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THE BLEACHING CLAYS

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P. G. NUTTING

WASHINGTON

1933

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The Bleaching Clays

By P. G. Nutting

Abstract

Bleaching clays of both the naturally active and the activable types are abundant and widely distributed in this country south of latitude 38. Neither type occurs in glaciated areas.

Three chief source materials are recognized - volcanic ash and certain igneous rocks that are low in silica and high in bases and partly decomposed and the marine secondary mineral glauconite. Partial leaching with dilute acids renders these highly active bleaching agents. The naturally active clays may be derived from the same source materials by long leaching in fresh water, assisted in some cases by plant acids. Active bleaching clays result when bases in the surfaces of the clay particles are replaced by the hydrogen and hydroxyl of acid. These are driven off as water by heat, leaving the open bonds essential for bleaching. Bleaching power is at a maximum when only part of the bases are removed. If the leaching of bases is carried too far, the material degenerates into an ordinary clay or into a less active complex of hydrous oxides.

There appears to be a fixed upper limit to bleaching power closely approached by many treated bentonites available in great quantities. The best naturally active clays, treated slag, and various synthetic bleaching media are considerably lower in bleaching power. A few clays may be prepared in granular form from the percolation process of bleaching. A few bentonites slake in water without leaving hard granules and are adapted to the mud process, requiring no grinding. Although there is an insistent demand for more powerful bleaching agents for treating valuable products such as lubricants and cotton oil, no clay capable of higher activity than many of the bentonites is likely to be found, nor is any process of activation yet discovered more effective than mild acid leaching. Synthetic bleaching media, treated slag, and activated alumina will serve other purposes but are not good bleaching agents.

The study of bleaching power here recorded included a study of the vapor pressure of hydrous clays and of their thermal dehydration. These properties bear directly on their adsorbing and bleaching properties. Each clay has its own characteristic weight-humidity and weight-temperature curves, which may be interpreted in terms of energy of adsorption.

The testing of bleaching clays covers not only the bleaching power and hydration but acid solubility and identification of the acid-soluble constituents. A table of test data is given covering a few of the 200 clays studied. Much further work remains to be done relating to standard methods of testing and to the application of active clays to other purposes than decolorizing, such as solvent recovery, catalysis, and desiccation.

Introduction

Although bleaching clay or fuller's earth is produced in considerable quantity by many independent operators, it has received very little intensive study. Not much is known of the seat of the decolorizing action nor of its nature except that it is a selective adsorption or some kind. An active clay can be distinguished from one that is inactive by actual test of its bleaching or adsorbing power. Some clays are inactive until leached with acid; others have their activity much diminished by the same treatment. Many of the naturally active clays are improved by acid treatment. Producers of bleaching clays operate entirely by cut and try methods. The study here reported was undertaken to find the fundamental properties of such clays as a part of a comprehensive study of the relations between oil, silica, and water. Many thanks are due to the various producers mentioned for their whole-hearted cooperation in supplying clay samples and data and for permission to visit their plants and deposits. Members of the Geological Survey staff, C. S. Ross in particular, have made many helpful comments.

The clay materials that are the characteristic materials of clays, soils, and shales have been studied at the Survey for several years past. These include such classes as kaolinite, halloysite, beidellite, nontronite, and montmorillonite. The dominant mineral in many regions of profound weathering and especially in china and paper clays is kaolinite, the characteristic mineral of kaolin. The kaolins have been subdivided into nacrite, dickite, and kaolinite-anoxite by Ross and Kerr.^{1/} All these have essentially the same chemical composition ($2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), but they differ from one another slightly in internal structure as revealed by X-ray spectra. Kaolinite is commonly but not invariably derived from the feldspars $(\text{K}, \text{Na}, \text{Ca})\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. The kaolin minerals are dehydrated abruptly at temperatures between 500° and 600° C. Before dehydration they do not absorb water or bleach oil, nor can either the kaolins or feldspars be activated by acid treatment. Dehydration disrupts the structure (shown by X-ray) and imparts a slight adsorbing power. The crystalline inactive kaolin minerals appear to be the product of extreme weathering of many kinds of igneous rocks and are highly stable.

The bleaching clays appear to be composed chiefly of the less stable and less completely weathered clay minerals. They are characterized by high contents of loosely held water and by partial solubility in dilute ordinary acids, such as hydrochloric or sulphuric acid. The water is largely adsorbed water and is removable by heating to 200° C., but water of constitution and probably water of crystallization are also present. On the other hand, inactive clays, such as kaolin, retain almost all their water up to a red heat (500° C.) and then lose it abruptly within a short temperature range. Moderate dehydration to 200° C. is sufficient to develop the full bleaching power of the active clays, but heating to 600° - 800° C. destroys that power; hence we infer that it is the water driven

^{1/} Ross, C. R., and Kerr, P. F., The kaolin minerals: U.S. Geol. Survey Prof. Paper 165, pp. 151-176, 1930.

off between 50° and 200° C. that must be present in bleaching clays and must be driven off to induce bleaching power. Acid-leached clays require similar heat treatment following acid treatment and washing to bring out their full bleaching power.

Most bleaching clays are improved by acid leaching; a few are rendered less active by such leaching, and a few of the best are inactive until leached. The solubility of bleaching clays in acid runs from 10 to 30 percent, and the material removed is chiefly iron and alumina. The alkalies and alkaline earths are readily soluble if present but rarely appear in large amounts in active clays. In contrast we may cite the insolubility in acids of the alkalies in feldspars and of the alumina in kaolin. The replacement of a base in the surface of a mineral by the hydrogen of water or of an acid, followed by the removal of that hydrogen (by heating) to leave an open bond, appears to be the essential in producing an actively absorbing (bleaching) surface.

The thermal dehydration curves of the bleaching clays (see below) are all of the zeolite-silica gel type. They show definitely that neither the kaolins nor halloysite is present in any appreciable amount. Clay minerals characterized by acid-soluble (or replaceable) bases, low refractive index, open lattice structure, and high silica:alumina ratio may be present, but the evidence either way is not decisive, as these minerals give flat dehydration curves that are easily suppressed by excess hydrous silica or alumina. Many or possibly all of the bleaching clays would go over to kaolins if sufficiently leached and given sufficient time to take on water of constitution. A few clays have been thus transformed (from bleaching clay to china clay) in the laboratory by water treatment alone. The structure and probable origin of the bleaching clays are discussed farther on in this paper.

Occurrence and production

The great quantities of bleaching clay used in the East for refining cotton oil and petroleum lubricants come chiefly from the Georgia-Florida district extending from Macon, Ga., to Ocala, Fla., and centering in a 50-mile tract astride the Georgia-Florida line northwest of Tallahassee. Plants at Attapulcus, Ga., and Quincy, Fla., each produce more than 10,000 tons a month of finished clay, used chiefly on petroleum. At Macon and Ocala are plants producing clay that is used chiefly in refining cotton oil.

North of central Georgia and east of the Missouri River the only commercial production to my knowledge is at Olmstead, Ill. (near Cairo) where quantities of clay rather high in iron ore are mined by one of the large oil companies for its own use. Glaciated areas appear to contain no commercial deposits of bleaching clays.

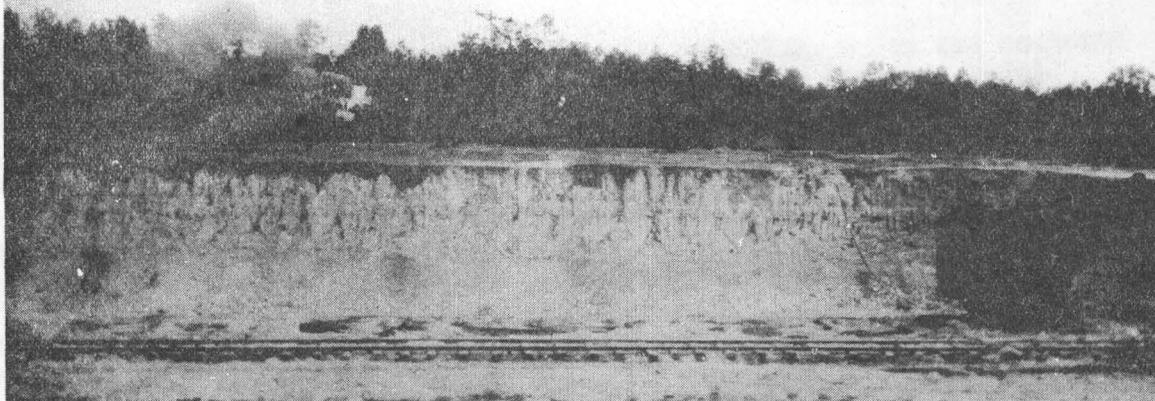


Figure 1.--Twiggs clay member of the Barnwell formation (upper Eocene). Clay deposit of the General Reduction Co., near Macon, Ga., being worked in 1931. Photograph by P. G. Nutting.

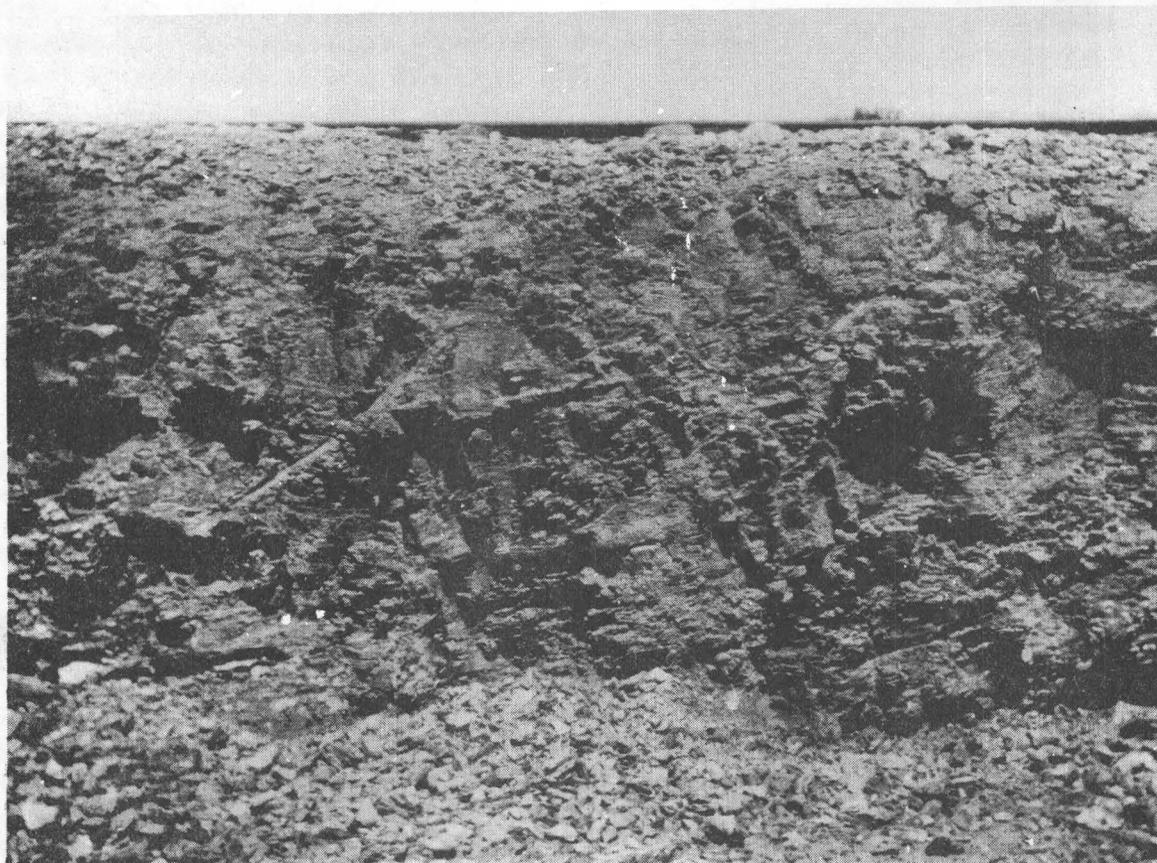


Figure 2.--Hawthorn formation (lower Miocene). Fresh worked clay bank Floridin Co.'s deposit at Quincy, Fla. Photograph by P. G. Nutting at 15 feet. Note pressure bedding but absence of sedimentary bedding.

The larger worked deposits of the West are near Creede, Colo.; near San Antonio, Tex.; in central Utah (Aurora); in western Nevada near Death Valley; near Chambers, Ariz.; and near Tehachapi, Calif. Clay from Death Valley is sold to refiners in Pennsylvania, and Arizona clay prepared in Los Angeles has been shipped to England, the original home of fuller's earth. English clay is imported chiefly for refining lard. A Bavarian treated clay is imported for refining cotton oil. There are several good deposits in Japan, used locally.

There is no dearth of good clay, and each producer has several deposits in reserve mapped ready for work. A 50-acre tract does not last long where worked with steam shovels at the rate of 500 tons a day, and when the overburden becomes too thick (15 feet) or the clay too thin (5 feet) another tract is opened and perhaps a new mill is built in another location. The clay beds already located are sufficient to supply even a largely increased demand for many years, and there is every reason to believe that the enormous deposits of the Southeast and the far West are practically inexhaustible.

The worked deposits are mostly 10 to 20 feet thick and (in the East) covered with soil and vegetation. Beneath is usually a bed of sand, and below this test drills sometimes show a second bed of active clay, too deep to be profitably worked. Sandy clay is not worked in this country, for the jills used are of the flour-mill type and sand removal would add materially to the expense of production. The Bavarian treated clay is screened as a thin mud before treating with acid, washing, drying, and milling. 2/ Although the bulk of the present domestic output consists of low-priced clay for decolorizing petroleum and cotton oil and is merely dried and milled, the domestic market calls for considerable clay of high strength and efficiency and low retention which will yield a stable product. Doubtless the chief advances of the near future will be the development of high-grade special clays to meet these domestic demands.

The clays; preparation and use

The active clays are all light gray when dry; some have a faint bluish or greenish or yellowish tint. They are, of course, much darker when fresh and moist. Most of them dry at room temperature to hard blocks without cracking, but a few—for example, the clay at Macon, Ga. — become rather friable. To the eye or touch they cannot be distinguished from kaolin or bentonite, but a lump of active clay placed in water does not swell nor slake nor become plastic, like many clays and soils. As mined they are very moist but not plastic. At one bed near Attapulcus, Ga., the good clay shades to a puttylike consistency (recognized by the test drillers) at the thin edge.

2/ Burghardt, O., Activated bleaching clays: Ind. and Eng. Chemistry, vol. 23, No. 7, pp. 800-802, July 1931.

The ultimate grains of these clays are very small. They are microscopic or submicroscopic in size, but X-ray diffraction patterns show that practically all clays are composed largely of particles having some crystalline structure. What one sees under the moderate magnification of a binocular microscope is a mass of rounded opaque lumps whose size depends only upon the crushing and sifting the clay has undergone.

Certain bleaching clays are valued only because they can be prepared in granular form (16-30 mesh, 30-60, 60-100, 100-200, and 200 up are the commercial sizes) not broken down by handling or by burning for reuse. Clays in granular form are used in percolation filtering, the topped and dewaxed oil passing slowly down through 4 to 10 feet of granular clay. The first oil to come through is water-white; then come green, yellow, orange, and red oils, which are afterward blended to obtain the color desired. In the "contact" method of bleaching, very finely ground earth (usually 200 mesh) is mixed with the oil in sufficient quantity to give the desired color, the mixture is well agitated for a half hour, and then the clay is separated in a filter press. The contact method is in general use except in a few of the older refineries.

Most bleaching is done at high temperatures (150° - 200° C.) to insure maximum efficiency, particularly in working with viscous oils and fats. This temperature is sufficient to expel the residual H. and OH ions in the clay, and hence clay so used need not be entirely dehydrated. The clay may even be injected as mud into the hot still. But when bleaching clay is to be used cold on mineral oils such as gasoline or lubricants it must be thoroughly dried by heating for some time to about 175° C. Many highly active clays when used dry, however, will crack white neutral oils, gasoline, or fused paraffin. The cracked portions are at once absorbed by the clay, leaving the filtrate still water-white but unstable toward light. It is claimed that the hot wet method of bleaching produces oils more stable toward light. Storage in the dark improves the stability of light-sensitive filtered oils.

Source and origin of bleaching clays

The weathering of most igneous rocks, such as dunite, granite, basalt, and rhyolite, is a very complex process, partly physical and partly chemical. Water penetrates between individual mineral crystals and into cleavage planes and surfaces of structural discontinuity within the crystals. The water carries H and OH ions, dissolved oxygen, carbon dioxide, organic acids, and miscellaneous dissolved salts, but simple solution appears to be the dominant factor in decomposition by weathering. The surfaces that are wet may be hydrated or dissolved away or may exchange bases and other ions for the H and OH of the water. Drying partly removes material in solution and suspension and makes easier the subsequent entry of water. Periodic wetting and drying or drainage is therefore much more effective in decomposing the rocks than a permanently arid or permanently submerged condition.

Mechanical decomposition (softening) is only the first step in weathering. Chemical decomposition and leaching continue, removing alkali and alkaline-earth bases and silica and leaving behind the sesquioxides Al_2O_3 and Fe_2O_3 , their silicates, and crystalline quartz, which are the chief constituents of fully weathered rocks. Climate, vegetation, and bacterial action influence the end product, which is usually either a soil or an inactive clay containing water of crystallization.

The residual soils in the immediate vicinity of Washington are the result of weathering of granites, gneisses, and locally of gabbro. Of these products the most activable are the yellow and green soils containing excess quartz, usually unaltered, but little mica or alkali-rich feldspars; these yield the most active bleaches. The ash-gray variety composed largely of kaolin is far less activable, and a dark-green material high in mica and a white nearly pure feldspar rock could not be activated even by leaching with acid.

The solid residues of rock weathering have most open bonds and are most highly absorbent when the decomposition and leaching are far advanced but before the highly stable end products are approached. Decomposed (in place) and partly leached granite from Washington, D. C., diabase from Virginia, and dunite from Webster, N. C., were found to be active filtering media. By carrying the leaching a little further by boiling in several changes of distilled water or by treating with dilute acid, each of these materials was converted into an excellent bleaching earth. Many soils possess considerable bleaching power.

The composition of the mother rock naturally affects the number and strength of the open bonds on the surfaces of the residual grains. Out of the almost infinite variety of such rocks, it is difficult and probably useless to select those which weather to the most active residuals in the average climate, but laboratory studies have shown which types of residual material are the most active when conditioned to maximum strength. These are derived from the magnesian and ferromagnesian silicates. If fully activated silica (silica gel) is taken as standard, other dehydrated amorphous oxides (Fe, Mg, Al, etc.) are about on a par with it in activity as a bleaching agent and so is hydrous aluminum silicate that has been dehydrated by ignition. Some magnesium-bearing aluminosilicate clays are twice as active, and many iron and magnesium bearing silicates exceed it by 50 percent.

The beds of commercial bleaching clays are probably the accumulated wash of decomposed igneous rocks. The associated sand and mica may well have been separated and deposited elsewhere by gently flowing water. The active clay might have become soil had it been exposed to the organic acids of vegetation. Although probably deposited in water and always kept saturated, it has not become reduced to pure aluminosilicate (Kaolin) with or without inert iron oxide, because chemical conditions (see below) were unfavorable.

Most of the clay deposits that are being worked commercially contain in themselves little evidence as to the mode of their deposition. One at Quincy, Fla. (Hawthorn formation), 3/ shown distinctly an old stream bed with two laterals filled with sandy peat extending from top to bottom (about 20 feet) of the active clay. Whether these stream deposits were laid down at the time the active clay was deposited or subsequently is not entirely clear, but they were probably filled in later. They are evidently not offshore marine deposits. In a neighboring bed the well-preserved skeleton of a manatee was found near one edge. The clay bed being worked east of Macon, Ga., (Twiggs clay member of the Eocene Barnwell formation; 4/ see fig. 1), is thick and horizontal and suggests a deposit in the bed of a lake. The extreme clarity of any water in contact with any of these active clays is noteworthy. Evidently no suspension is stable under conditions now existing in the clay bed, nor does running water take up active clay. A stream will trickle down over a steep bank of active clay (Attapulcus, Ga., May 1931) without becoming at all muddy.

Finally must be mentioned the synthetic bleaching media, the amorphous oxides and silicates. Such hydroxides as $Al(OH)_3$ or $(OH)_4$, if precipitated in water, washed free from salt, and thoroughly dried, possess good adsorptive powers. Commercial "dialized iron" merely dried and ground is in this class, as are activated alumina and silica gel. Silicates are easily prepared in a similar manner by mixing dilute solutions of a metallic chloride, for example, with a dilute solution of water glass. These "silicates" adsorb like the amorphous oxides, cracking some oils and filtering water-white until exhausted. Adsorbents of this nature are useful chiefly for the recovery of solvent vapors, as they do not yield an intermediate series of green, yellow, and red oils. Many are effective bleaching agents for vegetable oils and for fats, but they are too expensive to compete with the naturally active clays in petroleum filtration.

3/ For a description of the Hawthorn formation see Cooke, C. W., and Mosson, Stuart, Geology of Florida: Florida Geol. Survey Twentieth Ann. Rept., pp. 115-137, 1929.

4/ The Twiggs clay member is described in Cooke, C. W., and Shearer, H. K., Deposits of Claiborne and Jackson age in Georgia: U. S. Geol. Survey Prof. Paper 120, pp. 41-81, and Shearer, H. K., A report on the bauxite and fuller's earth of the Coastal Plain of Georgia: Georgia Geol. Survey Bull. 31, 1917.

Seat and origin of bleaching action

The property of selective adsorption is by no means limited to the bleaching clays. Active surfaces may be produced on many minerals by suitable means. Even pure quartz beach sand may be activated by etching the grain surfaces with caustic soda or hydrofluoric acid or with water at high temperatures. The Tensleep oil sand, or Wyoming, is almost pure quartz with grain surfaces naturally active. These surfaces have adsorbed tarry substances from the oil such that a brown layer 0.75 micron thick cannot be washed off by even the most powerful solvents. If it is removed by chromic acid ("wet combustion"), a white roughened surface is left which is active and will reabsorb a similar layer if left a few hours in Tensleep crude oil. The oil sand of Bradford, Pa., also has active surfaces but with more or less alumina and ferrous oxide associated with the surfaces of the quartz grains, which are very rough and irregular.

The basic constituents of many natural minerals -- for example, serpentine, greensand, glauconite, and the zeolites -- are easily removable by ordinary acids, leaving hydrated, more or less impure silica behind. This residue, after thorough washing to remove all free irons except H and OH, followed by thorough drying at 190° - 200° C. to expel these, is found to be an active adsorbent or bleaching medium.

Clays of apparently similar chemical composition may be either highly active bleaching agents or entirely inactive. On the other hand, clays differing widely in composition may be similar in bleaching power. Nor is the molecular structure as revealed by X-rays a safe guide, for an inactive clay after activation by chemical treatment generally shows little or no change in structure by activation. However, a knowledge of structural type, as discussed later in this section, is a valuable guide in the study of activation.

As the bleaching action is essentially a selective adsorption of coloring matter on exposed solid surfaces in contact with the liquid to be decolorized, such surfaces must be the seat of the bleaching action. Study of active and inactive surfaces and particularly of the activation of inactive surfaces leads to the conclusion that it is the presence on a surface of open bonds or free valencies that make them selectively adsorbing. Any solid adsorbs every fluid that wets it in the sense that near the boundary surface internal pressure, density, and viscosity are increased. In certain combinations these effects are heightened by chemical affinity. A greased surface holds diamonds rather than quartz pebbles. A clean quartz grain prefers water to oil, but a tar-coated grain or grain of coke prefers oil to water.

For fulling cloth (removing grease) a highly active earth is not necessary. The fuller's earth mined near Clinton, Mass., used for fulling cloth for many years, appears to be nothing but a very fine glacial silt. It has no filtering or bleaching power for petroleum, as the grain surfaces are not activated.

In the cases just mentioned the adsorbed coating may be removed by solvents without chemical change of the adsorbed material. But the coloring matter on a used filter cannot be removed (except the loosely held outer layers) by even the most powerful solvents. It can be removed only by combustion -- that is, by converting it to carbon dioxide and water by igniting or by treating with chromic acid. It is this kind of adsorption which is thought to occur when open bonds are present. These open bonds may be limited to the visible surface (activated quartz grains) or may occur on the walls of submicroscopic pores (silica gel) or of lamellar cleavage surfaces. In a few minerals bases may be leached out even from the interior of grain structures, yielding bleaching earths of the most valued type.

The production of active surfaces on solid minerals is very simple in theory. It is apparently sufficient that the surface be attacked by a reagent which leaves the acid and basic constituents out of balance on that surface. In quartz the mere etching away of a part of a surface layer appears to leave open bonds -- bonds that were previously attached to atoms which have been removed. The minerals of basaltic rocks (calcic plagioclase, augite, olvine, etc.), serpentine, and blast-furnace slag readily part with their basic constituents when treated with an ordinary acid, and only pure or nearly pure silica remains. Pure kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, roasted at 600°C ., and goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, roasted at 300°C ., give up their H and OH as water and become active like silica gel but not water-absorbent. Commercial active clays, either raw or acid-leached, are considerably lowered in bleaching power (to about two thirds) after ignition to 800°C .

Some untreated natural clays are nearly as active bleaching agents as any treated clays or as any that can be produced in the laboratory. (See test data, below.) Natural weathering must have been accomplished mainly by nearly pure water. In rare instances the activated mineral may have been exposed to solutions from which it could adsorb material, enhancing its bleaching power. The fundamental problem is therefore to determine what pure or nearly pure water may do to decomposed rock.

The solubility of a decomposed granite from Washington, D. C., was found to be about 50 parts per million, and saturation is approached in about 20 hours at 80°C. (steam bath.) At ordinary temperature (25°C.) saturation is about 35 parts per million and is approached only in a week or two. The initial solubility of fresh material is about twice as great as the ultimate solubility reached after long-continued washing. Two weeks' treatment at 80°C. gave no higher concentration than two days. A solution boiled down in the clay gave no increase in concentration, but a clear, filtered solution at (50 parts per million) may be concentrated in pyrex or platinum to several thousand parts per million before precipitation begins. Decomposed diabase and dunite and commercial bleaching clays from Florida and Death Valley gave solubilities and supersaturations of the same order of magnitude. Bentonite shows a much higher initial solubility (350 parts per million) but also approaches 50 parts per million after repeated washes. Amorphous silica (gel) has a constant solubility of about 180 parts per million. Solutions of this concentration may be concentrated (with care) to 16,000 parts per million before precipitation begins.

During weathering rock surfaces are exposed to thin films of moisture, which are dilute but nearly-saturated solutions. Alumina and ferric oxide appear to be the most resistant to weathering in the absence of vegetation, but where vegetation and the organic acids derived from decaying vegetation are present even these may be removed, releasing more silica in soluble form. Slightly less resistant are quartz and the potash feldspars, and calcium, magnesium, and sodium complexes in general yield readily.

Leaching with acid removes bases from many decomposed igneous rocks but tends to leave grain structures with the original edges and corners intact, as the residual silica is insoluble, whereas in pure water, on the contrary, it appears to yield indefinitely until exhausted or equilibrium is reached. Diluting the acids assists the dissociation and removal of the soluble components. In treating commercial clays with acid about 20 percent hydrochloric acid or sulphuric acid is preferred, and the mass is kept hot and stirred for some hours or over night. Under such conditions silica is one of the least soluble constituents, and there is a tendency in many clays to leave too pure a silica for the best activation. The gentler action of weaker acids or of a salt solution leaves more active ions and alumina as silicates. Aluminum chloride, chromic acid, and oxalic acid solutions have given excellent results with minerals that yield too readily to the stronger acids.

Conditions during weathering are also favorable to the colloidal dispersion of the constituents, whereas conditions during the artificial acid treatment are not. In a colloidal suspension near its isoelectric point, the particles do not settle nearly as readily as they do if any excess of either positive or negative ions is present. It follows, therefore, that near the isoelectric point physical decomposition is favored. In natural weathering the adsorbed film of water, except in rare instances, remains near its isoelectric point--a condition favoring the escape and removal of ions and small particles from the mineral surfaces. In the decomposed and claylike weathered products of granite, dunite, and diabase the free particles constituting most of the suspension after extended treatment with pure water consist largely of iron oxide, which has been set free by the water treatment. By water treatment alone the clay materials of the rocks just mentioned have been converted into good bleaching earths, and commercial bleaching clays and bentonites have been converted into plastic clays resembling ball clays.

The interchange of ions between a solid mineral surface and the solution in contact with it also takes place much more freely near the isoelectric point. On the surface of a silicate crystal ions of the silicates are freely displaced by OH and other anions. The net result is that the free colloidal complexes (grains of silicates) represent a wide variety in composition and in properties. This interchange has been intensively studied by Mattson ^{5/} in connection with ionic equilibria in soils.

Vegetation affects the course of decomposition and the composition of the end products by supplying free weak acids and substances for a rich bacterial growth. Plant acids dissolve sesquioxides, silicates, bases, and even metals more freely than they are attacked in simple weathering, but such products are usually stored and partly returned to the soil instead of being carried away. Most soils possess some bleaching power, if screened to remove coarse material and treated with chromic acid to remove organic matter--in fact, some diabase soils approach the best commercial clays in activity.

Soil, active clay, and inactive (kaolin) clay beds lie in contact in some places with little or no intermediate gradation. In many deposits of this type even tree roots in shallow soil do not penetrate the active clay beneath. Soil supporting luxuriant vegetation, resting on partly kaolinized feldspar without half an inch of gradation, is not unusual in the South. On the other hand, roots of plants penetrate decomposed granite, even the highly active varieties, freely.

^{5/} Mattson, Sante, The laws of soil colloidal behavior, V: Soil Science, vol. 31, p. 319, 1931.

The decomposed granite still contains much of its slightly soluble bases and hence may serve as plant food. The beds of bleaching clay, on the other hand, consist of only the finest material which has been superficially leached of all water-soluble constituents by long contact with excess water, deposited in water, and kept saturated with water nearly free from ions other than H and OH. Soil represents an unstable chemical (ionic) composition which is continually varying within a considerable range. The active clay beds of the East and South also represent an unstable equilibrium but one which has become stabilized for that particular environment through the removal and absence of practically all exchangeable ions from the surfaces of the clay particles and the presence of considerable bound, interstitial water. Many of the active clays of the far West are only incompletely leached. The ceramic clays of the ball-clay type represent an approach to the true chemical equilibrium (with water), having all their bonds satisfied. Deposits of active clay may shade off into inactive clay and goil at their thin edges when ionic interchange with acid and base ions is provided. Why active and inactive clays are laid down in separate beds in the same basin remains to be explained but may provisionally be attributed to long-period climatic changes, the bleaching clays being less completely leached than the ordinary clays.

Susceptibility to molecular breakdown by weathering or chemical treatment, which is the basis of activation, is of course largely a matter of the molecular structure of the original mineral. The structure of many silicates has been tentatively established, but the stability of such structures toward removal of individual atoms and atomic groups has received little attention. The little that is known may be briefly sketched.

Acid and basic atoms alternate in all these structures. The ease with which bases may be removed or replaced of course varies widely with the nature of the structure as well as with the particular base affected. In some open lattices, such as the zeolites and some clays, replacement of certain ions may be effected without destroying the lattice. Lamellar and fibrous structures are common and are readily broken down. Breakdown and replacement of bases are often superficial only.

Bragg ^{6/} and his coworkers have considered the following five classes of structures for the silicate minerals, which form a convenient basis for considering stability. The comments relating to ease of breakdown are my own.

^{6/} Bragg, W. L., The structure of silicates: Zeitschr. Kryst., vol. 74, pp. 237-305. 1930; cf. p. 300.

I. The orthosilicates, composed of independent SiO_4 groups. In this class minerals such as olivine yield very readily to weathering and to chemicals.

II. Diorthosilicates, ring structures (beryl), and other complex orthosilicates. These are fairly stable toward weathering and do not readily exchange bases.

III. Silicon-oxygen chains, as in the pyroxenes and amphiboles. These minerals yield rather readily to weathering, and under suitable conditions the bases of their alteration products are largely replaceable by the hydrogen of acids and of water.

IV. Silicon-oxygen sheets of the micaceous minerals. Many of these minerals of micaceous habit are extremely resistant to activation methods on their faces. Neither muscovite, biotite, vermiculite, nor kaolinite can be made into good filtering media by leaching. Similarly needles (actinolite) and fibers (asbestos) do not yield to the simpler activation methods, on their larger faces at least.

V. Three-dimensional silicon-oxygen networks. This class includes extreme types of stability. Quartz is very resistant and stable, but the zeolites readily exchange bases with no alteration in structure. This group should be subdivided.

Bragg's rough classification appears to be more suitable than any other yet offered to serve as the basis of the intensive study of structural stability and atomic or ionic interchangeability necessary to clear up the study of active minerals. Structural stability chiefly concerns weathering; chemical stability relates to leaching and base exchange.

Igneous rocks are the ultimate source of probably all the bleaching clays. In such rocks the minerals most readily converted to active clays are the complex augites, hornblendes (class III), biotites, and olivines. Feldspars tend to alter to kaolinitic (nonactive) materials, but under favorable conditions they too may alter to the type of clay material that is capable of becoming active under the proper conditions. The large commercial beds are all sedimentary deposits derived from weathered rock material. Mines in Arkansas, worked until about 20 years ago, are igneous ferromagnesian (basic) dikes about 4 feet thick and nearly vertical where the minerals have been weathered in place and the original composition is evident from the retained structure. ^{7/} Igneous rocks of

^{7/} Miser, H. D., Developed deposits of fuller's earth in Arkansas: U. S. Geol. Survey Bull. 530, pp. 207-220, 1913.

the same general type in which the feldspars are dominant weather in this region to plastic clays; and those in which nephelite is in excess weather to bauxite. The Arkansas deposits are no longer worked, nor is any other bed of rock decomposed in place, as the expense of sorting and sifting is too great to compete with vast deposits of sedimentary clay of equally good quality already sorted and sifted by the processes of nature. Here in Washington different varieties of decomposed rock may be noted, not far apart.

The bleaching clays of the Georgia-Florida region were probably formed in embayments along the coast, and the material must have been derived from the weathering rocks of the Piedmont and Blue Ridge region to the north. Rocks composed wholly or even dominantly of amphiboles, pyroxenes, or olivine are of only local occurrence in this region, and feldspathic rocks are dominant. For this reason it is unlikely that the active clays of the Georgia-Florida region have been derived wholly or even dominantly from ferromagnesian (basic) minerals, like the active clays of Arkansas. Therefore the development of the active clays of the Georgia-Florida region has probably been controlled by conditions of weathering and deposition, rather than by derivation from the type of minerals (ferromagnesian) that most readily yield active clays.

The relation between Bragg's classification of silicate structures and activation is illustrated by the action of acids on serpentines and vermiculites. Ordinary green serpentine treated with hydrochloric acid yields its magnesium and iron, leaving active, nearly pure silica. When the rock is treated with hydrofluoric acid, the silica and iron yield to solution, leaving a white active magnesian residue. Both the silica and the magnesia residues are fairly good filters for oil. But fibrous serpentine (asbeston) low in iron and alumina does not yield to hydrochloric acid and is not activated by it. It yields readily to hydrofluoric acid, leaving a finely divided active magnesian residue. Raw vermiculite yields readily to either hydrochloric acid or hydrofluoric acid, without destruction of its micaceous structure, but neither residue is active toward oil.

This evidence supports the view that activation consists in removing one or more constituents from an associated solid complex. It is usually associated water that is removed to leave open bonds, but it may be almost any element or group, or simply an interchange. Fibrous structures that yield in but a single dimension and micaceous structures that are unyielding in one dimension (Bragg's class IV) are probably not exceptions to the general rule.

The formation and stability of the active silicates

The bleaching action of certain clays is only a special case of union between oppositely charged ions or molecular aggregates. In general, a positively charged group unites with a negatively charged group. If either group consists of solid particles or a porous solid, the other may be ultramicroscopic, ionic, or even molecular, and attachment to the solid (adsorption) removes it from solution or suspension. We are here dealing with systems of which one component (the clay) consists of relatively large aggregates, while the other (the adsorbed material) usually consists of single molecules or small groups of colored molecules in solution or suspension. In this section are considered more in detail the action of water on silicates and the conditions necessary for the stability of the wet active clays.

In general any solid particle in suspension in a liquid will migrate either with or against an electric current when a potential gradient is applied. If the particles are large enough to be seen with a microscope the movement may be seen (cataphoresis), the velocities being commonly a few microns per second per volt per centimeter. In ordinary electrolysis there is a similar but invisible movement of ions (charged atoms or groups of atoms). When a visible particle is moving in an electrolyte, acid or base may be added till the movement is reversed. When no motion occurs, the particle is at its isoelectric point, and its total charge is zero.

Charged particles tend to unite, positive with negative, if both are present, just as do ions in solution in ordinary chemistry. This union of acidoid particles with basic colored ions in suspension, for example, is the basis of the filtering or bleaching action of active clays. But while the small chemical ions are single, the large charged particles tend to collect neighboring ions and so neutralize their charges and become less active. Further, the external ions tend to react with individual component ions at the surface of the large particles and neutralize their charges and tend to break down their structure if that is weak.

Starting with the simplest case we may quote Mattson: ^{8/} "In general all inert substances charge themselves negatively in water. This may be accounted for by assuming the electrical forces within the oriented, interfacial layers of molecules to be such as to attract and fix the OH ions of the water while the H ions (or any other cation which may have displaced the H ion) remains free and diffused into the surrounding water, which then assumes a corresponding positive charge." Or it may be simply assumed that the bond attaching the OH ion is more powerful or more readily attached than that attaching the H atom (it is part of a potential double bond).

^{8/} Mattson, Sante, Isoelectric precipitates: Soil Science, December 1930, p. 463.

Thus clay particles in water tend to surround themselves with an atmosphere of charged ions--some from their own material if any are free but supplemented by H, OH, and other ions from the water. As the H is small and mobile while the OH tends to remain with the silica, there is a marked tendency for H to diffuse away from the silicate particle and be replaced by other less mobile bases if these are available. The very high dielectric constant of water assists this action. Alumina and ferric oxide are most like the silica and even less soluble in water, so they tend to remain with it to the last.

At the isoelectric point a particle does not migrate either with or against an electric current. Hence the total charge, consisting of that within the solid particle plus the ions on its surface and in its atmosphere must be zero. Ions (for example, H^+) may be escaping with the current, but others must be joining the aggregate at the same rate. In a large excess of pure water mineral particles must in time closely approach their isoelectric points, bases at or near the surface have mostly escaped, and the ion atmosphere must (owing to mass action) consist chiefly of H^+ and OH^- . When bases are locked in the interiors of the grains and either time or water has been insufficient for the complete removal of bases or of silica in excess of the 1:2 ratio, then clays of beidellite-montmorillonite type may result. When both time and water supply have been ample for such removal, many silicates may go to hydrous aluminum silicates of the kaolin type. These in pure water have a hydrogen-hydroxyl ion concentration near the isoelectric point and in sufficient time may crystallize to kaolinite.

The eastern active clays have been rather thoroughly leached at the grain surfaces but have apparently been weathered under such conditions and laid down so rapidly that the bases have been leached away only at the surface and after deposition, the supply of water (locked in) has been very small, and the isoelectric point could not therefore be attained. In the western active clays there has been even less leaching, a more rapid deposition, and a more limited supply of water.

It is worth noting that when the OH ions are forcibly removed from kaolinite by heating above $500^{\circ} C.$, the residue having open bonds is a very good filter and is partly soluble in ordinary acids. The solubility in acid after ignition may be used to estimate the fraction of kaolinite in a mixed clay. The filtering power of ignited kaolinite, as would be expected, is similar to that of amorphous silica and alumina and about half that of the best neutral earths; and such material yields but little of the intermediate yellow and red grades of oil in filtering.

The bleaching clays, then, consist of particles of mixed aluminosilicates of somewhat variable composition but belonging to the less stable group of clay minerals whose surfaces are only partly balanced with removable ions. Water and weathering have prepared these surfaces, and lack of time or of a sufficient supply of suitable ions has prevented their complete leaching and recrystallization into permanent stable units (secondary silicates). Activation consists simply in the removal of the ions loosely held at the surface, so that in filtration other chosen ions or charged aggregates may be adsorbed and thus removed from solution or suspension.

The clays under consideration here are then accumulations of the miscellae of suspensions. Of the many types possible, considering the nature of the original source rock and of subsequent weathering and water treatment, at least three may be distinguished:

1. Clays consisting of basoid particles whose surfaces have been leached to unsaturation, the open bonds temporarily holding ions, chiefly hydrogen and hydroxyl.
2. Clays consisting of basoid particles with surfaces either unleached or covered with adsorbed bases. Groups 1 and 2 commonly have an alumina-silica ratio greater than 1:2--that is, 1:3 to 1:5.
3. Kaolinitic clays composed of particles leached free from bases and hydrated to $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Ordinary clays consist largely of Al_2O_3 and smaller but variable quantities of Fe_2O_3 , combined with SiO_2 and H_2O in variable proportions. If the proportion of silica is low and hydrous oxides are abundant, they may lean either toward laterite or toward bauxite, according to which oxide is in excess.

Most active clays do not slake in water, although bentonites and ball clays slake readily. This property is significant. Colloidal suspensions precipitated by electrolytes (acid, basic, or salt solutions) readily break down physically in water, even after drying to a hard lump. Hence precipitation by sea water is not a probably method of deposition of the active clays.

Nonslaking dried sediments may be obtained by precipitating one colloid by another--for example, an acid clay or diatomite by dialyzed iron, all electrolytes being excluded. This is evidence, though not conclusive, that the active clays consist of positive and negative particles nicely balanced in sufficient proportion to give a nonslaking character to the whole mass. Material from decomposed ferromagnesian igneous rocks, thoroughly leached in a large excess of rather pure water, would give rise to such a combination. Particles that were smaller and more easily leached would be adsorbed by particles less leached, thus neutralizing and precipitating them. The base-exchange properties of the active clays are not pronounced, as this theory would require. They are highly stable toward water and give up a few ions to it.

The sedimentary active clays are also highly impermeable to water and probably for much the same reason that they do not slake in water--namely, that the grain surfaces are interlocked by chemical bonds. Other factors are the fineness of grain and fineness of pores between and through the grains. Water cannot pass through a channel less than 0.01 millimeter in diameter, for such a duct is choked by adsorbed water. Bentonite slakes readily but is impervious to water when confined so that it is unable to expand, because its pores are too small to permit water to pass through them.

The complex silicates constituting the active clays range from slightly acid aluminosilicates to those that are only partly leached and decidedly basoid. In the latter class acid treatment is indicated to remove the excess of the stronger bases K, Na, and Ca by replacing them by H. Good natural filters may be composed largely of silicates rich in magnesia but are more commonly compounds of alumina, iron, and silica. After an acid treatment, thorough washing is required to remove all salts formed, because otherwise these may be adsorbed in preference to the colored ions to be removed in the bleaching process. A wash with even dilute alkali (KOH) will ruin a filter; but a final dilute acid wash is not seriously detrimental.

An active bleaching clay placed in a hydrocarbon containing no oxygen atoms (such as petroleum) will adsorb colored ions of the nature of $-C_nH_{2n+1}$, detached parts of multiply-bonded carbon chains or rings. If these are not present, a good filter will break out (crack) and adsorb parts of even saturated chains or rings. If the filter is not completely dry, H and Oh ions remain on its surface and its activity is much reduced, so that it adsorbs only the blackest hydrocarbon groups and passes the yellow and red fractions.

Filtering a hydrocarbon containing oxygen atoms to a water-white color is much more difficult. In this class are the animal and vegetable fats and oils, fatty acids, and esters. The colored groups are probably as readily adsorbed, but the efficiency of the filter is unavoidably reduced by H and OH ions already adsorbed, so that the less active greens and yellows are not removed. If an alcohol (high in OH) is added to petroleum even a good petroleum-bleaching clay has almost no power to filter it. There appears to be some advantage in using the more siliceous type of filters, which have a higher capacity for OH adsorption and combination. Also there appears to be a selective advantage in high temperatures, which appear to drive off OH more readily than hydrocarbons from an active surface. It might be thought that the carboxyl radical $-\text{COOH}$ of the fatty acids would be more readily adsorbed on siliceous surfaces, but this is weakly negative and probably seldom colored or adsorbed.

Association with water - Hygroscopicity

Water is associated with minerals in many different ways, often difficult to determine. It may be adsorbed on surfaces, absorbed in minute pores or angles, or be simply in solution in the mineral. It may be water of crystallization in molecular association, or water of constitution in chemical combination as H and OH ions. In any of these forms it may be driven off by heat. It is to be regarded as an additional oxide, but one more readily dissociated and more easily vaporized or replaced than most others. In chemical analyses it is customary to regard water not removed by heating to 110°C . for some time as combined water, that driven off below 110°C . being either free moisture or adsorbed water, but in many analyses such a division cannot be made. Some adsorbed water is not driven off even at 200°C ., and some hydrates break up and release water below 100°C .

The significance of the association of water in bleaching clays is that where bonded hydrogen and hydroxyl ions are driven off from solids they leave open bonds, whether or not such removal results in structural breakdown or is reversible. The vapor pressure of bonded water is always less than that of free water; hence a study of vapor pressures and various percentages of water present gives a measure of the degree of association. Heats of wetting also give a measure of bond number and strength, but those heats are only a few calories, experimental difficulties are great, and corrections and uncertainties are large, so that this method is little used.

Clay exposed to a given relative humidity reaches a fixed weight. That weight is always the same whether equilibrium is reached from a dryer or moister condition and nearly the same whether the clay is in lump form or powdered. The curve of weight plotted against humidity is not a straight line, as for simple solutions (Henry's law), but is somewhat S-shaped, indicating some chemical association of water with clay. Typical curves are reproduced in figures 3, 4, and 5.

These curves suffice to show the wide difference in response to water vapor. Pure silica gel represents one extreme type of response; a powdered chemical salt, like potassium chloride, the other extreme. The salts take up no water--that is, their vapor pressure remains practically nil--up to a limiting high humidity, above which they take it up freely and go into solution. The clay curves are all intermediate and S-shaped. Of two high-grade clays, that from Chambers, Ariz., is one extreme in taking up the most water, while the other, from Death Valley, takes up the least. The curve for acid-treated serpentine has the silica gel type of shoulder at its upper end but has the toe (0-20% humidity) of a clay type of curve, convex upward.

To have a vapor pressure approaching saturation most clays must have a high water content, the affinity of clay for water being high. On the other hand, a clay mud will lose water even in a saturated atmosphere in a closed glass vessel. There may be clear water above the settled mud, but the loss of water goes on just the same in a perfectly smooth curve at a steadily decreasing rate. A hard block of dried clay of course gains water in a saturated atmosphere. The block and the mud eventually (in a year or two) approach the same water content, which is not far from that found in commercial clay beds when mined. A mud of powdered glass, on the other hand, neither gains nor loses water in a saturated atmosphere, but a salt or a sulphuric acid solution continually gains water under like conditions.

The energy and pressure connected with the adsorption of water vapor are of interest. If saturated water vapor is in contact only with liquid water and an inactive solid such as glass, the work RT in calories per mole (18 grams), or $RT/18$ calories per gram, will condense the vapor to liquid. T is the absolute temperature and R the constant 1.985. At $26^\circ \text{C.} = 26 + 273 = 299^\circ$ absolute, this work is 32.9 cal/gm. As soon as the vapor is condensed, internal forces pulling the molecules together do the additional work $RT \cdot d \log C / d \log T$, amounting (at 26°C.) to 548.9 cal/gm, called the internal work. The sum $548.9 + 32.9 = 581.8$ is the total heat of vaporation. The concentration C refers to the water vapor in grams per cubic centimeter.

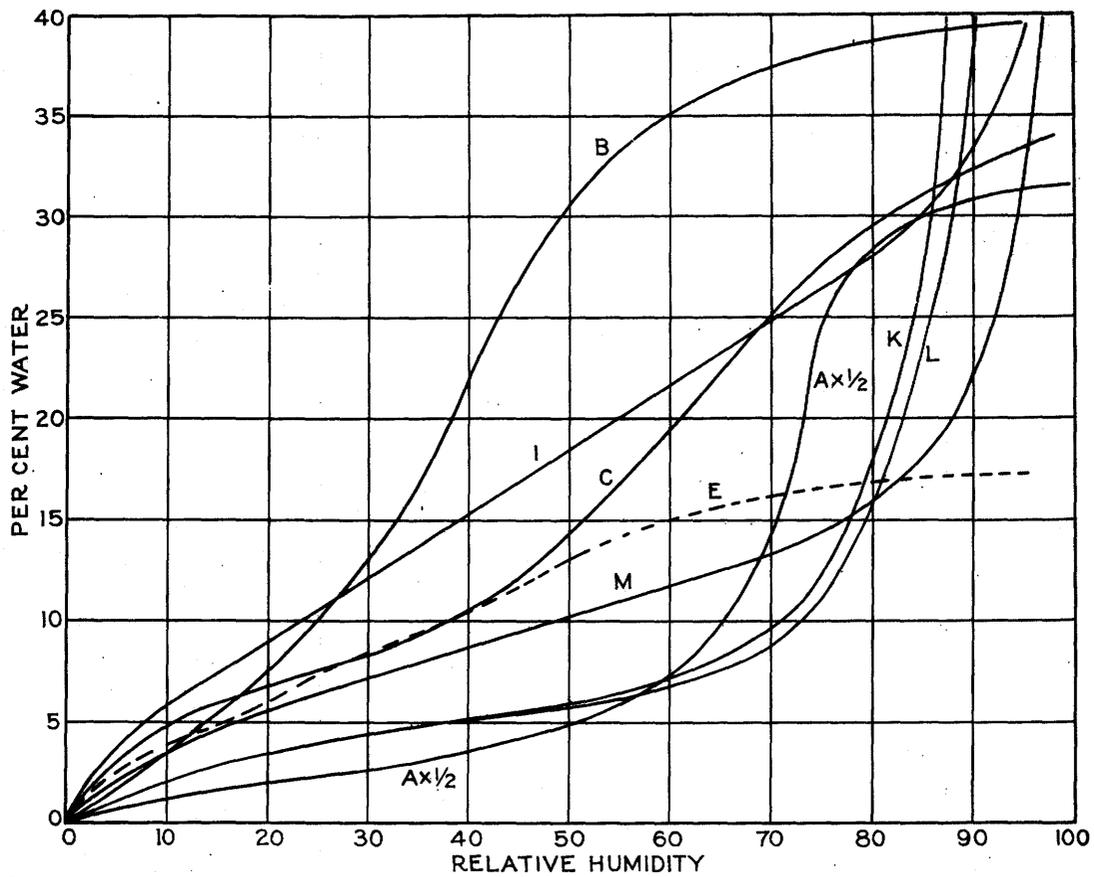


Figure 3.—Weight-humidity curves. Notation of table 2.

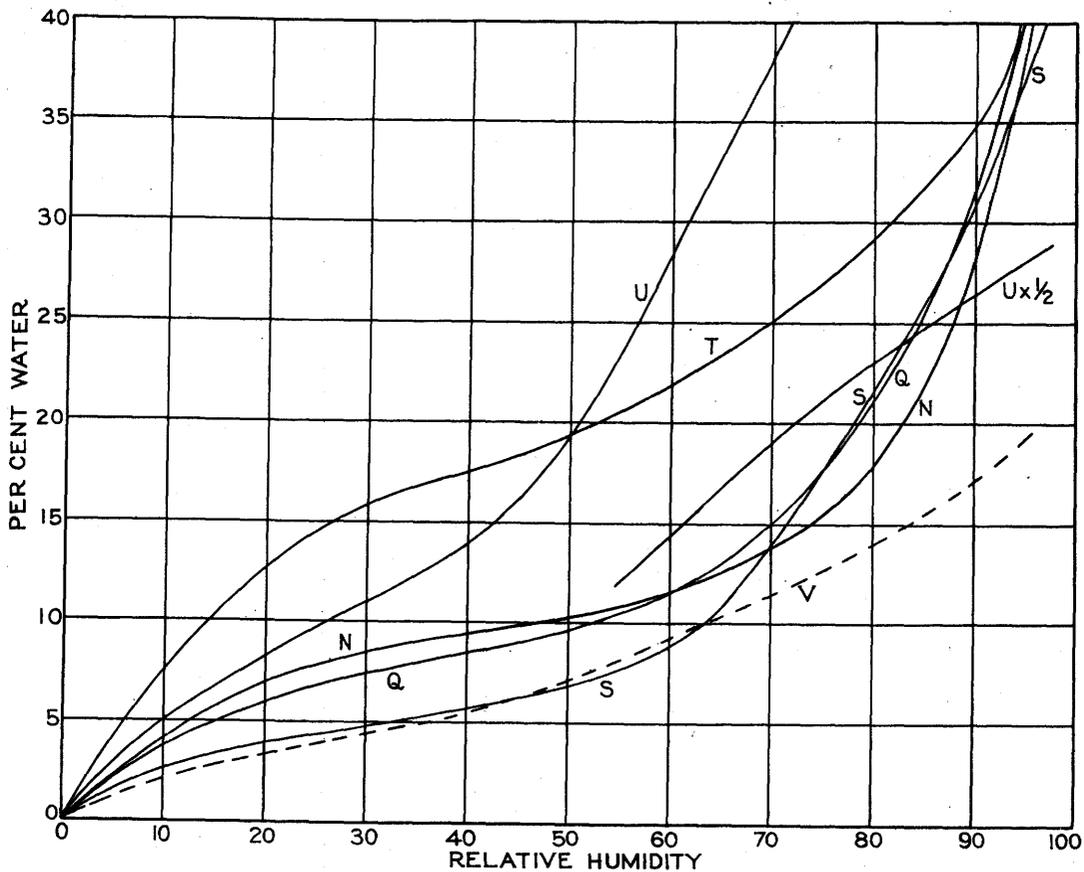


Figure 4.—Weight-humidity curves of clays. Notation of table 2.

With an adsorbed film of water in equilibrium with unsaturated water vapor in a glass enclosure, the extra work of condensation is $RT \log (p/P)$ or $RT \log H$, where H is the relative humidity and p is the vapor pressure, less than the saturation pressure P . This extra work or energy is due to adsorption, the total external work being $RT \log H$ to bring the vapor to saturation, plus RT to condense it to liquid, or $RT (1 + \log H)$ altogether. The expression $RT \log H$ for external work due to adsorption may be shown by statistical methods to hold whenever the contact is between water vapor and liquid water (at least one layer of molecules of water adsorbed) and whenever capillary or other forces are negligible--that is, except at high water contents. At 26°C . the extra energy is as follows:

Table 1.--Energy of association with water

H%	$-\log H$	cal/gm	H%	$-\log H$	cal/gm
1	4.6052	151.85	50	0.6932	22.86
2	3.9120	128.99	60	.5108	16.84
5	2.9957	98.78	70	.3572	11.78
10	2.3026	75.92	80	.2231	7.36
15	1.8971	62.55	90	.1053	3.47
20	1.6094	53.07	95	.0513	1.69
30	1.2040	39.70	100	.00	.00
40	.9163	30.21			

The third column of this table gives the external energy in calories per gram of water adsorbed when the water content is such as to be in equilibrium with the relative humidity of the first column. Curves such as those of figure 3 then, with this table, supply data for finding a relation between adsorption energy and water content or thickness of film if the surface is known. As would be expected, the energy is very high for the first moisture adsorbed but falls off rapidly as the thickness increases. The form of these energy-concentration (percent water) curves suggests an exponential, and in figure 5 is plotted $\log H$ against $\log C$ for permutite.

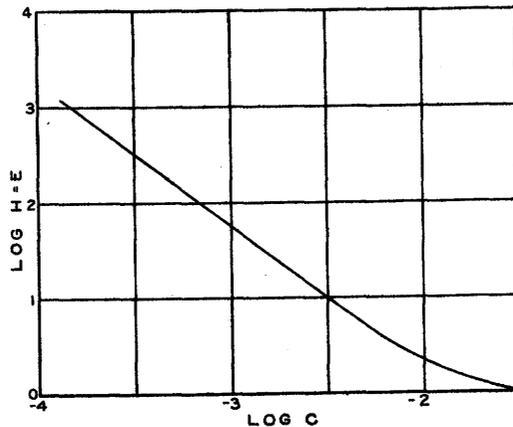


Figure 5.--Energy-log concentration, permutite.

The first eight points lie on a perfectly straight line $E = \log H = -2.788 - 1.515 \log C$ or $dE/dC = -1.515/C$. The rate of falling off of energy (or pressure) is therefore inversely proportional to the thickness of the adsorbed layer. This law holds up to a concentration of 13 percent moisture in permutite. At higher percentages of water either the law breaks down or other effects (such as capillarity) enter. All the observed curves for the clays and simple amorphous oxides show this simple linear relation $E = \log H = A + B \log C$ for the lower humidities and water concentrations.

In differential form, this relation is $dH/H (= dp/p = B dC/C)$, which states that the percentage increase in vapor pressure is directly proportional to the percentage increase in concentration of water in clay. Rewritten as $dE/dC = B/C$ the law states that the rate of falling off of energy with thickness (or the attraction between contiguous layers of adsorbed water) varies inversely as the thickness of the adsorbed layer of water (which is proportional to C for C small). The constant B is a measure of that rate of falling off of energy with thickness and hence must be closely related to the orienting power, for water molecules, of the adsorbing active surface of the solid. The constant A/B is likewise a measure of the extreme thickness at which the adsorptive force is appreciable ($E = 0, \log C = A/B$)--that is, it is a measure of maximum concentration adsorbed from a water-saturated atmosphere ($p = P, H = 1, E = \log H = 0$).

The well-known empirical law of Freundlich, $q = ap^n$, for the quantity of liquid q adsorbed from a gas or vapor at a pressure p , may be translated into the law discussed above and similarly interpreted, as quantity adsorbed, thickness of adsorbed layer (at low concentrations), and concentration are all proportional to one another, and the logarithmic derivative is the same whichever variable is used. If vapor pressure p is measured in terms of saturation pressure P , its logarithmic derivative is also not affected. Our constant B is the reciprocal of Freundlich's n . His formula states that the vapor pressure of an adsorbed layer is simply proportional to some power of its thickness.

Heat treatment, leaching with acid, and hydration modify the weight-humidity curves. In figure 6 are shown curves for serpentine raw, ignited to 800°C ., and leached to white, nearly pure silica with hydrochloric acid. The original grains were 150 mesh, a clear dark green.

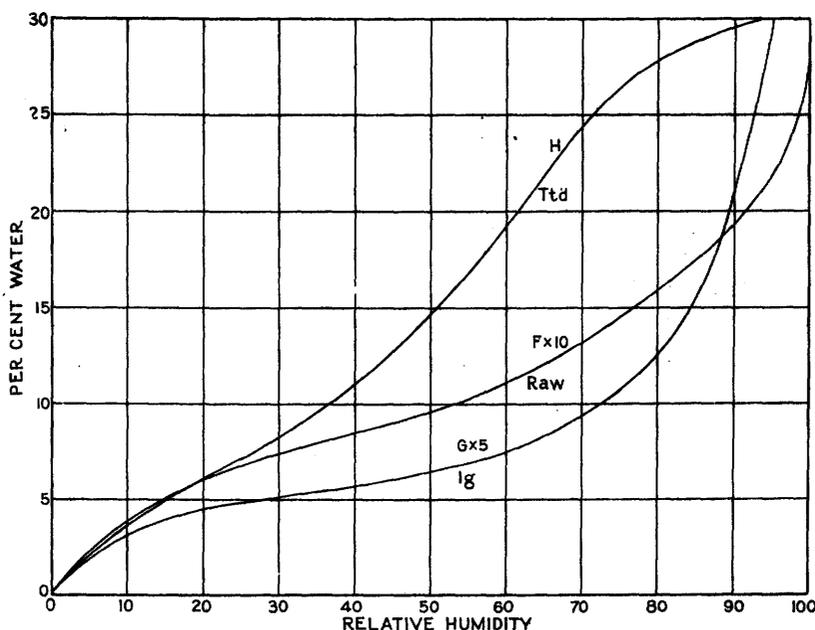


Figure 6.--Weight-humidity, treated serpentine. Raw, untreated grains. Ig, ignited to 800°C . in air. Ttd, HCl leached until white, then washed free from chloride. Note different vertical scales for percent moisture. (See table 2.)

Ignition nearly doubles the water adsorption and affects that at high humidities most. Acid treatment increases water adsorption more than ten times and gives a curve similar to that for silica gel.

A possible variation of hydration with size of grain was sought by using the Quincy earth in the 30-60 mesh commercial grade in comparison with the same material ground to pass 300 mesh (0.05 millimeter). The amount of water taken up was very nearly the same for the powdered and granular clays for all humidities from 0 up to 50 percent. Either the increased surface due to powdering is negligibly small in comparison with the active pore surfaces, or else the new surfaces are inactive. Between humidities of 60 and 95 percent the coarse material took up about 1 percent more moisture than the fine. Similar but less precise results had previously been obtained with bentonite. The fines in that experiment were obtained by evaporating a suspension that had not settled in months and pulverizing the dried residue. The close agreement in the results of the two experiments indicates that the extremely fine material remaining in suspension has essentially the same composition and character as the mass from which it was derived. (Compare O and P of table 2.)

Freshly treated raw clays and most synthetic active silicates are known to become somewhat less active in time. The effect of ageing on the amount of water taken up was studied with a silicate precipitated by chromic acid, freshly made and after 30 months. There was no change in moisture adsorption at a humidity of 30 percent. At humidities from 0 to 30 percent the aged material took up a little more water than the fresh; above 30 percent it took up less, with a steadily increasing divergence. At 90 percent humidity the fresh material took on 62.3 percent of water, the aged but 37.5 percent. Probably few other materials exhibit so large an ageing effect. The results indicate that the change with time is not merely a closing of some open bonds but is explained by more active but fewer bonds in aged material. (Compare K and L, table 2.)

A test was made of the reversibility of the water left in an active clay at zero humidity, usually between 3 and 10 percent. A powdered clay was put in the usual P_2O_5 desiccator until constant weight was reached, then heated to about $200^\circ C.$ to drive off part of the remaining moisture, then put back in the desiccator. In a week it had regained over half the water driven off by heat, proving that it was able to take water even from fresh P_2O_5 , which has a vapor pressure below a billionth of an atmosphere. The residual moisture in clays therefore represents a definite equilibrium, which is at least partly reversible. Ignition ($800^\circ C.$) destroys the avidity of most silicates for water for a time, and after a moderate heating most active clays are much more powerful desiccants than even P_2O_5 .

In table 2 are presented data on hydration for several synthetic amorphous oxides, simple natural minerals, and bleaching clays. They are perfectly definite and repeatable values, approached from either higher or lower humidities for the same sample of material, but the method of preparation of a material may profoundly influence its dehydration curve. Part of the data on serpentine and analcite were published in an earlier paper, 9/ in which various details of the method used may be found.

9/ Nutting, P. G., The association of water with serpentine: Washington Acad. Sci. Jour., vol. 18, pp. 81-89, 1928.

Table 2.- Moisture content at various humidities
(Percent by weight)

Relative humidity (percent)	A	B	C	D	E	F	G	H	I	K
5	1.5	1.7	3.0	1.1	2.6	0.24	0.39	2.0	3.7	1.20
10	2.5	3.4	4.8	2.0	4.0	.39	.62	3.5	6.0	2.10
20	4.0	7.5	6.9	3.3	6.0	.60	.90	6.0	9.1	3.41
30	5.4	12.8	8.3	4.6	8.2	.73	1.03	8.2	12.2	4.39
40	7.5	22.1	10.5	5.8	10.7	.82	1.13	10.9	15.5	5.14
50	9.8	30.5	14.3	8.1	13.1	.95	1.28	14.6	18.8	6.02
60	14.5	35.1	19.3	11.3	14.9	1.11	1.51	18.9	21.9	7.20
70	28.4	37.3	24.8	13.7	16.2	1.32	1.89	24.3	25.1	9.4
80	57.3	38.5	29.6	14.5	16.9	1.59	2.52	27.8	28.3	17.8
90	61.9	39.4	32.5	15.9	17.2	1.94	4.22	29.5	33.6	62.3
95	62.8	39.8	33.4	18.5	17.3	2.16	5.90	30.1	38.5	
Ig.800°		-9.3		-10.6		-17.6	.00	-8.3		
Relative humidity (percent)	M	N	O	P	Q	R	S	T	U	V
5	2.19	2.25	3.01	3.10	2.2	2.2	1.6	4.0	2.8	1.2
10	3.52	4.15	4.74	4.86	3.7	3.7	2.6	7.5	5.0	2.1
20	5.48	6.90	6.69	6.80	5.8	5.8	3.8	12.8	8.2	3.3
30	7.12	8.45	7.91	7.99	7.3	7.3	4.6	15.8	11.1	4.2
40	8.70	9.35	8.78	8.79	8.4	8.4	5.6	17.4	13.8	5.4
50	10.2	10.2	10.4	9.83	9.6	9.6	6.8	19.3	19.2	7.0
60	11.7	11.5	13.2	11.5	11.8	11.8	8.7	21.8	28.6	8.9
70	13.3	13.7	16.1	14.5	15.0	14.6	13.7	25.0	38.3	11.3
80	16.3	17.9	20.6	19.2	20.7	18.7	21.6	29.1	46.4	13.9
90	22.4	28.6	33.2	31.3	31.3	26.6	30.9	34.6	53.1	17.0
95	31.4	38.5	46.4	43.9	40.8	33.1	37.2	41.1	56.2	19.3
Ig.800°	-19.9	-10.9	-9.4	-8.7	-6.7	-.6	-5.7	-9.5	-10.2	-11.5

- A. Silica gel, ion-free, prepared by Nutting, 1928, 100 mesh.
- B. Silica gel, commercial (Patrick), crushed to 100 mesh.
- C. Al_2O_3 from pure $Al(OH)_3$, prepared by Nutting, 1928, 100 mesh.
- D. Activated alumina, from Aluminum Co. of America, 1931, 150 mesh.
- E. Fe_2O_3 from $FeCl_3$ dialyzed ion-free by Nutting, 1931, 150 mesh.
- F. Raw serpentine, 150-300 mesh, clear yellowish green. SiO_2 35.6%,
MgO 39.9, Al_2O_3 2.5, Fe_2O_3 4.6, FeO 2.0 (F. A. Gonyer).
- G. Ignited serpentine from same stock as F.
- H. Serpentine from same stock digested in HCl and washed. White.
- I. Bentonite (otaylite), California, white, crude. SiO_2 50.3%, Al_2O_3
16.0, CaO and MgO 7.8, H_2O 25.6.
- K. "Chromium silicate." A greenish-yellow synthetic preparation of
silica gel made from water glass precipitated with CrO_3 solution,
100 mesh. Fresh.
- L. The same stock 2 1/2 years old, showing age effect.
- M. Permutite, Folin preparation, old stock, white, 100 mesh.
- N. Fuller's earth, Quincy, Fla., raw clay dried and powdered to 150 mesh.
- O. Fuller's earth, Quincy, Fla., commercial 30-60 mesh.
- P. Fuller's earth, same as O but finely powdered.
- Q. Clay from Macon, Ga., General Reduction Co., raw clay fresh ground
to 150 mesh.
- R. Clay from Macon, Ga., baked at 200° F., then ground to 150 mesh.
- S. Clay from Macon, Ga., ground fresh clay, HCl leached, then washed.
- T. Clay from Chambers, Ariz., Filtrol Co., raw clay ground to 150 mesh.
- U. Clay from Chambers, Ariz., same clay acid-treated, then washed.
- V. Clay from Nevada near Death Valley, Calif., high in Mg, raw clay ground
to 150 mesh.

The synthetic amorphous oxides SiO_2 , Al_2O_3 , and Fe_2O_3 are characterized by humidity curves having pronounced shoulders at high humidities (70-95 percent). SiO_2 hydrated to $Si(OH)_4$ would contain 37.5 percent H_2O . Both the silica gels studied take up more than that at 95 percent humidity, indicating that the water is adsorbed as well as combined, and the reversibility at room temperature indicates that little if any is combined with the silica. Similarly for the pure Al_2O_3 , $Al(OH)_3$ is 30.7 percent H_2O , and the amorphous form takes up 33.4 percent at 95 percent humidity. And instead of 25.2 percent H_2O in $Fe(OH)_3$, the prepared oxide takes up 18.5 percent H_2O at 95 percent humidity.

On the other hand, the curves for the naturally active clays and the complex synthetic silicates point steeply upward at humidities approaching saturation. Ignited serpentine has a curve of the clay type, but acid-leached serpentine has the characteristics of silica gel, as it should after removal of the stronger bases.

Conversely, moist clays have a definite vapor pressure corresponding to each percentage of water retained. That vapor pressure is approximately 25 millimeters times the relative humidity with which the clay is in equilibrium, as observations were made near 26° C. Curves of the simple oxide type, such as that for silica gel, indicate that a definite equilibrium concentration is attained at saturation pressure. A thin mud of water suspension of materials of this class, placed in a saturated atmosphere, will neither gain nor lose water. On the other hand, humidity curves of the active clay type seem to overshoot the saturation line, and muds of such clays will lose water in a saturated atmosphere until equilibrium with saturated water vapor is reached, generally when the clay has consolidated into fairly hard lumps. Soils, which always contain some active colloidal material, according to these observations would never take up water vapor from the atmosphere. On the other hand, if wet with liquid water (rain) to a mud they tend to rid themselves of the excess and will provide a saturated atmosphere for plant roots under surroundings far less humid and until they are themselves fairly dry.

Association with water - Hydrothermal relations

As hydrous minerals are heated they gradually lose water - first free water, then adsorbed and combined water, H and Oh ions. At 800° C. all but a very few minerals are anhydrous. The curves of dehydration with increase in temperature vary widely in form, from a smooth continuous slope to curves having steep shoulders characteristic of definite minerals containing water in molecular proportions. The dehydration-temperature curves are useful in studying the composition and structure of clays. In particular they give valuable clues to the nature of water association and hence to the activity of the clay as a filtering agent.

Hydrothermal curves are perfectly definite and repeatable but are reversible within a reasonable time only at the lower temperatures (below about 200° C.). Kaolinite, which parts with 2H₂O abruptly at about 500° C. (a low red heat), with loss of crystal structure, was thought to have irreversible properties, but heating with water in an autoclave to 300° C. in time restores the combined water and crystal structure.^{10/} It is probable, therefore, that the reversion would occur even at ordinary temperatures, given sufficient time (probably hundreds of years).

^{10/} Schachtschabel, Paul, Ueber Dehydratisierung und Rehydratisierung des Kaolins: Chemie der Erde, Band 4, pp. 395-419, 1928.

These thermal dehydration curves supply additional evidence that it is not chemical composition but structure which determines the behavior of a mineral toward water or other adsorbed substances. Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) shows the sharp shoulders ($469^\circ\text{--}483^\circ\text{C.}$) characteristic of pure hydrated salts. Allophane ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 3\text{--}5\text{H}_2\text{O}$), however, dehydrates (fig. 7) in a very smooth curve with no shoulders. The high-temperature kaolin mineral ("dickite" of the new classification of Ross and Kerr 11/) $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ also has a sharp shoulder at $500^\circ\text{--}545^\circ\text{C.}$ Impurities affect the shapes of these curves at temperatures below that of the sharp break (if there is one) and round off the shoulders but do not affect the temperature of the break. As little as 10 percent of the pure mineral diaspore or of a kaolinite in a mixed clay should show in a thermal analysis.

11/ Ross, C. S., and Kerr, P. F., The kaolin minerals: U. S. Geol. Survey Prof. Paper 165, pp. 151-176, 1931.

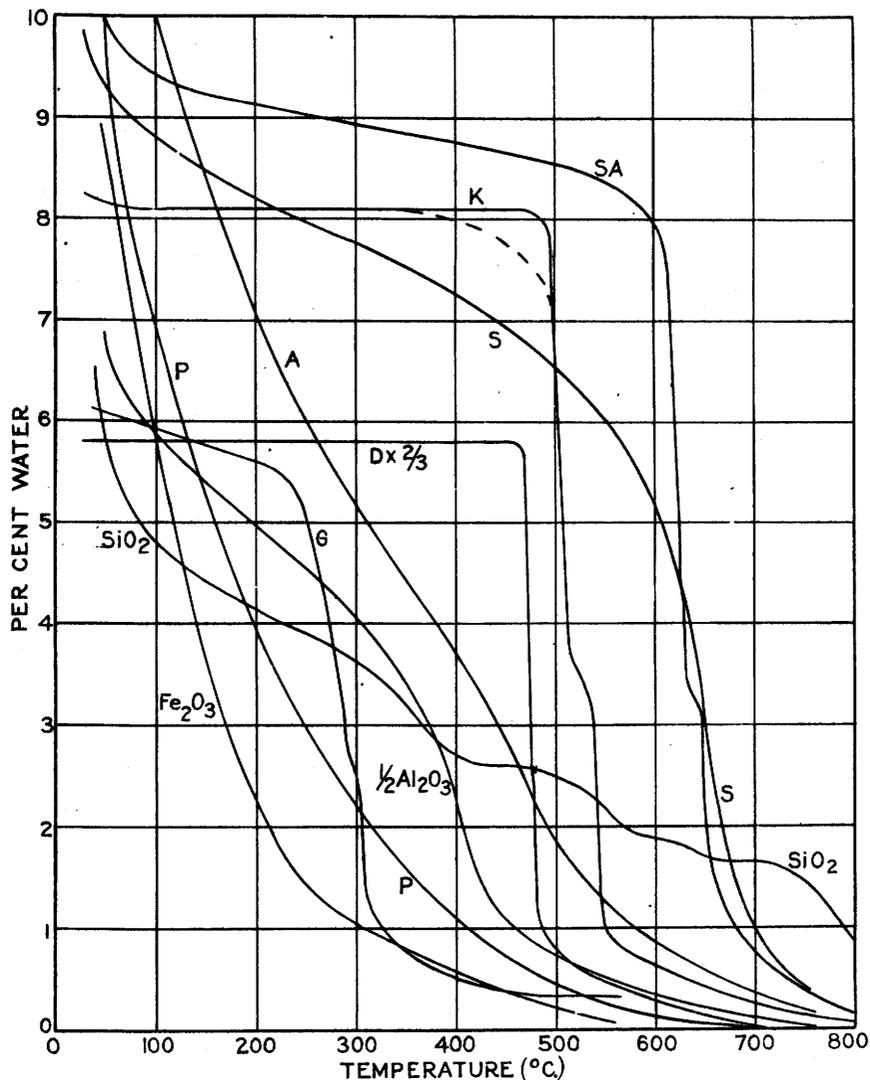


Figure 7.--Thermal dehydration curves of hydrous oxides. D, Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), from Rolla, Mo., selected by C. S. Ross; evidently very pure. G, Geothite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), alteration product from marcasite going over to hematite at $250^\circ\text{--}310^\circ\text{C}$. K, Kaolin mineral ("dickite"), fairly pure, from Chihuahua, Mexico; the rounded shoulder (dotted) is for a similar kaolin (slightly impure) from a hot spring near Bishop, Calif. A, Allophane ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2.3\text{--}5\text{H}_2\text{O}$); note absence of shoulders. S, Serpentine containing some iron and alumina. SiO_2 , Al_2O_3 , Fe_2O_3 , amorphous oxides prepared from precipitated hydrates and carefully freed from salts. Al_2O_3 is plotted $\times 1/2$. P, Permutite (Folin), so-called artificial zeolite, prepared by fusion for water softening by base exchange. SA, Asbestos serpentine containing but 0.3 percent of iron. (See table 3.)

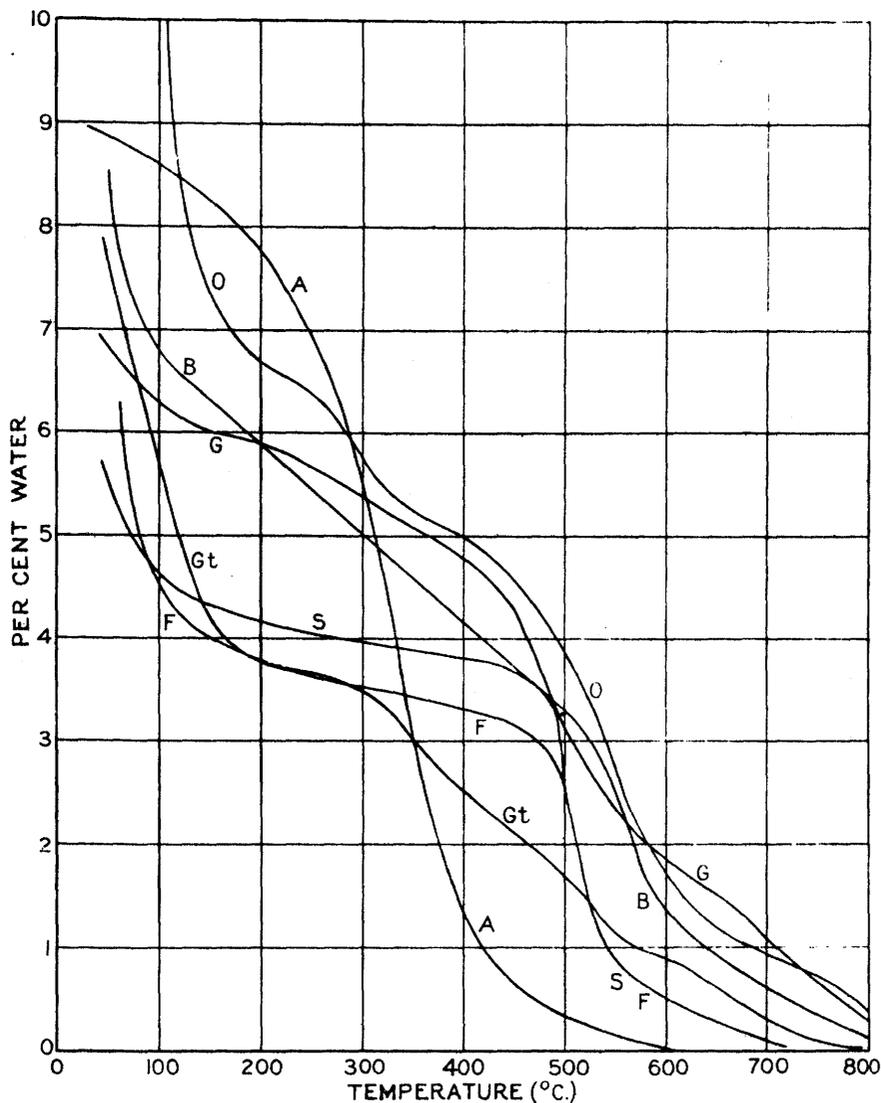


Figure 8.--Thermal dehydration curves of related clay minerals. O, "Otaylite," a pure-white montmorillonite bentonite. A, Analcite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). B, Bavarian acid-treated commercial bleaching clay. G, Greensand, 0.10-0.15 millimeter, raw. Gt, Same greensand acid-leached, white. The curve for acid-leached serpentine is nearly identical with Gt. S, Gray silicic decomposed granite, from D. C., acid-leached; bleaching action low. F, Yellow-green iron-rich decomposed granite, D. C., acid-treated; high in bleaching power. (See table 3.)

Table 3.-- Thermal dehydration data of the hydrous oxides of Figures 7 and 8
(Percent by weight)

Temperature (°C.)	D	G	K	A	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P	Chabazite
50	16.7	12.2	16.3	28.0	11.8	27.7	17.4	20.1
100	16.6	12.0	16.2	20.0	9.6	23.6	11.7	14.1	22.6
150	16.6	11.5	16.2	16.3	8.8	21.7	7.5	10.4	16.3
200	16.5	11.2	16.2	13.8	8.3	19.9	4.5	7.8	11.4
250	16.4	10.1	16.2	12.0	7.8	18.3	2.9	6.0	8.3
300	16.3	5.0	16.2	10.4	7.3	16.3	2.1	4.3	6.2
350	16.3	1.6	16.2	8.9	6.3	13.7	1.6	2.0	4.6
400	16.2	1.0	16.2	7.5	5.4	9.5	1.2	2.2	3.4
450	15.9	.8	16.2	6.1	5.2	4.3	.8	1.5	2.5
500	1.6	.8	14.0	3.8	5.0	2.8	.5	.9	1.7
550	.9	.7	2.1	2.7	4.3	2.1	.2	.6	1.1
600	.5	.6	1.2	2.2	3.8	1.5	.0	.3	.8
650	.2	.3	.8	1.8	3.4	.9	.0	.1	.2
700	.1	.1	.5	1.2	3.3	.5	.0	.0	.0
750	.0	.0	.2	.5	2.9	.2	.0	.0	.0
800	.0	.0	.0	.0	1.7	.1	.0	.0	.0
Temperature (°C.)	Q	A	B	G	Gt	S	F	SA	
50	8.9	3.5	6.8	7.6	5.5	7.2	19.6	
100	10.5	8.6	6.8	6.3	5.7	4.6	4.5	18.8	
150	7.3	8.3	6.3	6.0	4.2	4.3	4.0	18.5	
200	6.7	7.7	5.9	5.9	3.8	4.2	3.8	18.3	
250	6.4	6.9	5.4	5.6	3.6	4.1	3.6	18.0	
300	5.7	5.5	5.0	5.4	3.5	4.0	3.5	17.8	
350	5.2	3.1	4.6	5.1	3.1	3.9	3.4	17.6	
400	5.0	1.4	4.2	4.8	2.5	3.8	3.3	17.4	
450	4.6	.6	3.7	4.3	2.1	3.7	3.1	17.3	
500	3.8	.3	3.3	3.1	1.7	2.5	2.5	17.2	
550	2.7	.1	2.5	2.3	1.1	.9	.9	17.1	
600	1.7	.0	1.3	1.8	.9	.5	.5	16.0	
650	1.2	.0	.9	1.5	.6	.3	.3	6.1	
700	.9	.0	.6	1.1	.3	.1	.1	1.5	
750	.7	.0	.3	.6	.1	.0	.0	.8	
800	.4	.0	.1	.3	.0	.0	.0	.3	

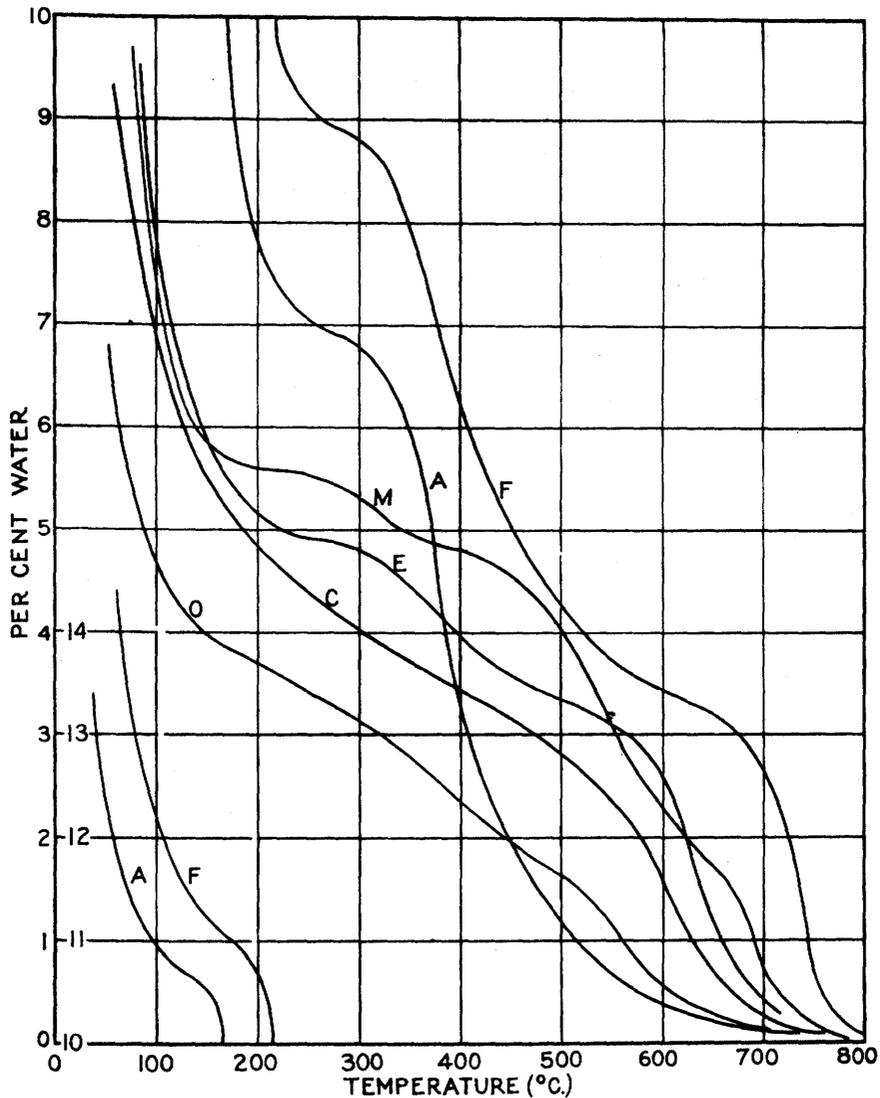


Figure 9.--Thermal dehydration curves of active clays. F, Commercial clay from Quincy, Fla. A, Clay from Attapulcus, Ga. M, Clay near Macon, Ga., submitted by the General Reduction Co. E, English fuller's earth recently imported for refining lard, XL brand. C, Commercial earth from Creede, Colo. O, Commercial earth from pit near Ocala, Fla., submitted by the Superior Earth Co. (See table 4.)

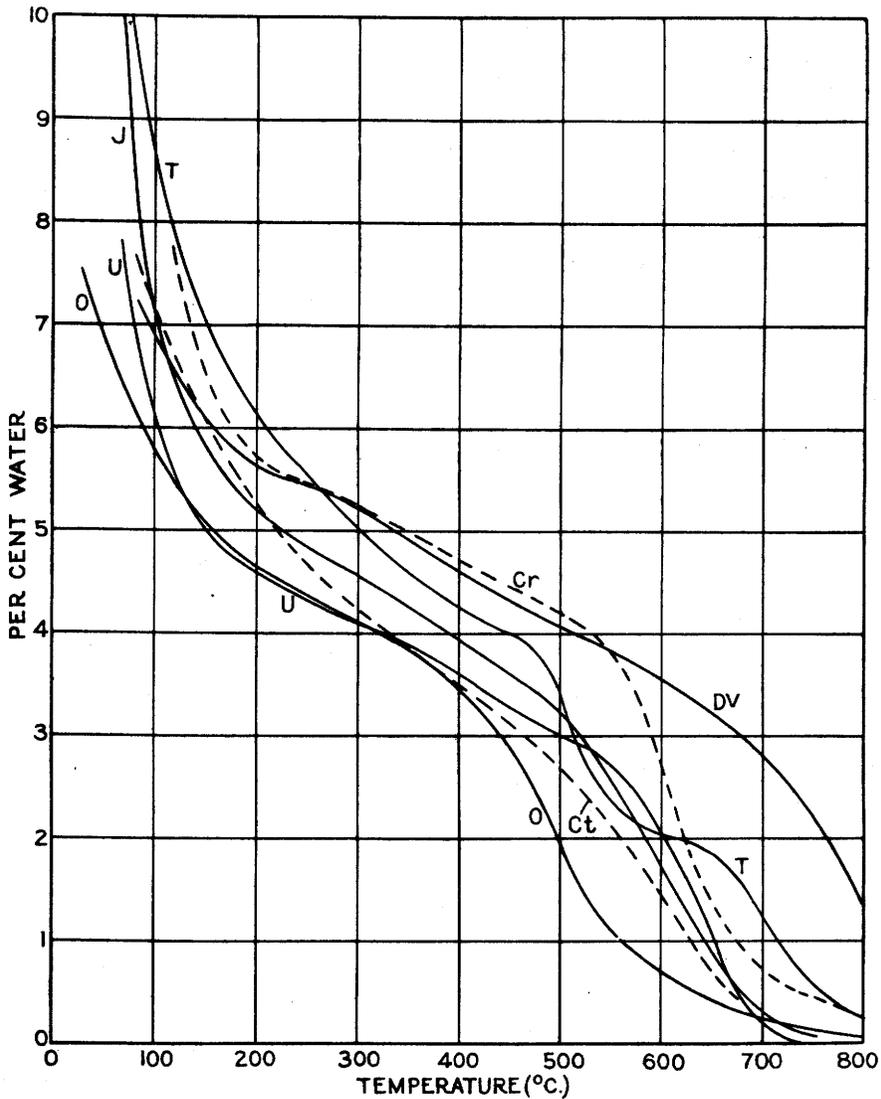


Figure 10.--Thermal dehydration curves of active clays. T, Untreated raw clay from tehachapi, Calif., from the Filtrol Co., Los Angeles. J, Japanese "acid clay" obtained through Prof. Yoshio Tanaka. U, Raw clay near Aurora, Utah, as used for refining petroleum, from Western Clay & Metals Co. The other clay supplied by this company for refining vegetable oils has a curve identical throughout except for a slight dip centered at 460° . O, Clay from Olmstead, Ill., mined and used by Sinclair Oil Co. DV, Magnesian clay from Nevada near Death Valley. Cr, Raw clay from Chambers, Ariz.; low in filtering power. Ct, Same clay acid-treated; highly active. (See table 4.)

Table 4.- Thermal (Percent by weight) Dehydration Data of the Active Clays of Figures 9 and 10

Temperature (° C.)	F	A	M	E	C	O	T	J	U	O	DV	Cr	Ct
50	15.8	12.6	11.8	12.8	9.8	7.0	11.5	11.6	9.8	6.9	8.0	...	8.0
100	12.2	11.0	7.4	7.9	6.9	4.7	8.6	7.2	6.2	5.8	6.9	8.8	7.2
150	11.2	10.5	5.8	5.9	5.5	4.0	7.0	5.8	5.0	5.1	6.1	6.5	6.1
200	10.7	7.8	5.6	5.2	4.8	3.7	6.1	5.2	4.6	4.7	5.6	5.7	5.2
250	9.1	7.1	5.6	4.9	4.4	3.4	5.5	4.8	4.3	4.4	5.4	5.4	4.7
300	8.8	6.8	5.3	4.8	4.0	3.1	5.0	4.6	4.1	4.1	5.2	5.2	4.2
350	7.9	5.9	4.9	4.4	3.7	2.8	4.6	4.2	3.9	3.8	4.9	5.0	3.8
400	6.4	3.3	4.8	4.0	3.4	2.4	4.3	3.9	3.6	3.4	4.6	4.7	3.5
450	5.0	1.9	4.6	3.6	3.2	1.9	4.0	3.6	3.3	2.9	2.9	4.4	3.1
500	4.3	1.2	4.0	3.4	2.8	1.6	3.4	3.2	3.0	1.9	1.9	4.2	2.7
550	3.7	.7	3.1	3.1	2.3	1.1	2.4	2.6	2.7	1.1	1.1	3.8	2.1
600	3.4	.4	2.2	2.6	1.6	.5	2.0	1.7	2.1	.7	.7	2.7	1.4
650	3.2	.2	1.7	1.2	.7	.3	1.8	.9	1.1	.4	.4	1.4	.7
700	2.9	.1	.7	.4	.2	.1	1.2	.3	.2	.2	.2	.7	.3
750	.7	.0	.2	.1	.1	.1	.6	.1	.0	.1	.1	.4	.1
800	.0	.0	.0	.0	.0	.0	.2	1.0	.0	.0	.0	.2	.0

These thermal dehydration curves are perhaps most striking in their individuality: each is unlike all the rest. A dozen of the commercial clays (figs. 9 and 10) have curves lying within a characteristic band between those of the clays from Macon and Death Valley above and that from Ocala below, but two of the most important clays, those from Attapulugus and Quincy, have curves well outside that band. These two curves resemble each other in their shoulders at 200° and 300° C., but the third shoulder at 700° on the Quincy clay is entirely absent on the Attapulugus clay (fig. 9). These two clays are mined less than 30 miles apart. The gray and green decomposed D. C. granites (S and F, fig. 8) are similar in form, but the gray holds more water in the range 100° - 500° C.

The curves for the artificial hydrous oxides Fe_2O_2 and Al_2O_3 (fig. 7) bear no apparent relation to the corresponding hydrated minerals goethite and diasporite, nor does the curve for the hydrated aluminosilicate (K, fig. 7) bear any resemblance to those for hydrous alumina or silicate. Some of the shoulders on various clay curves might be identified with those on the primary oxides, but not with any certainty. The acid leaching of a clay displaces its curve toward that for silica gel. This effect is most marked in clays (DV) and other minerals (greensand and serpentine) high in the easily removable magnesia.

Water driven off by heating to 50° C. is probably so loosely held that its removal opens no active bonds useful in bleaching. On the other hand, heating to 200° C. is sufficient to develop maximum bleaching power. In general this results in removing nearly all except the water of constitution, but without destruction of crystal structure. A higher temperature of dehydration may open additional valence bonds, but it must close others, as it does not further enhance bleaching power. Hence the quantity of water driven off in the temperature range from 50° to 200° C. should roughly correspond to bleaching power. The correlation is fairly good, as shown by the bleaching tests given below.

Although water of crystallization and water of constitution (H_2O , H, and OH) are driven off at the higher temperatures (300°-1,000° C.), by no means all the water driven off in that range is molecular water. Amorphous gel still contains considerable water, even at 800°, and several clays do also. A sharp shoulder in the dehydration curve is apparently the sole criterion for molecular water. A distinction cannot always be drawn, on the basis of dehydration curves, between adsorbed water, water of constitution, and water of crystallization. And of course adsorbed water shades off imperceptibly into adsorbed water in these curves, as the corresponding energies overlap.

The theory of the energy involved in dehydration is simple. In calories per gram molecule (q) it is

$$\frac{q}{R} = \frac{d \log C}{d(1/T)}$$

where R = 1.985, C is concentration of water in mineral (or any quantity proportional to it), and T is absolute temperature. Dividing q by 18, the molecular weight of water, gives the energy in calories per gram of water driven off. The curves give for kaolinite 3,442, for diaspore 3,857, and for goethite 601 calories per gram at the steepest part of the shoulder when combined water is being driven from the interiors of crystalline hydrates. Molecular proportions (calculated) correspond well with the observed percentages at these shoulders.

With the clays and other complex silicates there are no sharp shoulders (like those on the simpler hydrates) on the thermal dehydration curves. The general method of finding the energy of association as a function of water concentration in the sample is illustrated by figure 11 and table 5. As a typical example I have again chosen the artificial silicate permutite, data for which are given in figure 7 and column P in table 3.

Table 5.- Energies of dehydration of permutite

T_c	Concentration of H ₂ O	$1/T_a$	log C	q/R	cal/gm
50	0.201	0.003096	-1.6045	751.9	82.9
100	.141	.002681	-1.9590	877.2	96.7
150	.104	.002364	-2.2634	1,101.9	121.5
200	.078	.002114	-2.5511	1,315.8	145.1
300	.043	.001745	-3.1466	2,076.1	229.0
400	.022	.001486	-3.8167	3,409.0	375.9
500	.009	.001293	-4.7105	5,555.5	612.7
600	.003	.001145	-5.8092	12,307.7	1,357.3

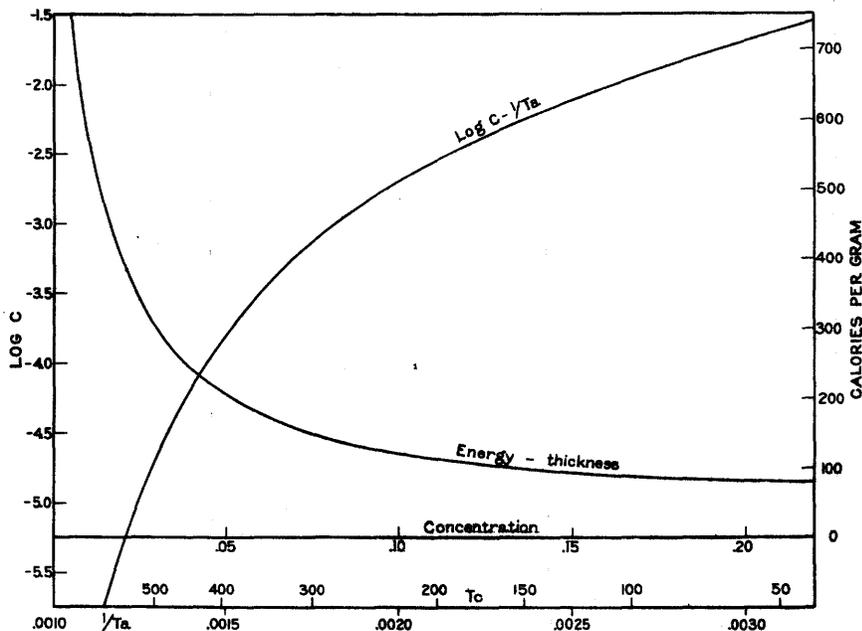


Figure 11.--Energy of dehydration of permutite.

In figure 11 are plotted $\log C$, the natural log of the water concentration, against reciprocal absolute temperatures $1/T_a$ ($T_a = T_c + 273$). From this curve the slope $d \log C / d(1/T_a)$ is found at each point. This is q/R , which is converted to calories per gram by the factor 0.11028 ($= 1.985 \div 18$). The energy-concentration curve is also plotted in figure 11 (left). It is a smooth curve, high for low percentages of moisture in the mineral and low and steadily falling for high percentages.

All the data on hydration and dehydration lend additional support to the hypothesis that each bleaching medium offers a wide range of continuously varying adsorbing properties. In the clays composition may vary widely from point to point over the surface. In the simpler synthetic amorphous oxides probably only the structure varies and the range of adsorbing powers is narrower. In permutite every basic ion, internal as well as on the surface, is considered exchangeable, but this material is not exceptional among bleaching agents nor in its relation to water.

The bleaching action

The rating of active minerals according to their bleaching efficiency is obviously a quite arbitrary matter, because the relative bleaching power of any series of clays will be different for every test liquid used. To avoid this arbitrariness, dyes dissolved in benzine have been used, but this standard test is too artificial. Even with a specific clay and test oil there is the question of which cut to choose as standard--whether water-white (complete filtration), complete exhaustion of filtering power, or intermediate filtration to green, yellow, orange, or some particular shade of red.

The tests here reported refer to complete filtration (to water-white), and the numerals under "Bleach rating" in table 6 are the ratios of volumes of oil so filtered to the volumes of clay so filtering it. Thus if 1 inch of clay filters 1.5 inches of oil water-white before going to green or yellow its rating is 1.5. The test oil was a high-gravity black natural petroleum, free from sulphur. Obviously this rating has little practical significance and was chosen partly for that reason.

Table 6.- Bleaching and solubility tests

	a/ Type	Bleach. rating		Acid- soluble (percent)	Soluble (scale of 10)			
		Raw	Treated		Fe	Al	Ca	Mg
Attapulugus, Ga.	M	0.8	0.5	18.6	4	4	1	1
Macon, Ga.	V	.5	.9	20.8	6	2	2	Tr.
Quincy, Fla.	M	.7	.6	25.6	4	3	3	Tr.
Ocala, Fla.	M,V	.6	.9	26.1	3	4	3	Tr.
Creede, Colo.	M,V	.8	1.2	11.1	6	3	1	0
San Antonio, Tex.	M	.8	1.1	11.1	6	3	1	Tr.
Olmstead, Ill.	M	.6	.3	23.3	7	3	0	Tr.
Aurora, Utah	M	1.4	1.2	10.9	4	3	2	1
Aurora, Utah	V	1.1	1.2	9.8	4	4	2	Tr.
Death Valley, Nev.	M	1.8	1.2	24.9	Tr.	1	1	8
Tehachapi, Calif.	V	1.1	1.1	13.1	4	4	Tr.	2
Chambers, Ariz.	M	.6	2.0	22.6	5	4	1	Tr.
English, XL	V	1.2	2.0	19.9	5	4	1	Tr.
Japanese acid	M,V	1.0	1.1	14.2	3	6	1	0
D.C. granite, green	M	.0	1.5	32.6	8	2	Tr.	0
D.C. granite, gray.	M	.4	1.0	13.7	5	5	Tr.	Tr.
N.C. dunite, treated.	M	1.2	1.2	40.0	5	0	0	5
Va. decomposed diabase.	M	.2	1.0	16.1	7	1	2	Tr.
Bentonite (otaylite), Calif.	M	.3	1.8	31.3	2	8	Tr.	0
Oklahoma, white	M	1.1	.8	9.1	0	6	4	Tr.
Riverside, Tex.	M	.6	1.1	11.2	4	2	2	2

a/ M, Mineral; V, vegetable.

The eastern clays would of course rate much higher on the practical basis of red oil. None of them are much improved by acid leaching, and the clay from Attapulugus is actually harmed. A number of our clays rate as high as the best English, Japanese, and German clays. Bavarian acid-leached clay tests 1.3 on this scale.

Silica gel and amorphous Al_2O_3 and Fe_2O_3 rate about 1.0 on this scale but are useless for filtering lubricants, because they cease filtering abruptly at the end of the water-white. For vegetable oils they are better, but their chief field of usefulness is in solvent recovery. A number of the western active clays and decomposed rocks are reduced almost to pure active silica by acid leaching.

The acid-soluble fraction of these clays ranges from 10 to 40 percent and bears no apparent relation to bleaching power. Rough analyses of the dissolved material (last four columns) shows that this is largely iron and alumina. Soluble calcium is always low, magnesium also except in two examples-both excellent bleaching materials.

Many of the most powerful bleaching clays will crack water-white gasoline, melted paraffin, and even highly refined and stabilized laxative mineral oil, immediately adsorbing the brown portion cracked out and leaving the liquid colorless.

Numerous specimens of active clays have been studied with a view to obtaining a basis for classification and developing possible relations between bleaching power and other properties and possible origin. Test data on the more interesting of these clays are given in table 7. The rating of activity is on the same scale as in table 6. Activity of the ignited raw clay is given for some of the specimens. Relative weights at room temperature and after heating to 160° and 800° C. show the percentage of moisture in these two ranges and indicate clay types. Kaolinitic clays lose their moisture in the higher range, bentonitic chiefly in the lower range (25°-160°). The complete dehydration curves show many significant details but require so much time to make that only a selected few have been run.

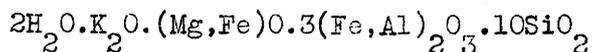
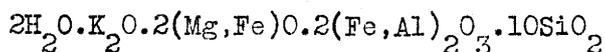
Table 7.- Miscellaneous clay tests

Clay	Bleach rating			Acid-soluble (percent)	Soluble (scale of 10)				Weight loss (percent)	
	Raw	Treated	Ignited		Fe	Al	Ca	Mg	25°-160°	160°-800°
1. Otay, Calif.	0.5	1.8	...	31.3	2	8	Tr.	0	11.3	5.2
2. Oklahoma	1.1	.8	...	9.1	0	6	4	Tr.	8.1	5.2
3. Texas	.6	1.1	...	11.3	4	2	2	2	5.2	6.0
4. Ga. bauxite	.5	.8	...	22.4	0	9	1	Tr.	.2	23.4
5. Midway, Fla.	.7	.8	...	33.0	2	2	6	Tr.	6.6	13.3
6. Tenn. bentonite	.4	1.3	...	4.7	4	3	3	0	3.7	6.4
7. Ala. bentonite	.4	1.3	...	8.5	5	4	1	0	13.1	8.5
8. Miss., Smith Co.	.8	1.2	...	7.9	5	3	2	Tr.	3.5	5.0
9. Miss., Tippah Co.	.8	1.0	...	27.5	4	6	0	Tr.	5.4	5.3
10. Miss., bauxite	.0	.4	...	26.0	5	5	Tr.	0
11. Okla. bentonite	.5	1.7	...	37.9	5	4	1	0	12.0	12.0
12. Woodward, Okla.	.6	1.7	...	41.0	5	4	1	0	13.1	11.2
13. Silver Cliff, Colo.	.8	2.0	...	30.7	1	7	1	1	14.4	5.6
14. Santa Rita, N.Mex.	.8	1.5	...	21.7	1	8	1	1	12.2	6.5
15. Saline Co., Ark.	.8	1.6	...	22.5	3	5	2	0	14.6	6.9
16. Gordon, Ga.	1.0	1.2	0.9	3.6	0	5	5	0	.9	15.4
17. N.C. nontronite	.0	1.6	...	55.0	8	2	0	0	18.5	9.0
18. Ga. halloysite	1.0	1.4	1.0	42.9	0	10	Tr.	0	9.4	14.2
19. Permutite	1.1	1.7	...	53.0	0	10	0	0
20. Cordelc, Ga.	1.3	1.3	1.2	15.1	4	5	1	Tr.	2.0	8.8
21. Durant, Ga.	.6	.3	.8	11.5	0	10	0	0	.4	13.8
22. Fort Valley, Ga.	.3	.4	1.2	6.5	0	10	0	0	.3	13.1
23. Musselwhite, Ga.	.9	1.8	.3	30.6	5	5	1	Tr.	5.4	8.6
24. Md. glauconite	1.4	1.5	.7	38.3	10	0	Tr.	Tr.	3.5	5.9
25. Clarendon, Tex.	.8	1.3	.8	18.9	5	4	1	0	5.6	6.0
26. Fort Gaines, Ga.	1.3	1.4	1.2	4.5	5	4	1	0	4.3	6.0
27. St. Paul, Minn.	1.4	1.8	.4	26.4	6	3	1	0	1.6	6.2
28. Laurel, Miss.	.7	2.0	.4	41.4	4	4	2	0	16.8	6.2
29. Ga. bentonite	1.0	1.9	.6	20.9	3	5	2	Tr.	2.7	7.2
30. Wrens, Ga.	1.2	1.2	1.2	20.4	5	3	2	Tr.	15.0	5.4
31. Oglethorpe, Ga.	1.0	1.4	1.2	6.9	7	Tr.	3	0	1.3	3.6
32. Tennille, Ga.	1.2	1.3	1.2	17.1	7	Tr.	3	0	9.1	5.3
33. Westcliffe, Colo.	1.3	1.9	.7	31.5	0	7	2	1	16.1	4.8
34. N. J. glauconite	1.2	1.3	.3	43.4	9	1	0	0	1.9	5.1
35. Commercial bentonite	.7	1.3	.7	19.7	3	5	2	Tr.	6.3	5.9

1. Bentonite from Otay, near San Diego, Calif. Supplied by the Standard Oil Co. of California. Treated and used by that company.
2. A white Oklahoma clay sent in by Max B. Miller.
3. Riverside, Tex., from Continental Oil Co.
4. A Georgia Bauxite having some bleaching power.
5. Midway, Fla. Clay mined by the Fullers Earth Co. of Cleveland. One of the first known deposits of active clay.
6. A greenish-gray Ordovician bentonite near Evansville, Tenn.
7. A similar red bentonite near Birmingham, Ala.
8. White active clay from Smith County, Miss.
9. A greenish-gray clay from Tippah County, Miss.
10. Bauxitic clay from same locality as 9.
11. White Oklahoma bentonite.
12. Pink bentonite from Woodward, Okla. Note similarity to No. 11 shown by the test.
13. Pink bentonite (volcanic ash) from Silver Cliff, Colo. Similar in appearance to No. 33.
14. Volcanic ash from Santa Rita, N. Mex., very possibly from the same horizon as Nos. 13 and 33.
15. Bentonite from Saline County, Ark., submitted by John C. Branner.
16. White kaolinitic clay near Gordon, Ga.
17. Olive-green nontronite from Sandy Ridge, N. C.
18. Halloysite near Rome, Ga.
19. Synthetic zeolite (permutite), Folin preparation.
- 20 - 23. Hard gray clays near Cordele, Durant, Fort Valley, and Musselwhite, Ga.
24. Dark-green glauconite from Lyons Wharf, Md.
25. An active clay near Clarendon, Tex.
26. A light-yellowish clay near Fort Gaines, Ga.
27. A dark-green silt from an excavation in St. Paul, Minn.
28. Bentonite from the vicinity of Laurel, Miss. Byram marl.
29. An Ordovician bentonite from Chickamauga, Ga.
- 30 - 32. Active clays near Wrens, Oglethorpe, and Tennille, Ga.
33. A pink volcanic ash from Westcliffe, Colo.
34. Glauconite (greensand) near Sewell, N. J.
35. Gray commercial (Wyoming?) bentonite having pronounced swelling and gel-forming properties.

Only a few of these clays are highly active without acid treatment, rated by the water-white bleach of cold crude petroleum. Conspicuous in this class are the glauconites (24,34). The clays from Cordele, Fort Gaines, St. Paul, Wrens, and Tennille (20, 26, 27, 30, 32) also show this character and may all be derived in part from glauconite or its counterpart, the waxy green clay not uncommon in decomposed igneous rocks.

All true glauconites have been shown by Ross^{12/} to lie between the two end members



The thermal hydration curve of the clay from Fort Gaines is almost identical with that of marine glauconite.

Another interesting and perhaps commercially important class or subclass is the group of clays whose activity is but slightly affected by either acid leaching or ignition. The list is the same as before, with the omission of St. Paul. A glauconitic origin subsequently modified by lime or kaolin (from decomposed feldspar) is indicated. Kaolinite is inactive until ignited. Clays of this type would best withstand burning for reuse.

The bentonitic (volcanic ash) type of clays respond best to acid leaching. Properly prepared, they are not excelled in activity by any clay or synthetic bleach. Otaylite and the clay from Chambers, Ariz., the only clays acid-treated and marketed on a large scale in this country, are far western. The eastern market is largely supplied by imported acid-leached German clay. This also, according to Kerr, ^{13/} is largely an impure bentonite from decomposed volcanic ash. Bentonites were therefore given particular attention in this study. Clays 6, 7, 11, 12, 13, 14, 15, 23, 29, 33, and 35 are known to be bentonites; 3, 8, 23, and 25 behave like bentonites diluted with other clays. Halloysite (18) activates like a bentonite but has a dehydration curve entirely different in character, with a large loss (12 percent) in moisture at 470° C., whereas the bentonite curves have a small but pronounced shoulder at 570° C.

^{12/} Ross, C. S., The optical properties and chemical composition of glauconite: U. S. Nat. Mus. Proc., vol. 69, art. 2, 1926.

^{13/} Kerr, P. F., Montmorillonite or smectite as constituents of fuller's earth and bentonite: Am. Mineralogist, vol. 17, p. 192, 1932.

Bentonitic clays of high grade are widely distributed, and each deposit usually extends over a large area but is not very thick. Thickness, overburden, and location with reference to markets will be dominant factors in future production. Clays of this class respond much more readily to attack by acid than the glauconites.

The active clays of northern Florida and southwestern Georgia are in a distinct class by themselves, characterized by fair bleaching power without other treatment than drying and grinding and being unaffected by acid bleaching. Electrodialysis to remove soluble salts nearly doubled (0.7 to 1.3) the bleaching power of the clay mined at Quincy and Attapulcus, Ga., and Ocala, Fla. Leaching in a large quantity of hot distilled water was found to give a similar enhancement of bleaching power. A third method was to mix sawdust with clay, wet to a mud, and allow bacterial action to take its course. Clay thus treated also rates 1.3. Other clays are either unaffected or harmed by this excessive water leaching.

Washing an active clay in hard water of course destroys its bleaching power, for it provides the cation-hungry open bonds with cations, thereby destroying their affinity for the black particles in oil. An acid-leached clay must be washed in water kept below pH 7.0. So long as the wash water is kept acid, cations cannot be adsorbed by the clay surfaces but must remain in solution. If the wash water is allowed to become alkaline, anion acceptors are provided, and cations are adsorbed by the clay. If only hard water is available for washing acid-leached clays, it should be kept well on the acid side of neutrality.

Many important problems connected with the bleaching action of clays remain to be investigated. Why do some clays crack even saturated pure paraffines, whereas others do not? Why do some clays cease bleaching abruptly, and others give a long series of intermediate green, yellow, orange, and red oils? What is the optimum acid leach? Why is the bleaching power of some clays unaffected by ignition, which destroys that of many others? One clay is inactive on hot crude oil when raw but highly active when acid-leached; on cotton oil, however, its behavior is just the reverse, and on cold crude oil it is highly active either raw or acid-treated. Some clays leave the bleached oil stable toward light and air; others leave it unstable. What is the value of active clay as a catalyst, for the recovery of solvent vapors, or for water softening?

Maximum bleaching powers and efficiencies

Some questions of considerable practical interest are frequently asked, such as (1) What naturally active clays are the best, and are much better ones likely to be discovered? (2) Among the treated clays, which respond best to treatment, what is their maximum activity, and what treatment gives best activation at least expense? (3) By what process may other types of clays be converted into bleaching clays, and which of such processes are commercially feasible? (4) What are the possibilities of producing synthetic bleaching media? Although these questions may be tentatively answered with some assurance as a result of the laboratory studies here recorded, complete answers must await the results of much further study. The results thus far indicate that the market structure is not likely to be upset or even seriously disturbed by new developments in any line.

Natural bleaching clays.- Tests of scores of samples from all parts of this country and from several foreign countries indicate that the maximum bleaching power to be expected of any natural bleaching clay is about 1.6 to 1.8 on the scale used in table 7. This rating is approached by a number of selected western clays. This statement applies to clays treated only by milling and dehydrating to 180° C. (= 350° F.) just before using. The bleaching power of clay thus dried is two to three times that of the same clay merely room-dried at say 30 percent relative humidity. The lower-grade eastern clays retain their large market through lower transportation and production costs. Selected natural minerals, pulverized and subjected to treatment simulating weathering, may be made to approach but not to exceed this apparently fixed limit to bleaching power.

Tests of samples through vertical and lateral sections of clay deposits indicate wide variation in filtering power, in some deposits within a few feet. Check tests in the field are readily made with simple apparatus and must be made in most deposits to avoid including poor material, with consequent loss in quality of the product.

Many otherwise excellent bleaching clays contain grit and other inactive material (such as quartz and feldspar grains and kaolin). At the present time in this country such clays cannot be considered commercial sources, on account of the expense of screening. There appears to be an almost unlimited quantity of excellent clay available which requires no screening and can be mined, dried, and milled at less than the cost of screening.

Treated clays.— Clays treated with acid to remove their excess bases and thus (after dehydration) provide their surfaces with open bonds appear also to approach a fixed minimum of filtering power, which is about 2.0 on the scale of table 7. I have studied the activation of many different clays with various acids but have never been able to exceed this limit. The maximum is a little higher for a natural complex oxide (mixed with silicate) than for any of the similar component oxides, fully activated. Starting with a complex alteration product composed of ferromagnesian silicate, screened and thoroughly water-leached free from water-soluble bases, it seems to make little difference whether the iron oxide, the silica, or the magnesia is partly removed to leave open bonds. Activation depends very little on what acid is used or what oxides are left, so long as the clay is attacked.

A wide variation of decomposed rocks, base-containing clays, bentonites, and some partly altered volcanic ashes are available for conversion to high-grade bleaching clays by acid treatment. Some yield too readily, going over to nearly pure silica, which is not a good oil bleach. Diatomite with simple washing or no treatment at all is in this class. At the other extreme are rock powders, very resistant to acid, and ordinary (brick)clays which have gone too far and would require roasting before yielding to acid treatment. There is no lack of material available. Probably the best sources of raw material are decomposed rocks ranging from ferromagnesian diabases to dunites. In this field preliminary work and check tests are indispensable to rational production. The cost of screening is not prohibitive when acid treatment is to follow and a high-grade product made.

Synthetic bleaching media.— A great many hydrous oxides may be readily prepared by chemical methods. Dehydration by simple heating leaves these in active form, but their bleaching power is no higher than that of many natural clays. Nor is there apparently any advantage in precipitating any two or three oxides together. The chief field of such synthetic preparations appears to be the recovery of valuable solvent vapors, for which they are well suited, as they are efficient and can be reused indefinitely.

The chief advancements to be looked for in the bleaching-earth industry lie not in the discovery of new beds or more powerful earths, nor in the development of new methods of treating clays, nor yet in the creation of synthetic products, but rather in the preparation at low cost for special purposes of special clays having a minimum cracking power and minimum retention, with a maximum of decolorizing or deodorizing power, together with the property of leaving a stable filtrate.