60, p. 7–142.   (Chem. Abs., v. 45, 6130$^d$, 1951.)

Jenny, Hans, 1932, Studies of the mechanism of ion exchange in colloidal Al silicates: Jour. Phys. Chemistry, v. 36, p. 2217–2258.
——— 1936, Simple kinetic theory of ionic exchange; pt. 1—Ions of equal valency: Jour. Phys. Chemistry, v. 40, no. 4, p. 501–517.
——— 1942, Base exchange in soils and in other disperse systems: Chronica Bot., v. 7, p. 67–68.
Jenny, Hans, and Ayers, A. D., 1939, The influence of the degree of saturation of soil colloids on the nutrient intake by roots: Soil Sci., v. 48, p. 443–459.
Jenny, Hans, and Engabaly, M. M., 1943, Cation and anion interchange with zinc-montmorillonite clays: Jour. Phys. Chemistry, v. 47, p. 399–410.
Jenny, Hans, Overstreet, Roy, and Ayers, A. D., 1939, Contact depletion of barley roots as revealed by radioactive indicators: Soil Sci., v. 48, p. 9–24.
Jenny, Hans, and Reitemeier, R. F., 1935, Ionic exchange in relation to the stability of colloidal systems: Jour. Phys. Chemistry, v. 39, p. 593–604.
Jensen, J. H., 1951, Organization and activities of subcommittee on waste disposal and decontamination: Indus. and Eng. Chemistry, v. 43, no. 7, p. 1500–1501.
Jirgensons, B., and Straumanis, M. E., 1954, A short textbook of colloid chemistry: New York, John Wiley & Sons, Inc., 420 p. [Copyright, 1954. Quoted with permission on p. 5.]
Joffe, J. S., and Levine, A. K., 1947, Fixation of potassium in relation to the exchange capacity of soils: Soil Sci., v. 63, no. 3, p. 241–247.
Johnson, A. L., 1949, Surface area and its effect on exchange capacity of montmorillonite: Am. Ceramic Soc. Jour., v. 32, p. 210–214.
Johnson, J. R., Fulkerson, S. D., McVay, T. N., and Warde, J. M., 1956, Heat experiments for self-fixation of radioactive wastes in clay-flux mixtures, in Sanitary Eng. Conf., Cincinnati, 1955: U.S. Atomic Energy Comm. TID-7517(pt. 1b), p. 339–351.
Johnson, A. L., and Lawrence, W. G., 1942, Fundamental study of clay; pt. 4—Surface area and its effect on exchange capacity of kaolinite: Am. Ceramic Soc. Jour., v. 25, p. 344–346.
Jordan, J. W., 1949, Organophillic bentonites; pt. 1—Swelling in organic liquids: Jour. Phys. and Colloid Chemistry, v. 53, p. 294–306.
Jordan, J. W., Hook, B. J., and Finlayson, C. M., 1950, Organophilic bentonites; pt. 2—Organic liquid gels: Jour. Phys. and Colloid Chemistry, v. 54, p. 1196–1208.
Joseph, A. B., 1954, Technical considerations of sea disposal, in Sanitary Eng. Conf., Baltimore 1954: U.S. Atomic Energy Comm. WASH-275, p. 284–299.
——— 1956, Land disposal of atomic reactor wastes: Am. Water Works Assoc. Jour., v. 48, no. 5, p. 538–544.
Joseph, A. B., and Morgan, J. M., Jr., 1954, Compilation of current information regarding the disposal of radioactive wastes: U.S. Atomic Energy Comm. Contract AT (30-1) 1477, 32 p.
Jurinak, J. J., and Bauer, Norman, 1956, Thermodynamics of zinc adsorption on calcite, dolomite, and magnesite type minerals: Soil Sci. Soc. of America Proc., v. 20, no. 4, p. 466–471.
Kaufman, W. J., 1952, Removal of radioisotopes by sewage treatment processes: U.S. Atomic Energy Comm. WASH-129, p. 34–37.
Kaufman, W. J., Orcutt, R. G., and Klein, Gerhard, 1956, Underground movement of radioactive wastes, Prog. Rept. 1, covering period July 1, 1954 to June 30, 1955: U.S. Atomic Energy Comm. AECU-3115, 87 p.

Keller, W. D., 1955, The principles of chemical weathering: Columbia, Mo., Lucas Brothers Pub., 88 p.

Kelley, W. P., 1943, Mattson's papers on the laws of soil colloidal behavior—review and comments: Soil Sci., v. 56, p. 443–456.

—— 1948, Cation exchange in soils: New York, Reinhold Pub. Corp., 144 p.

Kelley, W. P., and Brown, S. M., 1924, Replaceable bases in soils: California Univ., Agr. Expt. Sta. Tech. Paper 15, p. 1–39.

——1925, Base exchange in relation to alkali soils: Soil Sci., v. 20, p. 477–495.

—— 1926, Ion exchange in relation to soil acidity: Soil Sci., v. 21, p. 289–302.

—— 1934, Principles governing the reclamation of alkali soils: California Univ., Agr. Expt. Sta. Hilgardia, v. 8, p. 149–177.

Kelley, W. P., and Cummins, A. B., 1921, Chemical effects of salts on soils: Soil Sci., v. 11, p. 139–159.

Kelley, W. P., and Jenny, Hans, 1936, The relation of crystal structure to base exchange and its bearing on base exchange in soils: Soil Sci., v. 41, p. 367–382.

Kenny, A. W., 1956, The safe disposal of radioactive wastes: World Health Organization Bull., v. 14, p. 1007–1060.

Kerr, H. W., 1928, The nature of base exchange and soil acidity: Am. Soc. Agronomy Jour., v. 20, p. 309–335.

Kerr, P. F., and Hamilton, P. K., 1949, Glossary of clay mineral names; Preliminary report No. 1 of Am. Petroleum Inst. Research Proj. 49: New York, Columbia Univ. Press, 66 p.; rev. 1951.

Kerr, P. F., Hamilton, P. K., and Pill, R. J., 1950, Analytical data on reference clay minerals, Preliminary report No. 7, Sec. 1, of Am. Petroleum Inst. Research Proj. 49: New York, Columbia Univ. Press, 70 p.

Kiefer, Charles, 1947, Origin of the charge of suspensions of phyllitic minerals and its relation to their surface lattice structure: Acad. Sci. [Paris] Comptes rendus, v. 225, p. 1071–1073.

Kilcawley, E. J., and Clark, H. M., 1955, Radioactivity in water supply sources—Measurement and removal, in Proc. 10th Indus. Waste Conf., 1955: Purdue Univ. Eng. Bull. 89, p. 363–380.

Kinet, Joseph, 1943, Present knowledge of disperse phases, especially the colloidal state: Chimie des peintures, v. 6, p. 82–93, (Chem. Abs., v. 38, 3530$^9$, 1944.)

Kingery, W. D., 1950, Fundamental study of phosphate bonding in refractories; pt. 3—Phosphate adsorption by clay and bond migration: Am. Ceramic Soc. Jour., v. 33, p. 247–250.

Kingery, W. D., Halden, F. A., and Kurkjian, C. R., 1955, Base-exchange capacity of talc: Jour. Phys. Chemistry, v. 59, no. 4, p. 378–380.

Kiselev, A. V., 1945, The work and heat of adsorption: Acta Physicochimica [U.S.S.R.], v. 20, p. 947–968.   (Chem. Abs., v. 40, 3677$^6$, 1946.)

—— 1946, Thermodynamics of adsorption processes: Uspekhi Khimyii, [U.S.S.R.] v. 15, p. 456–484.   (Chem. Abs., v. 41, 1139$^i$, 1947.)

Kitazaki, Umeka, 1951, Glauconite-bearing strata of the Noto Peninsula; pt. 2—Crystal structure of glauconite with special reference to its genesis: Research Inst. Nat. Resources [Japan] Misc. rept. 23, p. 38–47.   (Chem. Abs., v. 47, 451$^i$, 1953.)

Kittrell, F. W., 1952, Radioactive waste disposal to public sewers: Sewage and Indus. Wastes, v. 24, no. 8, p. 985–993.

Kittsley, S. L., 1955, Physical chemistry: New York, Barnes and Noble, 209 p.

Koizumi, Mitsue, 1953, Water in minerals; pt. 1—The differential thermal analysis curves and the dehydration curves of zeolites: Mineralog. Jour. [Japan], v. 1, p. 36–47.

Kolthoff, I. M., 1936, Adsorption on ionic lattices: Jour. Phys. Chemistry, v. 40, no. 8, p. 1027–1040.

Krishnamoorthy, C., Davis, L. E., and Overstreet, Roy, 1948, Ionic exchange equations derived from statistical thermodynamics: Science, v. 108, p. 439.

Krishnamoorthy, C., and Overstreet, Roy, 1950, An experimental evaluation of ion-exchange relationships: Soil Sci., v. 69, p. 41–53.

Krishnamurti, K., 1954, A new adsorption equation: Research Correspondence, Suppl. to Research [London], v. 7, no. 4, p. S25–26. (Chem. Abs., v. 49, 2812$^b$, 1955.)

Kunin, Robert, 1958, Ion exchange resins: 2d ed., New York, John Wiley and Sons, 466 p.

Kunin, Robert, and McGarvey, F. X., 1953, Eighth annual chemical engineering unit operations review; Ion exchange: Indus. and Eng. Chemistry, v. 45, p. 83–88.

————— 1954, Ninth annual chemical engineering unit operations review; Ion exchange: Indus. and Eng. Chemistry, v. 46, p. 118–125.

————— 1955, Tenth annual review of unit operations in chemical engineering; Ion exchange: Indus. and Eng. Chemistry, v. 47, p. 565–575.

Kurbatov, J. D., Kulp, J. L., and Mack, Edward, Jr., 1945, Adsorption of strontium and barium ions and their exchange on hydrous ferric oxide: Am. Chem. Soc. Jour., v. 67, p. 1923–1929.

Kuron, H., and Jung, Alexius, 1940, Methods of determining adsorptive capacity of soils and soil colloids: Bodenkunde und Pflanzenernährung, v. 21–22, p. 568–574. (Chem. Abs., v. 37, 2115$^3$, 1943.)

Laatsch, W., 1941, The fixation of phosphoric acid by clays: Bodenkunde und Pflanzenernährung, v. 23, p. 17–31. (Chem. Abs., v. 36, 1949$^6$, 1942.)

Lacy, W. J., 1952a, Metal-dust slurries and clay slurries as removal agents: U.S. Atomic Energy Comm. Tech. Inf. Serv. Report WASH–129, p. 96–100.

————— 1952b, Removal of radioactive material from water by slurrying with powdered metal: Am. Water Works Assoc. Jour., v. 44, pt. 2, p. 824–828.

————— 1953, Removing radioactive materials from water by coagulation: Water and Sewage Works, v. 100, p. 410–411.

————— 1954, Decontamination of radioactively contaminated water by slurrying with clay: Indus. and Eng. Chemistry, v. 46, p. 1061–1065.

Langmuir, Irving, 1915, Chemical reactions at low pressure: Am. Chem. Soc. Jour., v. 37, p. 1139–1167.

————— 1918, Adsorption of gases on glass, mica, and platinum: Am. Chem. Soc. Jour., v. 40, p. 1361–1403.

Lauderdale, R. A., 1951, Treatment of radioactive water by phosphate precipitation: Indus. and Eng. Chemistry, v. 43, no. 7, p. 1538–1540.

————— 1952, Decontamination of radioactive water: U.S. Atomic Energy Comm. WASH–129, p. 1–4.

Lauderdale, R. A., and Emmons, E. H., 1951, A method for decontaminating small volumes of water: Am. Water Works Assoc. Jour., v. 43, p. 327–331.

Levine, A. K., and Joffe, J. S., 1947, Fixation of K in relation to exchange capacity of soils; pt. 5—Mechanism of fixation: Soil Sci., v. 63, p. 407–416.

Lewis, D. R., 1950, Analytical data on reference clay materials; Prelim. rept. No. 7, sec. 3, of Am. Petroleum Inst. Research Proj. 49: New York, Columbia Univ. Press, 160 p.

————— 1952, Ion-exchange reactions of clays, in Grim, R. E., ed., Natl. Conf. Clays and Clay Minerals, 1st, Proc.: California Dept. Nat. Resources, Div. Mines Bull. 169, p. 54–69.

Lieberman, J. A., 1955, Disposal of radioactive wastes—a growing problem: Civil Eng., v. 25, p. 44–47.

Longchambon, Henri, 1937, Sur certaines caractéristiques de la sépiolite d'Ampandandrava et la formule des sépiolites: Soc. française minéralogie Bull., v. 60, p. 232–276.

Loutit, J. F., 1954, Radiation hazards of atomic energy, in Rotblat, J., ed., Atomic energy—a survey: London, Taylor and Francis, p. 40–42.

Love, S. K., 1951, Natural radioactivity of water: Indus. and Eng. Chemistry, v. 43, p.1541–1544.

Love, S. K., and White, W. F., 1955, Water-quality problems in nuclear development; Prepr. 179 of Nuclear Eng. and Science Cong., Cleveland 1955: Am. Inst. Chem. Engineers, 11 p.

Lowe, C. S., Bentz, L. L., Heiks, J. R., Mead, F. C., Jr., and others, 1954, Decontamination of liquid wastes by iron sulfide, iron hydroxide, and calcium phosphate precipitations: U.S. Atomic Energy Comm. AECD–3632, MLM–662 (rev.), 21 p.

Lowe, C. S., McEwan, M., Mead, F. C., Jr., and Orban, E., 1956, Research on reactor waste disposal: U.S. Atomic Energy Comm. AECD–4066, Inf. Report, 29 p.

Lutz, J. F., 1938, The effect of iron on some physico-chemical properties of bentonite suspensions: Soil Sci. Soc. America Proc., v. 3, p. 7–12.

MacEwan, D. M. C., 1947, The nomenclature of the halloysite minerals: Mineralog. Mag., v. 28, p. 36–44.

———— 1948, Complexes of clays with organic compounds; pt. 1—Complex formation between montmorillonite and halloysite and certain organic liquids: Faraday Soc. Trans., v. 44, p. 349–367.

———— 1949, Interlamellar adsorption; pt. 1—Natural adsorbents: Soc. chim. France Bull., p. D37–40.   (Chem. Abs., v. 43, 5254$^i$, 1949.)

———— 1950, Solvation of clay minerals in relation to crystal structure; Interlamellar adsorption by clay minerals: Internat. Cong. Soil Sci. Trans., v. 1, p. 107–108.

———— 1951, The montmorillonite minerals, in Brindley, G. W., ed., X-ray identification and crystal structures of clay minerals: London, The Mineralog. Soc. (Clay Minerals Group), Taylor and Francis, Ltd., p. 86–137

———— 1952, Interlamellar sorption by clay minerals, in Grim, R. E., ed., Natl. Conf. Clays and Clay Technology, 1st, Berkeley 1952 Proc.,: California Div. Mines Bull. 169, p. 78–85.

MacEwan, D. M. C., and Amoros, J. L., 1950, X-ray investigation of clays: Anales edafol. y fisiol. vegetal, v. 9, p. 363–379.

Maegdefrau, E., and Hofmann, U., 1937, Die Kristallstruktur des Montmorillonits: Zeitschr. Kristallographie, v. 98, p. 299–323.

Magistad, O. C., and Burgess, P. S., 1928, The use of alcoholic salt solutions for the determination of replaceable bases in calcareous soils: Ariz. Agr. Expt. Sta. Tech. Bull. 20, p. 481–497.

Magistad, O. C., Fireman, Milton, and Mabry, Betty, 1944, Comparison of base-exchange equations founded on the law of mass action: Soil Sci., v. 57, p. 371–379.

Malquori, Alberto, 1942, Properties of base exchange and swelling in the evaluation of the surface activity of clays; Ricerca sci. ed progresso techn. v. 13, p. 777–782.   (Chem. Abs., v. 3893$^5$, 1944.)

Malquori, Alberto, and De Angelis, Giorgio, 1948, Ammonium ion exchangers: Chimica appl. Annales, v. 38, p. 469–481.   (Chem. Abs., v. 44, 4166$^h$, 1950.)

Manowitz, Bernard, and Hatch, L. P., 1954, Processes for high-level waste disposal: Nuclear Eng., pt. 2, Chem. Eng. Prog. Symposium Ser., no. 12, v. 50.

Manowitz, Bernard; Richards, Powell; and Horrigan, Robert, 1955, Vapor compression evaporation handles radioactive waste disposal: Chem. Eng., v. 62, p. 194–196.

Marshall, C. E., 1931, Clays as minerals and as colloids: Ceramic Soc. [Great Britain] Trans., v. 30, p. 81–96.

―――― 1935a, Mineralogical methods for the study of silts and clays; Zeitschr. Kristallographie, v. 90, p. 8–34. (In English.)

―――― 1935b, Layer lattices and base-exchange clays: Zeitschr. Kristallographie, v. 91, p. 433–449. (In English.)

―――― 1936, Soil science and mineralogy: Soil Sci. Soc. America Proc., v. 1, p. 23–31.

―――― 1937, The colloidal properties of the clays as related to their crystal structure: Jour. Phys. Chem., v. 41, p. 935.

―――― 1948, Ionization of calcium from soil colloids and its bearing on soil relations: Soil Sci., v. 65, p. 57–68.

―――― 1949, The colloid chemistry of the silicate minerals: New York, Academic Press, 195 p.

―――― 1950, The electrochemistry of the clay minerals in relation to pedology: Internat. Cong. Soil Sci., 4th, Trans., v. 1, p. 71–82.

Marshall, C. E., and Gupta, R. S., 1933, Base-exchange equilibria in clays: Soc. Chem. Industry Jour. [London], v. 52, p. 433–443T.

Marshall, C. E., and Krinbill, C. A., 1942, The clays as colloidal electrolytes: Jour. Phys. Chemistry, v. 46, p. 1077–1090.

Marshall, C. E., and Upchurch, W. J., 1953, Free energy in cation interchange as illustrated by plant root substrate relationships: Jour. Phys. Chemistry, v. 57, p. 618–621.

Martin, J. C., Overstreet, Roy, and Hoagland, D. R., 1946, K fixation in soils in replaceable and non-replaceable forms in relation to chemical reactions in the soil: Soil Sci. Soc. America Proc., 1945, v. 10, p. 94–101.

Martínez, F. B., 1950, Methods for obtaining analysis, testing, and properties of zeolites: Anales edafol. y fisiol. vegetal [Madrid], v. 9. p. 29–81.

Mason, Brian, 1952, Principles of geochemistry; New York, John Wiley and Sons, 276 p.

Mathieson, A. McL., and Walker, G. F., 1954, Crystal structure of Mg-vermiculite: Am. Mineralogist, v. 39, p. 231–255.

Mattson, Sante, 1929, The laws of soil colloidal behavior, pt. 1: Soil Sci., v. 28, p. 179–220.

―――― 1930, The laws of soil colloidal behavior; pt.3—Isoelectric precipitates: Soil Sci., v. 30, p. 459–495.

―――― 1932, The laws of soil colloidal behavior; pt. 9—Amphoteric reactions and isoelectric weathering: Soil Sci., v. 34, p. 209–240.

―――― 1942, Laws of ion exchange: Lantbruks-Högskolans Annaler, v. 10, p. 56–73. (Chem. Abs., v. 38, 4855[2], 1944.)

―――― 1954, Solubility relations of soil colloids: Internat., Symposium Reactivity of Solids, Gothenburg 1952, Proc., pt. 1, p. 369–372. (In English.)

Mattson, Sante, and Larsson, K. G., 1944–1945, Laws of ionic exchange; pt. 2—The valence effect in relation to micellar ion concentration and base saturation of Donnan systems: Lantbruks-Högskolans Annaler [Upsala], v. 12, p. 222–229.

―――― 1946, The laws of soil colloidal behavior; pt. 24—Donnan equilibria in soil formation: Soil Sci., v. 61, p. 313–330.

Mawson, C. A., 1956, Waste disposal into the ground *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations Pub., 1956. IX. 1. v. 9, p. 676–678.

Mazurak, A. P., 1953, Aggregation of colloidal clay from Hesperia sandy loam as affected by univalent and calcium ions: Soil Sci., v. 76, p. 181–191.

McAuliffe, C. D., Hall, M. S., Dean, L. A., and Hendricks, S. B., 1947, Exchange reactions between phosphate and soils: Soil Sci. Soc. America Proc., v. 12, p. 119–123.

McBain, J. W., 1950 Colloid science: Boston, D. C. Heath and Company, 450 p.

McConnell, Duncan, 1950, The crystal chemistry of montmorillonite: Am. Mineralogist, v. 35, p. 166–172.

McGeorge, W. T., 1945, The base exchange-pH relationships in semiarid soils: Soil Sci., v. 59, p. 271–275.

McHenry, J. R., 1955, Adsorption and retention of strontium by soils of the Hanford project: Contract W–31–109–eng–52, HW–34499, 36 p.

——— 1954, (Decl. Jan. 6, 1956) Adsorption and retention of cesium by soils of the Hanford project: Contract W–31–109–eng–52, HW–31011, 41 p.

McHenry, J. R., Rhodes, D. W., and Rowe, P. P., 1956, Chemical and physical reactions of radioactive liquid wastes with soils, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1a), p. 170–190.

McMurchy, R. C., 1934, The crystal structure of chlorite minerals: Zeitschr. Kristallographie, v. 88, p. 420–432.    (In English).

McVay, T. N., Hamner, R. L., and Haydon, M. P., 1956, Fixation of radioactive wastes in clay-flux mixes, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1b), p. 335–338.

Mehlich, Adolf, 1942, Rapid estimation of base-exchange properties of soils: Soil Sci., v. 53, p. 1–14.

——— 1945, Effect of type of soil colloid on cation-adsorption capacity and on exchangeable H and Ca as measured by different methods: Soil Sci., v. 60, p. 289–304.

——— 1950, Cation exchange-anion exchange ratios of kaolinitic soil colloids: Internat. Cong. Soil Sci., 4th, Amsterdam 1950, Trans., v. 1, p. 133–135.

Mehmel, M., 1935, Ueber die Struktur von Halloysit und Metahalloysit: Zeitschr. Kristallographie, v. 90, p. 35–43.

Melsted, S. W., and Bray, R. H., 1947, Base-exchange equilibriums in soils and other exchange materials: Soil Sci., v. 63, p. 209–225.

Migeon, Georges, 1936, Contribution a l'étude de la définition des sépiolites: Soc. Française minéralogie Bull., v. 59, p. 6–134.

Miller, H. S., Fahnoe, F., and Peterson, W. R., 1954, Survey of radioactive-waste disposal practices: Nucleonics, v. 12, no. 1, p. 68.

Milligan, W. O., and Mill, G. S., 1955, Colloids and surface behavior: Indus. and Eng. Chemistry, v. 47, p. 614–625.

Mitra, R. P., and Rajagopalan, K. S., 1952, Origin of the base-exchange capacity of clays and significance of its upper limiting value: Soil Sci., v. 73, p. 349–360.

Mokrushin, S. G., 1945, Application of the Maxwell-Boltzmann distribution law to colloid chemistry: Zhur. obshch. khim. (U.S.S.R.), v. 15, p. 259–268. (English summary.)

Mookerjee, Shankarananda, and Mukherjee, S. K., 1953, Ionic antagonism in exchange reactions of clays; pt. 1—Symmetry values of colloidal clay salts with cationic mixtures: Indian Soc. Soil Sci. Jour., v. 1, p. 95–104.

———— 1954, Ionic antagonism in exchange reactions of clays; pt. 2—Competition between two cations in the replacement of a third cation from clay salts: Indian Soc. Soil Sci. Jour., v. 2, p. 29–36.

Mooney, R. W., Keenan, A. G., and Wood, L. A., 1952, Adsorption of water vapor by montmorillonite; pt. 1—Heat of desorption and application: Am. Chem. Soc. Jour., v. 74, p. 1367–1371.

Morel, Robert, 1954, The distribution of adsorbed cations of varying sizes on clays: Acad. sci. [Paris] Comptes rendus, v. 239, p. 1846–1848.

Morgante, Sergio, 1945, Zeolites of the Dessie and Diredawa countries: Atti ist. veneto sci., v. 104, pt. 2., p. 405–425. (Chem. Abs., v. 44, 6776ᵉ, 1950.)

Morris, J. C., and Carritt, J. B., 1948, Contamination of water supplies by radioactive substances: New England Water Works Assoc. Jour., v. 62, p. 1–9.

Mortland, M. M., and Erickson, A. E., 1956, Surface reactions of clay minerals: Soil Sci. Soc. America Proc., v. 20, p. 476–479.

Mortland, M. M., and Mellor, J. L., 1954, Conductometric titration of soils for cation-exchange capacity: Soil Sci. Soc. America Proc., v. 18, p. 363–364.

Morton, Roy J., 1955, Waste disposal problems, in Sanitary Eng. Conf., Baltimore 1954: U.S. Atomic Energy Comm. WASH–275, p. 320–329.

Morton, R. J., and Struxness, E. G., 1956, Ground disposal of radioactive wastes: Am. Jour. Public Health, v. 46, p. 156–163.

Mukherjee, J. N., 1921, Origin of the charge of a colloidal particle and its neutralization by electrolytes: Faraday Soc. Trans., v. 16, app. 103–115.

Mukherjee, S. K., and Ganguly, A. K., 1944, Studies on base exchange; pt. 2— Comparison of different methods of estimating base-exchange capacities and of lime requirement of hydrogen clays, acid soils, and partly and completely desaturated soils: Indian Jour. Agr. Sci. v., 14, p. 203–209.

———— Base-exchange capacity and crystalline structure of silicate minerals related to soils and clays: Indian Jour. Physics, v. 24, p. 233–256.

Mukherjee, J. N., Mitra, R. P., Chatterjee, B., and Mukherjee, S. K., 1942, Nature of reactions responsible for soil acidity; pt. 8—Acid character of H clay in relation to some problems of soil science: Indian Jour. Agr. Sci., v. 12, p. 86–104.

Muto, Yoshio, 1942, A simple model treatment of the adsorption of surface-active electrolytes: Phys.-Math. Soc. Japan Jour., v. 16, p. 104–107. (Chem. Abs., v. 41, 7200ᵉ, 1947.)

Nachod, F. C., and Schubert, Jack, 1956, Ion exchange technology: New York, Academic Press, 660 p.

Nagelschmidt, G., 1938, Rod-shaped clay particles: Nature, v. 142, p. 114–115.

———— 1944, The mineralogy of soil colloids: Imperial Bur. Soil Sci. Tech. Comm., v. 42, 33 p.

Nakahira, Mitsuoki, 1953, Recent studies on clay minerals: Japanese Chemistry Jour., v. 7, p. 226–231. (Chem. Abs., v. 48, 13569ⁱ, 1954.)

Neel, J. W., Olafson, J. H., Allen, J. S., Gillooly, B. E., Nishita, Hideo, and Larson, K. H., 1953, Soil-plant interrelationships with respect to uptake of fission products: U.S. Atomic Energy Comm. UCLA–247, p. 4–44.

Nesbitt, J. B., Kaufman, W. J., McCauley, R. E., and Eliassen, Rolf, 1952, Removal of radioactive strontium from water by phosphate coagulation: U.S. Atomic Energy Comm. NYO–4435, p. 3–128.

Newell, J. F., and Christenson, C. W., 1951, Radioactive waste disposal: Sewage and Indus. Wastes, v. 23, p. 861–877.

Nikol'skiĭ, B. P., and Paramonova, V. I., 1939, Laws of the exchange of ions between a solid phase and a solution: Uspekhi Khimii [U.S.S.R.], v. 8, p. 1535–1567.   (Chem. Abs., v. 35, 362⁵, 1941.)

Nishita, Hideo, Kowalewsky, B. W., and Larson, K. H., 1954, Fixation and extractability of fission products contaminating various soils and clays; pt. 1—$Sr^{89}$, $Sr^{90}$, $Y^{91}$, $Ru^{106}$, $Cs^{137}$, and $Ce^{144}$: U.S. Atomic Energy Comm. UCLA–282, 32 p.

Norrish, K. and Quirk, J., 1954, Crystalline swelling of montmorillonite: Nature, v. 173, p. 255–257.

Nutting, P. G., 1931, Adsorption and base exchange: Washington Acad. Sci. Jour. v., 21, p. 33–36.

———— 1943a, Adsorbent clays, their distribution, properties, production, and uses: U.S. Geol. Survey Bull. 928–C, p. 127–221.

———— 1943b, The action of some aqueous solutions on clays of the montmorillonite groups: U.S. Geol. Survey Prof. Paper 197–F, p. 219–235.

Oak Ridge Natl. Lab., 1953, Health physics division quarterly progress report for period ending January 20, 1953: U.S. Atomic Energy Comm.   ORNL–1488, 13 p.

———— 1956, Health physics division semiannual progress report for period ending January 31, 1955: U.S. Atomic Energy Comm.   ORNL–1860, 29 p.

Oden, Sven, 1916, General introduction to the chemistry and physical chemistry of clays: Upsala univ. geol. inst. Bull, v. 15, p. 175–194.

Opler, A. and Hiester, N. K., 1954, Tables for predicting the performance of fixed bed ion exchange and similar mass transfer processes: Palo Alto, Calif., Stanford Research Inst.

Orcutt, R. G., Kaufman, W. J., and Klein, G., 1956, The movement of radio-strontium through natural porous media *in* Progress report No. 2 covering period July 1, 1955 to June 30, 1956: U.S. Atomic Energy Comm. AECU–3608, 58 p.

Orcutt, R. G., Naor, I., Klein, G., and Kaufman, W. J., 1956, Hydraulic and ion-exchange phenomena in the underground movement of radio-strontium, *in* Sanitary Eng. Conf., Cincinnati, 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1a), p. 191–211.

Orcutt, R. G., Rifai, M. N. E., Klein, G., and Kaufman, W. J., 1957, Underground movement of radioactive wastes: Sewage and Indus. Wastes, v. 29, p. 791–804.

Ormsby, W. C., and Sand, L. B., 1954, Base-exchange, an analytical tool for mixed layer aggregates, *in* Swineford, Ada, and Plummer, N. V., eds., Natl. Conf. Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.: Natl. Research Council Pub. 327, p. 254–263.

Osthaus, B. B., 1954, Chemical determination of tethrahedral ions in nontronite and montmorillonite, *in* Swineford, Ada, and Plummer, N. V., eds., Natl. Conf. Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.: Natl. Research Council Pub. 327, p. 404–417.

Page, J. B., and Baver, L. D., 1939, Ionic size in relation to fixation of cations by colloidal clay: Soil Sci. Soc. America Proc., v. 4, p. 150–155.

Palange, R. C., Robeck, G. G., and Henderson, C., 1956, Radioactivity in stream pollution: Indus. and Eng. Chemistry, v. 48, p. 1847–1850.

Paneth, F. A., 1948, Exchange of ions between crystal surfaces and solutions: Jour. chimie phys., v. 45, p. 205–211.   (Chem. Abs., v. 43, 6047ᵈ, 1949.)

Paramonova, V. I., 1940, The effect of acids and bases on the adsorption capacity of soils and of glauconite: Kolloid zhur. [U.S.S.R.], v. 6, p. 259–274. (Chem. Abs., v. 35, 2655⁵, 1941.)

Paramonova, V. I., Grigorov, O. N., and Nikol'skiĭ, B. P., 1940, The effect of pH on base exchange in chernozem: Kolloid zhur. [U.S.S.R.], v. 6, p. 249–258. (Chem. Abs., v. 35, 2657², 1941.)

Patrick, W. A., 1956, Use of artificial clays in removal and fixation of radioactive nuclides, in Sanitary Eng. Conf., Cincinnati, 1955: U.S. Atomic Energy Comm. TID–7517(pt. lb), p. 368–373.

Pauling, Linus, 1930a, The structure of micas and related minerals: Natl. Acad. Sci. Proc. [U.S.], v. 16, p. 123–129.

———— 1930b, The structure of the chlorites: Natl. Acad. Sci. Proc. [U.S.], v. 16, p. 578–582.

Paver, H., and Marshall, C. E., 1934, The role of alumina in the reactions of clays: Soc. Chem. Industry Jour. [London], v. 53, p. 750–760.

Pavlovschi, Gh., 1937–1938, The Donnan equilibrium and base-exchange phenomena: Acad. sci. Roumaine Bull., v. 19, p. 226–233. (Chem. Abs., v. 34, 4845³, 1940.)

Peech, Michael, 1945, Determination of exchangeable cations and exchange capacity of soils; Rapid micro-methods utilizing centrifuge and spectrophotometer: Soil Sci., v. 59, p. 25–38.

Perkins, A. T., 1945, Phosphate fixation by soil minerals, pt. 4: Kansas Acad. Sci. Trans., v. 48, p. 209–217.

———— 1949, Reactions of muscovite, bentonite, and their treated residues: Soil Sci., v. 67, p. 41–46.

———— 1952, Determination of cation-exchange capacity of soils by use of versenate: Soil Sci., v. 74, p. 443–446.

Perring, J. K., 1956, The cooling of underground fission wastes: Harwell, England, Atomic Energy Research Establishment C/R 1294.

Phelps, G. W., 1947, Practical applications of clay colloid theory: Ceramic Age, v. 50, p. 119–120.

Powell, Sheppard T., 1954, What part does chemical coagulation play in today's water-treatment practices?: Power, v. 98, p. 80–82, 216, 218, 220.

Pratt, P. F., and Holowaychuk, N., 1954, A comparison of NH₄OAc, Ba(OAc)₂ and buffered BaCl₂ methods of determining cation-exchange capacity: Soil Sci. Soc. America Proc., v. 18, p. 365–368.

Rabinerson, A. I., 1938, Structure formation in soil colloids and methods for its investigation: Vsesoyuz. Akad. Sel'sko-Khoz. Nauk Lenina, Nauch.-issledov. Inst. Udobrenïĭ, Agrotech. i Agropoch. Gedroĭtsa, Trudy Leningrad. Otdel., 1938, pt. 2, p. 427–438. (Chem. Abs., v. 36, 7204³, 1942.)

Ralston, A. W., 1946, Structure and properties of solutions of colloidal electrolytes: New York Acad. Sci. Annals, v. 46, p. 351–369.

Randall, Merle, and Cann, J. Y., 1930, Micelles and base exchange: Chem. Rev., v. 7, p. 369–406.

Raney, W. A., and Hoover, C. D., 1946, The release of artificially fixed potassium from kaolinitic and montmorillinitic soils: Soil Sci. Soc. America Proc., v. 11, p. 231–237.

Rankama, Kalervo, and Sahama, T. G., 1950, Geochemistry: Chicago, Univ. Chicago Press, 912 p.

Rediske, J. H., and Hungate, F. P., 1956, The absorption of fission products by plants, in Internat. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, Proc.: United Nations Pub., v. 13, p. 354–356.

Reiche, Parry, 1950, A survey of weathering processes and products: New Mexico Univ. Pub. in Geology, no. 3, Albuquerque, New Mexico University Press, 95 p.

Renn, C. E., 1956a, Ultimate disposal of radioactive reactor wastes in the oceans, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID-7517(pt. 1a), p. 53–56.

———— 1956b, Disposal of radioactive wastes at sea, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1. v. 9, p. 718–721.

Repenning, C. A., 1959, Geologic summary of the San Juan Basin, New Mexico, with reference to disposal of liquid radioactive waste: U.S. Geol. Survey TEI–603, 57 p.

Rios, E. G., and Ruiz, J. C., 1954, Thermodynamic properties of ion exchange: Anales edafol. y fisiol. vegetal [Madrid], v. 13, p. 791–841.

Robertson, H. S., 1951, The microstructure of clay minerals: Tonindustrie-Zeitung, v. 175, p. 2–6.   (Chem. Abs., v. 45, 3768[h], 1951.)

Robertson, R. H. S., and Ward, R. M., 1951, The assay of pharmaceutical clays: Jour. Pharmacy and Pharmacology, v. 3, p. 27–35.

Robinson, G. C., 1958, Summary of summer work on the incorporation of radioactive isotopes in ceramic masses: ORNL Central Files 58–4–74, 21 p.

Robinson, G. W., 1949, Soils—their origin, constitution, and classification: 3d ed., London, Thomas Murby and Co., 573 p.

Rodger, W. A., 1954, Radioactive wastes—treatment, use, disposal: Chem. Eng. Progress, v. 50, p. 263–266.

Roedder, Edwin, 1957, Atomic waste disposal by injection into aquifers: Nuclear Eng. and Sci. Conf., 2d, Philadelphia 1957, Paper 57–NESC–1, New York, prepr. published by Am. Soc. Mech. Eng.

Ross, C. S., 1928, The mineralogy of clays: Internat. Cong. Soil Sci., 1st, v. 4, p. 555–561.

————, 1960, Review of the relationship in the montmorillonite group of clay minerals, *in* Ingerson, Earl, ed., Natl. Conf. Clays and Clay Minerals, 7th, Washington, D.C., 1958: New York, Pergamon Press, p. 225–227.

Ross, C. S., and Hendricks, S. B., 1941, Clay minerals of the montmorillonite group; their mineral and chemical relationships and the factors controlling base exchange: Soil Sci. Soc. America Proc., v. 6, p. 58–62.

———— 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: U.S. Geol. Survey Prof. Paper 205–B, p. 23–79.

Ross, C. S., and Kerr, Paul F., 1931, The kaolin minerals: U.S. Geol. Survey Prof. Paper 165–E, p. 151–180.

———— 1934, Halloysite and allophane: U.S. Geol. Survey Prof. Paper 185–G, p. 135–148.

Ross, C. S., and Shannon, E. V., 1925, The chemical composition and optical properties of beidellite: Washington Acad. Sci. Jour., v. 15, p. 467–468.

———— 1926, Minerals of bentonite and related clays, and their physical properties: Am. Ceram. Soc. Jour., v. 9, p. 77–96.

Rostenbach, R. E., 1956, Radioactive waste disposal at Hanford: Sewage and Indus. Wastes, v. 28, p. 280–286.

Rothe, Edmond, 1940, Several phenomena of concentration of radioactivity: Acad. sci. [Paris] Comptes rendus, v. 211, p. 753–756.

Ruiz, J. C., and González, J. de D. L., 1955, Adsorption of water by layered silicate minerals: Anales edafol. y fisiol. vegetal [Madrid], v. 14, p. 249–267. (English summary.)

Russell, G. C., and Low, P. F., 1954, Reaction of phosphate with kaolinite in dilute solution: Soil Sci. Soc. America Proc., v. 18, p. 22–25.

Russell, R. G., and Pearce, D. W., 1943, Fractionation of the rare earths by zeolite action: Am. Chem. Soc. Jour., v. 65, p. 595–600.

Sabatier, M., 1949, Investigations of glauconite: Bull. Soc. française minéralogie, v. 72, p. 475–542.

Saidel, Teador, 1943, Interpretation of experimental results on exchange reactions: Bodenkunde und Pflanzenernährung, v. 29, p. 232–244.

Samuelson, Olof, 1953, Ion exchangers in analytical chemistry: New York, John Wiley and Sons, 264 p.

Sand, L. B., and Ormsby, W. C., 1954, Evaluation of methods for quantitative analysis of halloysite-kaolinite clays, in Swineford, Ada, and Plummer, N. V., eds., Natl, Conf. on Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.,: Natl. Research Council Pub. 327, p. 280.

Sawhney, B. L., Jackson, M. L., and Corey, R. B., 1959, Cation-exchange capacity determination of soils as influenced by the cation species: Soil Sci., v. 87, p. 243–248.

Schachtschabel, Paul, 1940, Investigation of the adsorption of clay minerals and organic soil-colloids and the determination of these colloid portions and their adsorption in soil: Kolloid-Beihefte, v. 51, p. 199–276.

——— 1942, Investigations of sorption in soils: Forschungsdienst, v. 16, p. 87–90.

Schoen, U., 1953, Identification of clay by phosphate fixation and cation exchange: Zeitschr. Pflanzenernährung, Düngung und Bodenkunde, v. 63, p. 1–17. (Chem. Abs., v. 48, 5409$^j$, 1954.)

Schofield, R. K., 1940, Clay mineral structures and their physical significance: Ceramic Soc. [Great Britain], Trans. v. 39, p. 147–158.

——— 1949, Calculation of surface area of clays from measurements of negative adsorption: Ceramic Soc. [Great Britain], Trans. v. 48, p. 207–213.

——— 1952, Soil colloids: Chemistry and Industry [London], no. 4, p. 76–78.

Schofield, R. K., and Samson, H. R., 1953, Deflocculation of kaolinite and the accompanying changeover from positive to negative chloride adsorption: Clay Minerals Bull. 2, p. 45–50.

Schuffelen, A. C., and Middelburg, H. A., 1953, Ionic exchange interrelations in soils in crops; pt. 1 — Ion selectivity in soils: Netherlands Jour. Agr. Sci., v. 1, p. 97–110. (Chem. Abs., v. 48, 11698$^e$, 1954.)

Schwartz, A. M., and Perry, J. W., 1949, Surface-active agents, their chemistry and technology: New York, Interscience Publishers, 579 p.

Schweitzer, G. K., and Jackson, Morrison, no date, Radiocolloids: U.S. Atomic Energy Comm. Report ORO–48, Tennessee Univ., 28 p.

Seligman, Henry (pt. 1), Dunster, H. J., (pt. 2), and Fair, D. R. R., and McLean, A. S. (pt. 3), 1956, The discharge of radioactive waste products in the Irish Sea: Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1. v. 9, p. 701–711.

Shannon, R. L., 1950, Radioactive waste disposal—a bibliography of unclassified literature: U.S. Atomic Energy Comm. ORE TID–375, 8 p.

Sharov, V. S., 1939, Contradictions in contemporary colloid chemistry of soils and their source: Pochvovodenie [U.S.S.R.], no. 6, p. 121–135. (Chem. Abs., v. 35, 3377$^7$, 1941.)

Shukla, K. P., 1944, Influence of exchangeable ions on the dispersion of soil: Current Sci., v. 13, p. 45.

Siegel, J. M., 1946, Nuclei formed in fission—Decay characteristics, fission yields, and chain relationships: Am. Chem. Soc. Jour., v. 68, p. 2411–2442.

Sieling, Dale H., 1947, Role of kaolin in anion sorption and exchange: Soil Sci. Soc. America Proc., 1946, v. 11, p. 161–170.

Simon, G. P., 1956, The evaluation of montmorillonite clay for the pickup and fixation of MFP activity in the presence of boric acid: U.S. Atomic Energy Comm. BNL–2388, 13 p.

Smulikowski, Kazimierz, 1954, The problem of glauconite: Polska Akad. Nauk, Kom. Geol., Archiw. Mineralog., v. 18, p. 21–120.   (In English.)

Snell, F. D., 1943, Surface-active agents: Indus. and Eng. Chem., v. 35, p. 107–117.

Speil, S., 1940, Effect of adsorbed electrolytes on properties of monodisperse clay-water systems: Am. Ceramic Soc. Jour., v. 23, p. 33.

Stanford, G., and Pierre, W. H., 1946, The relation of potassium fixation to ammonium fixation: Soil Sci. Soc. America Proc., v. 11, p. 155–160.

Stern, O., 1924, Zur Theorie der elektrolytischen Doppelschicht: Zeitschr. Elektrochem., v. 30, p. 508–516.

Stewart, G. D., 1953, Samples of soil from Arco, Idaho: U.S. Atomic Energy Comm. MLM–401, 7 p.

Stout, P. R., 1939, Alterations in the crystal structure of clay minerals as a result of phosphate fixation: Soil Sci. Soc. America Proc., v. 4, p. 177–182.

Straub, C. P., 1951, Removal of radioactive materials from waste solutions: Sewage and Indus. Wastes, v. 23, p. 188–193.

Straub, C. P., 1952, Water decontamination studies: U.S. Atomic Energy Comm. WASH–129, p. 84–89.

——— 1953, Treatment and disposal of liquid radioactive wastes, *in* Rudolfs, Willem, ed., Industrial wastes—their disposal and treatment: New York, Reinhold Publishing Corp., p. 450–470.

——— 1956, Problems of radioactive waste disposal: Sewage and Indus. Wastes, v. 28, p. 787–794.

Straub, C. P., and Krieger, H. L., 1954, Removal of radioisotopes from waste solutions—Soil suspension studies, *in* Proc. 8th Indus. Waste Conf., 1953,: Purdue Univ. Eng. Ext. Ser. 83, p. 415–438.

Straub, C. P., Lacy, W. J., and Morton, R. J., 1956, Methods for decontamination of low-level radioactive liquid wastes, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1., v. 9, p. 24–27.

Straub, C. P., Morton, R. J., and Placak, O. R., 1951, Studies on the removal of radioactive contaminants from water: Am. Water Works Assoc. Jour., v. 43, p. 773–792.

Stremme, H., 1911, On allophane, halloysite, and montmorillonite:   Centralbl. Mineralogie, Geologie, und Paleontologie, No. 7, p. 205–211.

Struxness, E. G., and Blomeke, J. O., 1958, Multipurpose processing and ultimate disposal of radioactive wastes, *in* Internat. Conf. Peaceful Uses Atomic Energy, 2d, Geneva 1958, Proc.: United Nations Pub., v. 18, p. 43–45.

Struxness, E. G., Morton, R. J., and Straub, C. P., 1956, Disposal of high-level radioactive liquid wastes in terrestrial pits, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1., v. 9, p. 684–691.

Sudo, Toshio, 1955, Clay minerals with long spacings: Geol. Soc. Japan Jour., v. 61, p. 200–207.   (English summary.)

Tesdahl, T. C., Lowe, C. S., Mead, F. C., and Murphy, E. L., 1954, Fixation of mixed-fission products activity by soils of the Savannah River Project: U.S. Atomic Energy Comm. MLM–665, 18 p.

Tezak, Bozo, 1952, The general scheme for the mechanism of coagulation and peptization processes: Arhiv za Kemiju i Tehnologiju [Yugoslavia], v. 24, p. 25–28.   (English summary.)

Theis, C. V., 1955, Geologic and hydrologic factors in ground disposal of waste, *in* Sanitary Eng. Conf., Baltimore 1954: U.S. Atomic Energy Comm. WASH–275, p. 261–283.

—— 1956a, Problems of ground disposal of nuclear wastes, *in* Internat. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Proc.: United Nations, Pub. 1956. IX. 1. v. 9, p. 679–683.

—— 1956b, A review of the ground-water geology of the major waste-producing sites: U.S. Atomic Energy Comm. TID–7517(pt. 1a), p. 116–131.

Thomas, H. A., Jr., 1956, Disposal of low-level liquid radioactive wastes in inland waterways: U.S. Atomic Energy Comm. TID–7517 (pt. 1b), p. 457–470.

Thomas, H. C., 1944, Heterogeneous ion exchange in a flowing system: Am. Chem. Soc. Jour., v. 66, p. 1664–1666.

Thomas, H. C., and Frysinger, Galen R., 1956, Ion exchange: Ann. Rev. Phys. Chemistry, v. 7, p. 151–152.

Thomas, H. C., and Gaines, G. L., Jr., 1954, The thermodynamics of ion exchange on clay minerals—a preliminary report on the system montmorillonite-cesium-strontium, *in* Swineford, Ada and Plummer, N. V., eds., Natl. Conf. Clays and Clay Minerals, 2d, Columbia, Mo., 1953, Proc.: Natl. Research Council Pub. 327, p. 398–403.

Thomas, R. G., Rex, E. H., and Christenson, C. W., 1956, Studies on fixation of radioactivity in fired clays, *in* Sanitary Eng. Conf., Cincinnati, 1955: U.S. Atomic Energy TID–7517(pt. 1b), p. 352–367.

Thompson, H. S., 1850, On the absorbent power of the soil: Royal Agr. Soc. Jour., v. 11, p. 68–74.

Thugutt, S. J., 1948, Zeolites—chemical properties and origin: Polsk. Tow Geol. Rocznik, Soc. geol. Pologne Ann. 18, p. 5–35. (In English.)

—— 1949, The views of Gustav Bischof on the origin of zeolites—an historical note: Acad. sci. lettres (Varsovie) Comptes rendus, v. 42, p. 147–148. (In English.)

Thurston, W. R., 1956, Summary of Princeton Conference on disposal of high-level radioactive waste products in geologic structures, *in* Sanitary Eng. Conf., Cincinnati 1955: U.S. Atomic Energy Comm. TID–7517(pt. 1a), p. 47–52.

Tiselius, Arne, 1936, Adsorption and diffusion in zeolite crystals: Jour. Phys. Chemistry, v. 40, p. 223–232.

Trapnell, B. M. W., 1955, Chemisorption: New York, Academic Press, 265 p.

Troelstra, S. A., 1954, Colloid chemistry: Ann. Rev. Phys. Chemistry, v. 5, p. 291–312.

Truog, Emil, 1946, A proposed system of names, abbreviations, symbols, and formulas for designating the soil base-exchange substances and their acids and salts: Soil Sci. Soc. America, Proc., v. 10, p. 341–343.

Tschapek, M., and Butschkowskyj, M., 1952, The origin of the binary electrical coating in clay minerals: Inst. nac. inv. ciencias nat. y Mus Argentino ciencias nat. "Bernardino Rivadavia" Commun., Ser. Cienc. geol., v. 1, p. 1–19.

Tsyurpa, I. G., 1946, The kinetics of exchange reactions of cations: Pochvovodenie [U.S.S.R.], p. 309–314. (Chem. Abs., v. 41, 826ᵉ, 1947.)

Turner, F. J., and Verhoogen, Jean, 1951, Igneous and metamorphic petrology: 1st ed., New York, McGraw-Hill Book Co., 602 p.

Tyulin, A. F., and Malomakhova, T. A., 1952, Colloid-chemical adsorption of phosphates in soils and clay minerals: Pochvovedenie [U.S.S.R.], p. 514–527. (Chem. Abs., v. 7, 1879ᵍ, 1953.)

U.S. Department of Agriculture, 1954, Determination of the properties of saline and alkali soils: U.S. Dept. Agriculture Handb. 60, p. 19–20.

Vageler, P., and Waltersdorf, J., 1930, Beiträge zur Frage des Basenaustausches und der Aziditäten: Zeitschr. Pflanzenernährung u. Düngung, A. 15, p. 329–342.

Van Bemmelen, J. M., 1888, Absorption compounds and the absorptive power of the soil: Landw. Versuchs Stat., v. 35, p. 69–136. Abs., Chem. Soc. Jour. [London], v. 54, pt. 2, p. 985–986.

Van Olphen, H., 1950, A tentative method for the determination of the base-exchange capacity of clays: Internat. Cong. Soil Sci., 4th, Amsterdam 1950, Trans., v. 2, p. 97–99.

Vanselow, A. P., 1932a, Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids and zeolites: Soil Sci., v. 33, p. 95–113.

———— 1932b, The utilization of the base-exchange reaction for the determination of activity coefficients in mixed electrolytes, Am. Chem. Soc. Jour., v. 54, p. 1307–1311.

Van Nostrand's Scientific Encyclopedia, 1947: 2d ed., New York, D. Van Nostrand Company, 1600 p.

Vermeulen, T., and Hiester, N. K., 1954, Ion exchange and adsorption column kinetics with uniform partial pre-saturation, Jour. Chem. Phys., v. 22, p. 96–101.

Vernadsky, W., 1924, La Géochimie: Paris, Librairie Felix Alcan, 404 p.

Voet, Andr., 1936, Colloidal solutions in concentrated electrolytes: Jour. Phys. Chemistry, v. 40, p. 307–315.

Volk, N. J., 1934, The fixation of potash in difficultly available form in soils: Soil Sci., v. 37, p. 267.

Voress, H. E., Davis, T. F., and Hubbard, T. N., Jr., 1958, Radioactive waste processing and disposal—a bibliography of selected report literature: U.S. Atomic Energy Comm.   TID–3311, 123 p.

Walker, G. F., 1949, Water layers in vermiculite: Nature, v. 163, p. 726.

———— 1951, Vermiculites and some related mixed-layer minerals, *in* Brindley, G. W., ed., X-ray identification and structure of the clay minerals: London, The Mineralogical Society (Clay Minerals Group), Taylor and Francis, Ltd., p. 199–223.

Walker, G. F., and Milne, A., 1950, Hydration of vermiculite saturated with various cations: Internat. Cong. Soil Sci., 4th, Amsterdam 1950, Trans., v. 2, p. 62–67.

Walton, H. F., 1941, Ion exchange between solids and solutions: Franklin Inst. Jour., v. 232, p. 306–334.

Warde, J. M. ,and Richardson, Raymond, 1955a, Waste disposal—Vital to atomic power development: Mining Eng., v. 7, p. 458–461.

———— 1955b, Waste disposal is vital to atomic power development: Jour. Metals, v. 7, p. 1090–1092.

Waterlot, Gerard,1955, Ion-exchange phenomena in the aquifer of the Cobrieux limestone: Soc. géol. du Nord (Lille) Ann., v. 75, p. 173–181.   (Chem. Abs., v. 51, 3881ᵉ, 1957.)

Way, J. T. ,1850, 1852, On the power of soils to absorb manure: Royal Agr. Soc. (England) Jour., v. 11, p. 313–379; v. 13, p. 123–143.

Weaver, C. E., 1953, A classification of the 2:1 clay minerals: Am. Mineralogist, v. 38, p. 698–706.

———— 1958, A discussion of the origin of clay minerals in sedimentary rocks, *in* Swineford, Ada, ed., Natl. Conf. Clays and Clay Minerals, 5th, Urbana 1956, Proc.,: Natl. Research Council Pub. 566, p. 159–173.

Webster's New International Dictionary, 1951: 2d ed., Springfield, Mass., G. & C. Merriam Co., p. 498.   [Quoted on p. 36]

Wells, A. F., Structural inorganic chemistry: 2d .ed., Oxford, Clarendon Press, 590 p.

Wey, Raymond, 1953, The adsorption of phosphate anions by montmorillonite: Acad. Sci. [Paris] Comptes rendus v. 236, p. 1298–1300.

Whitney, R. S., and Peech, Michael, 1952, Ion activities in sodium-clay suspensions: Soil Sci. Soc. America Proc., v. 16, p. 117–122.

Whitt, D. M., and Baver, L. D., 1937, Particle size in relation to base exchange and hydration properties of Putnam clay: Am. Soc. Agronomy Jour., v. 29, p. 905–916.

Wiegner, Georg, 1936, Ionenumtausch und struktur, in Internat. Cong. Soil Science, 3d, Oxford [England] 1935, trans.: London, T. Murphy & Co. p. 5–28.

Wiegner, Georg, and Jenny, Hans, 1927, Ueber Basenaustausch an Permutiten: Kolloid Zeitschr., v. 42, p. 268–272.

Wiklander, Lambert, 1946, Studies of ionic exchange with special reference to the conditions in soils: Lantbruks-Högskolans Ann. [Upsala], v. 14, p. 1–171. (Chem. Abs., v. 41, 3561$^i$, 1947.)

———— 1950, Fixation of potassium by clays saturated with different cations: Soil Sci., v. 69, p. 261–268.

———— 1955a, Cation and anion exchange phenomena, in Bear, F. E., ed., Chemistry of the Soil: New York, Reinhold Pub. Corp., p. 107–148.

———— 1955b, Cation exchange in clay and soil: Iva [Stockholm], v. 26, p. 198–207. (Chem. Abs., v. 50, 4435$^e$, 1956.)

Wiklander, Lambert, and Hallgren, Gunnar, 1944–1945, The dispersion of soil colloids: Lantbruks-Högskolans Ann. [Upsala], v. 12, p. 230–250. (Chem. Abs., v. 39, 4421$^2$, 1945.)

Wolman, Abel, 1957, Disposal of radioactive wastes: Am. Water Works Assoc. Jour., v. 49, p. 505–511.

Wolman, Abel, and Gorman, A. E., 1955, Disposing of radioactive wastes: Mech. Eng., v. 77, p. 321–324.

———— 1956, The management and disposal of radioactive wastes, in Internat. Conf. Peaceful Uses of Atomic Energy, Geneva 1955, Proc.: New York, United Nations, Pub. 1956. IX. 1. v. 9, p. 9–16.

Wolman, Abel, Gorman ,A. E., and Lieberman, J. A., 1956, Disposal of radioactive wastes in the U.S. Atomic Energy program: U.S. Atomic Energy Comm. WASH–408, 14 p.

Woodruff, C. M., 1955, Ionic equilibria between clay and dilute salt solutions: Soil Sci., Soc. America Proc., v. 19, p. 36–40.

Yoder, H. S., and Eugster, H. P., 1955, Synthetic and natural muscovites: Geochim. et Cosmochim. Acta, v. 8, p. 225–280.

Yusupova, S. M., 1946, On the characteristics of montmorillonite: Akad. Nauk SSSR (Doklady) Comptes rendus, v. 51, p. 631–634. (In English.)

Zel'dovich, Ya. B., 1949, The theory of Freundlich's adsorption isotherms: Akad. Nauk. (SSSR), Problemy kinetiki i kataliza, v. 7, p. 238–247. (Chem. Abs., v. 49, 32$^d$, 1955.)

Zettlemoyer, A. C., Young, G. J., and Chessick, J. J., 1955, The surface chemistry of silicate minerals; pt. 3—Heats of immersion of bentonite in water: Jour. Phys. Chemistry, v. 59, p. 962–966.

Zhukov, I. l., and Brodskaya, N. I., 1949, Connection between exchange capacity and electrokinetic potential: Kolloid. Zhur., v. 11, p. 322–327. (Chem. Abs, v. 44, 904$^a$, 1950.)

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